GMELIN HANDBOOK
OF INORGANIC CHEMISTRY

Pt

SUPPLEMENT VOLUME A 1

TECHNOLOGY

1986

Periodic Table of the Elements with the Gmelin System Numbers

1 H 2																1 H 2	2 He 1
3 Li 20	4 Be 26											5 B 13	6 C 14	7 N 4	8 O 3	9 F 5	10 Ne 1
11 Na 21	12 Mg 27											13 Al 35	14 Si 15	15 P 16	16 S 9	17 Cl 6	18 Ar 1
19 * K 22	20 Ca 28	21 Sc 39	22 Ti 41	23 V 48	24 Cr 52	25 Mn 56	26 Fe 59	27 Co 58	28 Ni 57	29 Cu 60	30 Zn 32	31 Ga 36	32 Ge 45	33 As 17	34 Se 10	35 Br 7	36 Kr 1
37 Rb 24	38 Sr 29	39 Y 39	40 Zr 42	41 Nb 49	42 Mo 53	43 Tc 69	44 Ru 63	45 Rh 64	46 Pd 65	47 Ag 61	48 Cd 33	49 In 37	50 Sn 46	51 Sb 18	52 Te 11	53 I 8	54 Xe 1
55 Cs 25	56 Ba 30	57** La 39	72 Hf 43	73 Ta 50	74 W 54	75 Re 70	76 Os 66	77 Ir 67	78 Pt 68	79 Au 62	80 Hg 34	81 Tl 38	82 Pb 47	83 Bi 19	84 Po 12	85 At	86 Rn 1
87 Fr	88 Ra 31	89*** Ac 40	104 71	105 71													

* NH_4 23

**Lanthanides 39	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
***Actinides	90 Th 44	91 Pa 51	92 U 55	93 Np 71	94 Pu 71	95 Am 71	96 Cm 71	97 Bk 71	98 Cf 71	99 Es 71	100 Fm 71	101 Md 71	102 No 71	103 Lr 71

A Key to the Gmelin System is given on the Inside Back Cover

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8th Edition

Volumes published on Platinum-Group Metals

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* Iridium Suppl. Vol. 1 (Metal, Alloys) – 1978
° Iridium Suppl. Vol. 2 (Compounds) – 1978

Os * Osmium Main Volume – 1939
Osmium Suppl. Vol. 1 – 1980

Pd * Palladium 1 (Element) – 1941
* Palladium 2 (Compounds) – 1942

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* Platinum Suppl. Vol. A 1 (Technology of Platinum-Group Metals) – 1986
(present volume)

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* Ruthenium Suppl. Vol. – 1970

* Completely or ° partially in German

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8th Edition

Gmelin Handbuch der Anorganischen Chemie

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Prepared and issued by
Gmelin-Institut für Anorganische Chemie
der Max-Planck-Gesellschaft
zur Förderung der Wissenschaften
Director: Ekkehard Fluck

Founded by
Leopold Gmelin
8th Edition
8th Edition begun under the auspices of the
Deutsche Chemische Gesellschaft by R. J. Meyer
Continued by
E. H. E. Pietsch and A. Kotowski, and by
Margot Becke-Goehring

Springer-Verlag Berlin Heidelberg GmbH

Gmelin-Institut für Anorganische Chemie
der Max-Planck-Gesellschaft zur Förderung der Wissenschaften

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Gmelin Handbook of Inorganic Chemistry

8th Edition

Pt

Platinum

Supplement Volume A 1

Technology of Platinum-Group Metals

With 37 illustrations

AUTHORS

G. J. Bernfeld, Council for Mineral Technology, Randburg, Republic of South Africa
A. J. Bird, Johnson Matthey Research Centre, Reading, Great Britain
R. I. Edwards, Council for Mineral Technology, Randburg, Republic of South Africa
Hartmut Köpf, Technische Universität Berlin
Petra Köpf-Maier, Universität Ulm, Bundesrepublik Deutschland
Christoph J. Raub, Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, Bundesrepublik Deutschland
W. A. M. te Riele, Council for Mineral Technology, Randburg, Republic of South Africa
Franz Simon, Degussa AG, Schwäbisch Gmünd, Bundesrepublik Deutschland
Walter Westwood, Johnson Matthey Research Centre, Reading, Great Britain

EDITORS

Gary J. K. Acres, Johnson Matthey Corporate Development (Technology), London, Great Britain
Kurt Swars, Gelnhausen, Bundesrepublik Deutschland

System Number 65

Springer-Verlag Berlin Heidelberg GmbH

AUTHORS OF THIS VOLUME

R. I. Edwards, W. A. M. te Riele, G. J. Bernfeld	pp. 1/23
W. Westwood	pp. 24/65
C. J. Raub	pp. 66/68, 77/91
F. Simon	pp. 68/77
A. J. Bird	pp. 92/317
P. Köpf-Maier, H. Köpf	pp. 318/338

LITERATURE CLOSING DATE: 1983, FOR CHAPTER 5: 1982
IN SOME CASES MORE RECENT DATA HAVE BEEN CONSIDERED

Library of Congress Catalog Card Number: Agr 25-1383

ISBN 978-3-662-10280-0 ISBN 978-3-662-10278-7 (eBook)
DOI 10.1007/978-3-662-10278-7

Originally published by Springer-Verlag Berlin Heidelberg New York Tokyo in 1985.
Softcover reprint of the hardcover 8th edition 1985

Preface

Like most supplement volumes of the platinum-group metal series, Platinum Suppl. Vol. A 1 has been written by an international team of specialists. It comprises technological data of all six platinum-group metals and their technically relevant alloys and compounds.

The volume starts with a review on the recovery of the platinum-group metals (23 pages); the next 42 pages are devoted to processes for separating and refining the PGM in order to obtain metals of high purity. The electrodeposition of the PGM and their alloys is treated on 26 pages. The by far most extensive section deals with PGM and their alloys and compounds in catalysis. After a historical survey and a list of important reviews on PGM catalysis, the catalytic properties of the metals are treated in a general way, followed by unsupported metals and alloys including preparation of catalysts and their reactions in various industrial processes. The role of supported metals and alloys is described in a similar manner. This is followed by an extensive description of the preparation and the reactions of PGM compounds with various nonmetals and their catalytically active role in a number of industrial processes (226 pages).

The last chapter (21 pages) is a compilation of data on the medical use of cytostatic platinum compounds.

Gelnhausen, December 1985 Kurt Swars

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Technology of the Platinum-Group Metals

1 Review on the Recovery of the Platinum-Group Metals

1.1 Historical Perspective

No definite date can be ascribed to the discovery of platinum; rather it became gradually known to the Western World as a distinct metal of unique properties over a period of two centuries, between 1500 and 1700. The first source to be exploited was the placer deposits in New Granada (now Colombia) where it was initially regarded as a nuisance in the gold extraction operations. By about 1750 however it was beginning to be exploited for its own sake and had found uses for decorative purposes.

The development of the technology of these metals can be divided into four stages:

Period of Discovery, 1750 to 1820

During this period major progress was made in separating the various platinum metals and in establishing many of the basic characteristics of their chemistry. Thus, for example Scheffer established in 1751 the fact that NH_4^+ ions precipitated Pt as an insoluble salt from Cl^- solutions – a technique used in its recovery and refining up to the present day. By 1804 various techniques had been used to isolate five of the six metals (Pt, Pd, Rh, Os, Ir) from Colombian ores.

At the same time much attention was also paid to the physical metallurgy of the new metals, especially of Pt and to methods of fabricating them.

The techniques of extraction, refining, and fabrication developed during this period thus laid the foundation for the industrial exploitation of the metals.

First Industrial Period 1820 to 1900

This period is distinguished by four major developments in the industrial applications of the platinum metals. These were:

(a) The development of industrial-scale integrated refining processes for the metals. Starting with Breant in 1822, these processes included steps such as aqua regia leaching, distillation of Os, precipitation of Pt as $(NH_4)_2PtCl_6$ and precipitation of Pd as $PdCl_2(NH_3)_2$.

(b) The establishment of industrial companies whose major business was the extraction, refining, and fabrication of the platinum metals. These include Johnson Matthey, Hereaus, and Desmontis Quennessen early in the period, and Bishop and Baker-Engelhard later on.

(c) The establishment of international trade in the metals and their ores, firstly from Colombia alone, but later and almost exclusively from new deposits in Russia.

(d) The development of satisfactory methods of fabricating the metals and their usage as corrosion-resisting linings, especially in sulphuric acid boilers – the major use for Pt till after the turn of the century.

Second Industrial Period 1900 to 1960

Platinum metals were obtained from a wide variety of sources during this period. Placer deposits in Colombia and Russia were still exploited, but the recovery of byproduct platinum metals from Cu-Ni ores from Sudbury, Canada became an important source from about 1920 and by the late 1930s this source was dominant in the market. This situation continued until the late 1940s, when deposits in South Africa and, somewhat later, in Russia, also of the Cu-Ni sulphide type, became of increasing importance.

During this period the refining processes developed during the nineteenth century became standardised to a large extent. This is best illustrated by the Inco process which with minor variations was almost universally used until the 1970s.

Because of the change in the nature of the ores from which PGM were derived, new methods also had to be developed for the early stages of concentration. These techniques only reached their full maturity with the development of the South African and Russian deposits, however.

Uses of the PGM continued to grow during this period and their catalytic properties began to be exploited, firstly in the production of H_2SO_4, then the oxidation of NH_3 to HNO_3, and thereafter in a whole range of new industrial processes.

The Modern Period

This period bas been marked by the vast increase in the range and amount of usage of the PGM. Accompanying this has been the virtual elimination of primary sources of PGM other than Cu-Ni sulphide deposits, and the dominance of the Russian and South African deposits.

At the same time the recovery of the metals from secondary materials, i.e. their recycling, has become a major factor in the industry. The secondary refining industry is probably almost as large as the primary, and will probably continue to expand in the future.

Technologies have been developed to a high level of sophistication to extract and concentrate the metals from ores containing only a few parts per million into concentrates.

Beginning in about 1970, the principles and techniques of modern inorganic chemistry have been used very effectively to analyse the conventional process for the refining of the concentrates and to improve these methods. A feature of newer refining processes has been the introduction of solvent extraction and ion-exchange methods to the industry, and it appears probable that these techniques will become standard within the industry in the near future.

1.2 Sources of Platinum Metals

Primary Metal

As outlined previously, various sources have at various times dominated the supply of PGM. From about 1960 onwards, PGM associated with Cu-Ni deposits became by far the dominant source, and today about 98% of the total world production of primary PGM is derived from only three sources, i.e. sulphide deposits in Canada, USSR, and South Africa.

These three sources have in common a low PGM grade (2 to 10 ppm), and in general a very close association between the PGM minerals and the base metal sulphide minerals. This means that, in general, recovery of the PGM separately form the base metal sulphides is not possible by physical methods such as gravity separation. Thus, the major amount of PGM is recovered as a byproduct ot the processes used for recovery of the much larger amounts of base metals that accompany them.

In other respects these three deposits are somewhat different. In the case of the Russian and Canadian deposits, the ratio of (Cu + Ni)/PGM is so high that these deposits are in essence mined for their base metal content, the PGM being merely byproducts. In the Bushveld Igneous Complex (BIC) deposits in South Africa, the reverse is true, ~60% of the revenue being obtained from the PGM, and <40% from the base metals.

In addition, Pt is the major PGM found in South African ores, whereas Pd is the major in Russia and Canada. South Africa therefore dominates the world Pt market whereas the USSR dominates the Pd market.

A further source of supply is beginning to be exploited in South Africa. This is the "UG-2" chromitite seam, underlying the main Merensky Reef. This contains a low sulphide mineralisation in a chromitite seam, and, associated with these sulphides are PGM. The ratio of individual PGM in this ore is quite distinct to that of the Merensky Reef, and it is in particular much richer in Ru and Rh than the Merensky.

The reserves of PGM available in South Africa are reputed to be in excess of 42000 t. This includes those in the Merensky Reef and the UG-2 reef, where exploitation has only just begun.

Secondary Metals

The consumption of PGM by industry increased by a factor of ~50 between 1930 and 1980. This vast increase in consumption has been matched by the growth of the secondary metal industry since most of the metals are used in products from which they may eventually be recovered for recycling. The major uses of the metals today are as follows:

> electrical and electronic usage 40%; chemical industry (catalysts) 30%; auto-exhaust catalysts 10%; petrochemical catalysts 10%; fabricated ware 10%.

Recycled material from these uses falls into one of two categories:

(I) high and medium grade scrap includes supported and gauze catalysts, fabricated ware, etc., and usually has a PGM content of >10%, or is associated with an easily separated substrate (e.g. carbon supported catalysts). These materials can be recycled directly to a secondary refinery for treatment and recovery of the individual PGM.

(II) low-grade scrap. This includes much material from the electronics industry in the way of obsolete equipment and production scrap, and the PGM are usually present in low amounts on mixed metallic/non-metallic materials. Certain low-grade catalysts, e.g. auto-exhaust catalists, alumina-supported petroleum catalists, etc. also fall into this category, as well as low-grade byproducts from the secondary refiners themselves. These materials are usually treated by Pd or Cu smelters, and are removed from the base metal circuits in the form of byproducts where they may be sufficiently concentrated to allow final refining to take place.

By 1981 it is estimated that ~100 t p.a. of PGM scrap in one form or another was being recycled via secondary metal refiners. This may be compared with total world production of new metal of ~200 t p.a. in that year.

1.3 The Production of PGM Concentrates from Sulphide Ore-bodies

Almost all ores that are treated today for their PGM content contain less than 10 ppm PGM in association with a relatively large amount of Cu, Ni, and Fe sulphides. The initial steps in the recovery of the PGM are thus very closely related to the recovery of the associated base metals, and the processing only becomes distinct once a concentrate containing the PGM can be separated from the base metals.

The following description of the early stages in the processing of the ore applies to the South African producers. The technology used by Russian and Canadian producers is similar in principle but does vary somewhat in detail, as a result of the slightly differing mineralogy of these deposits.

The ore is first crushed and then milled to the desired "liberation" size. On South African ores of a relatively fine-grained character, this is usually 75% <70 μm. The finely ground ore may then be treated by a gravity separation technique to remove some of the PGM (±20%) as a rich As/Te heavy mineral concentrate, although this is by no means essential. This concentrate is rich enough to be treated directly by the PGM refinery.

The sulphide minerals are then recovered from the ore by froth flotation. Usually ~5 to 10% of the ore appears in the concentrate, and this contains ±80% of the PGM and Cu and Ni sulphides. The grade of PGM in the concentrate is thus ~100 ppm and the nickel content 5 to 10%.

The flotation process may be varied to include differential flotation of Ni and Cu minerals. Thus, at Inco, it has been found possible to selectively float chalcopyrite, pendlandite, and pyrrhotite to produce separate concentrates for processing. This may be a distinct advantage for further processing, especially if the PGM are only of minor economic significance, but this does not apply to South African ores.

Further upgrading of the concentrate usually takes place by smelting. This was formerly done in blast furnaces, but all new plants have been built on the basis of electric smelting.

The concentrate, dried and sometimes agglomerated, is fed via chutes between the electrodes to form a cold top.

The electrodes usually in an in-line pattern, are spaced ~1.5 to 2 m apart, and heating takes place by means of the ohmic resistance of the molten slag layer between the electrodes. The sulphide minerals melt and collect at the bottom of the furnace as a matte layer, which is tapped off intermittently while slag runs over an end weir continuously.

Typical operation is at a temperature of 1250 to 1350°C. The composition of the matte produced – "green matte" is dependent on the Ni and Cu content of the concentrate. In South Africa a typical composition would be Fe 40%, Ni 20%, Cu 10%, S 30%, PGM 500 to 1000 ppm. Recovery of valuable metals in the matte is very high – usually $>98\%$, so that the slag is normally discarded, although at Rustenburg Platinum Mines (RPM) a slag grinding/flotation circuit was formerly used.

Although the operation is in essence a melting, some incidental oxidation of sulphur takes place, and the furnace off-gases contain a low concentration, 1 to 2%, of SO_2. This is of considerable concern from the atmospheric pollution that results. Furnace gas is also very dusty and is cleaned before discharge to atmosphere via a tall stock, the dust being returned to the furnace.

The matte phase formed in this operation is an excellent collector of the precious metals, and losses in the slag are almost entirely due to mechanical causes (entrainment of matte prills). It is also an excellent collector of various other minor constituents of the ore, such as Se, Te, As, Sb, Pb, Co, Bi, etc., and these are thus concentrated along with the PGM.

The next step in the processing is the converting operation in which S in the green matte is partly oxidised to SO_2, and Fe oxidised in the presence of SiO_2, to form a fayalite slag. This operation is usually carried out in convertors of the Pierce-Smith type although rotary top-blown convertors are also used. Converting practice also varies somewhat from plant to plant, depending on the route that will be used to process the white matte. On South African plants it is usual to produce a matte with a composition of Ni 50%, Cu 25%, S 22%, Fe 1 to 2%, PGM 2000 to 4000 ppm.

A rich SO_2 stream is produced from the convertor during the blowing, but the production is, of course, intermittent, and this leads to problems in controlling the conversion to H_2SO_4 on smaller plants. On larger plants, a number of convertors are operated in a staggered fashion giving a reasonably steady SO_2 stream.

The slag from the converting operation contains considerable oxidised and entrained Cu and Ni values, and is returned to the smelter where the entrainment settles out and oxides are recovered by reactions such as $NiO + FeS \rightarrow NiS + FeO$.

A number of alternative methods to the electric smelting/converting route are practised outside South Africa. In Botswana a Cu-Ni concentrate is flash-roasted by the Outokumpu route to produce a matte which is low in PGM.

In Canada and the USSR, where separate Cu and Ni concentrates are produced, a rather different philosophy is followed. Cu concentrates are smelted and converted to blister copper along the line practised in conventional copper practice. Cu anodes are then electro-refined and the PGM recovered from the anode mud formed during the electrolysis.

The Ni concentrates are roasted in fluidised bed roasters to remove S virtually completely. The dead-roasted concentrate is then selectively reduced with coke in an electric furnace to produce Ni metal and an iron-oxide slag. The associated PGM are reduced into the metal and are thus concentrated in the Ni. Ni is then refined either by electro-refining or by the Mond carbonyl process. In either case the PGM are recovered from the residues (anode slimes or carbonylation residue) remaining after the bulk of the Ni has been refined away.

Most Pt, if not other PGM, is however, produced by the route previously described, i.e. smelting and converting to produce a high-grade Cu-Ni matte. This is treated further in one of two ways:

(a) direct matte leaching in which the Cu, Ni, and S are removed by leaching processes of which several are practised, or

(b) by the matte slow-cooling/magnetic separation route.

Direct matte leaching processes may be divided into two types: oxidative leaching and non-oxidative leaching. In the oxidative processes, mattes are finely ground and then leached under mildly acidic or buffered pH conditions using O_2 under pressure. Cu and Ni sulphides are converted into their corresponding sulphates. The processes are usually staged so that initially only Ni is dissolved, leaving Cu and residual Ni sulphides to be dissolved under more stringent conditions. The PGM, because of their nobility and tendency to passivate strongly in H_2SO_4 solutions tend to remain in the insoluble fraction together with a number of other minor constituents of the matte. Nevertheless, because of their high value, the solutions obtained from the leaching processing must be treated, usually by cementation with Cu scrap, to recover the small PGM content. The Cu und Ni are recovered from solution by electrowinning or H_2 reduction processes.

In the non-oxidative process of Falconbridge, finely divided matte is leached with hydrochloric acid. Ni, Co, and any Fe in the matte are dissolved and H_2S is produced; the residue consisting of Cu sulphides and PGM and other constituents of the matte. This is then roasted to produce $CuSO_4$ which is leached leaving a PGM-enriched residue.

Typically, the matte-leach residue or PGM concentrates produced by these routes are complex materials, containing, besides PGM, substantial quantities of other metals. These include Cu, Ni, Fe, and SiO_2 in major quantities, and smaller amounts of Se, Te, As, Sb, Bi, Sn, Co, etc. The PGM content of the material can vary widely, depending upon the efficiency of the leach and the actual leach process used. Normally, a concentrate grade of between 20% and 50% is achieved, and this is suitable for further treatment in the refinery.

Higher grade and simpler to treat concentrates are obtained by the matte slow-cooling process. In this, molten matte is cast into covered moulds and allowed to cool and solidify over a period of 2 to 4 d. During this slow-cooling, the matte crystallises into sulphide and Ni-rich phases in accordance with the phase – equilibrium diagram. The PGM and Au with some other constituents, notably As and Sb, have a strong tendency to migrate into the metallic phase and, provided the cooling is slow enough to allow equilibrium to be approached, up to 98% will collect in this phase.

The slow-cooled matte is then crushed and milled, and the metallic fraction separated from the sulphides by magnetic means. Typically, the magnetic fraction comprises 5 to 10% of the original mass of matte. The PGM content of the magnetics is correspondingly increased, to the 2 to 4% level.

This metallic material can now be leached under non-oxidising conditions to remove the bulk of the nickel, leaving some Cu und Ni sulphides with the PGM. This can be further upgraded by leaching under oxidising conditions to give a final concentrate containing 40% to 60% PGM, the remainder being largely Cu and Ni.

The small amount of PGM reporting with the sulphides is recovered from the matte leach circuit as a low-grade concentrate together with Se, Te, and Ag. The material is treated in a manner similar to that described for anode slimes (see below) to separate the metals and produce a high-grade PGM concentrate.

1.4 Production of PGM Concentrates from Low-Grade Scrap and Other Minor Sources

The Copper Smelting – Refining Route

Considerable amounts of copper-based precious metals bearing scrap are processed by secondary copper refiners. The main precious metals involved are Ag and Au, but Pd, Rh, Ru, and Pt are also used in printed circuits and contacts, etc.

Such scrap materials are normally incinerated to remove non-metallics such as insulation, etc. and then smelted in the copper reverberatory furnace, together with ores, other copper scrap, and fluxes. The Cu matte produced in this way is blown in a convertor to remove Fe, S, and other impurities, and then cast into anodes for electro-refining.

The anode slime produced from the electro-refining process is greatly enriched in the precious metals and would contain, after preliminary removal of Cu contamination, 10 to 25% Ag, 1 to 2% Au, and usually <1% PGM together with Pb, Sn, Cu and other metals and metalloids. This material may be treated by roasting and leaching operations to remove Se and Te if these are present in significant amounts before being smelted in the Doré furnace.

This is a small reverberatory furnace in which the material is melted and can be reacted with various oxidising fluxes which remove almost all of the base metal impurities, thus producing Ag bullion, which contains Au and the PGM.

The Ag bullion is then electro-refined in Moebuis or Tums cells to produce fine Ag crystals. The Ag anode slime still contains considerable Ag as well als Au and the PGM, and this is leached in HNO_3 to remove Ag as the nitrate. Evaporation of this solution to the point of fusion of silver nitrate precipitates any PGM dissolved, as oxides.

The Au/PGM concentrate resulting from this is treated in different ways depending upon its composition. Material low in PGM may be melted and cast in anodes and electro-refined by the Wohwill process. In this case the PGM accumulate in the electrolyte which must be periodically removed, and Au precipitated, and the PGM recovered from solutions.

Material having a higher PGM content is usually dissolved directly in aqua regia or HCl/Cl_2. The Au is then precipitated by selective reduction with SO_2 or, more recently, is removed by selective solvent extraction.

In either case a solid PGM concentrate is not obtained, but rather an impure solution containing the PGM.

Treatment of PGM-rich Doré metals is most often done in assocation with refining of other PGM scraps.

The Lead Smelting and Refining Route

The Pb smelting process has very favourable thermodynamics for both the collection of precious metals and their subsequent recovery from the Pb bullion.

Large lead smelters, such as the one of Metallurgie Hoboken Overpelt (MHO) at Hoboken are very flexible in operation, and handle a wide variety of Pb and Cu containing scrap materials. These materials can contain small amounts of PGM, but because of the large scale of operation the total quantity produced per annum can be significant.

Scrap materials are blended with lead concentrates and fluxes and smelted in blast furnaces. The result of this operation is to produce, usually, four liquid phases: a slag which is discarded; a matte which contains most of the Cu in the charge; a speiss containing Ni, Cu, and the speiss-forming elements As, Sb, and Sn, and a Pb bullion. Most of the Au and Ag in the charge report to the Pb bullion, and are recovered from there as Zn alloys by the Parkes Pb bullion purification process.

The PGM report mainly to the speiss, and since the quantity of this material produced is usually a small fraction of the mass of the feed material, they are considerably enriched in this phase. The treatment of speisses varies considerably and processes ranging from totally hydrometallurgical to pyrometallurgical are used. One route uses pyrometallurgical processes to oxidise As, Sb, Pb, etc. and to remove them as fumes and slags, so producing a Cu-Ni alloy containing the PGM. This is then leached to produce a Cu-Ni sulphate solution leaving the PGM as an enriched residue, which is then refined in the normal way.

Small captive Pb smelters are usually used to process precious metals containing scrap. The operations at Sheffield Smelters are typical. Scrap materials are calcined, mixed with PbO, S, and C, and smelted in an electric furnace. A discard slag, Cu matte, and a rich Pb-Ag bullion containing the PGM are produced.

The Pb-Ag bullion is then treated by cupellation to produce PbO for recycle to the smelt, and an Ag bullion which is electro-refined as described previously.

In both Cu and Pb smelting processes small additional amounts of primary PGM are recovered from the ores together with that contained in the scrap materials. The total amount of primary PGM produced from Cu and Pb ores is, however, not significant ($<1\%$) in terms of total world production. The amount of recycled material recovered in this way is in contrast, highly significant, and amounts to several thousand kg per annum.

Auto-Exhaust Catalysts

Recovery of PGM from automobile exhaust catalysts will become a distinct sector of the PGM industry in future in view of the considerable quantities of recovered PGM that will become available. It is estimated that from 1983 onwards upwards of 21000 kg per annum of PGMs in this form will be potentially recoverable in the USA alone. However, significant difficulties are expected in collecting spent catalyst for re-working.

The material contains 500 to 2000 ppm of PGM (Pt + Pd + Rh) on a refrectory base, either alumina or cordierite. The material can be treated directly by leaching with aqua regia or HCl/Cl_2, but the reagent consumption is high and recoveries seldom exceed 80%.

For this reason it appears likely that a smelting route will have to be used and numerous trials using conventional (submerged arc) and plasma smelting equipment have been performed. The material is blended with a flux and a collector metal oxide. Cu, Fe, and Pb have been suggested as collectors. Lime is used as the flux for high alumina materials, and a lime-silica mix for cordierite.

Smelting temperatures are much higher than normally used in either Pb or Cu metallurgy. The bullion produced in the process would have a PGM content of 1 to 10%, and would have to be upgraded by leaching or electro-refining to produce a concentrate amenable to final refining.

1.5 The Refining of Platinum Metal Concentrates

General Principles

Many of the processes that are still used today were originally developed early in the nineteenth century. It is only comparatively recently that the principles of modern inorganic chemistry have been applied to the understanding and the development of the process for the refining of the metals. The chief features of their chemistry relevant in the industrial processes are therefore briefly outlined below.

The transition metals in general, and the PGM in particular, are distinguished by two outstanding features. These are:

(a) The large number of stable oxidation states of the elements. These range from -2 to $+8$ for the platinum metals; the extreme cases being those of Ru and Os.

(b) The very large number of complexes formed by the metals with anionic and neutral ligands. This tendency is also carried to the extreme in the case of the PGM, so that in aqueous solutions at least, the simple metal ions are hardly ever encountered.

Most transition metals are classed as "A"-type in the definition of Bronsted-Lowry, i.e. they are "hard" Lewis acids and form σ-bonded complexes with "hard" Lewis bases such as F^-, NH_3, and O^{2-}. The PGM, on the other hand, are "soft" acids and tend to form π-bonded complexes with ligands such as S^{2-}, SCN^-, thiourea, phospines, etc. The type of complex formed is, however, greatly dependent on the oxidation state of the metal; the lower the oxidation state, the "softer" the behaviour of the metal. Thus Ru, for example, will form π-bonded complexes with ligands such as $(Ph)_3P$ in the $+2$ oxidation state, chloride complexes in the $+3$ and $+4$ oxidation states, and F^- complexes in the $+6$ and $+8$ states. Adjustment of the oxidation state of the metals to alter the stability of the complexes formed by the individual metals is a frequently used technique in the refining process.

The complexes of PGM differ from those of most transition metals in their reactivity. Ligand substitution reactions are almost instantanenous for all base metals except Cr^{III} and Co^{III}, but for PGM the rates of equivalent reactions range from slow to almost complete inertness. This is largely a function of the type of complex formed; square-planar complexes which can undergo S_N2 type reactions are fairly labile, whereas octahedral complexes where S_N1 type mechanisms dominate, are in comparison very inert. This is also often used in separating one PGM from another, but also complicates the process by preventing true equilibrium conditions to be obtained in an industrial process. Possibly the best known property of the PGM (together with Au) is their noble character. This is in practice a complex property which depends on both thermodynamic and kinetic effects.

All of the metals can only be dissolved under rather strongly oxidising conditions, even in complexing media such as HCl. The practical order of nobility of the metals is, however, much more strongly influenced by kinetic phenomena involving the formation and very slow dissolution of passivating layers, usually oxides.

For this reason Ru and Ir, for example, are normally immune to attack by aqua regia even though they are considerably less noble in the thermodynamic sense than Pt, which is fairly readily dissolved. Passivation phenomena are strongly influenced by alloying of the metals, and this technique is used both to enhance and eliminate passivation phenomena. Use is made of this property in the cementation process (separation from base metals), and in the separation of certain of the PGM from each other.

The Chemistry of Aqueous Chloride Solutions of the Metals

Since the PGM are most conveniently dissolved in HCl under oxidizing conditions, almost all refining operations are carried out in solutions containing high concentrations of Cl^- ions.

The stable oxidation states of the platinum metals in 1 M Cl^- solutions are shown in the table below.

redox potential	Ru	Rh	Pd	Os	Ir	Pt
reducing	+2	+3	+2	+2	+3	+2
↑	+3	+3	+2	+3	+3	+4
	+3	+3	+2	+4	+3	+4
	+4	+3	+2	+6	+4	+4
↓	+6	+4	+4	+8	+4	+4
oxidising	+8	+4	+4	+8	+4	+4

From this table it can be seen that control of the solution oxidation potential can be used to effect several separations. Under very highly oxidising conditions Os and Ru will be converted to the +8 oxidation state where they form the volatile tetroxides OsO_4 and RuO_4. These differ in their stability and by adjusting the potential again they may be separated. Pt can be separated from the others on the basis of the greater stability of the +4 oxidation state under mildly reducing conditions, and Ir separated from Pd and Rh on the same basis under more strongly oxidising conditions.

Many of the separations are based on the properties of the chloro-complex anions formed by the metals in Cl^- solutions. The complexes found in Cl^- solutions are listed for the metals in their most common oxidation states in the next table.

As can be seen from this table there are a number of differences in behaviour of the Cl^- complexes. In the first place, they differ considerably in their stability, Pt and Pd complexes being very stable, while those of Ir^{III}, Os^{III}, Rh^{III}, and Ru^{III} undergo aquation to form mixed aquo-chloro complexes at low Cl^- strenghts.

Secondly, the anionic change on the complexes are −2 for the +2 and +4 oxidation states and −3 for the +3 oxidation state.

metal	oxidin. state	complex formed low ⟵ Cl^- concentration		⟶ high
Ru	+3	$Ru_2OCl_8(H_2O)_2^{4-}$		$RuCl_6^{3-}$
	+4			$RuCl_6^{2-}$
Rh	+3	$Rh(H_2O)_6^{3+}$	$Rh(H_2O)_3Cl_3$	$RhCl_6^{3-}$
Pd	+2	$PdCl_4^{2-}$		$PdCl_4^{2-}$
Os	+3			$OsCl_6^{3-}$
	+4			$OsCl_6^{2-}$
Ir	+3	$Ir(H_2O)_3Cl_3$		$IrCl_6^{3-}$
	+4	$IrCl_6^{2-}$		$IrCl_6^{2-}$
Pt	+2	$PtCl_4^{2-}$		$PtCl_4^{2-}$
	+4	$PtCl_6^{2-}$		$PtCl_6^{2-}$

Both of these factors assist in separation by solvent extraction, ion exchange, and precipitation type reactions. For example, the large anion $PtCl_6^{2-}$ forms a series of very insoluble salts with large unipositive cations, and precipitation of $(NH_4)_2PtCl_6$ is a very important separation technique in the industry. Under conditions of low Cl^- strength and mildly reducing conditions, Ru, Os, Ir, and Rh will form mixed aquo-chloro complexes, whereas Pt and Pd will still be full anionic species. This can be used to effect group separations.

A further class of reactions which are important in the refining process involve ligand substitutions. The reactivity of the chloro complexes with other ligands is in the order $PdCl_4^{2-} \gg PtCl_4^{2-} > RhCl_6^{3-} > OsCl_6^{3-} > (Ru,Ir)Cl_6^{3-} \gg (Pt,Ir,Ru,Os)Cl_6^{2-}$.

Because of these very great differences in reactivity, it is possible to separate Pd for example from the metals by reactions such as $PdCl_4^{2-} + 2I^- \rightarrow PdI_2 + 4Cl^-$, and this type of reaction forms the general basis for separating Pd from the other metals.

The extreme inertness of the $PtCl_6^{2-}$ anion is used in the converse manner in operations such as the bromate hydrolysis (see below). During this separation $PtCl_6^{2-}$ is unchanged while the other metals undergo aquation and hydrolysis to be precipitated eventually as hydroxides.

The Standard Process

The process discussed in this section represents the classical process as it has been developed over the years. For Pt and Pd very little variation from this standard is practised, but for the other metals a greater variety of methods are still used.

The PGM concentrate is usually in the form of a finely divided powder containing metallics, oxides, sulphides, selenides, etc. This is usually roasted in oxidising conditions at a temperature between 600 and 900°C. This serves to remove the bulk of the S and Se contained in the concentrate. In addition, a substantial amount of oxidation of the metals occurs together with segregation of the minor metals from Pt and Pd. Thus following this operation the base metals are present mainly as oxides, as are Pd, Ru, Ir, and Rh, whereas Pt and Au are mainly in a metallic form.

The concentrate is then leached in HCl using either HNO_3 or Cl_2 as the oxidising agent. The objective of the leach is to dissolve as much of the primary metals (Pt, Pd) and Au as possible without effecting substantial co-dissolution of the minor metals. The concentration of the HCl acid used is thus between 4 M and 6 M, and under these conditions the oxidised portion of the metals is hardly attacked at all. It is normally found that over 90% of the Au and Pt content of the concentrate can be dissolved, 70 to 80% of the Pd (due to its greater extent of oxidation in the roast) and 10 to 20% of the minor metals, together with a variable proportion of the base metals.

The leach liquor is then filtered to remove the undissolved portion and evaporated to remove residual HNO_3 if this has been used in the leach. The free HCl concentration is adjusted to 1 to 3 M by dilution and any AgCl that precipitates is removed by filtration before the reduction of Au.

Au is precipitated by reduction to metal. This is usually done by bubbling SO_2 gas through the solution until Au precipitation is evident. Thereafter $FeSO_4$ solution is added slowly to reduce the remaining Au to metal without any danger of over-reduction and co-precipitation of PGM. In modern practice the solution potential is measured and this is used to control the addition of the reductant. The residual concentration of Au left in solution can be controlled to <5 ppm.

During the reduction Pd, Ir, Ru, and Os are reduced to their lower stable oxidation states, whereas Pt remains mainly as Pt^{IV}.

The purity ot the Au precipitated in this way is usually not high enough for sale. The major impurities are Ag and the PGM. The crude Au precipitate is usually treated by redissolving it in aqua regia and repeating the precipitation.

The solution, after precipitation and filtration of the Au, is in a form suitable for the precipitation of Pt, although it is now common practice to check and, if necessary, adjust solution potential before the precipitation is commenced.

Pt is precipitated as $(NH_4)_2PtCl_6$ by addition of NH_4Cl solution to the pregnant liquor. This is done slowly over a period of some hours, and a reasonable excess is finally added to depress the solubility of the Pt salt. The precipitation is close to quantitative and usually <50 ppm Pt remains in solution. Of the PGM, Ir has the greatest tendency to co-precipitation, but the crude salt usually contains small quantities of all of the PGM, as well as occluded base metal chlorides.

The crude salt is dried and calcined at 700°C to produce a crude Pt sponge of purity 97 to 99%. This is redissolved in aqua regia of HCl/Cl_2 and the resulting solution boiled down with NaCl to form sodium chloroplatinate, Na_2PtCl_6. This very soluble salt is then re-dissolved in water, and the solution purified by means of the "bromate hydrolysis". In this procedure $NaBrO_3$ and $NaHCO_3$ solutions are added. The solution potential is thus raised to a very high value as the pH is slowly increased to a final value near 7. Pt remains as $PtCl_6^{2-}$ while base metal and PGM complexes are converted into insoluble hydroxides which are removed by filtration. Pt is then precipitated from the purified solution, after acidification, as the ammonium salt as before.

The "bromate hydrolysis" residue usually contains a substantial amount of Pt either entrained in the rather gelatinous hydroxides or co-precipitated as hydroxide. It is therefore recycled to the beginning of the process to allow the Pt to be recovered.

The solution from the initial precipitation of Pt contains Pd, traces of Pt, most of the minor PGM originally dissolved and substantial quantities of base metal chlorides. This solution is neutralised while hot with aqueous NH_3. Pd is converted into the tetrammine complex, $Pd(NH_3)_4^{2+}$. Most base metals are hydrolysed (except Cu) to form hydroxides. The minor metals are partly amminated and partly precipitated. The solution is filtered and Pd precipitated as the sparingly soluble complex $Pd(NH_3)_2Cl_2$ on addition of HCl to $pH = 1$. Base metals are redissolved as chlorides and the PGM are also mainly soluble as mixed ammino-chloro complexes.

The crude "Pd-salt" is then purified by redissolution in cold aqueous NH_3. Small amounts of PGM ammine complexes co-precipitated with the Pd, are not redissolved and can be removed by filtration. Pd is then reprecipitated as $Pd(NH_3)_2Cl_2$, and this "salt" finally calcined to produce pure Pd sponge.

All effluent solutions from the refinery are treated with Zn in cementation vats to recover the PGM values they contain. This procedure is normally adequate to recover Pt and Pd. The minor metals, especially when present in solution as ammine complexes, are very slow to be reduced, and significant amounts of these metals are lost in the final effluent from the plant.

Zn cementation residues, the initial leach residues and other waste products are combined with PbO, C, and fluxes and smelted together to form a Pb bullion. Pd and Pt are very soluble in molten Pb, but the minor metals form intermetallic compounds with Pb and these crystallise from the melt as separate phases.

The Pb bullion is treated by a number of separate leaching steps as follows:

(a) An initial weak HNO_3 leach is used to dissolve most of the Pb, base metals, and Ag. This is treated to recover Ag as AgCl and Pb as $PbSO_4$. The $PbSO_4$ is then converted into $PbCO_3$ using Na_2CO_3 and recycled to the smelter.

(b) A second HNO_3 leach dissolves most of the remaining Pb and Pd in the residue. Pb is precipitated as the sulphate and Pd then recovered, after removal of HNO_3 by the route described previously.

(c) Pt and Au are then dissolved using aqua regia or HCl/Cl_2 and the solution is recycled to an appropriate point in the process.

The result of these operations is to produce a concentrate greatly enriched in the minor PGM, with Ru the major constituent at least for South African concentrates.

There are a number of different methods of treating such concentrates, and the following description represents only one among many that are in fact used at various refineries.

The concentrate is fused with a mixture of Na_2CO_3 and Na_2O_2 at 600 to 700°C. The PGM are oxidised to high oxidation states and form oxo-anions such as RuO_4^{2-}. The melt is cooled and allowed to solidify and then leached with water.

Ru and Os are dissolved as RuO_4^{2-} and OsO_4^{2-}, respectively, while Rh and Ir are precipitated as oxides. It is normal not to separate the oxides at this stage but to remove Ru and Os from the solution by oxidising them to the volatile tetroxides directly with Cl_2.

Ru and Os are further separated by collecting the tetroxides in HCl. Ru is reduced to the $+4$ oxidation state, but OsO_4 is not reduced and can be separated by redistillation. OsO_4 is then collected in alcoholic NaOH where it is reduced to OsO_4^{2-}.

Ru is recovered from the collecting solution by precipitation of $(NH_4)_2RuCl_6$, salt similar to the equivalent Pt salt except that is has a considerably greater solubility. Os is most often precipitated as $(NH_4)_2OsCl_6$ or OsO_2 and retained in that form since the metal tends to volatilise in air by formation of OsO_4.

The hydroxide residue, containing Ir and Rh is dissolved in HCl fo form $RhCl_6^{3-}$ and $IrCl_6^{2-}$. Ir is then precipitated as $(NH_4)_2IrCl_6$ by adding NH_4Cl solution.

Finally Rh is recovered by forming the pentammino-chloro complex $[Rh(NH_3)_5Cl]^{2+}$. This is done by heating the solution and adding aqueous NH_3 in the presence of alcohol as a catalyst. $[Rh(NH_3)_5H_2O]^{3+}$ is initially formed and the complex salt $[Rh(NH_3)_5Cl]Cl_2$ is precipitated on addition of HCl.

Alternative Classical Procedures

While the process described on pp. 10/1 represents that most widely used at least up until 1975, the chemistry of the PGM is obviously sufficiently versatile to support many other process options, a number of which are still used in various refineries. The list below does not include the more recent techniques of ion-exchange and solvent extraction.

The alternatives to the main classical procedures are listed in terms of their application to the separation of a particular metal or group of metals below.

Platinum. One of the major objections to the classical procedure for purification of Pt is the health hazard introduced during the handling of the metal in the salt form. This has led to a number of alterations to the basic procedure to alleviate this problem.

In one technique the salt is washed off the filter after the initial precipitation and the aqueous slurry reduced with HCOOH, NH_2OH or HN_2NH_2 to produce Pt^{II} which is soluble as $PtCl_4^{2-}$. The solution is then slowly oxidised to re-form $(NH_4)_2PtCl_6$, leaving the impurities in solution. An alternative is the direct reduction of $(NH_4)_2PtCl_6$ to Pt metal in aqueous media. This is accomplished with NH_2NH_2. The metal can be handled safely and is then purified by the bromate hydrolysis procedure. Final metal production takes place directly from the purified solution by reduction rather than by precipitation of the salt and calcination.

Palladium. The intitial precipitation of $Pd(NH_3)_2Cl_2$ is sometimes replaced by precipitation of $(NH_4)_2PdCl_6$. This is done by oxidising Pd^{II} to Pd^{IV} in the presence of NH_4Cl with HNO_3. The precipitation is not selective against most other PGM, but is useful if the mother liquor is highly contaminated with base metal chlorides. The initial "red salt" is then dissolved by boiling in water when Pd is reduced to Pd^{II} and further processed in the normal way. The final precipitation of $Pd(NH_3)_2Cl_2$ followed by calcination to produce metal sponge can also be replaced by direct reduction of $Pd(NH_3)_4^{2+}$ to metal using HCOOH.

A number of techniques are used to remove small quantities of Pd from solutions containing other PGM. Chief amongst these are the iodide and dimethylglyoxime precipitation techniques and these rely for their selectivity on the fast reaction kinetics of Pd.

Ruthenium and Osmium. Although these metals are almost always recovered by distillation of the tetroxides, there is considerable variation in the method used to achieve this.

Os can be selectively distilled from weakly acidic media using HNO_3 as the oxidant. Under these conditions RuO_4 is not formed.

Ru can also be oxidised to RuO_4 in acid medium ($pH \approx 1$) using very strong oxidising agents such as ClO_3^-, but it is obviously more difficult to achieve complete removal under these conditions than it is from alkaline conditions.

Ru is sometimes separated from the metals by hydrolysis. $NaBrO_3$ will oxidise RuO_2 to RuO_4^{2-} at $pH > 11$. The solubility of the other PGM and most base metals is very limited at this pH, and the ruthenate solution can thus be purified by filtration of the hydroxide residue. RuO_2

is then precipitated by reduction of the solution with ethanol, and this can be dissolved in the HCl and ammonium chlororuthenate, $(NH_4)_2RuCl_6$, finally precipitated.

Iridium. A wide variety of techniques are used to purify Ir solutions. These almost always involve the selective removal of the contaminating elements in the solution by precipitation reactions. This is a reflection of the extremely inert character of the Ir complexes which allows removal of contaminants by reactions which are thermodynamically unselective.

Rhodium. This metal is recovered and purified by a very wide range in procedure. This is not only a reflection of its very versatile chemistry, but perhaps also due to the generally rather poor results obtained by all of these techniques in terms of overall yield and single-pass purity. Some of the major alternative techniques used in the processing of rhodium-rich materials are:

(1) Bisulphate fusion techniques.

Here the concentrate is roasted to convert as much of the PGM as possible into oxides. The calcine is then sintered at 400 to 500°C with $NaHSO_4$. Rh is converted into water-soluble $Rh_2(SO_4)_3$. Other PGM oxides are not attacked or are converted into hydroxides when the cooled sinter is leached with hot water, but base metals are taken into solution. Rh is present in the leach solution mainly as the yellow aquo ion $Rh(H_2O)_6^{3+}$ – one of the few cases where aquo ions of the PGM are present in more than trace amounts.

Rh is precipitated from the solution by hydrolysis as the "hydroxide" at $pH = 5$, and is then redissolved in HCl for further processing.

(2) Formic acid precipitation.

Rh is sometimes finally precipitated from its purified chloride solution by reduction with HCOOH. This reduction has been shown to proceed through the intermediate formation of a Rh^I carbonyl complex, which is unstable and decomposes to metal. The reduction is fairly selective against most base metals and Ir and Ru but not against Pt, Pd, Ag, or Au. The method therefore is used only as a final precipitation from previously purified solutions.

(3) Complex precipitation techniques.

Rh forms a wide variety of slightly soluble complex salts and a number of purification techniques involve the formation of such complexes.

Inco has made use of the hexanitro complex salt $Na(NH_4)_2Rh(NO_2)_6$ extensively in its refinery, mainly as technique for removing base metal contamination from rhodium.

The hexachloro complex $RhCl_6^{3-}$ can also be precipitated in a fairly selective manner; the ammonium salt, $(NH_4)_3RhCl_6$, is, however, rather soluble so that yields are poor. Very much better yields are obtained by the use of ethylenediamine which precipitates the salt $[enH_2^{2+} \cdot enH^+] = RhCl_6^3$. This salt can be redissolved in aqua regia which oxidises the en, so releasing the Rh chloro anion.

The "chloropentammine" precipitation technique discussed previously is sometimes followed by conversion of the salt to the nitropentammine nitrate, $[Rh(NO_2)Cl_5](NO_3)_2$. This latter salt can be recrystallised well, its solubility increasing rapidly with temperature. Very high purity Rh can be made using this technique.

(4) Chlorination techniques.

Rh is sometimes treated by dry chlorination to convert it to a polymeric $(RhCl_3)_n$. This is extremely insoluble and may be partially purified of other PGM and base metals by leaching with aqua regia. The chloride is then reduced to metal which, if not of the required purity, is redissolved and the solution further purified.

1.6 Solvent Extraction Techniques

General Principles

Although the application of solvent extraction procedures to the refining of the PGM is relatively new, these methods have become well established in the industry and are of sufficient importance to justify a full description.

Solvent extraction procedures are almost always applied to chloride solutions of the PGM. As shown previously, the metals are almost always present in such solutions as anionic complexes, and thus the major techniques of use in the purification of the metals is anion exchange.

Anion exchange separation of the PGM is based on two features:

(1) Separation of full chloro complexes on the basis of differences in anionic charge and size. In general, the greater the equivalent weight of the anion, the easier it is to extract into a nonpolar solvent by means of an anion exchange reaction such as $MCl_m^{n-} + nR^+Cl^- \rightleftharpoons R_n^+MCl_m + nCl^-$ (R^+ is an organic, soluble cation).

(2) Separation of the metals on the basis of differences in stability of their chloro complexes. In solutions of low chloride strength it is possible to separate Rh and Pt, for example, by "aquating" the Rh chloro complex to form the non-extractable neutral complex $Rh(H_2O)_3Cl_3$. $PtCl_6^{2-}$ is not affected, and can be easily extracted. Because the PGM have such slow reaction kinetics, these separations depend upon achieving the desired equilibrium state before extraction takes place; adjustment to equilibrium will not happen automatically during the extraction process as occurs during anion exchange of base metal chlorides.

Complex formation extraction procedures have also been used in PGM refining. However, because of the very slow reaction kinetics of most of the PGM, these techniques are only suited to the extraction of Au and Pd, and have found industrial application only in the latter case. Typically, this type of extraction proceeds by a reaction $PdCl_4^{2-} + 2L \rightarrow PdCl_2L_2 + 2Cl^-$ where L is an organic, soluble ligand usually containing an S, N, or P atom.

Cation-exchange procedures have very little application in PGM refining, and these are confined to the minor role of removal of base metal impurities.

Anion Exchange

Anion exchange solvent extraction systems can be classified in terms of their increasing ability to extract anions as follows:

(1) Very weak base systems (solvating extractants). These are distinguished by their ability to extract anions only out of strongly acid solutions. Included in this group are reagents such as ethers, alcohols, and esters, such as tributyl phosphate (TBP). They are only able to extract anions of a high equivalent weight and are thus useful reagents in separating those PGM which form such anions. Typical examples are:

(a) The use of alcohols and ethers in extracting Au as the $AuCl_4^-$ anion, from strongly acid (6 M HCl) media; (b) the use of TBP in separating PGM chloro complexes of the type MCl_6^{2-} from MCl_6^{3-} anions.

A very useful feature of such systems is the simplicity of the back-extraction procedure; the extracted metal is recovered simply by washing the solvent with a very dilute acid when the equilibrium is reversed; for example $(TBP)_2H_2PtCl_6 \rightarrow 2(TBP) + 2H^+ + PtCl_6^{2-}$.

The solvents are usually employed at high concentration (50% to 100%) so that capacities are generally high, varying from 25 to 50 g/l extracted metal.

The major systems of this type now in use are as follows:

separation	solvent system
Au – PGM	long-chain alcohols (C_8 to C_{12})
Au – PGM	dibutyl "carbitol" (ether)
Au – PGM	MIBK (ketone)
Pt^{IV} – PGM^{III}	TBP
Ir^{IV} – Rh^{III}	TBP
$RuNOCl_5^{2-}$ – Rh^{III}, Ir^{III}	TBP

The extraction coefficients for the extracted metals range in the above systems between 5 and 100, so that a countercurrent extraction system is usually employed to obtain a high degree of extraction.

(2) Weak base (amine) systems. These extractants (primary, secondary, and tertiary amines) are typical weak bases and are protonated up to a pH value ranging between 3 and 5. They are thus capable of extracting metals by anion exchange from rather weakly acidic solutions. The extraction coefficients for PGM chloro complex anions obtainable with these systems are very much greater than is the case with first group extractants, and ranges from 10^2 to 10^4. Thus the extraction procedure is simpler than in the first case, but the selectivity obtainable is correspondingly much less. Nevertheless, because the extractions may be performed from solutions low in Cl^-, the separations obtained can be greatly improved by prior "conditioning" to aquate those metal complexes it is not desired to extract. A typical example of this approach is the separation of Pt and Pd from the other PGM (and base metals) using a secondary or tertiary amine. The solution is heated for several hours prior to extraction, allowing the trivalent PGM complexes to aquate, while base metals form simple aquo ions. $PtCl_6^{2-}$ and $PdCl_4^{2-}$ are then extracted with high efficiency while the other PGM and base metals are hardly extracted at all.

Back-extraction (stripping) of the metal from the solvent phase is very much more complex with these extractants than with the first group, and this represents a major disadvantage of their use. Several different approaches have been used for the back-extraction process:

(a) Stripping with alkali: $(RH^+)_2PtCl_6^{2-} + 2\,NaOH \rightarrow 2\,R + 2\,H_2O + Na_2PtCl_6(aq)$.

This can be used in a limited range of circumstances, mainly for Pt. The free base amine is a powerful ligand, however, and re-extraction may take place by complex formation. Thus, in the case of $PdCl_4^{2-}$ the reaction $(RH^+)_2PdCl_4 + 2\,NaOH \rightarrow PdCl_2R_2 + 2\,H_2O + 2\,NaCl$ takes place very readily, and the extraction is virtually irreversible.

(b) Stripping by ion exchange. The extraction equilibrium may be reversed in the presence of high concentrations of chloride ion: $(RH^+)_2PtCl_6 + 2\,Cl^- \rightleftharpoons 2\,RH^+Cl^- + PtCl_6^{2-}$ but this is usually an inefficient method of stripping. The back-extraction equilibria are more favourable if another highly extractable anion such as ClO_4^- is used, and complete recovery of $PtCl_6^{2-}$ can be obtained in two stages of stripping. The solvent must subsequently be regenerated by alkali stripping of ClO_4^-, and this is an obvious disadvantage.

(c) Stripping by complex formation. Here the extracted metal complex is extracted with an aqueous solution of a powerful neutral ligand, for example thiourea (TU). In the case of Pt, reduction to Pt^{II} takes place and a Pt^{II}-TU cationic complex is formed which is soluble in the aqueous solution. Further processing of such solutions presents difficulties, however.

(d) Stripping by reduction. Certain of the metals can be extracted as M^{IV}complexes and stripped from the solvent by reduction to the trivalent oxidation state. An example is Ir which is well extracted as $IrCl_6^{2-}$. It can be stripped by reduction to Ir^{III} with SO_2 or another fast reductant.

In other cases, reduction to metal directly from the organic phase has been proposed as a method of recovering the PGM, although it seems unlikely that this could be of great value in practice, except perhaps for Au.

Despite the several drawbacks, amine extraction systems have often been proposed for commercial processes, and in some cases are used in practice. Listed below are some of the processes for which they have been employed.

separation	solvent system	stripping method
PGM/base metal	primary amine	reduction to metal
Pt + Pd/PGM	2° + 3° amines	$HCl/HClO_4$
	tertiary amino acid	HCl
Pt/PGM	2° amine	alkali
$RuNOCl_5^{2-}$	3° amine	alkali
Ir^{IV}/Rh^{III}	3° amine	reduction (SO_2)

Amine extractants are usually employed in dilute solution (5% to 10%) in an inert solvent, as the ion pair formed is usually not very soluble in an organic solvent. The capacity is thus usually restricted to 5 to 10 g/l extracted metal.

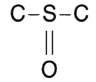
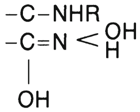
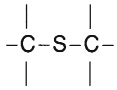
(3) Strong base systems (quarternary ammonium bases). These systems are in general very similar to the weak base systems. The chief differences are:

(a) The extractant is always cationic, i.e. there is no "free base" and the extracted metal cannot be stripped by alkalis.

(b) Correspondingly these extractants cannot form complexes with the extracted metals and their use is thus somewhat less prone to poisoning by irreversible extraction via complex formation. In other respects there is little difference in behaviour to that of the tertiary amine system and potentially they could be used in the same way. Very little attention has, however, been paid to this group of extractants for use in the PGM refining process.

Ligand Exchange Systems for Pd Extraction

Ligand exchange extraction system could be used for Au, Pd, and possibly Pt^{II}. Anion exchange systems are so simple in the case of Au and Pt, however, that there would be little incentive in developing ligand exchange extractants for these metals, and their use has therefore been confined to the extraction of Pd. Many long-chain organic molecules are known to complex Pd well. These include the following types of compound:

alkenes	$-C=C-$	sulphoxides	 $C-\underset{\displaystyle O}{\underset{\|}{S}}-C$
nitriles	$-C\equiv N$		
amines	$-C-NHR$		
oximes	 $-\underset{\displaystyle OH}{\underset{\mid}{C}}=N<^{OH}_{H}$		
		sulphides	 $-\underset{\mid}{\overset{\mid}{C}}-S-\underset{\mid}{\overset{\mid}{C}}-$

These are all typical soft Lewis bases capable of forming strong bonds with Pd^{II}.

Of the above, amines, oximes, sulphides, and sulphoxides have received the most attention. Amines will, of course, only form complexes with Pd^{II} at fairly high pH values and will extract other PGM by an anion exchange mechanism at lower pH values. Their use is thus restricted to one of acting as a "catalyst" for increasing the rate of extraction of Pd by other ligand exchange solvents, notably the oximes. Commercial oximes have been proposed for this application, notably Lix 64 N, an aromatic oxime. The extraction rate is apparently sufficiently great to allow the use of continuous flow equipment.

Since the formation of the complex involves removal of a proton from the hydroxy-oxime group, the equilibrium will be pH-dependent, and Pd can therefore be stripped with fairly concentrated HCl.

The reagent is used as a 5% solution in an inert solvent so that the capacity for Pd is restricted to a low value of ~10 g/l.

Organic sulphides are more commonly used. Both hexyl and octyl sulphides have been found to give a satisfactory rate of extraction, although this is always fairly slow (60 to 120 min for complete extraction). The equilibrium coefficient is in this case not pH-dependent and is so high ($>10^5$) that the extent of extraction obtained is determined by kinetic factors alone. The selectivity of the solvent is, of course, based only on kinetics, but the rate of extraction of the PGM other than Pd^{II} is so slow that virtually none is extracted even after extended periods.

The complex formed is $PdCl_2L_2$, where $L = R-S-R$, and as this is virtually nonpolar, it has excellent solubility in organic solvents. This allows the extractant to be used in high concentration (50 to 100%) and up to 100 g/l Pd can be extracted.

The solvent can only be stripped by a further ligand exchange reaction; NH_3 is usually employed. This converts the Pd complex into the tetrammine, $Pd(NH_3)_4^{2+}$, which dissolves in the aqueous phase. Pd is recovered from the strip solution by conventional means.

Commercial Solvent Extraction Processes

Several complete flowsheets for the refining of the PGM (and Au) have now been published; this is in addition to the extensive use of certain solvent extraction procedures within a conventional refinery.

The flowsheet of the Council for Mineral Technology (Mintek, formerly the National Institute for Metallurgy – NIM) makes the most extensive use of solvent extraction. An alloying technique is used to render all metals soluble in HCl/Cl_2. The leach solution is then treated by a series of solvent extraction processes:

(a) Au is extracted from 6 M HCl with a long-chain alcohol, isodecanol (mixed isomers of decanol). The loaded solvent is washed with weak HCl and stripped with alkali to produce a very concentrated pure Au solution.

(b) Pd is next extracted using di-n-hexylsulphide in a batch contactor. The solvent is washed and stripped with 15% NH_3 solution. Pd is precipitated from the strip liquor either as $Pd(NH_3)_2Cl_2$ or by HCOOH reduction.

(c) The solution is then treated with SO_2 to reduce Os, Ru, and Ir to their trivalent oxidation states and Pt^{IV} extracted with an amine or preferably TBP. The strip solution is then subjected to the bromate hydrolysis procedure and Pt precipitated by conventional means.

(d) The solution is boiled with HNO_3 to remove Os as OsO_4 and this is recovered by conventional means. The solution is then reduced with HCOOH and the Ru converted into the $RuNOCl_5^{2-}$ anion. This is extracted with TBP and stripped with water. The strip solution is made alkaline and oxidised with bromate to convert the Ru to RuO_4^{2-}. This is then reduced to RuO_2 with ethanol. The product is treated by conventional means if it requires further purification.

(e) The solution is then oxidised with Cl_2 to oxidise Ir to Ir^{IV}, which is then extracted with TBP. The solvent is stripped with water and Ir precipitated as $(NH_4)_2IrCl_6$.

(f) Finally, Rh is recovered by conventional techniques.

The Inco process is very similar in principle to the Mintek process.

Total dissolution of the concentrate is achieved by a three-stage process in which the insoluble residue from the first leach is treated by Na_2O_2 fusion and the fusion mixture leached and combined with the previous leach. The leach liquor is treated initially by an oxidative hydrolysis. This precipitates most of the base metals while Os and Ru are distilled as tetroxides and recovered by conventional means.

Au is then extracted in a counter-current contactor using dibutyl "carbitol" as the extractant, and is reduced directly to metal from the solvent using a hot aqueous solution of oxalic acid.

Pd is then extracted from the liquor using di-octyl sulphide (25% in an aromatic diluent). The remaining details of the process appear to follow closely those outlined for the Mintek process.

Rh and Ir are recovered by conventional methods, although it is apparently planned to introduce a TBP solvent extraction step for Ir^{IV}/Rh^{III} separation as well.

The Matthey Rustenburg Refiners (MRR) process is somewhat different in the details of the solvent extraction procedures, although the same general philosophy is evident. Here incoming materials are subjected to a dry chlorination procedure before leaching; this apparently activates the material ensuring a high leach extent for all the PGM. Once again Ru and Os are removed by distillation before solvent extraction procedures are used.

Au is extracted using methylisobutyl ketone (MIBK) in a similar fashion to that described previously. The method of stripping is not known.

Pd is then extracted with LIX 64N, catalysed with a long-chain amine. Pd is stripped with 6M HCl and the dilute strip liquor concentrated by means of ion-exchange. The ion-exchange resin is in turn eluted with NH_3 and the Pd tetrammine solution treated further by conventional means. The solution is then reduced and Pt extracted using Amberlite LA2, a commercial secondary amine. This is stripped with NaOH at $pH = 4$ to 5. The Pt solution obtained needs further purification before final precipitation of the metal. The solution is then oxidised and Ir extracted, again using an amine. This is stripped by reduction with SO_2. The strip liquor is treated by conventional methods. Rh is purified and finally recovered by conventional methods.

1.7 Other Modern Techniques

Pre-Leach Treatments

PGM concentrates usually contain a high percentage of base metals and the PGM are only partially soluble in HCl/Cl_2 or aqua regia. The development of new separation techniques such as solvent extraction which are capable of separating all the metals has motivated much research into methods of increasing the solubility of the PGM. In addition it has been found that the solvent extraction procedures are often adversely affected by the presence of base metals in high concentration and methods of removing these before the PGM leach has been developed.

In patents issued to MRR, a method of simultaneously removing base metals and activating the PGM is revealed. This involves a high-temperature chlorination in which base metals are volatilised and the PGM alloyed to form a concentrate totally soluble in HCl/Cl_2. In an alternative method, MRR have patented a process in which the PGM concentrate is roasted with H_2SO_4 under conditions where base metals are solubilised, but not the PGM.

Falconbridge use a process in which the concentrate is treated with H_2S in aqueous media. This concentrate is then subjected to a leach with Cl_2 gas under conditions of controlled redox potential to dissolve the base metals separately from the PGM. The residue is mostly soluble in HCl/Cl_2.

In the process of Mintek, the PGM concentrate is first melted in an induction furnace and silica and some base oxides removed as a slag. For certain concentrates, rich in the high melting-point metals, iron may be added to lower the liquidus of the alloy. The PGM are then alloyed with Al to form a low melting point alloy which is very brittle. It is crushed and leached in HCl to remove most of the base metals and to produce a very active PGM residue easily soluble in HCl/Cl_2.

In secondary metal refining, methods of producing finely divided PGM alloys have been developed. These are "atomisation" techniques, where the liquid metal is broken up into fine droplets by means of a high velocity water jet. This increases the surface area of the metal and thus increases the rate of leaching.

Chlorine/Hydrochloric Acid Leaching

The use of Cl_2 as the oxidant rather than HNO_3 has a number of advantages, and is rapidly supplanting the use of aqua regia as the leaching medium for PGM. Serveral chlorine leaching systems have been described:

(1) Pressure leaching – the leach vessel is closed and chlorine fed in on demand to maintain a pressure of 0.5 to 2 bar in the vessel.

(2) "Soxhlet" leaching, in which the PGM are placed in a permeable basket above the leach solution. The vessel is heated to boiling point and Cl_2 fed in. Cl_2-saturated HCl condenses above the basket and PGM leach liquor flows out of the basket into the main vessel below. It is claimed that in this way the leach rate is increased as the metal is never in contact with high concentrations of PGM chlorides and therefore does not tend to passivate.

(3) "Vortex" leaching, in which finely-divided PGM are suspended in HCl in a non-baffled vessel fitted with a high-speed agitator. Cl_2 is fed into the top of the reactor on demand at a pressure of a few Pa. The vortex formed ensures good gas/liquid contacting.

At a few refineries other leach systems are used for special purposes. For different materials such as Rh-rich alloys, a Br_2/HBr acid leach is used. This is apparently less susceptible to passivation than the HCl/Cl_2 leach. For special purposes Au and Pd are sometimes dissolved in NaCl solutions using Cl_2 as the oxidant. This is useful in catalyst and plating salt manufacture where the sodium salt of the PGM chloro acid is required.

Ion Exchange

The PGM leach usually contains high concentrations of Pt, Pd, and Ru, and ion exchange methods are thus not applicable to these metals. Ion exchange has been used for the separation of the minor constituents of such leach solutions, notably Au and Ir.

Au ion exchange systems have been based on the use of very weakly basic groups, such as esters. One of the most successful is the commercial resin Amberlite XAD-7. This has very good selectivity towards Au, a reasonable capacity, and is easily eluted with a mixture of acetone and HCl. Because of the ease of operation of the system, it is a potential competitor to the solvent extraction procedures already described.

Ion exchange separation of Ir from Rh is based on the absorption of $IrCl_6^{2-}$ on strong or weak base resins. These have a fairly good selectivity towards Ir^{IV} and the resin capacity is in excess of 100 g/l resin. Ir is usually eluted by reduction with SO_2 under conditions leading to the formation of an Ir^{III}-sulphito complex. The eluate obtained is usually not pure enough to allow direct production of metal, and could only be considered as a partial purification/concentration step.

The use of resins to recover PGM from dilute solutions arising during the course of refining operations has received a great deal of attention. While both strong base and weak base conventional resins have been used, the emphasis has been placed on the development of special resins more selective towards the PGM. These fall into two classes:

(1) Complexing resins where the functional group is isothio-uronium or similar. These are undoubtedly very selective towards the PGM, but have very slow reaction kinetics, especially if the PGM are already strongly complexed. Thus Pt and Pd are usually quickly absorbed, but Rh and Ir much more slowly. The resins may be eluted with a strong complexing agent such as thio-urea, but there appears to be little advantage in doing this, and the metals are usually recovered by burning the resin.

(2) Reducing resins are based on strongly reducing groups such as $-BH_3$. Subject to operating in the correct pH range, the PGM are reduced to metal within the pores of the resin and thus immobilised. The metals must be recovered by incineration. The capacity is greatly affected by the presence in solution of reducible base metal species, e.g. Fe^{3+}, and are thus not suitable for highly contaminated solutions.

It was initially hoped that the use of resins would supplant that of Zn reduction, which is both expensive and not entirely successful, especially in the case of the minor metals. However, resins have in general proved to be disappointing in this regard, for the same reasons as the failure of the reduction process, i.e. slow kinetics.

1.8 Analytical Techniques

The development of modern instrumental methods for the analysis of metals in general and PGM in particular has had a very great effect on the refining process, allowing quicker production of purer metals.

The major instrumental method employed in control of the process is atomic absorption. This allows "plant" solution samples to be analysed for a variety of metals within a very short time of receipt. It is thus used extensively for process control purposes.

It is probable that in future atomic absorption (AA) will be replaced by one of the newer techniques such as that employing induced coupled plasma (ICP) which are capable of performing simultaneous multi-element analyses.

The analysis of solid samples has also advanced greatly. X-ray fluorescence (XRF) techniques are useful for determining major elements present in materials such as slags and residues. Emission spectroscopy is the major method used for determination of impurities in pure metal products. Further development of the technique may in future make mass spectroscopy an attractive and simpler technique to use for this purpose.

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2 High Purity Platinum-Group Metals

2.1 Introduction

The availability of high purity platinum-group metals is of prime importance to those investigating the structures and properties of these elements, many of which are profoundly affected by the nature, concentration and distribution of the impurities present. Concentration of impurities and defects at the grain boundaries can strongly influence the mechanical characteristics of the metals. By arc/electron beam melting and zone refining in high vacuum significant purification of all the platinum-group metals commercially available could be achieved [1].

The platinum-group metal powders produced by the normal chemical precipitation techniques have levels of impurities, which vary according to the refining method used, and the efficiency of the separation operations. Table I gives typical figures obtained by emission spectroscopy using D.C. arc excitation for impurities in ppm by weight for platinum-group metal powders [2]; for levels of detection see Table IV, p. 26.

Table I

	PGM	Au	Mg	Al	Si	Ca	Cr	Mn	Fe	Ni	Cu	Ag	Sn	Pb
ruthenium	200	—	5	2	100	5	5	2	100	5	5	5	—	—
rhodium	200	—	1	—	1	1	1	—	50	5	10	5	1	—
palladium	300	50	1	20	30	1	—	1	50	5	5	10	5	10
osmium	50	—	5	20	1	5	5	1	50	5	5	1	—	—
iridium	500	—	1	—	10	5	10	—	20	5	5	1	—	20
platinum	200	20	1	5	100	5	10	—	5	5	5	10	5	—

Table II gives figures for the impurities present in different grades of commercial refined metals to Soviet State Standard [3].

By modifications of the chemical precipitation, refining procedures and the introduction of separation techniques depending on the impurities present, sponges with very low metallic impurities can be obtained as shown in Table III [4].

Table III

element	maximum total metallic impurities	element	maximum total metallic impurities
platinum powder	10 ppm	palladium powder	15 ppm
platinum wire	20 ppm	palladium wire	30 ppm
platinum sheet	20 ppm	palladium sheet	25 ppm
iridium powder	20 ppm	rhodium powder	30 ppm (PGM 20 ppm)
osmium powder	10 ppm	ruthenium powder	30 ppm

Table II

metal	Soviet State Standard (GOST)	host metal not less than %	impurities ppm by weight										
			PGM	Au	Pb	Fe	Si	Sn	Al	Ba	Sb	oxygen and volatiles	total
Ru A-1	12343 to	99.95	200	—	50	100	50	—	50	50	—	—	500
Ru A-2	12366	99.90	500	—	100	200	100	—	50	50	—	—	1000
Rh A-1	12342 to	99.95	200	—	50	100	50	—	—	50	—	100	500
Rh A-2	12366	99.90	300	—	50	200	50	—	—	50	—	200	1000
Pd A-1*)	12340 to	99.95	250	50	50	100	50	10	50	—	—	500	500
Pd A-2*)	12366	99.90	500	100	50	200	50	50	50	—	—	—	1000
Os A-1	12339 to	99.95	200	—	—	100	—	—	—	—	—	—	500
Os A-2	12366	99.90	500	—	—	300	—	—	—	—	—	—	1000
Ir A-1	12338 to	99.95	200	—	50	100	20	—	50	10	—	100	500
Ir A-2	12366	99.90	450	—	100	200	50	—	50	50	—	100	1000
Pt A-1*)	14837 to	99.95	250	50	50	100	50	10	50	—	10	—	500
Pt A-2*)	12366	99.90	500	50	50	100	50	50	50	—	50	—	1000

*) Refined ingot metal.

The levels of detection (in ppm) by the techniques employed, of the impurity elements commonly associated with the metals are given in Table IV.

Table IV

impurity element	Ru	Rh	Pd	Os	Ir	Pt
Al	1	1	1	<1	1	1
Ba	2	1	1	1	3	1
Be	<1	<1	<1	1	<1	<1
Bi	2	1	1	2	2	<1
B	5	3	1	3	3	<1
Cd	<1	2	<1	—	3	1
Ca	<1	<1	<1	<1	<1	<1
Cr	1	<1	<1	1	1	<1
Co	2	1	2	1	1	1
Cu	<1	<1	<1	<1	<1	<1
Au	1	1	1	1	<1	<1
Ir	10	<1	10	10	—	5
Fe	1	1	1	1	2	1
Pb	1	1	2	7	3	1
Li	<1	2	<1	—	<1	<1
Mg	<1	<1	<1	<1	<1	<1
Mn	<1	<1	<1	1	<1	<1
Mo	2	1	2	3	10	1
Ni	3	1	2	2	1	1
Pd	<1	<1	—	<1	<1	<1
Os	20	10	10	—	10	5
Pt	1	2	5	2	2	—
Ru	—	10	10	10	7	5
Rh	1	—	3	1	2	2
Si	1	1	1	1	2	<1
Ag	<1	<1	<1	<1	<1	<1
Na	2	5	<1	20	2	<1
Sn	3	1	2	2	3	1
Ti	2	1	2	2	2	2
V	3	1	2	3	3	1
Zn	5	<1	1	1	5	1

The National Bureau of Standards reference material SRM No. 680 high purity platinum has the following recommended values in ppm by weight [5]:

Table V

Cu	Ag	Pd	Pb	Fe	Ni	Au	Mg	Zr	Rh	Ir	O
0.1	<0.1	0.2	<1.0	0.7	<1.0	<1.0	<1.0	<0.1	<0.2	<0.01	4.0

Elements known to be present for which figures are not given include aluminium, calcium, sodium and tin.

Significant concentrations of carbon, oxygen, nitrogen, hydrogen and sulphur, not detected in the normal spectrographic examination, may also be present in all materials which have not been treated for their removal by vacuum melting or zone refining techniques. Typical gas contents of production materials after melting and drawing into wire are given in Table VI in ppm by weight [6].

Table VI

	platinum	iridium	palladium	rhodium
hydrogen	1	1 to 10	1 to 80	2
oxygen	10 to 30	10 to 150	100 to 300	40
nitrogen	<1	1 to 5	10 to 50	1

Zone melting with single crystal growth is accompanied by purification as shown in Table VII [4]. This results from selective evaporation and transport of impurities to the end of the sample.

Platinum metals at high temperatures can dissolve considerable amounts of carbon which, on solidification, precipitates as graphite. Carbon diffuses rapidly through heated membranes of platinum and palladium even though the solubility in the fomer metal is less than 0.02% by weight at 1700°C [9]. Palladium takes up more than 0.4% by weight of carbon at 1400°C and this interstitial solubility hardens it considerably and distends the lattice. The solubility of carbon in Ru, Rh and Ir at 1256°C is quoted as 0.112%, 0.07% and 0.0025% and at 820°C 0.0009%, 0.00067% and 0.000328%, respectively [10]. Constitutional diagrams for C/Ru, C/Rh, C/Pd, and information on the solubilities of carbon in osmium, iridium and platinum are available [11].

Table VII
Analysis of impurities in platinum-group metals in ppm by weight.

impurity	Ru			Os			Rh		
	refined powder	arc melted	electron beam melted	refined powder	arc melted	electron beam melted	refined powder	arc melted	electron beam melted
Pt	10	10	10	30	7	7	200	150	100
Pd	10	10	10	1	21	1	1	1	1
Ir	10	—	10	60	27	10	30	30	10
Rh	40	10	10	3	3	3	—	—	—
Cu	10	10	5	5	5	1	10	10	5
Fe	10	10	8	60	18	18	10	10	8
Si	30	30	20	50	—	40	10	—	—
Mg	30	—	6	3	3	2	—	—	—
Al	20	—	—	56	20	8	—	—	—
Na	10	—	—	10	—	—	20	—	—
Pb	10	—	—	—	—	—	20	—	—
S	—	40	—	—	—	—	—	100	—
C	300 250	200 170	100 50	—	—	—	20	10	10
O	— —	150 200	80 60	—	—	—	—	30	30
H	—	9	2	—	—	—	—	1	1

Mass spectrographic analysis of three-pass zone-refined platinum is given in Table VIII [8].

Table VIII

element	content (weight) ppm	element	content (weight) ppm	element	content (weight) ppm	element	content (weight) ppm
Li	<0.0002	V	0.25	Ru	0.3	Dy	<0.01
Be	<0.02	Cr	2.5	Rh	15.0	Ho	<0.003
B	0.0003	Mn	0.6	Pd	0.6	Er	<0.008
C	10.0	Fe	3.0	Ag	0.012	Tm	<0.003
H_2	1.5	Co	0.3	Cd	<0.025	Yb	<0.06
O_2	10.0	Ni	2.5	In	0.03	Lu	<0.003
N_2	3.0	Cu	0.05	Sb	<0.004	Hf	<0.05
F	<0.003	Zn	0.05	Sn	0.08	Ta	<5.0
Na	<0.06	Ga	0.01	Te	<0.008	W	5.0
Mg	<0.06	Ge	<0.004	I	<0.002	Re	<0.02
Al	7.0	As	0.01	Cs	<0.002	Os	<0.08
Si	7.0	Se	<0.003	Ba	<0.003	Ir	0.3
P	0.002	Br	0.008	La	<0.002	Au	<0.3
S	0.2	Rb	<0.01	Ce	<0.002	Hg	<0.15
Cl	0.4	Sr	<0.003	Pr	<0.002	Tl	<0.15
K	0.1	Y	<0.01	Nd	<0.01	Pb	<0.6
Ca	0.05	Zr	2.5	Sm	<0.01	Bi	<0.06
Sc	<0.03	Nb	1.0	Eu	<0.005	Th	<0.07
Ti	2.5	Mo	<0.3	Gd	<0.01	U	<0.07
				Tb	<0.003		

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2.2 Production of Pure Platinum-Group Metals

2.2.1 Commercial Refining Using Sequential Precipitation

The commercial refining procedures used in two of the European refineries are shown in flow charts. **Fig. 1** and **Fig. 2**, p. 32, show the INCO's Acton Refinery Scheme. Additional stages to produce high purity metals are indicated by dotted lines.

The Matthey Rustenberg Refinery Scheme shown in **Fig. 3** (a and b), pp. 33/4, illustrates the process used to produce semi-refined metals via a different route, but does not give details of the final refining stages for the individual metals.

By careful attention to process details and close analytical control during the commercial refining operations, involving redissolving and reprecipitation where necessary, the platinum-group metals can be produced on a routine basis with less than 200 ppm of spectrographically determined impurities. These levels of impurities can be greatly reduced by the chemical precipitation and/or zone refining techniques described later (dotted lines in Figg. 1, 2 and 3).

R. J. Dowsing (Metals Mater. **1980** No. 7, pp. 32/42).

2.2.2 Solvent Extraction Methods

There are two major mechanisms (outer-sphere ionic and inner-sphere coordination) which operate for the ligand-ligand solvent extraction separation of metal species in solution, with particular reference to the platinum-group metals [1]. Separations are carried out in chloride solution which is at present the only effective medium for dissolving platinum-group metals. In the MRR scheme gold and base metals are separated using MIBK, palladium with a hydroxyamine plus accelerator, osmium and ruthenium by distillation as volatile tetraoxides, platinum using an alkylamine in reduced solution, iridium also using alkylamine in oxidised solution and rhodium by resin ion exchange. This scheme is shown in **Fig. 4**, p. 35, with additional stages of chemical precipitation and float zone refining to produce high purity materials (see later sections).

In the INCO scheme ruthenium and osmium are separated by the normal distillation techniques as tetroxides, gold extracted with dibutyl carbitol, palladium with di-N-octyl sulphide and platinum with tributylphosphate in reduced solution. By reoxidation of the platinum raffinate, iridium could be selectively separated from rhodium by tributylphosphate [2]. The scheme is illustrated in **Fig. 5**, p. 36, with additional purification stages to produce high purity materials.

In the Lonhro solvent extraction route gold is precipitated with SO_2, platinum plus palladium extracted with an acetic acid derivative of a secondary amine, osmium is distilled as oxide, ruthenium extracted as a nitrosyl complex by a tertiary amine and rhodium plus iridium recovered from the ruthenium raffinate by ion exchange with a strong base resin. From this resin iridium is selectively eluted with water saturated with SO_2. By reoxidation of the iridium a solution is obtained which can be solvent extracted using tributylphosphate and iridium recovered by water stripping [2]. This scheme is illustrated in **Fig. 6**, p. 37, with additional purification stages. Patents relating to solvent extraction processes are available [3 to 12].

Using solvent extraction/distillation processes, solutions of the individual platinum-group metals are obtained with very low levels of contaminating metals. The extraction, washing and stripping stages all need to be checked using ICP emission spectroscopy or appropriate atomic absorption methods to ensure that the necessary separations and purification levels have been achieved. The metals are produced by chemical precipitation and/or zone refining techniques described later.

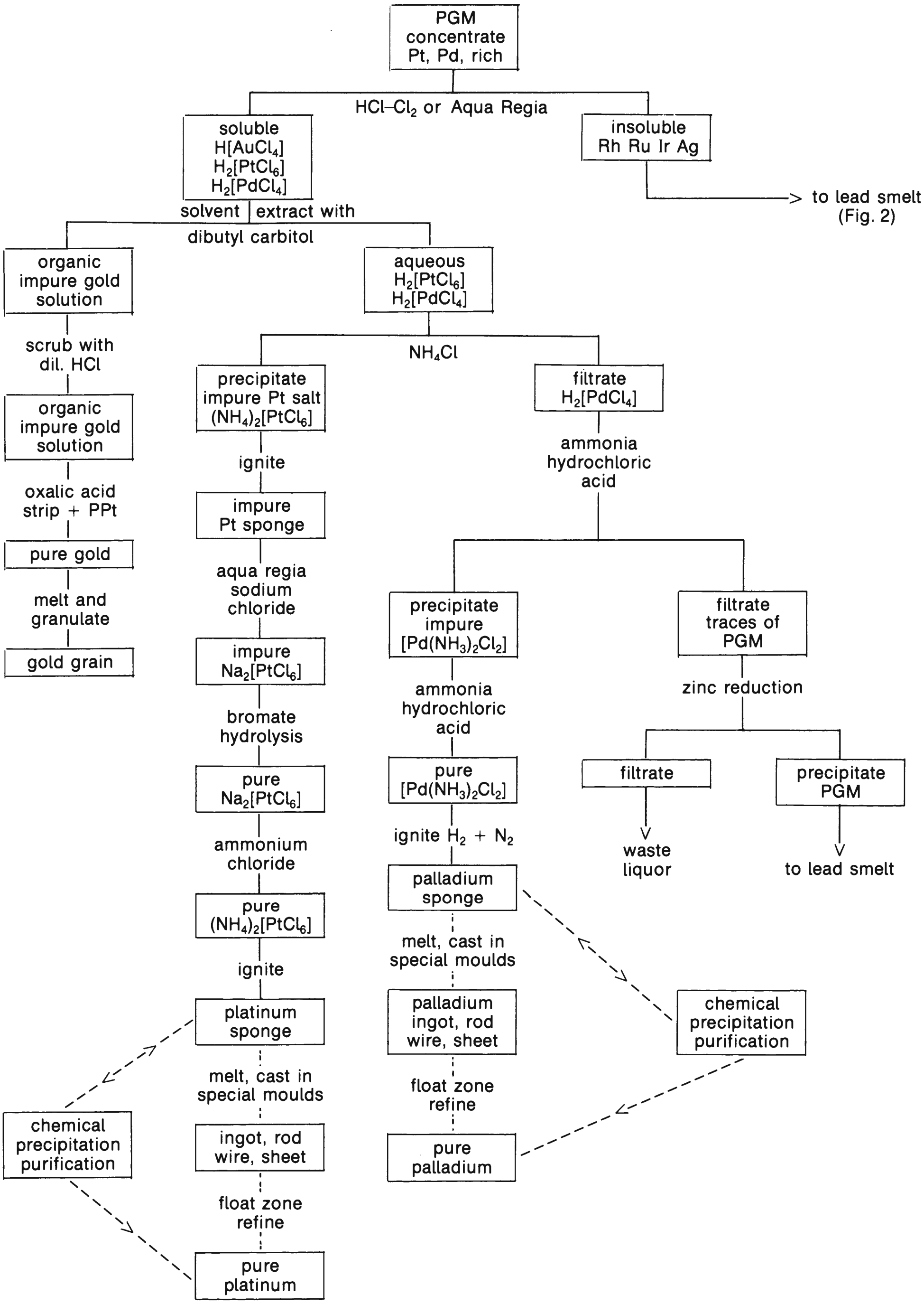

Fig. 1. Pure platinum and palladium starting with the INCO (Acton) (Refinery) route.

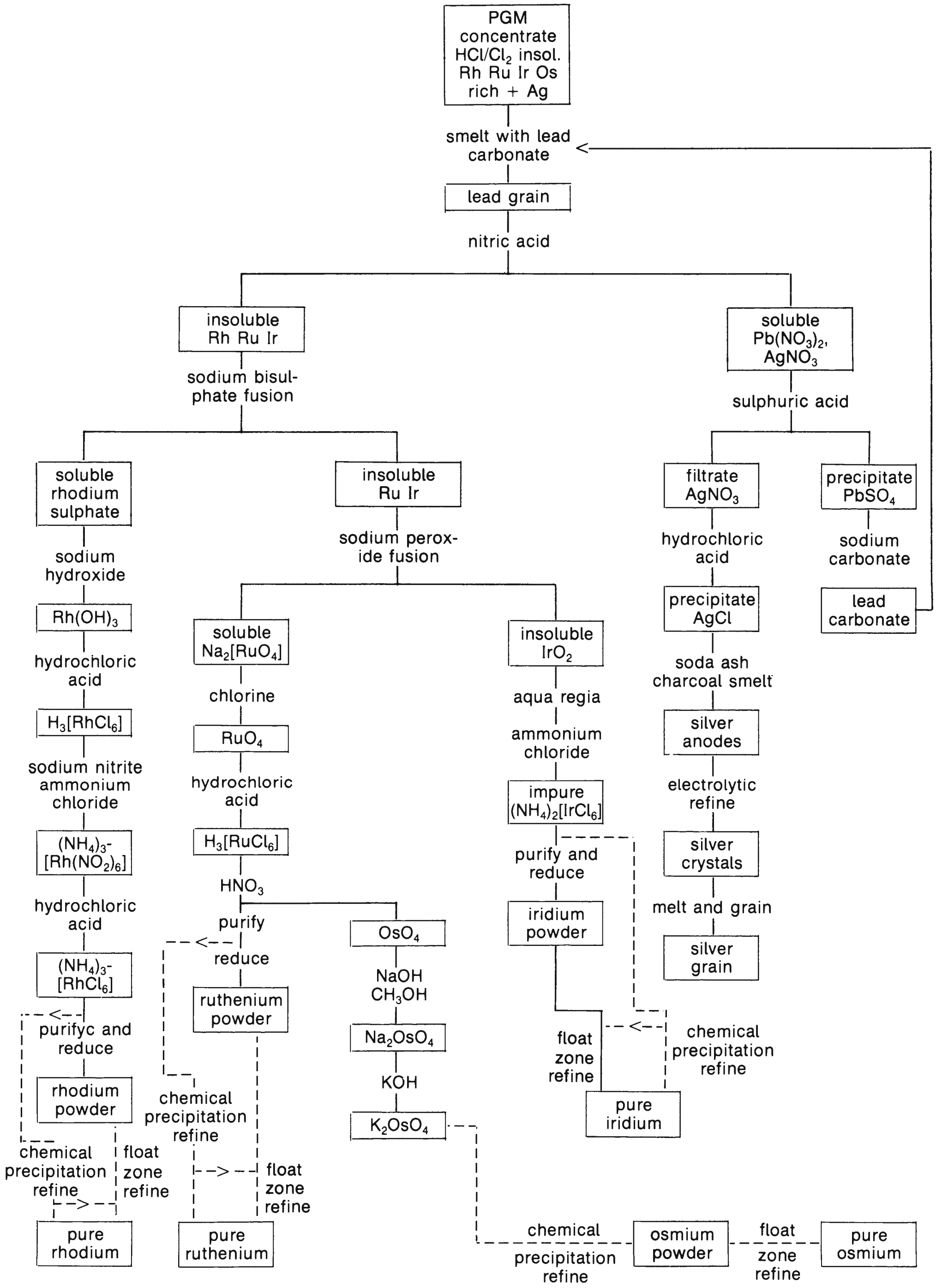

Fig. 2. Pure rhodium, ruthenium and osmium starting with the INCO route.

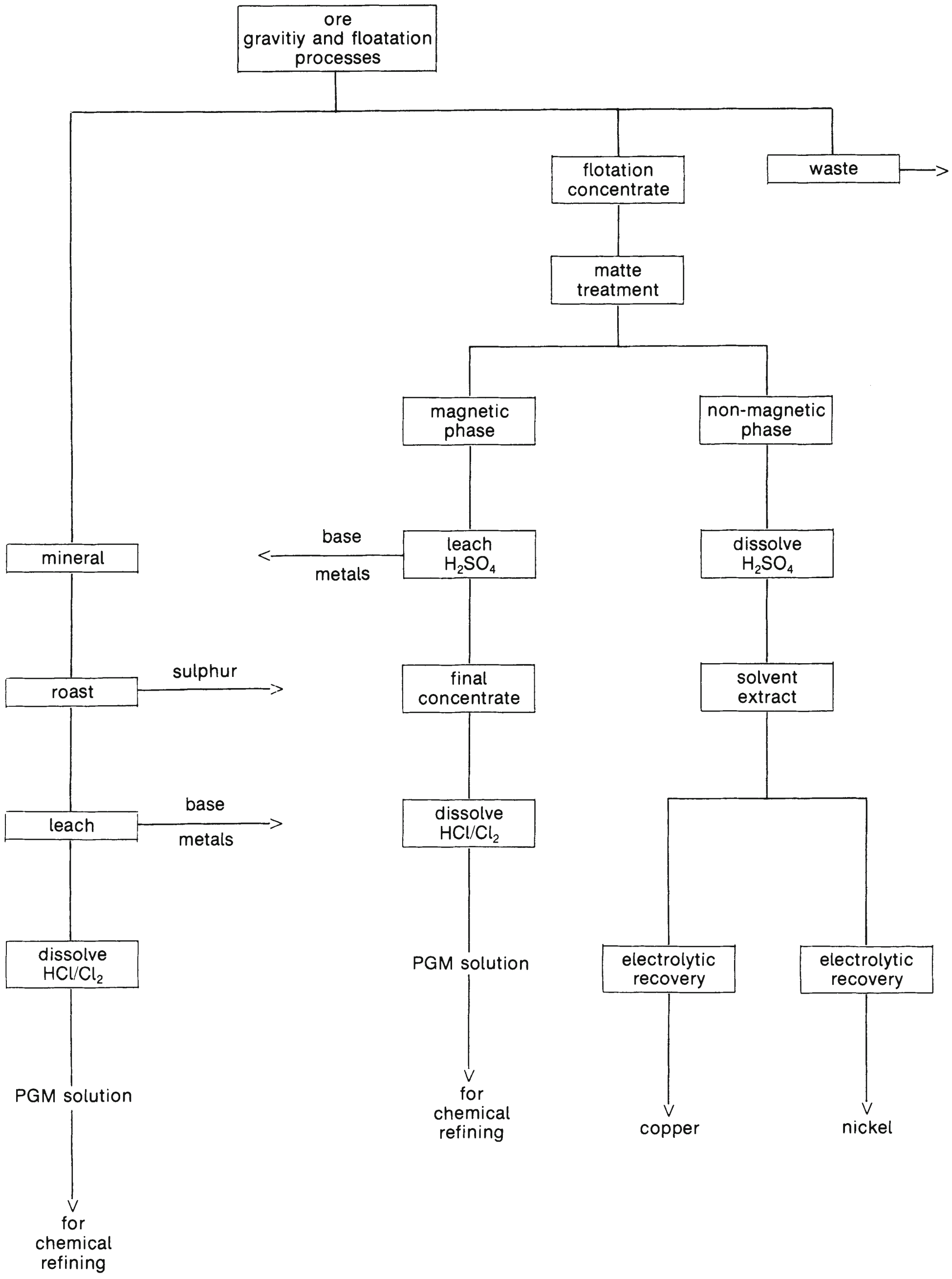

Fig. 3a. Rustenburg ore treatment.

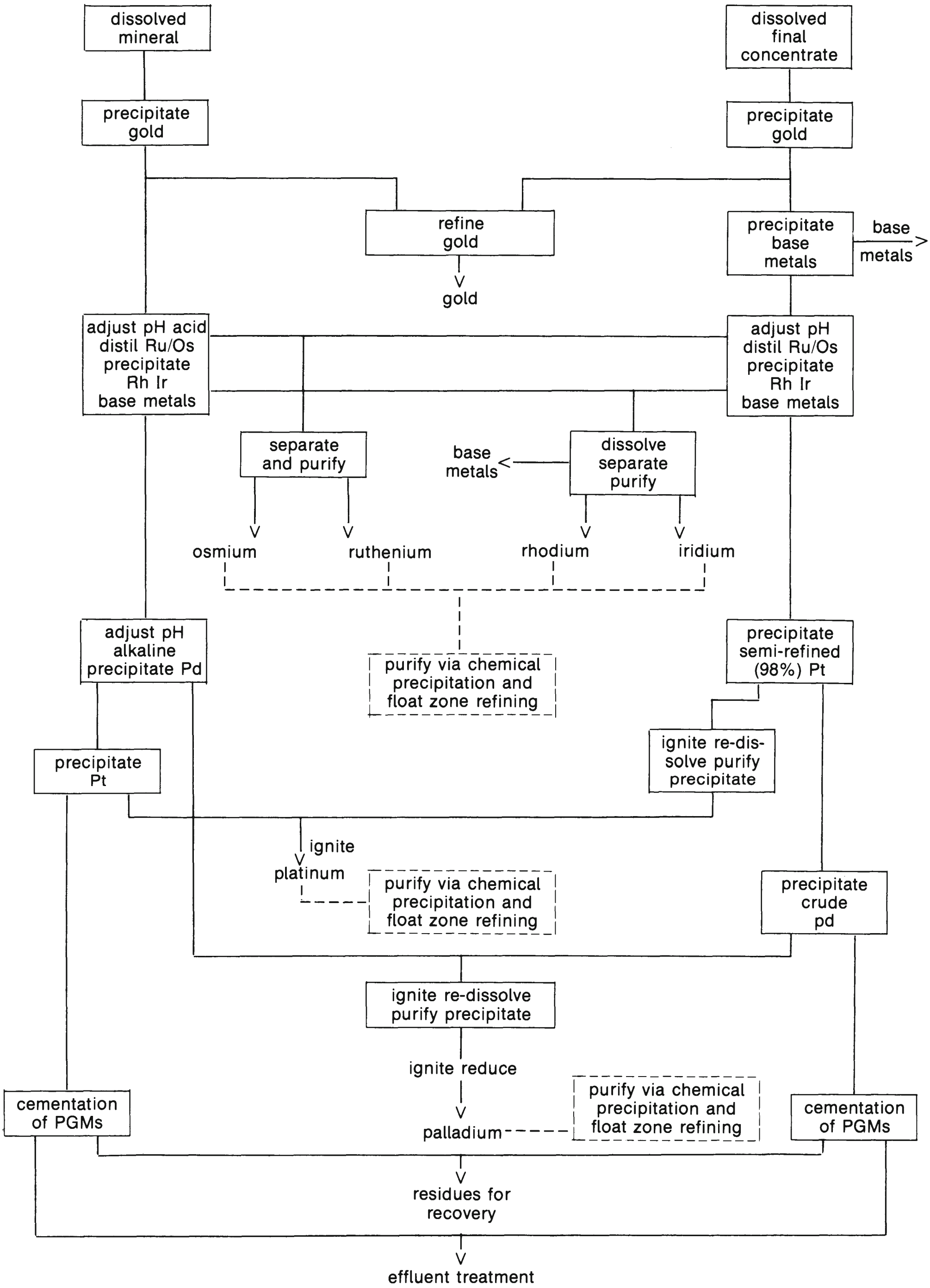

Fig. 3b. Pure PGMs starting with the MRR chemical refining scheme.

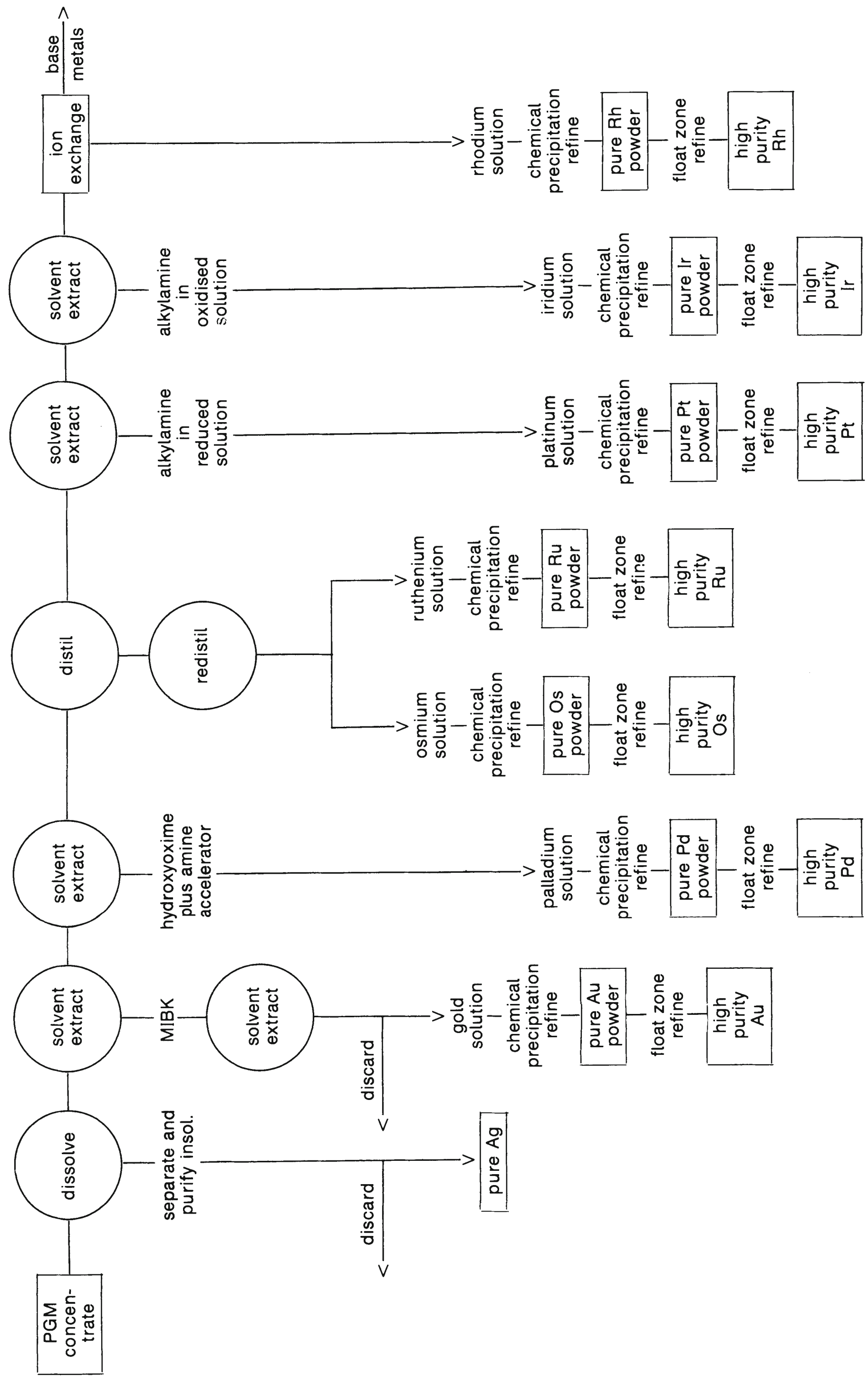

Fig. 4. High purity PGM using MRR solvent extraction process scheme.

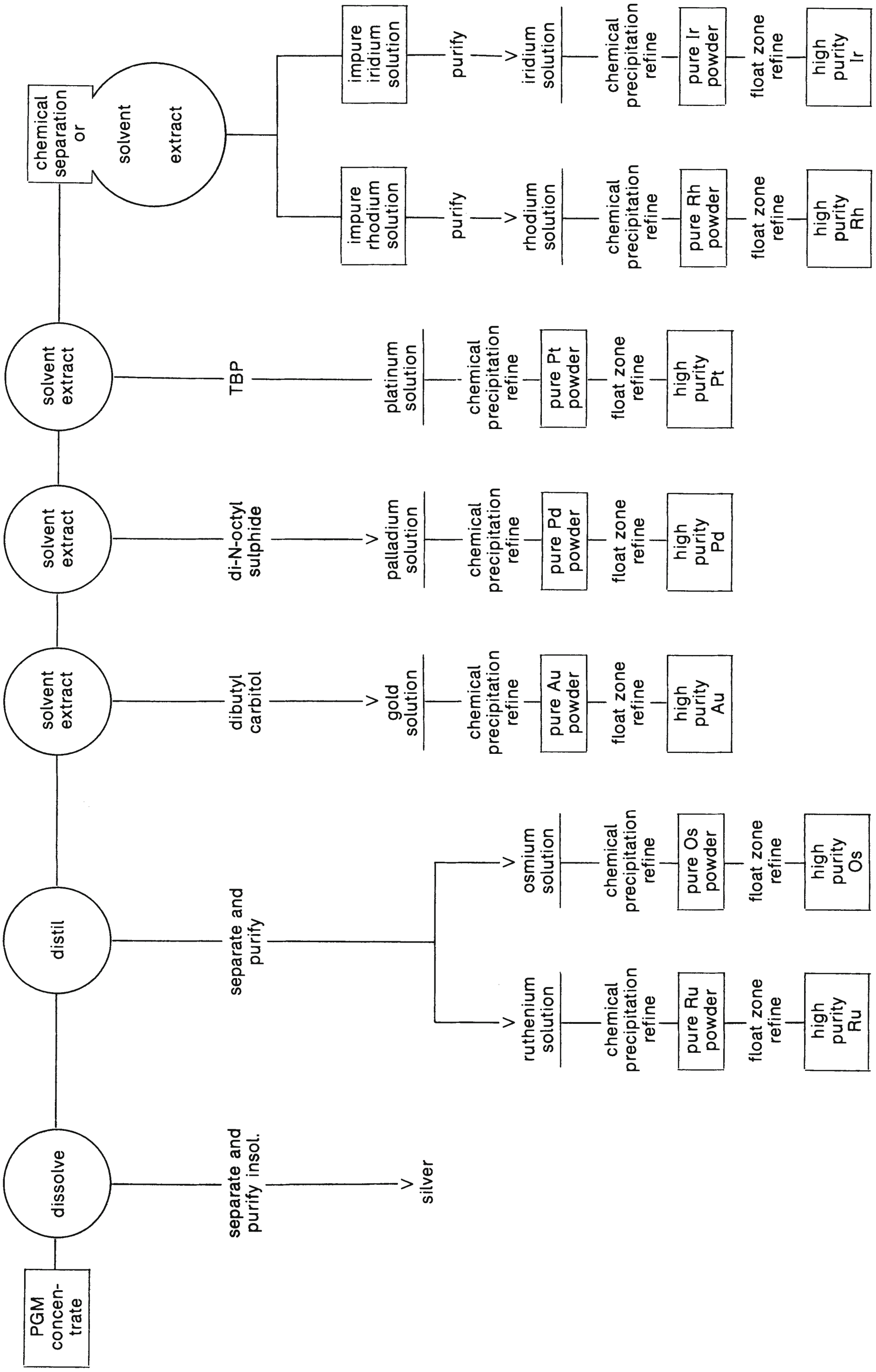

Fig. 5. High purity PGM using INCO's solvent extraction process scheme.

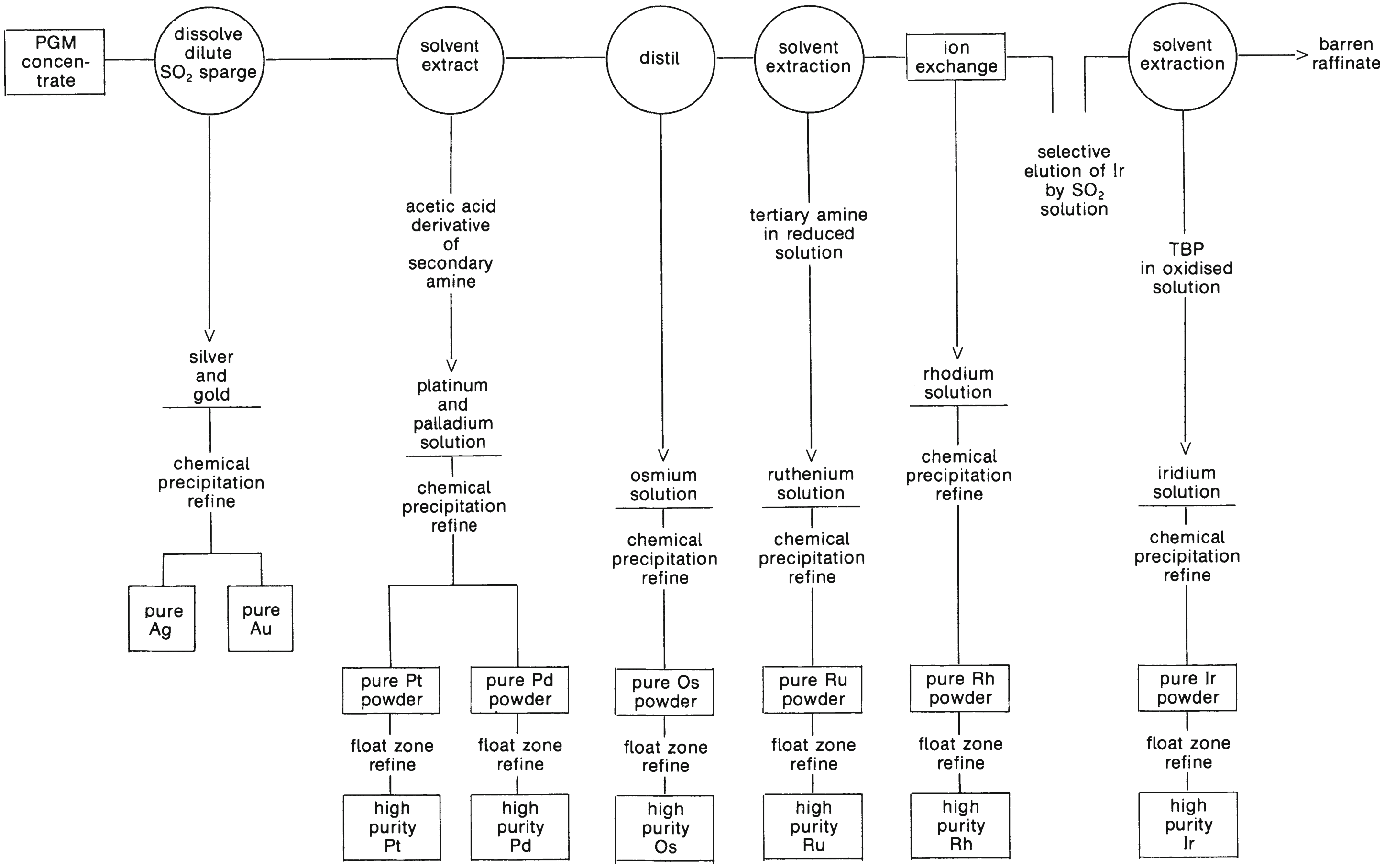

Fig. 6. High purity PGM using Lonhro solvent extraction process scheme.

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2.3 Preparation of High Purity Platinum-Group Metal Powders by Chemical Precipitation Methods

In the preparation of pure materials scrupulous attention to detail is essential to avoid contamination. The apparatus used should be reserved for this purpose alone and the reagents used must be of high purity. Methods for contamination control and production of pure reagents have been reported [1]. In addition, sub-boiling distillation techniques for the production of pure reagent acids and pure water, the preparation of clean bottles, reagent storage, laboratory design and ventilation requirements are of importance [3].

Platinum

The impurities present in normal production platinum powder (see Table I, p. 24) are silicon, palladium, rhodium and iridium together with low levels of aluminium, calcium, chromium, copper, gold, iron, mangesium, nickel, silver and tin. All of these can be reduced to extremely low levels (<10 ppm total) by dissolving the platinum, separation of palladium as iodide and precipitation of platinum as ammonium hexachloroplatinum(2−) which is ignited to platinum powder [2].

The production platinum powder is dissolved in hydrochloric acid plus chlorine. When only a trace of material remains undissolved (silica, platinum, iridium, etc.) the solution is cooled, filtered, and then evaporated to low bulk to remove excess acid. After diluting, and cooling, any palladium is precipitated as iodide using a small volume of diluted hydriodic acid (rhodium is also precipitated). The precipitate is filtered off and the filtrate heated to 90°C. A hot, filtered solution of ammonium chloride is added to the hot chloroplatinic acid to precipitate the platinum as ammonium hexachloroplatinum(2−). The first 5% and last 5% of the precipitate is discarded. When cool, the yellow salt is filtered and washed with 10% ammonium chloride solution. The salt is placed in a clean silica dish, heated slowly to 700°C and maintained at this temperature to decompose the ammonium hexachloroplatinum(2−) to platinum powder. When cool the powder is transferred to a polypropylene bottle, thoroughly mixed and then screened through a polythene or nylon screen and returned to the bottle. Soluble salts can be removed by washing with dilute hydrochloric acid and water if required but this is not necessary if the powder is to be melted subsequently [2].

If silica is present in the powder it can be remvoved by treatment with hydrofluoric/hydrochloric acid solution in a polypropylene container. The powder is then washed by decantation using demineralized water, and filtered on a polypropylene funnel with a terylene filter. After drying, mixing and screening it is stored in a polypropylene bottle. Insoluble residues, precipitated platinum-group metals and filtrates plus washings should be treated for recovery of precious metals [2].

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Palladium

High purity palladium powder can be produced from normal production powder which is dissolved in hydrochloric acid plus chlorine and evaporated to low volume to remove excess acid or from the chloropalladous acid obtained during the refining operations. Reaction of chloropalladous acid, H_2PdCl_4, with ammonia precipitates the pink salt $[Pd(NH_3)_4][PdCl_4]$ which is insoluble in water and on heating with excess ammonia it redissolves to give very soluble $[Pd(NH_3)_4]Cl_2$. Addition of hydrochloric acid to the solution of tetramminepalladium(2+) chloride precipitates the diamminepalladium(2+) chloride which can be ignited under reducing conditions to give palladium metal powder.

Diamminepalladium(2+) dichloride, selected on the basis of spectrographic analyses, is stirred with cold water and ammonia solution is added until only a small amount of diammine remains undissolved. The filtered solution is treated with a small volume of pure hydrochloric acid to reprecipitate a little diammine which forms slowly on standing. A small volume of the filtered tetrammine solution is precipitated completely with pure hydrochloric acid, filtered, washed, ignited, reduced with hydrogen and tested spectrographically for impurities.

If the palladium powder does not reach the specified impurity level the precipitation of diammine in the bulk solution with hydrochloric acid followed by filtration is repeated. When the diammine produces palladium powder of adequate impurity level the bulk of diammine is precipitated in the cold with pure hydrochloric acid. The diammine is filtered, washed with 10% hydrochloric acid and ignited at 700°C in silica trays to remove ammonium salts. The palladium powder is placed in a silica furnace tube from which air is displaced by nitrogen. The nitrogen is replaced by hydrogen and the powder heated to 300°C. When the reduction is completed the palladium is cooled under hydrogen which is replaced by nitrogen when the tube is cold. The powder is transferred to a polypropylene bottle, thoroughly mixed, screened through a polythene or nylon screen and returned to the bottle. Soluble salts can be removed by washing with dilute hydrochloric acid and water if required but this is not necessary if the powder is to be melted. The precautions necessary to avoid contamination must be observed. Ignited residues, filtrates and washings should be treated for recovery of precious metals.

S. I. Ginsburg, N. A. Ezerskaya, I. V. Prokof'eva, N. V. Fedorenko, V. I. Shlenskaya, N. K. Bel'skii (Analytical Chemistry of Platinum Metals, Wiley, New York 1975, p. 125).

Ruthenium

In normal refining operations ruthenium is separated by distillation of ruthenium tetroxide which is absorbed in dilute hydrochloric acid to give a solution of various polymeric oxo- and hydroxochloro Ru complexes, which is the starting material for producing high purity ruthenium [1]. The "ruthenium chloride" solution is heated with sodium chlorate to produce volatile ruthenium tetroxide which is distilled and carried over with chlorine into dilute hydrochloric acid to form "chlororuthenic acid" which is then converted into ammonium "chlororuthenate" by ammonium chloride [2, 3]. The ammonium "chlororuthenate" is then heated in air to convert it to the oxide and reduced with hydrogen to give ruthenium powder. As an alternative procedure, if the ruthenium powder produced by the normal refining process is spectrogaphically free from other platinum-group metals the silicon, iron and other base metals can be removed by treatment with hydrofluoric acid and hydrochloric acid.

The ruthenium trichloride plus water is placed in the distillation flask and dilute hydrochloric acid in the receiver flasks. The final receiver contains caustic soda to collect any osmium which may be distilled over.

Chlorine gas is bubbled slowly through the solution which is gently heated and sodium chlorate solution (25% W/V) is added slowly. A yellow vapour of ruthenium tetroxide is distilled over and absorbed in the hydrochloric acid. The addition of sodium chlorate solution is continued a little at a time and the solution in the distillation flask heated to boiling until it becomes almost colourless. With the chlorine stream continuing the receiver flasks are heated in turn to boiling point and then allowed to cool. It is essential that all of the ruthenium tetroxide is absorbed and converted to ruthenium chloride as shown by the absence of any oily drops or layers.

The contents of the receiver flasks are combined, evaporated to approximately half the volume, cooled and filtered. Ammonium chloride is dissolved in hot water, filtered and added to the chlororuthenic acid, the solution is stirred until cool and the crystals of ammonium chlororuthenate are filtered on a terylene filter, washed with ammonium chloride solution, transferred to a silica tray and dried at 60°C.

The chlororuthenate is heated at 600°C to convert it to ruthenium oxide, and cooled. The oxide is placed in small silica trays inside a silica tube into which nitrogen and hydrogen can be admitted. The nitrogen supply is turned on to displace the air and the silica tube heated. The nitrogen is replaced by hydrogen, the tube heated slowly to 700°C until the oxide is all reduced to metal. With the hydrogen still flowing the tube is cooled to room temperature, and the hydrogen replaced by nitrogen. The ruthenium powder is removed from the trays, thoroughly mixed and screened through a plastic sieve.

If the alternative procedure using ruthenium sponge is employed, or if the impurity level is above specification from the above procedure the powder is placed in a polypropylene container, stirred with 30% hydrofluoric acid and allowed to stand overnight. The powder is then washed by decantation and filtered on a polypropylene funnel with a terylene filter. When the washings are neutral the powder is transferred to a flask, and boiled gently under a reflux condenser with 50% hydrochloric acid. The powder is washed by decantation, filtered, dried in a platinum dish, mixed thoroughly, sieved and stored in polythene bottles. The precautions necessary to avoid contamination by impurities must be observed [1, 2, 3].

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Rhodium

High purity rhodium can be prepared from pentamminechlororhodium(2+) chloride (Claus salt). A method for the preparation in which rhodium trichloride is heated for 3 h with a solution of ammonium chloride and ammonium carbonate has been described [1]. The resulting mixture of yellow pentammine chloride and the tetramminedichlororhodium(2+) chloride is separated by recrystallization. A preparative method in which chlorine is passed over a heated mixture of rhodium powder and sodium chloride to produce sodium hexachlororhodium(3−) is available [2]. Claus salt is prepared from this by boiling with ammonium chloride and hydrochloric acid. In an alternative route, soluble pentamminechlororhodium(2+) sulphate is treated with hydrochloric acid to give pentamminechlororhodium(2+) chloride. In each case the Claus salt is tested for impurities and the appropriate purification treatment depends on the impurities present.

The Claus salt is redissolved in sodium hydroxide solution and palladium can be precipitated as iodide, iridium from oxidised solution as ammonium hexachloroiridium(2−) and many base metals as sulphides. Other metals are separated by repeated recrystallization of the sodium hexachlororhodium(3−). After reprecipitating the Claus salt with ammonium chloride and hydrochloric acid it is then filtered, washed well with ammonium chloride solution and dried. The salt is placed in silica trays in an ignition tube from which air is displaced by nitrogen. Hydrogen then replaces the nitrogen and the salt is calcined at 750°C to produce rhodium metal. After cooling and replacing the hydrogen with nitrogen the powder is removed from the silica trays, screened through a plastic sieve and thoroughly mixed. If silica is present the powder is placed in a polypropylene container and allowed to stand overnight in a hydrochloric acid and hydrofluoric acid mixture, then thoroughly washed with pure water, dried, ignited in hydrogen as previously, rescreened and mixed before storage in a polythene container. The precautions necessary to avoid contamination by impurities must be observed [1, 2].

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Osmium

Osmium is distilled as osmium tetroxide from solutions by a wide variety of oxidizing agents, of which nitric acid is the most usual. (Osmium and ruthenium tetroxides can be separated using distillation from nitric acid.)

The osmium tetroxide is collected in dilute sodium hydroxide solution, forming sodium perosmate which is readily reduced to osmate using ethanol. Ruthenium insolubles are formed and removed by filtration. The osmium is then precipitated as potassium osmate by addition of potassium hydroxide solution. The filtered potassium osmate can be recrystallized by dissolving in sodium hydroxide, adding ethanol to remove remaining ruthenium and then retreating with potassium hydroxide until an adequate level of metallic impurities is attained.

The solid, purple-coloured potassium osmate is amminated using solid pure ammonium chloride. The two solids are mixed together to produce to yellow-coloured "Fremy Salt" $[OsO_2(NH_3)_4]Cl_2$ which is only sparingly soluble in water and potassium choride. The salt readily decomposes in aqueous solution forming OsO_4 and possibly OsO_2.

By igniting Fremy Salt in a nitrogen atmosphere at 700°C a mixture of osmium metal and potassium chloride is obtained. The potassium chloride can be removed on washing by decantation with hydrochloric acid and hot water. By treatment with hydrofluoric acid in a polypropylene container any silica present can be removed.

Gmelin Handbuch der Anorganischen Chemie, "Osmium" Suppl. Vol. 1, 1980.

Iridium

Insoluble ammonium hexachloroiridium(2−) can be reduced by oxalate to produce soluble ammonium hexachloroiridium(3−) [1]. In slightly acid solution any platinum, palladium and rhodium can then be precipitated using mercurous chloride and removed by filtration [2]. Most of base metals present can be precipitated as sulphides. After boiling off any hydrogen sulphide this solution can then be reoxidised using nitric acid and the ammonium hexachloroiridium(2−) reprecipitated with ammonium chloride. A sample of the crystals is examined spectrographically for impurities and if the level is too high the appropriate stage of the purification is repeated. When the level of impurities required is achieved the ammonium hexachloroiridium(2−) crystals are filtered off, washed with 10% ammonium chloride solution, dried and ignited at 700°C, followed by reduction and cooling in hydrogen. (The usual precautions to avoid explosion must be observed.) Any soluble salts and silica can be removed if the powder is not to be melted, by treatment with hydrochloric acid/hydrofluoric acid in a polypropylene container. After reignition and reduction with hydrogen, the powder is screened through a plastic sieve, thoroughly mixed and stored in a polythene container. The precautions necessary to avoid contamination by impurities must be observed [1, 2].

References:

[1] E. N. Sloth, C. S. Garner (J. Chem. Phys. **22** [1954] 2064/6). – [2] S. I. Ginzburg, N. A. Ezerskaya, I. V. Prokof'eva, N. V. Fedorenko, V. I. Shlenskaya, N. K. Bel'skii (Analytical Chemistry of Platinum Metals, Wiley, New York 1975, p. 422).

2.4 Melting, Casting and Mechanical Working

The melting, casting and mechanical working of the pure platinum-group metals powders to produce sheet, rod and wire must be carried out under carefully controlled conditions to avoid pick-up of impurities and to produce sound castings free from porosity. High-frequency induction furnace melting in zircon crucibles with suitable control of melting conditions to deal with oxygen pick-up can be employed [1]. The National Bureau of Standards platinum 680 was prepared by induction-melting of high-purity platinum sponge in a zirconium silicate crucible and casting into a platinum-lined water-cooled copper mould [2] (material 681 was cast into a graphite mould).

Hot platinum readily alloys with any iron with which it is in contact, and the iron diffuses rapidly below the surface [3]. Thus, the operations of hot forging or hot rolling always contaminate a platinum ingot, so that after these operations it is essential to scalp all materials. Any subsequent surface contamination introduced during rolling or wire drawing must be removed by some means such as heavy aqua regia etching before any annealing is carried out, otherwise the iron may diffuse deeply into the mass.

To avoid oxidation, palladium is melted under an inert atmosphere and is cast, forged and worked under similar carefully controlled conditions to avoid contamination.

The high-melting point metals are produced by hot pressing, forging and working under very clean conditions to avoid oxidation and contamination. Alternatively they can be melted in a water-cooled copper mould using argon arc or plasma [1, 2, 3].

References:

[1] D. McDonald (Platinum Metals Rev. **2** [1958] 55/60). – [2] National Bureau of Standards U.S. (Stand. Ref. Mater. No. 680/681 [1967]). – [3] J. C. Chaston (Platinum Metals Rev. **15** [1971] 122/8).

2.5 Thin Films of High Purity Platinum-Group Metals

Thin films of high purity platinum-group metals can be deposited on various substrates using chemical vapour deposition, electrodeposition from aqueous solutions or fused salts, vacuum evaporation and sputtering techniques. In all cases high purity platinum-group metals or compounds produced by the chemical refining routes are required. Further purification of the starting materials by vacuum zone refining may also be required.

2.5.1 Volatilization Methods

Methods involving sublimation of volatile compounds of platinum-group metals and subsequent pyrolysis of these compounds to form the metals are of little value except in special circumstances since the temperatures of sublimation and decomposition are too close for effective separations.

Moreover, many base metals show similar behaviour. The compounds used fall into three distinct classes:

(1) halides,
(2) carbonyls and carbonyl halides,
(3) organometallic complexes which can be subdivided into
  a) acetylacetonato and substituted complexes,
  b) cyclopentadienyl, cyclooctadienyl and cyclooctatrienyl complexes,
  c) alkyl and aryl derivatives.

Most of the compounds referred to are available commercially but preparation of pure platinum-group metals via this route is more expensive than via the chemical and solvent extraction routes described previously. Also, the metals derived from such compounds are often contaminated with amorphous carbon which requires oxidative removal. The main application of metals derived via this route is where these deposits are required on selected substrates such as glass, plastics and refractory metals not readily coated by other means. The throwing power of chemical vapour deposition processes is high, and coating thicknesses can be varied and well-controlled over a wide range. Table IX, pp. 45/6, gives data on a number of these compounds [1 to 14].

References:

[1] J. P. Heffer (Johnson Matthey Chemicals, private communication). – [2] H. Zeiss (ACS. Monogr. Ser. No. 147 [1959]). – [3] A. O. Fink (U.S. 2576289 [1959]). – [4] E. O. Fischer, W. Hafner, Union Carbide Corp. (Brit. 829574 [1960]; U.S. 2953386 [1960]). – [5] N. V. Phillips Gloeilampenfabrieken (Brit. 304396 [1927]).

[6] W. Hieber, H. Heusinger, O. Vohler (Chem. Ber. **90** [1957] 2425/34). – [7] R. L. van Hemert, L. B. Spendlove, R. E. Sievers (J. Electrochem. Soc. **112** [1965] 1123/6). – [8] R. W. Moshier, R. E. Sievers, L. B. Spendlove (U.S. 3356527 [1967]). – [9] C. F. Powell, J. H. Oxley, J. M. Blocher (Vapour Deposition, Wiley, New York 1966, p. 313). – [10] J. S. Anderson (Quart. Rev. [London] **1** [1947] 331/57).

[11] J. N. Criscione (ML-TDR 64-173- Pt. III [1964] 33). – [12] B. A. Machlin, J. C. Withers (Proc. Conf. Chem. Vapour Deposit. Refract. Metals Alloys Compounds, Gatlinburg, Tenn., 1967, p. 161). – [13] C. F. Powell, J. H. Oxley, J. M. Blocher (Vapour Deposition, Wiley, New York 1966, p. 311). – [14] A. E. van Arkel (Metallwirtschaft **13** [1934] 405). – [15] N. V. Phillips Gloeilampenfabrieken (Brit. 280697 [1927]).

[16] E. C. Marboe (U.S. 2430520 [1947]). – [17] A. A. Grinberg, I. N. Chapurskii (Zh. Neorgan. Khim. **4** [1959] 314/8; Russ. J. Inorg. Chem. **4** [1959] 137/9). – [18] J. A. McCleverty, G. Wilkinson (Inorg. Syn. **8** [1966] 211/3). – [19] F. Bonati, G. Wilkinson (J. Chem. Soc. **1964** 3156). – [20] R. Cramer (J. Am. Chem. Soc. **86** [1964] 217/22; Inorg. Chem. **1** [1962] 722/3).

[21] M. Dub (Organometallic Compounds, Vol. 1, 2nd Ed., Springer, Berlin 1966, p. 630). – [22] B. L. Shaw, S. D. Robinson (Tetrahedron Letters **1964** 1301). – [23] R. W. Moshier (U.S. 3356527 [1967]). – [24] A. A. Grinberg, L. K. Simonova (Zh. Prikl. Khim. **26** [1953] 880/2; J. Appl. Chem. [USSR] **26** [1953] 801/3). – [25] A. K. Chatterjee, R. C. Menzies, J. R. Steel, F. W. Youdale (J. Chem. Soc. **1958** 1706).

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[31] J. A. Papke, C. D. Stevenson (Proc. Conf. Chem. Vapour Deposit. Refract. Mater., Gatlinburg, Tenn., 1967, p. 193). – [32] G. Pannetier, R. Bonnaire, P. Fougeroux, P. Alépée (J. Less-Common Metals **21** [1970] 103/13). – [33] G. Pannetier, R. Bonnaire, P. Fougeroux (J. Less-Common Metals **21** [1970] 437/8).

Pyrolysis of Halides

Iridium halides have been used for chemical vapour deposition of iridium on graphite to protect it from oxidation at high temperatures (~2000°C). The trichloride is vapourised at 150 to 300°C and carried in a stream of hydrogen mixed with carbon monoxide to the substrate which is heated to 825 to 975°C. Using iridium hexachloride carried in a stream of argon, carbon monoxide and hydrogen at low pressure rates of deposition of 0.5 mL/h were achieved. Of the other platinum group metals which have volatile halides only osmium tetrachloride has a volatilisation temperature and decomposition temperature sufficiently far apart to be potentially useful for chemical vapour deposition.

Table IX

metal	compound	formula	sublimation temperature	decomposition temperature	Ref.
Ru	carbonyl	$Ru_2(CO)_9$	—	150°C	[2]
	carbonyl chloride	$Ru(CO)Cl$	—	—	[3]
	di-aryl complexes	$[(Ph_2)_2Ru]X_2$ $X = ClO_4$, I or BPh_4	—	—	[4]
Rh	carbonyl	$Rh_2(CO)_8$	—	—	[5]
	carbonyl chloride	$Rh_2(CO)_4Cl_2$	100°C	140°C	[6, 18]
	bis trifluoroacetylacetonato rhodium(III)	$Rh(CH_3COCHCOCF_3)_3$	150°C/0.1 Torr	270°C	[7, 8]
	dicarbonylacetylacetonato rhodium(III)	$Rh(CO)_2(CH_3COCHCOCH_3)$	50°C/0.02 Torr	160°C	[19]
	bis(ethylene)acetylacetonato rhodium	$(C_2H_4)_2Rh(CH_3COCHCOCH_3)$	65°C/0.05 Torr	150°C	[20]
Pd	bis acetylacetonato palladium(II)	$Pd(CH_3COCHCOCH_3)_2$	160°C/0.1 Torr	360°C	[9, 24]
	bis trifluoroacetylacetonato palladium(II)	$Pd(CH_3COCHCOCF_3)_2$	150°C/0.1 Torr	270°C	[8]
	bis hexafluoroacetylacetonato palladium(II)	$Pd(CF_3COCHCOCF_3)_2$	60°C/0.1 Torr	230°C	[8]

Table IX (continued)

metal	compound	formula	sublimation temperature	decomposition temperature	Ref.
Pt	platinum carbonyl chloride	$Pt(CO)_2Cl_2$	~100°C	500°C	[13, 14, 15]
	bis acetylacetonato platinum(II)	$Pt(CH_3COCHCOCH_3)_2$	170°C	420°C	[16, 17]
	bis trifluoroacetylacetonato platinum(II)	$Pt(CF_3COCHCOCH_3)_2$	150°C	270°C	[1, 8]
	bis hexafluoroacetylacetonato platinum(II)	$Pt(CF_3COCHCOCF_3)_2$	50°C	240°C	[1, 8]
	bis(2,2′,6,6′-tetramethyl-3,5-heptanedionato)platinum(II)	$Pt(C_4H_9COCH_2COC_4H_9)_2$	115°C	140°C	[1]
	acetylacetonato 8-(acetylacetonyl)-cyclooct-4-enyl platinum(II)	$C_8H_{12}Pt(CH_3COCHCOCH_3)_2$	180°C	350°C	[1, 26]
	2,2′,6,6′-tetramethyl-3,5-heptanedionato trimethyl platinum(IV)	$(CH_3)_3Pt(C_4H_9COCHCOC_4H_9)$	145°C	160°C	[1, 25]
	cyclopentadienyl-trimethyl platinum(IV)	$C_5H_5Pt(CH_3)_3$	20°C	260°C	[27, 28, 29]
Ir	iridium trichloride, tetrachloride, tribromide and hexafluoride	$IrCl_3$, $IrCl_4$, $IrBr_3$, IrF_6	150 to 300°C	700 to 800°C	[11, 12]
	tris acetylacetonato iridium(III)	$(CH_3COCHCOCH_3)_3Ir$	180°C/0.1 Torr	350 to 400°C	[30]
	cyclo octadienyl complexes	$[(C_8H_{12})IrOCH_3]_2$ $(C_8H_{12})IrCOCH_3{=}COCH_3$	115 to 120°C/ 0.1 Torr	600°C	[1, 21, 23] [31, 32, 33]
Os	osmium carbonyl	$Os_2(CO)_9$	224°C	—	[10]
	osmium carbonyl bromide	$Os_2(CO)_2Br_2$	—	—	[3]

Pyrolysis of Carbonyls and Carbonyl Halides

Metal carbonyls are prepared by treating free metal or suitable compounds with carbon monoxide. Ru, Rh, Os and Ir form carbonyls (as do V, Cr, Mn, Fe, Co, Ni, Mo, W and Re); Ru, Rh, Pd, Os, Ir and Pt form carbonyl halides (as do Mn, Fe, Co, Ni, Cu, Re, Au and Hg).

The carbonyl halides of the platinum group metals are generally used because of their greater volatility at low temperatures (except palladium carbonyl halides which are too unstable). The carbonyl chlorides show greater thermal stability than the carbonyl bromides or carbonyl iodides. Preparation is carried out using carbon monoxide on the di-, tri- or tetrahalides, at 140 to 270°C, or on finely divided metals with chlorine and carbon monoxide at 600°C (or carbon dioxide and carbon tetrachloride). The carbonyl chlorides volatilised at 100 to 120°C are decomposed at 0.01 to 0.02 Torr on surfaces heated to 600°C. At higher pressures carbon monoxide can be used as a carrier gas with a vapourisation temperature of 135 to 145°C and a decomposition temperature of 500°C. By reducing the metal carbonyl halide with hydrogen using separate streams of hydrogen and compound in carrier gas, vapourisation temperatures of 100 to 125°C and decomposition temperatures around 125°C can be employed.

Pyrolysis of Acetylacetonato and Fluoroacetylacetonato Complexes

The bis-acetylacetonato palladium(II) undergoes some thermal decomposition in the vapouriser which may be suppressed by the addition of acetylacetone, acetone, acetic acid or anhydride, but this has not been investigated [1]. The trifluoro- or hexafluoroacetylacetonato complexes of rhodium can be reduced by hydrogen at atmospheric pressure and temperatures as low as 250°C [2]. The process is potentially cyclic, free chelating agent being regenerated.

References:

[1] C. F. Powell, J. H. Oxley, J. M. Blocher (Vapour Deposition, Wiley, New York 1966, p. 313). – [2] R. W. Moshier, R. E. Sievers, L. B. Spendlove (U.S. 3356527 [1967]).

Pyrolysis of Cyclopentadienyls

In addition to ruthenium, rhodium, iridium and osmium many base metals (Ti, V, Cr, Mn, Fe, Co, Ni, Mo, W, Nb, Ta, Re) form similar complexes. The trimethylcyclopentadienyl platinum(IV) compound sublimes in vacuum at room temperature.

R. L. Mack, D. J. Kozikoski, R. D. Stevenson (ML-TDR-64-206-Pt. II [1965]).

Pyrolysis of Alkyl and Aryl Derivatives

Platinum is the only member of the group so far reported as forming an alkyl. It decomposes at high temperature before melting. Many other elements form alkyls some of which are used (e.g., tributyl aluminium and trialkyl borons) in large quantities for commercial plating [1, 2]. Hence it is necessary to use high purity starting materials to obtain thin films of high purity.

Table X, p. 48, gives a comparative summary of the evaluation of platinum compounds used for chemical vapour deposition, and Table XI, p. 49, shows the type of deposit obtained on various substrates using bis-acetylacetonato platinum(II) [3].

Table X

compound	formula	sublimation temp. in °C	decomposition temp. in °C	deposit
(1) dichloroplatinum	$PtCl_2$	did not sublime	620	none
(2) platinum carbonyl chloride	$Pt(CO)_2Cl_2$	~100/760	500	coarse, crystalline, poorly adherent
(3) bis-acetylacetonato platinum(II)	$Pt(acac)_2$	170	420	smooth, bright, adherence generally good
(4) bis-trifluoroacetylacetonato platinum(II)	$Pt(tfacac)_2$	150	270	smooth, bright, adherence good but only marginally better than (3)
(5) bis-hexafluoroacetylacetonato platinum(II)	$Pt(hfacac)_2$	50	240	
(6) bis-2,2′,6,6′-tetramethyl-3,5-heptadionato platinum(II)	$Pt(isovac)_2$	115	140	smooth, bright, no advantage over (3) except lower temperature
(7) acetylacetonato [8-(acetylacetonyl)]cyclooct-4-enyl platinum(II)	$C_8H_{12}Pt(acac)_2$	180	350	smooth but dark, carbonaceous deposit, good adherence
(8) 2,2′,6,6′-tetramethyl-3,5-heptadionatotrimethyl platinum(IV)	$(CH_3)_3Pt(isovac)$	145	160	smooth, bright but no advantage except lower temperature; difficult preparation compared with (6)
(9) cyclopentadienyltrimethyl platinum(IV)	$C_5H_5Pt(CH_3)_3$	20	260	good deposit but no advantages

acac = $CH_3COCHCOCH_3$, tfacac = $CF_3COCHCOCH_3$, hfacac = $CF_3COCHCOCF_3$, isovac = $C_4H_9COCHCOC_4H_9$.

Table XI

substrate	type of deposit	adher- ence	conduc- tivity	remarks
glass sheet	metallic mirror	variable	excellent	no chemical bond, only weak van der Waals type bonds
glass sheet (sandblasted)	matte grey	excellent	excellent	"keyed" to rough surface
glass ballotini	light matte grey	good	excellent	self-supporting spherical films
sintox	light matte grey	excellent	excellent	"keyed" to rough surface
ceramic, unglazed biscuit	dull grey	good	good	"keyed" to rough surface
ceramic, glazed biscuit	bright grey	good	n.d.	a chemical bond probably formed between the glaze and the deposit
porcelain, unglazed	dull grey	excellent	excellent	"keyed" to rough surface
porcelain, glazed	bright metallic	good	excellent	
porous alumina tube	bright metallic	excellent	usually good but some poor	appeared to possess preferred routes for vapour through the matrix
silica	bright metallic	good	excellent	good conductivity
graphite	dull grey	poor	n.d.	although a rough surface substrate it was very powdery
copper	metallic mirror	poor	n.d.	poor adherence due to lack of any chemical bond and only weak physical bond
nickel	bright metallic	poor	n.d.	
niobium (etched)	bright	non-adherent	n.d.	probably due to inherent on substrate oxide film
niobium (sandblasted)	dull	non-adherent	n.d.	

n.d. = not determined.

Of the compounds referred to in Table X, p. 48, the bis(ethylene) acetylacetonato rhodium is easy to prepare in good yield and produces excellent deposits of rhodium. The cyclooctadienyl complexes of iridium produce acceptable deposits but the intermediate cyclooctadienyl dichlorohydrido iridium dimer $[(C_8H_{12})IrHCl_2]_2$ produced during the preparation is unstable in light and oxygen [4, 5]. By carrying out the reaction in nitrogen in the dark, satisfactory yields of the hydrido complex can be obtained. The bis-acetylacetonato palladium compound can be prepared in good yield and it behaves like the analogous platinum compound for chemical vapour deposition [6].

References:

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2.5.2 Electrodeposition

Aqueous electroplating of platinum-group metals is a well established method of producing thin, bright, adherent films on substrates. Plating baths and conditions for the electrodeposition of the platinum metals have been published [1, 2]. The fundamental electrochemistry of electrodeposition of precious metals is reviewed in a paper which also gives references to many of the basic plating solutions [3]. Although electrodeposition can produce high purity cathode material, information on the impurity levels in the films is generally not available.

Electrodeposition from fused salts is of increasing value. The electrodeposition of iridium from a molten mixture of sodium and potassium cyanides using an iridium anode and deposition of platinum, iridium and ruthenium from molten cyanides have been described [4, 5]. Investigation at the U.S. Bureau of Mines showed that iridium, rhodium and ruthenium can be electrodeposited from molten cyanides under an inert atmosphere, whilst platinum and palladium require the presence of air [6]. A separation scheme for rhodium, iridium, ruthenium and osmium is based on selective extraction into liquid metals and alloys [7]. Rhodium can be separated from iridium by selective extraction into tin or bismuth from molten (K, Na)CN [8]. The authors of these papers do not provide information on the purification effect of electrodeposition from molten cyanides but a significant reduction in impurities present in the fused salt plated deposit of platinum compared with those present in the original platinum anodes has been found (see Table XII; n.d. = not detected) [9].

Table XII

impurities	Au	B	Ca	Cu	Fe	Pb	Mg	Mn	Ni	Si	Ag	Zn	total
anode, ppm	50	5	<1	20	70	2	<1	<1	7	10	30	10	207
plated, ppm	7	n.d.	<1	5	9	n.d.	<1	n.d.	9	<1	1	n.d.	31

References:

[1] J. Fischer, D. E. Weimer (Precious Metal Plating, Draper, Teddington 1964). – [2] F. H. Reid (Trans. Inst. Metal Finish. **48** [1970] 115/23). – [3] J. A. Harrison, J. Thompson (Electro-

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2.5.3 Vacuum Evaporation and Sputtering

A review of the available techniques for depositing platinum-group metals on substrates includes vacuum evaporation, sputtering and the planar magnetism sputtering technique for attaining high deposition rates [1, 2]. The behaviour of impurities is not referred to, but by choice of suitable target materials, films in the range of a few atomic layers up to 1 μm of high purity metals can be expected.

References:

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2.6 Zone Refining of Platinum-Group Metals

2.6.1 General Remarks

High purity platinum-group metals are required for industrial usage in the preparation of thin film deposits for micro-solid-state electronic circuits and thermometry. The purest available platinum-group metals produced by chemical refining techniques still contain small amounts of metallic impurities such as calcium, copper, iron, magnesium, silver and other platinum-group elements. In addition silicon, carbon, oxygen and hydrogen are present either on the surface or the bulk of the metal, and can on melting, or high temperature treatment, react with the primary metal and with each other to form solid solutions and low-melting eutectics with the platinum metal, resulting in thin grain boundary layers [1]. Brittle chemical compounds may also be produced. Intercrystalline oxidation of impurities or the formation of weakly bound phases can initiate brittle fracture during working. Purification arising from selective evaporation of impurities and transportation to the ends of the sample has produced single crystals of the platinum metals in high purity form which then exhibit very high plasticity.

Techniques for producing single crystals of the platinum metals involve a preliminary melting of the purest available sponge on a water-cooled copper hearth in an arc or electron beam furnace under a vacuum of 1.33×10^{-3} to 1.33×10^{-4} Pa, or in a water-cooled silver boat using a 30 kW r.f. generator at a frequency of 3 MHz [2]. Rods can be sintered in a hydrogen atmosphere at high temperatures and furnace-melted rods can be rotary forged to produce starting blanks of round cross sections [3]. Rods made in silver boats can be stretched into uniform cylinders using a floating zone refiner [2].

Float zone refining in which surface tension holds a molten zone of liquid in a sample whose axis is vertical overcomes any difficulty of contamination by the container [4]. Heating can be by electron bombardment in vacuum, or where the metals have a high vapour pressure at the melting point (>13.3 Pa) by r.f. induction heating in an inert atmosphere. The stability of the molten zone is a function of the radius of the rods, the length of the molten zone, the surface tension and density of the liquid and the shape of the liquid-solid interface. Although relationships have been derived between these factors which ban be used as a guide to the design of apparatus, operating experience shows that there are experimental parameters which have a significant effect on stability [5, 6]. The process parameters which are appropriate for electron-beam melting of rhodium, iridium and ruthenium have been published [3]. To avoid production of internal stresses in the single crystals the cooling rate can be controlled by resistance heating or the crystals can be subsequently annealed.

References:

[1] E. M. Savitskii, V. Polyakova, N. B. Gorina (Platinum Metals Rev. **23** [1979] 57/65, 59). – [2] S. Hornfeldt, J. B. Ketterson, L. R. Windmiller (J. Cryst. Growth **5** [1969] 289/93). – [3] E. Savitskii, V. Polyakova, N. Gorina, N. Roshan (Physical Metallurgy of Platinum Metals [MIR Publ., Moscow], Pergamon 1978, p. 99). – [4] W. G. Pfann (Zone Melting, 2nd Ed., Wiley, New York 1966). – [5] W. Heywang (Z. Naturforsch. **11a** [1956] 238/42).

[6] P. H. Keck, M. Green, M. L. Polk (J. Appl. Phys. **24** [1953] 1479/81).

2.6.2 Platinum

A platinum bar was purified by vacuum annealing for 24 h at 1273°C and 6.65×10^{-5} Pa followed by zone refining in an electron beam refiner at 1.33×10^{-4} Pa. The whole of the zone-refined section of the bar was converted with its axis showing a preference for $\langle 100 \rangle$. The emission spectrographic analyses of the original, vacuum heated, vacuum melted and two zone refined sections (after 12 passes) are shown in Table XIII (all concentrations in ppm atomic, n.d. = not detected).

Table XIII

element	original bar	vacuum heated	vacuum melted	pure zone – refined ZRI	end of zone refined
Pd	20	10	8	n.d.	n.d.
Rh	—	4	2	n.d.	n.d.
Al	n.d.	10	n.d.	n.d.	n.d.
Cu	2	3	3	n.d.	3
Fe	20	14	4	<4	4
Mg	<8	8	<8	<8	<8
Si	7	7	<7	<7	<7
Ag	<2	2	2	n.d.	n.d.

The authors also gave the mass spectrographic analyses (Table XIV) for the original bar and the pure zone refined ZRI mentioned in Table XIII.

The ratio of the specific resistances at 300 and 4.2 K was used as a measure of evaluating purity. It represents the total contribution of chemical impurities and lattice defects (vacancies, interstitial atoms, dislocations) and omits that of impurity atoms which are present not in solid solution but at grain boundaries and in the inclusions.

Table XIV

element	ppm atomic mass spectrograph on original bar	 mass spectrograph on ZRI*)
Pb	<0.4	<0.6
Au	0.3	0.2
Pt	base	base
W	<0.04	0.07
Ta	<0.3	—
Pd	2.7	<0.04
Ag	0.06	<0.02
Rh	0.3	0.3
Cu	0.05	<0.05
Ni	1.5	0.15
Fe	20	3
Cr	1.2	0.4
Ti	<1.4	<0.13
Ca	3	—
S	3	—
P	1	—
Si	7	<2
Al	10	1
Mg	3	<0.1
Na	1	—
O	30	30
N	10	—
B	4	—
C	—	100
Bi	—	<0.1

*) Many elements with <0.05 ppm have been omitted.

The resistance ratio of the original platinum bar was 90; after annealing 750, and after zone refining 1100. By giving two more passes in a residual oygen environment at a pressure of 1.33×10^{-2} Pa a ratio of approximately 1350 was achieved and by giving two more zone passes in the residual hydrogen pressure of 1.33×10^{-2} Pa a ratio of $R_{4.2}=1600$ was obtained. (The actual measurements of $R_{4.2}$ along the length of the bar are shown in a graph.) Further chemical treatment produced a ratio $R_{4.2}=3200$.

The authors' main conclusions were:

(1) The major impurities limiting resistance ratio in commercially available 99.999% pure platinum are iron, carbon and palladium.

(2) Palladium can be substantially reduced by melting and zone refining.

(3) Iron content can be reduced by zone melting.

(4) The electron scattering due to iron can be reduced by oxygenation.

(5) Carbon content cannot be reduced by zone refining.

(6) $R_{4.2}$ may be significantly improved by hydrogenation.

J. S. Shah, D. M. Brookbanks (Platinum Metals Rev. **16** [1972] 94/100).

2.6.3 Palladium

The benefit of melting palladium in a water-cooled silver boat in an atmosphere of oxygen at 4.66×10^4 Pa followed by zone refining at 600 Torr was shown. The crystal was then annealed at 1100°C in air for 15 min. This crystal was found to have a residual resistance ratio of 2400 compared with a ratio of 950 for a crystal annealed in vacuum [1].

In a programm of r.f. float zone refining of palladium in air using a 450 kHz 10 kW generator, the starting material in the form of 1 mm wire was 99.999% Pd which by emission spectrography contained Fe (4 ppm), Si (2 ppm), Ca (1 ppm), Cu, Mg, and Ag each <1 ppm. Two rods were treated and on one the resistance ratio was measured at positions along the bar after 25, 35 and 65 passes in air. On the other bar 125 passes in air were made and similar measurements carried out. The authors apply two types of corrections to the resistance ratio at 4.2 K to get a proper estimate of the residual resistivity at zero K: (1) corrections due to electron-electron scattering and (2) corrections due to the finite size of the specimen. The minimum residual resistivity ratio after 65 passes was $R_{4.2} = 10000$ and $R_0 = 25000$. After 125 passes $R_{4.2}$ was 11000 and $R_0 = 31000$. The minimum residual resistivity occurred near the centre of the traverse, instead of at the lead end as in a zone-refined rod, suggesting that zone refining was not the dominant process in the purification. The authors concluded that the presence of oxygen during melting was essential for the refining process since zoning in an inert atmosphere and annealing in oxygen do not show a similar large improvement. The float zoned palladium crystals grown in air produce large de Haas-van Alphen oscillations, suggesting that lattice imperfections such as mosaic structure are near a minimum [2].

Palladium crystals have been grown utilising vapour-solid equilibria. Solid $PdCl_2$ was heated to ~900°C in a vitreous silica tube in a slow stream of argon. The vapour passed along the tube to a higher temperature area where the palladium chloride was decomposed to give hexagonal and triangular platelets and long filamentary single crystals or whiskers some of which were straight while others were helical [3].

References:

[1] S. Hornfeldt, J. B. Ketterson, L. R. Windmiller (J. Cryst. Growth **5** [1969] 289/93). – [2] N. B. Sandesara, J. J. Vuillemin (Met. Trans. B **8** [1977] 693). – [3] R. A. Landise (The Growth of Single Crystals Prentice-Hall, Englewood Cliffs, N.J., 1970).

2.6.4 Rhodium

Rhodium single crystals with a residual resistivity ratio of 2200 have been produced [1]. Starting with rhodium powder containing 12 ppm of impurities the metal was sintered and melted in water-cooled silver boats by r.f. heating in an atmosphere of argon at 4.66×10^4 Pa. It was noted that when the rhodium powder would not heat in the r.f. field, presumably due to a surface layer of oxide, the addition of a small piece of pure rhodium wire at one end of the charge would form a nucleation point from which the material could be melted. Zone refining in vacuum (1.33×10^{-5} Pa) was followed by annealing at 1200°C in vacuum, reheating in air at 1500°C in the concentrator and finally at 1100°C in air. Other investigators list the process parameters for electron beam zone melting of rhodium and show the effect of arc melting and electron beam melting on impurities (see Table XV) [2, 3].

Rhodium single crystals have been produced from 99.99% sponge by three vertical zone passes at a rate of ~5 cm/h in a vacuum of 1.33×10^{-5} Pa. Starting with crystals whose ratio varied between $200 \leqq RRR \leqq 1000$ the resistance ratio was increased to 2400 by heating to 1400°C for ~6 h in an oxygen atmosphere, independently of the starting ratios. In addition the ratios could be reduced back to the original values by a simple heat treatment in hydrogen. The oxygenation was thought to be a bulk effect which caused the oxygen to diffuse into the rhodium lattice where combination with major impurities created a complex (or precipitate) with a smaller electronic scattering cross section. This conclusion was supported by spark source mass spectrometric analysis data which showed very little difference in the major impurities in a rhodium crystal before and after oxygen annealing [4].

Table XV

element	impurities in ppm/wt refined powder	arc melting	electron-beam melting
Pt	200	150	100
Pd	1	1	1
Ir	30	30	10
Cu	10	10	5
Fe	10	10	8
Si	10	—	—
Na	20	—	—
Pb	20	—	—
S	—	100	—
C	20	10	10
O	—	30	30
H	—	1	1

When searching for the possible superconductivity of rhodium the Jülich low temperature team discovered in a sample of commercial high purity rhodium which had a residual resistivity ratio of 50 a weak diamagnetic signal around 20 mK, which increased with decreasing temperature and reached a full superconductive value around 200 μK. Another sample of high purity rhodium sponge was consolidated by r.f. induction melting in a water-cooled copper boat. A sample was annealed for 15 h at 2020 K in ultra-high vacuum (10^{-8} Pa). The residual resistivity ratio and the impurities present by emission spectrometry and mass spectrometry are listed in Table XVI [5].

Table XVI

Optical Emission[a] and Mass[b] Spectrometry Analysis of 2 Rh Samples (RRR = residual resistivity ratio):

sample	RRR = 50[e]		RRR = 450[f]	
analysis[c] number	optical emission 1	mass 2	optical emission 3	mass 4
element	impurity level, atomic ppm[d]			
C	—	~1000	—	~1000
N	—	4	—	7
O	—	20	—	~30
Na	—	1	—	1.5
Mg	<4	1	<4	—
Al	<4	4	—	4
Si	4	~43	<4	24
P	—	—	—	2
S	—	121	—	~100
K	—	—	—	2
Ca	<2.5	0.5	8	1
Ti	—	2	—	—
V	—	0.5	—	1.5
Cr	2	2	<2	1.5
Mn	—	0.8	<2	0.5
Fe	2	13	<2	12
Co	—	0.5	—	0.4
Ni	—	2	—	2.5
Cu	12	250	1.5	200
Zn	—	5	—	—
Zr	—	~20	—	0.5
Ru	—	1.5	—	~11
Ce	—	~6	—	~2
W	—	64	—	—
Ir	—	1.5	1	21
Pt	—	1.5	—	1
Pb	<0.5	—	—	—

[a] Data from Johnson Matthey Chemical Ltd. – [b] Data from H. Beske, ZCH, KFA Jülich. – [c] Analyses 1, 2 and 4 were made on the final sample, analysis 3 on the starting sponge. – [d] The limit of detection for mass spectrometry is 0.5 atomic ppm, for optical spectrography in general 1 wt ppm (osmium, ruthenium 10 ppm, tungsten 100 ppm). – [e] This sample was arc-melted with a tungsten electrode in a beryllium-copper mould. – [f] This sample was r.f. induction-melted in a water-cooled boat crucible made from copper.

With the sample having a R of 450, sharp signals were obtained which could be attributed unambiguously to the volume superconductivity of rhodium. The superconducting transition temperature in rhodium (325 μK) is approximately three orders of magnitude below those of the neighbour elements iridium (0.1 K) and ruthenium (0.49 K) [5].

References:

[1] S. Hornfeldt, J. B. Ketterson, L. R. Windmiller (J. Cryst. Growth **5** [1969] 289/93). – [2] E. Savitskii, V. Polyakova, N. Gorina, N. Roshan (Physical Metallurgy of Platinum Metals [MIR Publ. Moscow], Pergamon, New York 1978, p. 99). – [3] E. M. Savitskii, V. Polyakova, N. B. Gorina (Platinum Metals Rev. **23** [1979] 57/65, 59). – [4] J. J. Rubin, D. L. Malm (J. Vac. Sci. Technol. **11** [1974] 389). – [5] Ch. Buchal, J. M. Welter (Platinum Metals Rev. **27** [1983] 170/4).

2.6.5 Iridium

Details of the parameters used for electron-beam zone melting of iridium, together with a photograph of a single crystal bent at room temperature to illustrate its considerable plasticity, have been recorded [1].

The production of single crystals of iridium which were subsequently used in the study of the high temperature tensile properties has been described. Rods, 4 mm diameter, 15 cm long which had been formed by swaging high purity arc-melted ingots at 1400°C were outgassed in the electron-bombardment furnace for 20 h at 2000°C in a vacuum of 1.33×10^{-4} Pa. The crystal was melted in the same furnace and after up to 25 passes became stable enough to form a single crystal. The final zoning was carried out at ~1.5 mm/min in a vacuum between 1.3 and 4×10^{-4} Pa using an emission current of 100 mA at 280 to 300 W [2].

The stress/strain curves for iridium single crystals are compared with those obtained earlier and the effect of impurities which aid crack propagation in single crystals by significantly increasing the critical resolved shear stress is considered. At high temperatures iridium was shown to be a metal of exceptional strength but at low temperatures it was found to be brittle. The brittleness was attributed as at least partly due to impurities which, using the Argonne National Laboratory figures quoted, show that the iridium used was less pure than that used by earlier investigators [3].

References:

[1] E. Savitskii, V. Polyakova, N. Gorina, N. Roshan (Physical Metallurgy of Platinum Metals [MIR Publ. Moscow], Pergamon, New York 1978, p. 99). – [2] C. A. Brookes, J. H. Greenwood, J. L. Routbort (J. Inst. Metals **98** [1970] 27/31). – [3] P. Haasen, H. Hieber, B. L. Mordike (Z. Metallk. **56** [1965] 832/41).

2.6.6 Ruthenium

Polycrystalline ruthenium rod suffers from brittle fracture when bent at room temperature but single crystal ruthenium produced under specified conditions can be bent by hand through more than 90° [1]. Figures obtained for the impurities in refined powder, arc melted and electron beam melted ruthenium are given in Table XVII [4].

Table XVII

element	impurities in ppm/wt refined powder	arc melted	electron-beam melted
Pt	10	10	10
Pd	10	10	10
Ir	10	—	10
Rh	40	10	10
Cu	10	10	5
Fe	10	10	8
Si	30	30	20
Mg	30	—	6
Al	20	—	—
Na	10	—	—
Pb	10	—	—
S	—	40	—
C	300	200	100
	250	170	50
O	—	150	80
	—	200	60
H	—	9	2

The two-stage production of ruthenium single crystal, from 99.9% material has been described. In the first stage the powder was degassed and electron-beam melted in water-cooled copper boats to give ingots 7 mm diameter by 8 mm long. These were then zone refined at a gas pressure between 6.67×10^{-5} Pa and 6.67×10^{-4} Pa during melting. The molten zone produced by electron beam was moved at a rate of 3.5 to 4 mm/min. In powders containing oxygen there was decarbonisation accompanied by the evolution of carbon monoxide. For the ruthenium single crystals produced the residual resistivity ratio was 2500 [2]. A later paper reports on the production of single crystals of ruthenium by zone melting in an electric field. The material used was vacuum melted rods, 8 mm diameter and 110 mm long, with a resistivity ratio of 500. There were seven zone passes at a rate of 3 mm/min with a current density of 1000 to 2000 A/cm^2,and an electric field of 0.15 V/cm. The greatest purification was achieved where zone movement was in the opposite direction to that of the electric field, see Table XVIII [3].

The temperature dependence of the resistivity was measured on single crystal ruthenium with a residual resistivity ratio of ~1100 using specimens spark machined with a cross section of 1.3×1.3 mm and length up to 12 mm. The resistivity of ruthenium specimens of different orientation was shown to be temperature-dependent: the resistivity anisotropy $\varrho\langle 1210\rangle/\varrho\langle 0001\rangle$ being greater than unity throughout the range of temperature studied, reaching ~1.3 when $T \geqq 100$ K and with a minimum at ~50 K indicating a change in the direction of conduction electron scattering.

Attention has been drawn to the anisotropic characteristics of the ruthenium single crystals. The hardness on different single crystal faces are 100 and 250 kg/mm^2; the thermal

Table XVIII

process	residual resistivity ratio start of cast	 middle of cast	 end of cast
zone melted without electric field	1300	1000	900
in electric field – same direction	1050	1100	1200
in electric field – opposite direction	1900	1500	650

diffusivity of single crystal ruthenium on samples cut parallel to and at right angles to the c-axis was shown to be temperature-dependent and to decrease with increasing temperature and electrical resistivity measurements showed the temperature dependence of the ratio ϱ_1/ϱ_{11} to be 1.45. The thermionic emission also showed anisotropy, the work function of electrons (eV) for polycrystalline material being 4.68 and for (0001), $(10\bar{1}0)$ and $(11\bar{2}4)$ single crystal faces being 5.40, 5.14, and 4.52, respectively. Oxygen and hydrogen adsorption and desorption on electrode samples in 1N sulphuric acid were studied. The curves for hydrogen adsorption on ruthenium (0001) and $(11\bar{2}0)$ faces show a maximum which is responsible for the presence of hydrogen in the bound form on a ruthenium surface. Oxygen desorption from ruthenium (0001) and $(11\bar{2}0)$ faces differ by 3 to 4 times [4].

References:

[1] E. Savitskii, V. Polyakova, N. Gorina, N. Roshan (Physical Metallurgy of Platinum Metals [MIR Publ. Moscow], Pergamon, New York 1978, p. 99). – [2] V. M. Azhazha, G. P. Kovtun, V. I. Makarov (Izv. Akad. Nauk SSSR Metally **1973** No. 6, pp. 165/9; Russ. Met. **1973** No. 6, pp. 97/9). – [3] V. M. Azhazha, G. P. Kovtun, V. A. Yelenskiy, N. V. Volkenshteyn, V. Ye. Startsev, V. I. Cherepanov (Fiz. Metal. Metalloved. **41** [1976] 888/90; Phys. Metals Metallog. **41** No. 4 [1976] 188/91). – [4] E. M. Savitskii, V. P. Polyakova, N. B. Gorina (Platinum Metals Rev. **23** [1979] 57/65).

2.6.7 Osmium

Osmium single crystals with a residual resistivity ratio of 2400 have been produced starting with 99.8% osmium and using the two-stage purification technique (degassing and melting by electron beam in water-cooled copper boats in vacuum and zone refining by electron beam heating, as for ruthenium) [1].

The effect of electron-beam melting on the removal of impurities from osmium is shown in Table XIX [2].

The anisotropic characteristics of osmium single crystals have ben referred to. The hardness of different single crystal faces was 350 and 600 kg/mm^2. The anisotropy in thermal properties was found to decrease continuously with increasing temperature and the electrical resistivity on samples cut parallel and perpendicular to the c-axis showed the temperature dependence of ϱ_1/ϱ_{11} to be 1.6 for osmium at 1000 K. Magnetic susceptibility of osmium single crystals between 4.2 and 273 K is independent of the magnetic field direction for the plane perpendicular to the c-axis but in the plane parallel to the c-axis there is 180° anisotropy depending on the crystallographic direction. The magnetic susceptibility ratio is higher if the field is parallel to the c-axis. Hydrogen absorption is 3 times and oxygen 10 times greater on (0001) than on $(11\bar{2}4)$ faces. Oxygen desorption differs by about 8 times for osmium (0001) and $(11\bar{2}4)$ faces [3].

Table XIX

element	impurities in ppm/wt		
	refined powder	arc melted	electron-beam melted
Pt	30	7	7
Pd	1	21	1
Ir	60	27	10
Rh	3	3	3
Cu	5	5	1
Fe	60	18	18
Si	50	—	40
Mg	3	3	2
Al	56	20	8
Na	10	—	—

References:

[1] V. M. Azhazha, G. P. Kovtun, V. I. Makarov (Izv. Akad. Nauk SSSR Metally **1973** No. 6, pp. 165/9; Russ. Met. **1973** No. 6, pp. 97/9). – [2] E. M. Savitskii, V. Polyakova, N. B. Gorina (Platinum Metals Rev. **23** No. 2 [1979] 59). – [3] E. M. Savitskii, V. P. Polyakova, N. B. Gorina (Platinum Metals Rev. **23** No. 2 [1979] 57/65).

2.7 Testing High Purity Platinum-Group Metals

Review

Methods used for the detection of impurities in high purity platinum-group metals include optical emission spectroscopy (arc, hollow-cathode and plasma excitation) atomic absorption spectroscopy, spark source mass spectroscopy and activation analysis. Electrical measurements of EMF, thermal coefficient of resistivity (TCR) and residual resistivity ratio (RRR) provide very sensitive but not specific tests for impurities present in the metals. Vacuum fusion methods are used to determine gaseous impurities and combustion techniques for carbon and sulphur contents.

Where the metals have to be dissolved, as in plasma spectroscopy and atomic spectroscopy methods, high purity reagents are necessary and "blank" measurements must be taken into account [1, 2]. Clean laboratory conditions, to avoid contamination are essential [3]. For the elements which will not dissolve readily, the pressure dissolution technique can be employed. The use of pressure bombs lined with noble metals, quartz, P.T.F.E., or glassy carbon has been described and attention drawn to the impurities which may arise from the lining material [4].

Solution techniques have the advantage of using much larger samples than arc emission spectrographic methods and thereby reduce the problem of heterogeneity, but the risk of introduction of impurities from reagents and apparatus, thereby producing high blank values, makes the detection of low levels of impurities more difficult.

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Spectrographic Methods

The arc/spark optical emission spectrographic method for the determination of impurities in platinum-group metals is described and selected methods in atomic spectrophotometry are given by [1, 2]. Emission spectroscopic methods for the analysis of pure platinum-group metals are described in which wavelengths of analytical lines and lower limits of detection for the quantitative determination of impurities by the fractional vaporization technique are given by [3, 4]. Techniques for the preparation of calibration standards are also provided. For platinum and palladium with less complex spectra than the other platinum-group metals, direct reading spectroscopy is advantageous and more rapid than the techniques where photographic recording is employed. Other spectrographic techniques for the determination of impurities in palladium, rhodium and platinum are published [5].

A chemicospectral method of determining impurities in palladium and platinum involves separation of the major element palladium by extracting the dimethylglyoxime complex in chloroform and the major element platinum by precipitation with ammonium chloride. The impurities remaining in solution are evaporated onto strontium nitrate and calcined at 350°C, prior to arc emission spectroscopy [6]. Palladium can be extracted with dipentylsulphide to determine 26 impurity elements in high purity metal [7]. Palladium can also be separated as $PdCl_2$ from nitrate solution prior to determination of impurities spectrographically [8]. A method for determining impurities in platinum involves extracting the major element using tetraoctylammonium bromide [9]. Platinum and rhodium can be separated as anionic chloride complexes and the impurities eluted from the cation exchange resin and determined spectrographically [10].

Atmospheric pressure inductively coupled plasma (ICP) can be used as an ion source. Ions are extracted from the bulk plasma through an aperture, typically of 0.5 mm diameter into the vacuum system and analysed in a quadrupole mass analyser with a pulse-counting ion detector, followed by a multi-channel scale data system [11]. The authors also refer to the possibility of laser ablation from solids as an excitation source followed by analysis in the mass analyser which if successful would produce a method of very great sensitivity for elemental and isotopic analysis.

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Activation Methods

Activation techniques which can provide information on impurities at the nanogram level are of great value in laboratories where these facilities are available. The theoretical and practical aspects of activation methods for the noble metal industry have been considered including the determination of impurities and the special case of surface analysis [1]. The scope and limitations of neutron activation analysis of platinum-group metals have been studied. The problems of standards, carriers and chemical yield were emphasized and types of radiation detectors recommended [2].

A critical review of neutron activation and tracer methods for the determination of the noble metals covering publications up to 1965 is available [3]. This includes a number of references to the testing for impurity levels in the individual platinum-group metals. Details of radioactivation methods for the determination of impurities in pure platinum metals have been presented [4].

A technique for the simultaneous determination of osmium, ruthenium, iridium and gold in platinum in which 100 mg samples of platinum were irradiated for 11 d at a thermal neutron flux of 4 to 10^{11} $n \cdot cm^{-2} \cdot s^{-1}$ has been described. The samples were pressure-dissolved in aqua regia before irradiation. Ruthenium and osmium were separated by distillation, gold was extracted with ethyl acetate, and iridium was determined in the remaining aqueous phase both by γ-spectroscopy, or directly after decay of platinum activity, or after extracting the platinum/tin chloride complex with ethyl acetate. The lower limits of detection were approximately 0.5 ppm Ru, 0.2 ppm Os, ~0.1 ppm Au and 0.1 ppm Ir. After separation of platinum from iridium the sensitivity for Ir was <10 ppb [5].

A number of other techniques employing destructive methods on which separations involving extraction, distillation, ion exchange and chromatography are used together with direct instrumental methods have been described. For platinum-group metals references [6, 7, 8]; for platinum [2, 9 to 19]; for palladium [20, 21]; for rhodium [22, 23] and for osmium [24, 25].

Analysis of rhodium by activation with thermal neutrons has been shown to be limited. Alternatively, the simultaneous determination of 35 elements in rhodium by non-destructive activation analysis with 10 MeV protons has been described [26].

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Mass Spectrograph Methods

Spark-source spectrographic techniques are capable of determining most elements in the Periodic Table at concentrations in the neighbourhood of 1 ppb atomic fraction. The high sensitivity and the approximate equality of sensitivity for all elements are useful features of the technique. Where the impurities are not homogeneously distributed and a small amount of material is consumed in the analysis this could lead to inaccuracies in results for the bulk of the material. As with other techniques, preliminary separation of the major element or concentration methods for impurities can be employed.

Glow discharge mass spectra are generally simpler than spark source mass spectra of similar samples, since the excitation processes in the glow discharge are such that there is only a very small production of doubly charged ions. Sample consumption rates are said to be sufficient to ensure bulk analysis [1].

An isotope dilution and spark source mass spectrometry technique has been used for the simultaneous determination of silver, palladium, copper, nickel and lead in 250 mg of platinum [2]. The method was applied to the analysis of NBS Standard Reference Material Platinum 681. The possible application of stable isotope dilution mass spectrometry to the analysis of noble metals has been discussed and the characteristics of the spark source mass spectrometric method of analysis summarised together with its application to the analysis of platinum and gold [3, 4].

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The Atom Probe

The concept, operating characteristics, and limitations of the atom probe (a field-ion microscope with a time of flight mass spectrometer), has been described together with the ways in which it can be used in the microstructural and microchemical analysis of materials.

S. S. Brenner, M. K. Miller (J. Metals **35** No. 3 [1983] 54/63).

Gas Analysis

Oxygen, hydrogen and nitrogen are determined in platinum-group metals by the vacuum fusion method. Parameters quoted for platinum are a temperature of 1850°C, a specimen weight of 0.5 to 1 g and extraction time of 15 min [1]. A selective review of methods for the determination of gases in metals gives details of the preparation of samples, equipment, molten metal baths, and low-pressure analysis of evolved gases using fractional freeze-out, selective reagents or mass spectrometer techniques [2 to 9]. Atmospheric pressure analysis can be achieved using the classical gas analysis methods or by the use of gas chromatography [10 to 15]. Commercial equipment is available using temperatures of 2000 to 3000°C and a single-use graphite crucible. The evolved carbon monoxide, nitrogen and hydrogen are carried by inert gas through appropriate traps and columns and measured using thermal conductitvity or infrared detectors. Radioactivation techniques for oxygen and spark-source mass spectrometry methods for nitrogen, oxygen and hydrogen can also be employed [16, 17].

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Determination of Carbon and Sulphur

These elements are usually determined by combustion in purified oxygen using induction heating. Tungsten or tungsten plus tin can assist in producing rapid and complete melting.

The evolved carbon dioxide, carbon monoxide and sulphur dioxide are measured using thermal conductivity or infrared detectors. The output of the detectors is integrated and displayed as ppm of carbon or sulphur. Commercial instruments are available with BCD output for computer connection and with automatic weight correction.

Electrical Resistivity and Electromotive Force Tests for Purity

An indirect indication of the purity of platinum, or at least freedom from certain deleterious, although unnamed, impurities is obtained by measuring the ratio of electrical resistivities at the triple point of water (0.01°C) and at 100°C (the boiling point of water). For platinum resistance thermometers the completed thermometer must have a value of the resistance ration R(100°C)/R(0°C) not less than 1.39250 (IPTS-68) [1]. Equipment for the test is described by [2]. Bridges and potentiometric methods for temperature measurement are described in "Temperature, Its Measurement and Control in Science and Industry" [3]. The surface of the wire is cleaned by aqua regia etch and it is then annealed, before measurement of resistance [2, 4]. Nearly all the common impurities in platinum depress the resistivity ratio. It is stated that gold at 100 ppm by weight reduces the ratio by 0.07% and silicon at 1 ppm by weight has as damaging an effect on the temperature coefficient as 10 ppm of gold [5]. Iron which alloys very readily with hot platinum and chromium came next after silicon in their damaging effect on the temperature coefficient. It is suggested that the relationship between effective impurities and the temperature coefficient of resistance is additive to the effects of the individual impurities and the relationship is essentially linear [6].

In the case of single crystals a common method for evaluating purity is to determine the residual resistivity ratio by measuring specific resistivities at 300 and 4.2 K. At liquid helium temperature (4.2 K) the resistivity of a single crystal is determined mainly by the chemical impurities present in solid solution but lattice defects also contribute. Practical details for the determination of residual resistivity ratios of the individual platinum-group metals are given in the section on zone refining. A non-contact method for measuring electrical resistivity is described [7].

A rapid and useful test used by most producers when the metal is available in wire form is to couple it with a wire of known high purity and to measure the emf produced when the junction is heated to high temperature (usually 1000°C). In the case of platinum the National Bureau of Standards Reference Material SRM 680 is a useful standard. The presence in the platinum wire under test of 10 ppm of iron produces an emf of ~15 μV, of silicon ~10 μV and of iridium ~8 μV [5]. The effects are additive. The effects on the emf caused by impurities in the test wire versus NBS platinum 27 have been listed [6].

It should be noted that although gold as an impurity reduces the temperature coefficient of resistivity of pure platinum, it changes the sign of the thermoelectric power relative to pure platinum thereby making it appear purer than it really is.

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3 Electrodeposition of the Platinum-Group Metals

General Literature:

F. H. Reid, Platinum Metal Plating – A Process and Applicational Survey, Trans. Inst. Metal Finish. **48** [1970] 115/23.

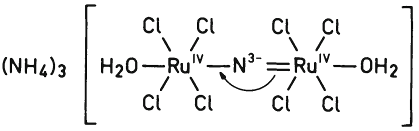
F. H. Reid, Electrodeposition of the Platinum-Group Metals, Met. Rev. **8** [1963] 167/211.

3.1 Electrodeposition of Ruthenium

Mainly due to the relative low prize of Ru its electrodeposition has been investigated extensively. Nevertheless up to now electrodeposited Ru has found only limited industrial application [1, 2, 3]. From extensive investigations on the electrodeposition of Ru from aqueous electrolytes based on solutions of simple Ru salts and nitrosyl derivatives, the sulphamate solution developed as the most promising for practical uses [4]. During this work the following electrolytes have been examined:

Ru nitrosylchloride in a) acid chloride solution and b) acid sulphate solution; Ru nitrosylsulphate; Ru^{IV} nitrosylsulphate; Ru sulphate; Ru phosphate; Ru nitrosylsulphamate; Ru sulphamate; Na tetranitro-nitrosylruthenate in a) aqueous solution, b) acid sulphate or phosphate solution and c) as solution obtained by reaction with sulphamic acid; ammonium nitrosylpentachlororuthenate in a) aqueous solution, b) acid sulphate, phosphate or ammoniacal solutions and c) as solutions in sulphamic acid. In the paper details of the preparation of these electrolytes have been listed [4].

The Ru nitrosylsulphamate solution was tested in the following range: Ru content 2.5 to 50 g/l, current density 2.0 to 8.0 A/dm^2, temperature 20 to 90°C, sulphamic acid 10 to 5 g/l. The current efficiency of metal deposition decreases from ~20% at 90°C to 0.5% at 20°C, or from 20% at 3 A/dm^2 to 6% at 8 A/dm^2 and from 3% at 10 g/l Ru to ~2% at 50 g/l. Due to the development of RuO_4 at the anode, 5 g/l of Ru were set as the optimum concentration. All other salt solutions investigated proved inferior to this electrolyte. Internal stress in the deposits is in the range of 20 to 40 t/in^2, varying with current density. The microhardness was estimated as 800 DPN. Deposits tend to grow with preferred orientation, basal planes parallel to the surface of the base metal [4]. Deposits from the Ru nitrosylsulphamate and ammonium nitrosylpentachlororuthenate type of solutions were tested for their possible use for slip-rings. They proved to have at least the same wear behaviour as Rh coatings [5, p. 12]. A decisive step forward was achieved by the development of a new type of electrolyte. The basic compound whose synthesis is described is a binuclear N-bridged complex having the structural formula



$$(NH_4)_3\left[H_2O-\overset{Cl\ \ Cl}{\underset{Cl\ \ Cl}{Ru^{IV}}}-N^{3-}=\overset{Cl\ \ Cl}{\underset{Cl\ \ Cl}{Ru^{IV}}}-OH_2\right]$$

named “RuNC” [6, p. 187]. The cathode efficiency at pH=1 changes from ~60% at 2 A/dm^2 to 25% at 7 A/dm^2, the corresponding deposition rates are 8 and 12 μm/h [6, p. 188]. There is only a slight variation of current efficiency with Ru concentration, but it increases strongly with temperature up to nearly 100% at 90°C [6, p. 189]. Deposits at a thickness <2.5 μm are bright and have, relative to polished Ag, a total reflectivity of 55 to 65% and specular reflectivities of 35 to 50%. Microhardness (H_v) varies from 750 to 850 kg/mm^2 (surface) to 900 to 1100 kg/mm^2 (microsection). After a 30 min heat treatment at 700°C, hardness drops by ~40%. Internal stress is 60 to 85 kg/mm^2. The majority of deposits with a thickness ≧2.5 μm showed cracks at the edges, but at 1.5 μm deposits were completely crackfree [6, p. 190]. The deposition of Ru from a nitrosylchloride and sulphamic acid bath, similar to [4], was studied by [7]. Typical current efficiencies ($RuNOCl_3 \cdot 5H_2O$ 8 g/l, NH_2SO_3H 12 g/l, 60 to 80°C) are: 23.8% (1 A/dm^2, 60°C), 41% (1 A/dm^2, 80°C) and 28.6% (4 A/dm^2, 80°C).

Recommended plating conditions [7, p. 1040]:

Ru nitrosylchloride ($RuNOCl_3 \cdot 5H_2O$) 10 g/l, Ru metal content 3.5 to 4.5 g/l, sulphamic acid (NH_2SO_3H) 10 to 20 g/l; temperature 50 to 65°C, current density 0.5 to 1.5 A/dm^2, anode Pt; yield (A/min) 5 to 8 mg, efficiency ~30%, maximum thickness 7.6 μm; basis material gold flash.

These conditions yield a bright deposit, but over 2.5 μm thickness cracking is observed [7, p. 1040]. A variation of the electrolyte used by [6], by adding a small amount of acetic acid, is discussed by [8]. It produces bright adherent deposits up to 1.5 μm thick at a current efficiency of 60%.

At about the same time as [6], a bath based on the $K_3[Ru_2NCl_8(H_2O)_2]$ complex was proposed by [9]. Best results were obtained with 7.5 A/ft^2 (~0.8 A/dm^2) current density at 70°C and pH between 1.0 and 1.5. Deposits were shining and adherent up to a thickness of 0.00025 inch (6.2 μm). Current efficiency at pH = 1.5 and 17 g/l Ru is near 100%. Under optimum conditions deposits are free from pores and cracks. Stress as measured with a spiral contractometer varied from 100 000 to 120 000 lb/in^2. Stress increased as pH of the electrolyte decreased [9].

The state of the art of electroplating Ru is reviewed together with own experiments on two commercially available electrolytes by [3]; typical data are:

basic complex	$(NH_4)_3[Ru_2^{IV}NCl_8(H_2O_2)_2]$	$Ru^{III}(NO)(NH_2SO_3)_3$
Ru content (in g/l)	10 to 12	5 to 6
In content (in g/l)	ε	—
pH	1.5	1.0
temperature (in °C)	65	70
current density (in A/dm^2)	1	5
current efficiency (in %)		
1 A/dm^2	70	14
5 A/dm^2	58	8
deposition rate (in μm/min)		
1 A/dm^2	0.09	0.02
5 A/dm^2	0.37	0.07

Deposits from both electrolytes are comparable. Differences are explained by the In content of the electrolyte [3, p. 102]. For good adhesion on Cu, Ni and their alloys a gold strike of less than 0.5 μm thickness is necessary. For Fe, Ni, Al, Zn or even Mg and their alloys a Ni layer on top of the gold strike is recommended. The gold strike also reduces the tendency of cracking. By applying thicker intermediate fine gold layers crack-free Ru deposits up to 7.5 μm can be obtained. Microhardness of deposits at 5 to 10 μm is ~500 daN/mm^2, the contact resistance at 1 N load in air 3.5 mΩ, after annealing in H_2 at 800°C, 2.0 mΩ.

Confirming earlier observations [6, p. 189], [3, p. 104] postulates from contact resistance measurements a thin RuO_2 film on the as-deposited layers. The characteristics of deposits from "RuNC" type plating solutions for reed contacts were evaluated by [2]. The electrolyte remained stable with constant cathode efficiency unaffected by either solution agitation or metallic contamination. Deposits of 1 μm Ru on 1 μm soft Au remained crack-free after thermal shock testing. The introduction of a diaphragm to separate the anolyte and catholyte in order to maintain the Ru in a stable valence state and to prevent formation of RuO_4 proved to be very successful [2, p. 42]. For low-force, low-voltage applications Ru is less suited as a contact material than Au, as contact resistance increases in an unstable manner, depending on the surrounding atmosphere. Ru layers fail in wear tests by brittle fracture after a few cycles. The introduction of a very thin (soft or hard) gold layer on top of at least one Ru surface of the mating pair dramatically improves the wear resistance of the combination and assures the stability of the long-term contact resistance [1].

Smooth and bright deposits can be obtained from cyanide melts. Prior to its electrodeposition the metal was dissolved in the electrolyte by passing alternating current between two Ru electrodes suspended in the molten salt. The concentration of this 30 cm^3 bath was 0.5 wt%. The electrolyte was a 53 NaCN/47 wt% KCN melt at 560°C. Operating conditions were: current density 0.5 to 1.8 A/dm^2, cathodic current efficiency 11 to 45%, deposition rate 0.1 to 0.6 mils/h (2.5 to 15 $\mu m/h$). The hardness of the layers was 610 to 935 KHN_{25G}. Adhesion on Cu, Mo, Ni and Pt is good. Smoother deposits are obtained by periodic reverse plating. The thickest sound deposit obtained in this way is 2.5 mils (50 μm). Deposits tended to be nodular [10].

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3.2 Electrodeposition of Rhodium

Introduction

Rhodium belongs to the so-called light platinum metals. Regarding electroplating of the platinum-group metals rhodium is the most important one for decorative and technical purposes. Only palladium gained a similar importance as a substitute for gold in the last 5 years since the gold price went up drastically. Rhodium metal and electrodeposits of rhodium are extremely noble with high corrosion resistance; they are resistant to most common acids and alcaline solutions.

Rhodium deposits exhibit a nearly total tarnish resistance [1], also against sulphur and organic vapours [2], up to 400°C [3] without losing brightness. Rhodium electrodeposits show high hardness ($H_V = 800$ to 1000 kg/mm^2), good wearing properties and a low and constant contact resistance which make the deposits suitable for various contact applications. Because of the high reflectivity of light, rhodium deposits have a white and brilliant appearance which is similar to that of silver. Therefore rhodium is being used as a finishing layer for decorative and technical purposes [1, 2, 3].

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Applications of Rhodium Electrodeposits

Decorative Applications. Because of the white colour and the high reflectivity for light which is only 10% less than that of silver [1], thin rhodium deposits are used as a finishing layer on top of white gold alloys, nickel and on silver [2, 3] for jewelry. In contrast to deposits of chromium, nickel and platinum the reflectivity of rhodium changes depending on wave length of light nearly in the same ratio as the reflectivity of silver. By that circumstance the silver-like colour of rhodium is caused [4].

The layer thickness of rhodium used as decorative tarnish-resistant film for silverware and jewelry is in the range of 0.13 to 0.25 μm.

Other decorative uses are for scientific and surgical instruments.

Technical Applications. Rhodium deposits are used on top of iron-base alloys for dry reed contact applications [5, 13], over a silver electrodeposit on the current-carrying and sliding contact surfaces of co-axial line assemblies [6], in homopolar generators [7], for electromechanical multiposition switches (uniselectors) [8], in high frequency technology [9] and for special types of printed circuits [10]. Other electrical and electronical applications are described in [11, 12, 18]. Electrodeposition of rhodium for slip-ring surfaces is mentioned in [14, 28]; rhodium electroplates are used in light-house beacons [15], rhodium plated Langmuir probes for space research applications [16]. Other technical applications of rhodium electroplates are for cinema projectors and IR reflectors because of the reflecting surface, heat-resisting properties and tarnish-free characteristics. In this field deposit thicknesses of 0.125 to 0.25 μm are applied [17]. Recommended Rh thicknesses for different technical applications are listed in [18]. The production and application of rhodium on top of titanium as insoluble anode is mentioned in [19]. Rhodium plating is used for electrical contacts, especially sliding contacts which are required to operate reliably after periods of inactivity [27].

Switches in radio communication and radar control gear are rhodium plated [28].

Gold plated connectors are rhodium plated to provide better wear resistance [29]. Rhodium plated iridium crucibles used for growing single crystals of calcium tungstate etc. exhibit longer life time than iridium alone [30].

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Historical Survey on Rhodium Plating

Rhodium was discovered in 1804 by Wollaston. In 1842 H. B. Leeson filed a patent, in which electrodeposition of rhodium was described among other topics [1]. In 1891, Juley, Leidie and E. Smith tried to deposit rhodium from chloride containing solutions [2, 3]. Marino applied a patent in 1912 for an electrolyte on chloride basis with organic and inorganic additives [2]. Rhodium plating was described basically by [4, 5]. Rhodium electrolytes were commercially available since 1930.

Rhodium plating became very important for the electronic equipment developed since World War II.

More recently the history and development of rhodium plating was reported by [6, 7].

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Aqueous Electrolytes for Electrodeposition of Rhodium

All described aqueous electroplating systems of economical importance for rhodium work at low pH values; they may be based on sulphate, phosphate, sulphate-phosphate, sulphate-sulphite, sulphamate, chloride, nitrate, fluoroborate or perchlorate.

Rhodium is the only platinum metal which can be easily deposited from simple solutions in a pleasant form with high current efficiency. The purity of such solutions is of major importance because of the colour of the deposits. Therefore Rh baths are traded in the form of special concentrates which are diluted in acid.

It is necessary to use very pure rhodium salts. Metallic and/or organic impurities usually affect the white and pleasant colour of the deposits. The influence of metallic impurities was investigated by [1] and is listed in [2].

The most important systems regarding their applicability for decorative and technical purposes are sulphate, phosphate, sulphate-phosphate or sulphate-sulphite based baths.

References:

[1] S. Dorner, L. Froels (Galvanotechnik **49** [1958] 229, 539). – [2] R. Weiner, A. v. Krusenstjern (Edelmetallgalvanotechnik, Vol. 14, Leuze, Saulgau, Ger., 1970, pp. 292/3).

Rhodium Sulphate Electrolytes. Rhodium sulphate electrolytes are mostly used for technical applications. The greyish white deposits are achieved with relatively high deposition speed. By the aid of additives, especially sulphur-containing compounds, crack-free thick deposits up to 20 μm with a Vickers hardness of 800 to 1000 kg/mm² can be achieved.

In sulphate baths rhodium is being used as a solution of the yellow threevalent $Rh_2(SO_4)_3 \cdot 14H_2O$ which is considered to be of complex structure [12]. It is not clear if and how the rhodium is complexed in the ready made-up sulphate bath [13].

The red Rhodium sulphate $Rh_2(SO_4)_3 \cdot 6H_2O$ is not appropriate for electroplating baths. As this salt is generated from the yellow salt by heating, rhodium baths should not be overheated or locally overheated by poor stirring. The most advantageous working temperature for sulphate baths is in the range of 40 to 60°C at current densities between 1 and 10 A/dm². To avoid internal stress in rhodium deposits from low concentrated electrolytes the current density of 0.5 to 1 A/dm² should not be exceeded.

All sulphate electrolytes with low rhodium concentrations are also used to a certain extent for decorative purposes for the deposition of thin deposits.

For decorative applications baths with ~2 g/l Rh are used for layer thicknesses of 0.2 to 1 μm. Thicker deposits from such electrolytes are usually not obtainable because of high internal stress. For thicker deposits baths with 5 to 10 g/l Rh are recommended. For technical applications baths with up to 100 g/l Rh are known, but there are also baths for that purpose with only 2 g/l Rh.

If rhodium deposits are micro-cracked this may indicate that the metal content is too low and/or the acid concentration in the electrolyte is too high leading to low current efficiency.

In rhodium sulphate baths the best current efficiency can be achieved with high rhodium concentration, electrolyte movement and temperature, and with low acid concentration and current density. So current efficiencies of more than 90% can be achieved. The optimal working conditions are not only influenced by technical parameters but also by economic points of view.

Because Rh baths work with insoluble anodes the rhodium is replenished by an Rh concentrate. By this the acid content increases and the current efficiency decreases. To obtain optimal deposits the acid concentration in the bath has to be controlled. Sulphate baths show higher current efficiencies than comparable phosphate baths [5].

Electrolytes for Technical Purposes. Rhodium sulphate electrolytes for technical applications are distinguished from sulphate electrolytes for decorative purposes mainly by higher metal contents and special additives.

Typical sulphate electrolytes for technical applications have the following composition [1]: Rh (as sulphate) 5 to 10 g/l, sulphuric acid (1.84 g/ml) 50 to 100 g/l; cathodic current density 0.5 to 3 A/dm², electrolyte temperature 20 to 50°C, anodes Pt or platinized Ti.

The dependence of current efficiency on rhodium concentration is described in [1]. Increases of current efficiency up to 30% can be observed at increasing rhodium concentrations up to 16 g/l. The electrolyte contains 35 g/l H_2SO_4 at 35°C at a current density of 3.9 A/dm². The dependence of the current efficiency in sulphate baths on rhodium concentration, current density and on the kind of movement were investigated by [10].

A barrel plating version of a rhodium sulphate bath for technical applications is according to [8]: Rh (as sulphate) 2.6 to 5.2 g/l, sulphuric acid ~80 ml/l, temperature 40 to 50°C, current density 0.5 to 2 A/dm^2.

Rhodium electrolytes for technical applications have to be very pure [2]. To reduce the tendency of cracking, additives of selenic acid [3, 6] and magnesium sulphate [4] are recommended. To reduce the discharge of hydrogen (to increase current efficiency) addition of maleinic acid and quinone is mentioned in [1, 7].

For technical purposes baths with 2 to 3 g/l of rhodium can be used with 30 ml sulphuric acid per 1 l bath at 50°C and at 1 to 2 A/dm^2 cathodical current density [5]. In baths with 5.25 g/l Rh as sulphate and 50 to 100 g/l H_2SO_4 current densities up to 30 A/dm^2 are applicable [11].

A bath for the deposition of thick crack-free rhodium layers contains rhodium not only as a sulphate but also as a sulphite complex. At rhodium concentrations of 2 to 10 g/l and 20 to 100 g/l conc. sulphuric acid, ductile and crack-free deposits up to 25 μm are obtained at 20 to 60°C and current densities of 0.5 to 5 A/dm^2. The current efficiency is reported to be 20 to 70%. The sulphite complex of rhodium is said to be the advantageous factor of the bath [14].

Electrolytes for Decorative Purposes. A typical sulphate electrolyte for decorative applications according consists of: Rh (as sulphate) 2.5 g/l, sulphuric acid (1.84 g/ml) 20 to 50 g/l; cathodic current density 0.5 to 3 A/dm^2, temperature 30 to 60°C, anodes Pt or platinized Ti. Deposits of a maximum thickness of 0.5 μm are achievable with a high tendency for cracking. The cathodic current efficiency lies in the range of 20 to 40% [1]. There are also electrolytes with rhodium contents of 1 to 2 g/l or 5 to 10 g/l, respectively [9]. Current densities of 1 to 11 A/dm^2 at 2 to 2.5 g/l Rh and ~20 g/l H_2SO_4 are applicable [2].

Sulphate baths with 50 to 160 g/l H_2SO_4 and high current densities of 2 to 10 A/dm^2 can be applied [11].

A barrel-plating version is mentioned by [8]: Rh (as sulphate) 1 g/l, sulphuric acid 80 ml/l, current density 0.5 to 2 A/dm^2, temperature 40 to 50°C.

References:

[1] H. W. Dettner, J. Elze, E. Raub (Handbuch der Galvanotechnik, Vol. 2, Hanser, München 1966, pp. 433/4). – [2] J. Fischer (Galvanische Edelmetallüberzüge, Leuze, Saulgau, Ger., 1960). – [3] F. H. Reid (Trans. Inst. Metal Finish. **36** III [1959] 74/81; C.A. **1959** 14775). – [4] Sel-Rex-Corporation (Ger. 1068081 [1960]). – [5] M. Danemark, Y. Rusconi (Galvanotechnik Oberflächenschutz **3** [1962] 287/301).

[6] F. H. Reid (Metalloberfläche **15** [1961] 33/7). – [7] R. Weiner, A. v. Krusenstjern (Edelmetallgalvanotechnik, Vol. 14, Leuze, Saulgau, Ger., 1970, pp. 291/355). – [8] E. A. Parker (Metal Finish. Guidebook Directory A **82** I [1984] 298/301). – [9] J. Fischer, F. Leonhard (Metall **10** [1956] 608/17). – [10] E. Parker (Plating **42** [1955] 882/92).

[11] Kirk-Othmer Encycl. Chem. Technol. 3rd Ed. **8** [1979] 852. – [12] F. H. Reid (Bull. Inst. Metal Finish. **6** [1956] 107/42; C.A. **1956** 16473). – [13] G. Hänsel (Metalloberfläche **20** [1966] 67/70). – [14] E. Kreuter, W. Zilske, Deutsche Gold- und Silber-Scheideanstalt (Ger. 1922421 [1969/71]; C.A. **74** [1971] No. 37802).

Rhodium Phosphate Electrolytes. This type of electrolyte is appropriate for deposition of special white and brilliant deposits for decorative applications, e.g. eye-glass frames, watch cases and jewelry. Usual deposit thicknesses are <0.5 μm because of internal stress by incorporation of hydrogen and because of comparatively low deposition speed.

A typical all-phosphate electrolyte is according to [1]: Rh (as phosphate) 2.5 g/l, phosphoric acid (1.71 g/ml) 20 to 50 g/l; cathodic current density 0.5 to 3 A/dm^2, temperature 30 to 60°C, anodes Pt or platinized Ti.

According to [2, 3] current densities up to 5 A/dm^2 are usable. In [4] contents of 55 to 115 g/l of phosphoric acid and applicable current densities of 2.0 to 15 A/dm^2 are mentioned.

Aluminium chloride, chromium (III) chloride, lithium and mangnesium chloride can be used as additives in phosphate (or sulphate) based baths. In a bath with 2 g/l rhodium as sulphate, 40 g/l conc. sulphuric acid and 1 g/l chloride, brilliant hazy-free deposits were achieved at 1 A/dm^2. The chlorides are said to be responsible for the pleasant white colour of the deposits [5].

References:

[1] H. W. Dettner, J. Elze, E. Raub (Handbuch der Galvonotechnik, Vol. 2, Hanser, München 1966, pp. 433/4). – [2] J. Fischer (Galvanische Edelmetallüberzüge, Vol. 5, Leuze, Saulgau, Ger., 1960). – [3] R. Weiner, A. v. Krusenstjern (Edelmetallgalvanotechnik, Vol. 14, Leuze, Saulgau, Ger., 1970, p. 294). – [4] Kirk-Othmer Encycl. Chem. Technol. 3rd Ed. **8** [1979] 852. – [5] W. Engelhardt, W. Zilske, Deutsche Gold- und Silber-Scheideanstalt (Ger. 2329578 [1973/75]; Brit. 1402521 [1975]; Fr. 2232618 [1975]; Japan. Kokai 75-33125 [1975]; Neth. 74-05208 [1974]; U.S. 3902978 [1975]; C.A. **82** [1975] No. 131068).

Rhodium Phosphate-Sulphate Electrolyte. Electrolytes on phosphate-sulphate basis are used for decorative purposes. They are manufactured by dissolving rhodium sulphate in phosphoric acid or by dissolving rhodium phosphate in sulphuric acid [1].

Mostly rhodium phosphate is dissolved in sulphuric acid.

A typical bath contains Rh (as phosphate) 2 g/l, sulphuric acid (1.84 g/ml) $\leqq$40 ml/l; cathodic current density $\leqq$15 A/dm^2. The deposits are very white. During the lifetime of the bath the content of free acid increases and the current efficiency diminishes, this effect is severer than in sulphate baths [2].

Mixed electrolytes of rhodium phosphate in sulphuric acid have good throwing power [3].

In baths with 1 to 10 g/l rhodium as phosphate and/or sulphate, 20 to 200 g/l sulphuric and/or phosphoric acid and aromatic sulphonic acid additives, extremely brilliant white deposits can be obtained at current densities of 0.5 to 5 A/dm^2 and temperatures $\geqq$60°C [4].

References:

[1] J. Fischer (Galvanische Edelmetallüberzüge, Vol. 5, Leuze, Saulgau, Ger., 1960). – [2] M. Danemark, Y. Rusconi (Galvanotechnik Oberflächenschutz **3** [1962] 287/301). – [3] K. Schumpelt (J. Electrodeposit. Tech. Soc. **13** No. 24 [1937] 1/6). – [4] E. Kreutzer, W. Kuhn, W. Zilske (Eur. 0056590 [1983]; Ger. 3100997 [1981/82]; Braz. Degussa A.-G. 82-00158 [1982]; Japan. 57-137492 [1982]; U.S. 4402802 [1982]; C.A. **97** [1982] No. 117483).

Other Electrolytes for Electrodeposition of Rhodium. In this group sulphamate, chloride, nitrate, nitrite, fluoroborate and perchlorate based electrolytes are described briefly. These electrolytes are of inferior practical and economical importance. For completion they are listed here.

Sulphamate Baths. The baths are prepared by dissolving basic rhodium sulphate in the presence of sulphamate [1]. Deposits which can be obtained within a relatively wide temperature range have low internal stress [2].

A bath consisting of sulphamic and sulphuric acid and rhodium as $Rh(NH_3)_3(NO_2)_3$ with a current efficiency of less than 20% is described in [3]. The relatively high throwing power of a Rh sulphamate bath is mentioned in [4]. High current efficiencies at low current densities are claimed by [5], but the efficiency dropped to 15% already at 2 A/dm^2. Sulphamate electrolytes with 20 to 50 g/l Rh and 30 g/l of free sulphamic acid are mentioned by [6].

References:

[1] R. Weiner, A. v. Krusenstjern (Edelmetallgalvanotechnik, Vol. 14, Leuze, Saulgau, Ger., 1970, p. 294). – [2] D. G. Foulke, E. C. Rinker (Galvanotechnik **56** [1965] 679/84). – [3] R. Kunce, S. I. Khotyanovich, J. Matulis (Lietuvos TSR Mokslu Akad. Darbai B **1975** No. 4, pp. 69/76). – [4] B. Mazza, P. Pedeferri, A. Alberti Oggioni (Symp. Sulphamic Acid Its Electromet. Appl., Milan 1966, pp. 53/6). – [5] G. Hänsel (Metalloberfläche **20** [1966] 67/70).

[6] B. Gaida (Galvanotechnik in Frage und Antwort, 4th Ed., Leuze, Saulgau, Ger., 1983, pp. 259/60).

Chloride Baths. A bath containing 1% $RhCl_3$ at pH ≈ 2 gives light grey and compact deposits at 0.2 A/dm^2 and black and powdery deposits at 1.5 A/dm^2 [1].

Hydrazine contents $\leqq 10$ g/l at pH $= 0.5$ decreased the current efficiency in hydrochloric solutions to less than 1% of the starting value [2]. A bath containing aminochloride is described as not sufficiently stable and inferior to baths containing phosphate or sulphate [3]. A chloride-phosphate bath with 10 mol/l $RhCl_3$, 100 mol/l NH_4Cl and 4 mol/l H_3PO_4 is used to achieve bright, compact, adherent deposits at 0.5 A/dm^2 with a current efficiency of ~100% [4].

References:

[1] A. A. Sutyagina, N. P. Matveiko, G. D. Vovchenko (Vestn. Mosk. Univ. Ser. II Khim. **13** [1972] 414/6; Moscow Univ. Chem. Bull. **27** No. 4 [1972] 32/4). – [2] M. V. Pokrovskaya, B. S. Krasikov (Vestn. Leningr. Univ. Fiz. Khim. **23** No. 4 [1968] 152/4). – [3] V. P. Yakovenko (Elektrokhim. Osazhdenie Primen. Prokrytii Dragotsennymi Redk. Metal. **1972** 115/8; Ref. Zh. Khim. **1973** No. 11 L311; C.A **80** [1974] No. 103101). – [4] L. F. Kozin, Yu. F. Balybin, A. K. Dzhasymbekov (Izv. Akad. Nauk Kaz.SSR Ser. Khim. **25** No. 6 [1975] 32/8).

Nitrate and Nitrite Baths. The following electrolytes were proposed [1]:

1) Rhodiumammonium nitrate 5 g/l, H_2SO_4 20 ml/l, $NaNO_2$ 120 g/l; temperature 25°C, current density 0.2 to 0.5 A/dm^2.

2) Rhodiumnitrite 8.5 g/l, H_2SO_4 33 ml/l; temperature 40°C, current density 0.5 A/dm^2.

An electrolyte containing Rh as diamminodinitrite is mentioned in [2, 3, 4].

References:

[1] R. H. Atkinson, A. R. Raper (Metal Ind. [N.Y.] **32** [1934], 119/21). – [2] W. Keitel, H. E. Zschiegner (Trans. Electrochem. Soc. **59** [1953] 273/5). – [3] L. M. Gerasimovich, S. I. Khotyanovich (Issled. Obl. Osazhdeniya Metal. Mater. 18th Resp. Konf. Elektrokhim. Litovsk.SSR, Vilnius 1981, pp. 188/91). – [4] R. Kunce, S. I. Khotyanovich, J. Matulis (Lietuvos TSR Mokslu Akad. Darbai B **1975** No. 4, pp. 69/76).

Fluoroborate and Fluoride Containing Baths. Baths with 20 to 90 g/l Rh and 85 ml of fluoroboric acid (30%) are reported in [1]. A bath containing NH_4F and ammonium borate to provide bright crack-free coatings with low internal stress is mentioned in [2].

References:

[1] F. Reid (Bull. Inst. Metal Finish. **6** [1956] 1075/9). – [2] Takiuchi, Takashi, Nakayama, Shunichi, Yamada Keiichi (Japan. 74-25531 [1969/74], Japan. Kokai 69-10225 [1969]).

Perchlorate Baths. Baths with 15 g/l Rh as $Rh(ClO_4)_3$ in solutions of 1 to 30% $HClO_4$ at 48°C have current efficiencies of 80 to 100% at a current density of 0.4 A/dm^2.

F. M. Lever, E. G. Towndrow (Brit. 856867 [1960]).

Polyphosphate Baths. In a tripolyphosphate bath consisting of 10 g/l $RhCl_3$, 100 g/l NH_4Cl and 150 g/l $Na_5P_3O_{10}$ at ph = 6 to 8, the addition of $Na_5P_3O_{10}$ leads to higher stability of the chloro-aquo complex of Rh^{III} [1]. Addition of a polyphosphoric acid or an alkali or ammonium salt of the polyphosphoric acid to a solution containing a rhodium salt renders this solution appropriate to deposit Rh/Au alloys [2].

References:

[1] A. K. Dzhasymbekov, L. F. Kozin, Yu. F. Balybin (Vestn. Akad. Nauk Kaz.SSR **1975** No. 9, pp. 73/5). – [2] K. Ohkubo, H. Mokoujima (U.S. 3515651 [1970]).

Miscellaneous Electrolytes. In experiments to deposit Rh from alkaline solutions, additions of ammoniumoxalate, citrate, tartrate, or benzoate, respectively, were considered to be necessary.

Baker (U.S. 2057475 [1936]).

Electrolytes for Deposition of Rhodium Alloys

The importance of rhodium alloys for technical or decorative purposes is comparatively low.

Alloys with Other Platinum Metals. A bath on the basis of sulphamic acid for the deposition of rhodium/platinum alloys contains rhodium as sulphate, phosphate or sulphamate, whereas platinum is contained as platinum diamminodinitrite [1]. Another electrolyte for obtaining mixed Rh/Pt layers is based on chlorides. It contained 5% H_2PtCl_6 and 2% $RhCl_3$; current densities of ~2 A/dm^2 were applied. The deposits contained 2 to 87.5% Rh [2]. Rh/Pt deposits are obtained from solutions containing ~1.5% ($H_2PtCl_6 + RhCl_3$), acidified by 3N H_2SO_4 with varying atomic ratios of Pt and Rh [3].

For the electrodeposition of rhodium/iridium alloys, the electrolyte contains 2 mol/l NaCl at pH = 0.5 at 25°C [4].

Rhodium/palladium alloys were investigated by [8].

Alloys with Non-precious Metals. Rhodium/cobalt alloys with at least 90% cobalt are being used for magnetic memories [5].

For rhodium/nickel alloys with 5 to 70% Rh, the electrolyte is based on rhodium and nickel sulphamates at pH = 3.5 to 4.0 and current densities of 1 to 4 A/dm^2 at 50°C. Deposits of 5 to

10 μm were obtained containing 10 to 30% rhodium [6]. Rhodium/nickel deposits are also described by [8].

A rhodium/rhenium alloy electrodeposition where rhenium also acts as a brightener is described in [7].

Rhodium/indium and rhodium/nickel alloys were obtained from sulphuric and sulphamic acid solutions at current densities of 0.8 to 1.0 A/dm^2. The deposits were dense and adherent [9].

Rhodium/copper alloy deposits were obtained from a molar H_2SO_4 solution containing 0.02 to 2×10^{-4} mol Rh^{III} sulphate and 0.625 mol Cu^{II} sulphate at a temperature range of 20 to 40°C [10].

Rhodium/tungsten deposits are mentioned in [8].

References:

[1] OMF California Inc. (Ger. Offen. 2226699 [1972]). – [2] A. M. Skundin, E. K. Khodzhaeva, V. S. Bagotskii (Elektrokhimiya **6** [1970] 1133/5; Soviet Electrochem. **6** [1970] 1100/2). – [3] B. I. Podlovchenko, L. Aliua (Elektrokhimiya **8** [1972] 460/4; Soviet Electrochem. **8** [1972] 450/3). – [4] B. S. Krasikov, V. S. Krivonos (Zh. Prikl. Khim. **39** [1966] 1332/8; J. Appl. Chem. [USSR] **39** [1966] 1244/9). – [5] M. Bratoeva, E. Todorinov (Galvanotechnik **69** [1978] 589/92).

[6] I. I. Kadaner, G. N. Jarmolenko (Khim. Khim. Tekhnol. **23** [1980] 1277/9). – [7] P. Stevens, G. R. Lurie, Oxy Metal Finish. Corp. (U.S. 3890210 [1972/73]; Ger. 2429274 [1973/75]; Fr. 2234390 [1975]; C.A. **82** [1975] No. 131067). – [8] L. I. Kadaner, G. N. Yarmolenko, N. A. Slipukh, N. Ya. Khramtsova (Teor. Prakt. Elektroosazhdeniya Met. Splavov **1976** 14/6; Ref. Zh. Khim. **1979** No. 44353). – [9] N. V. Evdokimova, P. M. Vyacheslavov, O. G. Lokshtanova (Elektrokhimiya **15** [1979] 173/5; Soviet Electrochem. **15** [1979] 145/7; C.A. **91** [1979] No. 65141). – [10] B. S. Krasikov, S. V. Yakovleva (Zh. Prikl. Khim. **53** [1980] 830/3; J. Appl. Chem. [USSR] **53** [1980] 646/8).

Electrolytes for Electroless Deposition of Rhodium

The electroless deposition of rhodium is of minor importance.

A survey of electroless plating of platinum-group metals is given by [1].

The immersion plating of rhodium on copper from chloride solutions with 5 g/l Rh, 250 ml/l HCl (32%) at 25°C yields deposit thicknesses $\leqq 2.5$ μm. A sealing process seems to be necessary [2, 5]. In a diluted rhodium(II) chloride solution copper of a printed circuit board was rhodium-covered by immersion plating. The deposit is not compact [3].

Rhodium/cobalt alloy deposits were obtained in an alkaline bath with hydrazine as reducing agent [4].

References:

[1] P. G. L Vivian (Electroplat. Metal Finish. **23** No. 11 [1970] 20/2, 24/6, 28). – [2] R. W. Johnson (J. Electrochem. Soc. **108** [1961] 632/5). – [3] L. A. Suchoff (in: H. W. Dettner, J. Elze, Handbuch der Galvanotechnik, Vol. 2, Hanser, München 1966, p. 753). – [4] Ya. I. Val'syuene (Lietuvos TSR Mosklu Akad. Darbai B **1976** No. 1, pp. 13/20). – [5] N. Hall (Metal Finish. Guidebook Directory A **82** I [1984] 423).

Electrodeposition of Rhodium from Molten Salts

The electrodeposition of rhodium from molten salts was considered to be successful to obtain low-stressed thick deposits, especially to protect refractory metals such as molybdenum at high temperatures in an oxidising atmosphere. Other applications are considered to be in aerospace industry [1]. The importance of the molten-salt process for rhodium deposition seems to be limited to some special applications.

Alkali Cyanide Melts. First experiments were made in 1962 by [2] who found that under the chosen conditions deposition of Rh was possible only for a few hours. To obtain satisfactory deposits of rhodium an inert gas atmosphere is necessary [3].

A fused-salt electrolyte was prepared by dissolving 0.9 wt% Rh in molten NaCN. The plating was achieved at 600°C under Ar. Compact soft Rh deposits of $\sim 20\ \mu m$ thickness were obtained at a current density of 1 A/dm^2 with a cathodic current efficiency of 80%, at a current density of 1.5 A/dm^2 with an efficiency of more than 90%. In the latter case the deposit was partially nonadherent. The fused-salt electrolyte has excellent throwing power. It is assumed that rhodium ions of the valence +1 are present in the electrolyte and discharged on the cathode. Substrates to be plated were molybdenum, tungsten, nickel, Inconel, 4130 carbon steel and stainless steel. A good oxidation protection on air for molybdenum is reported to be achieved by 12.5 μm Rh up to 1270°C, i.e. 700°C above the normal oxidation temperature of the metal [1].

A eutectic mixture of 57 wt% NaCN and 43 wt% KCN is used for the electrodeposition of platinum metals [4]. Plating rhodium from a fused mixture of NaCN and KCN in an inert gas atmosphere, a cathodic efficiency of nearly 100% is reached. The optimum potential and current were detected by cyclic voltammetry and slow sweep linear polarisation techniques [5].

Alkali Chloride Melts. Rh is electrodeposited at 490°C from a NaCl–KCl–CsCl melt containing the Rh as a chloride. Relatively thick deposits can be achieved [6].

References:

[1] G. R. Smith, C. B. Kenahan, R. L. Andrews, D. Schlain (Plating **56** [1969] 805/8). – [2] R. N. Rhoda (Plating **49** [1962] 69/71). – [3] R. L. Andrews, C. B. Kenahan, D. Schlain (U.S. Bur. Mines Rept. Invest. No. 7023 [1967]). – [4] W. B. Harding (Plating **64** [1977] 48/55). – [5] D. R. Flinn, C. L. Manger (USBM-RI-8656 [1982]).

[6] N. A. Saltykova, A. B. Smirnov, A. N. Baraboshkin, S. N. Kotovskii (Fiz. Khim. Elektrokhim. Rasplavl. Tverd. Elektrolitov Tezisy Dokl. 7th Vses. Konf. Fiz. Khim. Ionnykh Rasplavov Tverd. Elektrolitov, Sverdlovsk 1979, Vol. 2, pp. 15/7).

3.3 Electrodeposition of Palladium

In spite of its light silvery colour, electrodeposited palladium has found extensive technical application only after the electronics industry discovered its potential value for substituting gold in separable connectors. One reason was that most of the gold electrolytes used in those early days of electronics for processing printed circuit boards attacked the adhesives and lifted the copper foil in the boards. The second advantage became even more important with rising gold price. Since the density of palladium is roughly one half and the price nearly one half of that of gold, a palladium layer of equal thickness costs about one quarter that of gold. Even if this advantage is reduced by the higher forming and operating costs of the electrolytes and the refining of scrap there is quite an economic incentive to use palladium instead of gold.

Today many suppliers of electroplated connectors and many users have accepted palladium as a contact material and it has been in use now for a long time [1 to 4]. As has been shown in a series of papers, the wear and contact properties of electrodeposited palladium are similar to that of gold [3, 4]. On the other hand the chemical properties are quite different since palladium is a transition metal. Contrary to gold, palladium metal and salts are quite active catalysts. This activity explains why it is in general more difficult to operate Pd electrolytes and why Pd deposits often show the so-called "brown powder effect", by which organic polymers (brown powders) form on the Pd surface from organic vapours by catalytic action of the Pd [3 to 8]. By using appropriate plastics or a thin gold layer on top of the Pd this effect can be reduced or even totally avoided; the contact properties of the system are improved [9 to 11].

General Properties of Palladium Electrodeposits

The electrical resistivity of electroplated palladium is between 10.7 and 15 $\mu\Omega\cdot$cm, this being higher than that of bulk Pd and nearly four times as high as that of "hard gold" (Au-Co, Au-Ni or Au-Fe layers), but similar to the value of 18 carat Au-Cu-Cd electrodeposits [12]. The contact resistance which is more important for applications than the resistivity of electrodeposited Pd is with 1 to 7 mΩ (depending on measuring) near that of hard gold [2, 4]. Depending on the surrounding atmosphere it increases up to 30 mΩ [13 to 19]. Under identical conditions, 18 carat Au-Cu-Cd layers are inferior since their resistance increases to nearly twice that of Pd. During annealing in air the contact resistance of Pd layers rises more slowly than that of gold deposits, which is explained by the lower diffusion coefficients of the substrate metals Cu, Ni and Zn in Pd. The diffusion coefficient is important for the solderability of Pd with Sn-Pb solder, as the Pd-Sn phase formed during soft soldering increases from 3 to 60 μm if the sample is stored for 25 d at 100°C [20, 21].

Wire wrap properties of electrodeposited Pd are similiar to those of hard gold layers, especially if the Pd is heat-treated.

Microhardness (H_v) of Pd electrodeposits varies between 150 and 600 kg/mm^2 depending on the deposition parameters [1, 2, 12, 18]. It rises immediately after deposition due to release of hydrogen and decreases at longer storage times. The internal stress of the Pd deposits is strongly influenced by the type of electrolyte and the deposition conditions. In general tensile stresses between 50 and 200 N/mm^2 are measured. Due to diffusion of H_2 and the corresponding volume change, they can increase from 100 to 400 N/mm^2. If cracks appear stresses are lowered to 50 N/mm^2 [1].

Sliding and wear behaviour of Pd layers has been extensively investigated by [3, 4, 17, 18, 22, 23] see **Fig. 7** according to [3]. For Pd-plated contacts see [24 to 30].

The sliding behaviour of Pd electrodeposits in contacts is comparable to that of hard gold. A thin top-layer of gold improves sliding and wear properties as does a combination of a non-wear-resistant Pd coating as a base covered with a porous wear-resistant Pd layer [31, 32]. For removal of codeposited hydrogen, deposits are often heat-treated for a short time at ~300°C.

Many investigations are concerned with the porosity of the coatings, but it is difficult to make a general statement, since porosity depends, among others, on the type of electrolyte, the deposition conditions, the base material and its pretreatment. There is agreement that with appropriate substrates and pretreatment coatings with identical porosity can be obtained at thicknesses equal to those of Au-Ni and Au-Co or Au-Fe layers. Codeposited hydrogen considerably influences porosity, as will be discussed later.

For electric contacts especially the tarnishing and corrosion behaviour is important. Exposure tests under practical conditions with cladded Pd and Pd alloys were made by [33, 34]. After up to 40 months' exposure, samples were tested by contact resistance measurements, Auger and ESCA investigations. In air-conditioned telephone central offices Pd and Pd alloys did not reveal any tarnishing, but tarnished in non-airconditioned offices. The layers observed consisted of dust particles containing salts of Ca, Na and Cl on hydrated $PdCl_2$ on Pd, and a mixed hydrated $PdCl_2$ and AgCl film on Pd-Ag surfaces [33]. The growth rate of the chloride film on Pd is parabolic with a rate constant of 1.11×10^{-11} cm^2/month. These results – the occurrence of contact resistance increasing chloride and sulphur containing tarnishing layers – were confirmed by other exposure tests [35, 36, 37].

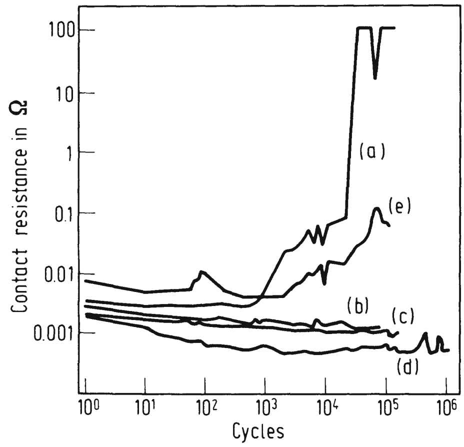

Fig. 7. Contact resistance versus fretting cycles determined using hemispherically-ended riders on flats. The wipe distance was 20 μm at a force of 50 g. Material combinations: (a) and (e) palladium versus palladium, (b) gold rider on palladium flat, (c) palladium rider on gold flat, (d) gold versus gold. (a), (b), (c) and (d) were unlubricated; (e) was lubricated with a thin film of polyphenylether obtained by withdrawal of contacts from a 0.5 per cent solution in a volatile solvent.

Hydrogen in Electrodeposited Palladium

Though the importance of dissolved hydrogen was know from the earliest deposition experiments, only in the last years a method for its quantitative determination was developed [38] which was adopted and developed further for investigations on direct current and pulse plated palladium [39].

Palladium dissolves appreciable quantities of hydrogen as a face-centred cubic α-Pd solid solution up to $H/Pd = 0.03$ at atmospheric pressure and room temperature. At higher H_2 concentrations the face-centred cubic β-PdH phase with $H/Pd \geqq 0.57$ is observed. Its lattice constant is by ~3.8% higher than that of the α-Pd-H solid solution. These data refer to equilibrium conditions [40]. In the highly distorted electrodeposited layers solubility is much higher.

There is a connection between stress in the deposits and the hydrogen dissolved. Furthermore, if during storage hydrogen diffuses from deposits with higher H/Pd ratios, the decomposition of the β phase and the accompanying change in volume may cause stresses and cracks in the layers, sometimes even days after deposition [41, 42].

Since the determination procedure for hydrogen by vacuum extraction works so slowly that it catches only part of the hydrogen diffusing very fast out of the deposit ($D_{O,H_2} \approx 1 \times 10^{-6}$ cm^2/s in β-PdH) an electrochemical method was developed which is very fast and permits the first hydrogen measurements within a few seconds after deposition. It utilises the electrochemical oxidation of the hydrogen diffusing from the palladium layers to determine its amount via the charge Q:

$Q = i(t)dt$ (i = anodic current, t = time). The anodisation of hydrogen is done in 1 N NaOH at a constant potential of +0.25 V, which is high enough to oxidise hydrogen but low enough to avoid other electrochemical reactions [38].

Palladium Electrodeposition Processes

There are only few comparable laboratory investigations that mention details of the electrolyte compositions, deposition parameters and properties of deposits [1, 4, 13, 38 to 43]. In other papers details of electrolyte composition or deposition parameters are lacking which makes an evaluation difficult [27, 28, 44, 45].

Seven electrolytes were tested by [2]: a) tetrammino-palladous nitrate, b) sodium palladonitrite, c) diamminodinitrito palladium (P salt), d) dicyanodiammino palladium, e) acid palladous chloride, f) palladous amminechloride and g) palladium sulphamate (developed by the Automatic Telephone and Electric Company). An acid electrolyte was described by [18], its practical application is discussed by [29]. A plating bath based on a unique complex of Pd and an aliphatic polyamine with 3 to 20 C atoms was patented by [46]. A so-called Pd-BTL-electrolyte and its application are reviewed by [27, 28]. Earlier an electrolyte with higher aliphatic polyamides as complexing agents was patented by [47] and an organic polyamine complexing agent by [48].

Acid $PdCl_2$/HCl and $Pd(NO_3)_2/H_2SO_4$ Electrolytes

In the $PdCl_2$/HCl electrolyte deposition occurs by the reaction $Pd^{2+} + 4Cl^- + 2H^+ \rightleftharpoons H_2PdCl_4$. The palladium is rather loosely bound, so it easily deposits without external current in a blackish powdery form on less noble metals. At current densities between 97 and 100%, palladium is electrodeposited as a compact layer with a microhardness (H_v) of ~250 to 350 kg/mm^2 which is crack-free even at higher thicknesses. The hydrogen content of the deposits is H/Pd <0.03 [40], and the structure is that of a slightly expanded face-centred cubic Pd lattice. The layers are fine crystalline and non-orientated with stress values of ~20 N/mm^2 at 7 μm thickness. Recently the deposition of Pd-Ag alloys from a LiCl containing electrolyte was discussed [65]. The emission of HCl vapours and the tendency to self-decomposition have prevented industrial use of these electrolytes.

These problems are avoided to a certain extent by an acid electrolyte based on $Pd(NO_3)_2/H_2SO_4$ [18, 29, 43]. As an additive this electrolyte contains Na sulphite. Dependent on the sulphite concentration and current density, the current efficiency for Pd deposition varies from 108% (0.01 mol/l Na_2SO_3, 1 A/dm^2) to 63% (0.2 mol/l Na_2SO_3, 2 A/dm^2). The S concentration of the electrodeposits increases from 0.15% (0.01 mol/1 Na_2SO_3, 1 A/dm^2) to 10% (0.2 mol/l Na_2SO_3, 1 A/dm^2), and the H/Pd ratio varies from 0.007 (0.01 mol/l Na_2SO_3, 1 A/dm^2) to 0.0006 (0.2 mol/l Na_2SO_3, 1 A/dm^2). The deposits have a microhardness (H_v) of 350 kg/mm^2, which can be increased to 430 kg/mm^2 by annealing 1 h at 100°C. After 1 h at 400°C it dropped to 200 kg/mm^2 [43]. Internal stresses even at 10 μm thickness never exceed 100 N/mm^2. Deposits usually need an Au or Pd prestrike [18, 29].

In general at low pH values all Pd electrolytes have a current efficiency of ~100% and a low H_2 concentrattion and low tensile strength. They have a tendency of self-decomposition and electroless deposition on base metals.

The Alkaline $Pd(NH_3)_4Cl_2$ Electrolyte

The alkaline $Pd(NH_3)_4Cl_2$ complex seems to be completely stable above pH = 7.5. Below pH = 6 the $Pd(NH_3)_2Cl_2$ form is stable. Palladium deposits at 1 to 5 A/dm^3 and −300 to −600 mV with a current efficiency of less than 100%. The potential current density curves show a strong temperature dependence explained by decreasing stability of the complex. Current efficiency increases from ~60% at 0.2 A/dm^2 to 90% at 2 A/dm^2 and from 82% at 25°C to 85% at 50°C. Deposits are highly stressed (100 to 200 N/mm^2) and tend to form cracks at higher thicknesses. Stress and hardness values decrease with deposition temperature and thickness. Layers deposited below 30°C show age hardening, often crack formation is observed. The hydrogen concentration of the deposits increases with current density but decreases with deposition temperature. It depends on the relative movement electrolyte/sample [38].

Deposits with H/Pd <0.1 exhibit metallic lustre. At H/Pd $\geqq 0.8$ they are powdery and black. The surface structure is influenced by addition of carbonic acids or their derivatives. By addition of benzoic and nicotinic acid and their derivatives, deposition potentials are shifted to more negative values, see **Fig. 8**. Citrates have a similar effect. If the citrate concentration is 0.5 mol/l, the hydrogen concentration increases from H/Pd = 0.02 to 0.08 at 2 A/dm^2. In general citrate reduces the tensile stress, but the deposits are still highly stressed (150 N/mm^2) and tend to crack. Benzoates and salicylates as well as heterocyclic N-containing compounds cause a sharp fibrous (110) orientation. At concentrations >5 mmol/l, phenacetine reduces tensile stress to values below deposits from addition-free electrolytes [41].

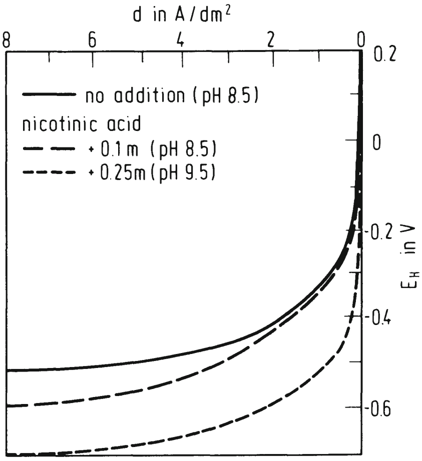

Fig. 8. Change of galvanodynamic current density/potential curves of the Pd $(NH_3)_4Cl_2$ electrolyte by addition of nicotinic acid; E_H = electrode potential, d = cathodic current density.

The Alkaline $Pd(NH_3)_2(NO_2)_2$ Electrolyte (P-Salt Type)

Electrolytes of this type are among the most widely used solutions for Pd electrodeposition. They work at pH values between 7.5 and 10, and Pd is electrodeposited at −300 to −700 mV forming dense and bright layers. At higher temperatures the deposition potential becomes more positive, at higher pH values more negative. The current efficiency for Pd deposition increases from ~40% at 20°C to nearly 60% at 60°C, correspondingly the H/Pd concentration drops from ~0.04 (20°C, 1 A/dm^2) to 0.005 (70°C, 1 A/dm^2), internal stresses of 250 to 300 N/mm^2 drop sharply with increasing deposition temperature and thickness, see **Fig. 9**, p. 82. There seems to be a certain relationship between hydrogen concentration and stress. At pH values between 7 and 8 insoluble Pd salts are incorporated in the deposit [38, 42].

By investigation of the deposits obtained by pulse (p.c.) and direct current (d.c.) plating results of [42] were confirmed in general. In pulse plating harder deposits are obtained than in d.c. plating. For thicknesses <2.5 μm, crack- and pore-free deposits are more readily obtained in p.c. than in d.c. plating [39].

Other Alkaline Pd Electrolytes

Interesting variations of Pd electrolytes with NH_3 as a complexing agent are electrolytes with amines [47] and aliphatic polyamines [46, 48]. Though it is not stated in the publication it must be assumed that the results published by [27, 28] are based on [46], the results of [45] are based on [48]; the results of [32] were achieved in an electrolyte proposed by [47]. Since many details of the proprietary electrolytes are not given in the papers it is impossible to compare the results which are sometimes contradictory. The practical aspects of running and controlling another proprietary electrolyte are discussed in detail by [30]. He stresses the use of ion chromatography, polarography and other electrochemical methods in on-line service.

A solution based on P salt contains 10 g/l P salt and 100 g/l ammoniumsulphamate; it operates at pH = 7.5 to 8.3, 32°C and 0.6 to 1 A/dm^2 with a cathode efficiency of 70% [49].

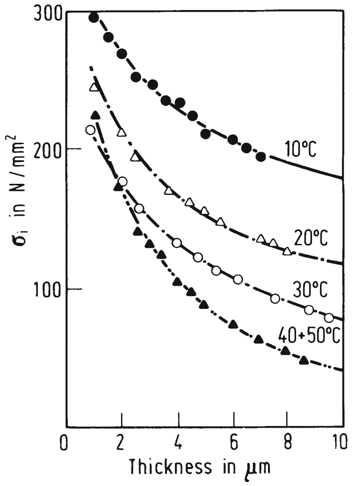

Fig. 9. Dependence of the internal stress σ_i on the thickness of Pd layers deposited from $Pd(NH_3)_2(NO_2)_2$ electrolytes at various temperatures (pH = 9; 1 A/dm^2).

Electrodeposition of Pd Alloys

The electrodeposition of Pd alloys has been reviewed by [50]. A process for the deposition of Pd together with other metals from ammoniacal solutions in a diaphragm cell was patented by [51]. In commercial use are electrolytes containing ammonia, Pd and Ni salts and various additions [52 to 58]. The influence of organic sulfo acids and their derivatives on Pd/Ni electrodeposition was studied by [58]. As shown in **Fig. 10**, at constant Pd and Ni concentration of the electrolyte the Ni concentration decreases and the H_2 concentration of the deposits increases with current density [56]. Depending on Ni concentration of the electrolyte, its pH value, the temperature, and the current density, the Pd concentration of the deposit can be varied from 40 to 100% [55]. Pd/Ni alloys up to 50% Ni with or without a final gold flash for contact applications were studied by [59]. After ageing one month in air, the contact resistance of the 50/50 alloy increased to 12 ± 8 µΩ. The films with a microhardness (Knoop) of 240 to 450 kg/mm^2 show good wear resistance and seem to be good underplatings for contacts as well as for decorative applications [59]. The use of Pd/Ni alloys coated with gold as an etch resist for printed circuit boards was discussed by [60]. The solderability of Pd/Ni coatings with a mildly activated flux was excellent even after ageing [54].

In a series of papers results with proprietary electrolytes are published [61, 62, 63]. Deposits from a "Pallinic" electrolyte (pH = 8.0 to 8.5) were found quite profitable, as an etch resist showing certain advantages vs. gold, e.g. better soldering behaviour, fewer gold needed and in general significant saving in factory production [61]. More information on the electrolyte „Pallinic" is published by [62]. Despite the fact that he lists the composition of the electrolyte he does not state the kind of additions, but lists salt compositions for high-speed and barrel-plating uses.

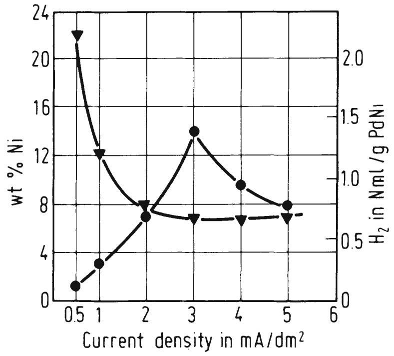

Fig. 10. Dependence of Ni content and H concentration of Pd-Ni deposits on current density at constant Pd and Ni concentration of the electrolyte.

Concentration of various Pallinic alloys [62].

Pallinic electrolyte for	high speed	decorative	barrel
Pd concentration, g/l	10 to 20	5 to 10	7 to 9
Ni, g/l	7 to 11	7 to 11	3 to 6
current density, A/dm²	2.0 to 50.0	0.5 to 2.0	0.2 to 1.0

The effect of the coating parameters is discussed, e.g. influence of pH value, nickel concentration in the electrolyte and current density. Among the contaminants Pb produces dull deposits at 5 to 10 ppm. Up to 50 ppm Cu does not affect the deposit, at 200 ppm and above Cu stripes are discernible. At more than 30 ppm Zn produces dark stripes. Cyanide reduces the effect of Pd additions due to complexing, organics tend to increase internal stress. The deposits are more ductile than acid hard gold or pure Pd and can be used at 0.5 μm as etch resist, for coating edge connectors instead of gold or replace Rh on rotary switch connections and touch button connections. For connectors a combination of 2 μm undercoat of "Pallinic" and 0.5 μm of hard gold is recommended. "Pallinic" also may replace Rh and Au in reed relays [62].

An investigation on the effectiveness of Pd-Ni (25 to 30% Ni) as a replacement for gold came to the conclusion that Pd-Ni is "very effective under certain circumstances but ineffective under other circumstances". It was suggested that 2.3 to 3 μm acid gold on copper for printed circuit boards for pore-free layers, a suitable alternative would be 3 to 5 μm Ni/1.5 to 2.0 μm Pd-Ni/0.2 to 0.3 μm acid gold [63].

A ternary alloy Pd-Ni-Co is in use for electronic applications. Deposits have a hardness (H_v) of ~370 to 400 kg/mm² but at the same time a relative high ductility (>5%). Their electrical resistivity is 20 μΩ·cm and the contact resistance 2 μΩ at 100 g load. Bondability and solderability are good [64].

The electrodeposition of Pd-Ag alloys was recently reviewed and supplemented by own results by [65]. There is still no commercial electrolyte available for Pd-Ag deposition. To study the mechanism of Pd-Ag alloy deposition for a better understandig of the process, deposition experiments were made on a rotating Cu cylinder. The electrolyte was a simple Pd-Ag nitrate/ammonia electrolyte, pH = 11.5. Alloy composition varied from 5 to 25% Ag, depending on deposition parameters, hardness (H_v = 400 kg/mm² at ~15% Ag) specific resistance ~35 μΩ·cm for 15 at% Ag, contact resistance ~2 μΩ at 20 g load [65].

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3.4 Electrodeposition of Osmium

Due to little technical interest, only few papers on the electrodeposition of osmium from aqueous electrolytes have appeared [1 to 4]. The high work function of osmium has led to a limited application in the form of thin layers on Mo and W wires in thermionic devices [5], and its high hardness (estimated to 1000 to 1500 DPN) and wear resistance suggested its use for "Reed-Switches" [4].

The earlier work was reviewed by [3] and [4]. The alkaline phosphate electrolyte with metallic Os anodes [1] produced nonadherent deposits and OsO_4 at the anode at current densities of 0.5 to 1 A/dm^2 with superimposed alternating current [3]. Other electrolytes based on Na_2OsCl_6 in alkaline or acid solutions were not very successful either. An improved hexachloro-osmate bath working at current efficiencies of 20 to 30% has a deposition rate of 4 μm/h but its pH value <1.5 makes it difficult to handle. A proprietary electrolyte produced by dissolving OsO_4 in sulphamic acid contains up to 1.2 g/l, operates at current densities between 1 and 2 A/dm^2 and temperatures of 75 to 80°C at pH$\approx$14. The cathodic current efficiency depends on the current density and the Os concentration of the electrolyte; it is 68.1% at 1 A/dm^2, pH = 13.7 to 13.8, 80°C (no agitation), cell voltage 2.0 V; the electrolyte contains 1.0 g/l of Os. Deposits are shiny, darker than Rh deposits, and show a bluish tint and excellent adhesion up to 1.3 μm. Above 2.5 μm they become dull but remain smooth and adherent [3, 6].

Another electrolyte was produced by reacting potassium hexachloro-osmate with a solution of KNO_2 in boiled-out, nitrogen-saturated water. The product is $K_2[Os(NO)(OH)(NO_2)_4]$. Electrolytes based on $K_2[Os(NO)(X)_5]$ were prepared by reacting $K_2[Os(NO)(OH)(NO_2)_4]$ with the corresponding halogen acids HX (X = Cl, Br, J). Electrolytes from these complexes behaved similarly. In addition these electrolytes contained sulphamic acid when the acidic range was studied [4].

Deposits of bright metallic Os were produced over the whole pH range from acidic to alkaline. Below pH = 7 and 60°C the current efficiency is 2% but rises rapidly with pH and temperature and decreases with increasing current density. The preferred operating conditions of this type of electrolyte are listed as: Os concentration 4 g/l, sulphamate concentration 25 g/l, pH = 12 to 13, cathodic current density 2 A/dm^2, electrolyte temperature 70°C, current efficiency (for Os^{II}) 8 to 12%, maximum plating rate 3 μm/h. Deposits are highly stressed and microcracked already at ~1 μm. Apparently during electrolysis, the electrolyte deteriorates by an anodic reaction which can be avoided at least partially by using a cell divided by a semipermeable diaphragm. From IR measurements reactions of NO and NO_2^- ligands in the Os complex with OH^- and NH_2SO_3H are assumed postulating a reversible nitrosyl-nitro conversion: $[Os(NO)L_m]^{n-} \underset{2H^+}{\overset{2OH^-}{\rightleftharpoons}} [Os(NO_2)L_m]^{(n+2)-}$ [4].

A molten cyanide bath has been described, but did not produce satisfactory results [7].

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3.5 Electrodeposition of Iridium

The electrodeposition of iridium has up to now not found wider technical application. This is mainly due to the fact that there are practically no aqueous electrolytes for depositing Ir at a reasonable thickness with satisfactory properties.

In general the electrolytes are based on chloro-iridic acid in the oxidised or reduced form (H_3IrCl_6) [1, 2, 3]. The metal is deposited in a wide pH range with fairly low current efficiencies, even if ammonia complexes are used [1]. The state of electroplating of Ir from aqueous electrolytes was experimentally tested, based on existing procedures and newly developed baths, and bromide electrolytes seemed to be most promising. The optimum plating conditions for this electrolyte are: Ir concentration 5 g/l, HBr concentration 0.1 mol/l, temperature 75°C, current density 0.15 A/dm^2. The microhardness of these deposits is 900 DPN, their total reflectivity (visible, silver=100%, up to 4 μm thickness) 61% and their specular reflectivity (visible, up to 1 μm thickness) 26%. The limiting thickness for an uncracked coating is 1 μm. The current efficiency depended on the substrate and varied from 65% on Cu to 45% on Ti, plating rate 1 μm/h. The electrolyte could be replenished by addition of IrO_2 as long as the acidity did not exceed 0.1 mol/l [2].

As advantages of this electrolyte are listed:

1) The electrolyte is stable and reproducible; 2) there is very little oxide formation on the anodes; 3) bright, smooth, adherent metallic deposits up to 10 μm are obtained on a variety of base metals including copper, brass, nickel, mild steel, molybdenum and titanium; 4) concentrations of 5 to 10 g/l of Ir are possible; 5) the cathode efficiency is 65% for deposition on most base metals, and 45% on Ti.

As disadvantages are stated:

1) The relatively high acidity of the solution; 2) evolution of small quantities of bromine at the anode, making the provision of fume extraction equipment desirable; 3) the maximum efficiency is obtained only at low current densities, giving a fairly low plating rate of 1 μm/h [2].

Another electrolyte is made up of aqueous solutions of iridium chloride and sulphamic acid. The plating efficiency in an electrolyte with 8.3 g/l $IrCl_3 \cdot 4H_2O$, 42 g/l NH_2SO_3H and a current density of 0.1 A/dm^2 increases from 6% at 30°C to 63% at 90°C. The influence of the sulphamic acid depends on the bath temperature: at 60°C there was no influence, but at 80°C the plating efficiency was inversely proportional to the sulphamic acid content. In general, current efficiency decreases at higher current densities, e.g. from 33% at 0.1 A/dm^2 to 24% at 0.3 A/dm^2. The influence of auxiliary alternating current electrodes upon Ir plating from this bath seems to cause an increase of efficiency (for optimum operating conditions see original publication). The maximum thickness obtainable is near 25 μm, however, deposits are highly stressed [4].

The deposition of Ir from a molten cyanide bath was described by [1, 5, 6]. The electrolytes were either NaCN or the NaCN-KCN eutectic (53 wt% NaCN) with melting points of 564 and 500°C, respectively. Attempts to dissolve Ir salts in the fused melt were unsuccessful, therefore, prior to electrodeposition, the Ir was dissolved by passing alternating current between two Ir electrodes suspended in the melt. A current of 0.3 A (60 Hz) through 30 ml of electrolyte for 1 h dissolved enough metal for subsequent electrodeposition. During deposition, the Ir concentration of the melt reached an equlibrium value of 0.3 to 0.4 wt%. The operating conditions of the Ir cyanide bath are given as salt NaCN, Ir concentration 0.3 wt%, temperature 600°C, current density 1.4 to 5 A/dm^2, cathodic current efficiency (for Ir^{2+}) 9 to 20%, deposition rate 2.5 to 12.5 μm/h, substrate Cu, Ni, Pt. Properties of deposits obtained are: Knoop hardness H_K (25 g) = 800 kg/mm^2, adherence good, appearance bright and smooth, thickest sound deposit 75 μm. The throwing power seems to be adequate to cover symmetrical specimens. Even at a current density of 1.5 A/dm^2 deposits were satisfactory. The current efficiency under these conditions was ~10% based on Ir^{III} [6].

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3.6 Electrodeposition of Platinum

F. H. Reid finishes his extensive review on the electroplating of platinum metals as follows: "There has so far been little interest in electrodeposition of the metal for electronic applications since in the majority of cases it offers no advantage in electrical or mechanical properties over less costly alternatives such as gold, palladium or rhodium" [1, p. 122]. Not much has changed in this situation ever since.

In an earlier review four main types of electrolytes are listed and discussed [2, p. 190]: 1) Platinic chloride (chloroplatinic acid), 2) diammino-dinitritoplatinum (platinum "P" salt), 3) alkali hydroxyplatinates.

Electrolytes Based on Platinic Chloride

The basic composition of the electrolyte is: Platinic chloride 5 g/l, diammonium hydrogenphosphate 46 g/l, disodium hydrogenphosphate 240 g/l, operation temperature 70°C, current density 1 A/dm^2 [2]. Despite the fact that it was considered an electrolyte well suited for making "flash" coatings [3] it was too unstable for practical service. After earlier investigations [4] it was extensively studied by [5] whose work proved to be of lasting influence on the electrodeposition of other Pt-group metals as well.

Chloroplatinic acid was prepared from Pt sponge, a solution containing only little free hydrochloric acid was used as a starting mixture. Platinum was used for cathodes and anodes. Another "2 diaphragm cell" contained a cathode surrounded by a porous porcelain pot of ~50 ml capacity. Great care was taken to heat the bath uniformly [5].

The control of the deposition rate was very difficult because it was influenced by the transport of chloroplatinous acid to the cathode and therefore was dependent on stirring and cathodic current. For the deposition mechanism two steps were suggested:

$$1)\ H_2PtCl_6 + 2e \rightarrow H_2PtCl_4 + 2Cl^-;\ 2)\ H_2PtCl_4 + 2e \rightarrow Pt + 2H^+ + 4Cl^-.$$

With convential stirring apparently only reaction 1) occurred, as the chloroplatinous acid was immediately re-oxidized to chloroplatinic acid at the anodes and no reduction to the metal could occur at the cathode. Within a temperature range of 40 to 70°C thermal convection currents provided enough stirring for satisfactory deposition. The use of a diaphragm complicated things even further, due to the interaction of chloroplatinous and chloroplatinic acid, complicated by frequent additions of chloroplatinic acid which tended to decrease the plating rate. Under satisfactory conditions the deposition rate ranged from 50 to 80% (for Pt^{IV}) for non-diaphragm cells, and for diaphragm cells it was 80 to 90%. Below these limits deposits tended to brittleness, above they were rough. The acid content of the bath should be kept between 240 and 260 g/l HCl. In the non-diaphragm cell the Pt content is nearly constant since it dissolves anodically at about the same speed as it is deposited cathodically. A method was devised for determining the critical chloroplatinous acid concentration by adding manganous sulphate and by potentiometric titration at room temperature with 0.1 N permanganate solution. For the production of ductile deposits there seemed to be a minimum rate of deposition, depending on the acidity of the electrolyte, namely from 0.7×10^{-3} in/h at 225 g/l HCl to 0.35×10^{-3} in/h at 290 g/l HCl. Below these values deposits were harder (250 to 350 KHN) and easily cracked. Up to a deposition rate of 1.0×10^{3} in/h they were ductile, at higher values they appeared spongy. Ductile deposits were not obtained below 220 g/l HCl. The electrolyte gave smooth layers, up to 0.013 inch thick. Wire cathodes from a bath with 213 g/l HCl (plating rate 0.39×10^{-3} in/h) showed blistering and brittleness. If the pH value was extremely high there was no blistering after heat treatment. Deposits from a conc. HCl solution were ductile (plating rate 0.52×10^{-3} in/h) after heat treatment at 1500°F (~815°C) in Ar [5, p. 8].

This is explained by the incorporation of hydrolytic matter from the bath, caused by the reaction $H_2PtCl_6 + 6H_2O \rightarrow H_2Pt(OH)_6 + 6HCl$.

Significant hydrolysis of chloroplatinic acid begins at $pH \approx 2.2$. A solution of chloroplatinous acid (free from chloroplatinic acid) had a hydrolysis pH of 3.6 to 3.7. From these measurements it was concluded that the ratio of the minimum acidity (required for the production of ductile Pt deposits) to the concentration corresponding to the hydrolysis pH of the respective salt is 950 to 1 for the chloroplatinic acid bath. This is equal to 3 pH units [5, p. 13]. Similar values were found for Ni electrolytes and are most likely valid also for Pd and Rh electrolytes [6]. The incorporation of hydrolytic matter is facilitated by colloidal particles at the cathode. Formation and transportation of these colloids as well as their influence on the deposit properties are discussed in [5, p. 16].

The anode current efficiency of anolytes containing 320 to 350 g/l HCl was 94 to 98% at 40 to 50°C [5].

As stated by [2] the use of these electrolytes will be restricted "to highly specialized applications by the very acidity of the electrolyte and the difficulty in controlling the conditions of deposition". Nevertheless, some Pt electrolytes in practical use today are of the highly acidic type.

It is important to stabilise Pt^{2+} as an amino complex to avoid oxidation to Pt^{4+}. Electrolytes on the basis of $Pt(NH_3)_2(NO_2(NO_2)_2$ or of the diammino-dinitrito-platinum ("P" salt) type have found practical application [7, p. 239].

Electrolytes Based on Diammino-dinitritoplatinum ("P" Salt)

A typical electrolyte of this type contains: platinum "P" salt 16.5 g/l, sodium nitrite 10 g/l, ammonium nitrate 100 g/l, ammonia (28%) 50 ml/l [8].

This electrolyte works at temperatures between 90 and 95°C and current densities of 3 to 20 A/dm^2 with a current efficiency of 15% [7]. Deposits tend to be dull and fairly porous [2, p. 191]. By using pulse-plating, 5 s cathodic followed by 2 s anodic cycles with a current density of 5 to 6 A/dm^2, lustrous deposits could be obtained up to 40 μm thickness [9]. Improvements are achieved if the ammonia is replaced by a sodium or potassium acetate/carbonate mixture [10] or by phosphoric acid [11]. Other electrolytes are based on "P" salt and sulphaminic acid [12], on mixtures of sulphuric and phosphoric acid [13] or on "P" salt and fluoroboric acid and sodium fluoroborate at operating temperatures of 70 to 90°C, current densities of 2 to 5 A/dm^2 and current efficiencies of 14 to 18%. Electrolytes of this type produce in 30 to 60 min fairly ductile layers, 4.6 to 7.6 μm thick, which are lustrous up to 6 μm thickness [7].

The sulphate/phosphate solutions are the most promising concerning stability in operation and storage [2, p. 192]. In electroplating experiments from solutions based on a wide range of Pt compounds, only complexes based on nitroplatinates of the general formula $K_2Pt(NO_2)_2X_{4-2}$ ($X = Cl^-$, SO_4^{2-}) showed promising results. Among other compounds, $K_2Pt(NO_2)_3Cl$, $K_2Pt(NO_2)_2Cl_2$, $K_2Pt(NO_2)Cl_3$ and $K_2Pt(NO_2)_2SO_4$, the corresponding perchlorato-nitritoplatinates, sulphato-dinitroplatinates of Na, NH_4, Li, Mg, Al, Ni and Zn, the potassium dinitroplatinates with acetate, borate, tartrate, citrate, fluoroborate, phosphate, sulphate and sulphaminate were synthesized and investigated. Nearly all of these gave electrodeposits of good quality with cathode efficiencies near 15%, but a solution containing sulphato-dinitroplatinous acid, $H_2Pt(NO_2)_2SO_4$ (DNS salt), produced optimum results. The salt is used at a Pt concentration of 4 g/l, the pH has to be kept below 2 and the current density below 20 A/ft^2 (~21.5 mA/cm^2). Between 30 and 70°C smooth bright deposits are obtained. At 50°C the deposition rate is 0.0001 inch in 2 h at 5 A/ft^2 (~5.4 mA/cm^2). For fast plating this time can be reduced to 30 min using a 15 g/l bath at 20 A/ft^2 (~21.5 mA/cm^2). Advantages of the bath are: 1) bright and smooth deposits, no need for polishing; 2) deposits up to 0.001 inch in thickness may readily be obtained; 3) the bath is stable and does not deteriorate on standing; 4) the bath can be used for plating on base metals [14].

Electrolytes Based on Alkali Hydroxyplatinates

The basic electrolyte of this type was discovered fairly early. Operating conditions are: sodium hexahydroxyplatinate 20 g/l; free sodium hydroxide 10 g/l; pH = 13; temperature 75°C; current density 0.8 A/dm^2. Lustrous deposits are obtained at thicknesses up to 0.001 inch with a hardness of ~400 DPN. A serious disadvantage of the solution is its instability due to decomposition of the Na salt according to $3\,Na_2Pt(OH)_6 \rightarrow Na_2O \cdot 3\,PtO_2 \cdot 6\,H_2O + NaOH + H_2O$ [15].

The bath can be improved by using KOH instead of NaOH. This electrolyte operates at 75°C and 0.75 A/dm^2 with a current efficiency of 100% [16].

The deposition of Pt from aqueous electrolytes has been reviewed in various publications on the electrodeposition of Pt metals and their alloys, the electrodeposition of the latter up to now being of no practical importance [17, 18]. In general Pt electrodeposition is treated very briefly, exceptions being [19 to 22], with [22] briefly discussing the analytical determination of Pt in electrolytes.

Electrodeposition of Pt from Salt Melts

The electrodeposition of Pt from salt melts was developed from early beginnings in 1937 [23] to a commercial process which is used today, especially to produce ductile, nonporous and heat-resistant Pt layers, e.g on Ti and Mo for anodes, electronic parts and the glass industry. For electrolyte preparation, pieces of Pt were dissolved by electrolysis at 0.5 A and 60 cycles in a mixture of 53 wt% NaCN and 47 wt% KCN, melting point 500°C. Layers 10 mil (250 μm) thick were plated with a current efficiency >90% at current densities between 0.3 and 0.5 A/dm^2. Deposition of successive layers was achieved by reversing the polarity of the electrodes for the first 15 min of operation of each additional period. The Knoop microhardness H_K (25 g) of the deposited Pt was between 85 and 95 kg/mm^2 [24]. A general review of the electrodeposition of platinum metals from molten salts, supplemented by own experimental work, is given by [25], who stated in conclusion "that there would be substantial engineering problems to be solved before the processes could be commercialized". In a later publication the plating of Pt from cyanide melts was more carefully investigated. The Pt was electrolised from straight cyanide melts or mixtures of cyanides with cyanates and carbonates. It was introduced into the melt either electrolytically via a soluble anode or as $Pt(CN)_2$ or $Na_2Pt(CN)_4$. The concentration was 0.5 wt% Pt, the current density 5 to 10 mA/cm^2, the cathode efficiency 60 to 90%. Deposits were columnar and soft. Their Knoop hardness H_K (100 g) was 50 to 60 kg/mm^2, the ultimate tensile strength 300 MPa. The electrolytes have a high surface tension, so bubbles are difficult to remove. Especially above 650°C electrolytes are unstable, probably due to decomposition of the bivalent Pt complex according to $2Pt(CN)_4^{2-} \rightarrow Pt(CN)_6^{2-} + Pt^0 + 2CN^-$. The rate at which Pt^{2+} decomposes is reduced by lowering the melt temperature by using cyanide/cyanate mixtures. The author recommends a mixed cyanate/cyanide electrolyte operating at 450°C [26]. From a similar melt Pt-Ir alloy deposits can be obtained, see **Fig. 11** [26, p. 33]. Results of coating refractory metals and graphite with Pt layers up to 63.5 μm thick for technical applications are reported by [27, pp. 39, 42]. A production process for fused-salt platinum electroplating as applied to the continuous cladding of Mo wire has been described. The author concluded that "it now can be stated with confidence that fused-salt plating has emerged from being a critical laboratory technique to a useful and economical method of applying platinum coatings with unique properties to a variety of substrates" [28, pp. 124, 128].

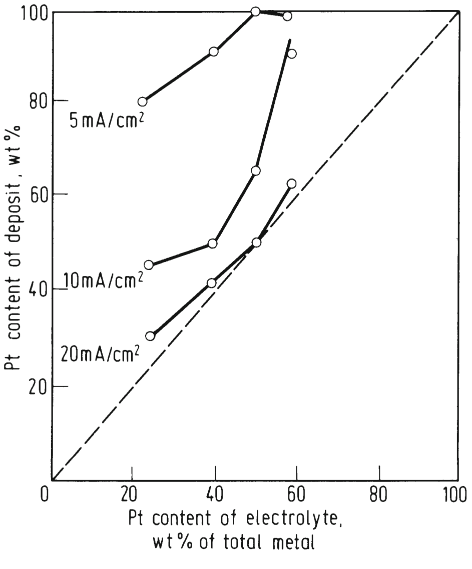

Fig. 11. Plot of platinum content of a platinum-iridium alloy electrodeposit vs. platinum content of electrolyte expressed as percent of platinum plus iridium in electrolyte. Electrolyte is equal mass mixture of NaCN and KCN. Platinum added as $Na_2Pt(CN)_4$ and iridium added as $K_3Ir(CN)_6$.

Direct current, current reversal and pulse plating all produced columnar structures of Pt layers deposited from a cyanide melt [29]. The technical application of fused cyanide electrolysis for coating Ti anodes of Mo and W wire for the electronic industry is described by [30, 31].

The methods for coating various substrates with platinum by vacuum deposition, thermal decomposition, chemical vapour plating, electroless plating, aqueous electroplating, fused-salt electroplating, metallic bonding and metallising are reviewed and evaluated. There is a difference between methods for the production of thin films (below 1 μm) and for layers thicker than 20 μm. Fused-salt electroplating is listed in the second group. The advantage cited is a stress-free and ductile deposit up to 200 μm thickness. The disadvantage is that only substrates can be coated which can withstand the high temperature of the fused salt, e.g. Ti, Ta, Nb, Mo, W or graphite [32, pp. 51, 52].

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4 Platinum-Group Metals, Alloys and Compounds in Catalysis

4.1 Introduction

Ostwald defined a catalyst, about 1900, as "a substance that alters the velocity of a reaction without appearing in the end products", and from this it follows that by increasing the velocity of a desired reaction with respect to that of an unwanted side reaction, the formation of a desired product may be enhanced. It is this ability to modify the rates of competing reactions that is the keystone to the greatly expanded chemical and petroleum industries of today, whose products, worldwide, are valued in billions of dollars. It is a startling fact that about 90% of all chemical manufacturing processes are catalytic, and that they account for 15 to 20% of all manufactured goods produced in the United States [1]. Sulphuric acid, ammonia, nitric acid, the aromatic hydrocarbons, methanol and ethyleneglycol are all manufactured by catalytic processes, while chlorine production utilizes energy saving anodes and cathodes, and others, such as ethylene and terephthalic acid, contain catalytic clean-up steps to improve their purity before further processing. All of these compounds are in the top 30 chemicals produced in the United States and are manufactured on the billions of pounds per annum scale [2]. In 1979 world crude oil consumption averaged 64×10^6 bbl (barrels) per day, the United States share being 2.9×10^6 bbl per day, and all of this was processed by an industry that consists almost entirely of a series of catalytic processes, such as cracking, reforming, desulphurisation, isomerisation, polymerisation, and alkylation [3].

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4.1.1 The Historical Background to Platinum-Group Metal Catalysis

The history of catalysis may be divided into three periods:

(I) from antiquity to 1836, the year in which Berzelius reviewed the then known catalytic phenomena, noted their similarity and coined the term "catalysis";

(II) the advance of scientific knowledge of catalysis during which the relationship of catalytic phenomena to the steadily expanding fields of physical chemistry (thermodynamics and kinetics) and inorganic/organic chemistry (reaction paths etc.) were demonstrated;

(III) the development of industrial catalysis, when the knowledge gained in the second period was applied to the founding of large industries based on catalysis [1].

The second period lasted from 1836 to about 1920 and the third period has lasted until the present day. Inevitably each period has overlapped the succeeding one and no sharp boundaries between them can be drawn. For example, some would claim that a new era in catalysis is just starting where the empirical formulation of industrial catalysts, with subsequent scientific explanation of their action, is being replaced by the organised development of catalysts from well understood physical and chemical principles [2, 3, 4].

Apart from Green's survey of catalysis, which takes the history only as far as 1929, no general history of catalysis appears to exist. Robertson [5] has reviewed the early history of catalysis up to 1840, while McDonald and Hunt [6] have considered the contribution which the platinum-group metals have made to the subject from the researches of Davy to the present day. The history of industrial catalysis, particularly the petroleum, petrochemical and automotive uses of catalysis has been well reviewed by Heinemann [7], and Donath [8] has written a history of catalysis in coal liquefaction. Chaston [9] has looked at the technological progress of catalysis over the last twenty-five years and finally the history of ideas and concepts in catalysis is to be found in the papers of Robertson [10] and Schwab [11]. Use of all these references has been made in the following brief, mainly tabular, history of platinum metal catalysis.

The First Period to 1836

The very earliest use that man made of catalysis must have been the enzymatic conversion of sugar into alcohol, fermentation under anaerobic conditions. Later the aerobic conversion of alcohol to acetic acid (vinegar) was found, probably by accident. Fermentation may have been discovered in neolithic times prior to the discovery of the metallurgies of bronze and iron. By 500 BC fats were being hydrolysed by the catalytic action of potash for the manufacture of soap in the Mediterranean region [12], and the conversion of alcohol into ether using sulphuric acid as catalyst came somewhat later, although it was only recorded in 1552 by Gessner [1].

The first reaction in which the principle of catalysis was recognised was during the investigation of the oxidation of carbon monoxide and metals by Mrs. Fulhame in 1794. She noticed that the presence of water was essential to the process, but was not consumed during the reaction.

Activity quickened in the early years of the new century with notable investigations by Kirchoff, Thenard, the two Davys, Döbereiner, Dulong etc. It was in 1817 that H. Davy described the catalytic properties of platinum for the first time [14]. Subsequently the platinum-group metals played a crucial role in the discovery and description of catalytic phenomena leading to the reviews of Faraday in 1834 and Berzelius in 1836, and the use of the term catalysis by the latter [15]. The following table shows the course of catalysis up to 1836, and the part played by the platinum-group metals.

discovery	investigator	date	catalyst	Ref.
alcohol to ether	Gessner	1552	H_2SO_4	[1]
SO_2 to SO_3		1740s	NO_x	[1]
oxidation of CO oxidation of metals	Mrs. Fulhame	1794	H_2O	[1]
dehydrogenation of ethanol	Priestly, van Marum	1790s	metallic catalysts	[5]
action of NO_x in SO_2 and SO_3	Clement and Desormes	1806	NO_x	[1]
hydrolysis of starch to sugars	Kirchoff	1812	H_2SO_4	[1]
decomposition of ammonia	Thenard	1813	Fe, Cu, Ag, Au, Pt	[5, 6]
oxidation of H_2, coal gas, C_2H_5OH, $(C_2H_5)_2O$	Humphrey Davy	1817	Pt, Pd wires	[1,5,6,14]
decomposition of hydrogen peroxide	Thenard	1818	alkalies	[1, 5]

discovery	investigator	date	catalyst	Ref.
platinum black prepared; oxidation of C_2H_5OH to CH_3COOH	Edmund Davy	1820	Pt	[1, 5, 6]
platinum sponge prepared; oxidation of C_2H_5OH and H_2	Döbereiner	1822/23	Pt	[1, 5, 6]
oxidation of C_2H_5OH and H_2	Dulong, Thenard	1823	Ag, Au, Pd, Rh, Ir, glass	[1, 6]
combination of H_2 and Cl_2	Turner	1824	Pt	[1]
investigation of supported catalysts	Döbereiner, Henry	1824	Pt	[1, 6, 13]
poisoning of catalysts	Henry	1825	Pt	[1]
selectivity of Pt in oxidation reactions discovered	Henry	1825	Pt	[1, 6]
oxidation of SO_2 over heterogeneous catalyst	Phillips	1831	Pt	[1, 5, 6]
isolation of first enzyme catalyst, diastase	Payer, Persoz	1833	organic	[1]
isolation of second enzyme catalyst, emulsin	Liebig	1835	organic	[1]
review of catalytic phenomena	Faraday, Berzelius	1834/36	—	[1, 6]

The Second Period, 1836 Onwards

Emphasis in scientific thought changed during the second period. The organic chemists' description and classification of organic reactions, together with the discovery of the laws of thermodynamics and kinetics eclipsed the efforts of those chemists trying to understand the phenomena of catalysis. Discoveries of new catalytic reactions were made, but depended purely on chance. Attempts were made to utilize catalytic reactions industrially with mixed results. Sometimes the attempt was successful, for example, with Groebe's discovery of the mercury-catalysed oxidation of naphthalene to phthalic anhydride [1] which revolutionised the dyestuff industry with the synthesis of indigo. On other occasions the attempt was less successful, as when Kuhlmann tried to manufacture sulphuric and nitric acids catalytically with platinum catalysts. Failures were almost always due to an inadequate understanding of how pressure and temperature affected reaction equilibria and kinetics, and of the part played by trace quantities of the metalloids in the poisoning of catalysts.

The key to catalytic poisoning had been given by Faraday in 1834 [1, 6] when he noted that catalysis with platinum only occurs on a clean metal surface, that the rate of reaction is affected by the state of division of the catalyst, by the purity of the reactants, and that some substances cause temporary loss of activity while others permanently damage the catalyst. However, before Faraday's theory of catalytic action could affect the course of catalysis, two other ideas, Berzelius' theory of catalytic force and de la Rive's and Gmelin's theory of intermediate compound formation [5], had to be shown to be inadequate. This took until the end of the century.

The first successful application of thermodynamics and kinetics to industrial catalysis only came with the investigations of ammonia synthesis from nitrogen and hydrogen by Ostwald, Haber and Nernst between 1904 and 1907. These discoveries inaugurated the period of industrial application of catalysis which, together with theoretical investigations, has continued to the present day.

The Third Industrial Period, 1838 Onwards

Although the first industrial catalytic process, the manufacture of sulphuric acid, was a gaseous homogeneous system, virtually all subsequent processes have used heterogeneous catalysts. In recent times liquid-phase homogeneous systems have made their appearance. Platinum-group metals have been prominent in both heterogeneously and homogeneously catalysed processes during this period.

In inorganic catalysis PGM have been used in sulphuric acid manufacture (Pt, 1840 to 1940), nitric acid production (1840 onwards), ammonia synthesis research (Pt 1881 and Os 1907), hydrogen peroxide manufacture (Pd 1950 onwards) and chlorine production (Ru 1970 onwards). PGM usage in organic chemical processes include petroleum refining (Pt in reforming catalysts), petrochemicals (Pd in ethylene cleanups, Pd in oxidation of ethylene to acetaldehyde and acetic acid, Rh in low-pressure hydroformylation), fine chemicals (organic function hydrogenation with Pt and Pd) and plastics, fibres and resins (Pt and Pd for nylon intermediates, Pd for terephthalic acid purification).

New fields of PGM usage have opened up in the last ten years, in energy generation with platinised catalysts in fuel cells [16 to 18], and platinum-rhodium-palladium catalysts for pollution control [19 to 22]. Future areas of application include possibilities for hydrocarbon fuel synthesis (Ru, Fischer-Tropsch catalysis) [23], catalytic combustion (Pt) [24] and in electricity generation by nuclear power (Pt for heavy water production) [25, 26].

The following table shows the principal PGM catalysed processes developed for commercial use in the past 150 years with the approximate date of commercialisation.

discovery	investigator/ operator	date	catalyst	Ref.
oxidation of SO_2 to SO_3	Kuhlmann	1838	Pt	[10]
oxidation of NH_2 to nitric acid	Kuhlmann	1838	Pt	[10]
ammonia synthesis experiments	Johnson	1881	Pt	[6]
ammonia synthesis experiments	Haber	1907	Os	[6]
synthesis of high melting hydrocarbons	Pichler	1938	Ru	[7]

discovery	investigator/ operator	date	catalyst	Ref.
reforming catalysts	Haensel	1950	Pt	[7]
acetylene removal from ethylene		1950s	Pd	
acetaldehyde production by oxidation of ethylene	Wacker	1960	Pd/Cu	[7]
bimetallic reforming catalysts		1967	Pt/Re	[7]
emission control catalysts		1976	Pt/Pd or Pt/Rh	[7]
high stability zeolite cracking catalysts		1977	Pt	[7]
hydroformylation of olefins	Wilkinson	1978	Rh	
carbonylation of methanol	Union Carbide	1978	Rh	
$C_4H_6 + C_2H_4$ to 1,4-hexadiene		1970s	Rh	
fuel cell		1980	Pt	

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4.1.2 Catalyst Literature

The literature of platinum metal catalysis is very large, but somewhat scattered throughout the general catalytic literature. It is the purpose of this section to list the more accessible information sources. In 1940 Berkman, Morrell and Egloff [1] could cover the whole field of catalysis in one rather large volume. By 1954 Emmett [2] required seven volumes, since when authors have contented themselves with covering some aspect of the subject. General, elementary accounts of catalysis are to be found in [3, 4] while encyclopedic texts covering most aspects of catalytic phenomena are to be found in [5, 6]. More advanced texts dealing with heterogeneous catalysis [7] and catalysis over metals [8] review the experimental and theoretical literature to 1967 and 1962, respectively. Corresponding texts for homogeneous catalysis are to be found in [9, 10, 11]. Books which treat specific topics such as hydrogenation etc. are to be found in [12 to 17, 28, 29]. Reviews of fundamental research are given in [18, 19], and of experimental technique in [20]. The area of industrial catalysis including PGM catalysis was surveyed by [21]; in a similar area [22] gives the practical catalyst chemist a great deal of information on commercial catalysts and processes, while [23] deal less with catalysts and more with process conditions. The Royal Society of Chemistry publish Specialist Periodical Reports on Catalysis which contain articles dealing with subjects as diverse as hydrogenation on Pt stepped surfaces, catalytic oxidation with PGM complexes in solution, and catalyst preparation [24 to 27].

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Congress, Symposia etc., Reports

A large amount of information concerning specific catalytic properties of the PGM are reported at congresses, symposia and meetings. With the more international gatherings the proceedings are usually published, and being state of the art contributions, invariably contain a useful review of that particular subject in the introduction.

The foremost reports are those of the International Congress on Catalysis held every four years. They are devoted to the more academic and fundamental aspects of research on catalytic phenomena and have been the forum for reporting progress on the theory of catalytic mechanisms. To date seven congresses have been held [1 to 7].

Two symposia dealing with catalyst preparation have been published [8, 9], two on the relationships between heterogeneous and homogeneous catalysts [10, 11], and two on the loss of activity and selectivity of catalysts [12, 13]. Among the many meetings held on homogeneous catalysis two have been published of interest [14, 15], and many papers dealing with the subject are to be found in the published proceedings of the Organic Reactions Catalysis Society together with papers on heterogeneous catalysis, catalyst characterisation etc. [16 to 23].

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Patent Literature Reviews

Although the patent literature on the preparation and properties of PGM catalysts is extremely large it has been very poorly reviewed. Catalyst manufacture and hydrogenation catalysts have been reviewed by [1, 2], respectively, while reviews on fragrances and flavours [3], vitamin synthesis [4], and hydrogen manufacture [5] contain references to catalysts and processes using PGM.

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Periodical Literature

Original experimental work on catalysis over platinum-group metals is published in the Journal of Catalysis [1], Journal of Applied Catalysis [2], Journal of the Chemical Society [3], Journal of the American Chemical Society [4], and Journal of the Research Institute for Catalysis, Hokkaido University [5].

Catalytic reaction chemistry is frequently surveyed in Chemical Reviews [6] while Catalyst Reviews-Science and Engineering [7] emphasises a multi disciplinary approach to advances in catalyst theory, the technology, engineering and chemical aspects of reactions, reactors, modelling, analysis and statistical evaluations. Russian work in platinum-group metals catalysis is most frequently published in Kinetics and Catalysis [8] (English translation of Kinetika i Kataliz). Industrial and Engineering Chemistry is now published in three parts quarterly, under the titles "Fundamentals [9], Process Design and Development [10], and Product Research and Development" [11].

The physical characterisation of catalysts, now an important subject in its own right, is well catered for in a series of specialist journals which usually contain articles on the characterisation of platinum metal catalysts and their supports. These journals are Journal of Surface Science [12], Journal of Electron Spectroscopy and Related Phenomena [13], and the Journal of Colloid and Interfacial Science [14]. Scientists working on characterising catalysts, supports and reactions by infrared spectroscopy publish their work mainly in Transactions of the Faraday Society I [15]. The Journal of Chemical Technology and Biotechnology [17] bridges the field between enzyme/molecular catalysis and heterogeneous catalysis.

The only journal entirely devoted to the science and technology of the platinum-group metals is Platinum Metals Review [16], which is published quarterly and usually contains at least one article on platinum metal catalysis.

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Reviews of Platinum Metal Catalysis

The review paper literature for the whole field of catalysis of the six platinum-group metals and the industrial uses of platinum-group metal catalysts is not extensive, most of the papers being written before 1970. Papers reviewing areas of platinum metal catalysis abound and reference will be made to these in subsequent sections. Included in this section are reviews of platinum metal catalysis contained in the Gmelin Handbuch der Anorganischen Chemie.

The physical properties of the six platinum metals, much of it of use to the catalyst chemist, has been surveyed and the best values tabulated and published in the Engelhard Industries Technical Bulletin [1]. The physical and mechanical properties, chemistry and catalysis of these metals have been reviewed in a series of publications by the International Nickel Company between 1962 and 1968 [2 to 6]. An annotated bibliography of the catalysis of ruthenium, rhodium and iridium was published in 1959 and reviews the catalyst literature for these metals from 1881 to 1959 [7].

In a series of papers the general catalytic properties of the platinum-group metals for hydrogenation [8], dehydrogenation [9] and their place in synthetic organo-silicon chemistry [10] have been reviewed, and, in two more specialised papers, ruthenium catalysis [11] and osmium catalysed hydrogenations [12]. The use of ruthenium and osmium as hydrogenation catalysts has been reviewed by [13] and [14].

The industrial use of the platinum-group metals has been reviewed in [15 to 18].

The Gmelin Handbuch der Anorganischen Chemie has included much of the academic catalytic chemistry of the platinum metals known prior to the Second World War [19 to 27]. It refers, however, little of the technical catalytic chemistry discovered, mainly in Germany and the USA, between 1920 and 1940. Each of the platinum metals is treated in a separate volume, some of them such as platinum, in several parts. Reference to this literature may be had via the table below.

subject	Ref.	page
platinum black	[26]	391
platinum black preparation	[26]	393/7

subject	Ref.	page
platinum black properties	[26]	397/8
platinum sponge	[26]	398
ruthenium black	[26]	398
rhodium black	[26]	399
rhodium sponge	[26]	399
palladium black	[26]	399/400
palladium sponge	[26]	400/1
osmium black	[26]	401
iridium black	[26]	401
colloidal platinum metals	[26]	405/23
colloidal platinum	[26]	405/23
negative platinum sols	[26]	405/23
positive platinum sols	[26]	423
colloidal ruthenium	[26]	423/4
colloidal rhodium	[26]	424
colloidal palladium	[26]	425/7
colloidal osmium	[26]	427/8
colloidal iridium	[26]	428
catalytic hydrogenation over Pt sols	[26]	429
decomposition of hydrogen peroxide	[26]	429/30
oxidation of carbon monoxide	[26]	430
ammonia oxidation	[26]	849
decomposition of hydrogen peroxide	[26]	849
hydrogen cyanide synthesis	[26]	849
hydrogen sorption on wires, foils, etc.	[27]	7/9
platinum as a cathode	[27]	9
hydrogen sorption on platinum sponge	[27]	9/10
hydrogen sorption on platinum black	[27]	10/21
hydrogen sorption on platinum black by reduction of the oxide	[27]	21/2
hydrogen sorption by supported platinum	[27]	22/4
hydrogen sorption on platinum from thermally decomposed salts	[27]	24/5
hydrogen sorption by colloidal platinum	[27]	25
oxygen sorption on platinum wires, etc.	[27]	30/4
platinum as an anode	[27]	34/5
oxygen sorption on platinum sponge	[27]	35
oxygen sorption on platinum black	[27]	36/9
oxygen sorption on supported platinum	[27]	41

subject	Ref.	page
oxygen sorption on colloidal platinum	[27]	41
decomposition of oxygen compounds over ruthenium catalysts	[19]	24
Fischer-Tropsch catalysis over ruthenium	[19]	24
oxidation of isobutane, ethylene and propylene over ruthenium	[19]	24
decomposition of formates over ruthenium	[19]	24
oxidation of ethanol over ruthenium	[19]	24
benzene hydrogenation over ruthenium	[19]	24
dehydrogenation of cyclohexane over ruthenium	[19]	24
Fischer-Tropsch reaction over ruthenium	[20]	173
hydrogenolysis of ethane over ruthenium	[20]	173
hydrogenation over ruthenium	[20]	173
hydrogenation over mixed Ru/Pt oxides	[20]	173/4
hydrogenation of aliphatic aldehydes and ketones over Ru/C	[20]	174
hydrogenation of cellulose/starch over Ru/C	[20]	174
hydrogenation of 1,4-butanediol	[20]	174
hydrogenation of aromatic compounds over ruthenium	[20]	174/5
hydrogenation over Ru/Pt alloys	[20]	175
ruthenium halides and complexes as hydrogenation catalysts	[20]	175
deuteration reaction over ruthenium	[20]	175
isomerisation over ruthenium	[20]	176
ammonia oxidation over ruthenium	[20]	176
oxidation of olefins and aromatic nuclei over ruthenium complexes	[20]	176
ruthenium and alloys as electrocatalysts	[20]	176
decomposition of ozone, etc., over iridium	[25]	43
hydrogenation or organics over iridium	[25]	43
oxidation of NH_3, SO_2, CO over iridium	[25]	43
inversion of sugar over iridium	[25]	43
electrocatalyst for water decomposition	[21]	44
decomposition of oxygen-containing compounds over rhodium	[21]	44
synthesis of water, ammonia over rhodium	[21]	44
oxidation of SO_2 over rhodium	[21]	44
Fischer-Tropsch reaction over rhodium	[21]	44
decomposition of formates over rhodium	[21]	44
dehydrogenation of alcohols over rhodium	[21]	44
oxidation of ethanol over rhodium	[21]	44
benzene hydrogenation over rhodium	[21]	44
cyclohexane dehydrogenation over rhodium	[21]	44
hydrogen sorption on various forms of palladium	[22]	162/5

subject	Ref.	page
hydrogen sorption on palladium formed by oxide reduction	[22]	162/3
hydrogen sorption on supported palladium	[22]	163/4
hydrogen sorption on evaporated palladium	[22]	164
hydrogen sorption on low-pressure glow discharge produced palladium powder	[22]	164/5
hydrogen sorption on colloidal palladium	[22]	165
hydrogen reduction of palladium oxides	[22]	162
preparation of palladium powder by low-pressure glow discharge	[22]	164
preparation of palladium colloids	[22]	165
catalytic reactions of palladium with organic substances	[22]	256
nitrobenzene reduction over palladium	[22]	256
oxidation of benzene to phenol over palladium	[22]	256
sorption of oxygen on massive palladium	[22]	257
sorption of oxygen on palladium black	[22]	257/8

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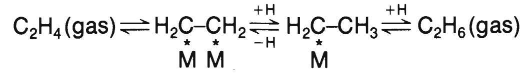
4.1.3 Platinum-Group Metal Catalysis

In order that a catalytic reaction may take place the reactants must come into close contact with the catalyst surface. Two types of close contact exist, physical sorption in which the molecules are held to the surface by forces like those which normally lead to the liquefaction of gases, and chemisorption in which the adsorbed molecule forms a chemical bond with the catalyst surface. For example, for the ortho-para hydrogen interconversion over ruthenium metal it is sufficient for the hydrogen molecule to enter the magnetic field of the paramagnetic ruthenium atoms by physical sorption, but for the cracking of hydrocarbons it is necessary for the compound to chemisorb to the catalyst surface [1].

Generally, to obtain catalytic reaction, the reactants must be chemisorbed on the catalyst surface. Reactions between olefins and hydrogen, for example, require the formation of surface organo-metallic intermediates.



$$C_2H_4(gas) \rightleftharpoons \underset{\underset{M}{*}}{H_2C}-\underset{\underset{M}{*}}{CH_2} \underset{-H}{\overset{+H}{\rightleftharpoons}} \underset{\underset{M}{*}}{H_2C}-CH_3 \overset{+H}{\rightleftharpoons} C_2H_6(gas)$$

Similar intermediates have been postulated for many other reactions. With ethylene hydrogenation there is only one product. Where more than one reaction path is possible mixed products will be formed and the path with the highest overall rate will contribute most to the product. Catalysts can only alter the rate at which reactions proceed and do not change the equilibrium which is attained. Different paths may be catalysed to different extents, and from this arises the concept of selectivity. Selectivity may be expressed as the ratio of the activities or rate constants [2].

The platinum-group metals are catalytically more active than the base metals for many reactions, but particularly for hydrogenation and oxidation reactions. **Fig. 12** illustrates the effect for ethylene hydrogenation [5].

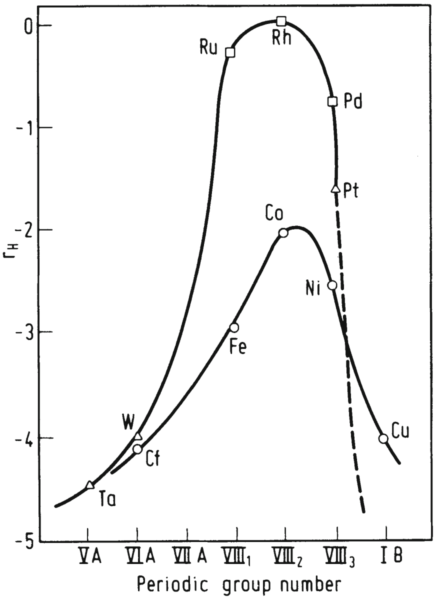


Fig. 12. Rate of ethylene hydrogenation r_H on various metals as a function of periodic group number (Rh = 1).

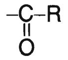
Each element also has specifically high activity for certain types of reaction (see table p. 106), and both the higher activity of the PGM and the differences between the PGM have been explained as a function of changing absorption strengths of the reactants with changing electron/atom ratios [3, 4, 5]. The concept was extended to cover the selectivity of PGM for the hydrogenation and hydroisomerisation of multiply unsaturated compounds [6]. Molecular orbital theory was used to explain the bonding of adsorbed species to catalyst surfaces and to draw distinctions between the bonding strengths of various sites on cubo-octahedral metal crystallites exposing (100) and (111) planes, such as may be present in supported industrial platinum metal catalysts [7, 8]. The importance of terrace, step and kink sites on platinum single crystals for hydrogenation and hydrogenolysis reactions was verified experimentally and the effect of a carbonaceous overlayer on the selectivity of platinum in these reactions was pointed out. A model for reforming reactions on working platinum reforming catalysts was developed proposing that 90 to 95% of the platinum surface is covered by a carbonaceous layer. The 5 to 10% of uncovered platinum surface occurs in patches within the carbonaceous layer and is responsible for the observed structure sensitivity of platinum in these reactions and the turnover rate, while the carbonaceous layer provides desorption and hydrogen transfer sites for other reactions. The theory may also explain the improvement in selectivity which platinum poisoned by a very small quantity of sulphur exhibits toward dehydrogenation/hydrogenation reactions compared to hydrogenolysis, by postulating that the sulphur will bond to the sites of highest energy (kink sites) which are responsible for C–C bond breaking, poisoning the site and decreasing the platinum catalysts activity for this reaction. The theory also emphasises the connection between the heterogeneous platinum surface, with its atomic steps and carbonaceous overlayer, and homogeneous systems with their single metal atoms or metal clusters surrounded by ligands which will break and form H–H and C–H bonds, but lack the ability of C–C bond breaking possessed by the highly uncoordinated kink atoms of metallic surfaces [9, 10]. The close connection between heterogeneous, homogeneous and cluster catalysis has been emphasised in articles by [11, 12, 13], and the 1974 and 1978 symposia devoted to the connections between homogeneous and heterogeneous catalysis [14, 15].

Although the surface chemistry outlined above controls the intimate details of the reaction, other processes can interfere with the activity and selectivity of the system. For instance, with a gas phase reaction the overall reaction may be split into the following steps: (1) diffusion of reactants to the surface, (2) adsorption, (3) surface reaction, (4) desorption, (5) diffusion of product away from surface [2].

The rate of reaction is a function of the catalyst surface area and in order to maximise surface area it is essential to use porous supports. When surface reaction, adsorption and desorption are fast compared to the rate of diffusion of reactants and products, the porosity of the catalyst may impose severe restraints on the diffusive process and large concentration gradients may result within the pore system. This may alter the kinetics of the process with changes in the apparent activation energy and even the stoichiometry of the reaction. Heterogeneous liquid phase catalytic systems impose two further diffusive barriers to the reaction, particularly when one of these reactants is gaseous. Flow of the gaseous reactant from the gas phase to the liquid phase, and from the bulk liquid to the catalyst particle is impeded by stagnant boundary layers surrounding both the gas bubble and the catalyst particle. Liquid phase homogeneous systems have the advantage of removing the mass transport barrier around the catalyst particle, but the gas-liquid barrier remains and may be a rate/selectivity determining step, particularly where the gaseous phase is multicomponent such as with hydroformylation reactions using CO/H_2 mixtures [2].

The effect of mass transport on reaction rates and selectivity in catalyst pores was considered first by [16] in a classic paper. [17, 18] make use of this paper in discussing mass transport in both gaseous and liquid phase systems. [19] has looked at mass transport in heterogeneous liquid phase systems and [20] have calculated the magnitude of the effect of reaction product poisoning on the fraction of catalyst surface available for reaction. [21 to 23] have examined the role of mass transport on activity and selectivity in liquid phase reactions and its effect on the design of platinum-group metal supported catalysts. More mathematical treatment of transport in porous catalysts is given by [24 to 26].

Reactions of the platinum-group metals:

reaction	2nd row			3rd row		
	Ru	Rh	Pd	Os	Ir	Pt
hydrogenation:						
$-C=C-$, $-C\equiv C-$ etc.	—	—	✓	—	—	✓
$R-C=O$	✓	✓	—	—	—	—
 $-\underset{\underset{O}{\|}}{C}-R$	—	—	✓	—	—	✓
NO_2	—	—	✓	—	—	✓
aromatic rings	✓	✓	—	—	—	—
dehydrogenation:	—	—	✓	—	—	✓
oxidation:						
mild	✓	—	✓	—	—	✓
deep	—	✓	—	—	—	✓
synthesis:						
ammonia	✓	—	—	—	—	—
methanol	—	—	✓	—	—	—
hydrocarbons	✓	—	—	—	—	—
acetic acid	—	✓	—	—	—	—
CO insertion:						
carbonylation	—	✓	—	—	✓	—
hydroformylation	✓	✓	—	—	✓	—
cis-hydroxylation:	—	—	—	✓	—	—

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Industrial Platinum Metal Catalysis

Any substance, in principle, may act as a catalyst for some chemical reaction, but in practice there are only a limited number of types of substances which are effective industrial catalysts. The following table shows the major industrial applications of catalysis in 1978.

application	catalyst	production capacity $t \times 10^6$	catalyst sales $\$ \times 10^6$ p.a.
petroleum refining	Pt, Pd, Ir, Si, Al, Re, Cr, Mo, W, Ni	434	364
fertilisers	Pt, Pd, Rh, Fe, Ni, Cr, Zn	24	46
bulk chemicals	Pd, Rh, V, Bi, Mo, Ag, Cu, Ni, Fe, Co	46	35
plastics	Cr, Fe, Al, Ti, Sn	19	118
fine chemicals	Pt, Pd, Rh, Ru, Ni, Cu	—	90
fats & oils	Ni, Cu	28	24
pollution control	Pt, Pd, Rh	—	230

Industrial catalysts can be gaseous, liquid or solid. The first industrial catalyst was a gas, nitric oxide used in the manufacture of sulphuric acid by the Lead Chamber Process. Liquid catalysts find a very large place in the refining industry where both sulphuric and hydrofluoric acids are active alkylation catalysts. Many homogeneous catalytic systems may be regarded as liquid catalysts simply because they are dissolved in a liquid medium.

The majority of industrial catalysts are solids consisting of either a single component such as a platinum anode [1] or platinum gauze [2] or of an active component, platinum, palladium etc. dispersed on an inert support, for example platinum dispersed on alumina for the control of air pollutants [3]. In some cases the support may be one of the active components of the catalyst, forming what are known as dual function catalysts [4, 5], and in this case the support is merely the component in the highest concentration. With bimetallic catalysts the active components are dispersed together on the support material. These catalysts can show enhanced activity-selectivity and one valuable combination appears to be that of a group IB metal (Cu, Ag, Au) with a group VIII metal (Fe, Co, Ni, Pd, Ru, Rh, Pt, Ir, Os) for hydrogenation reactions [6]. Similar effects have been discovered for some platinum metal combinations such as Pd-Au and Pt-Ir. The application of the Pt-Re combination has revolutionised the performance of platinum reforming catalysts in the refining of crude oil fractions [7, 8]. The catalyst maintains its performance by decreasing the rate of carbon fouling and increasing the period between regenerations. An improvement in sulphur poison resistance over that of platinum alone has also been achieved [9].

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The Catalyst in Use. The principal requirement of industrial catalysts is that they are stable and retain their activity-selectivity over long periods. To do this the catalyst support combination must be physically and chemically strong in the reaction medium. Deterioration of catalyst performance can usually be attributed to one or more of the following factors: (I) sintering of the active metal component, (II) change in surface composition of alloys, (III) poor mechanical strength of the support, (IV) catalyst poisoning.

The term sintering may be used to cover both changes in the metal particle size and the pore size distribution of the support. The predominant factors affecting sintering are temperature and composition of the ambient atmosphere. At sufficiently low temperature metastable metal crystallites remain isolated. At sufficiently high temperatures, however, surface diffusion will cause particle growth. The growth can occur by the contact of metal particles, migration of the metal particles across the surface of the support or gas phase metal vapourisation. Work by [1] and [2] has shown that these surface processes become important at temperatures of approximately one third to one half of the melting temperature of the metal. Support materials may also undergo sintering changes, changes of composition, and crystallographic phase. For example γ-aluminas undergo a range of phase changes between 400 and 1000°C to terminate as α-alumina. Parallel with these phase changes goes a decrease in support surface area from $\sim 200\ m^2/g$ for γ-alumina to $1\ m^2$ for an α-alumina. Such large decrements of surface area can trap the active metal centres within the support denying the reactants access.

The mechanism by which sintering of metal crystallites occurs is a matter for dispute. The theoretical aspects of sintering have been well covered, firstly for the particle migration theory [3 to 8] and secondly capillary-driven interparticle transport [9 to 11]. The first mechanism is confined to particles of less than 10 nm diameter. The second mechanism is a development of the classical Ostwald ripening theory [6].

The second theoretical model postulates sintering to occur via a three-step mechanism: (1) escape of metal atoms or molecules of metal compound such as oxide, from the metal crystallite to the support; (2) migration of these atoms along the support surface; (3) capture of migrating atoms by metal crystallites upon collision [12 to 15].

A full mathematical treatment of the theory is given in [12]. The two theories are not mutually exclusive and the view is generally taken that particle migration may well predominate for particles below 10 nm diameter, while interparticle transport accounts for the sintering of larger particles. In liquid-phase heterogeneous catalytic reactions a further mechanism of sintering is thought to operate via dissolution – redeposition. This mechanism is thought to be a principal mode of sintering in fuel cell catalysts [16].

The sintering of alumina supports with particular reference to platinum automobile exhaust catalysts has been reviewed by [17]. It has been suggested that the incomplete occupancy of tetrahedral sites could be responsible for the metastability of transitional aluminas [18]. The stabilisation of transitional aluminas with divalent ions has been studied. The diffusion of Al^{3+} cations can be retarded by the introduction of divalent ions into the tetrahedral sites of the spinel cubic lattice [19].

It has been conclusively shown that the catalytic activity of alloys is strongly dependent on composition [20 to 22]. There is also experimental evidence that enrichment of one component at the alloy surface occurs during reaction [20, 23 to 26]. The thermodynamic driving force for surface enrichment in alloys is the reduction of the surface free energy of the system. Two theories have been proposed to account for the phenomenon and are known as the "bond breaking theory" and the "lattice strain theory".

The bond breaking theory relates surface enrichment to the heats of sublimation of the two components. This theory has had considerable success in predicting the enrichment of copper-nickel [23], gold-platinum [27] and silver-palladium [28] alloy surfaces with copper, gold and silver, respectively. The lattice strain theory was devised for alloys where the components differ considerably in atomic size. So far it has not been proved unambiguously experimentally [29].

The exposure of alloy surfaces to chemisorbing gases can also give rise to surface enrichment by one component. For example, when gold-platinum alloys are equilibrated in high vacuum the surface is enriched with gold. However, exposure of the surface to carbon monoxide causes enrichment by platinum. With chemisorptive enrichment the component which forms the strongest chemisorption complex migrates to the surface [29].

The enrichment of surfaces by one component during reaction has been considered theoretically by Bouwman [29 to 32]. The subject was comprehensively reviewed by [33].

Platinum-group metals are generally used in a supported form, the catalyst containing a relatively low concentration of the active metal, usually 0.1 to 10%. The mechanical strength of the catalyst is a property of the support form, whether pellet, extrudate, granule etc., its chemical nature and the method of preparation.

Fig. 13, p. 110, relates strength, hardness, melting point and chemical composition. In general solids with low melting points have low hardness and strength while high melting solids have high hardness and strength. Because pelleting machinery is made of steel, this imposes a strength factor on the solids which can be manufactured into pellets and only the weakest groups of materials with Mohs hardness up to 4 can be satisfactorily pelleted. With harder materials it is necessary to add a third component with a Mohs hardness <4. A pellet, however, to be a successful catalyst support, must have a high surface area and hence must contain pores. The degree of pore structure or voidage can be related to the strength and pelletability of the material. The relationship is shown in **Fig. 14** [34].

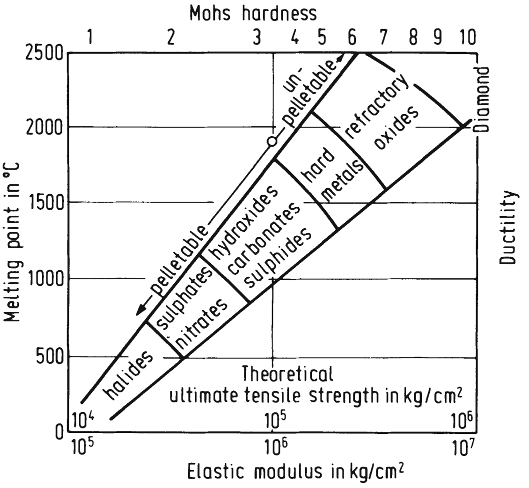


Fig. 13. Relation of strength, hardness and melting point for inorganic solids.

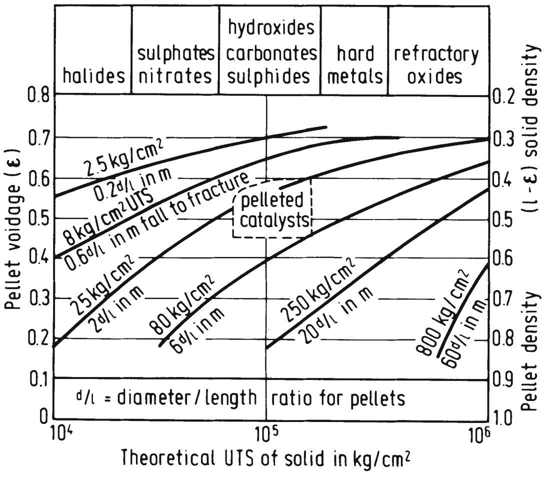
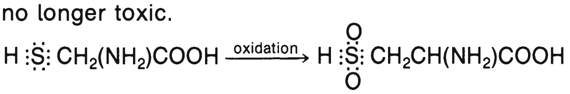


Fig. 14. Relation between ultimate tensile strength (UTS) requirements and pellet voidage and pelletability.

Unless the correct method of support impregnation is chosen it can give rise to chemical attack on the pellet material and cause a deterioration in the ability of the pellet to withstand the stresses imposed during use. As many platinum metal catalysts, particularly those intended for gas purification use, are impregnated so as to deposit the metal as a thin layer close to the surface of the pellet (so-called mantle inpregnation), the deterioration of the catalyst can start during transport from the catalyst manufacturer's factory to the customer's plant. Abrasion due to tumbling and rolling of the pellets can remove some, or in the extreme case of mantle impregnated catalysts, all of the outer metal-bearing layer, with consequent loss of both activity and platinum metal. Similar problems occur during reactor loading, the catalyst frequently being dropped a distance of several feet onto the catalyst bed below. The predominant problem at this stage is chipping, although powdering can also occur. The fines generated in loading can cause bed blockage and increased pressure drops. Once loaded the catalyst can be subject to chemical and physical strains imposed by the passage of reactants, the load of the superimposed catalyst bed and the movement of the bed caused by the expansion and contraction of both the catalyst bed and the reactor vessel. Although the discussion above has concentrated on pelleted catalysts, all catalysts are subject to degradation by attrition, particularly during use. For example, when powder catalysts are used in liquid phase reactions the shear imposed by the agitator can cause a reduction of particle size to such an extent that some of it passes the filters and is lost to the product [35].

The last mode by which the high activity and selectivity of the platinum-group metals may be lost is poisoning. Broadly poisoning may be defined as the covering of the active sites by some overlayer which is not catalytic for the required reaction. This definition covers all forms of chemical deactivation, classical poisoning by sulphur compounds etc., poisoning by a product, such as the poisoning of the pyridine hydrogenation by piperidine, and poisoning by a byproduct, for example poisoning of cracking catalysts by coke.

Maxted [36, 37] was one of the first to investigate the classical poisoning of platinum metal catalysts systematically. He found by working with the nonmetallic elements of groups V B and VI B and the base metals that the electronic structure of the molecule or atom was important in determining its ability to poison platinum metal catalysts. The nonmetallic elements operated by forming strong chemisorptive bonds with the atoms of the catalyst surface via free electron pairs in the valency shell [36, p. 137]. If the electron pairs can be shielded then the substance ceases to be toxic. For example cysteine is toxic to platinum catalysts, but if the unshielded pairs in the valency shell of the sulphur atom are oxidised they do not form strong bonds with the surface and are no longer toxic.



$$H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}:CH_2(NH_2)COOH \xrightarrow{\text{oxidation}} H:\underset{O}{\overset{O}{S}}:CH_2CH(NH_2)COOH$$

cysteine (toxic) cysteinic acid (nontoxic)

Catalysts poisoned by nonmetallic organic compounds could be detoxicated by treating the poisoned catalyst with perphosphoric acid, permolybdic acid, pertungstic acid, etc. [36, pp. 137/53].

The poisoning of platinum catalysts by metals was dependent on the structure of the d orbitals. The following table summarises the toxicity of metallic ions [36].

Organic poisons of the type investigated by Maxted may be introduced to the catalyst as inadvertant impurities in the reactant stream [38] or as deliberate additions to control the selectivity of the catalyst [39 to 42]. Recent work has tended to concentrate on the surface aspects of poisoning and in particular on the chemical state of the poisoned surface [43, 44].

The formation of poison molecules during reaction has two aspects, that of poisoning by the reactant molecule or its reaction products. Any substance which has unshielded electron pairs and which is desired, for example, to hydrogenate will act as a catalyst poison causing the rate of reaction to be very low indeed. Nitrogen and sulphur heterocyclics such as pyridine and thiophene, alkyldisulphides and sulphides, and alkylamines all tend to be very toxic to platinum-group metal catalysts and render the reduction of other substituent groups very slow [45]. Examining the hydrogenation of pyridine, a potent platinum-group metal poison, to piperidine, an even more toxic material, it was found that, by conducting the reduction in acidic media, shielded structures could be formed for both the reactant and product, allowing hydrogenation to proceed rapidly [36, p. 135].

metal ions tested					electronic occupation of external orbitals								toxicity towards platinum
Li^+	Be^{2+}	—	—	—	no d shell								nontoxic
Na^+	Mg^{2+}	Al^{3+}	—	—	no internal d shell								nontoxic
K^+	Ca^{2+}	—	—	—	3d	○	○	○	○	○	4s	○	nontoxic
Rb^+	Sr^{2+}	—	Zr^{4+}	—	4d	○	○	○	○	○	5s	○	nontoxic
Cs^+	Ba^{2+}	La^{3+}	—	—	5d	○	○	○	○	○	6s	○	nontoxic
—	—	Ce^{3+}	—	—	—	—	—	—	—	—	—	—	—
—	—	—	Th^{4+}	—	6d	○	○	○	○	○	7s	○	nontoxic
Cu^+	Zn^{2+}	—	—	—	3d	:⃝	:⃝	:⃝	:⃝	:⃝	4s	○	toxic
Cu^{2+}	—	—	—	—	3d	:⃝	:⃝	:⃝	:⃝	⊙	4s	○	toxic
Ag^+	Cd^{2+}	In^{3+}	—	—	4d	:⃝	:⃝	:⃝	:⃝	:⃝	5s	○	toxic
—	—	—	Sn^{2+}	—	4d	:⃝	:⃝	:⃝	:⃝	:⃝	5s	:⃝	toxic
Au^+	Hg^{2+}	—	—	—	5d	:⃝	:⃝	:⃝	:⃝	:⃝	6s	○	toxic
—	Hg^+	—	—	—	5d	:⃝	:⃝	:⃝	:⃝	:⃝	6s	⊙	toxic
—	—	Tl^+	Pb^{2+}	Bi^{3+}	5d	:⃝	:⃝	:⃝	:⃝	:⃝	6s	:⃝	toxic
Cr^{2+}	—	—	—	—	3d	⊙	⊙	⊙	⊙	○	4s	○	nontoxic
Cr^{3+}	—	—	—	—	3d	⊙	⊙	⊙	○	○	4s	○	nontoxic
Mn^{2+}	—	—	—	—	3d	⊙	⊙	⊙	⊙	⊙	4s	○	toxic
Fe^{2+}	—	—	—	—	3d	:⃝	⊙	⊙	⊙	⊙	4s	○	toxic
Co^{2+}	—	—	—	—	3d	:⃝	:⃝	⊙	⊙	⊙	4s	○	toxic
Ni^{2+}	—	—	—	—	3d	:⃝	:⃝	:⃝	⊙	⊙	4s	○	toxic

This procedure has become standard practice with toxic nitrogenous substrates, but is not open to use with sulphur containing materials. Indeed, many shielded sulphur compounds such as sulphoxides and sulphones, on hydrogenation yield highly toxic mercaptans [45].

The deactivation of catalysts by carbonaceous overlayers has been an important aspect of petroleum refining since catalysts were first used [46]. The formation of coke deposits occurs on both the acid cracking catalysts and platinum reforming catalysts. With dual function catalysts, platinum on acid treated alumina, coke can form on both functional sites. The formation of carbonaceous overlayers on acid catalysts was reviewed in [37, pp. 286/313]. The mechanism of carbonaceous overlayer formation on platinum has been ascribed to formation of partially dehydrogenated hydrocarbon species [47, 48]. Regeneration of coked catalysts has been reviewed in [37, pp. 348/81] for acid catalysts.

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The Catalyst in Development. The function of catalyst development is to ensure that the desirable features of stability for high activity and selectivity and long life are achieved in the commercial catalyst. This requires the correct choice of catalyst and of support, adequate design of the catalyst, and the eventual scale up of the catalyst for production. The choice of catalyst has been the subject of much literature, e.g. [1 to 7] which form the basis of the rest of this review. Besides the obvious metal catalytic component, choice of catalyst embraces also the economics of using the catalyst [8]. The high price of platinum metals (see table on p. 114) requires that the metal or compound be utilised to the full and that it is completely recovered after use. This will usually mean that the concentration of platinum-group metal in the reactor contents is in ppm and that the catalyst will be in a supported form.

Recent prices for platinum-group metals (in dollars):

metal	metal per troy oz	catalyst[*)] per kg
platinum	370	619
palladium	132	228
rhodium	820	1358
ruthenium	65	163
osmium	225	—

[*)] 5% on carbon-supported catalyst in 100 kg quantity, direct sale [9].

The design of catalysts is becoming more and more the main preoccupation of industrial catalyst chemists [7, 10]. The ability to modify catalysts logically has come about because of substantial progress in the development of techniques for the characterisation of catalysts and the willingness of industrial catalyst chemists to adapt them to the examination of real catalyst systems in operation [11]. Physical techniques may be applied to the four stages that make up an industrial catalytic process, namely process design, catalyst production and scale up and process trouble shooting [12, 13]. Other papers in [13] of interest to industrial catalyst designers are "The Characterisation of Industrial Catalysts with ESCA" (T. Edmonds, pp. 30/54), "The Application of Catalyst Characterisation to Problems arising in the Development of Catalysts" (R. J. Sampson, pp. 76/88) and "Catalyst Characterisation by Temperature and Voltage Programming" (B. D. McNicol, pp. 135/68).

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The Catalyst in a Process. Process design is obviously related to catalyst design. The major feature of catalyst design is the utilisation of metal and support chemistry to vary dispersion, distribution and chemistry of the catalytic centres. While process design and development is concerned with making use of reaction chemistry, reactor operation, and catalyst design to maximise the amount of product formed by suppressing side reactions. At the heart of any process is the reactor and it is the interaction of reactor operation and catalyst design which determines the course of the reaction chemistry.

Reactors come in all shapes and sizes and it is probably true to say that no two reactors are the same, although broad categories of reactor can be distinguished. Reactors may be classified, for example, according to the number of phases present (see table below).

phases	reactor type	method of surface area generation
gas-liquid	agitated vessel	impeller dispersion
	bubble column	bubble formation
liquid-liquid	spray reactors	droplet formation
	tray column	bubbles/drops at orifices
gas-solid	metal gauze beds, fitted bed, tubular fluidised bed	physical structure of catalyst mass, with gas-solid velocity difference
gas-liquid-solid	trickle bed	physical structure of catalyst
	agitated vessel	impeller dispersion

A broad examination of reactor technology has been given for a number of reactor types including batch reactors, continuous stirred tank reactors, thermal tubular reactors and fluid bed reactors [2]. The symbiosis between catalyst and reactor (automobile engine) has been examined by [3], while electrocatalytic reactors for both inorganic and organic reactants have been dealt with by [4, 5]. A dual temperature reactor for the enrichment of heavy water has been discussed by [6]. For a kinetic model for a slurry hydrogenator, see [7], the operating principles and results obtained with a loop reactor were described by [8]. Trickle column reactors for liquid phase continuous reactions were reviewed by [9].

With multiphase reactors it is essential that the phases be brought into intimate contact to enable transfer of reactants and products across the phase boundary. This requires the generation of the maximum interfacial area of contact. The generation of this area has been considered by [10, 11].

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The Regeneration and Recovery of Catalysts. The aim of regeneration and recovery is to recycle the active platinum catalyst metal centres. This requires that the catalyst is not chemically attacked by the reactants, that the catalyst particles can be separated from the product by a simple unit process such as filtration or centrifugation or that the catalyst activity can be regenerated in situ. The conditions under which palladium can be leached from palladium-carbon catalysts during hydrogenation of dinitrotoluene, a polyurethane intermediate, are described by [1]. The separation of catalyst from the product by filtration or centrifugation are standard processes, but one which is limited by the size of the pores in filter medium. Most powder catalysts for instance have particle sizes between 1 and 50 μ. However, fines generated during use can give particles of less than 1 μ, which will pass most filters. The addition of filter aids, such as Kieselgur, can help retain fines, but they cannot be used where it is intended to re-use the catalyst, and they can increase the platinum metal recovery charges. All of these operations are considered by [2] in a paper concerned with catalyst handling.

The methods used to recover the platinum from the support are in general proprietary secrets, but it is general knowledge that carbon-supported catalysts are recovered by burning the carbon, leaving a metal residue which is refined by standard procedures. Such procedures of catalyst recovery as have been published use aqua regia or sulphuric acid leaching. In the case of aqua regia the platinum metal dissolves leaving an insoluble support sludge, while with sulphuric acid the support (alumina) is dissolved leaving an insoluble metal residue. In the former case the support sludge is useless and its disposal forms a debit charge on the process, while with the latter a saleable product results (alum) giving a credit charge [3]. It has been estimated that platinum metal catalysts used in organic synthesis processes are recycled between 2 and 6 times per annum and that the cost of restoring the catalyst is close to 10 $ per lb for palladium catalysts and 6.5 $ per lb for platinum catalysts (USA 1978). Unsupported catalysts usually require little more than filtration from the process liquors, where this is necessary, and dissolution in aqua regia [4].

The regeneration of catalyst activity by the addition of fresh catalyst to the partially deactivated recycle catalyst is widely practiced with liquid phase reactions in the intermediates, fine chemicals and food industries. The petroleum industry, however, regenerates catalytic activity by the controlled oxidation of the carbonaceous deposits. For kinetics of controlled oxidative regeneration of coked catalysts, see [5]. Redispersion of the platinum metal by oxidation is also practiced [6].

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Catalyst Consumption. The collection of statistics on catalyst consumption in the developed world is not official policy in any country except Japan [4], and it is difficult to arrive at accurate assessments of world usage. Occasionally proprietary estimates are published. However, there is usually very little or no indication of how the estimates were arrived at, so that assessment of the accuracy of the data is not possible. An assessment of World Catalyst Sales for 1982 compiled by Chemical Hitech. Inc. is shown in Table 1, p. 117, it indicates total sales of all catalysts as $ 2.3 billion. Future growth of catalyst sales is forecast to increase at 5% per annum to 1990 giving a total world consumption of $ 4.3 billion in that year [1].

Figures for the United States consumption of catalysts are estimated and published by the technical press on a fairly regular basis [3 to 8], and these together with information on the major application of catalysis within the petroleum, petrochemical and chemical industries enable a broad brush picture of catalyst consumption in that country to be built up.

Table 2 indicates the major applications for catalysts in the USA during 1978, while Table 3, p. 118, shows the growth of catalyst sales for selected years from 1963 to 1980 with a forecast for 1986.

Table 1

Estimated Sales of Catalysts Worldwide in 1982 [1].

application	process	catalyst value $\times 10^6$ \$	percent of total value
petroleum refining	cracking	375.97	16.1
	reforming	153.90	6.6
	alkylation	141.19	6.1
	hydroprocessing	74.70	3.2
	hydrocracking	33.60	1.4
	polymerisation	5.50	0.2
	hydrogen production	4.14	0.2
chemical/petrochemical	polymerisation	461.40	9.5
	organic synthesis	279.78	12.0
	oxidation	158.65	6.8
	hydrogenation	75.93	3.2
	ammonia/methanol	61.03	2.6
	dehydrogenation	12.25	0.5
	synthesis gas	11.99	0.5
	others	131.50	5.6
captive consumption		354.09	15.2

Table 2

Major Applications of Catalysis in USA During 1978.

application	catalysts	production capacity $\times 10^6$ t	catalyst value $\times 10^6$ \$
petroleum refining	Pt, Pd, Ir, Re, Cr, Al, Co, Mo, W, Mo, H_2SO_4, HF	434 [2]	364 [2]
fertilizers	Pt, Pd, Rh, Fe, Ni, Cr, Cu, Zn	27 [2]	44 [3]
bulk chemicals	V, Bi, Mo, Ag, Cu, Ni, Pd, Rh, Fe, Co	65 [2]	43 [3]
plastics/resins etc.	Cr, Fe, Al, Ti, Sn, organic initiators	18 [3]	116 [3]
fine chemicals	Pt, Pd, Rh, Ru, Ni, Cu	—	90 [3]
fats & oils	Ni, Cu	28 [3]	24 [3]
pollution control	Pt, Pd, Rh	—	230 [4]
total			911

References to sources for the table are given in brackets.

Table 3

United States Catalyst Market 1963 to 1986 (sales in dollars).

application	1963	1972	1978	1980	1986
petroleum refining and pollution control	105 [7]	168 [5]	594 [3]	1002 [9]	1202 [9]
chemicals etc.	90 [8]	180 [6]	317 [4]	356 [9]	446 [9]
total	195	348	911	1358	1648
corrected to 1980 $*)	675	956	1147	1358	1648

References in brackets.

*) Inflation factors taken from Nelson Refinery Inflation Index published in Oil and Gas Journal, first issue of each month.

To enable a more accurate impression of catalyst sales to be made the figures are also shown in Table 3 corrected for inflation to 1980 values. On this basis the United States has experienced an approximate doubling of catalyst sales in the seventeen years from 1963 to 1980 and if the prediction is accurate will experience a growth of catalyst business of about two and one half times over the period 1963 to 1986.

As indicated in Table 2 platinum metal catalysts are used in all areas of catalyst application except those of plastics/resins and fats and oils. Some areas such as pollution control are almost exclusively the preserve of platinum metal catalysts.

The consumption of platinum metals in catalytic applications in the USA in 1977 to 1978 is shown in Table 4 by application, and Table 5 annually from 1976 to 1982. The value of platinum metal catalyst sales are given in Table 6 for the United States. These figures allow an estimate of platinum metal catalyst sales as a percentage of total catalyst sales to be made for the years 1963, 1972 and 1978.

1963	1972	1978
~12%	~18%	~40%

Platinum metal catalysts are, however, only one of the growing uses of platinum in industry, a subject which has been reviewed by [12], and from whose article Table 7, of the estimated annual consumption of platinum metals by all industries in the USA for the period 1979 to 1983, is reproduced.

Table 4

Consumption of Platinum Metals in Catalyst Applications for USA in 1977 to 1978 [3, 4, 10, 11].

application	Pt	Pd	Ru	Rh	Ir	Os
			(oz troy $\times 10^3$)			
petroleum refining	108	19	—	—	5.1	—
fertilizers	58	1	—	5.5	—	—
bulk chemicals	74	17	—	—	—	—
fine chemicals	18	128	12	15	5.1	0.2
pollution control	598	199	—	36	—	—

Table 5

Consumption of Platinum Metals for Catalysts in the United States in 1976 to 1990 (× 10^3 oz troy) [9, 10].

	1976	1977	1978	1979	1980	1981	1982*)	1986**)	1990**)
Pt	624	513	856	1072	780	613	478	1037	1122
Pd	329	295	364	447	319	240	223	370	420
Rh	—	21	—	—	—	39	—	85	89
Ir	—	10	—	—	—	3	—	16	18
Ru	—	12	—	—	—	54	—	29	34
Os	—	0.2	—	—	—	0.4	—	1.5	1.7

*) Estimated consumption. – **) Predictions made in 1978 based on 1977 consumption [10].

Table 6

Value of Platinum Metal Catalyst Sales in the United States (× 10^6 $) [3 to 8].

	1963	1972	1978
automobile pollution control	—	—	230
catalytic cracking	—	—	10
catalytic reforming	20	30	27
hydrocracking	—	6	12
gas purification	1	0.1	—
ammonia oxidation	2.5	9.7	17
organic synthesis	—	—	57
total	23.5	45.8	353

Table 7

Estimated Annual Consumption in the USA, 1979 to 1983.

application	ounces troy			
	platinum	palladium	rhodium	ruthenium
emission control catalysts for vehicles	750000	170000	36000	—
catalysts for chemical processing	130000	240000	18000	22000
electrical and electronic uses	127000	356000	15000	43000
jewellery	100000	18000	6000	6000
glass and glass fibre manufacture	70000	—	16000	—
catalysts for ammonia oxidation	56000	1000	5000	—

Table 7 (continued)

application	ounces troy platinum	 palladium	 rhodium	 ruthenium
dental and medical applications	34000	125000	—	—
catalysts for petroleum processing	25000	8700	600	150
fuel cells	16000	—	—	—

According to this data, 75% of the platinum used by industry is consumed by catalysis; 46% of palladium, 62% of rhodium and 31% of ruthenium is similarly used.

The mining and refining of platinum metals to supply these industrial needs are regularly reviewed in Platinum Metals Review [13 to 22], while platinum metal availability supply and demand patterns are reviewed, but less frequently [10, 11, 23, 24, 25].

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4.2 The Unsupported Metals and Metal Alloys

The unsupported metals and metal alloys are used in a wide variety of forms for both laboratory studies and industrial catalysis. Laboratory catalysts include single crystals, metal films, wire and foil, which form a group of clean surface catalysts, and colloidal metals, metal blacks, and metal powders in which the surface is variously contaminated by the reaction products formed during manufacture. Which form of clean metal surface is selected for laboratory work depends on the topic being studied. Only three metal forms have had significant use as industrial catalysts, metal blacks as hydrogenation catalysts, compacted metal powders in fuel cell electrodes, electrolysers, etc. and metal gauzes for high-temperature oxidation reactions such as nitric acid manufacture. The most extensive review of laboratory unsupported metallic catalysts is by [19], who discuss preparation, properties, nucleation and sintering of a wide range of unsupported catalysts.

Single Crystal Catalysts. Single crystals may be prepared to give preferred crystal planes on the surface. Data is given in [1] to the structure of ideal surface planes of metals of body-centred cubic, face-centred cubic and hexagonal close-packed structures out to the second order, and an appendix lists the crystal structures, lattice constants, and nearest neighbour distances for the six platinum-group metals.

Prepared single crystal surfaces contain at the monatomic level steps, terraces, kinks and vacancies, each of different catalytic properties. Steps and kinks of greater than monatomic dimensions undoubtedly occur, but in lower concentration. The influence of crystal face in catalysis was reviewed by [2], the clean single crystal surface approach to surface reactions six years later by [3]. Work to 1980 on reaction kinetics and mechanism on metal single crystal surfaces was summarised by [4] and [5] has recently reviewed his work on the catalytic properties of platinum-group metal single crystal surfaces. Heats of chemisorption of O_2, H_2, CO, CO_2 and N_2 on single crystal surfaces in comparison with polycrystalline films were listed by [8].

Metal Films. Metal films for catalytic purposes may be either continuous or discontinuous. In the latter the metal forms "islands" dispersed on the support, and if the metal concentration approximates to a monolayer, then the metal crystallites will be small enough to resemble traditional supported metal catalysts, but with very clean metal surfaces [1]. Films of up to 50 nm in thickness are usually discontinuous, and even up to 100 nm some discontinuity may be apparent. Above 100 nm the film is usually continuous, and approximate to massive metal surfaces in that the form and structure is similar to metal foils of the same thickness. The crystal structure of the film may vary between a perfectly epitaxed single crystal film and a polycrystalline randomly orientated film. The type of structure obtained will depend on the nature of the metal and support surfaces, as well as the preparation variables, such as support temperature, deposition rate, and impurity levels in both the metal and the vacuum system. Alloy polycrystalline films have been prepared for catalytic work; their preparation and properties have been reviewed by [6, 7], and their use as research catalyst surfaces was proposed. Selectivity effects for alloys in cracking-isomerisation, hydrogenation of C–O bonds and C–N bonds and oxidation of ethylene over PGM-group IB alloys were summarised by [9]. Heats of absorption of O_2, H_2, CO, CO_2 and N_2 on polycrystalline metal films have been tabulated by [8] for the individual platinum metals, and [10] have reviewed the chemisorption of CO, O_2 and H_2 on palladium-silver and palladium-gold alloys. Catalytic reactions on PGM alloys have been reviewed by [10] (palladium-silver and palladium-gold alloys and a series of hydrogen reactions), and by [11] for isotope exchange and desorption over platinum-gold films. The structure of alloy catalysts and the effect of structure on alkane hydrogenolysis and carbon monoxide hydrogenation have been reviewed by [17].

Foil, Wire and Ribbon. These forms are normally reserved for alloy work. Foils have been used extensively for electrochemical work, particularly the establishment of the surface composition under electrochemical conditions [1].

Cleaning the surface of wires, foils and ribbons is a difficult process. Hydrogen reduction at temperatures up to 350°C or argon ion bombardment can give rise to changes in the surface composition of alloys, while the use of high frequency discharge does not give an atomically clean surface.

Cold worked foils have been used to determine the effect of dislocations on catalytic reactivity [12]. The reactivity of hydrogen on palladium hydride phases was reviewed by [13], the hydrogen-oxygen reaction over Pt wires by [18].

According to [14] very thin platinum and platinum alloy foils have been proposed as industrial catalysts for ammonia oxidation. That they have not been used industrially is due to the superior robustness and higher space velocities which can be achieved with wire gauzes.

Metal Powders. The only satisfactory way to prepare clean metal powder surfaces is to crush metal crystals under high vacuum conditions [15]. Chemisorption complexes formed by CO and ethylene on clean platinum-tin alloys have been reviewed by [11].

Chemically reduced metal blacks do not have clean surfaces, but do provide high area metal and metal alloy surfaces suitable for chemisorption and catalytic studies comparable to those found in industrial catalysts. The chemisorption of CO, O_2 and H_2, the methane-deuterium exchange reaction, benzene hydrogenation and nitrobenzene reduction over chemically reduced palladium-gold and palladium-silver alloys was reviewed by [10]. Such work forms a bridge between the studies on clean highly characterised surfaces in ultrahigh vacuum and the dirty surfaces of industrial catalysts discussed in Sections 4.2.1 and 4.2.2 below.

Colloidal Metals. Platinum and palladium metal colloids have had a long history as laboratory catalysts, but today they are considered obsolete even for laboratory use. They were usually stabilised in aqueous media, although this was not essential and other liquid media have been used. The colloidal particles are 10^2 to 10^3 nm in diameter. When prepared without stabiliser the metal particles carry a negative charge and are prone to coagulation in the presence of electrolytes, particularly polyvalent ions.

Typical stabilisers are gelatin, polysaccharides or soluble synthetic polymers such as polyvinyl alcohol. Unstabilised metal sols may be prepared in concentrations up to 0.1 wt%, while stabilised sols of up to 50 wt% are known.

The advent of synthetic polymer stabilisers has allowed the preparation of sols in alcoholic and other media. All the early work on colloidal platinum-group metals was reviewed by [14], that on synthetic polymer-stabilised PGM colloids by [16].

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4.2.1 Preparation and Physical Properties of Industrial Unsupported Metal and Metal Alloy Catalysts

The physical form of the catalyst in each of the three industrial applications is different and arises from the needs of the application.

With ammonia oxidation the very high space velocity (contact time 10^{-3} to 10^{-4} s) and elevated temperature (875 to 925°C), requires a form of catalyst which offers minimum resistance to gas flow, but which is mechanically strong at high temperatures in oxidising atmospheres. Platinum metal gauzes are ideally suited to such an environment [1 to 8].

The electrochemical applications require high metal area permeable structures in the case of fuel cell electrodes [9 to 12], solid impermeable metal structures with or without a coating of finely divided platinum metal on the surface for electro-organic catalysts [13], water electrolysis [14, 15, 16] and electrodes for chlorine manufacture [17, 18].

Finely divided platinum-group metal blacks for pharmaceutical and fine chemical use must be highly active to be cost effective. However, the catalyst must be separable from the product, and as high catalytic activity arises from small particle size, some limit on the degree of dispersion must be placed on the metal black. This usually means using metal particles above 100 Å size, although in systems in which the metal aggregates during reaction smaller particle sizes can be tolerated [19, 20].

As a consequence of the physical form, each category of unsupported catalyst is manufactured in a different way. Ammonia oxidation gauzes are manufactured from wire by weaving techniques adapted from textile weaving. Metal blacks are on the whole made by chemical reduction of platinum metal salts usually in aqueous media, although some users of metal blacks prefer to produce the black in situ in the reaction medium by reduction of the metal oxides with hydrogen. This can frequently give higher catalyst activity and, because of the relative inertness of the oxides, it is safer to load a reactor with inflammable organics and metal oxide than with highly active metal black catalyst [20].

Metal electrodes can be smooth or coated. Smooth electrodes are constructed from the metal foil, sheet or in rare cases from metal gauze. Coated electrodes are manufactured by coating platinum metal or base metal foil, sheet or gauze electrode support structures with finely divided platinum metal. Two methods of coating are practiced, firstly electroplating platinum metal blacks from suitable baths and secondly by physically pressing a mixture of a preformed platinum metal black with a suitable binder, such as PTFE, onto the electrode support. The following sections discuss each of the methods outlined above in greater detail.

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4.2.1.1 Preparation of Metal Blacks

Basically four methods of making metal powders and blacks have been used: (1) Thermal decomposition of salts; (2) hydrogen reduction of oxides and hydroxides; (3) reduction of aqueous and nonaqueous solutions of metal salts with a reducing agent such as formaldehyde; (4) skeletal catalysts such as Raney metals. Each of the methods of preparation will be considered below for the metal blacks and metal alloy blacks, together with the physical properties (hydrogen chemisorption, crystallite size, etc.) and chemical properties (surface chemistry, alloy component, segregation, etc.). Historically, thermal decomposition was the first method of manufacturing platinum metal blacks and was used from the time of Davy and Döbereiner until fairly recently, when it was displaced by methods giving greater metal dispersion derived from oxide and salt reductions. Thermal decomposition is still practised for manufacturing supported catalysts. Skeletal catalysts made their entry to the field relatively late and have not been commercially successful as a means of manufacturing platinum metal blacks. However, their base metal counterparts nickel, cobalt and silver have been, and still are widely used industrially, and the potential for some of the newer (and cheaper) methods of preparing skeletal platinum catalysts for low volume, high margin products are good.

S. C. Davis, K. J. Klabunde (Chem. Rev. **82** [1982] 153/208).

Thermal Decomposition of Salts

Finely divided platinum-group metals may be prepared in catalytically active forms by igniting the ammonium chloro salts in hydrogen [1 to 4]. Ruthenium carbonyl has been decomposed thermally to give catalytic ruthenium powder [5], while [6] prefer ignition of the nitrate, oxalates, etc. at as low a temperature as is practical in order to obtain as high a metal surface area as is possible. The ignition of oxalates, nitrates, etc. is also mentioned [7]. Thermally produced catalysts in an unsupported form are no longer industrially important, indeed they declined in popularity in the first decades of this century when methods for producing much higher surface area material became available. During their short industrial career, however, they gave rise to several important catalytic processes such as sulphuric acid (platinum), ammonia synthesis (osmium) and nitric acid production (platinum).

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Hydrogen Reduction of Oxides and Hydroxides

The hydrogen reduction of oxides and hydroxides has long been practised as a means of producing highly active platinum metal catalysts. The activity of the metal black catalysts is dependent, firstly on the precise manner of manufacture of the hydroxide/oxide, and secondly on the conditions under which the hydroxide/oxide is reduced. For the purposes of this section the method of oxide preparation will be divided into (1) precipitated hydroxides (hydrated oxides) and (2) oxides produced by thermal fusion of a platinum metal salt with molten sodium nitrate (Adams platinum metal oxides). The finer points of hydroxide and oxide preparation will be discussed in Section 4.4.1.1.

Invariably the precipitated hydroxide/oxide preparations are reduced with hydrogen, although other reducing agents have occasionally been used. The reduction is carried out with the hydroxide suspended in water, through which hydrogen gas is passed. Dispersion of the hydrogen as fine bubbles is achieved by injecting it into the solution through a glass sinter. When the hydroxide has reduced, it is washed free of chloride or nitrate and the suspension carefully filtered. Drying is always at ambient temperature, sometimes in vacuo [1]. The same method has been used to pre-reduce Adams platinum metal oxides [2]. The detailed process of nucleation and particle growth during oxide reduction has been reviewed by [9].

One major problem with this method of preparation is that the metal black may absorb large quantities of hydrogen which oxidises during drying and can cause loss of surface area. This disadvantage may be overcome by carrying out the hydrogen reduction in situ in the reactor, and many believe that this results in a more active catalyst. In situ reduction has become the standard way of using Adams platinum metal oxides in organic hydrogenations, although it is known that hydrogen at atmospheric pressure will only reduce platinum and palladium oxides fully to the metal [2, 3]. Rhodium, iridium and ruthenium are partially reduced to the metal, elevated temperature (80 to 100°C) [4] or elevated pressure [5] being required for full reduction.

Stabilisation of pre-reduced platinum black has been achieved by [6], who after reducing the oxide, washed it with water, dried in vacuo and treated the resulting black with carbon dioxide.

Platinum oxides and blacks are still widely used as catalysts particularly where the compound is difficult to reduce, the product is likely to be absorbed by the support or the product poisons the catalyst [7]. Platinum metal blacks have also been employed as anode and cathode electrode catalysts for fuel cells, particularly in the USSR [8].

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Reduction of Aqueous Solutions of Metal Salts

Platinum-group metal salts in aqueous solution when treated with reducing agents such as formaldehyde, sodium formate, hydrazine, etc., precipitate a finely divided form of the metal. Most often the reduction is carried out in alkaline solution, although acidic reductions are not unknown. For methods of preparation up to 1920, see [1], for those to 1939, see [2, 3].

Loew [1, 4] manufactured platinum black by allowing a mixed solution of sodium hydroxide, chloroplatinic acid and formaldehyde to stand at room temperature for 12 h. Willstätter [5] modified Loew's method and extended its use to palladium [4]. Reduction of the metal solution by formaldehyde was conducted at 55 to 60°C, and potassium hydroxide was used, in place of the sodium hydroxide of Loew's method, to give an improved product. Detailed preparations of both platinum and palladium blacks are given by [4]. Further modifications have been introduced by [6] to reduce the tendency of the black to become colloidal during the washing step. Ruthenium black was prepared by the Willstätter method [7]. Ammoniacal palladous chloride was treated with formaldehyde and sodium hydroxide [8]. This method was used to prepare ruthenium blacks while investigating the effect of the method of preparation on the properties of the resulting black. It was concluded that the ruthenium salt chosen as starting material affected the dispersion of the black when measured by hydrogen absorption, and that the ruthenium black is a mixture of the metal and the oxide. The oxide content of the black can be reduced to zero at 580°C and 1 atm hydrogen, but the surface is reoxidised as soon as the metal is exposed to oxygen or air, and the water formed during reduction clings tenanciously to the metal surface even at 520°C [9]. Other reducing agents which have been used to prepare experimental platinum metal blacks include alcohols, ethers and esters [10], potassium in liquid ammonia (platinum [11] and iridium [12]), tribenzylsilane [13], sodium naphthalide [14 to 17] and sodium borohydride [18, 19, 20]. The latter reducing agent is believed to give, at least in part, a boride of the metal reduced from solution [20, 21]. All of the platinum metals may be prepared as blacks using sodium borohydride [18, 23], and this reagent is one of the most popular for the preparation of alloys from aqueous solutions of platinum-group metal chlorides or platinum-group metal-base metal chlorides. Ruthenium-palladium and ruthenium-platinum alloys [19, 22], and platinum-palladium, platinum-ruthenium, platinum-rhodium, platinum-iridium and palladium-gold alloys [23] were prepared by this method. When this method of manufacturing palladium-gold alloys was used, it was essential to add the mixed palladium and gold chlorides solution rapidly to a solution of sodium borohydride in sodium hydroxide. If slow addition of sodium borohydride to the mixed metal chlorides solution was tried, then the gold precipitated first [24]. In preparing palladium-gold and palladium-silver alloys, precipitation with hydrazine appears to be more effective in producing alloys than using sodium borohydride [25]. Binary and ternary intermetallic compounds can be formed by hydrazine or hypophosphorous acid reduction of stoichiometric quantities of the metal chlorides in aqueous solution [26].

A considerable amount of work has been undertaken by research workers in Eastern European countries into the effect of preparing platinum metal blacks in ultrasonic fields [27 to 30]. The effects of ultrasonic fields on inorganic chemical reactions were reviewed up to 1961. Regarding the effects of ultrasonics on the decomposition of chlorauric acid in aqueous solution to a gold sol, it was proposed that water is split by the ultrasonic field into $H+OH$. If oxygen is present in the solution the following reactions will ensue: $H+O_2 \rightarrow HO_2$; $HO_2+H \rightarrow 2OH$, and in the presence of a reducing agent $OH+e^- \rightarrow OH^-$ [27].

However, [28, 29] disagreed with the proposed mechanism and obtained reduction of chloroplatinic acid to platinum black without an ultrasonic field. He agreed with [27] that platinum black formed in an ultrasonic field is catalytically more active. Both authors studied the effect of chloroplatinic acid concentration on the catalytic activity of the platinum black so formed and concluded that it is only more active than normal blacks when it is precipitated from dilute solutions [27, 28, 29]. When the ultrasound reduction is conducted in the presence of the substrate the catalytic activity of palladium black is enhanced with respect to palladium blacks formed in an ultrasound field in the absence of substrate [30].

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Raney and Urushibara Skeletal Catalysts

Raney and Urushibara catalysts have been prepared predominantly as base metal catalysts, in particular as nickel catalysts, with wide applications in the fine chemicals, chemical intermediates and food industries. According to [1] the USA market for Raney nickel catalysts in 1978 was 1.5×10^6 lbs worth \$ 7.5×10^6.

Very little work on the corresponding platinum-group metal catalysts has been undertaken in the West. However, both Eastern European and Japanese scientists have investigated, and indeed continue to investigate the properties of the six platinum metal analogues with interesting results.

The first skeletal catalyst was discovered by Raney in 1925 by leaching a nickel-aluminium alloy with aqueous sodium hydroxide [2]. General methods of preparing Raney catalysts of various transition metals based on the original method, using caustic soda, caustic potash, etc., and currently seven different procedures exist given the labels W1 to W7 [3, 4]. Detailed preparations have been given by [3, 5, 6, 7].

The catalytic properties of Raney metals are functions of the non-catalytic alloying metal (Al, Mg, Zn, Bi, Si, etc.), the alloy composition, the method of leaching, and post-preparative treatments.

Alloys of the platinum-group metals with aluminium [8 to 16], zinc [12, 14], magnesium [14] and bismuth [17] have been used to manufacture starting alloys with platinum [9, 12, 13, 16, 17], palladium [12], rhodium [11, 14], ruthenium [8, 10], iridium [15, 16], osmium [15] and iridium-osmium [15] and platinum-iridium [16] alloys. Alloy composition affects the type of metallurgical compound formed, whether intermetallic or eutectic [18], and through this the physical-catalytic properties of the Raney metal catalyst. The surface area of a series of rhodium catalysts prepared from rhodium-aluminium alloys whose composition ranged from 5 to 60% rhodium (Rh_2Al_9 in excess aluminium to Rh_2Al_3) varied from 77 m^2/g for the low rhodium content alloys to 106 m^2/g for the high rhodium alloys. The pore volume was halved with the high rhodium content alloys, while the particle size of the metal increased from 1 to 2 μm to 30 to 50 μm over the same composition range [14].

Methods of leaching the alloys are different depending on the non-catalytic metal used in the starting alloy. With aluminium either caustic soda or caustic potash is used, while with magnesium it is usual to employ a weak organic acid, such as acetic acid [14]. Strong mineral acids such as nitric acid [14] or hydrochloric acid [12], are used with zinc alloys. Use of alkaline leaching agents with magnesium alloys normally results in low activity catalysts, although acid washing can improve the activity of such material. Alkaline leaching has been used with zinc alloys [19] and such catalysts have been found to be non-pyrophoric, but very active in hydrogenation reactions cf. Urushibara catalysts. Post-leaching treatments usually consist of treating the catalyst in the alkaline leach liquors with organic acids to raise the pH to between 7 and 8 before filtration [20].

In 1951 Urushibara discovered a new method of skeletal catalyst preparation. He treated solutions of a transition metal chloride with finely divided zinc (zinc dust). Reaction between the transition metal chloride and the zinc resulted in the transition metal being precipitated from solution as a fine powder [21]: $NiCl_2 + Zn \rightarrow ZnCl_2 + Ni$.

Metals precipitated in this way are usually inactive in hydrogenation reactions, although active in other catalytic reactions [21, pp. 221/35]. The lack of activity in hydrogenation reactions is caused by basic zinc chloride which is precipitated with the catalytic metal and acts as a poison [21, p. 11]. This can be overcome by resorting to high temperatures (80 to 176°C) and high initial hydrogen pressures (50 to 100 atm) [21, pp. 235/9] or by digesting the precipitated transition metal with further alkali or acid to remove the zinc contaminant as a soluble zinc salt:

$$Zn(OH)Cl + 3OH' \rightarrow [ZnO_2]'' + Cl' + 2H_2O$$
$$Zn(OH)Cl + HCl \rightarrow ZnCl_2 + H_2O$$

Neither acid or alkali treatment completely removes zinc contamination and in this respect the Urushibara catalysts resemble their Raney analogues. As with Raney catalysts the residual zinc oxide acts to retard the sintering of the small crystallites and so maintains the catalyst surface area and activity [21, p. 17].

Metals other than zinc may be used to precipitate the transition metal from solution, such as aluminium, magnesium, etc., indeed any metal that is more electropositive, and interestingly the catalytic properties of the Urushibara catalyst are different according to the metal used to precipitate it. This is thought to be a function of the epitaxy forced on the catalytic metal by the crystal structure of the precipitating metal. For example, Urushibara nickel precipitated on zinc is non-pyrophoric [21, p. 15].

Urushibara catalysts have found their main industrial applications in the pharmaceutical industry [21, 22] principally in Japan. The bulk of catalysts used have been base metal catalysts. However, palladium, rhodium, platinum and iridium catalysts have been prepared by the Urushibara procedure with aluminium and magnesium as precipitating agents [23]. It is claimed that Urushibara catalysts have advantages over Raney catalysts in that they have the catalytic properties of Raney catalysts, but can be prepared by a simpler, shorter process, are not sensitive to the impurities present in commercial grade reagents or the city water supply, can be stored as dry powders for very long time without activity loss, can be handled easily and can be prepared with modified catalytic activity simply by changing the preparative procedure [21, pp. 20/2].

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Promoted Metal Blacks

Three methods of promoting metal blacks have been tried according to the published literature.

(1) The promotion of platinum black, made by the hydrogen reduction of Adams platinum oxide, with alkaline earth metals; (2) the promotion of Raney nickel catalysts with platinum-group metals either by reaction of the catalyst with an aqueous solution of platinum-group metal chlorides prior to its use in a hydrogenation or the addition of chloroplatinic acid to the catalyst-substrate mixture immediately before hydrogenation; (3) the preparation of a Raney nickel-aluminium alloy containing the platinum-group promoter metal.

Alkaline earth chlorides were added to suspensions of Adams platinum oxide in various solvents and reduced to platinum black by molecular hydrogen. The resulting catalysts contained very small quantities of alkaline earth metals and were used to hydrogenate potassium maleate solution. Beryllium- and barium-doped catalysts showed almost no enhancement of catalytic activity, but magnesium, calcium and strontium promoted the hydrogenation in the sequence $Sr^{2+} \approx Ca^{2+} < Mg^{2+}$ [1].

The promoting effect of platinum-group metals on hydrogenations with Raney nickel catalysts has been investigated by two groups of workers, French [2, 3] and American [4 to 7]. Raney nickel could be promoted by platinum-group metals if the catalyst was treated with an alkaline solution of the platinum-group metal chloride prior to its use in a hydrogenation. Such catalysts, promoted with platinum, palladium, rhodium, ruthenium, iridium or osmium were very active for the hydrogenation of methyl-ethyl ketone and ethyl-acetoacetate. When the Raney nickel was promoted by treating it with acidic solutions of the platinum-group metal chlorides only iridium and osmium were active promoters [2].

In contradiction to this it was found that the addition of acidic chloroplatinic acid to the catalyst (Raney nickel)-substrate mixture just prior to hydrogenation, enhanced the rate of hydrogenation of nitroguanidine, nitrobenzene, of carbon-carbon double bonds in castor oil and linseed oil, and benzaldehyde [4]. Subsequently it was discovered that alkali poisons the nitro group reduction over platinum-promoted Raney nickel, but enhances the reduction of ketonic groups over the same catalyst [5, 6].

Further work showed that a larger enhancement of catalyst activity could be obtained by washing the catalyst with water immediately after promotion with alkaline platinum chloride solution [3]. Using the Lieber-Smith method of promoting Raney nickel, it was shown that even W6 Raney nickel could be substantially improved as a hydrogenation catalyst by promoting it with very small quantities of platinum (7.3×10^{-2} mmol Pt per g Ni) [7].

Promotion of Raney nickel with palladium has been achieved by adding it to the nickel-aluminium melt. The ratio of nickel to palladium was 450:1 (0.2% palladium based on the nickel). The aluminium alloy was leached with sodium hydroxide and the palladium-promoted Raney nickel catalyst used to hydrogenate 4,4′-dinitrodiphenylether to 4,4′-diaminodiphenylether with 100% selectivity. The catalyst was able to operate continuously for 700 h (1 month) at a catalyst consumption rate of 0.4 to 0.5 g per kg product [8].

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Pseudo-organometallic or Solvated Metal Atom Dispersed (SMAD) Catalysts

This method of metal black manufacture is presently of academic interest only, but the technique employed, of higher vacuum metal evaporation, is of widespread industrial application in coating technology and the catalytic properties of the blacks are sufficiently different to hold out the possibility of eventual industrial application.

To prepare the blacks, metal atoms are evaporated under high vacuum ($<10^{-5}$ Torr) and mixed with a stream of organic substrate molecules. The two streams co-condense on the cold (-196°C) reactor walls. Here the metal atoms react with the organic substrate to form unstable solvated metal atoms or pseudo-organometallic complexes. Once deposition ceases the condensate is warmed, when decomposition of the metal atom adduct takes place and a slurry of a metal black in solvent is formed. Organic substrates such as pentane, toluene, benzene, tetrahydrofuran, etc., have been employed to form unstable solvated metal atom adducts [1].

The reactor designed for the preparation has been fully described [2, 3] while the theory and operation have been explained by [4]. Rotating reactor vessels for use with metal vapour reactions with solutions of solid or liquid substrates have been devised [5, 6] and a commercial reactor is made by G.V. Planar Ltd. In some cases where the intermediate adduct is temperature-stable it may be hydrolysed to the metal after removal from the reactor [7].

By appropriate use of various strength solvating agents, the metal blacks can be tailored to give varying degrees of activity and selectivity in hydrogenation, isomerisation and disproportionation catalysis [1, 8], and the technique has now been extended to allow manufacture of supported catalysts [9]. A large number of metals have been prepared as metal blacks by this process including nickel, platinum, and palladium [7, 9].

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Nascent Platinum Metal Blacks

If an aqueous solution of a platinum metal chloride, such as chloroplatinic acid, is treated with molecular hydrogen, reduction of the salt will take place, and as this has been known for a long time, a precipitated black will result. When platinum metal chloride reduction with molecular hydrogen takes place in the presence of the organic substrate molecule to be hydrogenated, a stage occurs which is not present when the reduction is conducted in the absence of the substrate. This stage takes the form of an aqueous sol of Pt^0 nuclei with exceptionally high catalytic activity, up to 50 times greater than that of the corresponding black precipitated in the absence of substrate [1]. The enhanced activity is not simply a function of greater catalyst surface area. These catalysts have been termed "nascent" platinum blacks [1, 2, 3].

The method of their manufacture is extremely simple. The calculated quantity of chloroplatinic acid and 0.001 mol of the unsaturated compound is dissolved in 20 ml water. This solution is agitated and molecular hydrogen passed through the solution at 50°C and atmospheric pressure. Nascent platinum black forms during the initial induction period prior to hydrogenation of the unsaturated compound. Examination of the solution during this induction period showed that it scattered light. Simultaneously with the hydrogenation of the substrate, precipitation of platinum black occurred. The activity of the "nascent" platinum black is dependent on the concentration of the platinum salt, and the type of organic substrate [1]. Platinum, palladium and rhodium have all been shown to exhibit this type of behaviour in both hydrogenation reactions [1, 2] and hydrogen peroxide decomposition [3].

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Physical Properties of Platinum-Group Metal Blacks

The Russians were the first to establish a relationship between the physical and the catalytic properties of metals [1], and Breskov [2] was the first to systematically investigate the relationship between catalytic activity and metal particle size (dispersion). Since then the advent of new methods of measuring the physical properties of catalysts has led to a better understanding of these relationships and, indeed, has helped in the designing of better catalysts [3].

The preparation, reactivity and characterisation of small metal particles including the stability, structure, sintering, magnetic and electronic properties of small metal particles were reviewed by [4]. In the catalytically important area of structure, attention is drawn to the preference, according to theoretical considerations, for small numbers of atoms (13 to 2000 atoms) to stabilise in the form of icosohedra because of the higher average atomic coordination number attainable in this structure. Some experimental evidence in support of this has been forthcoming [4, pp. 171/2].

The electronic properties of small metal particles has received a large amount of attention. Bonding in small particles is different to that for the bulk metal. For example, the atomic configuration of palladium is $4d^{10}\ 5s^0$ and in small particles bonding is due principally to the 5s orbitals, which overlap to produce stronger bonding molecular orbitals than can be obtained with the 4d molecular orbitals. This leads to a $4d^9\ 5s^1$ configuration for Pd_2, $4d^{9.4}\ 5s^{0.6}$ for Pd_8 to Pd_{10} and $4d^{9.6}\ 5s^{0.4}$ for the bulk metal. The effect of particle size changes on catalytic activity due to changes in electron configuration should, therefore, be negligible for any, but the smallest metal cluster ($<Pd_{10}$). However, it should be remembered that stepped, kinked and isolated atom sites, present in real metal particles, will show a variety of bonding orbitals that may well be related to changes in catalytic activity [4, pp. 174/5].

On a more practical note, the dispersion of metal particles is most frequently measured by either X-ray diffraction line broadening or by a gas sorption method. X-ray line broadening measurements of dispersion are usually quoted as crystallite sizes (diameter in Å), while gas sorption methods give dispersion as a surface (metal) area (in m^2 per g catalyst) or occasionally as an average particle diameter (in Å or nm). Thus, for example, the sintering of metal blacks may be presented as an increase in metal crystallite size or as a decrease in surface area [6].

The degree of dispersion to be expected for the platinum-group metals when formed into metal blacks, excluding skeletal catalysts which are considered later, are given in the following table.

method of preparation	metal	crystallite size (Å)	surface area (m^2/g cat.)	gas	Ref.
Willstätter	Pt	85	11.7 to 15.3	Kr	[7]
Willstätter	Pt	—	22.2 to 31.7	N_2	[8]
Zelinskii	Ru	—	65.3 to 78.5	N_2	[9]
			38.3 to 75.6	H_2	
Zelinskii	Pt	—	18.3	H_2	[10]
			19.2	N_2	
Zelinskii	Os	—	76.2	H_2	[11]
			75.2	N_2	
Frampton	Pt	—	12 to 19	H_2	[12]
			20	N_2	
Frampton	Pd	—	16 to 19	H_2	
			17	N_2	
Frampton	Pt	—	12	H_2	[10]
			12.7	N_2	
Frampton	Pt	—	20 to 50	N_2	[13]
$NaBH_4$	Pt	—	5.4	N_2	
	Ru	—	21.9 to 24.5	N_2	
$NaBH_4$	Pt	—	7 to 15	N_2	[12]
	Pd	—	23 to 32	N_2	
$Ca(BH_4)_2$	Pt	—	12 to 22	N_2	
	Pd	—	28 to 34	N_2	
N_2H_4	Pt	—	6 to 13	N_2	
	Pd	—	22 to 31	N_2	
$TiCl_2$	Pt	—	22	N_2	
	Pd	—	28	N_2	
$CeCl_3$	Pt	—	26	N_2	
	Pd	—	30	N_2	
$NaBH_4$	Pt	—	4.9	N_2	[25]
	Pd	—	14.3	N_2	
	Ir	—	57.3	N_2	
	Os	—	17.2	N_2	
	Rh	—	28.1	N_2	
	Ru	—	74.4	N_2	
Na naphthalide	Pd	30 to 60	—	—	[14]

Willstätter method: reduction with NaOH or KOH and HCHO; Zelinskii method: reduction with NH_4OH and HCHO; Frampton method: reduction of oxide with H_2.

Very rarely an investigator publishes details of the effect of variables, such as reactant concentration or temperature changes, on the dispersion and catalytic activity of the metal black. According to [15] the reduction of chloroplatinate ion (Pt^{IV}) with alkaline formaldehyde can take two courses depending on the reaction conditions: $PtCl_6^{2-} + 2HCHO + 6OH^- \rightarrow Pt + 2HCOO^- + 4H_2O + 6Cl^-$ and $PtCl_6^{2-} + HCHO + 6OH^- \rightarrow Pt + CO_3^{2-} + 4H_2O + 6Cl^-$. Adding the reductant (formaldehyde) to alkaline chloroplatinic acid solution always gave inactive low surface area blacks (2.5 to 6.9 m^2/g Pt), while addition of a chloroplatinic acid-formaldehyde mixture to the alkali gave a very active high area black (31.7 m^2/g Pt). Lowering the molar ratio of HCHO : Pt from 6 : 1 to 3 : 1 decreased the metal area from 22.2 to 25.2 m^2/g. Examination of the nucleation at pH = 9 showed that better control and reproducibility of the metal black crystallite size could be achieved if the nucleation of the platinum solution was separated from the growth phase. Consequently they carried out a preliminary nucleation stage at room temperature in sodium carbonate solution (pH = 9) for 10 min followed by a growth stage at pH > 12 in hot (90°C) sodium hydroxide (full preparation details are given in the original paper). No advantage to dispersion or catalytic activity could be detected from preparing the catalyst in an inert (nitrogen) atmosphere [8].

In a similar detailed examination, this time of ultrasonic vibration, on dispersion of metal blacks prepared by the Willstätter method, it was concluded that only a high frequency ultrasonic field affected the dispersion of palladium and platinum blacks during the preparation stage. The metal area of a platinum black increased from 11.7 m^2/g to 15.2 and 19.0 m^2/g after ultrasonic treatment with 548 and 3000 kHz [16].

Post-preparation treatment of platinum and palladium blacks formed in the absence of an ultrasonic field, with ultrasonics (20 to 3000 kHz) failed to give any improvement in either dispersion or catalytic activity [7].

All platinum-group metal blacks once exposed to air are covered with a layer of oxygen, in some cases, for example ruthenium black, it is a layer of oxide. Some methods of preparation produce a metal black containing substantial quantities of oxides, and because of both of these factors, it has become customary to hydrogen-reduce a metal black immediately prior to its use, particularly when measuring its physical properties. Hydrogen reduction of platinum-group metal blacks at elevated temperatures can result in a substantial loss of surface area. Thus, a platinum black heated at 300°C in hydrogen showed a decline in surface area from 18.3 to 1.6 m^2/g, while a ruthenium black reduced at temperatures >500°C in 20 Torr partial pressure of hydrogen suffered only moderate surface area loss from 75.6 to 66.5 m^2/g (see table below). Increasing either the reduction time or the hydrogen partial pressure has a far more disastrous effect on dispersion, than changes in reduction temperature [9, 10]. A contrary effect of hydrogen reduction on dispersion was found with an osmium black by increasing the temperature of hydrogen reduction from 200 to 300°C. This was ascribed to the reduction of oxides unreduced at 200°C. Further increase of reduction temperature to 400°C caused a loss of surface area due to sintering. Osmium black only severely sinters when adsorbed hydrogen is completely removed from the metal surface at 520°C. The results are to be found in the following table [9, 10, 11].

catalyst	time (h)	temp. (°C)	H_2 pressure (Torr)	surface area (m^2/g)
Pt	3	75	760	18.3
Pt	3	100	760	14.5
Pt	3	200	760	2.5
Pt	3	300	760	1.6
Ru I	0	—	—	75.6

catalyst	time (h)	temp. (°C)	H_2 pressure (Torr)	surface area (m^2/g)
Ru I	1	570	20	66.5
Ru I	1	600	60	64.9
Ru I	1	516	200	4.1
Ru I	6	580	20	1.7
Ru II	0	—	—	38.3
Ru II	1	510	20	33.0
Ru II	1	580	60	2.0
Ru II	1	580	200	2.4
Ru II	1	580	760	1.0
Os	—	200	470	64.5
Os	—	300	470	75.2
Os	—	400	470	30.9

Ru I and Ru II are two samples of ruthenium black.

From the adsorption of hydrogen on the surfaces of ruthenium [9] and osmium [11] blacks it was concluded that in both metals hydrogen exists in three forms. Weakly bonded α, which can be desorbed isothermally, strongly bonded β^1, which in the case of ruthenium desorbs between 500 and 600°C and between these two forms the moderately strongly bonded β form which desorbs from ruthenium surfaces between 30 and 360°C. The amount of each form for various reduction conditions are shown in the table below.

metal	conditions of catalyst treatment			forms of adsorbed H_2 %		
	time (h)	H_2 pressure (Torr)	temperature (°C)	α	β	β^1
Ru I	1	20	570	5	67	28
Ru I	1	60	600	5	69	26
Ru I	1	200	516	9	64	27
Ru I	6	20	580	7	81	12
Ru II	1	20	510	4	69	27
Ru II	1	60	580	5	31	64
Ru II	1	200	580	5	51	44
Ru II	1	760	580	27	47	26
Os	—	470	350	8	86	6

Ru I and II are two samples of ruthenium black.

Many platinum-group metal blacks will aggregate when treated with hydrogen or oxygen, particularly when suspended in aqueous media (see for example [8, p. 159]) and most retain this loose structure when dried. Commercial palladium blacks form loose relatively open-structured ensembles, and when these are treated with hydrogen at room temperature they aggregate more closely to form a single macroscopic aggregate. These macroscopic aggregates may be easily decomposed into smaller ensembles by either mechanical or ultrasonic vibrations. Co-ordination number typical of normally aggregated palladium blacks is ~3, while that for the macroscopic aggregates has been calculated to be up to 12, suggesting close well-ordered packing. One result of aggregation should be to lower the surface area available for catalytic reaction. The theoretical percentage loss in surface available for reaction can be calculated from the formula 50 N/K + 1 where N = coordination number, K = R/d, R = palladium particle radius, and d = diameter of a reactant molecule. **Fig. 15** [17] shows the available surface area for reaction as a function of palladium particle radius for molecular diameters ranging from 0.07 to 0.6 nm, assuming that N = 0 or 12 [17, 18].

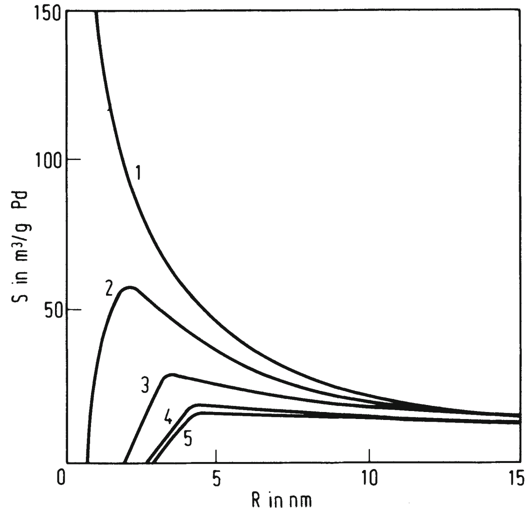

Fig. 15. The specific surface area (S) of unsupported palladium that is available for adsorption by molecules of length d normal to the surface, assuming N is 12. Curve 1: d = 0.07 nm; 2: d = 0.2 nm; 3: d = 0.4 nm; 4: d = 0.57 nm; 5: d = 0.6 nm. Similar sets of curves can be drawn for other values of N and for other materials.

Heating any of the samples of palladium black in hydrogen at temperatures above ambient caused sintering with a permanent loss of surface area. For example, a sample with a surface area of 68 m^2/g fell to 48.6 m^2/g when treated with hydrogen at 90°C [19].

No sintering of platinum black was observable when it was treated with hydrogen at room temperature. Some sintering occurred when the hydrogen treatment at room temperature was followed by heating in air at 360°C for 30 min then, after flushing with helium, treating with hydrogen at ambient temperature. The greatest degree of sintering was found when the sample was heated to 360°C in hydrogen and held at this temperature for 25 min [20].

Ruthenium, rhodium, platinum, iridium and osmium have been prepared as Raney skeletal catalysts. (No record has been found in Chemical Abstracts to the preparation of palladium in a skeletal form since 1950.)

The effects of various starting alloy compositions on the physical properties of Raney rhodium are shown in the table on p. 137. V is the pore volume, H_2(ads.) the amount of adsorbed hydrogen, and E the Rh–H bond energy; $s_{cum.}$ are cumulative surface areas calculated on the basis of different pore models; s_{el} is the specific surface determined from the amount of H_2 adsorbed at 15°C [21]. Particle size of the rhodium catalyst was shown also to be dependent on alloy composition, increasing from 1 to 2 μm with alloys of 5 wt% rhodium content to 30 to 50 μm with alloys of 60 wt% Rh content [21].

Rh (wt%)	phase composition	s_{BET} m²/g	s_{cum} m²/g	10^{-3} V cm³/g	H_2(ads.), cm³/g 15°C	30°C	45°C	60°C	E (kJ/mol) Θ = 0.05	Θ = 0.5	Θ = 0.9	s_{el} m²/g
5	Al; Rh_2Al_9	106	79	128	23.5	23.2	22.5	21.9	248	238	227	92
15	Al; Rh_2Al_9	90	—	129	22.0	20.9	19.4	18.8	247	237	224	85
20	Al; Rh_2Al_9	95	—	119	21.5	20.9	19.8	18.2	248	239	224	83
25	Al; Rh_2Al_9	90	—	—	20.9	19.9	18.9	18.6	247	237	224	81
30	Al; Rh_2Al_9	91	75	126	24.3	23.9	22.8	22.4	247	237	226	94
37	Al; Rh_2Al_9	80	—	—	24.4	23.8	22.5	21.1	248	238	224	95
45	Rh_2Al_9	84	—	80	23.9	23.5	22.0	21.1	247	237	224	93
50	Rh_2Al_9; $RhAl_3$	82	47	74	24.0	23.6	23.2	22.2	248	236	226	93
54	Rh_2Al_9; $RhAl_3$	82	—	80	21.0	20.0	19.1	18.7	248	237	227	81
60	$RhAl_3$	77	43	69	22.3	20.7	19.1	18.9	247	238	226	86
5	Mg; Rh_7Mg_{44}	72	80	157	22.7	22.5	22.1	21.9	247	237	224	88
14	Mg; Rh_7Mg_{44}	95	—	151	22.0	21.5	19.5	18.7	247	239	225	85
26	Mg; Rh_7Mg_{44}	84	58	128	20.7	19.8	19.2	18.6	248	239	223	80
35	Rh_7Mg_{44}; Mg	75	51	—	19.7	18.8	17.9	17.6	248	236	227	76
45	Rh_7Mg_{44}	80	65	124	20.3	20.0	19.5	17.5	248	237	224	78
60	$RhMg_3$; Rh_2Mg_5	56	34	24	16.0	15.5	14.3	13.8	248	239	224	62
30	Rh_5Zn_{21}	—	—	—	25.8	24.9	24.0	23.6	247	236	224	98

With Raney platinum and iridium surface areas of 33 m^2/g for platinum and 50 m^2/g for iridium were obtained by the charging curve method of hydrogen sorption. Some iridium aluminide was detectable in the catalyst by X-ray diffraction. Scanning electron microscopy (SEM) revealed that the morphology of the two catalysts was different. The platinum catalyst consisted of aggregates of fine particles, while the iridium catalyst formed much larger needles, suggesting orientated crystal growth in the starting alloy [22].

A surface area of some 54 m^2/g was obtained for iridium. Raney osmium had an area of 30 m^2/g. When these catalysts were aged by treating them with a cathodic polarisation of 5 mA at 80°C, so that the surface was saturated with hydrogen, both metals sintered, the loss of surface area being about 29% (38.5 m^2/g after ageing) for iridium and 54% for osmium (13.9 m^2/g after ageing) [23].

Pyrophoric Raney ruthenium when treated with 600 Torr partial pressure of hydrogen at 300°C for 3 h gave a stable surface area of 30.7 m^2/g by N_2 BET method. Hydrogen and carbon monoxide chemisorption experiments showed that only 57% of this area or 17.5 m^2/g could be ascribed to ruthenium metal surfaces [24].

The preferred method of preparing platinum metal alloy blacks is by reduction of the chloro salts with sodium borohydride. The resulting materials are invariably contaminated with boron, for example, up to 2000 ppm boron were reported in palladium-gold alloys prepared by this procedure [32]. Whether the boron is a component in the alloy or not is an unanswered question, but it is known that all six platinum-group metals will form compounds with boron [30], and phase diagrams for palladium, platinum, rhodium and ruthenium with boron exist [31]. Preparation of the borides of Pd, Pt and Rh by $NaBH_4$ reduction has been claimed by [16].

Palladium-ruthenium [26], platinum-ruthenium [25], platinum-palladium [25], platinum-rhodium [25] and palladium-gold [25] alloys were reported by sodium borohydride reduction. In the case of palladium-ruthenium and platinum-ruthenium alloys a post-preparative treatment in hydrogen at 300°C for 3 h was given, the other alloys were used as prepared. Physical data for the Pt-Ru, Pt-Pd, Pt-Rh and Pt-Au alloys are shown in the table below. The surface area of the palladium-ruthenium blacks was reported as being between 8 and 12 m^2/g after treatment in hydrogen [26].

alloy composition (wt%)	lattice spacing a_0 (Å)	surface area (m^2/g)
100 Pt	3.916	4.9
Pt-20.0 Pd	3.904	3.6
Pt-33.0 Pd	3.899	3.3
Pt-49.3 Pd	3.894	6.0
Pt-65.2 Pd	3.892	6.2
100 Pd	3.890	14.3
Pt-10 Rh	3.89	13.7
Pt-15.8 Rh	3.90	34.9
Pt-27.3 Rh	3.86	16.2
Pt-49.9 Rh	3.85	21.7
Pt-72.6 Rh	3.82	23.6
Pt-90.1 Rh	3.81	25.7
100 Rh	3.80	28.1
Pt- 8.9 Ru	3.90	12.0
Pt-16.3 Ru	3.90	13.1
Pt-19.9 Ru	3.89	9.7
Pt-28.2 Ru	3.88	13.7
Pt-59.7 Ru	3.87	18.3
100 Ru	2.70	74.4

alloy composition (wt%)	lattice spacing a_0 (Å)	surface area (m^2/g)	alloy composition (wt%)	lattice spacing a_0 (Å)	surface area (m^2/g)
Pd-10.9 Au	3.90	16.8	Pd-33.5 Au	3.92	8.0
Pd-15.5 Au	3.89	8.3	Pd-50.5 Au	3.94	12.4
Pd-19.7 Au	3.89	8.6	Pd-59.0 Au	3.98	12.9
Pd-25.7 Au	3.89	18.0	Pd-79.0 Au	4.02	10.4
Pd-29.2 Au	3.92	10.7	100 Au	4.08	5.0

The chemisorption of oxygen and carbon monoxide on palladium-gold and palladium-silver alloys was reviewed by [27]. Surface enrichment is considered as one factor in explaining the results.

Hydrazine was used as a reducing agent in preparing palladium-gold [28], platinum-gold [28, 29] and palladium-copper alloys [29]. The alloys consisted almost entirely of the intermetallic compounds $PtAu_3$ and $PdCu_3$ of ~100 Å crystallite size. The proof of alloying with Hoffman's palladium-silver and platinum-gold materials, was obtained by comparing the theoretical melting point of alloys of a given composition, obtained from the solidus-liquidus curve of the phase diagram, with the observed melting point of the material. The data is reproduced in the table below. The observed melting point of mixtures of palladium and silver, and of platinum and gold was that of silver (960°C) or gold (1062°C).

example No.	wt. of Pt solution in g	wt. of Au solution in g	percent Pt in alloy	reducing agent and amount dissolved in 100 ml H_2O	observed melting point (°C)	theor. melting point (°C)
4	24	176	10	50 g hydrazine hydrate	1080	1080
5	50	150	21.4	50 g hydrazine hydrate	1121	1129
6	68	132	30	50 g hydrazine hydrate	1204	1200
7	110	90	50	50 g hydrazine hydrate	1330	1330
8	130	70	60	50 g hydrazine hydrate	1426	1390
9	148	52	70	50 g hydrazine hydrate	1398	1425
10	168	32	80	50 g hydrazine hydrate	1525	1550
11	184	16	90	50 g hydrazine hydrate	1700	1683
12	110	90	50	25 g hydroquinone, 25 g sodium borohydride	1332	1330
13	50	150	21.4	25 g hydrazine sulphate, 25 g sodium borohydride	1127	1129
14	110	90	50	25 g sodium borohydride, 25 g sulphurous acid	1330	1330
15	110	90	50	25 g sodium sulphite, 25 g sodium borohydride	1337	1330
16	110	90	50	25 g sodium borohydride, 25 g zinc dust	1338	1330

example No.	wt. of Pt solution in g	wt. of Au solution in g	percent Pt in alloy	reducing agent and amount dissolved in 100 ml H_2O	observed melting point (°C)	theor. melting point (°C)
17 1)	110	90	50	25 g sodium hydrosulphite, 25 g ferrous sulphate	1341	1330
18	15	85	10	4 g hydrazine hydrate	1175	1200
19	27	73	20	4 g hydrazine hydrate	1360	1350
20	40	60	30	4 g hydrazine hydrate	1403	1400
21	50	50	40	4 g hydrazine hydrate	1454	1450
22	60	40	50	4 g hydrazine hydrate	1490	1475
23	70	30	60	4 g hydrazine hydrate	1495	1500
24	77	23	70	4 g hydrazine hydrate	1515	1520
25	87	13	80	4 g hydrazine hydrate	1541	1540
26	93	7	90	4 g hydrazine hydrate	1570	1550
27	60	40	50	25 g hypophosphorous acid, 2 g hydroquinone	1482	1475
28	60	40	50	25 g hypophosphorous acid, 2 g hydrazine sulphate	1480	1475
29	60	40	50	25 g hydrophosphorous acid, 2 g sulphurous acid	1490	1475
30	60	40	50	25 g hydrophosphorous acid, 2 g sodium sulphite	1481	1475
31	60	40	50	25 g hydrophosphorous acid, 2 g zinc dust	1476	1475
32	60	40	50	2 g sodium hydrosulphite, 2 g ferrous sulphate	1468	1475

1) pH adjusted to ∼5.5 with NaOH before adding reducing agent.

Platinum-iridium [22] and iridium-osmium alloys [23] were prepared by the Raney method. The surface areas of the alloys are given in the table below. Differences in the morphology of the platinum and iridium catalysts were found by scanning electron microscopy. The platinum and platinum rich materials formed aggregates of fine particles while the iridium and iridium rich catalysts formed large needle-like crystals.

alloy composition wt% Pt	wt% Os	crystallite size (Å)	surface area (m^2/g) freshly prepared	aged
100	—	3.875	31	—
90	—	3.869	21	—
75	—	3.864	54	—
50	—	3.851	54	—
40	—	3.848	50	—

alloy composition wt% Pt	 wt% Os	crystallite size (Å)	surface area (m^2/g) freshly prepared	 aged
25	—	3.840	50	—
10	—	3.828	60	—
0	—	3.813	50	—
—	100	—	30.0	13.9
—	90	—	35.6	18.3
—	75	—	42.0	22.7
—	60	—	42.6	26.5
—	40	—	45.9	27.1
—	25	—	51.6	32.2
—	10	—	53.3	34.4
—	0	—	54.1	38.5

Aged catalysts had been held cathodically at 5 mA current for 33 h at 80°C. The surface was hydrogen saturated for the whole of this time.

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4.2.1.2 Gauze Manufacture and Properties

Industrial ammonia oxidation gauzes are manufactured from platinum alloy wires on standard looms. Two platinum alloys are employed, 10% rhodium-platinum and 5% rhodium-5% palladium-90% platinum which are woven to gauzes of the standard 1024 mesh per cm^2, with one of the two standard wire diameters of 0.06 mm or 0.076 mm. Impurity metals in the alloy wires are restricted to 100 ppm Au, 200 ppm Fe and 100 ppm total other metallic impurities. Many plants operate with upwards of 20, 30 or 40 gauzes, which are composed of pads of 2, 3 or 4 individual gauzes spotwelded together. Nonstandard gauzes can be woven from platinum wire or 5% rhodium-platinum for special purposes.

The physical properties of platinum, 5% rhodium-platinum and 10% rhodium-platinum gauzes are given in the table below [1].

composition	apertures per cm^2	nominal wire diam. (mm)	free space per m^2	approx. weight per unit area $oz.tr/ft^2$	g/m^2
Pt	1024	0.06	2.3×10^3 cm^2	1.24	415
5% Rh/Pt	1024	0.06	2.3×10^3 cm^2	1.20	400
10% Rh/Pt	1024	0.06	2.3×10^3 cm^2	1.15	386

In addition to the oxidation gauzes most plants contain base metal support gauzes and palladium-gold (80% Pd-20% Au) gauzes which act as collectors or getters for platinum and rhodium volatilised from the oxidation gauzes during operation. The collector gauzes are manufactured on standard looms from wire of 0.09 or 0.06 mm. By using a mix of collector gauzes, with both heavy and light gauge gauzes, the most economical recovery can be attained [2, 3].

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4.2.1.3 Electrode Fabrication

Platinum-group metal electrodes have a variety of uses in electrochemical applications where corrosion resistance and catalytic activity are required. The use of platinised electrodes as voltage references is described by [1], whilst the preparation of platinised platinum with high surface area characteristics is reviewed in [2]. The various mechanisms proposed for electrochemical activation of platinum electrodes are reviewed by [3]. It was concluded that impurity desorption is the most important result of brief activation treatments. Improved activity may also be obtained by "activating" electrodes by alternate oxidizing and reducing treatments.

The surface reactions of the platinum-group metals and alloys with respect to oxygen have been examined by [4, 5]. The mechanisms of oxygen evolution and reduction, and the role played by absorbed ions at anodes and cathodes are extremely complex. It is generally agreed that reactions on noble metal electrodes proceed via partial coverage of oxide, possibly little more than monatomic layers. The experimental techniques employed to study these surface films and interfaces have been reviewed by [6].

A number of noble metal/noble metal and noble metal/base metal alloys have been shown to exhibit enhanced activity for the anodic oxidation of hydrogen and methanol [7].

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4.2.2 Reactions

Platinum-group metals are catalytically active over very wide ranges of processing conditions and unsupported platinum metals are applied in situations at the extremity of their range such as very high or very low temperatures, very corrosive media or the processing of expensive substrates where loss of product by contamination or absorption on a support cannot be tolerated.

Platinum oxidation gauges for nitric acid manufacture, operate at temperatures between 800 and 900°C in extremely oxidising conditions [1] and where platinum metal losses occur to the gas phase, probably as a platinum oxide, causing weakening and eventually breakage of the gauze catalyst [2, 3]. Alloying with other platinum-group metals, principally rhodium, can cut this loss from 0.88 to 0.53 oz troy (~27.4 to ~16.5 g) Pt per 10^5 lbs (45300 kg) NH_3. Under the same conditions cobalt, in a platinum-cobalt alloy catalyst, was rapidly oxidised and the initial low platinum loss quickly rose to that for pure platinum [2]. Platinum loss from pure platinum and 10% rhodium-platinum gauges are shown in **Fig. 16**, p. 144, taken from [3].

At the other temperature extreme, ruthenium blacks are used to catalyse the ortho-para hydrogen conversion at temperatures as low as −196°C, an essential step in the growing market for liquid hydrogen [5].

Corrosion to the active metal catalyst component in liquid phase reactions can be even more disastrous of catalyst activity and product integrity than platinum losses with gauzes.

Very little is published on this topic, but it is a widespread phenomenon and is especially noticeable with base metal (Ni, Cu) catalysts and supported metal catalysts [6, 7, 8]. Corrosion is connected with the pH of the system and the presence of oxidising agents and complexing ions. Pourbaix has published much that is instructive in analysing catalyst systems for potential solubility situations [9, 11]. Solutions to solubility problems have varied, maintaining a high flux of hydrogen at the catalyst surface, above that required for reactions, was the solution adopted by [6] and is mentioned by [7], while making the metal cathodic has been proposed in the patent literature [8]. Solution of platinum, in phosphoric acid fuel cells at 200°C, followed by redeposition, is a major mode of fuel cell catalyst sintering [12]. Base metal catalysts in the first row of group VIII (Fe, Co, Ni) and group IB (Cu) are more easily brought into solution, and rendered inactive by the conditions prevailing within many liquid phase systems, than their platinum metal counterparts. This is illustrated by **Figg. 17**, **18**, **19** and **20**, pp. 145/6, which give the domains of corrosion, immunity and passivation for copper, nickel, palladium and platinum at potentials E [11].

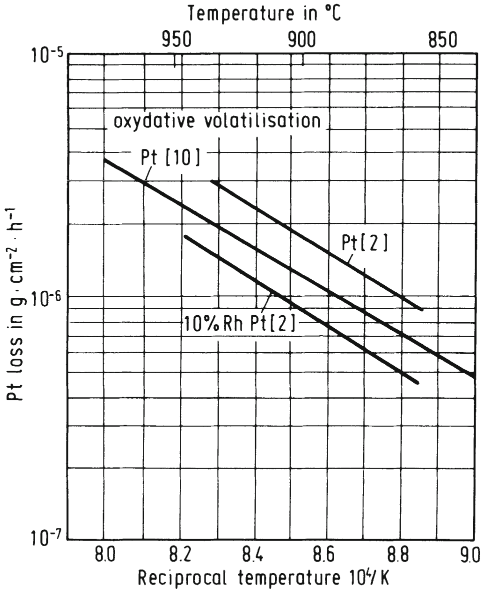

Fig. 16. Arrhenius plots of platinum weight losses at gauze operating temperatures, comparing results obtained by oxidative volatilisation of platinum [10] with metal losses from gauzes under plant conditions [2]. Good agreement is observed indicating that oxygen plays a large part in causing metal loss from gauzes.

Platinum metal blacks found their main application in the production of pharmaceuticals between 1940 and 1970, and, although some processes still require metal blacks, there is a general trend towards their replacement by supported catalysts or more frequently homogeneous catalysts [13, 14]. The chief reason for the survival of metal blacks in this area is where there is an overriding need to prevent product contamination by catalyst corrosion products, and of preventing loss of expensive product to the pore system of a support.

Early use of platinum and alloy metal blacks in fuel cells has given way to their supported counterparts as the necessary skills of catalyst manufacture and electrode fabrication have been obtained [15].

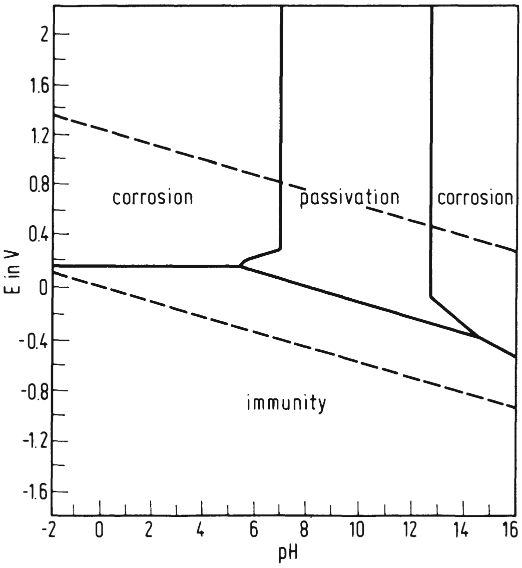

Fig. 17. Domains of corrosion, immunity and passivation of copper, at 25°C.

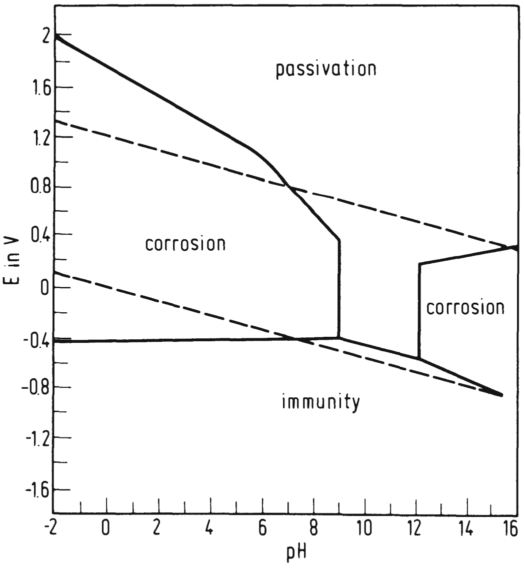

Fig. 18. Theoretical domains of corrosion, immunity and passivation of nickel, at 25°C.

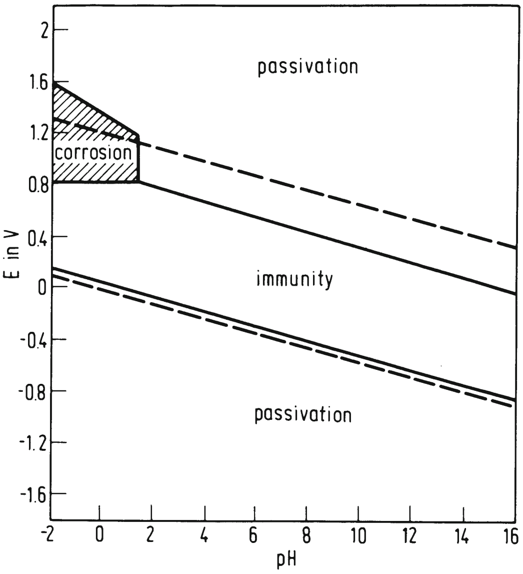

Fig. 19. Theoretical domains of corrosion, immunity and passivation of palladium, at 25°C.

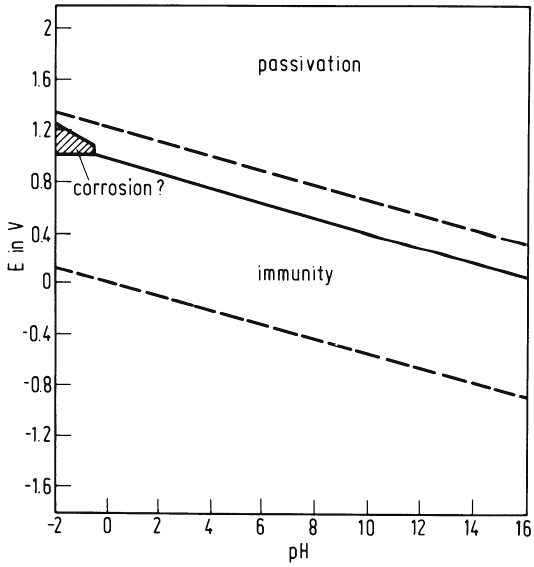

Fig. 20. Theoretical domains of corrosion, immunity and passivation of platinum, at 25°C.

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4.2.2.1 Hydrogenation

Finely divided platinum-group metal catalysts were used almost exclusively by the fine chemical industry for hydrogenation and dehydrogenation reactions (Section 4.2.2.2). In both of these types of reaction selectivity was always more important than activity, so much so that in order to make catalysts more selective, poisoning for example was frequently resorted to, and a spectrum of poisoning agents were used ranging from iron and lead salts to mixtures of quinoline and sulphur. The successful design of a process and catalyst, for say a pharmaceutical hydrogenation, required a knowledge of both the thermodynamic selectivity of the platinum metals and of how selectivity is modified by changes in kinetics induced by mass transfer. The latter can be achieved either by varying reaction parameters, such as temperature and pressure, or a reactor parameter, such as agitation, or both. This section reviews the information available on the kinetics and thermodynamic selectivity of the platinum metals, catalyst modifications to achieve better selectivity and higher activity, and kinetically induced selectivity.

The effect of alloying on the selectivity of platinum-group metals has been considered by [1, 2, 3] mainly from the electronic contribution that the alloying metal has on the d band character, and by [4]. More qualitative descriptions of activity and selectivity of the platinum metals in hydrogenation reactions have been given by [5 to 9]. The approach of the first three authors is that of classifying the hydrogenation reactions by organic functional groups, and noting the selectivity/activity patterns obtained when a spectrum of organic compounds containing a particular functional group are hydrogenated over any one or more of the six platinum metals. Reviews of the catalytic hydrogenation of functional groups containing information on platinum catalysis for (I) addition of hydrogen to carbon-carbon multiple bonds including olefins, acetylenes, dienes, polyenes, enynes, diynes, allenes, aromatic hydrocarbons, α,β-unsaturated carbonyls, polyene acids, aldehydes and ketones [10], (II) acetylene compounds [11], (III) reduction of indoles, etc. [12], (IV) hydrogenation of double bonds in steroids [13], and (V) the hydrogenation of small carbon rings (3, 4 and 5 carbon atoms) [14] have appeared. Information on cis-trans isomerisation during hydrogenation and hydrogenation of optically active compounds is contained in a review [15].

Large numbers of papers have been published dealing with the hydrogenation of a particular organic function, or a spectrum of organic functions over one or more platinum metal blacks. The following references are given to illustrate the type of information available from this source, but are not exhaustive.

In the hydrogenation of nitriles, both the particular nitrile and the chosen platinum metal determined the product spectrum. With proprionitrile, rhodium gave predominantly the secondary amine, while platinum and palladium produced the tertiary amine. When benzonitrile was hydrogenated no tertiary amine was formed, and palladium gave the highest yield of the monoamine, benzylamine. Platinum, however, gave large quantities of dibenzylamine [16].

Hydrogenation of aromatic nitro compounds over Adams iridium oxide, reduced to the metal in situ, produces large amounts of the arylhydroxylamine. Thus, with p-bromonitrobenzene in ethanol, an 83% yield of p-bromophenylhydroxylamine was obtained [17]. However, [18] found that hydrogenation of nitrobenzene over iridium gave only low yields of phenylhydroxylamine. Iridium gave the highest yield at 16 to 19%, while platinum only produced 3%. Rhodium and palladium gave variable yields depending on whether the metal black or oxide was used. Palladium black gave 9% phenylhydroxylamine, but palladium oxide only 3%; rhodium black produced 1% of this material, while rhodium oxide gave 10%. Under the conditions used, both oxides would be expected to reduce the metal.

Hydrogenation of acetylenic triols over platinum black, made in situ by reduction of Adams platinum oxide, resulted in 85 to 95% yields of the corresponding cis-olefinic triols [19]. The hydrogenation of simple acetylenes (pentynes, hexynes and heptynes) over palladium, platinum, and rhodium also produced cis-olefins [20]. Palladium black isomerised any α-olefin to near the equilibrium mixture of isomers. In the reduction of di-2-cyclopenten-1-yl acetylene over platinum, the triple bond was reduced to the olefin first, followed by reduction of the cyclic double bonds without isomerisation. With palladium, triple bond hydrogenation gave the cis-olefins, followed by isomerisation and hydrogenation of the ring double bonds, together with saturation of the non-ring double bond [21].

Acetophenone was hydrogenated over platinum black and 1-phenylethanol obtained in 90% yield. Pressure was 1 atm and temperature was ambient. Reduction of acetophenone over ruthenium dioxide at 100°C and 1000 psi (67.44 kg/cm^2) gave 1-cyclohexylethanol in 88% yield [22]. The hydrogenation of methyl cyclohexanones and cresols to methylcyclohexanols over platinum black, produced by in situ reduction of Adams platinum oxide, gave substantially the most stable isomer of the corresponding methylcyclohexanol, 61% trans-2-methylcyclohexanol from 2-methylcyclohexanone and o-cresol, 75% cis-3-methylcyclohexanol from 3-methylcyclohexanone and m-cresol, and 63 to 65% trans-4-methylcyclohexanol from 4-methylcyclohexanone and p-cresol [23].

In a study of ruthenium catalysis, a spectrum of organic compounds was hydrogenated at either 1 atm H_2 pressure and 35°C or 100 atm and 150°C over ruthenium black, made by prereduction of ruthenium dioxide at 80 to 90°C. The results are shown in the tables on pp. 149/51 [24].

In situ reduction of ruthenium hydroxide has been used to provide a ruthenium black catalyst for 2,5-dimethylpyrrole reduction at 400 psi (~27 kg/cm^2) and 75 to 150°C [25]. The hydrogenation of pyridines, principally over ruthenium and platinum blacks, has been reviewed by [26].

In the most comprehensive investigation of alloy catalysts for liquid phase hydrogenations the effects of alloying were examined: (I) two platinum metals, (II) a base metal with a platinum metal and (III) a base metal with two platinum metals on the hydrogenation of a range of organic functions. **Fig. 21**, p. 152, illustrates the type of activity-composition plots obtained while the following table is a list of alloy combinations used by the authors [27].

Alloy combinations used for hydrogenations:

Pt-Ru
Pt-Ir
Pt-Rh
Pt-Pd
Pd-Ru
Pd-Rh
Rh-Ru
Pd-Ni
Pd-Co
Pt-Ni
Pt-Co
Pt-Fe
Pt-Cu
Pt-Ru-Ni

Hydrogenation of Organic Compounds by Ru Catalyst.

Normal pressure:

acceptor	mol × 10^{-2}	catalyzer (g)	solvent (ml)	activator (g)	absorbed H_2 in 1 h from start (ml)	theoretical amount at 20°C (ml) and name of product
acetone	1.0	0.1	(a) 20	10% NaOH 1.0	(35)	240 isopropylalcohol
			(b) 20	10% NaOH 1.0	195.0	
			(c) 20	10% NaOH 1.0	(55)	
			(d) 20	10% NaOH 1.0	83.2	
methyl ethyl ketone	1.0	0.1	(a) 20	10% NaOH 1.0	(40)	240 sec.-butanol
cyclohexanone	1.0	0.1	(a) 20	10% NaOH 1.0	(60)	240 cyclohexanol
			(b) 20	10% NaOH 1.0	212	
anthraquinone	0.25	0.1	(b) 20	10% NaOH 1.0	(20)	60 anthrahydroquinone
allyl alcohol	1.0	0.1	(a) 20	—	31.3	240 propylalcohol
			(b) 20	—	201.5	
			(c) 20	—	192.0	
			(d) 20	—	112.0	
maleic acid	1.0	0.1	(a) 20	—	26.0	240 succinic acid
			(b) 20	—	(37)	
nitrobenzene	1.0	0.1	(a) 20	10% CH_3COOH 1.0	57	720 aniline
			(b) 20	10% CH_3COOH 1.0	207.0	
			(c) 20	10% CH_3COOH 1.0	52.0	
			(d) 20	10% CH_3COOH 1.0	47.0	
o-nitrophenol	1.0	0.1	(b) 20	10% CH_3COOH 1.0	(60)	720 o-aminophenol
p-nitrophenol	1.0	0.1	(b) 20	10% CH_3COOH 1.0	(120)	720 p-aminophenol

acceptor	mol × 10^{-2}	catalyzer (g)	solvent (ml)	activator (g)	absorbed H_2 in 1 h from start (ml)	theoretical amount at 20°C (ml) and name of the product
m-dinitrobenzene	0.1	0.1	(a) 20	10% CH_3COOH 1.0	(45)	144 m-phenylenediamine
acetonitrile	1.5	0.1	(a) 20	10% NH_3 1.0	104.0	480 ethylamine
			(b) 20	10% NH_3 1.0	52.5	
			(d) 20	10% NH_3 1.0	35.0	
benzonitrile	1.5	0.1	(a) 20	10% NH_3 1.0	4.0	480 benzylamine
mesityl oxide	1.0	0.1	(a) 20	10% NaOH 1.0	(120)	480 methylisobutylcarbinol
citronellal	1.0	0.1	(a) 20	10% NaOH 1.0	69.0	3,7-dimethyloctan-1-al 240 citronellol 240 3,7-dimethyloctan-1-ol 480

(a) water, (b) alcohol, (c) decalin, (d) n-hexane.
The figures in brackets indicate the time (min) needed for completion of hydrogenation reaction.

Hydrogenation of Organic Compounds by Ru Catalyst.

Elevated pressure:

acceptor	mol × 10^{-1}	solvent (ml) and activator (g)	catalyzer (g)	reaction temp. (°C)	completing time of hydrogenation (min)	product and yield in %	
acetone	1.0	(a) 30 10% NaOH 1.0	(A) 0.1 (B) 0.1 0.1	38 to 40	15 5 20	isopropylalcohol	98
methyl ethyl ketone	1.0	10% NaOH 1.0	0.1	38 to 40	17	sec.-butanol	95
crotonaldehyde	1.0	10% NaOH 1.0	0.1	120 to 122	68	n-butanol	86
cyclohexanone	1.0	10% NaOH 1.0	0.1	38 to 40	17	cyclohexanol	96
benzaldehyde	1.0	10% NaOH 1.0	0.1	120 to 122	44	cyclohexylcarbinol	91.5
cinnamaldehyde	1.0	(a) 30	0.1	120 to 122	86	3-cyclohexylpropyl alcohol	88.5
citronellal	1.0	(a) 30	0.1	60 to 65 120 to 125	56 32	citronellol 3,7-dimethyloctan-1-ol	82.0 98
mesityloxide	1.0	(a) 30	0.1	38 to 40 120 to 122	35 14	methylisobutyl ketone methylisobutyl carbinol	92 91
allylalcohol	1.0	(a) 30	0.1	38 to 40	25	propylalcohol	97
geraniol	1.0	(a) 30	0.1	120 to 122	62	2,6-dimethyloctan-1-ol	—
benzene	1.0	(a) 30	0.1	120 to 122	16	cyclohexane	92
phenol	1.0	(a) 30	0.1	120 to 122	16	cyclohexanol	96
p-nitrophenol	1.0	(a) 30	0.1	120 to 122	72	4-aminocyclohexanol	—
dextrine	1.0	50%	0.1	120 to 122 140 to 142	50 20	sorbitol	95

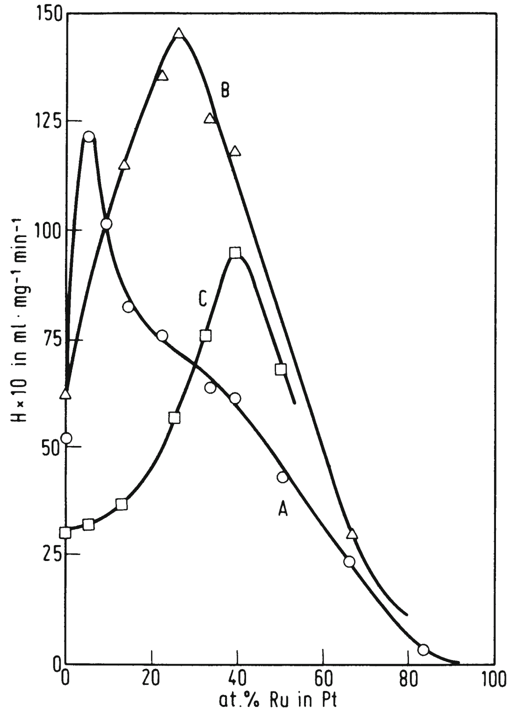

Fig. 21. Rates of hydrogen uptake (H) of methylbutynol (A), maleic acid (B) and cyclohexene (C), using Ru-Pt oxides.

An extensive review of the catalytic properties of palladium-silver and palladium-gold alloys in the form of blacks, films, foils and wires has been published by [28] and selectivity in hydrogenation, hydrogenolysis and oxidation reactions over alloy catalysts has been made by [29]. Binary platinum metal alloys as catalysts in liquid phase hydrogenations were examined by [30, 31].

From the point of view of liquid-phase hydrogenation catalysis the most important platinum metal alloy is platinum-rhodium. The hydrogenation of nitrobenzene, nitropropane, benzilic acid, aniline, cyclohexanone oxime, acetoacetic ester, and 2-acetylbutyrolactone over this catalyst combination was described by [30, 31], while changes in the catalytic activity and selectivity of these two metals for a very large spectrum of organic functions in hydrogenation and hydrogenolysis reactions were systematically investigated by [32 to 39]. The platinum-rhodium alloy is particularly recommended for selective hydrogenations in which labile carbon-oxygen functions are to be protected during reduction of other organic groups [40, 41]. The composition at which either maximum activity or selectivity occurs is different for each organic function, and even for the same function attached to different carbon skeletons. Frequently increasing hydrogen pressure will help to protect carbon-oxygen groups prone to hydrogenolysis [40]. The hydrogenation of aliphatic nitriles over a 50% rhodium-50% platinum alloy gave 83% of the primary amine [42].

Platinum-ruthenium blacks have been investigated as catalysts for the hydrogenation of unsaturated compounds, cyclic ketones and pyridine. The results are shown in the following table [43].

reactant	solvent	reactant (moles)	oxide (mg)	E.F.[d]	optimum Ru content[a] (at.%)
2-methylbut-3-yn-2-ol[b]	CH_3OH	0.8	10	2.5	3
maleic acid	CH_3OH	1.8	50	2.5	20
cyclohexene	CH_3OH	1.5	10	3.0	30
cyclohexanone[c]	C_2H_5OH–HCl	0.5	50	3.5	30
acetophenone[c]	CH_3OH–HCl	3.4	50	3.0	30
pyridine	CH_3OH–HCl	0.25	50	1.5	3

[a] Approximate Ru content, as at.% of total metal, at which rate is a maximum. – [b] Products not analysed. – [c] Reduced to corresponding secondary alcohol. – [d] Enhancement factor, defined as maximum rate/rate for PtO_2.

For kinetics of methane-deuterium exchange over palladium-ruthenium powder alloys see [44], the decomposition of hydrogen peroxide over binary platinum metal alloys was investigated by [45].

Platinum was promoted by preparing Adams platinum oxide from chloroplatinic acid containing various amounts of the alkaline earth metals as their chlorides. Improvements were consistently found for these promoted catalysts in the hydrogenation of maleic acid and methyl butynol whether the catalyst was platinum oxide reduced in situ or prereduced platinum black. Addition of alkaline earth chloride to prereduced unpromoted platinum black and to hydrogenation reactions catalysed by unpromoted blacks were unsuccesful. The promoted catalysts were also more stable in storage and in use. The table on p. 155 indicates the degree of promotion of platinum (S is the specific surface) [46].

Although many attempts have been made in Europe and USA to assess the effect of preparation method on the activity and selectivity of supported catalysts, these results are not always applicable with blacks and it is only in the USSR that systematic attempts have been made to determine the effect or preparation variables on unsupported catalysts.

A sample of commercial platinum black gave 90% ethylbutyrate and 10% ethyl β-hydroxybutyrate when used to hydrogenate ethylacetoacetate, while platinum oxide reduced in situ in the hydrogenation medium, and a prereduced platinum black (from platinum oxide) gave 100% ethyl β-hydroxybutyrate, but the cause of this disparity in selectivity was not investigated. Hydrogenation of methylbutynol over ruthenium black caused some hydrogenolysis to give isopentane. When the catalyst was heated to 300°C in hydrogen, the surface area declined and the rate of hydrogenation decreased sixfold over the catalyst treated normally in hydrogen at 100°C. Hydrogenolysis, however, increased from 13.4% with the normal catalyst to 28.6% when heat treated at 300°C [48]. With platinum and palladium blacks, made by reduction of the chlorides with a variety of reducing agents, in general catalytic activity increased as dispersion increased, but highly dispersed platinum black made by reduction with cerous chloride was less active than less well dispersed titanous chloride-reduced material. A similar pattern was shown by both platinum and palladium blacks in the reduction of the acetylenic bond in methylbutynol. The following table shows the catalytic results of this investigation [49]. With platinum and palladium blacks produced by Willstätter's method in an ultrasonic field of various frequencies from 20 kHz to 3 MHz, and by hydrogen reduction of chloroplatinic acid in ultrasonics of 21 kHz, catalytic activity, for hydrogen peroxide decomposition and 1-hexene hydrogenation, was proportional to the concentration of the chloroplatinic acid for hydrogen-reduced material and was dependent on the nature of the gas atmosphere with formaldehyde-reduced platinum and palladium. The following tables show the effect of platinum concentration, and ultrasonic frequency on platinum and palladium black activity [50, 51].

Dependence of the total activity of the platinum blacks on the concentration of the chloroplatinic acid solutions being reduced (catalysts prepared in a shaken reactor or in an ultrasonic field):

Pt in H_2PtCl_6 solution wt%	total activity, 10^{-3} mol·g^{-1}·s^{-1}			
	decomposition of H_2O_2		hydrogenation of hex-1-ene	
	catalyst obtained in a shaken reactor	catalyst obtained in an ultrasonic field	catalyst obtained in a shaken reactor	catalyst obtained in an ultrasonic field
0.05	0.31	0.72	—	—
0.10	0.28	0.44	0.19	0.25
0.25	0.21	0.065	0.17	0.071
0.50	0.27	0.062	0.068	0.049

Relative total activity of platinum US-blacks (total activity of catalyst obtained in the absence of ultrasonic field taken as 100%):

catalytic process	US-blacks						
	N_2			air			H_2
	3 MHz	548 kHz	20 kHz	3 MHz	548 kHz	20 kHz	3 MHz
decomposition of H_2O_2	260	175	135	116	226	226	195
hydrogenation of hex-1-ene	138	104	113	70	87	90	110
oxidation of ethanol	140	84	74	125	110	118	60

Relative total activity of platinum US-blacks (total activity of catalyst obtained in the absence of ultrasonic field taken as 100%):

catalytic process	US-blacks						
	N_2			air			H_2
	3 MHz	548 kHz	20 kHz	3 MHz	548 kHz	20 kHz	3 MHz
decomposition of H_2O_2	100	200	320	58	158	—	150
hydrogenation of hex-1-ene	175	140	130	70	79	84	150
oxidation of ethanol	79	135	240	30	173	—	82

Sodium borohydride reduction of platinum-metal chloro salts gave highly active catalysts for the hydrogenation of 1-octene [52]. The activity of these catalysts could be exceeded by employing tribenzylsilane as reducing agent. The rates of hydrogenation of 1-octene by the platinum metals prepared by the method of [52] are given in the table on p. 157 [53].

Structures, Chemical Compositions, and Specific Activities of PtO_2 and Platinum Black.

additive	MCl_2:Pt (wt%)	crystal size, Å		mean grain size, µm		S, m^2/g		impurity content, wt%								rate of hydrogenation, $ml \cdot min^{-1} \cdot g^{-1}$	
								Na^+		Be^{2+}		Mg^{2+}		Ca^{2+}			
		PtO_2	Pt	PtO_2	Pt	PtO_2	Pt	PtO_2	Pt	PtO_2	Pt	PtO_2	Pt	PtO_2	Pt	of potassium maleate	of ethynyldimethyl methanol
$BeCl_2$	0	26	94	34	54	49	13	~1	<0.01	—	—	<0.01	<0.01	<0.03	<0.03	16	119
	1	20	51	—	—	—	—	~1	<0.01	~1	~1	0.1	—	0.01	<0.01	76	235
	2	20	46	—	13	71	22	~1	<0.01	~1	~1	0.1	—	0.01	—	135	314
	5	—	47	—	—	—	27	—	<0.01	—	≫1	—	—	—	—	161	416
	10	—	54	—	—	—	30	—	<0.01	—	≫1	—	—	—	—	167	552
	20	22	54	5	6	87	35	~1	<0.01	≫1	≫1	0.1	<0.01	0.01	<0.01	167	644
$MgCl_2$	1	19	51	—	—	47	27	>0.01	<0.01	—	0.003	~1	>0.1	~0.1	<0.1	73	235
	2	15	52	—	—	—	29	>0.01	<0.01	—	0.003	≫1	≧1	~0.1	<0.1	89	268
	5	—	53	—	—	—	29	>0.01	<0.01	—	0.001	—	≧1	~0.1	<0.1	94	668
	10	10	52	—	—	—	30	>0.01	<0.01	—	0.001	≫1	≧1	~0.1	<0.1	112	686
	20	—	53	12	15	78	39	>0.01	<0.01	—	0.001	≫1	≧1	0.1	<0.1	119	744
$CaCl_2$	1	20	—	—	—	52	26	~1	—	0.001	—	<0.1	—	~1	—	42	249
	2	20	67	—	—	—	29	~1	<0.01	—	—	<0.1	<0.1	~1	≧1	47	276
	5	25	59	—	—	—	31	~1	<0.01	—	—	—	<0.1	—	≧1	58	341
	10	20	48	—	—	74	33	~1	<0.01	—	—	0.1	<0.1	>1	~0.1	69	360
	20	—	53	16	16	—	39	~0.3	<0.01	—	—	—	<0.1	—	~0.1	75	366
$SrCl_2$	1	20	56	—	—	50	21	~1	<0.01	0.001	0.001	0.1	<0.1	<1	—	39	282
	2	20	54	—	—	—	32	~1	<0.01	—	0.001	—	<0.1	—	<0.1	49	303
	5	—	55	—	—	—	37	—	<0.01	—	0.001	—	<0.1	—	<0.1	61	389
	10	19	54	—	—	—	40	~1	<0.01	—	0.001	0.1	<0.1	—	<0.1	64	391
	20	—	—	15	16	60	40	~0.3	<0.01	—	0.001	—	<0.1	—	<0.1	78	391
$BaCl_2$	1	25	—	—	—	—	—	1	<0.01	—	—	0.1	—	0.01	0.01	65	219
	2	24	51	—	—	43	24	—	<0.01	—	—	0.1	0.01	0.01	—	68	235
	5	—	53	—	—	—	27	—	<0.01	—	—	—	—	—	—	70	235
	10	26	48	—	—	61	35	—	<0.01	—	—	—	—	0.01	—	80	193
	20	—	43	11	12	—	39	~0.01	<0.01	—	—	0.1	—	—	—	85	235

Specific Activities and Linear Dimensions of Catalyst Grains and Metal Particles in the Catalysts.

catalyst	reducing agent	average size		PM		PONP		1-hexene		DMEC			
		catalyst grain, μm	metal particle in catalyst, Å	W	K	W	K	W	K	–C≡C–		=C=C=	
										W	K	W	K
Pt from PtO_2	H_2	54.0	147	20	0.5	34	1.7	130	6.5	75	3.7	100	5.0
Pt black	$N_2H_4 \cdot H_2O$	34.0	215	4	0.3	16	1.2	74	6.1	42	3.2	58	4.5
	$NaBH_4$	38.0	187	3	0.2	22	1.5	92	6.1	36	2.4	65	4.3
	$Ca(BH_4)_2$	15.0	127	9	0.8	54	4.5	125	10.4	102	9.0	171	14.2
	$TiCl_3$	0.5	38	63	3.0	360	16.3	800	36.4	360	16.3	1200	54.5
	$CeCl_3$	0.3	32	90	3.5	330	12.7	980	37.7	300	11.5	1185	45.6
Pd from PdO	H_2	14.0	263	92	2.4	47	2.5	150	7.9	100	5.3	96	5.6
Pd black	$N_2H_4 \cdot H_2O$	21.0	161	80	2.6	60	1.9	240	7.7	96	3.1	68	2.2
	$NaBH_4$	24.0	156	70	2.2	66	2.1	175	5.5	110	3.4	70	2.2
	NaH_2PO_3	25.0	135	124	3.4	118	3.4	300	8.6	200	5.0	160	4.6
	$Ca(BH_4)_2$	10.0	147	134	4.8	176	6.3	326	11.6	239	19.1	176	6.3
	$TiCl_3$	0.3	54	720	25.7	870	31.0	1750	62.5	2850	101.8	2670	95.3
	$CeCl_3$	0.1	50	900	30.0	1050	35.0	1900	63.0	2820	94.0	2880	96.0

W is the specific activity in ml/g catalyst·min; K is the specific activity in ml/m^2 metal·min. Abbreviations: PM = potassium maleate, PONP = potassium o-nitrophenolate, DMEC = dimethylethynylcarbinol.

metal[a]	compound used	time, min[b] 50%	100%
ruthenium	$RuCl_3$	70	(170)
rhodium	$RhCl_3$	7	20
palladium	$PdCl_3$	16	(90)
osmium	OsO_4	45	(110)
iridium	$IrCl_4$	32	(80)
platinum	H_2PtCl_6	9	17
(platinic oxide)	PtO_2	14	27

[a] 0.2 mmol for 40 mmol of 1-octene. – [b] Values in parentheses are estimated times for complete reaction.

Modifications to the selectivity and activity of platinum metal blacks brought about by reaction variables such as temperature, pressure and amount of catalyst are well known and comment on them here will be restricted to noting the principle reviews and a few examples. General accounts and reviews of the effect of these factors have been given by [5, 7, 8, 9] for both supported and unsupported catalysts where the results are frequently very similar. The effect of temperature in the hydrogenation of p-cresol to isomeric methylcyclohexanols over platinum black was small, but there was a definite tendency towards increased formation of the trans isomer as the temperature was increased (58% at 26°C and 63% at 100°C). Changes in selectivity have also been noted with increases in reaction pressure [23]. Rhodium black at 50 psi (~3.372 kg/cm^2) hydrogenates propionitrile in 77% yield to dipentylamine, while at 1400 psi (~94.419 kg/cm^2) over this catalyst the product is 100% pentylamine [42]. The early literature was extensively reviewed for effects caused by changes in the catalyst-to-substrate ratio [54]. In the catalytic hydrogenation of pyridines, with these compounds a solvent is frequently essential. Thus, with nicotinic acid extensive decarboxylation occurs in the absence of solvent. Satisfactory hydrogenation without decarboxylation could, however, be achieved by carrying out the reaction with aqueous sodium bicarbonate solution as solvent. Again the reduction of 2-β-hydroxyethylpyridine over ruthenium black took 4 h in the absence of solvent, but was complete in less than 5 min when ethanol was used as solvent [26]. Large solvent effects were obtained in the hydrogenation of ethylacetoacetate over platinum black. The results are shown in the table below [47].

Hydrogenation of ethylacetoacetate over platinum black:

solvent	product % ethyl-butyrate	% ethyl-β-hydroxy-butyrate
water	90	10
hexane	92	8
acetic acid	95	5
ethylether	47	53
tetrahydrofuran	52	48

Certain metals, when added to a platinum catalysed hydrogenation of an aliphatic or aromatic aldehyde, can improve the activity and selectivity of the reaction. The best additives appear to be iron salts or zinc acetate, although manganese, cobalt, nickel, chromium, vanadium, osmium, palladium, uranium and even sodium hydroxide modified the behaviour of platinum in aldehyde hydrogenations. Ferrous salts or zinc acetate were used to accelerate the rate of hydrogenation of benzaldehyde and heptaldehyde, and to modify the selectivity of unsaturated aldehyde reductions, to produce high yields of the unsaturated alcohols [55 to 58]. These results were confirmed by [59, 60]. Stannous chloride had a much greater promoting effect on the hydrogenation of valeraldehyde than ferrous salts, and also accelerated the reduction of acetone and ethyl cinnamate, but not cyclohexene. The stannous chloride promoted hydrogenation of valeraldehyde over platinum passed through its maximum activity at 25°C, temperatures above or below this giving decreased rates. Ethanol proved to be the best solvent for the promoted hydrogenation [55 to 58]. Using promoters with heptaldehyde as substrate and platinum black catalysts, confirmed that stannous chloride is a potent promoter of aldehyde hydrogenation. Also gaseous oxygen can function as a promoter of aldehyde reductions [60]. Ferric chloride can modify the behaviour of platinum black towards ethylacetoacetate hydrogenation. With a sample of commercial platinum black the product distribution was 90% ethylbutyrate and 10% ethyl β-hydroxybutyrate, when a small quantity of ferric chloride was added to the hydrogenation the product was 100% ethyl β-hydroxybutyrate. Promotion of nitrile hydrogenation by lithium hydroxide has also been reported. Adiponitrile was hydrogenated over rhodium black and a 35% yield of hexamethylenediamine was obtained which was increased to 85% by the addition of lithium hydroxide [42].

Almost all work on the effect of agitation on the activity and selectivity has been conducted with supported catalysts. However, the results of such studies are generally applicable to liquid phase hydrogenations and papers such as [61] or [62] should be consulted for details. A more detailed description of reactor parameters including agitation in catalytic hydrogenation has been given by [63]. In the hydrogenation of acrylic acid and decomposition of hydrogen peroxide, ultrasonics improved the rate of hydrogenation by a factor of 2 over platinum black and a factor of 3 over palladium black. Hydrogen peroxide decomposition increased by factors of 10 over platinum black and 2.5 over rhodium black [64].

Sources of hydrogen for catalytic reductions other than gaseous hydrogen may be utilised with platinum-group metals, where hydrogen bound chemically in a compound such as cyclohexene, isopropanol, hydrazine, etc., may be used to hydrogenate carbon-carbon double and triple bonds, nitro groups, nitriles, etc. The subject was reviewed up to 1974 by [65], for a review about hydrazine as a hydrogen source in hydrogen transfer catalysis, see [66]. The place of platinum-metal catalysts in silicon chemistry, including hydrosilyation of olefins, addition of silanes to olefins, diolefins and substituted olefins, hydrosilylation of olefins, addition to nitrosofunctions, dehydrogenation of silanes and carbon-silicon bond cleavage was reviewed by [67].

Raney ruthenium was highly active in ammonia synthesis at temperatures between 250 and 350°C. Addition of potassium (0.97 mmol/g catalyst) to the Raney catalyst caused a tenfold increase in activity between 100 and 300°C without a change in activation energy (19 kcal/mol). Surface area of the potassium-treated Raney catalyst decreased to one third of its original value [68]. In an ammonia synthesis catalyst only a portion of the aluminium content of the alloy is removed by leaching and the remaining aluminium promotes the catalyst's ammonia synthesis properties [62].

The promotion of Raney nickel catalysts by platinum-group metals has attracted some attention from both academic and industrial workers, although they have never achieved an important industrial use. It was discovered, early in 1936, that treating Raney nickel with alkaline chloroplatinic acid increased the rate of hydrogenation of methyl-ethylketone. Subsequent experiment showed that not all of the platinum-group metals were as effective as platinum in enhancing catalyst activity. Thus in the hydrogenation of ethylacetoacetate the order of enhancement was $Pt \approx Os \approx Ir > Ru \approx Rh > Pd$ [70].

In the hydrogenation of nitroguanidine, nitrobenzene, benzaldehyde and unsaturated natural oils, up to nine times the activity of Raney nickel could be obtained by treating the base metal catalyst with minute amounts of platinum. The enhancement of activity was general for a large range of organic functions [71 to 74].

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Catalysis in the Fine Chemicals Industry

Fine chemicals can be defined as "chemicals that are manufactured to high and well defined standards of purity" [1]. The industry includes the manufacturing of pharmaceuticals, flavourings, fragrances and perfumes, food chemicals, agricultural chemicals, photographic chemicals, anti-oxidants for the rubber industry, dye stuffs and such like. From the point of view of the use of unsupported platinum metal catalysts the list may be shortened to physiologically active substances for the pharmaceutical industry and fragrances, etc., for the cosmetic industry.

Both industries were founded on natural products, the pharmaceutical industry being the first to produce and use synthetic materials. With the inception of synthetic routes to firstly natural chemicals and later to physiologically active non-natural substances, hydrogenation became an important unit operation and unsupported finely divided platinum metals were widely used in industrial liquid-phase reactions for the first time. Improvements in the manufacture of supported catalysts and the discovery of homogeneous platinum metal catalysts resulting in better utilisation of the platinum metal active centres, coupled with a better understanding of the factors controlling their activity and selectivity, has led to the replacement of unsupported catalysts, until today when virtually no unsupported finely divided catalysts are used in fine chemical production.

The global sale of human and vetinary drugs produced in the USA reached \$ 17×10^9 in 1978 with the domestic market accounting for the lions's share of \$ 9.9×10^9 [2]. The fragrances market is an altogether smaller business, perfume and flavour materials having sales of \$ 0.21×10^9 in 1977 [3]. The quantity of materials produced also differs in the two industries, most pharmaceuticals being produced in pounds (lbs) per annum quantities [4], while fragrances are produced in the ton or hundreds of tons per annum scale [3]. This has meant that production is usually based on batch processing rather than continuous production and generally pressures of operation are low, both factors favouring platinum metal catalysts.

Review articles have appeared dealing with parmaceuticals [2] and flavourings and fragrances [3], the synthesis of fine chemicals with platinum metal catalysts [5], the use of platinum and palladium in the pharmaceutical industry [4], monohydric alcohols in the flavouring and fragrance industry [6], and the total synthesis of vitamins employing palladium catalysis [7].

Some of the more important synthetic routes to pharmaceutical fragrance products are outlined below, together with a number of processes utilising platinum metal catalysts for the hydrogenation of organic functions in natural or seminatural products.

Pseudoionone and β-Ionone. The preparation of pseudoionone and β-ionone from acetylene and acetone has been outlined in [6 to 8], with the detailed chemistry given in [9], while an alternative route starting with isoprene was described by [10]. Both routes converge at the dehydrolinalool stage. The acetone-acetylene route or Roche process was described in detail by [8].

One of the important steps in this synthesis, the hydrogenation of acetylenic bonds to olefinic bonds, occurred at an early stage in the preparation with the reduction of methylbutynol over a lead or bismuth poisoned palladium black catalyst [11].

Materials important to the fragrance industry are formed at several points in the synthesis, methylheptenone, citral and β-ionone. Also others may be made by hydrogenation of intermediates over poisoned palladium black catalysts such as linalool, linalylacetate, tetrahydrolinalool. Analogues and homologues of linalool, citral and ionone can be produced by substituting another ketone for acetone. By esterifying dehydrolinalool with cinnamic acid, benzoic acid, etc., followed by selective hydrogenation over lead poisoned palladium black, a whole range of linalool esters are made available to the perfumer. Citral forms one of the starting points for vitamin A, vitamin A ester and vitamin E production. The following table shows the US consumption of citral, linalool, geraniol, etc., for various years.

product	year	production (lbs)	comments
citral	1969	3×10^5	—
ionone (for perfumes)	1967	8.5×10^5	from 1.2×10^6 lbs citral
vitamin A & ester	1967	1.7×10^6	from 5.6×10^6 lbs citral
vitamin E	1967	6.4×10^5	from 1.6×10^6 lbs citral
linalool & esters	1962	1.1×10^6	—

product	year	production (lbs)	comments
geraniol	1969	2.3×10^6	—
citronellol	1969	9×10^5	from 10^6 lbs citronellal
hydroxycitronellal	1969	5.5×10^5	from 6×10^5 lbs citronellal

Vitamin A. The key step in the production of vitamin A and its analogues is the selective hydrogenation of the highly unsaturated intermediates in the chain of synthesis, e.g. 1,6-dihydroxy-3,7-dimethyl-9-(2^1,2^1,6^1-trimethylcyclohexenyl)-2,7-nonadiene-4-yne to vitamin A [4].

The hydrogenation originally used a lead poisoned palladium black catalyst [11], but this has now been replaced by a calcium carbonate supported palladium catalyst.

Vitamin B_6-Pyridoxine. The hydrogenation is carried out in two stages. Firstly, hydrogenation of a nitro group is accomplished over platinum black prepared by the in-situ reduction of Adams platinum oxide. The solvent is 95% ethanol-water. The product is crystallised, dissolved in glacial acetic acid and the nitrile group reduced over a mixed catalyst system consisting of Adams platinum oxide and 5% palladium on charcoal [4, 12].

Dihydrostreptomycin. Hydrogenation of the free aldehyde group in the sugar fraction of the streptomycin molecule, to an alcohol group, allows this valuable antibiotic to be prescribed for patients who have become sensitive to streptomycin itself. The product, dihydrostreptomycin, is as active as the parent molecule [4].

The hydrogenation is conducted in an aqueous medium at room temperature and under atmospheric pressure of hydrogen with either a platinum or palladium black catalyst [13].

Cortisone. This drug is manufactured from bile acids and involves the hydrogenation of a 12-ketosteroid to a 12-hydroxysteroid [4]. The reduction is carried out in methanol solution over a platinum black catalyst at room temperature and 1 atm hydrogen pressure. The yield of cortisone is between 80 and 90% of theoretical [14].

Ephedrine. Ephedrine or laevo-1-phenyl-2-methylaminopropanol-1 is obtained by the reductive amination of laevo phenylpropanolone with methylamine.

The starting material 1-phenylpropanolone is obtained by fermentation of sugar in the presence of benzaldehyde (Neuberg fermentation). The reductive amination was conducted over a colloidal platinum catalyst at room temperature and pressure in the presence of a 33% methylamine solution [15].

Vitamin B_2. Riboflavin is produced by reductively condensing tetraacetyl-d-ribonitrile and 4,5-dimethylaniline in the presence of a palladium black catalyst to form N-tetra-acetyl-d-ribityl-4,5-dimethylaniline [4]. Coupling the latter with p-nitrophenyldiazoniumchloride and reducing the reaction product in the presence of platinum black to form 1-N-tetra-acetyl-ribitylamino-2-amino-4,5-dimethylbenzene. This is then reacted with 5,5-dichlorobarbituric acid to form tetra-acetylriboflavin, which can be hydrolysed to riboflavin [16].

β-Phenylethyl Alcohol. Palladium black together with Raney nickel has been used as a mixed catalyst for the hydrogenation of styrene oxide to perfumery grade β-phenylethanol. Only very small quantities of palladium are required to activate the nickel catalyst (0.5% palladium, 99.5% Raney nickel). The temperature of the reduction is 30 to 40°C at a hydrogen pressure of 50 psi (~ 3.4 kg/cm^2) rising to 200 psi (~ 13.5 kg/cm^2). The yield of β-phenylethanol was 91%. Lower yields were obtained when either catalyst component, Raney nickel or palladium black was used alone [17].

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Hydrogen Production by Electrolysis

Hydrogen is made mainly from natural gas and petroleum fractions, with petroleum refining accounting for most of this manufacture. However, production of hydrogen and oxygen by the electrolysis of water has also been used industrially for many years. This is mainly due to requirements for high purity products in, for example, the food industry, or where relatively small uses preclude building large scale reformer plants. Hydrogen is also formed as a by-product in the chlorine/caustic soda manufacturing industry during the electrolysis of brine solutions [1].

The economics of hydrogen production techniques have been assessed by [2]. The possibility of using hydrogen as a means of energy distribution substituted for natural gas was examined by [3]. It was concluded that electrolysis using off-peak nuclear energy could be viable in the period 1990 to 2000 in the UK [4].

Progress in a water electrolysis programme conducted by the European Communities has been reviewed. A number of promising concepts have been developed to the small prototype stage and long term testing is in progress [5].

Methods of increasing the efficiency and lowering the capitcal cost of state of the art electrolysers by catalysing their electrodes are reviewed. The oxygen and hydrogen evolution characteristics of precious metal and various base metal electrodes are compared [6].

Electrolysers using a solid polymer electrolyte (SPE) such as perfluorosulphonic acid polymer have found a number of applications including spacecraft and submarines [7]. In these cells, catalysts are deposited directly on to the polymer membrane. Methods of depositing noble metal catalysts and their performance characteristics are discussed. The anodic overvoltage was found to increase in the order $Ir < Rh < Rh/Pt < Pt/Ru < Pt < Pd$ [8].

Using a cathode and anode of Pt and Ir, respectively, the cell voltage was 1.56 to 1.59 V at 500 mA/cm^2 and 90°C, corresponding to a thermal efficiency of 93 to 95% [8].

Oxygen evolution and reduction reactions are the chief causes of efficiency losses in electrolysers and fuel cells. The kinetic parameters of this electrode have been studied [7, 9, 10].

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4.2.2.2 Dehydrogenation

Dehydrogenation reactions have a broad synthetic utility, being used to oxidise alcohols to aldehydes and ketones, hydrazo to azo compounds, removal of hydrogen from heterocyclic rings, removal of hydrogen from carbocyclic rings, dehydrocyclisation etc. Only dehydrocyclisation and removal of hydrogen from carbocyclic and heterocyclic ring systems employ platinum-group metals. Dehydrocyclisation forms an important area of petroleum refining catalytic chemistry utilising supported platinum and palladium catalysts, and has been reviewed by [1]. This section will concern itself only with hydrogen removal from carbocyclic and heterocyclic ring systems and the formation of secondary and tertiary amines by dehydrogenative coupling of primary and secondary amines.

The catalytic dehydrogenation of polycyclic hydroaromatic compounds has recently been reviewed and contains a section devoted to the dehydrogenation of these compounds over platinum metal catalysts. The temperature at which dehydrogenation occurs is a function of the structure of the hydroaromatic compound, and can be as low as 80°C, although normally temperatures of ~250 to 300°C in the absence of solvent are used. When a solvent is present the reaction is carried out at the reflux temperature. Some solvents can act as hydrogen acceptors to remove hydrogen from the reaction zone. In their absence the reaction medium is usually swept by a stream of inert gas, such as nitrogen, to remove hydrogen and provide stirring of the reaction mixture. Cumene, p-cymene, decalin, nitrobenzene, naphthalene, quinoline and 1-methylnaphthalene have all been used as solvents, but the recently introduced polyglycol ethers, such as diglyme and triglyme have the advantage of a wide reflux temperature range and, because of their solubility in water, are easily removed from the product mixture [2].

The most effective catalysts are palladium and platinum. Unsubstituted hydroaromatic molecules usually dehydrogenate smoothly with good yields of the corresponding aromatic compound. Five-membered fused rings generally fail to dehydrogenate, and the same is true of any six-membered ring which is incapable of becoming a fully aromatic arene. The first stage of dehydrogenation is frequently that of disproportionation. For example, octalin forms decalin and tetralin in a 2:1 ratio and 9,10-dihydroanthracene disproportionates to anthracene and 1,2,3,4-tetrahydroanthracene.

For detailed descriptions of the dehydrogenation of hydroaromatic compounds over platinum and palladium black, see [6 to 20].

Subsequently decalin and tetralin dehydrogenate to give naphthalene, but the reaction rate with decalin is much lower than that of either octalin or tetralin.

Substituted hydroaromatics can lose or rearrange substituents, although this is not generally a problem with alkyl substituents. Dehydrogenation of alkyl side chains occurs only rarely. Halogen atoms are normally lost during dehydrogenation, and decarboxylation of carboxylic acid substitution is fairly frequent. Polycyclic alcohols will undergo both dehydrogenation and dehydration to yield the corresponding polycyclic aromatic hydrocarbons. Polycyclic ketones generally dehydrogenate to give phenols, although some dehydration may occur. α-Tetralone partially dehydrogenates to 50% α-naphthol and 50% naphthalene over platinum black. Only 58% of the starting material dehydrogenated [3].

The dehydrogenation of both sulphur and nitrogen containing heterocyclics has been reviewed. As with hydroaromatics, both platinum and palladium are good dehydrogenation catalysts. Temperatures of operation range from 200 to 300°C [4].

Primary and secondary amines may be dehydrogenated with coupling to form in high yield unsymmetrical secondary and tertiary amines over palladium black. Temperatures of up to 250°C are used with stirring. Reaction times are between 3 and 20 h. Results obtained with a variety of primary and secondary amines are shown in the following tables [5].

Products of the reactions of primary and secondary amines [5]:

amines $R^1CH_2NHR^2$ R^1	R^2	temp., °C	time, h	product yield (%)[a] $(R^1CH_2)_2NR^2$	$R^1CH{=}NCH_2R^1$	conversion (%)[d]
C_6H_5	H	80	5	45	45	90
$CH_2{=}CH$	H	25	5	—	95[b]	95
C_6H_5	CH_3	120	20	85	—	28
H	C_6H_5	120	20	98	—	7
CH_3	C_6H_5	150	48	98	—	5
n-C_3H_7	CH_3	160	5	85[c]	—	70

[a] Yields based on unrecovered amines. – [b] $CH_3CH_2CH{=}NCH_2CH{=}CH_2$. – [c] Another product was $(n\text{-}C_4H_9)_3N$ (8%). – [d] Conversions based on unrecovered amines are easily improved by prolonged reaction time or higher temperature.

Reactions of secondary amines with either primary amines or secondary amines [5]:

amines $R^1CH_2NHR^2$ R^1	R^2	R^3NHR^4 R^3	R^4	temp., °C	time, h	product yield (%)[a] R^1CH_2-NHR^3R^4	$R^1CH{=}NR^3$	conversion (%)[b]
C_6H_5	CH_3	n-C_6H_{13}	H	120	10	55	30	37
C_6H_5	CH_3	C_6H_{11}	H	120	10	10	90	40
C_6H_5	CH_3	C_6H_5	H	120	20	48	52	40
C_6H_5	CH_3	$H_2N(CH_2)_2$	H	120	10	95	—	24
H	C_6H_5	n-C_6H_{13}	H	120	40	98	—	5

amines				temp., °C	time, h	product yield (%)[a]		conversion (%)[b]
$R^1CH_2NHR^2$		R^3NHR^4				R^1CH_2-NHR^3R^4	$R^1CH{=}NR^3$	
R^1	R^2	R^3	R^4					
n-C_3H_7	CH_3	n-C_6H_{13}	H	160	7	75	—	45
C_6H_5	CH_3	n-$CH_3(CH_2)_3$	CH_3	120	10	80	—	55
C_6H_5	CH_3	$(CH_2)_5$	—	130	10	97	—	90
C_6H_5	CH_3	$(CH_2)_4$	—	130	10	75	—	75
n-C_3H_7	CH_3	$(CH_2)_5$	—	160	5	98	—	85

[a] Yields based on unrecovered amines. – [b] Conversions based on unrecovered amines are easily improved by prolonged reaction time or higher temperature.

Early work on catalytic dehydrogenation was reviewed up to 1948 [21].

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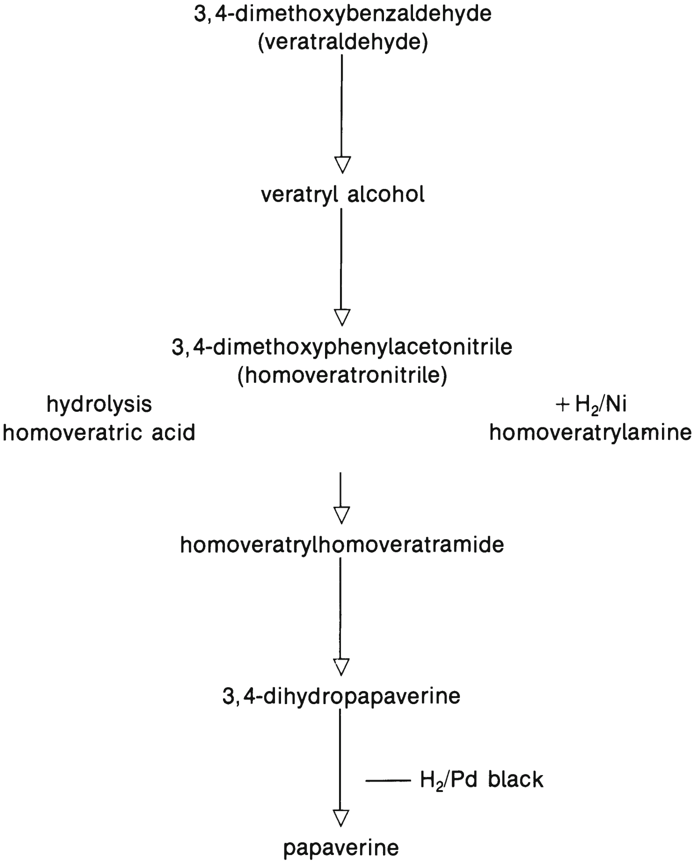
Dehydrogenation in the Pharmaceutical Industry

Dehydrogenation is not a widespread practice in the pharmaceutical industry. The most notable example is that of the production of papaverine. The supply of papaverine from opium was insufficient to satisfy the medical uses and efforts were made to manufacture the drug by a purely synthetic route. One successful method was started with a cheap organic 3,4-dimethoxybenzaldehyde (veratraldehyde). The preparation is shown in outline below [1]. The conversion of 3,4-dihydropapaverine by dehydrogenation to papaverine was originally discovered by [2] and subsequently modified by [1]. It employs tetralin as solvent at a temperature of 240 to 250°C. Yields of 95% theoretical for this stage have been obtained.

Outline preparation of papaverine from veratraldehyde:



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4.2.2.3 Oxidation

Oxidation is one of the mainstays of the present chemical industry. Fifteen of the top fifty chemicals produced in the USA in 1981 were manufactured wholly or in part by oxidative processes, and accounted for 28% by weight of their total production. The inorganics (sulphuric acid, nitric acid and ammonium nitrate) made up three quarters of the weight of chemicals produced by oxidative routes [1].

Platinum has had a long history of use in oxidation reactions starting at the beginning of the nineteenth century and continuing to the present day. In the inorganic field the oxidation of ammonia, ammonia plus methane, carbon monoxide and sulphur dioxide have all been catalysed over platinum, and only in the last case, sulphur dioxide oxidation, have base metals become the predominant catalyst type [2].

With organic reactants, oxidation over platinum metals tends towards complete oxidation to carbon dioxide and water, so that the industrial catalyst chemist, concerned mainly with oxygen insertion reactions for the manufacture of oxygenated products, has turned almost exclusively to the base metals and their oxides as catalysts [3]. Attempts continue, however, to modify the catalytic properties of the platinum metals to improve the selectivity for oxygen insertion and solutions to some of the problems which are given in Sections 4.3 and 4.4.

The number of large-scale chemical oxidation processes using unsupported platinum or platinum-alloy catalysts is limited. In general only two commercial systems are in use, firstly the oxidation of ammonia to nitric oxide as the first stage in the production of nitric acid and hence nitrogenous fertilisers, and secondly, the oxidation of ammonia and methane to form hydrocyanic acid as a precursor to the formation of acrylonitrile and its derivatives.

Both processes are important industrially. Annual capacity of nitric acid for 1963, 1966 and 1971 is shown in the table below. The weight of platinum and its alloys in use to maintain these industries makes unsupported catalysts the major industrial user of platinum. The catalyst is normally employed in the form of woven gauze [4].

The process of oxidation causes physical modifications in the catalyst resulting in facetting and the formation of surface growth. Chemical interactions also occur resulting in a loss of platinum from the catalyst. The lifetime of the catalysts used is limited by several factors, such as loss of mechanical strength, or loss of activity resulting from surface rhodium enrichment or poisoning.

Estimated world nitric acid production capacity (million MT. 100% HNO_3) [4]:

	1963	1966	1971
West Europe	10.1	12.5	15.4
North America	3.8	6.4	8.8
Latin America	0.6	0.6	0.8
Asia	1.8	2.5	4.0
Africa	0.6	1.0	1.8
Australia	0.1	0.1	0.3
socialist countries	3.8	5.0	8.0
total:	20.8	28.1	39.1

Liquid phase oxidations over unsupported platinum metals are rare, but one small industrial use is that of the insertion of a tertiary 12a-hydroxyl group into a pharmaceutical, dedimethylamine-12a-desoxytetracycline, to produce dedimethylaminotetracycline. The catalyst is platinum black prepared by prehydrogenating Adams platinum oxide:

Catalytic oxidation has been considered from a theoretical point of view [6, 7, 8], while technical reviews of ammonia oxidation have been published by [2, 4, 9]. The Andrusov process for hydrogen cyanide has also been reviewed by [2].

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Ammonia Oxidation

The oxidation of ammonia to nitric oxide over platinum gauze catalysts became a commercial process in the early years of the twentieth century largely due to the work of Ostwald [1]. The process rapidly gained importance with the development of the synthetic ammonia industry and the nitrate requirements for munitions in blockaded Germany during the First World War. Industrial plants were mainly atmospheric pressure plants during the early days [2].

During the past 70 years the process and catalysts used have not changed substantially although the pressure of operation and capacity of plants has increased. Some plant constructors have opted for high pressure (7 to 10 atm) operation (mainly in the USA), whilst others operate at medium pressure (3 to 5 atm). The most recent plant installations have opted for an integrated plant with medium pressure oxidation and high pressure adsorption with plant capacities of up to 2000 t/d.

The basis of the process has been described by many authors, and can be written in simple form as (1) $4NH_3+5O_2 \rightarrow 4NO+6H_2O$, $\Delta H_{298}=-216.7$ kcal. If a mixture of ~10% ammonia and air are passed over a platinum or platinum-alloy catalyst with a degree of preheat sufficient to reach a temperature of 900°C, then a nitric oxide yield from reaction (1) of the order of 95% will occur. Alternative side reactions can occur: (2) $4NH_3+3O_2 \rightarrow 2N_2+6H_2O$, $\Delta H_{298}=-302$ kcal; (3) $4NH_3+6NO \rightarrow 5N_2+6H_2O$, $\Delta H_{298}=-432$ kcal. The lower enthalpy of reaction (2) favours the formation of nitric oxide at high temperatures [3].

The precise mechanism by which the reaction (2) occurs has not been positively identified. Three main theories have been developed over the years. An early theory by [5] was developed and the reaction of ammonia with absorbed oxygen proposed as follows: $NH_3+O \rightarrow NH+H_2O$; $2NH+2O_2 \rightarrow 2HNO_2 \rightarrow NO+NO_2+H_2O$ [4]. This is generally called the imide theory.

The nitroxyl theory involves the reaction of ammonia with molecular oxygen: $NH_3+O_2 \rightarrow HNO+H_2O$; $HNO+O_2 \rightarrow HNO_3$ [7, 8].

However, if oxygen is absorbed it is generally accepted to be in atomic form.

A third theory requires that hydroxylamine be formed initially and hence: $NH_3+O \rightarrow NH_2OH$; $NH_2OH+O_2 \rightarrow HNO_2+H_2O$. In this instance experimental evidence was obtained of hydroxylamine in the product when ammonia was oxidised over a platinum wire at low pressures [9].

Throughout the decades the catalyst alloy used has been studied with the aim of producing stronger, more active, more poison-resistant and lower platinum-loss catalysts. 5% Rh/Pt and 10% Rh/Pt alloys were found to be most advantageous [10]. In a comprehensive paper the effects of rhodium content, temperature and flow rate, and the effect of catalyst loading on conversion efficiency were recorded [11]. More recent papers record the yield obtained over a further range of platinum-alloy catalysts and again demonstrate the superiority of rhodium alloys for the oxidation of ammonia [12, 13].

The effects of use on the catalyst surface have been examined by many workers. Scanning and transmission microscopy was used to examine the outgrowth described by [14] and the surface was described in terms of morphology and rhodium content, relating surface structure and chemistry to efficiency [3]. Surface attack occurs initially at grain boundaries and mobile promontories are formed on rhodium containing alloys, but not on pure platinum [15]. Hollow surface outgrowth was found on rhodium alloys employed in ammonia oxidation and cyanide production [16].

Under reaction conditions, on 10% Rh/Pt wires oxidising ammonia-air mixtures in the controlled atmosphere at temperatures of 890 to 925°C, the surface of the wire was remarkably mobile, knolls and promontory outgrowths occurring and moving along the wire length, coalescing and forming outgrowths and crystalline platelets akin to those seen on working and spent gauzes [15]. The subject of morphological change has been reviewed [34] and a "phase diagram", reproduced below as **Fig. 22**, of catalytic etching features produced on platinum during ammonia oxidation reactions was published [35].

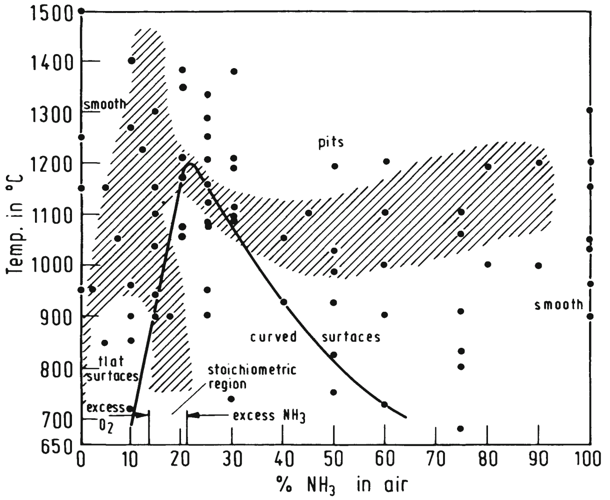

Fig. 22. Phase diagram for catalytic etching of Pt in NH_3 oxidation. Points represent scanning electron microscope observations of 0.010 inch diameter wires which had been heated in NH_3/air for 1 h; the curve indicates the "adiabatic" wire temperature which would be obtained by reaction heat alone.

More recently the redispersion of rhodium and rhodium-platinum particles and the surface enrichment of rhodium-platinum particles with rhodium under typical ammonia oxidation conditions were examined [33, 36].

The losses experienced during use have been studied over a long period by [10], and more recently a theory to explain the losses was proposed by [17, 18]. Its correlation varies from measured volumes by a factor of 4 according to [16].

Examinations of the parameters affecting the overall performance of the ammonia oxidation reaction have been made by [3, 13, 19, 20, 21]. Mathematical treatments based upon the kinetics of the reaction have been undertaken. The rate-controlling step was determined to be mass transfer to the catalyst surface [22], flow effects were studied by [18]. For work on reactor and plant design see [23]. A model taking into account ageing, feed temperature, ammonia contact, gas charge and gauze parameters was developed by [24].

Since ammonia oxidation first became a commercial process for the manufacture of nitric acid, plant design, materials of construction and costings have received a great deal of attention. In recent years many papers describing the latest plant designs and constructions have been published. A new plant installation at U.S. Steel's nitrogen plant was described in 1958 [25], a new high pressure plant in 1960 [26] and 1961 [27]. More general papers on the choice of new plant and costings were published by [28, 29, 30], while some work has been published on the estimation of catalyst requirements [31]. For the recovery of platinum lost during oxidation the use of catchment or "getter" alloys is described which can recover up to 60% of the lost platinum [32].

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Hydrogen Cyanide Formation

Hydrogen cyanide requirements are related to the demand for acrylonitrile and its derivatives which account for the majority of the hydrocyanic acid produced. Several commercially feasible routes are available for the production of HCN, but in practise only two are employed [1]. Of the two processes, one, the "Andrussow" process accounts for most of the world production; it was first described in [2]. There are many variants of the basic concept to be found in the patent literature [3 to 6]. In general an unsupported Rh/Pt alloy catalyst is used, although Pt supported on "beryl" can also be used.

The Andrussow process may be operated in two slightly differing ways. Both are used.

The basic process may be expressed as: $NH_3 + CH_4 \rightarrow HCN + 3H_2 - 60$ kcal. The reaction is highly endothermic and hence heat must be added to maintain the reaction at 1000 to 1200°C. Problems of carbon deposition have also been noted [7]. Despite these difficulties, the process has been used for large scale production [8].

The more common approach is to operate with an air addition to the fuel gas to produce an autothermal process viz: $NH_3 + CH_4 + \frac{3}{2}O_2 \rightarrow HCN + 3H_2O + 115$ kcal. The highly exothermic nature of the reaction allows the catalyst to run at 900 to 1100°C and be self-sustaining [1]. The feed gas employed is normally 13% methane, 10 to 12% ammonia, the balance being air. For satisfactory operation the feed gas is preheated to 400 to 500°C prior to passage over the gauze catalyst [9]. The catalyst normally comprises layers of 5 or 10% Rh/Pt alloy woven to 1024 mesh from 0.06 or 0.076 mm wire [10]. Optimum conversion is normally obtained with catalyst contact times of the order of 0.3 ms [10]; such reaction yielding HCN with a conversion of 60 to 67% based on ammonia, and 53% based on methane, in a single pass [1].

The mechanism of the reaction has been a subject addressed by several authors. A similar scheme to that proposed for ammonia oxidation to nitric oxide is: (1) $NH_3 + O_2 \rightarrow NH_3 \cdot O_2 \rightarrow HNO + H_2O$; (2) $HNO + CH_4 \rightarrow HNO \cdot H_2CH_2 \rightarrow HN \cdot CH_2 + H_2O$; (3) $HN \cdot CH_2 \rightarrow HCN + H_2$ [11].

A portion of the methane may be oxidised to CO and H_2O, possibly via H_2CO as an intermediate. It was suggested that HCN may be formed through methylamine as an intermediate viz: $H_2CO + NH_3 \rightarrow H_2CNH + H_2O$ [12]. The reaction results in morphological changes in the catalyst and an accompanying loss of Pt – normally ~0.6 g/t [10].

Several other authors have examined the process in detail. Attempts to calculate catalyst requirements based upon the hypothesis that NH_3 diffusion was the controlling step, were made by [13, 14], attempts to optimise HCN yield by mathematical correlation by [15]. This work was continued and yield related to contact time. The relationships between catalyst activity, campaign life, morphological changes, crystal structures and gauze impurities were examined [16].

The structure of used gauze catalysts was examined proposing a mechanism by which the porous and friable used gauze structure could be formed [18] examining the physical and chemical character of catalyst gauzes, it has been claimed that additions of H_2S improve early campaign yields and that the structures of catalysts treated in this way are different [18].

Whilst most plants operate at atmospheric pressure, it was recorded by [18] that operation pressures of 2 to 3 atm could improve yield by 7 to 9% from work by [19].

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4.2.2.4 Energy Generation

Platinum-group metals are widely used as catalysts in low and intermediate temperature fuel cell power generators. Currently, a considerable research effort is in progress to harness solar radiation for hydrogen production or direct electricity generation, although commercial systems for the latter are generally considered to be some years away [1].

The fuel cell is a device for converting chemical energy directly to electrical energy. In its simplest form, it is the direct converse of water electrolysis. The first experiments involved the use of platinised platinum foil in tubes of oxygen. A number of these in series proved capable of providing sufficient voltage and current to electrolyse solutions [2, 3].

The fuel cell is essentially an engine, in that fuel and oxidant are supplied to it from external containers, and power is produced as long as reagent flow continues. This distinguishes them from batteries, which store energy in situ, and cannot be easily replenished except by recharging electrically or mechanically. The mode of operation of fuel cells and the function of the catalyst have been described by [4]. For developments in fuel cell technology over the past 25 years, see [5]. Early work which led to the development of fuel cells for spacecraft powerplants in Apollo and the Space Shuttle Orbiter are recollected, together with later work on cells for terrestrial application and speculation on future courses of research [6].

A review of reformer systems to convert hydrocarbons to hydrogen for consumption in fuel cells, and hybrid cells, such as zinc air where battery electrodes (zinc or aluminium) are used in conjuction with fuel cell electrodes and atmospheric oxygen, to produce batteries with exceptional energy density, is given in [7]. An assessment of air cathodes for this application has been made by [8].

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Fuel Cells. Since the fuel cell is an electrochemical device rather than a heat engine, it is not limited by the effect of the Carnot cycle. Whereas the most efficient large power stations, for example, are limited to 33 to 36% overall thermal efficiency, the fuel cell has the potential for considerably higher efficiency. In practice, energy losses are encountered in (1) fuel processing (that is, converting a hydrocarbon or coal fuel into hydrogen), (2) as ohmic resistive losses in the fuel cell, and (3) in converting the direct current output of the fuel cell into alternating current to feed into the load. Existing fuel cells are operating at up to 45% overall efficiency. Additional major benefits are that the efficiency is maintained for a range of outputs as low as 20% of maximum rated output, and for units ranging in size form a few kW up to multi-MW.

A considerable effort has been made in the past to utilise fuels directly in the fuel cell without reforming. The use of platinum-group metals in cells fuelled by hydrogen, ammonia, hydrazines and hydrocarbons was described by [1, 7], a fuel cell running on propane and methane by [9]. Research into direct oxidation of hydrazine as a fuel resulted in the construction of a number of units of up to 5 kW, although problems associated with handling the fuel have resulted in applications being very limited. Direct oxidation of methanol fuel in both acidic and alkaline electrolytes have been studied intensively. It is generally agreed that binary and ternary alloys of platinum metals and platinum metal/base metals show increased activity over the pure metal, and that Pt + Sn and Pt + Ru are the most active binary electrodes [3, 4, 5].

Direct oxidation of ammonia fuel has been demonstrated, but no viable cells have been built. Hyrogen/oxygen fuel cells running on cracked ammonia have been postulated for transport applications [6].

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4.3 Supported Metal and Metal Alloy Catalysts

4.3.1 Preparation and Reactions

The industrial preparation of supported platinum metal catalysts is to a large extent proprietary information and is only described in any detail in the patent literature. This has been reviewed for the period 1970 to 1978 in [1] and [2]. Reviews of the science and technology of catalyst preparation are to be found in [3 to 6].

The range of reactions for which supported platinum metals are used is vast, covering the refining and chemical industries as well as pollution control. For the purposes of this section only two major applications are described; that of the role of supported catalysts in the refinery industry and in the control of pollution. To these are added a potentially important application to the manufacture of synthetic liquid fuels via the Fischer-Tropsch reaction.

Reviews of the use of supported platinum catalysts in the chemical industry are to be found in [6 to 10], while a review of industrially proven catalysts is given in [11].

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4.3.1.1 Catalysis in the Petroleum Industry

Most of the catalytic reactions of interest to the petroleum industry involve the making and breaking of both carbon/carbon bonds and carbon/hydrogen bonds. In the former class are the important hydrogenolysis reactions and metal catalysed cyclisation and structural isomerisation of hydrocarbon chains. In the latter category fall the hydrogenation/dehydrogenation reactions involving both cyclic and acyclic substrates. These latter reactions are also of importance in bifunctional catalysts since olefinic substrates are in general much more reactive than paraffinic substrates and can be produced as reaction intermediates in low and thermodynamically controllable quantities by metal catalysed reactions.

Although the octane improvement of petroleum naphthas constitutes by far the major use of such PGM catalysts, worldwide amounting to some 30% of the total refinery crude oil distillation capacity, other uses are far from insignificant. Almost without exception alumina or silica-alumina (including crystalline zeolitic silica-aluminas) supports are used. Many of these catalytic uses of the platinum-group metals have their counterparts in corresponding base metal catalysts. In this competition the platinum-group metals are generally preferred on the basis of superior performance which relates to their superior selectivity, activity and/or operating stability.

In particular the very high specific activity of the platinum-group metals implies that very low concentrations of material are required. On the other hand the controllable moderate hydrogenolysis activity of such catalysts, particularly those based upon platinum and palladium, means that the catalyst surface is to a significant extent self-cleansing and high molecular weight material, which otherwise would accumulate and physically block the active catalyst surface, tends to be removed.

A true appreciation of this uniqueness, which has led to the successful commercial application of the platinum-group metals and their potential for future application, may be derived from the vast amount of comparative information which has been accumulated over the past few years on the nature and extent of these metal catalysed reactions.

Platinum-group metal catalysts in the petroleum industry:

process	PGM	support	typical conditions	comments
aromatic hydrogenation				
benzene	Pt		50 to 60 bar 200 to 350°C	cyclohexane nylon intermediate
jet fuel kerosene	Pd	Al_2O_3 + halide	200 to 350°C 50 to 100 bar	smoke point and/or colorific value; may be combined with hydro-isomerisation
hydroforming				
monometallic	Pt	Al_2O_3 + halide	25 to 35 bar 450 to 525°C	octane No. improvement

process	PGM	support	typical conditions	comments
bimetallic	Pt	Al_2O_3+	10 to 30 bar	
	Re	halide	450 to 525°C	
	Ge			
	Sn			
	Pl			
	Ir			
hydrocracking				
heavy oils	Pt Pd	Y zeolite	100 to 150 bar	jet fuel and
low qualitiy	Pt	Al_2O_3+	350 to 425°C	naphtha
naphtha		halide		production, C_3&
selective	Pt	small pore		C_4, removal
naphtha	Pd	zeolite		of low octane No.
selective	Pt			linear paraffin
fuel oil	Pd			catalytic dewaxing
hydroisomerisation				
C_4 C_5 C_6	Pt	Al_2O_3	5 to 40 bar	octane No. improvement
		+halide	100 to 300°C	alkylation feed
C_8 aromatics	Pd	Y zeolite	10 to 15 bar	ortho and para
			375 to 450°C	xylenes
fuel oil	Pt	small pore	30 to 100 bar	catalytic dewaxing
lubricating oil	Pd	zeolite	250 to 400°C	pour point
jet fuel				improvement
aromatic dealkylation				
hydrodealkylation	Rh	Al_2O_3	350 to 450°C	benzene
steam dealkylation	Pt	Cr_2O_3	10 to 20 bar	xylenes
trans alkylation	Pd	zeolites		
purification (impurity)				
H_2 (O_2)	Pd		0 to 70°C	normally at RT[*)]
CO by oxidation	Pt	Al_2O_3	50 to 150°C	but higher with
CO by reduction	Ru Pt		250 to 400°C	CO 50 to 150% excess O_2
ethylene/propylene	Pd	Al_2O_3	C_2 30 to 120°C	0 to 300 ppm CO used
(acetylenes, dienes		(+Cr_2O_3)	C_3 150 to 200°C	to improve
100 to 1000 ppm)			10 to 30 bar	selectivity
butylenes	Pd	Al_2O_3	C_2 30 to 120°C	
(acetylenes, dienes)		(+Cr_2O_3)	C_3 150 to 200°C	
			10 to 30 bar	
regenerator of	0 to 100 ppm		550 to 700°C	SO_3 trapped by
the gas (CO, SO_2)	Pt		0 to 2 bar	Al_2O_3 and recycled
				to the reactor $CO \rightarrow CO_2$

[*)] RT = room temperature

Metal-catalysed Reactions

A number of excellent reviews of this subject have appeared recently. Some of these have dealt with metal-catalysed reaction in general [1 to 7] whereas others have emphasized more some of the aspects in the use of bimetallic catalysts [8 to 16].

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Ethylene Hydrogenation

The relative order of decreasing activities apparently is Rh > Ru > Pd > Pt > Co > Ni > Fe. In such a sequence the correlation plots suggest that Pd and Pt are less active because the reaction intermediates are less stable and form less readily, whereas for the Co > Ni > Fe trial the reaction intermediates are apparently too stable. This picture takes an added significance when one compares the relative rates of hydrogenation between acetylene and ethylene which is commercially important in the selective removal of acetylenes from pyrolytic olefine streams. The order of decreasing selective activity for acetylene hydrogenation is Pd > Pt > Rh > Ru > Os > Ir.

J. R. Katzer, G. C. Schmit (Chemistry of Catalytic Processes, McGraw-Hill, New York 1979).

Hydrogenolysis of Ethane

Ethane hydrogenolysis can be taken as the simplest possible case for rupturing carbon-carbon bonds. The relative order for decreasing reactivity is apparently Os > Ru > Rh > Ni > Ir > Co > Fe > Pt > Pd [1] although elsewhere the order is given as Os > Ru > Rh > Ir > Ni > Co > Pd > Pt [2].

Kinetic studies have shown that this reaction is approximately first order in ethane, but of variable negative order (−1 to −3) in hydrogen. That is to say the reaction is inhibited by hydrogen. This inhibition is associated with a mechanistic model in which the ethane substrate becomes more or less extensively dehydrogenated upon absorption, the extent in general tending to increase with atomic number. A further possible consequence of this hydrogen stripping is that an adsorption site involves a number of contiguous active metal atoms or an ensemble of atoms and as such is very susceptible to selective surface poisoning, for example, by adsorbed sulphur impurities. Yet another consequence is that such extensive molecular disruption implies strong adsorption and the possibilities of further secondary reaction such as carbon laydown and more extensive decomposition. It is interesting to note that Pt and Pd which are the most frequently used platinum-group metals are perhaps the least active for hydrogenolysis [3].

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Hydrogenolysis of Higher Hydrocarbons

For higher hydrocarbons both the activity and selectivity of the reaction are important. Hydrogenolysis may involve a simple molecule rupture into two fragments or more extensive degradation to nothing but methane.

The order for activity given for normal pentane is similar to that for ethane hydrogenolysis: Ru > Os > Rh > Ir > Ni > Co > Fe > Pt > Pd but for the extent of hydrogenolysis the order changes to Fe > Co > Ni > Os > Ru > Rh > Ir > Pt > Pd from which it is seen that the metals of the first transition series whilst having intermediate activity are less selective than those of the platinum group.

R. Montarnal, G. Martino (Rev. Inst. Franc. Petrole Ann. Combust. Liquides **32** [1977] 367).

Hydrogenolysis of Cyclic Hydrocarbons

The ability of the group VIII metals to interconvert cyclic and acyclic hydrocarbons forms the basis of their utility in petroleum refining and underlies the commercial processes of aromatisation, dearomatisation and hydrocracking. The combination of simultaneous cyclisation/decyclisation reactions also provides one basis for structural isomerisation. All of these reactions are closely related to the simple hydrogenolysis activity discussed above both with regard to the ordering of activity and the ordering of the extent of hydrogenolysis. The optimum combination of activity and selectivity under aromatisation conditions apparently lies in the vicinity of Pt or Ir. Pd is apparently not active enough, whereas Ru and Rh become too unselective. The specific activity and selectivity may be fine tuned by selective poisoning with controlled addition of sulphur or, as is more frequently the case, by the use of bimetallic combinations.

Rather pronounced effects are found for the relative reactivity of compounds with different ring sizes. Thus for platinum black the relative reactivity with ring size is given as $C_3 > C_4 > C_5 > C_7 \gg C_6$.

In particular the cylcohexanes will frequently inhibit ring opening of the other cyclic paraffins because of their lower intrinsic reactivity.

Z. Paal, P. Tetanyi (in: G. C. Bond, G. Webb, Catalysis, Vol. 5, A Specialist Periodical Report, Reactions of Hydrocarbons on Metallic Catalysts, The Royal Society of Chemistry, London 1982, pp. 80/126).

Gasoline Reforming

Many comprehensive and excellent reviews of this very important industrial process have been published [1 to 8]; of these the earlier reviews [1 to 4] concentrate on the use of platinum based catalysts which were introduced to the petroleum industry by Universal Oil Products (UOP) in 1949. This was a vastly improved version of the existing hydroforming processes of that time, which were based upon alumina supported chromia or molybdena catalysts. A significant step forward in the art of gasoline reforming occurred with the introduction of a bimetallic catalyst (Pt-Re/Al_2O_3) by Chevron Oil Co. in 1967. At the present time most reforming catalysts are based upon multimetallic combinations.

Naturally occurring petroleum naphthas and many intermediate product naphthas produced by hydrocracking of heavier oil cannot be used in a spark-ignited internal combustion engine because they tend to spontaneous ignition which gives rise to a loss in engine efficiency and the possibility of mechanical damage. This tendency towards spontaneous ignition, or "knocking", is dependent upon the composition of the fuel, some components apparently promoting the knocking tendency whereas others tend to inhibit the pre-ignition. Typically the knocking tendency is measured in a standardised variable compression single cylinder engine and the octane number represents the percentage of iso-octane (2, 2, 4-trimethylpentane) in a reference fuel blend of n-heptane and iso-octane which will cause knock at the same compression ratio as obtained with the unknown fuel mixture. Numbers above 100 are obtained by reference to agreed extrapolation of the critical compression ratio curves based upon standard reference fuels containing tetra-ethyl lead as an octane number enhancer. Many of the possible components of gasoline have been tested either as pure compounds or in suitable blends of reference fuels and individual component octane numbers have been evaluated and published as part of project 45 of the American Petroleum Institute. These tabulations show that the normal paraffins are by far the poorest components and become progressively worse as their molecular weight increases. Isomerisation of these normal paraffins leads to a modest improvement in quality depending upon the degree of branching which is introduced [9].

The next poorest class of component are the cyclic paraffins and again these become worse as side chains are added and the molecular weight increases. Introducing olefinic unsaturation leads to a marked increase in octane number which is even more pronounced in the case of poly-unsaturation. Highly olefinic gasolines, however, tend to spontaneously polymerise and deteriorate on storage, have objectionable smells and contribute to photochemically induced pollution. By far the highest octane components are the aromatics.

The improvement in product octane number therefore, entails either the removal of the lowest octane components or ideally their conversion to a higher octane component and hence the name of process-reforming. Important in any such reforming is the final yield of product and clearly reforming the low octane components is preferable to their removal. Since it is the volume yield of product which is of importance some yield loss will be inevitable due to volume shrinkage since the molar volume of an aromatic molecule for instance, is less than for the paraffinic precursor and in addition the removal of hydrogen entails a loss in weight yield. Under high hydrogen pressure conditions the naphtha to aromatics conversion is equilibrium-limited, but with a typical dual functional platinum catalyst takes place quite readily. More severe conditions have to be used for aromatisation or dehydrocyclisation of the paraffins and under these conditions hydrocracking becomes appreciable [4].

The earliest hydroforming catalysts based upon chromia or alumina were operated as a fully regeneration cyclic process. These catalysts were nonacidic and lacked isomerisation activity. They relied upon their dehydrogenation activity to improve octane number by a combination of paraffin dehydrocyclisation and olefin production. In the presence of feeds containing high levels of cyclopentane rings, however, such catalysts are rapidly deactivated. A significant improvement occurred with the introduction of molybdena on alumina catalysts which, being mildly acidic, had isomerisation activity and not only could take advantage of the gains to be obtained from paraffin isomerisation, but could also aromatise the cyclopentanes. Because of the acid activity such catalysts were normally operated with hydrogen diluent under a pressure of ~5 bar. Under these conditions paraffin aromatisation was less effective than for the chromia catalysts.

The next major step forward was the introduction of alumina supported platinum catalysts. For these the acidity and hence the isomerisation activity could be controlled and optimised by controlling the level of halogen combined with the alumina. Perhaps the superiority of the platinum based catalyst is best ascribed to the selective metal cyclisation activity of the platinum-group metals. In order to preserve this activity and thus enable reasonably extended process cycle times for semi-regenerating operation, it was found that both hydrogen diluent and relatively high pressures (30 to 50 bar) were required. Under these high pressures significant yield losses still occurred under high temperature conditions due to hydrocracking. This could be controlled only to a limited extent by small, but finite concentrations of sulphur in the feed (10 to 100 ppm) which served to control the metal catalysed hydrogenolysis activity, but not the bifunctional acid catalysed hydrocracking. Because of the acidic nature of such catalysts organic nitrogen in the feed had to be reduced to exceptionally low levels (<5 ppm) as did the moisture and oxygen content which otherwise led to a loss of halogen and acid isomerisation activity. Such control is normally facilitated by pretreatment of the feed over a base metal hydrotreating catalyst.

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Stability of Bimetallic Reforming Catalysts

The limiting reaction in catalytic reforming is the dehydrocyclisation or aromatisation of the low octane paraffinic components and in practice since paraffin conversion increases with molecular weight this means the limited conversion of the low molecular weight C_6 and C_7 paraffins.

Although paraffin (or olefin) cyclisation are known to take place on both acid and metal sites under normal reforming conditions the extent of reaction is markedly dependent upon Pt metal loading unlike simple isomerisation or even methyl cyclopentane dehydroisomerisation which appear to be independent of metal loading [1].

The stabilising effect of a second metal addition would therefore seem to depend upon three possible mechanisms:

(1) The initial activity is increased; (2) the rate of deactivation due to coke deposition is decreased; (3) the rate of loss in metal activity due to sintering of the highly dispersed active metal is decreased.

Ir increases the activity continuously, Re addition gives rise to an optimum ratio whilst Ge and Sn progressively poison the metal activity [2].

The longer a catalyst is used the less its activity and the greater is the laydown of strongly adsorbed carbonaceous matter or coke.

Such relationships may, however, not apply. The platinum/germanium combination accumulates coke faster than that of the germanium-free catalyst even though its stability is greater [2]. This apparent conflict may perhaps be resolved by recent work which shows that one must consider the relative effects of coke laid down upon the surface and that which is laid down upon the surface of the support. The coke laid down on the metal surface can be differentiated by the lower temperature at which it can be oxidatively removed [3]. Using a temperature-programmed oxidation technique the manner in which coke accumulates during use on a monometallic Pt/Al_2O_3 catalyst has been studied.

Activity testing of a wide series of catalysts coked to different extents by changing different reaction variables, e.g. pressure, temperature, time and hydrogen diluent ratio, all seemed to fit a unique relationship when correlated with carbon content. Surprising was that the coke first built up on the metal surface apparently reaching a constant saturation level before starting to accumulate on the support surface. Traditionally platinum has been supposed to function so as to keep the acidic surface clean [4].

Poor metal dispersion can be shown to lead to lower catalyst activity and it has been suggested that one possible role of bimetallic combinations is to limit their sintering, although there is no evidence that metal sintering normally occurs under reforming conditions. Sintering generally is due to faulty reduction procedures or occurs during regeneration in an oxidising environment. In such circumstances the presence of a second metal may be beneficial. In the case of Ir and Re combinations the higher melting point of the alloys would tend to inhibit sintering, although this cannot be said for the lower melting Ge and Sn alloys [5].

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Other Bifunctional Catalytic Processes

Butane to iso-Butane. Iso-butane may be reacted with n-butylenes in the presence of concentrated HF or H_2SO_4 to give a product rich in iso-octane of very high octane number. In situations where iso-butane is in short supply it is made by hydro-isomerisation of naturally occurring n-butane. Catalysts used include Pt on extensively halided alumina and more recently Pd on either a Y zeolite or one of the newer smaller poresize zeolites such as mordenite, erionite or zeolites of the ZSM series. Reaction is normally carried out under pressure (5 to 40 bar) with hydrogen diluent $(H_2/oil) \approx 4$ and at fairly low temperatures (100 to 300°C) [1 to 4].

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[1] F. G. Ciapetta, J. B. Hunter (Ind. Eng. Chem. **45** [1953] 147/55). – [2] F. E. Conden (Catalysis **6** [1958] 43). – [3] M. A. Lanewala, P. E. Pickert, A. P. Botton (J. Catal. **9** [1967] 95/7). – [4] J. P. Frank, J. F. Le Page, A. Roumegeous (in: New Horizons in Catalysis, Studies in Surface Science and Catalysis, Vol. 7b, Ethyl Aluminium Chlorides Anchored on Platinum Impregnated Alumina as Hyperacids for Isomerisation of Light Paraffins, Elsevier, Amsterdam 1981, pp. 1018/27).

C_5 and C_6 Hydroisomerisation. Isomerisation of these light paraffins is desirable for octane improvement. Whereas isomerisation normally will take place under gasoline reforming conditions thermodynamic equilibrium under these conditions is not particularly favourable for the most highly branched highest octane isomers. Isomerisation at lower temperatures with a much more acidic and more active catalyst is sometimes warranted. Catalyst and conditions used are similar to those used for converting n-butane [1 to 4].

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[1] F. G. Ciapetta, J. B. Hunter (Ind. Eng. Chem. **45** [1953] 147/55). – [2] F. E. Conden (Catalysis **6** [1958] 43). – [3] M. A. Lanewala, P. E. Pickert, A. P. Bolton (J. Catal. **9** [1967] 95/7). – [4] J. P. Frank, J. F. Le Page, A. Roumegeous (in: New Horizons in Catalysis, Studies in Surface Science and Catalysis, Vol. 7b, Ethyl Aluminium Chlorides Anchored on Platinum Impregnated Alumina as Hyperacids for Isomerisation of Light Paraffins, Elsevier, Amsterdam 1981, pp. 1018/27).

Hydroisomerisation of High Molecular Weight Paraffins. Naturally occurring petroleum oils frequently contain high concentrations of high molecular weight normal paraffins which crystallise out as paraffin wax at normal temperatures. Thus distillates used for either lubricating oil or fuel oil normally have to be dewaxed in order to lower their freezing point or "pour point". As an alternative to physical separation by cooling and wax removal by filtration they may be catalytically dewaxed altogether by shape selective cracking over Pd or Pt metal promoted small pore zeolite [1 to 4].

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[1] J. P. Frank, J. F. Le Page, A. Roumegous (in: New Horizons in Catalysis, Studies in Surface Science and Catalysis, Vol. 7b, Ethyl Aluminium Chlorides Anchored on Platinum Impregnated Alumina as Hyperacids for Isomerisation of Light Paraffins, Elsevier, Amsterdam 1981, pp. 1018/27). – [2] S. L. Meisel, J. P. McCulloagh, C. H. Lechthaler, P. B. Weisz (ACS Meeting **1977**). – [3] N. Y. Chen, R. L. Goring, H. R. Ireland, T. R. Stein (Oil Gas J. **75** [1977] 165). – [4] R. N. Bennett, G. J. Elkes, G. J. Wanless (Oil Gas J. **73** [1975] 69).

Isomerisation of C_8 Aromatics. The rapid increase in the use of polyester based fabrics has in no small measure been due to the introduction of C_8 aromatic isomerisation processes after 1968, which ensured an ample supply of relatively inexpensive para-xylene, the precursor of terphthalic acid which is one of the monomers used in polyester manufacture. Normally C_8 aromatic process streams derived, for example, from pyrolysis plants of platinum naphtha reforming units will contain substantial amounts of meta-xylene and ethylbenzene in addition to the more desirable isomers ortho-xylene and in particular para-xylene. These other isomers, however, may be isomerised over platinum or palladium bifunctional acidic catalysts. The xylenes are found to interconvert quite readily, the limiting reaction being the conversion of the ethyl-benzene. This latter conversion is thought to require prior hydrogenation to a cyclic naphthene and then acid catalysed isomerisation followed by dehydroisomerisation to the desired xylene isomers. Important side reactions which must be minimised are dealkylation of the aromatic and hydrocracking of the paraffinic components and naphthene intermediates. Typical conditions used are 375 to 450°C, 10 to 15 bar and 5 to 10 H_2/oil diluent. Originally Pt/SiO_2 [1] and Pt on halided alumina [2] were used. More recently there has been a change to zeolite containing catalysts [3, 4, 5] and even multimetallic catalysts [6]. The ultimate yield of para-xylene is thermodynamically limited. Typically the desired para-xylene is removed from the isomerisate either by fractional crystallisation or selective absorption and the depleted raffinate recycled to the isomerisation reactor.

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[1] H. F. Uhlig, W. C. Pfefferle (Advan. Chem. Ser. No. 97 [1970] 204). – [2] Anonymous (Erdöl Kohle Erdgas Petrochem. Brennst. Chem. **26** No. 6 [1973] 323). – [3] K. W. Cornely, S. G. Hindin, C. D. Keith, Engelhard Minerals and Chemicals Corp. (U.S. 3997618 [1976]). – [4] A. W. Chester, Y. F. Chu, Mobil Oil Corp. (U.S. 4283584 [1981]). – [5] U.S. 4300014 [1981].

[6] R. E. Rausch, Universal Oil Products Co. (U.S. 4024199 [1977]).

Hydrocracking. Hydrocracking is one way which the oil refiner has for adjusting the balance between his various product sales and entails the cracking of the heavier oil to more desirable lower boiling products such as gasoline, kerosine and jet fuel. Although base metal acidic catalysts are widely used platinum and palladium catalysts frequently show better activity and selectivity and improved product quality because of their superior hydrogenation-dehydrogenation activity. Hydrocracking is normally carried out in two-staged sequential reactors. In the first stage sulphur and nitrogen compounds which would deactivate an acidic catalyst are removed along with extensive hydrogenation of some of the aromatic rings and particularly the polyaromatic rings. Hydrocracking and aromatic hydrogenation are both highly exothermic reactions and it is desirable to try and equalize the hydrogen consumption and heat release between the separate stages. A base metal catalyst might be used in the first hydrotreating stage followed by use of a zeolite supported platinum-group metal, e.g. Pd/Y zeolite. Conditions typically are very severe (350 to 425°C, 100 to 150 bar) although temperatures are kept as low as possible in order to prolong catalyst life and processing cycles. More recently there has been a trend away from using hydrocracking processes towards a combination of catalytic cracking using zeolite containing catalysts in conjunction with extensive hydrotreating of the feed to such units. This change has come about in part because of the improved yields which are now possible with such zeolite containing catalytic cracking catalysts and in part because of the much higher quality of the gasoline so produced. This revised processing configuration is also more thermally efficient and requires less of the expensive hydrogen.

H. Pines (The Chemistry of Catalytic Hydrocarbon Conversions, Academic, New York 1981).

Hydrogenolysis Processes

The hydrogenolysis processes to be discussed in this section are to be differentiated from the hydrocracking discussed above in that the breaking of the carbon-carbon bonds takes place specifically on the metal surface rather than on the associated acidic sites of the metal catalyst support. Base metals in general are nonselective hydrogenolysis catalysts in that if a molecule reacts it is generally substantially degraded to the thermodynamically most stable product, methane. The platinum-group metals and especially rhodium, iridium and to a lesser extent platinum, are able to selectively split such molecules. All hydrogenolysis catalysts are highly susceptible to sulphur poisoning.

Hydrogenolysis of Alkanes. The aim of such a process is the selective production of ethane from higher molecular weight paraffinic feeds which could then be thermally dehydrogenated to ethylene. Working with n-butane selectivities greater than 80% to ethane were found for both iridium and rhodium on an alumina support. Somewhat better results were obtained when these metals were coimpregnated with platinum although platinum by itself proved somewhat nonselective and considerably less active.

J. R. Bernard, J. Bousquet, P. Tarber (Studies in Surface Science and Catalysis, Vol. 7, Elsevier, Amsterdam 1981, p. 149).

Toluene Dealkylation. In contrast to hydrocarbon streams derived from pyrolysis processes a typical platinum naphtha reformate contains relatively more toluene and higher molecular weight substituted benzenes rather than the more desirable benzene. The platinum-group metals have been shown to be highly selective toluene hydrodealkylation catalysts. Selectivities of the different metals follow the sequence Pd (100), Pt (97), Rh (97), Os (94), Ir (93), Ru (82).

Typical operating conditions are 1 to 20 bar and 500 to 550°C [1, 2, 3].

The possibility of using steam rather than hydrogen for the catalytic dealkylation of toluene has attracted much attention. The overall reaction is concomitant to combining the steam-methane reforming reaction with that of hydrodealkylation although the actual mechanism of the overall reaction may be quite different. Apart from requiring less of the expensive hydrogen reactant the steam reaction is far less exothermic than the hydrogenolysis reaction and should therefore be easier to control.

Selectivities for steam dealkylation have been found to the somewhat less than for straightforward hydrodealkylation: Pt–Pd (95 to 100), Rh, Ir (85 to 90), Ru, Os (60 to 70), Ni (40).

In terms of relative specific catalytic activity rhodium stands out particularly as shown by the following sequence for α-Al_2O_3 supported metals: Rh (100), Ru (52), Pd (34), Pt (21), Ir (14), Ni (9), Os (3).

However, for Pt, Rh and Pd the catalyst support has been found to have a major effect on catalyst activity suggesting that a bifunctional mechanism is involved. Thus for rhodium the activity found on various supports was Cr_2O_3 (130), γ-Al_2O_3 (100), α-Al_2O_3 (40 to 50), SiO_2, Al_2O_3 (15 to 40), SiO_2 (2 to 20).

For Ni, Co, Ru and possibly Ir, oxidation is a possibility since these metals will react with water to give a surface oxide [4, 5,6].

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Hydrogenation of Aromatics

Platinum-group metal catalysts, originally introduced for the aromatisation of petroleum fractions, are also used for the dearomatisation of such streams. This they are able to do by hydrogenation to the corresponding cyclo-alkane and this may possibly be combined with subsequent hydrogenolysis of these saturated rings giving the corresponding iso-alkanes. Platinum and palladium on alumina catalysts have been used at high pressures (50 to 60 bar) and relatively low temperatures (200 to 300°C). In order to maintain the highest possible activity these processes may be operated in two stages with prior desulfurisation. Processes used range from the purification of light solvents [1, 2] to the preparation of medicinal white oils and the dearomatisation of jet fuel kerosene [3].

When hydrogenating benzene over a platinum-group metal the reaction goes to completion. Cyclohexene will readily disproportionate over the platinum metals (particularly palladium) to give benzene and cyclohexane. Unsupported ruthenium catalysts are used in the presence of water. Under these conditions the ruthenium surface will be extensively oxidised and the strong planar adsorption of the benzene ring inhibited in favour of an "edge on" adsorption, the latter favouring sequential and partial hydrogenation [4, 5].

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Purification Processes

The high intrinsic activity and selectivity of the platinum-group metals make them suitable for catalytic removal of low concentrations of undesirable impurities from process streams.

Hydrogen Purification. Hydrogen is manufactured on a large scale by high-temperature gasification of organic matter to give a synthesis gas mixture of hydrogen and carbon monoxide. This is customarily followed by a CO shift reaction with steam to give a final mixture of hydrogen and carbon dioxide from which the carbon dioxide may be selectively absorbed. The CO shift reaction is thermodynamically limited and even after reaction at low temperature the resulting hydrogen will still contain traces of carbon monoxide. This is a potent poison for many hydrogenation catalysts which might use the hydrogen product and thus has to be removed. This can be done either by selective oxidation to carbon dioxide using a platinum catalyst of by reduction to methane using either a platinum or more usually a ruthenium catalyst.

For the selective oxidation of CO in the presence of hydrogen temperatures of 50 to 150°C are used with oxygen added 50 to 150 % in excess of stoichiometric requirements. Reduction of CO to methane is far less critical with respect to conditions at temperatures $>250°C$ [1, 2, 3].

Hydrogen may also be contaminated with air or oxygen. Although this can be removed by passage over hot (250 to 450°C) copper or nickel, palladium on alumina will catalyse this oxidation reaction at ambient temperatures and is the standard ingredient of catalytic purifiers used in hydrogen supply lines. The presence of CO may inhibit the selective oxygen reduction – typically with 10 and 1000 ppm CO; temperatures of 20 and 70°C, respectively, are required [1, 2, 3].

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Olefinic Stream. Olefinic streams frequently contain low concentrations of more highly unsaturated components which would severely impair the activity and selectivity of subsequent polymerisation catalysts. In order to meet the rigid specification associated with polymerisation grade materials these must first be removed by selective hydrogenation. Typical examples are the removal of acetylenes from ethylene, propylene, styrene and butadiene streams and the removal of butadiene from butylene streams [1 to 5].

Palladium supported on alumina would appear to be the catalyst of choice; chromia is sometimes added as a promoter. The selectivity is apparently favoured by having the metal as highly dispersed as possible and in order to maintain such high dispersions very low metal loadings (0.01 to 0.03 wt%) are customarily used [3,6]. Selectivity may be further improved by adding traces of CO (0 to 300 ppm). Conditions used for ethylene and propylene purification have thus been given as, for ethylene: 0.03% Pd/Al_2O_3, 25 atm, 30 to 120°C, with hydrogen added 100 to 500% of stoichiometric; for propylene: 0.03% Pd or $Pd\text{-}CR_2O_3/Al_2O_3$ 1300 to 4500, 1 to 20 atm, 150 to 200°C, with hydrogen added 300% of stoichiometric [7].

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Catalytic Cracking Regeneration. The use of platinum-group metals as combustion catalysts in association with silica alumina cracking catalysts is considered here as a purification process, in analogy with car exhaust purification catalysts since one reason for their use is to reduce emissions of carbon monoxide and sulphur oxides from the regenerator. In a real sense, however, they are rapidly becoming an integral part of the overall cracking process and although used only in very low concentrations (0 to 100 ppm) this process is carried out on such a large scale that their use is rapidly becoming a major application of platinum.

The silica alumina catalysed cracking of heavy oils is a highly endothermic reaction and the catalyst in use is very rapidly deactivated by the accumulation of a carbonaceous or coke deposit. The heat required for the cracking reaction is supplied by burning off this coke deposit in the regenerator and the heat of this combustion is transferred in part to the circulating catalyst and then to the reactor as sensible heat. This combustion reaction is much slower than the cracking reaction, so by far the greater part of the total catalyst inventory is being regenerated at any point in time. The regeneration is thermally not very efficient in that the exhaust gases contain a large percentage of partially combusted material in the form of carbon monoxide. The use of a combustion co-catalyst added to the silica-alumina cracking catalyst to promote both the rate and extent of combustion would therefore seem to be a natural solution. Unfortunately many good base metal oxidation catalysts, eg. Ni, if added in amounts necessary to promote the combustion reaction will also be catalytically active in the cracking reactor in a very undesirable way. These base metals promote extensive additional coke and gas formation and thus severely lower the selectivity to the desired hydrocarbon products. Platinum, however, because of its much higher intrinsic oxidation activity can be used in only trace amounts where it is still active under oxidising conditions and yet is probably deactivated so rapidly in the reactor that it does not depreciate the hydrocarbon product yield structure.

The possibility of using the platinum-group metals in this way is scarcely a new idea but with the recent increase in the use of zeolite containing cracking catalysts which make less coke and more stringent controls on permissible pollutant emissions increasing the thermal efficiency and lowering the CO and SO_x concentrations in the regenerator exhaust have taken on renewed significance and urgency [1, 10]. A recent estimate is that at least 40% of commercial catalytic cracking units now practice addition of platinum in some form or other. Many patents have been issued [2 to 7] covering the use of the different platinum-group metals in different forms and such an application has been discussed in the trade literature [8, 9].

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4.3.1.2 Automobile Emission Catalysts

There has been intermittant interest in the use of catalysts for the control of automobile exhaust emissions for at least 50 years [1]. The emission problems were solved by mechanical improvements to the engine and fuelling system until the mid 1970s, when mechanical improvements proved insufficient. The impetus behind this interest in the late 1960s und 1970s was the appearance of photochemical smog in Los Angeles initially, but later observed in other American cities, in Tokyo and London. This photochemical smog was formed by a series of complex reactions involving nitrogen oxides, ozone and hydrocarbons to produce peroxynitrates [2]. It was found that in the USA ~40% of this atmospheric NO_x and ~60% of atmospheric hydrocarbons were due to motor vehicles [3]. Almost 90% of atmospheric CO was also due to motor vehicle exhaust. The USA was thus amongst the first countries to introduce legislation to control automobile emissions with the Air Pollution Control Act (1955), Clean Air Act (1963), Air Quality Act (1967) and the Clean Air Act (1970), the most recent revision occurring in 1977 [4]. As a result of this legislation catalysts were first fitted to production cars to control emissions in 1978. Strict legislation has now been passed in other parts of the world including Japan, EEC countries, Sweden, Switzerland und Australia.

In general, exhaust emissions are measured over a cycle that simulates a typical urban driving schedule, the exhaust gas being continuously monitored as the vehicle is driven on a rolling road dynamometer. The gases collected are analysed for hydrocarbons, CO and NO_x. In the USA emissions control devices must meet the legislated standards for a minimum of 50000 miles. The conventional exhaust catalysts are poisoned rapidly by lead [5], and hence it has been necessary for lead free fuel to be introduced wherever catalysts are used, with the USA doing so in the early 1970s, although potentially lead tolerant catalyst systems will be described later. Exhaust catalysts are typically supported on ceramic honeycomb monoliths, or alumina pellets. Where a monolith is used, it is coated with a high surface area alumina prior to impregnation of the active catalyst components. Noble metals have been utilised commercially because of poor performance of base metal catalysts, due primarily to poisoning by sulphur in the exhaust stream [6].

The requirement for exhaust emission control catalysts from 1975 was to control CO and hydrocarbons which was accomplished by catalytic oxidation with air to carbon dioxide and water. Since the further tightening of legislation in the US in 1981, catalytic control of NO_x has become necessary. The catalysts used for CO/CH oxidation are generally based on platinum or platinum/palladium, with the addition of base metals for improving catalyst stability and performance. An excess of air is added to the exhaust stream prior to the catalyst by means of a pump or valve system [7].

The control of NO_x is more difficult as the decomposition to nitrogen is extremely slow, and reduction does not occur in the presence of an excess of oxygen. It is found necessary to run the engine close to stoichiometry and reduce the NO_x with CO or possibly CH [8]. Platinum is again used as the catalyst but is promoted by a second precious metal. Ruthenium has been proposed, but despite good initial results, the volatility of RuO_4 which is formed on lean excursions, that occur with even the best fuel management system, causes loss of active metal [9]. Rhodium is now used exclusively as the promoter for the reduction of NO_x. Both ruthenium and rhodium are able to reduce NO_x primarily to N_2 with little tendency to form ammonia, which is an undesirable byproduct [10]. NO_x ist controlled either by deliberately running the engine slightly rich and utilising a reduction catalyst which is then followed by air injection and an oxidation catalyst to reduce unreacted CH and CO (the dual bed system), or by controlling the fuelling system closer to stoichiometry when it is possible to reduce all these pollutants ("three way" catalysts). Both systems require accurate control of the air to fuel ratio being combusted within the engine which is obtained by means of a closed-loop feedback system that involves the use of an O_2- or Λ-sensor in the exhaust stream [11]. In practice it is found that for fuel metering systems using a carburettor, the fuelling hunts significantly around stoichiometry requiring a dual bed catalyst, while fuel injection systems may employ a single three way catalyst. This perturbation in fuelling has resulted in the incorporation of "oxygen gas storage components" within the catalyst which are capable of removing oxygen from active catalyst sites on lean excursions, and releasing it again during rich excursions [12].

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Catalytic Control of Diesel Emissions

The diesel, engine has advantages over gasoline engines in terms of reliability and efficiency. It does, however, suffer similar emission problems of unburnt hydrocarbons, CO and NO_x, although in general the CO and CH emissions are lower than with a gasoline engine. Additional problems with diesels are exhaust odour (which is caused by partially oxidised hydrocarbons), particulates (smoke) and potentially carcinogenic polynuclear hydrocarbons, all of which are present to a greater extent than with gasoline exhaust. As diesel exhaust is generally highly oxidising, this has precluded the use of the gasoline type of catalysts for NO_x control as oxygen poisoning inevitably occurs. For stationary units the catalysed reduction of NO_x with NH_3 may be used [1].

The control of CO, hydrocarbon and odour is readily undertaken by a platinum based oxidation catalyst [2, 3]. These catalysts will also dramatically reduce the emissions of carcinogenic polyaromatic hydrocarbons [4]. The emission of smoke in diesel exhaust is caused by particulate material composed of solid carbon impregnated with high molecular weight hydrocarbons, lower hydrocarbon aerosols, and residual ash from fuel inorganics. Conventional exhaust catalysts are ineffective in controlling these emissions, the momentum of the particulate causing it to avoid contact with the catalyst. Particulates may however be controlled by filtering them from the gas phase by means of monolithic unit with porous walls, alternate channels being closed at either the front or rear faces [5]. Thus the gas flow is caused to diffuse through a channel wall. The collected particulate is then oxidised during high temperature running of the engine. The particulate removal may also be undertaken using a catalysed filter [6]. An alternative method is to employ a wire mesh catalyst where the momentum of the particulates is sufficient to cause impingement on the catalyst, upon which catalytic oxidation takes place. Such a system has been shown to exhibit satisfactory performance for 50000 miles [7].

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Lead Tolerant Catalysts

As discussed above, the increasingly severe vehicle emission regulations introduced in the USA und Japan led to the introduction of precious metal catalysts to control unburned hydrocarbons, carbon monoxide and, later, oxides of nitrogen. ECE-15 legislation, applicable to the majority of European countries, is currently at a stage where emission standards can be met by engineering methods. However, further tightening of these standards is likely to necessitate catalytic control on the majority of cars.

Lead and the scavengers (1,2-dibromoethane and 1,2-dichloroethane) which are commonly added to gasoline cause deactivation of both base metal [1] and conventional precious metal catalysts [2, 3, 4]. In the USA and Japan, lead-free gasoline was introduced prior to the introduction of catalysts, but, until recently, no such commitment existed in Europe. This helped to create a situation of uncertainty which resulted in significant interest in the concept of a lead tolerant catalyst.

The importance of catalyst operating conditions, particularly temperature range, positioning and inlet oxygen level, in determining catalyst life in a leaded environment was stressed by [5 to 9], who studied the effect of these parameters in both rig and static engine tests. Fuel composition was also found to have a pronounced effect on catalyst life, as shown by research on fuels containing zero, or low levels of, scavengers [6 to 9].

In general, the observed rate and type of lead poisoning of catalysts have been explained in terms of the chemical nature and volatility of the lead compounds present in the exhaust stream [5, 6, 8, 9] – two main types of poisoning being cited, chemical poisoning and physical plugging or blocking. The effect of the scavengers themselves was, however, considered more important in explaining observations using Pt/Pd catalysts supported on alumina beads [7].

Where several combinations of precious metals have been considered for use in lead tolerant catalysts, pure platinum was found to be the most poison-resistant active phase [6, 8, 9], with high loadings (80 g/ft^3$\approx$2.8 g/l) giving superior performance to low loadings (25 g/ft^3$\approx$0.9 g/l) [6]. Addition of Pd was generally shown to be detrimental [4, 6, 10 to 13].

50000 km durability was demonstrated on two lead tolerant oxidation catalyst systems, tested under European conditions, with results inside the UBA (Umweltbundesamt Bundesrepublik Deutschland) proposals for a further tightening of ECE-15 legislation. One of these systems used pure platinum [8, 9] whilst the other was described only as precious metal [14]. Both catalysts used high cell density (600 cells/in.^{2}$\approx$93 cells/cm^2) metallic substrates.

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4.3.1.3 Control of Toxic Emissions, Odour and Solvent Streams

Legislation regarding emissions from nitric acid manufacturing plants exists in several countries [1]. In recent years, legislation has also been extended in certain countries to cover NO_x emission from other sources. Incomplete absorption of NO_x in water, after its formation by catalytic oxidation of NH_3 in the nitric acid manufacturing process, can result in the appearance of a reddish-brown plume of NO_2 in the tail gas from plants [2]. Because increasing the efficiency of absorption to the extent required to eliminate this plume is impracticable and uneconomic [3], and because of other factors, including a relatively high $NO_2{:}NO$ ratio compared with NO_x from other sources, and a high overall NO_x concentration, catalytic reduction of NO_x is especially attractive. This can be either selective or nonselective. The latter uses a fuel, such as natural gas or hydrogen, to reduce NO_x to N_2 and H_2O [4]. The catalytic processing of tail gas with CH_4 over supported noble metals to yield useful energy in the form of steam and/or power has been described as follows:

decolorisation $CH_4 + 4\,NO_2 \rightarrow 4\,NO + CO_2 + 2\,H_2O$; combustion $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$; abatement $CH_4 + 4\,NO \rightarrow CO_2 + 2\,H_2O + 2\,N_2$ [6].

The catalysts employed are normally based upon Rh/Pt and, over the years, many refinements have been made to improve their efficiency [3, 7, 8]. Selective catalytic reduction of NO_x by NH_3 [9] overcomes the need, encountered in the nonselective process, for a significant excess of fuel (typically 15%) [3].

Pt or base metal catalysts, typically vanadium compounds on a titania support, are used in this process:

$8\,NH_3 + 6\,NO_2 \rightarrow 7\,N_2 + 12\,H_2O$; $4\,NH_3 + 6\,NO \rightarrow 5\,N_2 + 6\,H_2O$; $4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O$ [10].

These and other (noncatalytic) methods of NO_x control have been reviewed [11, 12].

Organic fumes and odours may also be controlled by the use of catalysts. One of the first types of catalyst to be used in this application resembled an air filter element in appearance, consisting of thin ribbons of a high nickel alloy on which platinum or platinum alloys were supported. The ribbons were crimped into the form of a mat and activated prior to use. This system found application in the catalytic combustion of fumes from enamelling ovens [13, 14]. The next development was the use of a system based on stacked units of platinum impregnated porcelain rods [15]. A number of applications for the system have been discussed: curing operations on a resinous binder [15], waste gases from catalytic cracking plants [15, 16], tail gas from the phthalic anhydride process [15], and clean-up of emission from a paint stoving and bonderizing plant [17].

A major advance in this field occurred with the development of monolithic, ceramic, honeycomb materials and improved methods for impregnating them with platinum-group metals [18]. This system has been used for a wide range of applications [18] and a number of specific uses have been discussed in detail: control of odours from the processing of animal carcasses, fish and food [19, 20], oxidation of pollutants from ink drying ovens [21] and purification of injection moulding fumes [22]. Despite the increased pressure drop experienced with platinised alumina spheres as compared with the honeycomb type catalyst, there is some evidence that beds of small spheres could be more efficient than other supports in the control of organic air pollutants [23].

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4.3.1.4 Catalytic Combustion

The best known commercial application of catalytic combustion is in radiant burners for space heating systems [1]. The main component of these comprises a fibrous pad of quartz or alumina on which small quantities of platinum are dispersed, sometimes with a co-catalyst such as cobalt [1, 2]. Catalytic heaters have been designed for use with a wide variety of fuels including LPG, propane, butane and natural gas, and have found applications in industrial, agricultural and leisure markets where lower pollution or increased safety requirements over normal flame combustion are necessary.

Catalytic combustion has been applied in the gas turbine industry, both for ignition of jet engines and in the main combustors [3, 4]. Catalysts have been used to re-ignite jet engine combustors after flame-out due to transient conditions. The major potential use of catalyst in gas turbines, however, is to replace conventional flame combustions. The main advantage of such a system is that, as a direct result of the lower combustion reaction temperature, a much lower level of pollution, particularly nitrogen oxides, is achieved compared to a flame fired engine. Catalysts for use in this application must be capable of withstanding both continuous and transient operation at temperatures up to 1600°C without degradation and must have good attrition resistance and low back pressure properties. Such requirements mitigate in favour of monolithic catalysts and the use of both ceramic and metal support systems has been reported [3, 4], usually coated with platinum or platinum/palladium catalyst [5]. Although experimental catalytic gas turbines have been fitted to aircraft, commercialisation of these systems has yet to be realised.

The concept of an internal combustion engine in which the oxidation of the fuel is brought about by a catalyst has been reported to offer a number of advantages, including good fuel economy, low pollutant emissions and multifuel capability. The catalyst comprised a pure platinum gauze located either in the piston crown of a direct injection engine or, preferentially, in the pre-chamber of an indirect injection engine [6].

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4.3.1.5 Fischer-Tropsch Catalysis for Liquid Fuels

Between 215 and 315°C the platinum-group metals except platinum yield small quantities of low molecular weight hydrocarbons at atmospheric pressure when contacted with synthesis gas [1 to 4]. Of these ruthenium alone is capable of yielding significant quantities of low oxygen content waxes at elevated pressures [4]. Over unsupported, unpromoted ruthenium, synthesis gas conversion increased rapidly with increasing temperature and also with increasing pressure. Also the mean molecular weight of products increased with increasing pressure. A wax fraction was produced at 1000 bar with a melting point of 132 to 134°C and an average molecular weight of 23000 [5, 6].

The interaction of H_2 and CO over unsupported noble metal catalysts has been studied between 100 and 200°C at 1 bar. Under these conditions preferential CH_4 formation was noted and the order of activity Ru and Ru alloys $\gg$Rh$>$Pt and Pd was obtained.

It was suggested that alloying Ru with other noble metals offsets the catalytic performance in proportion to the Ru content of the alloy and that the alloying noble metal acted merely as a diluent [7].

The Fischer-Tropsch reaction has been studied over a series of well characterised SiO_2 supported Pt-Ru bimetallic clusters. It was concluded that under F-T conditions CO/H_2 interaction occurs only on Ru sites. The surface Pt atoms were inactive and acted merely as a diluent, while the F-T reaction on Ru is structure sensitive and is favoured by large Ru ensembles [8].

The behaviour of unsupported Ru-base metal alloy catalysts in the F-T reaction was studied by [9, 10]. Over Ru-Fe alloys containing more than 3% Fe, carbon laydown reduced the specific activity by a factor of 2 to 3 and shifted the selectivity to lighter end products. Such behaviour did not occur over pure Ru.

The effect of supported Ru catalysts on the F-T reaction has been examined at 4 bar between 175 and 300°C. The specific activity of supported Ru was dependent upon the nature of the support and on the metal loading. The specific activity for both CO conversion and CH_4

production increased with increasing particle size, obtained either by increasing the metal loading on a given support or by choosing a support which poorly dispersed the metal. Supported catalysts with large particles were similar to unsupported Ru in activity, but not in selectivity. Product selectivity, characterised by olefin/saturate ratio, length of hydrocarbon chain and tendency to produce branched-chain hydrocarbons, was a function of both the support and the metal loading. The degree of saturation in the products increased with increasing CO conversion. The length of the hydrocarbon chain was dependent upon temperature, pressure and the nature of the support, but not on the degree of CO conversion. Over a wide range of supports the most poorly dispersed catalysts were the most active [11]. Russian workers have studied the effect of particle size and metal-support interaction in the F-T synthesis over Ru catalysts. With Ru/Al_2O_3 catalysts of well characterised dispersion operating at $H_2/CO = 3$, 250°C and 10 bar, a decline in CO and CH_4 turnover numbers was observed with increasing dispersion. Chain growth was very little affected by the size of the Ru clusters present on the support, and an enhanced metal-support interaction at high metal dispersion may be responsible for diminished activity under these conditions [2].

The effect on the F-T activity of different dispersions of Ru metal when supported on γ-Al_2O_3 was studied between 200 and 275°C at 1 to 8 bar. Higher specific activities can be expected with an increase in average crystallite size, together with an increase in relative olefin content, and a higher average carbon number product [13]. Five of the platinum metals have been studied at 0.5 wt% loadings, high temperature and 21.4 bar pressure. The relative activities of the metals, based on conversion, decreased in the order $Ru > Rh > Os > Pt > Pd$.

Under these conditions Ru gave the highest yields of higher molecular weight hydrocarbons, with the other metals giving smaller amounts of these materials. The order of C_2 hydrocarbon production was $Ru > Pt > Rh > Os > Pd$.

However, these listings are not based on specific rate data since no metal areas were presented.

The performance of the group VIII metals supported on Al_2O_3 in the F-T reaction at 1 bar and 240 to 280°C have been compared. All of the catalysts were thoroughly characterised for metal area and specific activities were measured. Ordering the metals according to the average molecular weight of their hydrocarbon products gave $Ru > Rh > Pt > Pd$. The data were generated under different conditions [14].

The performance of a 0.5 wt% Ru/Al_2O_3 catalyst has been obtained in the F-T reaction under integral operation, thereby elucidating reactor performance as a function of process variables. Hydrogen/carbon monoxide mixtures (3/1, 2/1 and 1/1) and a 4/1 H_2/CO_2 mixture were used at 21.4 bar and 220 to 240°C with a space velocity of 300 h^{-1}. The molecular weight of the product decreased sharply with increasing H_2/CO ratio. Large yields of hard wax were produced at 1:1 H_2/CO ratio. Methane was the principal product with H_2/CO_2 feed. Reaction rate increased with total pressure to the 1.2 power.

The effect of alternative supports for Ru catalysts, e.g. Al_2O_3, SiO_2, SiO_2/Al_2O_3, Cr_2O_3/Al_2O_3, ThO_2, ThO_2/Al_2O_3 and NaX sieve has been examined. The length of the hydrocarbon chain and extent of olefin make were dependent on the nature of the support. Branched chain hydrocarbons were produced when using acidic supports such as silica-alumina or zeolites. This occurred via subsequent isomerisation of the initially formed straight-chain products [11].

By imposing strict maximum dimensions on metal particles enclosed in a Y zeolite matrix it is possible to restrict the hydrocarbon chain length in F-T synthesis. Hydrocarbon chain cut-off was claimed near C_2, C_6 and C_{11} using RuLaY, RuLaNaY and RuNaY catalysts, respectively, when operating at 200°C and 14 bar [17 to 20]. Because of a correlation between the number of C atoms in the largest chain produced and the diamter of the metal particles, selective F-T synthesis is achievable using Y zeolite chemistry. Small well characterised Ru metal particles (1.5 nm and 10 nm) have been placed inside the cages of HY zeolite and it has been found that the hydrocarbon products generated at 200°C and 20 bar under F-T conditions could be tailored to yield products in the range C_1 to C_9 by adjustment of the particle size, achieved by variation of the method by which $Ru_3(CO)_{12}$-HY was pre-treated. Moreover the particle size remained constant after the synthesis, unlike analogous Ru catalysts supported by SiO_2-Al_2O_3 which sintered readily [23].

The support and preparation factors which influence the maintenance of Ru clusters on the support after $Ru_3(CO)_{12}$ deposition have been discussed [25]. Rh carbonyl compounds deposited on various supports have produced selectively C_2 to C_4 alcohols and hydrocarbons [24].

Bifunctional catalysts incorporating an F-T function may be made by intimately mixing an F-T type active phase with, e.g., a shape selective zeolite such as Mobil's H-ZSM-5. In such a way modification of the F-T hydrocarbon product may occur in situ.

Ru/ZSM-5 catalysts prepared by a physical admixture of RuO_2 and ZSM-5 and by vacuum impregnation of $RuCl_3 \cdot 3H_2O$ have been made. Performing the F-T reaction on these materials at 294°C between 27 and 51 bar promoted aromatics formation, reduced the molecular weight of the hydrocarbons formed, and produced a high octane aromatic gasoline in good yield in a single step directly from synthesis gas [22].

Variation of the process parameters revealed that CH_4 was substantially reduced by higher pressure, shorter contact time, lower temperature and lower H_2/CO ratio and that aromatics production was greatly favoured by lower H_2/CO ratio at moderate temperature.

Ru/Al_2O_3 catalysts were operated at 1 bar under steady-state conditions. Addition of 10 ppm H_2S to the gas stream caused an increase in selectivity to C_2 products and a diminution in activity at 250°C. Removal of sulphur caused a partial recovery in catalyst activity [26, 27].

Alkali and sulphur addition on 1% Ru/Al_2O_3 catalyst in the F-T reaction, at 200°C and 260 ppm S as H_2S, and of alkali (10 wt%) diminished activity, but the effect was less marked when both were used [28].

Increasing the pressure reduced the effect of both S and alkali poisoning. Selectivity to C_5 products at 350°C on the alkaline catalyst was twice that on Ru/Al_2O_3, yielding products which were not predominantly n-paraffins for C numbers less than 12. The field of homogeneous F-T catalysis has been surveyed, with an appreciation of the likely role of such systems in the future [29].

As with heterogeneous noble metal catalyst the concept of dual coordination centres in a F-T catalyst system has led researchers to examine metal carbonyl cluster compounds as homogeneous F-T catalysts. $Ru_3(CO)_{12}$ [30], $Os_3(CO)_{12}$ [30] and $Rh_6(CO)_{16}$ [31] have been reported to catalyse the formation of hydrocarbon products from synthesis gas. $Os_3(CO)_{12}$ catalysed CH_4 formation under very mild conditions (140°C, 2 bar). However, at 300°C and 100 bar higher rates were observed, with products up to C_{30} detected. Under these conditions $Ru_3(CO)_{12}$ was even more effective for linear alkane production and three times more active. For $Ru_3(CO)_{12}$ in heptane 2.5 g of linear alkanes (C_3 to C_{30}) were produced per g Ru over 5 h at 300°C and 100 bar. No metallic Ru was detected. However, both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ cluster compounds broke down during the course of the reaction to give inactive homonuclear species [32].

In order to prevent disruption of the complex a tridentate ligand was used to complex or cap the three Ru centres, thus holding them together. Refluxing $Ru_3(CO)_{12}$ with methyltri-(di-n-butylphosphino)-silane in benzene gave the capped complex $Ru_3(CO)_9\{P(C_4H_9)_2\}_3SiCH_3$.

This complex when dissolved in heptane catalysed the formation of C_1 to C_4 at 300°C and 150 bar. After 300 h the catalyst was not recovered unchanged, but no mononuclear Ru species was detected [33].

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4.4 Platinum-Group Metal Compounds in Catalysis

The use of metal compounds as catalysts has a long and important history. Copper chloride was first used industrially to make chlorine by oxidation of hydrogen chloride in the 1870s [1], and has been revived recently as a means of recovering chlorine during the manufacture of vinyl chloride monomer from dichloroethylene [2]. Aluminium chloride was probably the first commercial cracking catalyst being used first in 1915. Clays were used from 1936 in place of aluminium chloride, and aluminosilicates in the form of zeolites are still used today [1]. The use of metal sulphides as catalysts arose from the need to process low purity, sulphur containing feedstocks in the early 1900s [4].

As time passed these early isolated examples of metal compound catalysts have increased in number to such an extent that at least one compound of each of the transition metals has found application as a catalyst. Compounds of the platinum-group metals were unknown as catalysts prior to 1939 when rhodium chloride and certain ammine complexes were shown to be active hydrogenation catalysts. Little more was done with platinum metal compounds until the 1950s when interest in organometallic chemistry arose and it was discovered that many platinum-group metal compounds were catalytically active. Progress was then very rapid, and when the catalytic properties of the platinum metal olefin complexes were reviewed in 1964, the author was able to quote examples of hydrogenation, isomerisation, polymerisation, and oxidation reactions, and include two examples of the industrial application of palladium olefin complexes, the Wacker process and the acetoxylation of ethylene to vinyl acetate [6]. Later rhodium was shown to be a hydroformylation catalyst many times more active and selective than cobalt. This property was exploited by two independent groups who discovered that the trialkylphosphine and triarylphosphine complexes of rhodium were even more active/selective than the chloro complexes [7, 8]. This gave rise to the present low pressure OXO process. So fast was the progress in homogeneous catalysis in the 1960s, that the UK Science Research Council reported that it expected half the heavy organic chemical processes in operation by 1990 would be catalysed homogeneously [9].

Although on a smaller scale, the use of platinum-group metal compounds in heterogeneous systems has also been explored. Although the use of platinum oxide as a catalyst had been claimed in 1922 [10], the compound was only a convenient means of producing in situ platinum black for hydrogenations, the use of platinum compounds as heterogeneous catalysts had to wait until 1965 when platinum metal sulphides were first used in reductive alkylation reactions [11]. Others soon followed with palladium cyanide being proposed as a polymerisation catalyst in the same year [12], palladium acetate as an acetoxylation catalyst in 1968 [13], palladium phosphide as a fuel cell catalyst in 1969 [14] and platinum silicide as a catalytic anode for chlorine manufacture in 1975 [15]. Ruthenium dioxide, in the form of "dimensionally stabilised anodes", has attained almost complete domination of the brine electrolysis industry for the manufacture of chlorine, caustic soda and chlorates [16].

Platinum-group metal spinels and perovskites, sulphides, carbides, nitrides, phosphides, silicides and borides have been proposed as catalytsts for various processes in coal conversions [17, 18].

Broadly the platinum-group metal compounds that are catalytically may be defined as

(I) the binary and ternary inorganic compounds, frequently nonstoichiometric, formed by platinum metals with the nonmetallic elements;
(II) the inorganic compounds formed by the OXO acids of the nonmetallic elements with the platinum metals;
(III) the organometallic compounds formed by the platinum metals with carbon monoxide, the organic hydrides and substituted hydrides of the nonmetals.

The nonmetals forming catalytic compounds with the platinum-group metals are: Cl, Br, I, Se, Te, B, Si (heterogeneous catalysts), As, Sb (homogeneous catalysts), O, N, S, P, C (heterogeneous and homogeneous catalysts).

Only a small proportion of the compounds contained within the above definition are catalytic. However, some of the simple inorganic compounds have achieved enormous industrial importance, such as ruthenium dioxide dimensionally stabilised anodes for chlorine manufacture [19, 20]. Others have found a use within small scale high value organic preparations such as the cis-hydroxylation of olefins by osmium tetroxide [21], or are still being investigated in the laboratory for potentially important industrial reactions [17, 18]. Palladium salts have been used in oxidation reactions and polymerisations and a whole range of organometallic platinum metal compounds are being explored as solution catalysts for hydrogenations, carbonylations, oxidations etc. [22]. In general the inorganic binary and ternary compounds find uses as heterogeneous catalysts and organometallic compounds as homogeneous solution catalysts. The oxo salts are used in both heterogeneous and homogeneous catalysis.

Comparisons can be drawn between catalysis over metal atoms and that over compounds. In both cases some form of bonding, of one or more of the reacting species, to the metal centre occurs. Much effort has been expended in understanding the origin of the bonding from which the catalytic properties arise. Molecular catalysis, as present in homogeneous reactions, has been reviewed in terms of molecular orbital theory [23, 24], while an approach based on band theory has been used to describe firstly the origin of conductivity and semiconductivity in crystalline compounds [25, 26, 27] and secondly the relationship of conductivity to catalytic activity [28]. More recently the main theoretical thrust seems to have been concentrated on descriptions of the electronic structure of metal-metal bonds in cluster compounds and small metal crystallites in nonmetallic catalysts [29 to 33].

On a more practical plane, platinum metal compounds may be used in a supported or unsupported form with a very wide variation in the degree of dispersion, from crystallites of several thousand Å diameter in the case of unsupported oxides or sulphides, to individual metal atom centres with the mononuclear metal complexes. Also the conditions under which metal compound catalysts are used can be categorised as gas phase or liquid phase in a similar way to metal catalysts. However, an extra degree of freedom is available to platinum metal compounds not found with metallic catalysts, in that many compound catalysts may be dissolved in the reaction mixture to give either mononuclear metal species or metal-metal bonded polynuclear clusters with highly directional bonds capable of the formation of, and reactions on, optically active compounds. Although this property can be exhibited by specially treated metallic catalysts it is usually very limited in its application. The close analogies between the metal and metal compound systems are shown in the following table.

degree of dispersion (increasing down table)	metal catalysts		compound catalysts	
	description of catalyst	industrial example	description of catalyst	industrial example
aggregate crystallites	unsupported metal blacks, wires etc.	hydrogenation of pharmaceuticals over Pt blacks; ammonia oxidation on gauzes	unsupported metal sulphides; metal oxide anodes	hydrogenation of nitrohaloaromatics; dimensionally stabilised anodes for chlorine
individual crystallites	supported metal catalysts	general hydrogenation catalysts; autoexhaust catalysts	supported oxides, sulphides etc.	reductive alkylation
metal clusters	supported metal alloys, e.g. Ru/Cu	petroleum refining catalysts	metal cluster compound catalysts	not used at present

degree of dispersion (increasing down table)	metal catalysts		compound catalysts	
	description of catalyst	industrial example	description of catalyst	industrial example
metal atoms	zeolite supported metal catalysts	petroleum refining catalysts	mononuclear metal complexes	asymmetric hydrogenation over Pt, Rh etc. complexes; OXO reaction over Rh

Aggregated Crystallites. As with the metal systems described in Section 4.2, platinum-group metal compounds were first used as heterogeneous catalysts in the unsupported form. This form of catalyst is extremely important industrially being the basis of the technology employed in (I), the chlorine industry, (II) control of NO_x emissions in the automobile exhaust purification system, and (III) the selective catalysts used in the fine chemicals industry, although in the latter cases replacement of the unsupported catalysts by more sophisticated supported forms has taken place.

Dimensionally stabilised anodes for brine electrolysis utilising platinum-group metal – valve metal mixed oxides were patented in 1967. Since then they have been applied to an ever greater volume of chlorine production until by 1979 these anode coatings were used for ~50% of world chlorine production [19]. The normal coating for chlorine anodes is ruthenium dioxide – titanium dioxide. The titanium dioxide in the form of rutile is isomorphous with ruthenium dioxide with which it forms a solid solution. Bonding to the titanium metal anode takes place via a ruthenium deficient rutile layer a few atoms thick. The oxide layer is oxygen deficient and exhibits quite a high conductivity [20].

The search for catalytic materials for incorporation in standard automobile exhaust clean-up systems to remove NO_x, has induced research workers to explore the use of ruthenium oxides, and in particular the complex oxides, such as the perovskites, barium ruthenate and lanthanum ruthenate. The method of preparation, high temperature firing of the oxides followed by grinding, gives rise to particles a few μm in diameter [34].

Platinum-group metal sulphides are frequently formed by hydrogen sulphide precipitation from solution. The resulting fine precipitates are dried and used as catalysts without further preparation as particles of a few μm diameter [35], as may be deduced from the ease with which they may be separated from reaction mixtures by filtration. Such bulk sulphides are frequently found to be amorphous [36].

Individual Crystallites. Supported dispersions of platinum metal oxides, sulphides, halides and acetates have been used industrially in many reactions. The usual supports are charcoal, alumina and silica gel. The aim of supporting these materials is to improve the degree of dispersion by providing a large surface area on which individual crystallites may be deposited, so increasing the activity of the catalyst.

The techniques available for the dispersion of simple compounds, such as halides and acetates, ensure that the integrity of the compound is preserverd during preparation [37, 38, 39]. With other techniques, used for the dispersion of sulphides [35] and complex oxides [34] it is not always so. This has been acknowledged by some workers, trying to improve the dispersion of barium/lanthanum ruthenates by impregnation of the support with barium/lanthanum nitrate, firing, then impregnating with a ruthenium salt, when they say "there is no direct evidence, however, that every ruthenium atom has been deposited in the vicinity of the stabilising oxide so as to ensure the formation of the ruthenate". More often than not it is assumed that the catalytic species is formed, if the catalyst shows the same catalytic properties as the unsupported compound [34].

Supported platinum-group metal compounds have not been exploited industrially as widely as their unsupported counterparts, but they make a notable contribution to both automobile pollution control catalysts (simple and complex oxides) and hydrogenation catalysts for the fine chemicals industry (sulphides).

Cluster Compounds. Cluster compounds have been defined as "frameworks of three or more metal atoms or ions surrounded and stabilised by ligands, commonly carbonyls, hydrides, phosphines and halides" [31]. The frameworks of metal atoms/ions are held spatially in definite configurations by metal-metal bonds. The metal atoms, which are close packed, form metal frameworks that are fragments of those found in metals, for instance, a face-centered cubic, body-centered cubic or hexagonal close-packed metal core with some of the peripheral faces capped by other different metal atoms. The following table gives a list of some of the metal frameworks that have been found, together with examples in which these structures have been found in platinum-group metal complexes.

number of metal atoms	structure of the metal atoms	examples containing platinum-group metal
3	triangle	$Os_3(CO)_{12}$
4	tetrahedra, squares, planar and bent diamonds	$Ir_4(CO)_{12}$
5	trigonal bipyramids, square pyramids	—
6	octahedra, planar rafts	$Os_6(CO)_{21}$
7	face capped octahedra	—
13	centred, reflected cube octrahedra	$[Rh_{13}(CO)_{24}H_3]^{2-}$
14	penta (face capped) body-centred cube	$[Rh_{14}(CO)_{22}]^{2-}$
19	pentagonal pyramids	$[Pt_{19}(CO)_{22}]^{4-}$
26	tricapped trigonal prism fragments of hexagonal close packing	$[Pt_{26}(CO)_{32}]^{2-}$
38	cube octahedra (face-centred cubic)	$[Pt_{38}(CO)_{44}H_x]^{2-}$

Metal cluster compounds are not currently used in industrial catalysis, but many have been investigated for catalytic activity. Some are not stable enough to be used catalytically, while others are stable enough to be reacted with ligands anchored to polymer silica and alumina surfaces. This feature gives the potential for cluster compounds to be used both homogeneously and heterogeneously. Although the catalytic activity of metal cluster compounds is largely unknown, they are thought by many to hold great potential as catalysts. For example, the opportunity to influence the properties of the compound by choice of ligand is greater with these compounds than with mononuclear complexes [31, 40]. Also the metal cluster bears a resemblance to molecules adsorbed on a metal crystallite, although this resemblance should not be taken too far [40].

As in any expanding field the literature of cluster compounds chemistry is voluminous. The chemistry of binuclear complexes has recently been reviewed [32], as have polynuclear complexes [33]. The catalytic properties of metal cluster compounds have been commented by [31], and the similarities between metal surfaces and metal clusters reviewed by [40].

Mononuclear Complexes. This is principally the field of solution of "homogeneous" catalysis. However, many of the complexes, like cluster compounds, may be heterogenised by anchoring them to support material surfaces. Industrially, homogeneous processes have attained a high level of maturity, while anchored catalytic systems have proved to be very disappointing primarily because few catalysts have retained their integrity during reaction. Also steric factors have a deleterious effect on the catalysts' activity/selectivity relationships. Here, because of the diverse nature of the mononuclear complexes involved, their catalysis has been considered in isolation from the other platinum-group metal compounds within a single heading "Homogeneous Catalysis" in Section 4.4.7.

Inorganic Molecular Compounds. Osmium and ruthenium tetroxides have long been used as stoichiometric oxidising agents [3, 42]. In the last two decades attempts have been made to make such oxidation reactions catalytic by lowering the amount of metal used and cycling it between the reduced lower valent state and reactive octavalent condition by means of cheap oxidising agents. A variety of such oxidising agents have been used to regenerate the tetroxide including air. The ruthenium compound is the more powerful oxidising agent, converting olefins to shorter chain aldehydes, ketones and carboxylic acids, while osmium tetroxide normally converts them to cis-diols. They have a number of specific industrial applications, particulary in sugar and steroid chemistry.

Both compounds have a tetrahedral structure and are monomeric in organic solvents, with a higher solubility in inert organic solvents than in water. This latter property enables them to be used in phase transfer catalysis.

The motivation for investigating and using platinum-group metal compounds as industrial catalysts has been threefold:

(I) the desire to initiate new types of reaction that are difficult or impossible over metal surfaces;
(II) the desire to improve the selectivity of catalysts in existing processes;
(III) the desire to process lower grade feedstocks without poisoning the catalyst.

The technology which has arisen now covers as wide a spectrum of reactions as those over metals and includes hydrogenation, dehydrogenation, oxidation, chlorination, dehydrochlorination, hydrosilylation, carbonylation, hydroformylation, polymerisation, isomerisation etc. Many reactions which have been considered to take place over "metallic" surfaces are now known to be mediated by surfaces which have been drastically modified by reaction with some impurity or reaction product. For example, sulphur compounds commonly desulphurise in hydrogenation systems to give hydrogen sulphide. This may react with a metal surface to give a sulphide layer or even the bulk sulphide. Some compound catalysts arise as a product of the catalyst preparation route, such as borides, while others, such as platinum metal hydrides can form under hydrogenation conditions, whenever the hydrogen flux to the surface is greater than the rate of consumption by the catalytic reaction. Under oxidation conditions some platinum metals will oxidise to give an oxide surface on which the reaction proceeds. A few compound catalysts are nonstoichiometric when manufactured, e.g. borides. Others assume a nonstoichiometric composition during reaction. It is this compositional variability which allows the precise tailoring of platinum-group metal compound catalysts.

Estimates of the total use of platinum-group metal compound catalysts by the chemical industry using published data are impossible. An estimate of their application can, however, be obtained by looking at the amount of product catalytically processed per annum. But it must be remembered that reaction over a platinum metal compound may not be the only preparative route. With homogeneous catalytic processes the estimates are fairly reliable; with heterogeneous catalytic processes the degree of reliability is much less. No estimate of the market for the use of platinum metal complex oxides for NO_x control in automobile exhaust systems can be made. The table below contains the results of such estimates for products processed over homogeneous and heterogeneous catalysts.

chemical products	catalytic metal	quantity of product ($\times 10^6$ t)
homogeneous catalysts:		
acetic acid	Rh, Ir, Mn	1.8
acetaldehyde	Pd	0.84
acetic anhydride	Pd	0.48
vinyl acetate	Pd	0.85
C_4 alcohols	Rh, Co	0.55
C_8 alcohols	Rh, Co	0.38
heterogeneous catalysts:		
antioxidants (by reductive alkylation)	Pd, Pt	0.065
herbicides	Pd, Pt	0.057
total		5.022

The total of 5.022×10^6 t of product represents about 15% of US production of organic chemicals for 1980.

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4.4.1 Platinum-Group Metal Hydrides

For the purposes of this section a hydride will be defined as a binary or ternary combination of metal/metals and hydrogen. Many metals will form stoichiometric binary compounds with hydrogen, which can be classified as (I) ionic, where the hydrogen assumes a strongly electronegative character, (II) covalent, where a nonpolar electron sharing bond is formed, or (III) metallic, in which the metallic properties of the element are retained, such as high thermal and electrical conductivity [1].

Some metallic hydrides are nonstoichiometric, particularly those of group VIII of the Periodic Table. Of the six platinum-group metals, palladium alone forms a simple binary hydride, while the other elements exhibit relatively low solubilities for hydrogen [2].

Ternary hydrides may be looked upon as the hydrides of intermetallic compounds or as simple binary hydrides with a second metallic element replacing a portion of the first metal.

Palladium hydride was the first metal hydride to be discovered, when Graham in 1866 found that palladium metal dissolved large quantities of hydrogen while in contact with a hydrogen gas atmosphere, a process which he called "occlusion". Somewhat later, in 1862, he found that palladium cathodes "occluded" hydrogen in electrolytic cells. Work by researchers subsequently has allowed the construction of a phase diagramm for bulk palladium (wires etc.), which is shown in **Fig. 23**, p. 204 [3].

Similar isotherms have been obtained with finely divided palladium blacks [4].

It is generally agreed that two hydride phases exist. The solid solution of hydrogen in palladium up to the section where the pressure remains constant is known as the α-phase. At the start of the section of constant pressure a new phase begins to nucleate known as the β-phase which grows by transformation of the α-phase. The two phases are coexistent over the constant pressure region which is known as the (α + β)-phase. Nucleation of the β-phase is complete by the point at which the pressure begins to rise again and the rising pressure region can be seen as the solution of hydrogen in the β-phase. The absorption/desorption isotherms show considerable hysteresis. Stoichiometric hydrides such as Pd_2H, Pd_3H, Pd_4H and Pd_8H have been claimed [4, pp. 15/8], but it is now known [3] that the hydride is nonstoichiometric with the α-phase maximum corresponding to a composition of $PdH_{0.03}$ and the β-phase corresponding to $PdH_{0.68}$, both at 1 atm hydrogen pressure and room temperature. The two-phase region disappears at temperatures >295.3°C, the critical temperature (T_c). The corresponding critical pressure (P_c) is 19.87 atm and the critical composition $PdH_{0.27}$. The rate of hydrogen adsorption/desorption is dependent on the catalytic activity of the Pd surface for H_2 dissociation [4, p. 19].

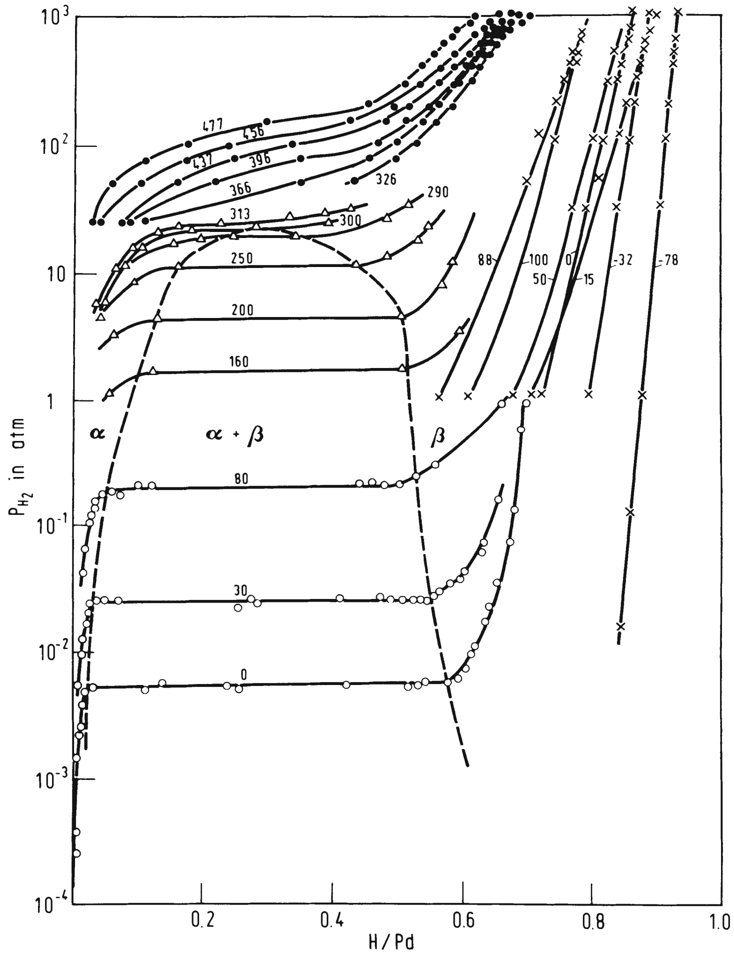

Fig. 23. Absorption isotherms of hydrogen in palladium, taken from different authors (see [3]).

Charging palladium with hydrogen changes both the topology and the shape of palladium specimens [4, pp. 43/9]. Electrical properties are also modified, the electrical resistance increasing by a factor of 1.8 in passing from palladium metal to palladium hydride $PdH_{0.7}$ [4, pp. 50/5]. The electrical potential of palladium cathodes also alters as their hydrogen content increases; this is shown in **Fig. 24**.

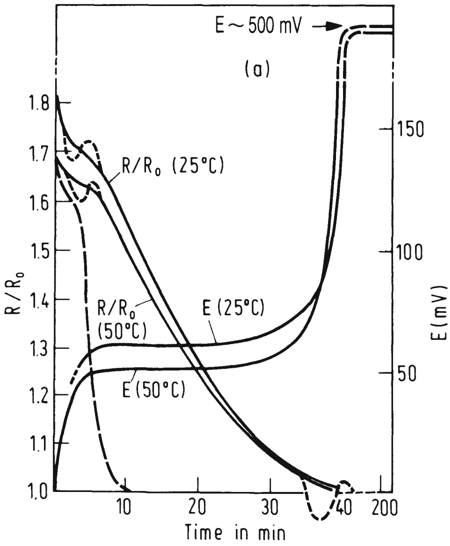

Fig. 24. Composite plot of results with previously hydrided specimens of 0.0122 cm diameter showing changes of R/R_0 and electrode potential E with time at 25°C and 50°C. Temporarily broken line indicates course of results obtained when the measuring current continuously passed through the specimen. Completely broken line indicates change of R/R_0 (measured by a.c.) during anodisation at 63.0 mA/cm^2 in 0.02N HCl (25°C).

The other platinum metals occlude hydrogen to a much smaller extent, the levels of occluded H_2 being shown in the table below.

temp.	H/Me				
in K	Ru	Rh	Os	Ir	Pt
293	—	0.025 to 0.03	0.11	0.10	0.005
373	0.04	0.02 to 0.03	0.07	0.13 to 0.14	0.007

Occlusion occurs to the greatest extent in iridium and osmium (H/Me = 0.1 to 0.14), ruthenium and rhodium will occlude between one quarter and one third the hydrogen of Ir and Os while platinum will occlude only about one twentieth as much hydrogen as the other two elements [5].

Considerable investigation of the effect on hydrogen absorption of alloying palladium with other elements has taken place. Near neighbour face-centred cubic metals, e.g. Au, Ag, Cu, Pt, Rh, Ir, Ni, form substantial solid solution alloys with palladium in which palladium and the other element are virtually interchangeable on any lattice site over the whole range of compositions [4, pp. 70/93]. In all cases the solubility of hydrogen is lower in the alloy than in palladium [4, 6].

Palladium/rare earth alloys have been shown to absorb considerable quantities of hydrogen and to form hydrides of the type $YPdH_3$ [7]. Platinum-group metals may also replace a portion of the nickel in $LaNi_5$ without seriously affecting hydride formation [8, 9]. Although both $LaNi_5$ and $LaNi_5H_6$ have catalytic activity, no investigation of the catalytic behaviour of any replacement alloy has been reported. Palladium and rhodium also form an alloy with cerium, $CeRh_{3-x}Pd_x$ [10]. This alloy absorbs hydrogen up to a value of x = 2.4 and the catalytic properties are thought to be connected with the stability of the hydride hydrogen atoms [11]. Data and methodology have been published for determining which intermetallic binary transition metal compounds will form stable hydrides [12, 13]. Rhodium forms stable hydrides with lithium hydride Li_4RhH_4; nothing is known of their catalytic properties [14].

In many ways palladium hydride differs from the majority of metallic hydrides. Hydrogen in palladium hydride is located in octahedral sites and it is the only metal to fill octahedral sites in preference to tetrahedral sites. Palladium hydride properties have been explained by three basic models:

(I) hydrogen atoms in the metal lattice; (II) as H^+ ions with the valency electron donated to the conduction band; (III) as H^- ions with an electron drawn from the conduction band.

The three models represent limiting cases, as the electron density distribution in the crystal would be expected to prevent complete charge separation and, at least, to leave partial charges on the hydrogen atom. Most properties of metallic hydrides can be explained either by model (II) or (III), while model (I) is thought to be valid only for the α-phase (or solid solution) region of the phase diagram. Hydrides in the alloy systems with platinum, silver and gold are believed to contain hydrogen in the protonic form (II). At low levels of the second metal, cubic α- and β-phase hydride are to be found up to a platinum content of 12 at.%, silver 30 at.% and gold 17 at.%. It is thought that both hydrogen and the second metallic element contribute to the electron content of the palladium 4d band [1].

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4.4.1.1 Platinum-Group Metal Hydride Preparation

Platinum-group metals and alloys may be hydrided by two methods:

(I) Absorption of hydrogen from gaseous atmospheres at pressures from ~0.01 to 1000 atm and temperatures up to the melting point of the metal; (II) electrolytic charging in which the specimen to be charged is made the cathode in an electrolytic cell. This method has the advantage that hydriding to higher levels at atmospheric pressure can be accomplished more easily than by gaseous equilibration [1, pp. 5/6].

Experimental techniques for obtaining isotherms by low-pressure gaseous hydrogen absorption are described in [2] and high-pressure gaseous absorption in [3]. The method of electrolytic charging by electrolysis in either dilute aqueous sulphuric acid (0 to 100°C) or ethanolic sulphuric acid (–77 to 0°C) is given in [4]. Hydriding palladium by decomposing formic acid on its surface has been practised by [5, 6]. With electrolytic and chemical methods of charging it is frequently necessary to activate the surface of the metal. Many methods have been used among which are charging the specimen electrolytically followed by rapid discharge [7], electrolytic anodisation [8, 9], heating in oxygen [10], or palladising with palladium black [9, 11]. Reactors suitable for charging palladium specimens and conducting catalytic reactions have been described by [12].

It has been discovered that if palladium metal is brought into physical contact with uranium, titanium, zirconium, thorium or cerium hydrides catalytic transfer of hydrogen to the palladium occurs giving the β-phase hydride. The catalytic hydrogen transfer reaction is much more rapid than the transfer from molecular gas phase hydrogen [13, 14].

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4.4.1.2 Reactions

The interpretation of heterogeneous catalytic hydrogen reactions and hydrogenations over the platinum metals has not, until recently taken into account the effect of dissolved hydrogen on the activity/selectivity of the reaction. This is particularly true of platinum-group metal hydrogenations conducted in the liquid phase where the possible effects of hydrogen dissolved in the metal surface on catalytic properties have largely been ignored. Whithin the range of gas phase reactions, however, self-poisoning of palladium by hydrogen was early noticed although no attempt was made to associate it with the ability of palladium to form hydrides [1]. Attention was drawn to the role of dissolved hydrogen in the self-poisoning of palladium catalysts, and many previous observations of loss of catalyst activity during hydrogenation were attributed to self-poisoning. Since then the observation has been confirmed in hydrogen reactions (para/orthohydrogen conversion, hydrogen/deuterium exchange etc.) and found in acetylene/olefin hydrogenations, isomerisations, formic acid decomposition etc. The original explanation is still basically tenable today that electrons from the dissolved hydrogen enter the unfilled 4d band of palladium. Filling of the d band continues with increasing dissolved hydrogen concentration until the 0.66 holes in the d band are filled at approximately $PdH_{0.6}$, the β-phase minimum. With palladium alloys, both the second metal and the hydrogen donate s electrons to the 4d band and the catalytic properties of the alloy become a function of the relative concentrations of the second element and hydrogen. In general once the d band of palladium is filled, the catalytic activity reaches a minimum [2].

Reviews of the catalytic activity of the palladium hydrides and of hydrogen effects in metal catalysts have been published in [1, 3].

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Hydrogen Reactions

Hydrogen reactions consist of four separate, but connected reactions: (I) hydrogen recombination $H + H \rightarrow H_2$; (II) para $H_2 \rightarrow$ ortho H_2 conversion; (III) ortho $D_2 \rightarrow$ para D_2 conversion; (IV) H_2/D_2 exchange $H_2 + D_2 \rightleftharpoons 2HD$.

All four reactions are discussed in [1]. They are simple reactions and since the reactant and products are chemically identical the derived rate expressions are without complication. H_2 molecules can be dissociated into H atoms by means of a radio frequency field. The hydrogen atoms in the gas phase may be caused to recombine catalytically at metal surfaces to reform molecular hydrogen. Apart from early work over palladium and platinum [2], in which the lower activity of the palladium is possibly attributed to hydride formation [1], the only extensive work on hydrogen recombination is that in [3]. Examining the recombination of hydrogen atoms over palladium and palladium-gold alloy foils (12, 31, 45, 72 and 100 at.% Au) at room temperature, it was found that palladium and the low gold alloys progressively lost catalytic activity. New and unannealed foils maintained activity for longer than annealed foils, while re-use of a foil after annealing caused rapid poisoning. The main results are shown in the following table from [4].

Coefficients of recombination, γ, of H atoms on Pd and Pd-Au foil catalysts[a]:

metal catalyst	γ		metal catalyst	γ	
	after a short exposure to H	after a long exposure to H[b]		after a short exposure to H	after a long exposure to H[b]
Pd	1.0×10^{-2}	1.2×10^{-3}	Pd55 Au45	1.0×10^{-2}	$(1.2/2.1) \times 10^{-3}$
Pd88 Au12[c]	9.5×10^{-3}	2.5×10^{-3}	Pd28 Au72	5.5×10^{-3}	1.5×10^{-3}
Pd69 Au31	1.2×10^{-2}	$(1.3/2.0) \times 10^{-3}$	Au	5.7×10^{-4}	5.8×10^{-4}

[a] $t \approx 20°C$; $p \approx 0.2$ Torr. – [b] Observed only for a first section of a cylindrical sample, near the atomic H source. – [c] 88 at.% Pd and 12 at.% Au.

The poisoning effect in palladium and the low gold alloys is attributed to hydride formation; hydrogen absorption-desorption on re-use causing metal crystallite disintegration with consequent activation of the surface for hydrogen dissolution.

A review has been published of the kinetics and mechanism of the para-hydrogen and ortho-deuterium conversions [1]. Although both conversions have been examined over the platinum-group metals, it is only in the case of palladium that the effect of dissolved hydrogen (hydride) on the conversion has been considered. Early work suggested that the rate of both para-hydrogen and ortho-deuterium over palladium was poisoned by the formation of palladium hydrides [5]. A re-examination found that as the d band of palladium was filled by electrons from the dissolved hydrogen, the activation energy rose from 4.3 to 11 kcal/mol. The results of para-hydrogen conversion over α-palladium hydride are given in the table below and are shown together with those for the β-palladium hydride in **Fig.25**.

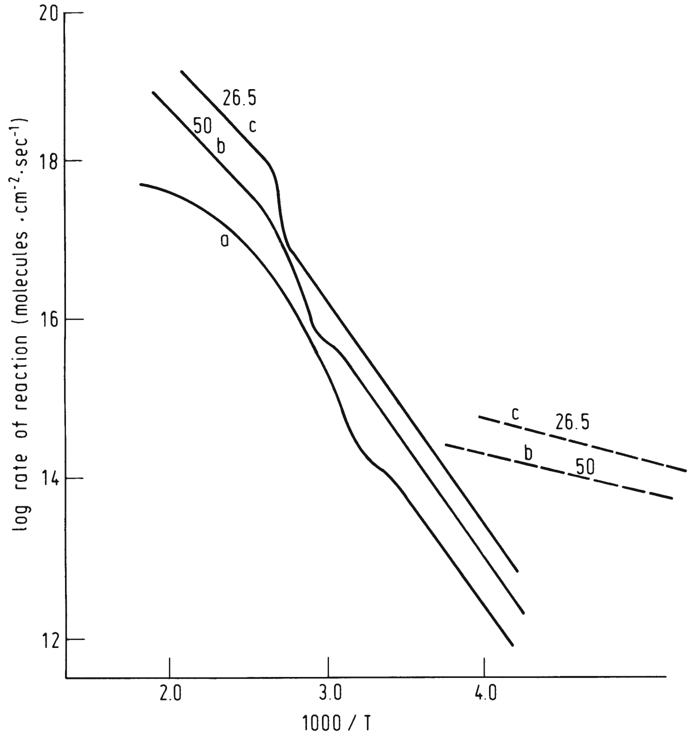

Fig. 25. Para-hydrogen conversion over α- and β-Pd hydride (dashed curves); P_{H_2} = (a) 6, (b) 50, (c) 26.5 Torr.

Para-hydrogen conversion over α-palladium hydride at 450 K:

pressure (Torr)	activation energy (kcal/mol)	pre-exponential factor (molecules·$cm^{-2}\cdot s^{-1}$)
265	9.5	2.9×10^{23}
55	9.3	1.4×10^{23}
6	6.3, 6.3	~1.5×10^{22}, 1.5×10^{22}
1.2	4.3	$5\ \times10^{20}$*)

*) observation of [6]

For the ortho-deuterium conversion (50 Torr) over β-palladium hydride, the logarithm of the reaction rate (molecules·$cm^{-2}\cdot s^{-1}$) rises linearly from ~11.9 to ~14.6 when 1000/T decreases from ~4.4 to ~3.4 [7].

A ten to one hundredfold decrease in reaction rate was observed as a break of slope in the Arrhenius plot just before the bulk formation of β-hydride. The authors accounted for this by assuming that β-phase hydride was formed at the catalyst sample prior to the bulk.

Mixtures of hydrogen and deuterium can be equilibrated over transition metals, and in particular the platinum-group metals, according to the equation $H_2+D_2=2HD$.

The equilibrium positions for the system have been calculated and confirmed by experiment. The value of the equilibrium constant varies with temperature. At room temperature the equilibrium composition of a mixture (50 at.% H_2, 50 at% D_2) is 26.2% H_2, 26.2% D_2 and 47.6% HD. The mechanism and kinetics of hydrogen-deuterium equilibration reactions over transition metals has been reviewed [1].

As for the hydrogen conversion reactions, hydrogen-deuterium exchange has been studied over all platinum-group metals, but it is only with palladium that the effect of dissolved hydrogen is taken into account. Considerable argument has taken place over the exact mechanism of hydrogen-deuterium exchange and this has been reviewed [1, 7]. The latter authors found that the activation energy for the exchange reaction over β-palladium hydride was 12.5 kcal/mol.

All four hydrogen reactions have been reviewed in [4].

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Olefin and Acetylene Isomerisation and Hydrogenation

The hydrogenation and isomerisation of simple mono-olefins, di-olefins and acetylenes over the platinum-group metals have been studied as model catalytic systems for a long time. A review has been published of the information, both practical and theoretical, gained on these systems [1]. Studies of the effect of hydrogen dissolved in the metal catalyst on these reactions are altogether rarer, despite the insight that they can reveal of the manner in which the platinum metals may act as catalysts. Ethylene, the simplest of the olefins, has been used more frequently than either other olefin or acetylene, as a model system. With the higher unsaturated hydrocarbons from C_4 onwards isomerisation, both positional and geometrical, becomes important, adding significantly to the practical difficulties of unravelling the spectrum of products, but giving, at least potentially, a large increase in the information to be gained [1, p. 256]. All six platinum metals will occlude hydrogen and the effect of dissolved hydrogen on olefin hydrogenation has been investigated. Acetylenes have only been studied over palladium hydride, although some work has been reported on Pd-Rh-Ce alloys where hydrogen solubility in the catalyst may affect the reaction activity. Some workers have examined the hydrogenation of ethylene and propylene at −78°C over palladium hydrides (containing α-hydride and (α + β)-hydride), and concluded that the rate of hydrogenation is the same whether hydrogen is added or not. The hydrogen for hydrogenation, therefore, would appear to come from the hydride and not from the gas phase, the rate of hydrogen transfer from the gas phase being extremely rapid. The rate of ethylene hydrogenation is also about five times greater than that for propylene, so that diffusion processes within the bulk hydride cannot be the rate-controlling step. The authors suggest that the rate-controlling step is the addition of adsorbed hydrogen atoms to adsorbed ethylene molecules or ethyl radicals [2, 3]. The diffusion of hydrogen within bulk palladium hydride was not rate-controlling at temperatures of 25 and 50°C, in the liquid phase hydrogenation of ethylene over palladium hydrides. Rates of hydrogen removal did not vary with the concentration of hydrogen in the metal, and were

3.6×10^{16} molecules·cm^{-2}·s^{-1} (0.079 ml·cm^{-2}·min^{-1}) and 3.4×10^{16} molecules·cm^{2}·s^{-1} (0.074 ml·cm^{-2}·min^{-1}) at 50°C [4]. The rate-controlling step in the hydrogenation appeared to be the rate of ethylene diffusion to the palladium hydride surface. The hydrogenation of ethylene over 480 Å thick films of palladium and palladium hydride has been studied; a tenfold increase in hydrogenation rate occurred for β-phase palladium hydride compared to palladium metal. The hydrogenation over β-palladium hydride was first order in hydrogen [5].

In the hydrogenation of acetylene over (α + β)-palladium hydride it has been found that the initial reaction of acetylene with palladium hydride is rapid and produces mainly ethane. As the reaction proceeds the rate of hydrogen removal decreases, and ethylene becomes the predominant product. The authors explain their results by supposing the surface to be poisoned by carbonaceous products [6]. Again hydrogen diffusion to the metal surface from inside the bulk palladium hydride is not seen as rate-limiting. A later study [7] of the same reaction over palladium, α-phase and β-phase palladium hydrides, suggests that selectivity over the β-phase is less than that over α-phase for ethylene formation, while over palladium metal the selectivity is very high. A dual mechanism is proposed for acetylene hydrogenation. Over β-phase hydride which will adsorb acetylene, but not ethylene, complete hydrogenation to ethane was proposed, while over α-phase a stepwise mechanism $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$ was considered to occur, with the high selectivity to ethylene arising from the absorptive thermodynamic factor [6].

The selectivities of Ru, Rh, Os, Ir and Pt containing occluded hydrogen compared to those for the same metals without occluded hydrogen are shown in **Fig. 26** [8, 9].

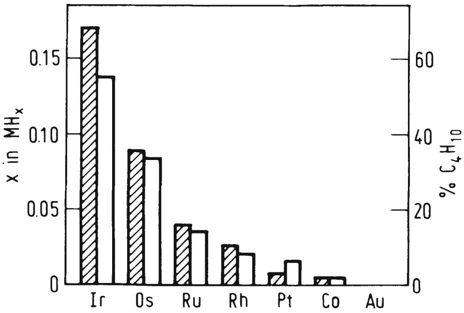

Fig. 26. Comparison of the extent of hydrogen occlusion in metal powders measured by butene titration at 373 K (left-hand ordinate, shaded columns) with the yields of butane, in 1,3-butadiene hydrogenation over metal-aluminas at 373 K (right-hand ordinate, open columns).

Dependence of selectivity in 1,3-butadiene hydrogenation on the extent of hydrogen occlusion in Ir powder and in iridium-alumina:

x in IrH$_x$	0.004	0.01	0.02	0.045 to 0.06	0.08	0.10	0.17
selectivity	1.00	0.91	0.82	0.47 to 0.80	0.76	0.65	0.55

It has been shown that by careful preparation iridium catalysts for 1,3-butadiene hydrogenation may be modified from low-selectivity catalysts (S = 0.2) to high-selectivity catalysts (S ≈ 1.0). Control of selectivity is achieved by altering the content of occluded hydrogen, low selectivity being associated with high occluded hydrogen contents and high selectivity with low occluded hydrogen content catalysts [8, 9].

The pseudobinary alloys MRh$_{3-x}$Pd$_x$, where M is Ce or Zr have been investigated as catalysts in the hydrogenation of l-octyne [11, 12]. A tentative attribution of the sudden change in selectivity for l-octene formation at x = 2.4 for the cerium alloy to a change in the ability of the alloy to absorb hydrogen is made [12].

In the reduction of the carbon-carbon double bonds in acrolein, allylcarbinol and methacrylic acid over palladium hydride, diffusion of hydrogen within palladium may be rate-controlling for these reactions [13, 14].

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Formic Acid Decomposition

An extensive review of the decomposition of formic acid has been published. The reaction is predominantly $HCOOH \rightarrow H_2 + CO_2$. Decomposition occurs over a wide range of transition metals including palladium, rhodium and platinum [1]. Only two reports of the catalytic decomposition of formic acid over hydrided surfaces exist, both with palladium as catalyst. Early workers found that the decomposition reaction slowed with time but was not due to the hydrogen content of the palladium. Specimens partially hydrided with hydrogen gas gave the same initial rates as hydrogen-free palladium. They attributed the poisoning of the decomposition to the deposition of formaldehyde formed by the reaction $2HCOOH \rightarrow HCHO + CO_2 + H_2O$. The temperature of decomposition was 50°C and conducted entirely in the liquid phase [2]. Later workers, however, studied the reaction over palladium and palladium hydride between 50 and 140°C (presumably in the vapour phase) and found that the activation energy changed with temperature and whether the catalyst was pretreated with hydrogen or not. At temperatures between 50 and 75°C the activation energy was 5.3 kcal/mol when the metal was not pretreated with hydrogen and 12 kcal/mol when pretreated. At 75 to 140°C the activation energy was 32.9 kcal/mol and was independent of pretreatment with hydrogen. They assigned the low activation energy to the α-phase of palladium hydride and the high activation energy to the β-phase [3].

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Other Reactions

The dissolution of palladium from carbon-supported catalysts during the hydrogenation of nitro-aromatic compounds has long been recognised to be an industrial problem. In a recent investigation of the phenomenon using a model system (ammonia and ammonium chloride) it was discovered that by converting the metal to the β-phase palladium hydride, dissolution ceased. The authors reasoned that hydriding the palladium changed its electrochemical potential, making it cathodic with respect to the carbon support, and so prevented corrosion of the metal. The conclusions were tested in an industrially significant reaction, the hydrogenation of 2,4-dinitrotoluene, and found to hold. When the hydrogenation was conducted under hydrogen mass transfer controlled conditions the formation of hydride was prevented and the catalytic metal dissolved. If the hydrogenation was controlled by the surface kinetics of the palladium catalyst metal and hydrogen arrived at the surface faster than it was consumed by the hydrogenation reaction, then the palladium metal became hydrided and palladium loss was prevented [1].

A similar solution to palladium solubility problems has been proposed in the formation of hydrogen peroxide from the elements, except that the metal is made cathodic by a voltage impressed externally, and not generated internally [2].

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4.4.2 Platinum-Group Metal Borides

Over 200 binary compounds of boron are known, exhibiting a wide range of structural types and stoichiometries. Equally numerous are the ternary and more complex borides with two metals or of a metal with boron and another nonmetallic element such as carbon [1]. Binary boride compounds have been used as catalysts in hydrogenation processes, at least in the laboratory, since the early 1950s [2], and proposals have been made to explore the range of boride compounds as potential catalysts in the very demanding hydrogenation of coal to liquid hydrocarbons. All six platinum-group metals are known to form at least one boride each [1, p. 702], those of osmium and iridium being least known, and include metal-rich borides such as Pd_3B and Pt_3B, boron-rich compounds such as Ru_2B_5 and Os_2B_5 and nonstoichiometric compounds, for example $RhB_{1.1}$ (see table below) [3, 4].

Borides of the platinum-group metals:

Ru_7B_3	Rh_7B_3	Pd_3B	(OsB)	$IrB_{1.1}$	Pt_3B
$Ru_{11}B_8$	(Rh_2B)	Pd_5B_2	OsB_2	(IrB_2)	Pt_2B
$RuB_{1.1}$	$RhB_{1.1}$	(Pd_2B)			Pt_3B_2
Ru_2B_3	(RhB_2)		Os_2B_5		PtB
RuB_2					
Ru_2B_5					

How catalytically active these compounds are for hydrogenation reactions is a matter of conjecture, as few of the pure phases have been prepared for catalytic purposes. Most "borides" tested catalytically have been prepared by the reduction of platinum-group metal chloride solutions with sodium or potassium borohydride, and although they have been shown to contain chemically bound boron, they are not chemically pure and are almost certainly mixtures of the boride/borides with the zerovalent metal [5]. The most important feature, which has given rise to interest in platinum-group metal borides as catalysts, is their apparent chemical inertness and hence their ability to withstand the rigours of high temperature and pressure, and the corrosive attack of hydrogen sulphide. Thus, it has been claimed that platinum boride (Pt_2B_3) is insoluble in hydrochloric, sulphuric and nitric acids, and alkali solutions. It does react, however, with molten alkali metal carbonates, hydroxides, and chlorates, but is inert to molten alkali metal nitrates [6].

Phase diagrams for the B-Pd, B-Pt, B-Rh and B-Ru systems have been published suggesting complex relationships between boron, the platinum-group metal and the boride compounds [7]. Additional information on these systems and the B-Os and B-Ir systems is available in [8] and its supplements [9, 10], although for B-Os and B-Ir the information is insufficient to allow the construction of even a tentative phase diagram.

Although complex borides have been proposed as catalysts, the only complexes containing a platinum-group metal that have been shown to be active catalysts are $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$. Both are active for hydrogenation and hydrogenolysis of cis-2-butene and hydrogenation of carbon monoxide. The nickel catalyst appears to be the more active of the two [11].

Metal rich compounds like Pd_3B and nonstoichiometric borides like $RhB_{1.1}$ "contain isolated boron at the centres of trigonal prisms of metal atoms". Compounds with higher boron contents, such as $Ru_{11}B_8$, contain branched chains of boron atoms. The structural classification of the PGM borides is shown in the table below. So little work has been done on the catalytic properties of well-defined platinum-group metal borides that the relationship between structure and activity is completely unknown. With platinum metal borides made by reduction of salts with alkali metal borohydrides only very weak lines are obtained by X-ray diffraction insufficient to allow any structural determination [1].

Structural classification of platinum-group metal borides:

boron arrangement	structure type	examples	closest B-B distance (Å)
isolated B atoms	Fe_3C	Pd_3B	>2.7
	Pd_5B_2	Pd_5B_2	~ 3.3
	Th_7Fe_3	Ru_7B_3 Rh_7B_3	~ 3.2
	anti NiAs	$RhB_{1.1}$ PtB	2.11 2.03
branched chain	$Ru_{11}B_8$	$Ru_{11}B_8$	1.68 (on chain) 1.70 (on branch)
layer networks	RuB_2	RuB_2 OsB_2	1.65 —

The stability of borides in sulphur-containing atmospheres increases towards the right of the Periodic Table; in general a high sulphur tolerance can be expected for group VIII metal borides [3].

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4.4.2.1 Preparation of Boride Catalysts

The most obvious preparative techniques are those which directly or indirectly lead to the combination of the two elements at high temperature [1, 2]. Such methods are of great value in the establishment of stoichiometry, structure and phase relationships, but are of very limited value in determining the catalytic properties of borides simply because the surface area of such thermally produced materials is so low [3]. Some catalytic work, however, on transition metal borides has been reported [4]. Russian and French workers have investigated the structure of boride catalysts by means of X-ray diffraction. With the platinum-group metal borides the situation is less satisfactory. Those materials that have been used catalytically have been in general prepared by precipitation with sodium borohydride. Such materials are difficult to characterise, the X-ray diffraction patterns are very diffuse, and their catalytic activity is known to be strongly influenced by the method of preparation [5, 6]. One report of preparing platinum metal borides by sodium hydroxide leaching of an alloy of boron and the platinum with aluminium, analogous to Raney skeleton metals, has appeared [7].

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Thermal Methods of Preparation

Eight methods of preparing metal borides by thermal combination have been given in the literature [1]:

(I) direct combination of the elements

$$M + nB \xrightarrow{1150^\circ C} > MB_n$$

(II) reduction of the metal oxide with boron or boron plus carbon

$$M_xO_y + (n + y)B \xrightarrow{1800^\circ C} M_xB_n + yBO$$

$$MO + 3B_2O_3 + 10C \xrightarrow{2000^\circ C} MB_6 + 10CO$$

(III) co-reduction with hydrogen
$MCl_x + n\,BCl_3 + (3n + x)H_2 \xrightarrow{1300^\circ C} MB_n + (6n + 2x)HCl$

(IV) reduction of a boron halide with a metal or metal plus hydrogen
$n\,BX_3 + (x+1)M \xrightarrow{1200^\circ C} MB_n + x\,MX\,3n/X$

(V) electrolytic deposition from fused salts

(VI) co-reduction with carbon
$M_2O_5 + B_2O_3 + 8C \xrightarrow{1500^\circ C} 2MB + 8CO$

(VII) reduction of metal oxide with boron carbide
$M_2O_3 + 3B_4C \xrightarrow{1600^\circ C} 2MB_6 + 3CO$

(VIII) co-reduction of mixed oxides by metals: two types of reaction are possible, either the metal oxide and boron are reduced by magnesium or aluminium or the boron trioxide can be reduced by the metal whose boride is required.

Potentially all of these methods are available for the thermal preparation of platinum-group metal borides. In practice, however, only two methods have been used, (I) the combination of the elements and (IV) the reduction of a boron halide with the metal plus hydrogen. Some workers have heated stoichiometric quantities of the platinum-group metal and boron in evacuated sealed silica capsules at 1000 to 1200°C [2], others, in order to avoid contamination of the platinum metal boride with the silicide, sintered stoichiometric amounts of metal and boron on boron nitride discs [3]. An arc furnace has been used to make ruthenium, rhodium, platinum, iridium and osmium borides [4, 5]. The platinum metal borides have also been prepared by the passage of boron tribromide vapour and hydrogen over the heated metals [2].

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Wet Chemical Methods of Preparation

The most important method for preparing catalytically active platinum-group metal borides is that of reacting either the metal chloride or the hydroxide with sodium, potassium or calcium borohydride. The order in which the reactants are mixed is important, especially with ruthenium and rhodium, as the platinum metal borides decompose solutions of BH_4^- ions [1]. The decomposition of sodium borohydride over the platinum-group metal borides has been studied and the following sequence of activities obtained: $Ru = Rh > Pt > Os > Ir \gg Pd$ [2].

When solutions of platinum-group metal chlorides are added to solutions of sodium borohydride the resulting borides decompose the borohydride solution, in the case of ruthenium and rhodium almost explosively. The normal mode of preparation of unsupported borides is, therefore, to add the borohydride solution to the platinum metal chloride in aqueous solution, usually at room temperature [1, 3 to 6]. By using ethanolic solutions, the rate of formation of the borides at room temperature can be slowed, ensuring complete reaction [7, 8]. The use of potassium and calcium borohydride has been pioneered by the Russians who found that hydrolysis of the calcium salt left some 10 to 16% calcium hydroxide in the resulting catalyst, improving its dispersion [3, 6].

The reduction of platinum metal chlorides absorbed on supports by sodium borohydride has been used to prepare supported boride catalysts [9, 10]. Some authors have reduced palladium hydroxide adsorbed on bone charcoal, alone and in the presence of polyvinyl alcohol, with sodium borohydride to give supported palladium boride catalysts. The unsupported analogues were made by reducing palladium hydroxide with or without polyvinyl alcohol to produce active palladium boride catalysts [11 to 13].

Complex hydrides of rhodium with either nickel or cobalt have been prepared by mixing ethanolic solutions of nickel or cobalt chlorides containing the stoichiometric quantity of rhodium with a fourfold molar excess of sodium borohydride under a nitrogen atmosphere. The material is pyrophoric when dry and must be stored in an inert atmosphere [14].

Platinum, palladium and rhodium borides have been made from the platinum metal-boron-aluminium alloys by leaching them with 10% sodium hydroxide [3].

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4.4.2.2 Chemical and Physical Properties

The chemical and physical properties of the catalytic platinum metal borides have not been extensively investigated, osmium, iridium and ruthenium have been entirely ignored from this viewpoint. Most workers assume, following the original publications, that reduction of platinum metal salts by sodium borohydride produces the pure metal [1], although others had already found, that samples of platinum, palladium and rhodium reduced with sodium borohydride contained fixed boron [2].

The first full analysis of platinum metal borides showed that palladium and rhodium borides approximated to M_3B while platinum boride was between Pt_2B and Pt_5B_2. The results are shown in the table below.

Hydrogen was evolved by the catalyst on heating, some 40 ml H_2 being produced by each gram of catalyst. The hydrogen was only weakly bonded to the catalyst, suggesting physical absorption rather than chemical bonding. In constrast a wide rather weak band in the infrared spectrum is ascribed to hydrogen-metal bonds [3].

salt	taken, g		analysis of products					
			weight%			atom fraction		
	salt	$NaBH_4$	M	B	H	M	B	H
$PdCl_2$	0.25	1.0	96.3	3.1	0.37	0.88	0.28	0.37
$RhCl_3$	0.25	1.0	92.8	2.9	0.40	0.90	0.29	0.40
H_2PtCl_6	0.25	1.0	95.7	2.28	0.42	0.48	0.21	0.42

Chinese workers analysed a palladium catalyst produced by the same method. They obtained a boron content of 1050 ppm (1.05 wt%) corresponding to $Pd_{10}B$, by atomic absorption spectrophotometric analysis. Analysis of the catalyst surface for boron by electron microprobe showed that the boron content was below 1%. The authors state that the boron content of the catalyst is too low for estimation by standard chemical techniques [4].

As instrumental analytical techniques have improved, the results have become more secure until now, it is possible to analyse complex boride hydride catalysts to reveal compounds of the type $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$.

The surface areas of palladium boride, rhodium boride and platinum boride catalysts were measured by the N_2 BET method as (in m²/g) 27 for platinum, 32 for palladium and 42 for rhodium [3]; 12.8 for platinum boride [6]; 13 for platinum boride, 35 for palladium boride, 30 for rhodium boride from the electrochemical charging curves [7]; 52 for platinum boride, 48 for palladium boride, 58 for rhodium boride (method of measurement not disclosed) [8]. The effect of using calcium borohydride, as well as the sodium salt, in the preparation of palladium and platinum catalysts is shown in the following table.

Physical properties of platinum and palladium catalysts prepared by sodium and calcium borohydride reduction [9]:

metal	reducing agent	metal area (m²/g)			crystallite size (Å)	agglomerate size (μm)
		N_2 BET	electrochemical			
			fresh	stabilised		
Pt	$NaBH_4$	12	15	7	187	38
	$Ca(BH_4)_2$	27	12	22	127	15
Pd	$NaBH_4$	29	32	23	156	24
	$Ca(BH_4)_2$	41	28	34	147	10

Electron microscope data indicated that sodium borohydride reduced catalysts consisted of small crystallites aggregated firmly into large agglomerates. The metal crystallites formed by calcium borohydride are much more loosely bound into aggregates, probably an effect of the 10% calcium hydroxide contained in the catalyst. All of the catalysts were microporous [9].

The bonding of hydrogen to the catalyst surface has been examined both for hydrogen sorbed during preparation and by electrochemical charging of the surface. Russian workers have discovered that hydrogen absorbed during catalyst preparation could be desorbed by mild heating (70 to 120°C). About 40 ml H_2 per g catalyst were desorbed. Desorption followed the equation $V = V_0 \cdot e^{-E/RT}$ and from it a value for the activation energy E was obtained of ~3 cal/mol suggesting physisorption [3]. But the bond strength of hydrogen chemisorbed on rhodium boride was measured by others as 58.8 kcal/mol, on platinum boride as 60.4 kcal/mol and on palladium boride as 64.9 kcal/mol.

References:

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4.4.2.3 Reactions

No general review of the catalytic reactions of platinum metal borides has been published, despite their having been used for hydrogenation, oxidation, hydrogen transfer catalysis, hydrogenolysis and methanation in both supported and unsupported forms. Hydrogenation reactions have centred around the reduction of carbon-carbon unsaturation with hydrogen and hydrogen transfer agents. Only two papers on the use of hydrogen transfer agents have been published [1, 2]. Little information is available on the selectivity of platinum metal borides in comparison with the equivalent platinum metal black. However, in the hydrogenation of crotonaldehyde, the boride was more selective than the metal black [3]. Complex borides of rhodium with cobalt and nickel will catalyse the hydrogenolysis of butenes, and methanate carbon monoxide [4]. The promotion of base metal catalysts with platinum metal borides has been investigated, but they seem to have little effect on either activity or selectivity. Although borides have been said to be prone to attack by oxygen [5] they have been shown to have useful properties as oxidation catalysts [6]. No use appears to have been made of the predicted high stability of boride catalysts to attack by sulphur compounds [7].

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Hydrogenations

Two studies of the catalytic activity of all six platinum-group metal borides have been made, one using octene-1 as substrate [1], the other α-β unsaturated aldehydes [2]. The order of catalytic activity of the platinum metal borides is given as Rh>Pt>Pd>Ir>Os>Ru [1], essentially the same as the order given by [3] for the hydrogenation of alkenes over the platinum metals.

Alkene and Acetylene Hydrogenation. 1-Hexane has been hydrogenated over platinum and palladium borides that have been prepared by precipitation from the chlorides with sodium borohydride and calcium borohydride. When made from sodium borohydride platinum is more active than palladium, however, with calcium borohydride preparations palladium is more active than platinum. Cyclopentadiene and cyclohexene have both been hydrogenated over palladium, platinum and rhodium borides. When the activities of the three boride catalysts were compared with those of the metal blacks in the same reactions, then it was found that the boride catalysts were about twice as active as the metal blacks and the sequence of activities of the borides is Pd > Pt > Rh [4].

Other hydrogenations of alkenes in the liquid phase have been studied: phenyl-1-cyclohexene and Pd_3B_2 [6], styrene and platinum boride [7] and platinum and palladium borides supported on charcoal with phenylacetylene and cyclohexene [8]. Where comparisons are made the boride catalysts are always more active than their metal counterparts.

Cis-but-2-ene has been hydrogenated over $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ at temperatures up to 500°C. Authors found no trace of the isomerisation products trans but-2-ene or but-1-ene. At temperatures below 90°C hydrogenation was incomplete over the Ni-Rh complex, but above this temperature the yield of n-butane was 100% [12].

Olefinic and Acetylenic Alcohols. Little work on the hydrogenation of either olefinic or acetylenic alcohols has been reported. Dimethylethynylcarbinol (DMEC) and eugenol have both been hydrogenated using platinum and palladium borides. With DMEC the hydrogenation showed two distinct stages corresponding to $-C{\equiv}C- \rightarrow -C{=}C-$ and $-C{=}C- \rightarrow -C-C-$. The second stage was always the more rapid over palladium boride, while the reverse was true of platinum boride [4, 8].

Saturated Aldehydes and Ketones. A series of aromatic aldehydes and ketones have been hydrogenated [6] over Pd_3B_2. The solvent used appears to be important in these hydrogenations, dioxane always being a poor solvent, ethanol a much better solvent. Hydrogenations over palladium boride irrespective of solvent being faster than over palladium black.

For the hydrogenation of saturated and unsaturated hydrocarbons, aldehydes and ketones with a platinum boride catalyst the reaction rates were in the sequence ketone > aldehyde. Side reactions such as hydrogenolysis and condensation were enhanced in acid solution, but were largely suppressed by alkalis [7].

Unsaturated Aldehydes und Ketones. Both crotonaldehyde and cinnamaldehyde have been hydrogenated (1 atm pressure, 20°C) over palladium, platinum and rhodium borides and their respective metal blacks. The metal blacks were always more active than the corresponding boride, in distinction to carbon-carbon double bond hydrogenation in hydrocarbons. The sequence of activities for the borides was reported as Rh > Pt > Pd [5], in agreement with the sequence for the platinum metals given by [3].

The selectivity for carbon-carbon double hydrogenation over that of aldehyde group reduction with crotonaldehyde has been examined over palladium, platinum and ruthenium borides. In water, methanol and hexane solvents the sequence was Pd > Pt > Ru. Hydrogenation of the carbon-carbon double bond was essentially complete in water and hexane solvents before reduction of the aldehyde function commenced. However, with methanol solvent considerable reduction of the aldehyde function took place at the same time as double bond hydrogenation [17]. Solvent effects were also found in the hydrogenation of cinnamaldehyde. This substrate could be hydrogenated in ethanol, but not in dioxane with palladium boride catalyst [6]. Chloroform, when used as a solvent in the palladium boride catalysed hydrogenation of cinnamaldehyde, increased the rate of aldehyde function reduction. Increased hydrogenation of the –CHO group could be obtained either by increasing the reaction temperature, or by adding acid. Addition of Zn^{2+} caused an enhanced rate of hydrogenation of carbon-carbon unsaturation, so as to give substantially 3-phenylpropionaldehyde [9].

While the addition of Co^{2+} increased the rate of aldehyde function reduction to give a mixture of 3-phenylpropanol and propylbenzene. In a similar study, but with mesityloxide and crotonaldehyde, it was found that the reaction sequence was olefin > ketone > aldehyde over platinum boride. Condensation and hydrogenolysis reactions were enhanced by acid conditions, and suppressed by alkaline conditions. Fe^{2+} addition to platinum boride hydrogenations of crotonaldehyde increased the rate of aldehyde reduction compared to that of the unsaturation, to such an extent as to give 70 to 78% yields of crotyl alcohol. Co^{2+} addition to the hydrogenation gave only 60% crotylalcohol. Neither Pt-Fe or Pt-Co coprecipitated catalysts gave crotylalcohol [9]. Others have quantitatively reduced the unsaturation in benzalacetophenone without attacking the ketonic function with palladium boride and dioxane solvent [6].

Saturated Nitriles. The hydrogenation of benzylcyanide over both palladium and platinum borides has been reported. The activity and lifetimes of the unsupported borides is superior to that of charcoal-supported platinum or palladium metals [8]. In the hydrogenation of propionitrile and butyronitrile over rhodium, ruthenium and platinum borides in water and isopropanol solvent, rhodium boride gives predominantly the secondary amine, while platinum borides form the tertiary amine almost exclusively. Ruthenium boride gives a mixture of primary, secondary and tertiary amine. Use of liquid ammonia or acetic anhydride gives the primary amine in very high yield (see tables below) [10].

Hydrogenation of propionitrile with platinum metal borides at 70°C and 2 atm H_2 pressure:

catalyst	solvent	time in h	mol% yield nitrile	primary amine	sec. amine	tert. amine
rhodium boride	water	16			61	39
	water[1]	16		14	86	
	isopropanol	16			66	34
	isopropanol[1]	16	31	29	35	5
	liquid NH_3	2		98		
	acetic acid	32	35		36	29
	acetic anhydride	72		100		
ruthenium boride	water	24			67	30
	water[1]	24		64	26	10
	isopropanol	24		50	43	7
	isopropanol[1]	24	11	69	19	
platinum boride	water	24			3	97
	water[1]	24			2	98
	isopropanol	24	50		3	49
	isopropanol[1]	24	54		1	45

[1] with added ammonia (ammonia : nitrile = 5 : 1)

Hydrogenation of butyronitrile with platinum metal borides at 70°C and atmospheric pressure:

catalyst	solvent	time in h	mol% yield			
			nitrile	primary amine	sec. amine	tert. amine
rhodium boride	water	16	3		59	38
	water[1]	16	2		98	
	isopropanol	24			62.5	37.5
	isopropanol[1]	24	21	27	52	
ruthenium boride	isopropanol	14	18	32	44	6
	isopropanol[1]	14	21	51	28	
platinum boride	isopropanol	14	62		8	30
	isopropanol[1]	14	64		6	30

[1] with added ammonia (ammonia:nitrile = 5:1)

Attempts to promote cobalt boride with rhodium, ruthenium or platinum borides improved activity marginally, but not the selectivity of the catalyst.

Unsaturated Nitriles of the hydrogenation of acrylonitrile over rhodium and ruthenium borides supported on carbon. The results, shown in the following table, indicate that the temperature is important in securing high conversions of acrylonitrile; allylamine was the main product [10].

Hydrogenation of acrylonitrile over carbon-supported rhodium boride and ruthenium boride at 70 to 140°C and 1 to 3 atm H_2 pressure in isopropanol with added ammonia (ammonia: nitrile = 5:1):

catalyst	temp. in °C	pressure in atm	time in h	mol% yield			
				AN	PN	n-allyl-amine	n-propyl-amine
rhodium boride	70	1	10	81		3	
	70	1	24	80		7	
	70	1	72	72	2	10	
	70	3	48	52		27	
	100	3	48	7	5	69	2
	140	3	48		13	44	
ruthenium boride	70	1	48	81		4	
	100	3	48	7	9	52	3
	140	3	48	24	14	22	12

AN = acrylonitrile, PN = propionitrile.

Pyrazolones. 3-Methyl-1-phenyl-4-(p-methoxybenzylidene)-5-pyrazolone and 1,2-diphenyl-4-benzylidene-3,5-pyrazoledione in ethanol solution have been hydrogenated over palladium boride catalyst at atmospheric pressure and room temperature. The only function hydrogenated was the carbon-carbon unsaturation. Palladium metal on carbon was very slow in these hydrogenations (2 to 12 h), but palladium boride completed the hydrogenation in 20 to 30 min [6].

Other Unsaturated Compounds. Cinnamic acid has been hydrogenated over palladium boride. The boride catalyst was more active than palladium black or palladium on carbon under the same conditions (1 atm H_2 pressure, room temperature) [6]. In the hydrogenation of potassium maleate in water solution platinum boride is between 6 and 10 times more active than palladium boride [4]. On the other hand palladium boride was about 7 times more active in the hydrogenation of dimethylmaleate in methanol, than either platinum or rhodium borides. The sequence of activities given is $Pd > Pt \approx Rh$ [5].

Nitro Compounds. Nitrobenzene has been reduced to aniline in the vapour phase at 200 to 210°C over platinum boride and palladium boride in 89 and 96% yield, respectively [8]. Potassium ortho-nitrophenate has been reduced in aqueous solution at 1 atm pressure and 20°C with platinum boride and palladium boride. Catalysts made from calcium borohydride were more active that those made from the sodium salt. Platinum boride was about three times more active than its palladium counterpart [4].

Other Hydrogenations. Hydrogenation of d-xylo-5-hexalusonate was much more selective over palladium boride than over palladium black or 5% palladium on charcoal [10].

$(Co_2B)_{10}RhH_4$ and $(Ni_2B)_{10}RhH_{15}$ will hydrogenolyse cis-but-2-ene and promote the hydrogenation of carbon monoxide at temperatures >200°C. The catalysts were stable in this reaction at 500°C for 48 h [12].

Hydrogen Transfer Catalysis. The platinum metal borides have been shown to be very active hydrogen transfer catalysts. For example 1-octene, 2-octene, 2,4,4-trimethyl-1-pentene, cyclohexene, cyclo-octene, norborene, 4-vinylcyclohexene, 3-hexyne and benzene were hydrogenated over platinum boride using sodium borohydride as a source of hydrogen [13, 14]. All six platinum metal borides are active catalysts for the transfer of hydrogen from sodium borohydride to the nitro group of nitrobenzene. Indeed the catalysts are so active that reduction of the aromatic ring was suspected. Platinum boride supported on carbon was an active catalyst in the hydrogenation of nitro aromatic compounds in general. Nitrobenzene gave aniline in 91% yield, p-nitrotoluene gave p-toluidine (96%), p-nitro-anisole gave p-anisidine (88%), p-nitrophenol gave p-aminophenol (83%), 1-nitronaphthalene gave 1-aminonaphthalene (91%), ethyl-p-nitrobenzoate gave ethyl-p-aminobenzoate (92%) and p-chloronitrobenzene gave p-chloroaniline (86%) [15].

Stereoselectivity in the hydrogenation of 4-t-butylcyclohexanone has been studied using refluxing isopropanol as the hydrogen transfer agent, over all six of the platinum metal borides in an unsupported form. The results are shown in the table below.

catalyst	reaction time (h)	% reduction of ketone	axial:equatorial alcohol ratio
ruthenium boride	96	80	49:51
osmium boride	75	63	50:50
rhodium boride	40	47	67:33
iridium boride	72	98	23:77
palladium boride	91	90	30:70
platinum boride	48	64	72:28

Under the same conditions palladium boride supported on carbon gave 15% cis-4-t-butylcyclohexanol and 7% trans-4-t-butylcyclohexanol, with the major product being p-t-butylphenol (55%) [16].

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Oxidations

The oxidation of 2,3,4,6-di-isopropylidene-L-sorbose as a 10% aqueous solution containing sodium bicarbonate at 85°C has been studied over (I) base metal catalysts promoted with palladium boride, (II) palladium boride on carbon with polyvinylalcohol and (III) palladium on carbon catalysts promoted with palladium boride. In all cases the principal oxidation product was the corresponding monocarboxylic acid [1].

Boride promoted base metal catalysts and palladium boride catalysts were much more effective than their palladium metal counterparts. The best catalysts were palladium boride promoted palladium catalysts containing polyvinyl alcohol and they have been the subject of patenting claims [2].

References:

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4.4.3 Platinum-Group Metal Compounds with Group IV Elements

This section deals with the catalytic chemistry of the inorganic compounds of the group IV nonmetallic elements, carbon and silicon. For the catalytic chemistry of the platinum metal organometallic compounds, Section 4.4.7, should be consulted.

Carbon and silicon form binary compounds with some of the platinum-group metals of the type M_yX_z where y and z can range from 1 in the case of carbon binary compounds [1] to 1 to 5 for silicon [2]. The binary carbides have a doubtful existence but the silicides are well characterised and are known to have catalytic properties. Ternary compounds of the type $T_aM_bX_c$, where T is a transition metal, M a nontransition metal, are known for carbon, but not for silicon. The ternary carbides have perovskite structures and it has been suggested that they should be catalytically active [3, 4].

Besides the monocarbides of the platinum metals a series of intercalate compounds have been found in which the platinum metal is held between the lattice layers of graphite. These materials are prepared by the reduction of the platinum metal chloride-graphite intercalates. Both the metal-graphite intercalates and the metal chloride intercalates have catalytic properties, particularly in such important reactions as the synthesis of ammonia and the Fischer-Tropsch reactions [5].

Some salts of the platinum-group metals have been used as heterogeneous catalysts, the most notable being the short chain length carboxylates of palladium in the oxidation of ethylene to vinylacetate. Palladium cyanide has been proposed as a catalyst for cyanation and polymerisation reactions.

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4.4.3.1 Carbides

Three types of carbides are known to exist: ionic, covalent and interstitial. The ionic carbides are primarily those of the alkali metals, alkaline earth metals, the lanthanides and the actinides, although one group formed by the action of acetylene on aqueous solutions of metal salts includes compounds (acetylides) formed by palladium and osmium [1, pp. 1204/10], [2, pp. 70/5]. On treatment with water or dilute acids ionic carbides decompose to give hydrocarbons such as methane, ethane, ethylene and acetylene. Covalent carbides are formed by the combination of carbon with a nonmetal such as boron or silicon, although some metal carbides, for example Be_2C, show at least partial covalent bonding [1, pp. 1214/5]. None of these materials possess catalytic activity.

Three types of void exist in packed layers of transition metal atoms, tetrahedral, octahedral and trigonal-prismatic. The interstitial carbides arise, like their hydride counterparts, by the filling of the octahedral or trigonal-prismatic holes with carbon. Where trigonal-prismatic voids are filled the structure is not close-packed, while close-packing does result from the filling of octahedral voids. Most interstitial carbides are formed by filling octahedral voids. In cubic close-packed structures the number of octahedral holes equals the number of atoms, and hence if all the holes are filled then compounds of the general formula MC result. When only half the octahedral voids are occupied by carbon, the formula is M_2C. However, in many cases the number of voids filled does not exactly correspond to either of the stoichiometries suggested above and nonstoichiometric compounds are formed. Although in theory carbides could be formed by filling tetrahedral holes, no carbides of this type are known.

Attempts to form the carbides of the group VIII elements by direct combination of the metal with carbon or reduction of the metal oxide with carbon have given rise to mixed results. Several carbides of iron and cobalt can be formed together with a single carbide of nickel, but no certainty exists as to the formation of the interstitial carbides of the platinum-group metals. No binary diagrams exist for the platinum metals – carbon systems. The platinum metal carbides were reviewed in 1968 and it was concluded that there were no reported binary carbides [3]. The formation of ruthenium and osmium carbides has been reported with hexagonal structure similar to tungsten carbide [4]. Although others were unable to repeat the preparation and suggested that the ruthenium and osmium carbides were tungsten carbide impurities [5], the original authors repeated their work showing that tungsten was not present [6]. The platinum-carbon and iridium-carbon systems have been investigated and eutectic points were found for both systems, but no evidence for compound formation [7].

The ternary perovskite carbides, known as Nowotny phases, have the general formula T_aM_bC where T is a transition metal and M is a nontransition metal. Perovskite carbides of the type T_3MC containing platinum-group metals are well established, as are those of type T_2M_4C. Examples of such materials are given in the table below.

platinum metal		compound	
	T_3MC	T_2M_4C	TMC_2
Pd	Pd_3AlC		
	Pd_3InC		
	Pd_3PbC		
Pt	Pt_3MgC		
	Pt_3AlC		
	Pt_3ZnC		
	Pt_3InC		
	Pt_3SnC		
	Pt_3PbC		
	Pt_3HgC		
Rh			$RhUC_2$
Ir			$IrUC_2$
Os		Os_2Zr_4C	

The carbide perovskite structure is the inverse of that found in the oxide perovskites in that the transition metal forms the principal structural element in the carbide perovskites, while the nonmetal, oxygen, performs this function in the oxide perovskites [3, 8].

It has been argued that unusual adsorption properties should result from such close-packed noble metal atoms in the perovskite carbides, leading to potentially useful catalysts for high temperature operation. As with all refractory materials the surface areas of samples prepared by the conventional means are low, and before they can be satisfactorily tested for catalytic activity, better dispersed material will have to be made. Some base metal carbides, e. g. tungsten carbide, have already been shown to possess catalytic activity in dehydrogenation, hydrogenolysis and isomerisation reactions, and there is every reason to believe that the perovskite carbides of the platinum metals may prove to be active catalysts [9].

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4.4.3.2 Graphite Intercalate Compounds

Many inorganic compounds will accept guest molecules or atoms within the voids of their structure, to form inclusion complexes. The guest molecules may simply be trapped within the host substance, or be physically or chemically bonded within the voids of the host material. Because there is no compulsion for the guest molecule to fill all of the voids to form a stable complex, inclusion complexes are frequently nonstoichiometric. Guest molecules or atoms may be accommodated in any one of five different modes, depending on the structure of the host substance: (I) molecules in isolated cavities, (II) molecules in parallel channels, (III) molecules between parallel chains, (IV) molecules between layers, (V) molecules in channel networks.

It is common practice to call such inclusion complexes, except those formed by molecules between layers, by the general label of "interstitial compounds". Those formed by molecules between layers are normally known as "intercalation or intercalate compounds". Of those substances which can accommodate guest molecules to form intercalate compounds, probably the best known are the layered silicates (vermiculites and micas) and graphite [1]. It is with the graphite intercalate compounds that we are concerned here.

Graphite forms three types of intercalate compounds. Firstly the nonconducting compounds containing graphite oxide or graphite monofluoride, secondly the conducting compounds predominantly ionic which retain all the characteristic graphite properties and lastly the residue compounds formed by removing the bulk of the guest molecules from the second type of graphite intercalate compounds. Residue compounds have properties which differ substantially from those of graphite. Only the second type of intercalate compound (the conducting type) are catalytically active. Among these are those made by intercalating platinum-group metal chlorides and sulphides between the graphite lattice planes; the table below gives a list of intercalate compounds formed by graphite with platinum metal compounds [2].

The most complete structural analysis made on a transition metal chloride-graphite intercalate is that carried out on ferric chloride-graphite. The structure of platinum metal chloride-graphite intercalates is identical, as is that of the palladium sulphide and oxide intercalates. The ferric chloride molecule tends to preserve its structure when intercalated into graphite. The ferric chloride ions are disposed centrally between the graphite layers forming a hexagonal net, as in normal ferric chloride. The ferric-ferric ion distance is essentially the same as in ferric chloride. They do not have a preferred position with respect to the carbon atoms, unlike the chloride ions [2].

Although transition metal chlorides can intercalate between each graphite layer, they frequently do not, one or more layers being missed. When all graphite layers are filled the intercalate compound is known as a stage 1 compound. A stage 2 compound is formed when every other layer is filled, stage 3 compound when every third layer is filled, and so on. Among transition metal compounds the only ones which will intercalate in graphite are those with incomplete d shells allowing the metal ion to bond via the electrons of the graphite upper conduction band [4].

The structure of transition metal-graphite compounds is at present open to doubt, and appears to depend on the reducing agent used. Hydrogen at elevated temperatures normally allows the metal to migrate from between the graphite layers to form metal crystallites supported on graphite. Reduction with organic anions such as sodium naphthalide at or near ambient temperature usually leaves the metal intercalated between the graphite layers. Very little is known of the structure of these transition metal-graphite intercalates or how the metal is bonded to the graphite, but they are known to possess unusual catalytic properties.

Platinum metal compound – graphite intercalates:

metal	compound	Ref.
Ru	$RuCl_3$	[1 to 6]
Rh	$RhCl_3$	[1, 2, 3, 5]
Pd	$PdCl_4$	[1 to 6]
	$PdS_{2.2}$	[1 to 5]
	PdO	[7]

metal	compound	Ref.
Pt	$PtCl_4$	[1 to 6]
Ir	$IrCl_3$	[7]
Os	$OsCl_3$	[6]

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Preparation of Platinum Metal Containing Graphite Intercalates

Graphite-metal compound intercalates are generally prepared by heating graphite with the metal compound at temperatures of 200 to 600°C in a vacuum or an inert atmosphere. When such compounds are formed, stage 1 intercalates (i.e. the highest degree of intercalation) are formed at the lowest temperature. Stage 2 and higher intercalates may be formed by heating stage 1 intercalates to a higher temperature than that of stage 1 formation or conducting the intercalation at temperatures above those at which stage 1 intercalates form. If heated to too high a temperature all intercalates will decompose to graphite and the metal compound. It is important therefore to ensure that temperatures attained during preparation and use are below those of the decomposition temperature.

Metal Chloride-Graphite Intercalates. Broad reviews of metal chloride-graphite intercalation procedures have been published [2, 3]. One worker conducted his preparations by sealing graphite and the metal chloride into a pressure tube which was then heated to 200 to 500°C after evacuation and sealing. The metal chloride, formed in situ by the chlorination of the metal, was sublimed onto cool graphite, then heated to the intercalation temperature [3]. Successful preparations of some compounds appear to be dependent on the presence of small amounts of free chlorine [1, p. 256]. In all preparations any excess metal chloride may be removed by sublimation, or by washing the impure intercalate with water and hydrochloric acid, followed by drying at 110°C or over phosphorus pentoxide.

Methods for the preparation of platinum metal chloride-graphite intercalates have appeared in the literature and details are contained in the table below.

compound	author	Ref.
$PdCl_4$	Croft	[5]
	Naito	[6]
	Lalancetti	[7]
	Novikov	[8]
$RuCl_3$	Croft	[5]
	Novikov	[8]
	Ichikawa	[9, 10]
$RhCl_3$	Croft	[5]
	Ichikawa	[10]

compound	author	Ref.
$PtCl_4$	Croft	[5]
	Lalancetti	[7]
	Novikov	[8]
$OsCl_3$	Ichikawa	[9]
	Novikov	[8]
	Postnikov	[1]
$IrCl_4$	Croft	[5]

Reduced Metal Chloride Intercalates. Certain reducing agents can reduce metal chlorides in metal chloride-graphite intercalates to the metal or a lower chloride. A variety of reducing agents (hydrogen, sodium borohydride, lithium aluminium hydride, sodium in liquid ammonia, lithium biphenyl, sodium naphthalide) have been studied with a number of base metal chloride-graphite intercalates, and it was concluded that the results depend on the reducing agent used and the stage of intercalation of the metal chloride-graphite intercalate. In most cases, even with stage 1 intercalates, the zerovalent metal state was formed either as a monolayer of metal, or small metal clusters between the graphite lattice planes. In both cases interaction between the graphite Π electrons and the metal atoms or clusters was found. Hydrogen, almost universally, caused separation of the metal from the graphite [12].

Platinum metal chloride intercalates have been reduced to the corresponding metal intercalates with lithium diphenyl reducing agent [7, 11]. $PdCl_4$-graphite and $PtCl_4$-graphite intercalates were reduced by this method at −50°C [7], while $OsCl_3$-graphite intercalate was reduced at temperatures close to 0°C [11].

Another favoured reducing agent is a metallic alkali metal, which besides acting as a reducing agent, frequently promotes the catalyst. $RuCl_3$-graphite and $OsCl_3$-graphite have been reduced to the metal with potassium [9, 13, 14], $RhCl_3$-graphite intercalate with sodium, potassium [9, 13, 14], $RhCl_3$-graphite intercalate with sodium, potassium and rubidium [10] and $PdCl_4$-graphite with sodium [6] and potassium [13]. The reduction is usually conducted at 300 to 350°C in vacuo, although it is really only necessary to exceed the melting point of the alkali metal (Na 98°C, K 64°C, Rb 39°C) to ensure reduction of the metal chloride. A temperature of 100°C was sufficient to reduce $RuCl_3$-graphite and $PdCl_4$-graphite with potassium [13].

Other Metal Compound-Graphite Intercalates. $PdS_{2.2}$-graphite intercalates have been prepared by heating graphite with palladium sulphide and excess sulphur at 570°C. After heating the graphite compound was extracted with carbon disulphide to remove excess sulphur, then with 6N nitric acid to remove any unused palladium sulphide [15]. The literature contains mention of a palladium oxide-graphite intercalate, but gives no method of preparation [6].

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Reactions

The catalytic reactions of platinum metal chloride-graphite and platinum metals-graphite intercalates may for convenience be divided into four broad groups:

(I) liquid phase hydrogenation; (II) hydrodesulphurisation, hydrodenitrification and hydrodealkylation reactions; (III) hydrogenation of carbon oxides etc.; (IV) ammonia synthesis.

The hydrogenation of carbon oxides and ammonia synthesis are potentially of more importance than either of the first two groups of reaction.

Liquid Phase Hydrogenation. Alkynes and 1,3-conjugated dienes have been hydrogenated over palladium-graphite and platinum-graphite intercalates. Both catalysts were almost completely selective for the hydrogenation of alkynes and dienes to olefins in the presence of excess alkenes. Hexyne (20%) in hexene (80%) was hydrogenated to give a product containing 99.9% hexene. No hexyne remained, neither was hexane formed nor any positional isomerisation of the double bond noticed. Hydrogenation of cyclohexylacetylene (20%) in 1-octene (80%) over palladium-graphite intercalate was not quite as successful, 4% octane and 0.1% cyclohexylethane being formed. 1,3-cyclo-octadiene in the presence of cyclo-octene was completely hydrogenated over palladium-graphite intercalate with the formation of 4.5%

cyclo-octane. Standard palladium and platinum on charcoal catalysts performed less efficiently than the graphite compound in all of these reactions. When tested in the gas-phase hydrogenation of propyne (10%) in propylene (70%) only 1.9% of propane was formed [1].

Hydrodesulphurisation, Hydrodenitrification, Hydrodealkylation. Sulphur compounds, such as methyl sulphide, thiophene etc., when passed in the vapour phase with hydrogen over potassium-promoted osmium metal-graphite intercalates at ~300°C are hydrodesulphurised to hydrocarbons [2]. Similarly hydrodenitrification of amines has been shown to take place over metal-graphite intercalates of the group VIII metals with no tendency to deposit coke or deactivate with heavy metal impurities [3]. Ethylbenzene has been hydrodealkylated at 350°C over group VIII metal-graphite intercalates to give 42% benzene and 58% toluene at a single pass conversion of 72% [4].

Hydrogenation of Carbon Oxides etc. Platinum metal-graphite compounds have been used as catalysts in a number of reactions with carbon oxides:

(I) formation of dimethylether from carbon dioxide and hydrogen; (II) the carbonylation of methanol to give acetic acid; (III) the synthesis of hydrocarbons from synthesis gas.

Carbon dioxide and hydrogen have been reacted over a palladium metal-graphite intercalate promoted with sodium metal to give dimethylether. Hydrogenolysis of methylformate (thought to be an intermediate in the reduction of CO_2) over the same catalyst also gave dimethylether. Rhodium, iridium and osmium metal-graphite intercalates were inacitve in the reduction of carbon dioxide, while the platinum metal-graphite compound was active, but not selective for dimethylether [5].

Both $IrCl_3$-graphite [6] and $RhCl_3$-graphite [7] compounds were active in the carbonylation of methanol at 200°C and 10 atm pressure. Over the rhodium compound 88.2 wt% of acetic was formed.

The synthesis of hydrocarbons over ruthenium-graphite, osmium-graphite, platinum-graphite and palladium-graphite intercalates promoted with potassium at 300°C and atmospheric pressure have been investigated. Single pass conversions were low at 12.8% (Ru-graphite), 11.1% (Os-graphite), 10.5% (Pt-graphite) and 6.0% (Pd-graphite). Ruthenium and osmium produced mainly methane (~89%) while platinum and palladium gave 68 to 77% C_2 hydrocarbons [8]. Such catalysts are claimed to be very resistant to deactivation by oxygen, and by nitrogen and sulphur compounds [9].

Ammonia Synthesis. Two research groups, one in Russia, one in Japan have studied the formation of ammonia over ruthenium-, osmium- and rhodium-graphite compounds with the aim of finding catalysts that will operate effectively under mild conditions.

The Russian workers examined the formation of ammonia over Fe-, Os- and Ru-graphite intercalates at temperatures between 250 and 400°C and 1 atm pressure.

Both osmium and ruthenium intercalates were as active as the iron compounds. The amount of alkali metal in the catalyst is an important factor of catalysis, the activity passing through a maximum as the level of alkali metal increases [10].

The Japanese workers have reacted nitrogen/hydrogen mixtures at 300°C over potassium-promoted ruthenium chloride and osmium chloride-graphite intercalates and obtained ammonia. The pressure in these experiments was subatmospheric (0.72 to 0.79 atm). The ruthenium compound had an initial rate of ammonia formation of 2.9 ml NH_3/h and converted 30% of a nitrogen/hydrogen mixture to ammonia in 10 h. The comparable figures for the osmium-graphite compound were 9 ml/h, and 60% conversion [11]. The use of rhodium trichloride-graphite intercalates promoted with sodium, potassium or rubidium is disclosed in a German patent [12]. The use of air as a nitrogen source is revealed in a French patent [13], and the production of ammonia at room temperature and pressure in a Japanese patent [14] over the same catalysts. The use of binary metal chloride intercalates such as $RuCl_3$-graphite with potassium promoter is said to produce a more effective catalyst [15]. It has also been discovered that paraffin hydrocarbons, such as methane, may be used directly as a source of hydrogen with air or nitrogen to make ammonia at 80 atm pressure and 350°C [16].

It is generally accepted that the alkali metals act as promoters by donating an electron to the metal atom of the graphite intercalate, thus facilitating the dissociation of the nitrogen molecule [17].

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4.4.3.3 Reactions of Carboxylate, Cyanide and Phthalocyanin Heterogeneous Catalysts

Platinum-group metal compounds are normally employed as catalysts in solution, although rarely they have been used heterogeneously in hydrogenation, oxidation and polymerisation reactions.

Palladium carboxylates and in particular the acetate have frequently been used as oxidation catalysts in the conversion of ethylene to acetaldehyde and vinylacetate. Both processes were originally practised with solution catalysts, which proved very corrosive. Much research time has been spent in the search for less corrosive heterogeneous catalysts utilising the same chemistry as the solution process, but in the gas phase. Although successful heterogeneous catalysts have been found for both processes, palladium-vanadium pentoxide for acetaldehyde and palladium-cupric chloride for vinyl acetate, only the latter has been used industrially and here replacement of the solution process is virtually complete. Two industrially important vinylacetate catalysts exist, the Bayer catalyst (palladium metal on a support) and the Hoechst or USI catalyst (palladium acetate plus a redox catalyst on a support) and it is the last that is of interest here. The catalyst may be prepared by impregnating carbon, alumina, silicagel, aluminosilicates, silicon carbide etc. with a solution of palladium acetate, cadmium acetate, potassium acetate, and a redox-metal acetate such as those of copper, manganese, iron, cobalt, cerium or uranium [1]. The catalyst preparation is sensitive to changes in the procedure, particularly to those in the drying stage. The reaction is operated in a tubular reactor with a fixed-bed catalyst at 175 to 200°C and 5 to 10 bar pressure. The explosion limit determines the oxygen content of the feed and hence the ethylene conversion of ~10%. Selectivities for the process of ~94% (based on the ethylene) can be attained with acetic acid conversions of ~20 to 35%. Plants of 150000 t p.a. (Hoechst) and 215000 t p.a. (USI) were started in 1975. The product requires multistep distillation to attain polymer grade purity [2].

Palladium cyanide has been proposed as a catalyst for polymerisation reactions [3, 4] and as a cyanation catalyst [5]. The catalyst is prepared by the method described in detail in [5] and [6]. At room temperature and pressure palladium cyanide gives a mixture of polymerised products with ethylene ranging from the dimer, butene, to low and high molecular weight polyethylene [7]. Propylene at 50 psi (~3.4 kg/cm^2) may be 1,3-polymerised to polypropylene containing ethylene groups [8], while α-olefins such as ethylene may be polymerised at 750 psi (~53 kg/cm^2) and 97°C to a polymer having an average molecular weight of 10^6 [3]. Nitriles have also been polymerised in the presence of unsaturated amines to a resin over this catalyst [4]. Palladous cyanide will also act as a catalyst in the cyanation of aryl halides. Thus, benzyl iodide can be converted to benzyl cyanide over palladous cyanide in 99% yield using potassium cyanide as the cyanating agent [5].

Platinum phthalocyanins may be activated by alkali metals like sodium to form active electron donor-acceptor catalysts (see Section 4.4.3.2) which will catalyse the conversion of carbon monoxide to C_1-C_5 hydrocarbons at 220°C. The main product is ethane and ethylene in 82% yield with minor amounts of propane (6%) and methane (10%) [9].

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4.4.3.4 Silicides

Silicon is too large to form Hägg interstitial compounds like carbon, and the silicides are considered to occupy an intermediate position between the interstitial and intermetallic compounds. They tend to form silicon-silicon bonds, particularly when the silicon content is high; for example RhSi contains chains of silicon atoms. In metal-rich silicides, the silicon atoms are completely surrounded by metal atoms, while in the silicon-rich compounds the metal atoms are completely surrounded by silicon atoms. Two extreme types of silicide are known, the first where silicon behaves like a metalloid forming substitutional compounds with the transition metals, the other extreme is that of the silicides of the more electropositive elements such as the alkali and alkaline earth metals.

Reviews of transition metal silicides, including the silicides of the platinum metals, are to be found in [1, 2, 3]. The chemistry of the binary compounds of silicon and the platinum metals is complex, some three dozen compounds having been discovered to date (see table below). Methods of preparation usually rely on the combination of the elements at elevated temperatures [1, 4 to 8], although heating the platinum metal with silica in a reducing atmosphere has been used [1]. Phase diagrams have been constructed for palladium-silicon [9, 10, 11], platinum-silicon [9, 12] and ruthenium-silicon [11], although the systems have not been completely explored. The silicides of osmium, ruthenium, iridium, and rhodium have been discussed [6, 9, 10, 12].

The platinum metal silicides have been commented on as potential high-temperature catalysts for coal conversion and there is evidence for their high-temperature stability in reducing atmospheres in the presence of sulphur compounds [13]. The only industrial use of the platinum-group silicides is as electrode coatings for the anodes of chlorine cells where they appear to reduce the overvoltage for chlorine generation [14]. For example an electrode of platinum silicide (Pt_3Si) on a graphite surface in a chlorine cell had an overvoltage of 0.05 V at 100 A/ft^2 (~15.5 A/cm^2), 0.09 V at 200 A/ft^2 (~31 A/cm^2) and 0.19 V at 500 A/ft^2 (~77.5 A/cm^2). To obtain the reduced overvoltage performance only partial coverage of the graphite electrode is necessary.

Silicides of the platinum-group metals:

element	Ref. [1]	Ref. [10]	Ref. [12]	Ref. [11]	Ref. [8]	Ref. [6]
Ru	Ru_3Si_2			Ru_3Si		
	$RuSi$			Ru_2Si		
	Ru_2Si_3					
Rh	Rh_3Si_2	Rh_3Si	Rh_5Si_3		Rh_4Si_5	Rh_2Si
	$RhSi$		Rh_2Si		Rh_3Si_4	
	$RhSi_2$					
Pd	Pd_3Si	Pd_9Si_4		Pd_5Si_2		
	Pd_2Si			Pd_9Si_2		
	$PdSi$					
Os	Os_2Si_3	$OsSi_2$				
	$OsSi$					
Ir	Ir_3Si_2	Ir_3Si		Ir_2Si		
	$IrSi$	$IrSi_3$				
	Ir_2Si_3					
	$IrSi_2$					
Pt	Pt_5Si_2					
	Pt_2Si	Pt_3Si	Pt_6Si_5			
	$PtSi$		Pt_7Si_3			
			Pt_4Si			

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4.4.3.5 Silicates

The platinum-group metals do not appear easily to form silicates of the conventional type by, for instance, the reaction of metal salts with silica at high temperature. The activity of Pd/SiO_2 catalysts for methanol synthesis may be due to the palladium forming a stable complex with the silica during preparation to give Pd^{II} ions at least on the surface of the catalyst [1]. However, it has been established that zeolite structures may be ion-exchanged with platinum-group metal salts to give catalysts in which the PGM ions retain their integrity during catalytic reaction. It is with this type of catalyst that this section is concerned.

Zeolites are one of the forms of aluminosilicate structures which abound in the mineral world. About 34 naturally occurring zeolites are known and about a further 100 have been synthesised. All are constructed from two basic building blocks, a tetrahedron of 4 oxygen anions surrounding either a silicon or an aluminium ion. These basic tetrahedra are arranged so that each oxygen is shared with another silica or alumina tetrahedron, giving a threedimensional lattice. The oxidation state of the oxygen ion is -2, while that of silicon is $+4$ and aluminium $+3$. The charge, therefore, on each silicon tetrahedron is balanced, but with the aluminium tetrahedra, each has a residual charge of -1 requiring a $+1$ charge from a cation to achieve neutrality. The usual cation is sodium, but these may be exchanged for other ions giving rise to the very useful ion exchange properties of zeolites.

The silica and alumina tetrahedra are geometrically combined to give more complicated open-framework structures with a variety of pore shapes and sizes. Pore diameters are determined by the size of the rings of oxygen ions; rings of 4, 6, 8, 10 and 12 oxygen atoms are known giving calculated apertures of 2.6, 3.6, 4.2 and 7.4 Å, respectively. Distortion of the oxygen framework can lower the effective aperture size. The only zeolites which have found major industrial applications are those with 8- or 12-membered oxygen rings, zeolites A, X and Y, erionite and synthetic mordenite. The structural aspects of zeolites have been discussed in [2, 3, 4] among others.

The zeolites have a high surface area, which in principle, allows a considerable amount of surface modification by, for example, ion exchange. The regular structure and ion exchange properties enable metal ions or functional groups in a variety of oxidation states and coordination geometries to be accommodated in a pore of known structure. These features, although known from the outset of zeolite catalysis, have remained unexploited, compared to the better known use of zeolites as solid acid catalysts, also when used as a means of dispersing transition metals, particularly the platinum-group metals, as very small crystallites in hydrocracking catalysts. Even then the amount was small, only some 0.5% of the total zeolite catalyst market going to hydrocracking catalysts [5]. Recently the catalytic properties of platinum-group metal ions, exchanged into the zeolitic component of fluid cracking catalysts (FCC), have been examined as combustion promoters. The loading of platinum-group metals is extremely low, 1 to 100 ppm. Despite this the combustion of coke on the deactivated FCC to carbon dioxide, rather than carbon monoxide, is so enhanced that it is possible to dispense with the conventional flue gas carbon monoxide incinerator [6, 7]. These catalysts have now been fully developed and are currently being applied to commercial cracking operations with success. The catalysis of platinum-group metal ion-exchanged zeolites has been reviewed in detail [8].

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Preparation

The normal form in which commercial zeolites are available is as the sodium form, and this imposes certain restrictions on the methods of preparation used in the manufacture of platinum-group metal ion catalysts. In aqueous media, at the usual zeolite/solution ratios, this results in pH's between 8 and 10, higher than that at which platinum-group metal chlorides commence hydrolysis to give hydroxypolycations and their polymerisation products in solution and colloidal metal hydroxides in suspension. Methods of preparation in which the zeolite is mixed with a solution of the salt in water either in just sufficient quantity to fill the zeolite pore volume, or in a large volumetric excess so that the zeolite absorbs the metal ion from solution are known as impregnation methods. Because of the diverse nature of the metal species in solution and suspension such methods usually lead to the metal ions being deposited both on the external surface as well as within the cavities of the zeolite. They are, however, widely practised despite the difficulties of characterising and replicating this type of catalyst [1 to 6]. Some authors have resorted to selective poisoning of the external metal ions in order to study the oxidation of methane by zeolite cavity palladium ions, for example [3].

When the pH of the metal salt solution is too low, some of the sodium may be replaced by hydrogen ions giving rise to acidic dual function catalysts, both by impregnation and ion-exchange methods. As this only normally happens when high metal loadings are being attempted, simple adjustment of the pH of the metal salt solution with sodium hydroxide usually suffices [1, 2, 7, 8]. Another means of overcoming deposition of hydroxymetal or the decationisation ot the zeolite is the use of platinum-group metal ammine salts. This deposits ions such as $[Ru(NH_3)_6]^{3+}$ at selected sites within the pore structure. Although some replacement of sodium by ammonium is to be expected [1, 2, 9 to 13]. The preparation of zeolite catalysts by ion exchange methods have been reviewed [14].

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Reactions

Platinum-group metal ion catalysts have been used for oxidation of carbon monoxide, alkanes, hydrogenation of alkenes and acetylene, dimerisation of ethylene, polymerisation of isobutylene, carbonylation of alcohols, and low-temperature water gas shift reactions. The use of zeolite-metal ion catalysts in a very wide range of reactions has been reviewed [1].

Hydrogenation. The hydrogenation of ethylene and acetylene over two rhodium catalysts (zeolite Y) in which 18% and 50%, respectively, of the cation was exchanged has been examined. Before measurement of the catalysts activity at room temperature, they were activated in vacuo (10^{-3} Torr) at various temperatures. Two peaks were observed in a plot of activity versus temperature of activation of ethylene, at ~200 to 250°C and 400°C, for both catalysts. With acetylene only a single peak at ~400°C was observed. From XPS and ESR data it was concluded that the low activation temperature (200°C) peak corresponds to catalysis over a Rh^{I} species, while that at high activation temperature (400°C) is due to rhodium metal. It would seem, therefore, that Rh^{I} species can be stabilised in the zeolite cage and is active for ethylene, but not acetylene hydrogenation in line with activity patterns found for homogeneous Rh^{I} complexes [2].

Oxidation. Very small quantities (1 to 100 ppm) of platinum-group metal ions, held within the cage of an ultrastable zeolite, promote the combustion of carbon monoxide to carbon dioxide, ensuring the emission-free regeneration of fluid cracking catalysts [3, 4]. The relative oxidation rates of the platinum-group metals have been determined by [5].

In the oxidation of methane over Pd^{II} ions the molecular sieve catalysts were active within 270 to 480°C, with activation energies of 25.4 kcal/mol for the low temperature reactions and 11.3 kcal/mol at the higher temperatures, where the reaction was thought to be diffusion-controlled. The catalytically active species was postulated to be square planar Pd^{II} ions in type II sites; ions within type I, I′ and II′ were seen as being inaccessible to methane molecules and therefore inactive [6].

The oxidation of alkenes has been studied over platinum-group metal ions stabilised within Y type zeolites. The gas phase oxidation of ethylene and propylene at low partial pressure has been studied over Pt^{II} and Pd^{II} catalysts [7]. In both cases only carbon dioxide and water were detected as oxidation products. It has been found that propylene could be oxidised to acetone in the liquid phase by Pd^{2+} in the presence of oxygen [8], but that the catalyst activity declined with time due to reduction of Pd^{2+} to Pd^0. When a Pd^{2+}/Cu^{2+} exchanged zeolite was used as catalyst the activity remained unchanged. When Pd^{2+}/Cu^{2+} catalysts were used to oxidise ethylene in the liquid phase, the main product was ethylene and the catalytic reaction mechanism paralleled the homogeneous Wacker reaction [9].

Polymerisation. Ethylene has been dimerised to butenes over Rh ions stabilised in a Y type zeolite. When the activity was plotted against activation temperature a single peak was observed at ~250°C corresponding to ESR and XPS data suggesting that the active catalytic species was a Rh^I ion. The isomer distribution was butene-1 2%, trans-2-butene 77% and cis-2-butene 21% after 2 h reaction at 20°C over Rh-Y zeolite activated at 250°C in vacuo [2].

Isobutylene has been polymerised over palladium and platinum zeolite catalysts at room temperature in an autoclave. Only zeolites with pore mouths larger than 5 Å were effective. The polymerised product was bimodal in molecular weight distribution with peaks at 250 and 3000 to 5000 [10].

Carbonylation and Hydroformylation. Hydroformylation of 1-hexene at 80°C under 50 to 100 atm CO/H_2 pressure in hexane solvent gave high selectivity for aldehyde formation with n-aldehyde/iso-aldehyde ratios of ~1.0. Examination of the catalyst by infrared showed bands which are characteristic of terminal and bridging carbonyl groups, but were not identical with those in the known carbonyl cluster compounds $Rh_4(Co)_{12}$ or $Rh_6(Co)_{16}$ [11, 12].

The Russians were the first to study the carbonylation of methanol over Rh ion-zeolite catalysts [13, 14, 15]. These authors found that a Na-X zeolite impregnated with 0.2% rhodium as rhodium trichloride was capable of carbonylating methanol at 250°C and 1 atm pressure providing methyliodide was present. In the absence of methyliodide the major product was dimethylether. When the reaction mixture of methanol, methyliodide and carbon monoxide was passed through the catalyst bed at a space velocity of 0.63 h^{-1} ($CH_3OH:CO=1.4$ to 2.0) methylacetate was formed with a selectivity of 87 to 90% (conversion 79%). The only by-product was dimethylether. The catalyst activity was equivalent to 46 to 52 g methylacetate per g Rh per h [13]. It was found that the method of preparation of the catalyst was important, ion-exchanged catalysts always giving better results than impregnated catalysts. Addition of 0.3% water to the feed stream increased the rate of reaction, but acetic anhydride decreased the activity of the catalyst. The optimum rhodium loading on the zeolite was 0.25 to 0.50% [14].

The Rh-X zeolite system has been used for the carbonylation of the first three aliphatic alcohols [15 to 18]. Methanol could be converted to methylacetate with a selectivity of >90% at temperatures between 160 and 240°C. The only by-product was dimethylether. Although the catalyst was prepared by the same method as in [13], its activity was some seven times greater than that of the Russian workers. Ethanol carbonylation was temperature-sensitive, selectivity falling from 99% at 110°C to 6% at 250°C. Above 200°C the main product was ethylene with small amounts of diethylether [16]. Attempts to carbonylate propan-2-ol at 160 and 200°C failed, the only product being propylene. The products dimethylether, diethylether, ethylene and propylene arise from dehydration of the respective alcohols, the zeolite providing the dehydration sites. The active carbonylation species appears to be an active acetyl rhodium complex of the type $Rh(CH_3CO)COX_2I^-$ held within the zeolite cavities [17].

A Rh-Y zeolite catalyst has been used to study the carbonylation of methane. The rate of methylacetate formation increased as the metal loading increased up to 0.6 wt% Rh. At loadings above this the rate decreased with time and the catalyst-support system was degraded. The rhodium species used to ion exchange the zeolite did not affect the catalyst activity despite the fact that the rhodium catalytic centre was associated with different counter ions. Activation of the catalyst by calcination in nitrogen or helium at 200°C removed the induction period to the carbonylation reaction. Calcination at 300°C reduced the activity, and calcination in hydrogen at 200°C destroyed the activity for carbonylation [19]. The kinetics of the methanol reaction were examined and a mechanism similar to that of the homogeneous reaction was proposed [20].

The carbonylation of higher alcohols has been shown to be sensitive to the imposed carbon monoxide pressure [21]. The compounds of a number of other metals act as promoters for the Rh-X zeolite-catalysed carbonylation reaction [22, 23, 24], and neither palladium nor platinum is active for carbonylation at 0.5 wt% loadings on X-type zeolite [25].

Ethylene has been successfully hydrocarboxylated to propylpropionate over a Na-X zeolite which had been ion-exchanged with group VIII metal ions. The activity and selectivity was highest for rhodium and decreased in the series $Rh > Pd > Ni > Co$. Allowing 100% conversions of ethylene in the presence of n-propanol and propyliodide at 250°C and 60 atm carbon monoxide pressure over Rh-X zeolite (1% Rh). The selectivity to propylpropionate was 98.7% [26].

Low-Temperature Water Gas Shift Catalysis. A study has been published of the low-temperature water gas shift properties of a ruthenium ion-zeolite combination. Several wide pore zeolites have been tried, but only X and Y types have proved to form active catalysts with ruthenium ions. If the ruthenium (III) hexamine exchanged X or Y zeolite is activated by heating it in synthesis gas at 250°C, it exhibits considerable low-temperature water gas shift activity. When heated in synthesis gas at 300°C the activity is lost, but is partially restored by increasing the activation temperature to 400°C.

$$\mathrm{Ru^{III}(inactive)} \xrightarrow{150^\circ C} \mathrm{Ru^{II}} \xrightarrow{220^\circ C} \mathrm{Ru^{I}(very\ active)} \xrightarrow{>290^\circ C} \mathrm{Ru^{0}(moderate\ activity)}$$

The high-temperature activation activity is thus thought to be associated with ruthenium metal crystallites [27, 28]. The active species in the low-temperature activated catalyst has been shown to be of the type $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ with $n < 3$. The catalytic activity of the Ru-X zeolite is greater than that of a commerical copper catalyst used under similar conditions. Temperature stability of the catalyst appears to be limited to the range 160 to 280°C. The acidity of the zeolite also has an effect on catalyst activity, low acidity types being preferred [27].

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4.4.4 Platinum-Group Metal Compounds with Group V Elemements

Although ruthenium and osmium nitrides have been reported [1, 2] and a rhodium surface nitride complex has been detected by infrared spectroscopy [3], none of them are of technical interest as catalysts, but the surface complexes undoubtedly play a part in the catalytic fixation of ammonia over these metals. Phosphorus, on the other hand, forms binary phosphides with each of the platinum-group metals that are characterised by hardness, high melting point, high thermal and electrical conductivity, metallic lustre and inertness to chemical attack [4]. The chemistry of the phosphides of the platinum-group metals is complex and incompletely explored. A list of the claimed compounds is to be found in the table below together with the relevant sources. In addition to the information for individual phosphides, phase diagrams are available for Pd-P [6, 7, 8], Rh-P [3, 8], Ru-P [6], and Pt-P [8, 10].

The normal method of platinum-group metal phosphide preparation is that of the combination of the metal, preferably in a finely divided form, with red phosphorus at elevated temperatures. However, the dispersion of the phosphide is poor and the catalytic activity low. Better dispersion is obtained if the phosphide is made by fusing a mixture of platinum metal black, aluminium and red phosphorus at 650 to 1000°C to form $PtP_2 \cdot 4AlP$, and extracting this with refluxing 6 to 12N sulphuric acid to leave a residue of PtP_2 [11]. Supported catalysts are usually made by absorbing a solution of a platinum-group metal compound onto alumina, removing the solvent and then treating the supported metal compound with phosphine at 250 to 300°C for 2 h [12].

Phosphides of ruthenium, rhodium, palladium and platinum have been used as catalysts in a wide variety of reactions in the laboratory such as hydrogenation, oxidation, polymerisation, hydroformylation and decomposition reactions.

Phosphides of the platinum-group metals:

metal	information source						
	[4]	[3, 5, 10]	[6]	[7]	[8]	[2]	[9]
Ru	Ru_2P		Ru_2P		Ru_2P	Ru_2P	
	RuP		RuP		RuP	RuP	
	RuP_2		RuP_2		RuP_2	RuP_2	
Rh	Rh_2P	Rh_2P			Rh_2P	Rh_2P	
	Rh_4P_3					Rh_4P_3	
					Rh_5P_4		
	RhP_2				RhP_2	RhP_2	
	RhP_3	RhP_3			RhP_3	RhP_3	
Pd				Pd_8P			
				Pd_6P			
				$Pd_{4.8}P$	Pd_5P		
	Pd_3P			Pd_3P	Pd_3P	Pd_3P	Pd_3P
				Pd_5P_2	Pd_5P_2		
	Pd_7P_3			Pd_7P_3			Pd_7P_3
	PdP_2			PdP_2	PdP_2	PdP_2	PdP_2
	PdP_3						
Os	OsP_2					OsP_2	
Ir	Ir_2P	Ir_2P			Ir_2P	Ir_2P	
	IrP_2				IrP_2		
	IrP_3					IrP_3	
Pt		$Pt_{20}P_7$	$Pt_{20}P_7$		$Pt_{20}P_7$		
	Pt_5P_2						
		Pt_2P	Pt_2P				
		PtP	PtP				
		Pt_3P_5	Pt_3P_5				
	PtP_3	PtP_2	PtP_2		PtP_2	PtP_2	PtP_2

Hydrogenation. Attempts have been made to hydrogenate ethylene, propylene, butene, acetylene and nitrobenzene in the gas or vapour phase over platinum metal phosphides. Ethylene and propylene were rapidly hydrogenated over ruthenium phosphide at temperatures >120°C, below this temperature no reaction took place. Acetylene behaved similarly, no reduction below 120°C, then progressively greater hydrogenation as the temperature was increased until at 175°C 16% of the acetylene was converted to ethylene. Both ruthenium and rhodium phosphides slowly hydrogenated acetylene to ethylene at temperatures >125°C when a mixture of acetylene and ethylene was passed over these catalysts. 1-Butene when passed over platinum, palladium of ruthenium phosphide was very slowly hydrogenated, but rhodium phosphide was inactive for this reaction. However, all of these catalysts were active for the isomerisation of 1-butene to cis/trans-2-butene. Butadiene was not hydrogenated by platinum metal phosphides [12].

In competitive hydrogenations of an olefin with acetylene the latter always suppressed the hydrogenation of the olefin. Nitrobenzene was hydrogenated over rhodium and ruthenium phosphides to give a 60% yield of aniline at 380°C [12].

Oxidation. Palladium phosphide has been used as an oxidation catalyst in the conversion of phosphine and arsine to their respective oxides. Platinum phosphide (PtP_2) has been tried as an anode catalyst in a fuel cell, fuelled by methanol, ethylene and hydrazine, the results are shown in comparison with those for a platinum metal electrode in the following table [13].

anode potential (V vs. SCE)	electrolyte	fuel					
		methanol		ethylene		hydrazine	
				anodic current (mA)			
		PtP_2	Pt	PtP_2	Pt	PtP_2	Pt
−0.9	1N NaOH					21	12
−0.8	1N NaOH					46	42
−0.7	1N NaOH					60	60
−0.6	1N NaOH					75	77
−0.5	1N NaOH					80	75
0.2	1N H_2SO_4	8	19	1	2		
0.3	1N H_2SO_4	19	33	2.5	1		
0.4	1N H_2SO_4	31	50	3	<1		
0.5	1N H_2SO_4	46	63	5	<1		

Polymerisation. An examination of the catalytic properties of platinum, palladium, rhodium and ruthenium phosphides in the dimerisation of isobutylene, ethylene, propylene and butadiene has appeared in the literature. Only isobutylene was dimerised to any extent, platinum phosphide giving a 15% conversion, while rhodium phosphide gave a 6% yield of 1- and 2-butenes at 175 to 200°C. Rhodium phosphide and platinum phosphide polymerise ethylene to low molecular weight polyethylene between 100 and 900 atm and 50 to 250°C. Polymerisation was greatest when 0.002 mol of hydrogen was added before injection of ethylene [12].

Hydroformylation. Attempts to hydroformylate propylene and acetylene over platinum metal phosphides at 150°C and 35 to 100 atm pressure were unsuccessful with ruthenium, rhodium and palladium phosphides [12].

Decomposition. In the decomposition of hydrogen peroxide over ruthenium phosphide catalysts, Ru_2P, RuP and RuP_2 prepared by reacting ruthenium metal with red phosphorus were somewhat less active than ruthenium powder. More active catalysts, comparable to some of the best silver catalysts, were prepared by leaching ruthenium aluminium phosphide in sulphuric acid [14].

Ruthenium antimonide had been shown to hydrogenate and isomerise butene-1 at 110 to 175°C. Conversions of 46 to 67% with 17% and 34% hydrogenation have been achieved [12].

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4.4.5 Platinum-Group Metal Compounds with Group VIA Elements

The section deals with the catalytic properties of compounds formed by the platinum-group metals with the elements of group VIA of the periodic table, oxygen, sulphur, selenium and tellurium. Although polonium forms compounds with the platinum-group elements [1, 2], these have no reported catalytic properties and are not considered further.

The physical properties of the group VIA elements are shown in the table below. The metallic character of the elements increases from the top to the bottom of the group, atomic and ionic radius increases in the same way, while the electronegativity decreases from oxygen to tellurium.

	O	S	Se	Te
atomic radius	0.73 Å	1.04 Å	1.17 Å	1.37 Å
ionic radius	1.39 Å	1.84 Å	1.98 Å	2.21 Å
electronegativity	3.46	2.50	2.48	2.01

As the atoms increase in size from oxygen to tellurium the screening effect of the inner electron shells becomes greater and the behaviour of the valency electrons changes. There is, for instance, a tendency for bonds formed by sulphur to have less ionic character than those of oxygen, and while many dioxides have a simple ionic structure, those of the corresponding disulphides are layer structures. This tendency is accentuated on passing from sulphur to tellurium.

Binary Chalcogenides. Metal oxides range from the suboxides of caesium and the transition metals such as titanium and chromium in which metal-metal bonding occurs, through the ionic oxides of the alkali, alkaline earth and the transition metals to the covalent higher oxides of chromium, manganese and ruthenium. All four main types of crystal structure (molecular, chain, layer and three-dimensional structures) are represented in the oxides. The majority of metal oxides are ionic with high co-ordination numbers. Sulphur, however, is only able to form ionic sulphides with the more electropositive metals, and few oxides and sulphides are isostructural. The selenides and tellurides are frequently isostructural with the corresponding sulphides. Sulphides, selenides and tellurides form only three of the four main structural types, molecular structures being absent. The following table contains examples of the structure types formed by the chalcogenides [3, 4].

type of structure	formula type and co-ordination numbers of M and X		structure	example			
infinite 3-dimensional	MX_3	6:2	ReO_3	WO_3			
complex	MX_2	8:4	fluorite	ZrO_2			
				UO_2			
		6:3	rutile	TiO_2			
				RuO_2			
				OsO_2			
				RhO_2			
				IrO_2			
				PtO_2			
	M_2X_3	6:4	corundum	Al_2O_3	**Rh_2S_3**		
				Rh_2O_3	**Ir_2S_3**		
	MX	6:6	sodium chloride	MgO	MgS	MgSe	MgTe
				FeO			
		6:6	nickel arsenide		FeS		
		6:6	pyrite or marcasite		FeS_2		
					OsS_2	**OsS_2**	**$OsTe_2$**
					RuS_2	**$RuSe_2$**	**$RuTe_2$**
				RhS_2	**IrS_2**	**$RhSe_2$**	
		4:4	zinc blende		ZnS		
			wurtzite	ZnO	ZnS		
		4:4	cooperite	**PdO**	**PdS**		
					PtS		
	MX_2	4:2	silica	GeO_2			
	M_2X	2:4	cuprite	Cu_2O			
		4:8	antifluorite	Na_2O	Na_2S		
layer structure	MX_2	6:3	cadmium iodide		**PtS_2**	**$PtSe_2$**	**$PtTe_2$**
					PdS_2		
			cadmium chloride		TaS_2		
		6:3	molybdenum sulphide		MoS_2		
chain structure				Sb_2O_3	Sb_2S_3		
molecular structure				**RuO_4**			
				OsO_4			

As can be seen from the table, the simple binary oxides of the platinum-group metals crystallise in the rutile or corundum structure, while the sulphides, selenides and tellurides crystallise either as infinite three-dimensional complexes of the pyrite form or as layer structures with the cadmium iodide form. The higher oxides of ruthenium and osmium (RuO_4 and OsO_4) form covalent molecular structures. The lower binary oxides of the platinum-group metals have a restricted catalytic chemistry being used as precursors for metal catalysts and as electrocatalysts in the chlorine industry. Ruthenium and osmium tetroxides are potent and highly selective catalysts in oxidation reactions. Binary sulphides, selenides and tellurides on the other hand have a wide use in hydrogenation reactions.

A few sulphides (e.g. Pd_4S) and many selenides and tellurides form alloy-like phases with metallic lustre, reflectivity and high electrical and heat conductivity. These intermetallic compounds have found few catalytic uses so far. Rhodium forms a sulphide $Rh_{17}S_{15}$ which is defective in that it is a zinc-blende type structure (MX) in which the sulphur atoms are close-packed with the metal atoms occupying the tetrahedral and octahedral holes. Similar selenides and tellurides of the platinum metals are known to exist. Again the catalytic chemistry of such compounds is almost entirely unexplored.

Complex Chalcogenides. Complex oxides, in which two or more different metal atoms are incorporated into the tetrahedral and octahedral holes left in close-packed oxide ion array, are formed by the platinum-group metals. Two groups of such oxides that frequently exhibit catalytic properties for oxidation and hydrogenation reactions are the spinels and perovskites.

Spinels. These materials are named after the naturally occurring mineral spinel, $MgAl_2O_4$. The general formula is AB_2X_4 where A and B are cations and X is the anion. A and B can be various metallic or nonmetallic elements and X is oxygen, sulphur, selenium or tellurium. Not all compounds of the general formula adopt the spinel structure, and this section ignores such non-spinel compounds. With oxides the unit cell contains 32 oxide ions in an almost perfect cubic close-packed array corresponding to the formula $A_8B_{16}O_{32}$.

Spinels crystallise in both the normal and inverse structures. The normal structure has 8 A atoms surrounded tetrahedrally by 4 oxygen atoms, and 15 B atoms surrounded octahedrally by 6 oxygen atoms.

Some spinels do not possess the normal structure and instead half the B atoms are in tetrahedral sites and half in the octahedral sites, while the A atoms all occupy octahedral sites. This structure is known as the inverse spinel structure. The normal and inverse spinel structures are two extremes or limiting cases of the structure and various degrees of inversion can be found.

Cation change and cation size are the two factors which determine whether the combination of atoms can form a spinel structure. With oxides of the formula AB_2O_4 the eight negative anions can be balanced by three different combinations of cationic charge:

$$A^{2+} + 2B^{3+} \text{ (2,3 spinels)}, \quad A^{4+} + 2B^{2+} \text{ (4,2 spinels)}, \quad A^{6+} + 2B^{+} \text{ (6,1 spinels)}$$

About four-fifths of all spinels are of the 2,3 form, 15% are 4,2 spinels and the remainder (6,1 spinels) constitute some 5%.

Among known 2,3 spinels are those containing O^{2-}, S^{2-}, Se^{2-} and Te^{2-} as anions with A^{2+} selected from Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg or Sn and B^{3+} from Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni and Rh. The ionic radii of the A^{2+} fall between 0.65 and 1.0 Å, except for Ca^{2+} and Hg^{2+} which will only form spinels with anions larger than oxygen (O^{2-} 1.4 Å), and the B^{3+} ions fall between 0.5 Å (Al^{3+}) and 0.81 Å (In^{3+}) with the majority between 0.6 and 0.76 Å.

4,2 spinels are formed by oxygen and sulphur ions. A^{4+} may be Ti, V, Mo, Si, Ge, Sn or Pb and B^{2+} can come from Mg, Mn, Fe, Co, Ni, Cu or Zn. 6,1 spinels are known to form oxide types only.

Whether a spinel occurs in the normal or inverse form is governed by a number of factors such as ion size, charge, Madelung energy etc. which interact in a complex manner. With the Madelung energy as the controlling factor, 2,3 spinels will be normal and the 4,2 spinels will be inverse. Inversion of the 2,3 structure will occur where the octahedral field stabilisation energy is greater than the Madelung energy or where the crystal field stabilisation energy equals the

Madelung energy, when polarisation becomes the controlling factor. The table below contains a list of spinel types formed by the ions of the group VII B, VIII and I B metals. Sulphospinels, in which sulphur replaces oxygen, are essentially the same as oxygen-containing spinels [3, 4, 5].

ion	radius	configuration			spinel type		
	(Å)		n-2,3	i-2,3	n-4,2	i-4,2	n-6,1
Ag^+	1.26	d^{10}					$MoAg_2O_4$
Au^{3+}	0.85	d^8		$CuAu_2O_4$			
Co^{2+}	0.72	d^7	$CoCr_2O_4$	$CoFe_2O_4$			
Co^{3+}	0.63	d^6	$ZnCo_2O_4$	$FeCo_2O_4$	$GeCo_2O_4$	$NiCo_2O_4$	
Cu^{2+}	0.72	d^9	$CuRh_2O_4$	$CuFe_2O_4$		$CuAl_2O_4$	
Mn^{2+}	0.80	d^5	$MnRh_2O_4$				
Mn^{3+}	0.66	d^4	$CdMn_2O_4$	$NiMn_2O_4$			
Mn^{4+}	0.60	d^3				VMn_2O_4	
Ni^{2+}	0.69	d^8	$NiRh_2O_4$	$NiCo_2O_4$	$GeNi_2O_4$		
Pd^{2+}	0.80	d^8	$PdRh_2O_4$			$RePd_2O_4$	
Pt^{2+}	0.80	d^8	$PtCr_2O_4$			$MnPt_2O_4$	
Re^{4+}	0.72	d^3				$ReCu_2O_4$ $ReCo_2O_4$	
Rh^{3+}	0.68	d^3	$PtRh_2O_4$				
Ru^{4+}	0.67	d^4				$RuCu_2O_4$	

Perovskites. Perovskites are compounds of the general formula ABX_3, or ABO_3 if only oxides are considered, where B is a small cation and A a larger cation. The B ions are octahedrally co-ordinated and occupy corner-shared octahedra. This comes about because in perovskites electrostatic energy is the stabilising force. The A ions occupy the space formed by the corner-shared octahedra. It has been found that, for contact to occur between the cations and the oxygen anions, the A and B ions must be compatible in size defined by a tolerance factor $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$ where R_A, R_B and R_O are the radii of the A ion, B ion and oxygen ion, respectively.

The A cation in the perovskite structure is co-ordinated by twelve oxygen ions and the B cation with six. It should, however, be remembered that this is the ideal structure and many perovskites do not have this exact structure at ambient temperatures, although they may adopt it at higher temperatures. The ideal structure would correspond to a value of the tolerance factor $t = 1.00$, but in practice it has been found to occur over the range $0.75 < t < 1.00$. The cations have also been found to have a minimum size of $R_A > 0.90$ Å and $R_B > 0.51$ Å. The total charge to be balanced in perovskite is -6 which allows cationic combinations of $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$, and $A^{3+}B^{3+}O_3$.

Compounds with A cationic vacancies can occur, but because the B containing octahedra are the structural basis of the perovskite structure, B defects are not tolerated. The following table contains a list of some of the perovskite structures formed by the group VII B, VIII and I B elements [3, 4, 5].

ion	radius (Å)	perovskite type		
		1.5	2.4	3.3
Ag^+	1.26	$AgNbO_3$		
Co^{3+}	0.63			$LaCoO_3$
Fe^{3+}	0.64			$LaFeO_3$
Mn^{3+}	0.66			$LaMnO_3$
Mn^{4+}	0.60		$BaMnO_4$	
Ni^{3+}	0.62			$LaNiO_3$
Rh^{3+}	0.68			$LaRhO_3$
Ru^{3+}	0.69			$LaRuO_3$
Ru^{4+}	0.67		$BaRuO_4$	

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4.4.5.1 Oxides

The platinum-group metal oxides have been utilised catalytically in three main areas. Firstly as precursors of platinum-group metal black catalysts. Although, in principle, any of the platinum-group metal oxides may be reduced to finely divided metal, because of the restrictions imposed by having to use commercially available salts and either hydrolysis chemistry or sodium nitrate fusion chemistry [1], the technically important oxides are PdO, Rh_2O_3, RuO_2, OsO_2, IrO_2 and PtO_2. Mixed oxides, such as RuO_2-PtO_2, can be made by these methods of preparation. The mixed oxides gave, on reduction, some of the earliest commercially available metal alloy catalysts [2, 3, 4].

Secondly, the oxides may be used as oxidation catalysts. The two higher oxides of osmium and ruthenium (OsO_4 and RuO_4) are the main platinum-group metal oxides used commercially [5 to 8], although some work, mainly experimental, has been carried out on the application of complex perovskite oxides, such as barium ruthenate and lanthanum ruthenate, to the oxidation of carbon monoxide by nitrogen oxides in autoexhaust streams [9].

Lastly, some of the platinum-group metal oxides have been used as anode coating materials. Ruthenium dioxide coatings for brine electrolysis anodes, both for chlorine and chlorate manufacture, have become part of the accepted technology in these industries. Besides saving power, by having lower chlorine overvoltages compared to conventional graphite electrodes, ruthenium dioxide coatings are also non-corrodable [10, 11]. Other platinum-group metal oxides have been developed for brine electrolysis anodes, with properties somewhat different to ruthenium dioxide coatings and two of them, iridium dioxide [12] and palladium oxide [13] have achieved commercial use. Anode oxide coating technology has been applied to mercury cells as well as diaphragm and membrane cells.

Both simple and complex oxides of the platinum-group metals have been studied for a variety of noncommercial reactions in which the oxide retains its identity. These reactions include oxidation of functional organic groups, hydrogenation, decomposition of hydrogen peroxide and nitrous oxide, exchange of deuterium between deuterium oxide and alkylbenzenes, and the photoelectrochemical decomposition of water.

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4.4.5.1.1 Oxides as Catalytic Metal Precursors

Platinum metal oxides occur as the precursors to metallic catalysts for three reasons:

(I) in the case of supported catalysts, where the platinum metal is impregnated into the support by a hydrolysis route; (II) with both supported and unsupported oxides, where reduction in the reaction mixture is used to obtain higher catalytic activity than can be obtained by a catalyst reduced during preparation; (III) for reasons of safety, where the introduction of a prereduced catalyst into a reaction mixture containing volatile organics is liable to cause a fire or an explosion. Although such hazards may be overcome by blanketing the reaction mixture with an inert gas, this may not always be a convenient or practical step and substitution of an oxide catalyst removes most of the problems.

With case (I) conversion to the metal may be accomplished by purely thermal means or with hydrogen gas as reductant or by the use of a "liquid" reducing agent such as hydrazine or formaldehyde. These methods have already been discussed in Section 4.3 and will not be considered further. Of necessity the other two cases require the use of hydrogen gas as reductant of the metal oxide.

The group VIII metal oxides of the second and third long periods can be reduced to the metal with hydrogen, but the ease of reduction differs for the six elements. Palladium(II) oxide is very easily reduced by hydrogen. Gas phase reduction occurs below room temperature even when the hydrogen partial pressure is low (50 Torr) and is almost always accompanied by the formation of palladium hydride. Care must always be taken to limit the temperature rise during reduction to prevent sintering and loss of surface area. Reduction with hydrogen in the presence of a liquid phase (solvent or substrate) can sometimes be a slow process as it depends on the solubility of hydrogen in the liquid. This may give rise to induction periods, during which both catalyst reduction and substrate hydrogenation may take place simultaneously [1].

Platinum dioxide is easily reduced by both gaseous and dissolved hydrogen at ambient temperature [1], but higher temperatures are required by the oxides of rhodium [1, 2], ruthenium [2, 3], iridium and osmium if gas phase reduction is used, or increased temperature and/or pressure in liquid phase reductions [4].

In the reduction of mixed oxides, the more easily reduced metal frequently aids in the reduction of the more refractory oxide, possibly because of hydrogen spillover. Thus some workers have found that although Adams ruthenium dioxide was not reduced by hydrogen under their experimental conditions, a mixed platinum-ruthenium oxide, containing 66 at% ruthenium, was reduced completely to the metal [2]. The reduction of binary and ternary oxides has also been discussed in general terms [5].

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Preparation of the Oxides

Hydrolysis. The usual method of making the platinum-group metal oxides by hydrolysis is to add alkali to the corresponding chloro salts, such as chloropalladous acid or rhodium trichloride in aqueous solution, until the pH reaches 8 at which point the metal precipitates as the hydrated oxide (hydroxide) [1, pp. 1574/5, 1591]. The precipitate is washed free of chloride ion and dried. Such oxides invariably contain bound chloride which may interfere with the catalytic properties of the oxide. Chloride-free oxides may be made by employing the nitrate of the metal in place of the chloro salt. It is not possible to prepare platinum dioxide by this route from chloroplatinic acid or its salts. The best method for this oxide is to replace all six chlorines around the platinum with hydroxyls by prolonged boiling of the chloroplatinate with sodium carbonate forming sodium hexahydroxyplatinate. This salt is then carefully acidified with acetic acid to precipitate white hydrated platinum dioxide which is washed and dried [1, p. 1591]. An alternative method is described in [1, pp. 1574/5]. The general hydrolysis chemistry of the chloro salts of the platinum metals has been reviewed by [6]. Catalytic oxides prepared by these methods are usually amorphous, showing little or no X-ray diffraction pattern. The particle size is normally <10 μ, with highly irregular particle shapes. Monodisperse metal oxide powders of spherical shape have been prepared by conducting the nucleation and growth stages of the hydrolysis in the presence of chelating agents such as nitrilotriacetic acid, triethanolamine, ethylene diaminetetracetic acid, etc. [7].

Alkali Nitrate Fusion. The decomposition of platinum metal chloro salts by molten sodium nitrate was first described for platinum dioxide [8]. The method was later improved [9] and this became the accepted preparative route for what became known as Adams Catalyst [10]. The basic method of preparation has been described a number of times and is particularly accessible in [11] and [12]. It consists of evaporating a solution of chloroplatinic acid onto solid sodium nitrate and fusing the dried mixture at 400 to 450°C. After evolution of nitrogen oxides ceases the melt is cooled and leached with water to give a fine brown powder. Platinum oxide prepared by this method has been found to give material which is not uniformly active from one preparation to another, and the method has been modified so that dried sodium nitrate-chloroplatinic acid mixture is added to molten sodium nitrate at 520°C to overcome the problem [13]. Rhodium-platinum mixed oxides have been prepared by a third modification of the method by adding the mixed metal chlorides as a solid to molten sodium nitrate at 420°C, then raising the temperature to 460 to 480°C for 10 min [14, 15]. The same method was employed in the manufacture of platinum-rhodium oxide [16, 17] and for the preparation of fifteen mixed oxides of the platinum metals with other platinum metals (e.g. Pt/Pd, Ir/Pt) and base metals (e.g. Fe/Pt, Co/Pd), and a single ternary oxide mixture Ni/Ru/Pt [2]. Platinum dioxide has been prepared by the Frampton method, but alkaline earth metals were added to the chloroplatinic acid before reaction [4]. The changes in the physical properties and chemical composition are shown in the following table.

additive	MCl_2:Pt (wt%)	crystal size (Å)	mean grain size	surface (m^2/g)	impurity content (wt%)			
					Na^+	Be^{2+}	Mg^{2+}	Ca^{2+}
		PtO_2	PtO_2	PtO_2	PtO_2	PtO_2	PtP_2	PtP_2
$BeCl_2$	0	25	34	49	~ 1	—	<0.01	<0.03
	1	20	—	—	~ 1	~ 1	0.1	0.1
	2	20	—	71	~ 1	~ 1	0.1	0.1
	5	—	—	—	—	—	—	—
	10	—	—	—	—	—	—	—
	20	22	5	87	~ 1	$\gg 1$	0.1	0.01
$MgCl_2$	1	19	—	47	>0.01	—	~ 1	~ 0.1
	2	15	—	—	>0.01	—	$\gg 1$	~ 0.1
	5	—	—	—	>0.01	—	—	~ 0.1
	10	10	—	—	>0.01	—	$\gg 1$	~ 0.1
	20	—	12	78	>0.01	—	$\gg 1$	0.1
$CaCl_2$	1	20	—	52	~ 1	0.001	<0.1	~ 1
	2	20	—	—	~ 1	—	<0.1	~ 1
	5	25	—	—	~ 1	—	—	—
	10	20	—	74	~ 1	—	0.1	>1
	20	—	16	—	~ 0.3	—	—	—
$SrCl_2$	1	20	—	50	~ 1	0.001	0.1	<1
	2	20	—	—	~ 1	—	—	—
	5	—	—	—	—	—	—	—
	10	19	—	—	~ 1	—	0.1	—
	20	—	15	60	~ 0.3	—	—	—
$BaCl_2$	1	25	—	—	1	—	0.1	0.01
	2	24	—	43	—	—	0.1	0.01
	5	—	—	—	—	—	—	—
	10	26	—	61	—	—	—	0.01
	20	—	11	—	~ 0.01	—	0.1	—

On reduction to the metal in the liquid phase by hydrogen, it was found that the addition of alkaline earth chlorides to the melt resulted in a more porous platinum black. The composition of platinum oxide made by the Adams method has been investigated and found to consist of a mixture of platinum, platinum dioxide and $Na_xPt_3O_4$ (a sodium-platinum bronze). Reduction of the mixture with hydrogen gave a mixture of platinum metal and $Na_xPt_3O_4$. Both the metal and the bronze are catalytically active [5].

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Reactions

Platinum-group metal oxides have long been used as the precursors to catalytically active metal blacks for liquid phase hydrogenations and electrode catalysts for fuel cells. Much of the information available on these subjects has been reviewed in Section 4.2.2. This section will deal with reactions in which the oxide precursor is reduced in situ in the reaction mixture. General reviews of the use of platinum metal oxides as catalyst precursors have been published in works devoted to the wider aspects of catalysis [1 to 6]. Most of the organic functional groups met with in the Fine Chemicals Industry can be hydrogenated over platinum metal oxides, even the more difficult reactions involving the hydrogenation of nitrogen or sulphur functions or the hydrogenation of simpler functions in the presence of nitrogen or sulphur functions. Thus the use of ruthenium dioxide for the hydrogenation of pyridines in neutral or slightly alkaline solvents has been recommended, although platinum dioxide may be used if acid is present. Ruthenium dioxide is also the catalyst of choice for the hydrogenation of aliphatic ketones to alcohols, and here the ketone function is sometimes reduced in preference to carbon-carbon double bond unsaturation. For example, provided that low temperature (60 to 65°C) and an alkaline solvent (10% sodium hydroxide in water) is used citronellal will be hydrogenated to citronellol in 82% yield. At 120 to 125°C hydrogenation of both organic functions takes place to give the saturated alcohol [8]. Ruthenium dioxide has been used to hydrogenate the aromatic nucleus in compounds having amine functions [9] and more recently it has been found that ruthenium, palladium and rhodium oxides can be used to hydrogenate pyrroles and pyridines [10]. Crude and refined sulphur-containing rosin acids have been hydrogenated over platinum dioxide [11]. Palladium oxide and platinum dioxide have been used as catalysts in the manufacture of hydrazine [12]. The sodium content of some platinum oxides can act as a poison for some hydrogenation reactions. In order to obtain a high activity for benzene hydrogenation, the reaction had to be conducted either in an acidic medium or with a sodium-free platinum oxide [13].

Mixed oxides have not received the same attention in the literature that the simple binary oxides have. The competitive hydrogenation and hydrogenolysis of unsaturation and oxygenated functions in organic compounds has been studied. It was found that the use of a mixed platinum-rhodium oxide (25% Pt, 75% Rh by weight) increased the rate of hydrogenation and decreased the rate of hydrogenolysis compared to that obtained over platinum dioxide [14 to 17]. The platinum-rhodium oxide system has been explored in greater detail. It was found that catalyst activity, product composition and resistance to poisoning was a function of the metal ratio in the catalyst. For many hydrogenations the mixed oxide catalyst was superior to either platinum dioxide or rhodium oxide [18 to 21].

For example, 75% Rh/25% Pt oxide hydrogenated acetophenone to cyclohexylethanol while platinum oxide caused both hydrogenation and hydrogenolysis. With diphenylether both dicyclohexylether and phenylcyclohexylether were formed. Minimum hydrogenolysis occurs at a composition of 70% Rh/30% Pt. Some work with platinum-iridium, platinum-ruthenium and platinum-palladium oxides showed that synergistic effects were general with these materials [19]. Some attempts have been made to give the subject a theoretical basis by attributing the systematic changes of activity with composition of oxide to electronic factors in the alloy produced by their reduction [22]. No direct evidence of alloying was found, although evidence was obtained, from the consumption of hydrogen during reduction of the mixed oxides, that both oxides were substantially reduced. Most of the work was conducted with platinum-ruthenium oxide [22 to 25] see **Figg. 27** to **29** and **Fig. 30**, p. 254 [24, 25]. Other purely platinum-group metal mixed oxides studied were Pt/Ir, Pt/Rh, Ru/Rh, Pd/Ru, Pd/Rh and Pd/Pt [22, 26]. Platinum metal-base metal systems were represented by Pd/Ni, Pt/Ni, Pt/Fe, Pt/Co, Pt/Cu, and Pd/Co [22, 27]. The ternary system Pt/Ru/Ni was also described [22].

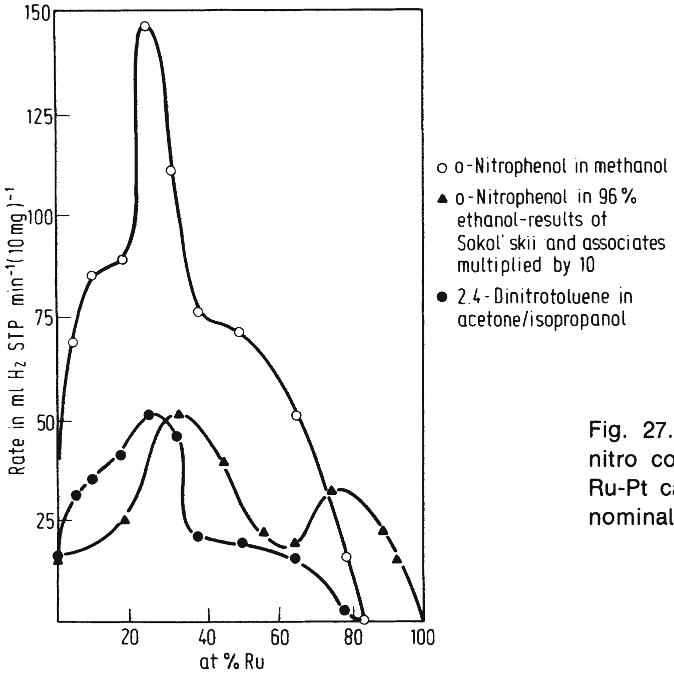

Fig. 27. Hydrogenation of aromatic nitro compounds in the presence of Ru-Pt catalysts (rates plotted against nominal composition).

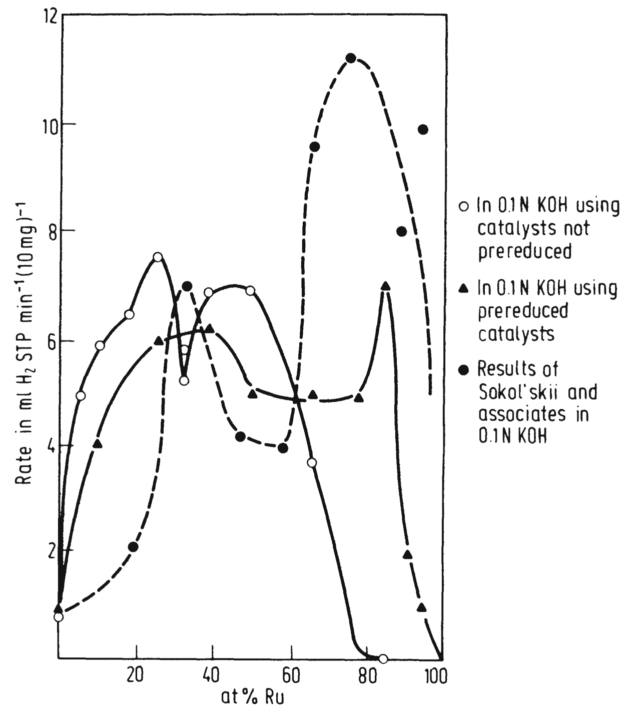

Fig. 28. Hydrogenation of o-nitrophenol in the presence of Ru-Pt catalysts.

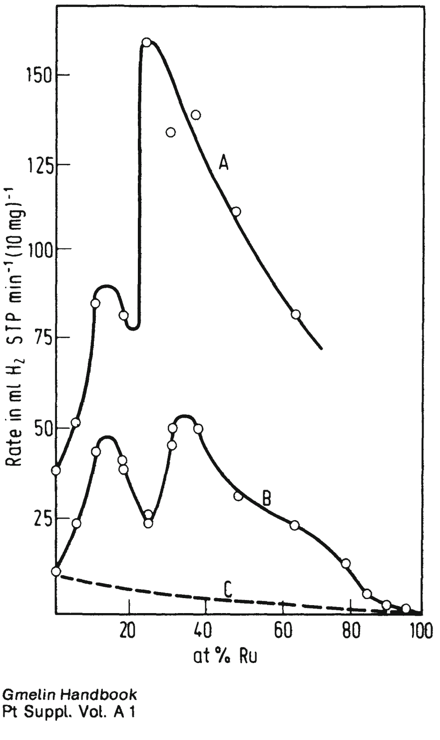

Fig. 29. Hydrogenation of nitrobenzene in the presence of Ru-Pt catalysts.

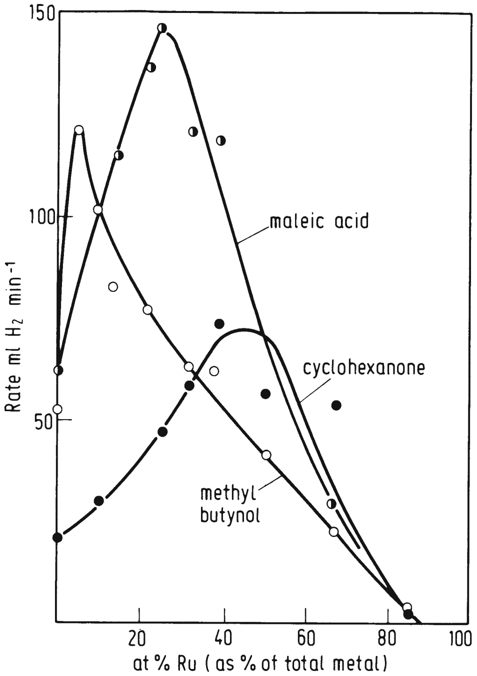

Fig. 30. Activity of reduced Ru-Pt oxides in the hydrogenation of methylbutynol, maleic acid and cyclohexanone.

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4.4.5.1.2 Oxides as Catalysts

It is only fairly recently that the platinum-group metal oxides have been used as catalysts, although the catalytic properties of osmium tetroxide were early exploited by organic chemists to form cis-diols from unsaturated hydrocarbons. The principal use of platinum metal oxides is for oxidation catalysis, but some work on hydrogenation, chlorination, decomposition reactions etc. has been reported. Oxidation has taken preference over other types of reaction simply because little was known about the complex oxides of the platinum metals and the simple binary oxides have limited stability in any atmosphere except those that are oxidising. Apart from osmium tetroxide, the only commercial use for the oxides is in spinels and perovskites for autoexhaust cleanup. Current work on the use of ruthenium dioxide as a catalyst in the photodecomposition of water looks promising, but its commercial exploitation is a very long way off. In general the metal oxides are used as heterogeneous catalysts in gas or vapour-phase reactions, liquid-phase reactions being in the main confined to oxidations with ruthenium and osmium tetroxide. It is for this reason that catalytic reactions with these two compounds are considered separately from the reactions over heterogeneous catalysts.

Preparation of Heterogeneous Oxides

The simple binary oxides are prepared by the methods given on pp. 249/51. However, ruthenium dioxide suitable for hydrogen peroxide decomposition has been prepared by the reduction of ruthenium tetroxide with hydrogen at 15 to 100 psi (~1 to ~6.7 kg/cm^2) and a temperature of 30 to 50°C [1]. Mixed ruthenium dioxide and titania has been prepared by the sodium hydroxide hydrolysis of an aqueous solution of the two chlorides [2]. Details of the preparation of single crystals of ruthenium dioxide, osmium dioxide and iridium dioxide and elaborations of these methods have been published [3].

Methods of synthesising complex oxides are usually adaptions of methods used by solid state chemists, designed to improve the surface area of the material. Solid state chemists prefer to work with single crystal material and aim, with their preparations, to achieve as little amorphous or poorly crystalline material as possible. Synthesis of complex oxides is normally attained by solid-state reactions, heating the intimately mixed oxides to elevated temperature (>500°C), sometimes under high pressures of oxygen (>100 atm):

$$2\,BaO_2 + Ru \xrightarrow{1000\text{ to }1200^\circ C} BaRuO_3 + BaO$$

A large number of papers have been published dealing with solid state reactions for the preparation of complex oxides [4 to 14]. Other methods, such as hydrothermal reactions, metathetical reactions involving exchange of anions between two reagent phases, and oxidising flux reactions have been described [14]. A chapter dealing with the preparation of complex oxides showing how solid-state preparation methods may be adapted to improve the surface area of these meterials for catalytic purposes has been published [15]. Preparations in which part of the anionic metal is replaced by another metal, e.g. $Ba(Ru_xTi_{1-x})O_3$, have been described [16], while materials have been described, in which the cation has been partially replaced by a second metal, e.g. $(Ba_{0.83}Sr_{0.17})RuO_3$ [5, 6].

The patent literature describes a very large number of catalyst preparations in which two metal oxides are reacted under conditions which may lead to the formation of complex oxides. However, although no indication is given that complex oxides are formed, such methods may prove of use to the catalyst chemist in the design of new catalysts and he should consult the patents mentioned in the next section for preparation information.

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Reactions

Concerning platinum-group metal containing complex oxides, one review discussed the properties of perovskite and perovskite-related oxides as gas phase oxidation-reduction catalysts [1], while the other was a wide ranging discussion of spinels and perovskites as catalysts in deep oxidation, oxidative dehydrogenation, hydrogenation reactions and as fuel cell catalysts [2]. Both reviews include a wide ranging discussion of mechanism and kinetics, but concentrate on the effect of oxide structure on the catalysis.

Hydrogenation. That the hydrogenation properties of Adams platinum oxide is dependent on its sodium content has long been known [3, 4], and although is was suspected that the sodium was present as "sodium platinate" [3], it was only with later investigations [5] that the presence of a platinum bronze was confirmed. This bronze $Na_xPt_3O_4$ was shown to be catalytically active for the hydrogenation of cyclopentenes and benzene. A second bronze $NaPt_3O_4$, although not present in Adams platinum oxide, was found to be active for both of the above substrates. Neither bronze was substantially decomposed during the hydrogenation reaction. The use of a calcium-platinum bronze as a hydrogenation catalyst has been patented [6].

Oxidation. Oxidation of unsaturated compounds to give aldehydes, ketones or carboxylic acids with either the simple binary oxides or complex oxides of the platinum metals, are to be found in the patent literature. Furfural was oxidised to furoic acid over platinum dioxide at 50 to 55°C in the liquid phase [7]. Using palladium hydroxide, propylene has been oxidised to malonic acid at 90 to 120°C and a total pressure of 3 to 10 atm. Both reactions utilised gaseous oxygen as the oxidant [8].

Complex oxides of palladium and vanadium supported on alumina were employed to oxidise ethylene to aldehydes and ketones in 69% yield at 140°C and 1 atm pressure [9]. Either air or oxygen could be used as oxidant. Unsaturated carboxylic acids have been formed by the oxidation of acrolein and methacrolein over a complex oxide catalyst of metal ratio $Mo_aP_bQ_cPd_d$ (where Q was Rb, Cs or K and a = 12.0, b, c, and d = 1 to 8) [10]. A bismuth, chromium and palladium complex oxide was used to oxidise toluene in the liquid phase and in the presence of acetic acid and sodium acetate to benzyl acetate at 85°C under pressure in 32% yield [11].

Automotive Catalysts. The current strategy for cleaning up the exhaust streams of automobiles relies almost exclusively on the concept of catalytic after-burning in which the pollutants, hydrocarbons, carbon monoxide and nitrogen oxides, are removed by reaction over a catalyst installed in the exhaust stream. Two systems have evolved. The first a purely oxidative system which removes hydrocarbons and carbon monoxide, but is ineffective for nitrogen-oxide removal, and a second system which, by operating the automobile engine in a narrow window around oxygen-fuel stoichiometry utilises a catalyst as an afterburner to complete combustion, reacting residual hydrocarbons and some carbon monoxide with residual oxygen and the remainder of the carbon monoxide with the nitrogen oxides. This system is known as the "Three Way System".

The principal oxidation catalyst in both cases is platinum-palladium or platinum-rhodium metal catalysts. Although attempts have been made to replace platinum metals by base metal oxides, notably base metal perovskites, none have been successfully commercialised, simply because the activity and durability of such materials have proved to be poorer than those ot the platinum metals. Replacement of some of the base metal in the perovskite by a platinum metal has led to some improvement in both activity and durability, and given rise to hopes, as yet unfulfilled, that catalysts may operate with lower platinum metal loadings. The table below contains details of the catalysts. Examination of such catalysts by X-ray photoelectron spectroscopy (XPES) shows that during oxidation excursions of the catalyst, the platinum is predominantly in the Pt^{IV} condition, while during reduction excursions it is mainly Pt^0.

base metal perovskite	PGM replacement	formula	Ref.
$LaCoO_3$	Pt	—	[12]
$La_{0.7}Pb_{0.3}MnO_3$	Pt	—	
$La_{0.8}Sr_{0.2}CoO_3$	Pt	$La_{0.8}Sr_{0.2}Co_{0.9}Pt_{0.1}O_3$	
$La_{0.7}Pb_{0.3}MnO_3$	Pt	≧1600 ppm Pt	[13]
$La_{0.7}Pb_{0.3}MnO_3$	Pt	30 to 300 ppm Pt	[14, 15]
$La_{1-x}Sr_x$	Pt		

"Three Way Catalysts" operate with either rhodium or ruthenium in the form of rhodites or ruthenates. Ruthenium metal catalysts lose ruthenium as RuO_3 and RuO_4 during oxidising excursions, leading to irreversible loss of activity for nitrogen oxide removal. One solution to this problem is to combine the ruthenium with rare earth and base metal oxides to form ruthenates, such as the perovskites $SrRuO_3$, $LaRuO_3$ and $BaRuO_3$ and the pyrochlore $Pb_2Ru_2O_{7-x}$ (with $x \approx 1$). Many ruthenates have short Ru-Ru distances indicating some metal-metal bonding, but it has been shown that the active species is the ruthenium ion [16]. The effect of stabilisation on the selectivity of the ruthenium component was studied by comparing ruthenium metal catalysts with $Pb_2Ru_2O_{7-x}$, $SrRuO_3$, $La_{0.8}K_{0.2}Mn_{0.94}Ru_{0.06}O_3$ and $La_{0.7}Pb_{0.3}Mn_{1-x}Ru_xO_3$ [16, 17, 18].

The activity and selectivity of perovskite cobaltates and niobates, and spinel aluminates in which a portion of the anion has been replaced by a platinum-group metal, have been studied in "Three Way Catalysts". The table below contains catalyst details. Perovskite catalysts, in which a portion of the oxygen has been replaced by a halogen and part of the base metal by a platinum metal, have been tested [23].

base metal perovskite	PGM replacement	formula	Ref.
$Sr_{0.2}La_{0.8}CoO_3$	Ru	$Sr_{0.2}La_{0.8}Co_{0.8}Ru_{0.2}O_3$	[19]
		$Sr_{0.2}La_{0.8}Co_{0.9}Ru_{0.1}O_3$	
	Pd	$Sr_{0.2}La_{0.8}Co_{0.9}Pd_{0.1}O_3$	
$KNbO_3$	Pt	$KNb_{0.9}Pt_{0.1}O_3$	[20]
$NdCoO_3$	Ir	$NdCo_{0.5}Cu_{0.25}Cr_{0.2}Ir_{0.05}O_3$	[21]
$Sr_{0.2}La_{0.8}CoO_3$	Ru	$Sr_{0.2}La_{0.8}Co_{0.9}Ru_{0.1}O_3$	[22]
$Sr_{0.2}La_{0.8}AlO_3$	Ru	$Sr_{0.2}La_{0.8}Al_{0.9}Ru_{0.1}O_3$	
$Sr_{0.4}La_{0.6}CoO_3$	Pt	$Sr_{0.4}La_{0.6}Co_{0.9}Pt_{0.1}O_3$	
	Rh	$Sr_{0.4}La_{0.6}Co_{0.9}Rh_{0.1}O_3$	
	Ru	$Sr_{0.4}La_{0.6}Co_{0.9}Ru_{0.1}O_3$	

Lanthanum rhodite ($LaRhO_3$) shows high activity for carbon monoxide oxidation and reduction of nitrogen oxides to ammonia under reducing conditions in auto exhausts [24, 25], while the activity of $La_{0.8}K_{0.2}Mn_{0.9}Ru_{0.1}O_3$ for the reduction of nitrogen oxides is known to be high [26]. Neither catalyst was tested under near-stoichiometric conditions such as pertain under three way catalyst conditions.

Photodissociation of Water. Artificial photosynthesis systems designed to produce useful chemical products using solar energy are in their infancy, with most work concentrating on the photodissociation of water. Currently two basic strategies exist. The first consists of a homogeneous photosensitiser system, which functions to transfer electrons between certain mediator materials, coupled to heterogeneous catalysts capable of using the oxidised and reduced forms of the mediators to liberate hydrogen and oxygen from water. The basic system of cycles is shown in **Fig. 31** [27].

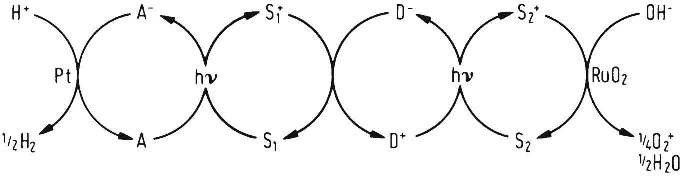

Fig. 31. During the photodissociation of water using coupled photosystems, photosystem I forms oxidised sensitiser (S_1^+) and reduced acceptor (A^-). A donor (D) recycles S_1^+ while platinum catalyses hydrogen formation via A^-. Photosystem 2 reduces the oxidised donor (D^+), forming oxidised sensitiser (S_2^+) which generates oxygen via a ruthenium dioxide catalyst.

The catalyst for systems evolving hydrogen is usually metallic platinum either colloidal or supported, but platinum dioxide has been used in one system. In oxygen-evolving systems the normal catalyst is ruthenium or iridium dioxide, either powder or colloidal if unsupported, or supported on titanium dioxide or zeolite. Manganese dioxide has also been tried. The following tables give details of the two homogeneous systems [27].

Hydrogen-evolving photosystems:

sensitiser	electron acceptor	electron donor	catalyst	quantum efficiency (% H_2)
$bipy_3Ru^{2+}$	methyl viologen	EDTA	Pt colloid	26
$bipy_3Ru^{2+}$	methyl viologen	cysteine	PtO_2	—
proflavine	methyl viologen	EDTA	Pt/asbestos	—
acridine yellow	methyl viologen	EDTA	Pt colloid	32
$ZnTMPyP^{4+}$	methyl viologen	EDTA	Pt colloid	60
$ZnTMPyP^{4+}$	none	EDTA	Pt colloid	7
$ZnTSPP^{4-}$	methyl viologen	EDTA	Pt colloid	2

Oxygen-evolving photosystems:

sensitiser	electron acceptor	catalyst	quantum efficiency (% O_2)
$bipy_3Ru^{2+}$	$Co(NH_3)Cl^{2+}$	RuO_2 powder	1.2
$bipy_3Ru^{2+}$	$Co(NH_3)Cl^{2+}$	RuO_2 colloid	20
$bipy_3Ru^{2+}$	$Co(NH_3)Cl^{2+}$	$CoSO_4$	8
$bipy_3Ru^{2+}$	$Co(NH_3)Cl^{2+}$	RuO_2/zeolite	5
$bipy_3Ru^{2+}$	$Co(NH_3)Cl^{2+}$	RuO_2/TiO_2	12
$bipy_3Ru^{2+}$	$Co(NH_3)Cl^{2+}$	MnO_2	—
$bipy_3Ru^{2+}$	$S_2O_8^{2-}$	RuO_2/TiO_2	—
$bipy_3Ru^{2+}$	$S_2O_8^{2-}$	IrO_2	14
$bipy_3Ru^{2+}$	Ti^{3+}	RuO_2 colloid	<1

$ZnTMPyP^{4+}$ = zinc tetra(N-methyl-4-pyridyl)porphine
$ZnTSPP^{4-}$ = zinc tetra(4-sulphophenyl)porphine

The second system is based on inorganic semiconductors in the form of macro electrodes or as colloidal particles. When irradiated with light of energy higher than that of the semiconductor band gap, an electron/hole pair is formed which can migrate to the semiconductor surface and liberate hydrogen and oxygen from water by reduction and oxidation, respectively. Once again a catalyst is required to couple the electron/hole pair to the substrate, water. The most common catalysts are platinum metal for the reduction cycle and ruthenium dioxide for the oxidation cycle. The system is set out schematically in **Fig. 32**, p. 260 [27].

Both systems have recently been reviewed where two of the problems which beset practical hydrogen/oxygen production by the homogeneous-colloidal systems currently favoured are pointed out. Firstly the gas product is evolved throughout the entire volume of the photolysis cell making collection very difficult. Secondly recovery of the catalyst is almost impossible. With semiconductor systems most of the suitable semiconductor materials are subject to photocorrosion, and those which are not will only absorb a small fraction of the solar spectrum, so reducing their efficiency. Some progress has been made in this area, however, with the discovery that loading the surface of cadmium sulphide with a highly efficient catalyst (ruthenium dioxide) very greatly improves stability [27]. Most of the key references to the photodissociation of water using platinum, ruthenium and iridium dioxides as catalysts are to be found in [28]. Palladium oxide and Fe-Rh oxide are suggested as catalysts in a review of systems for the photodissociation of water and where semiconducting d band oxides are sought which would yield the combination of stability, low electron affinity and moderate band gap suitable for a photoanode [29].

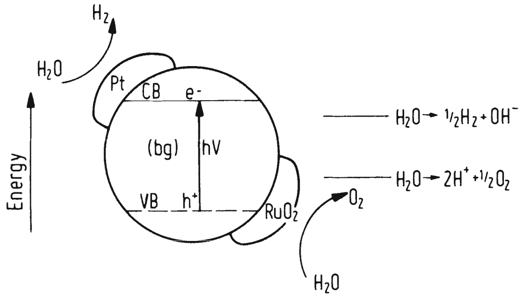

Fig. 32. Excitation of a semiconductor particle loaded with surface deposits of platinum and ruthenium dioxide promotes an electron into the conduction band (CB), enabling it to migrate throughout the particle. The platinum deposit can trap the electron and promote hydrogen formation. The hole remaining in the valence band travels to the particle surface where, if trapped by the ruthenium dioxide deposit, it can promote oxygen formation.

Other Reactions. A binary mixture of vanadium pentoxide and platinum oxide has been used to synthesise phthalonitrile by the condensation of phthalic anhydride with ammonia in the vapour phase, at a working temperature of 330 to 445°C, a contact time of 3 to 4 s, and a 5 to 50 molar excess of ammonia. Yields of 85 to 92% phthalonitrile have been obtained [30].

Toluene has been chlorinated in the presence of platinum dioxide catalyst, to give a higher yield of the p-chloro isomer than in chlorinations in the absence of the catalyst [31].

The deuteration of alkylbenzenes over $PtO_2 \cdot 2H_2O$, PdO, Rh_2O_3, $IrO_2 \cdot 2H_2O$ and $RuO_2 \cdot H_2O$ using deuterium oxide has been investigated [32].

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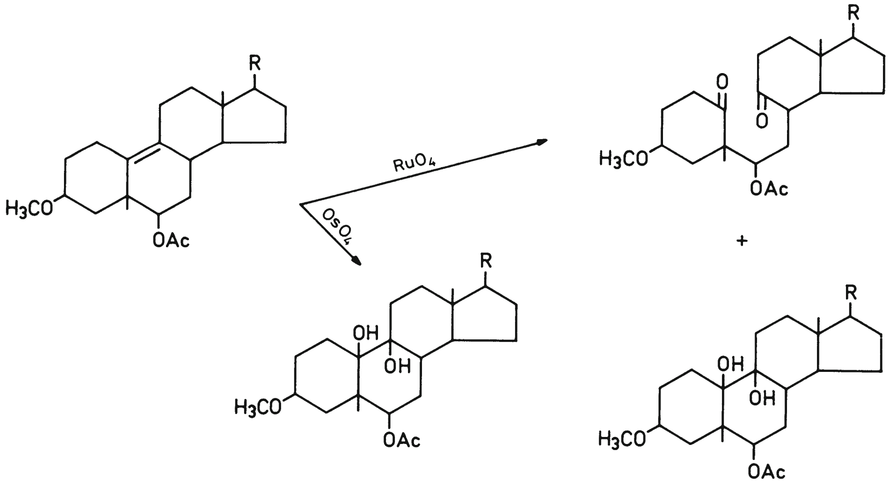
4.4.5.1.3 Ruthenates, Perruthenates, Ruthenium Tetroxide and Osmium Tetroxide as Oxidation Catalysts

The use of ruthenium tetroxide and osmium tetroxide as selective oxidising agents is now a well established procedure with organic chemists. Osmium tetroxide is without doubt the most reliable oxidant for the conversion of alkenes to the corresponding cis-diols. Ruthenium tetroxide on the other hand, being a more powerful oxidising agent, cleaves the double bond of alkenes to give ketones, aldehydes or carboxylic acids [1].



More recently investigation of the properties of the perruthenate ion Ru^{VIII}, ruthenate ion Ru^{VI} and the dioxotrichlororuthenate ion Ru^{V} as oxidation agents has been undertaken, and they have been found to be more selective in their reactions than the tetroxide from which they are derived.

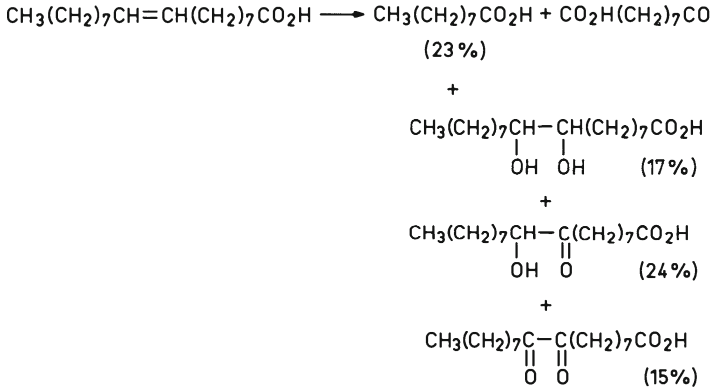
Aqueous solutions of ruthenium tetroxide are stable only at $pH<7$. Under alkaline conditions reduction takes place. At $pH=7$ to 12 it is reduced to the perruthenate ion, while at $pH>12$ reduction to ruthenate occurs [3].

$$4\,RuO_4 + 4\,OH^- \rightarrow 4\,RuO_4^- + 2\,H_2O + O_2$$
$$4\,RuO_4^- + 4\,OH^- \rightarrow 4\,RuO_4^{2-} + 2\,H_2O + O_2$$

The rates of these reactions are strongly dependent on factors other than the hydroxyl ion concentration, such as the purity of the chemicals, presence of catalysts and the cleanliness of the apparatus. This has given rise to some speculation as to the precise nature of the oxidising species present when ruthenium tetroxide is used catalytically under alkaline conditions, especially when the ruthenium tetroxide is generated by the oxidation of an Ru^{III} salt, such as the chloride, with for example sodium hypochlorite oxidising agent. The ability of each ruthenium species to oxidise organic functions is different, thus when perruthenate ion is reacted with oleic acid (molar ratio of oxidant:double bond 4:1) the double bonds were quantitatively cleaved, while the ruthenate ion at the same concentration did not react with the double bond. Concentration of the oxidant is also important. For example when perruthenate ion (oxidant:double bond 4:1) oxidises oleic acid, it forms the cleavage products quantitatively.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H \rightarrow CH_3(CH_2)_7CO_2H + HO_2C(CH_2)_7CO_2H$$

When the oxidant to double bond ratio is only 2:1, then as well as the cleavage products, partial oxidation products are formed [3].



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H \longrightarrow CH_3(CH_2)_7CO_2H + CO_2H(CH_2)_7CO_2H \; (23\%)$$
$$+ \; CH_3(CH_2)_7\underset{OH}{\underset{|}{C}}H-\underset{OH}{\underset{|}{C}}H(CH_2)_7CO_2H \; (17\%)$$
$$+ \; CH_3(CH_2)_7\underset{OH}{\underset{|}{C}}H-\underset{O}{\underset{\|}{C}}(CH_2)_7CO_2H \; (24\%)$$
$$+ \; CH_3(CH_2)_7\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}(CH_2)_7CO_2H \; (15\%)$$

In catalytic oxidations the ratio of ruthenium ion oxidant to oxidisable organic function is even lower, usually about 1:45 to 1:50, and it becomes unsafe to predict catalytic product distributions from the results of stoichiometric oxidation experiments, although they can give a general indication of the path that a catalytic oxidation will follow. Reviews of stoichiometric oxidations of organic functions by ruthenium oxidants [1, 2, 4], and by osmium tetroxide [5, 6, 7], have been published. In order to operate catalytically the osmium or ruthenium oxidant must be regenerable from its reduction product, for example osmium tetroxide from osmium dioxide. Both osmium tetroxide and ruthenium tetroxide may be regenerated in this way and certainly ruthenate ion (RuO_4^{2-}) can, but some doubt exists as to whether perruthenate (RuO_4^-) can be regenerated by the normal oxidising agents from its reduction product, the ruthenate ion (RuO_4^{2-}).

Some authors have found perruthenate in catalytic solutions of ruthenium salts oxidised at high pH by sodium hypochlorite and potassium persulphate, respectively [3, 8]. Others could find no perruthenate in alkaline solutions of ruthenium oxidised by potassium persulphate, and were unable to make the perruthenate ion catalytic with secondary oxidising agents such as chlorate, periodate and persulphate [2]. The formation of perruthenate only occurred when an alcohol was added to the alkaline ruthenium-persulphate mixture, and it was postulated that an alcohol-perruthenate complex was formed which acted as the catalyst [8].

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Preparation

The literature contains methods for the preparation of bulk quantities of osmium tetroxide [1], of ruthenium tetroxide [1, 2], metal ruthenate and perruthenates [1, 2, 3]. Bulk material is usually only prepared where large stoichiometric quantities of the oxidant are required, with catalytic reactions only small quantities of primary oxidant are required and these are usually generated in situ by the secondary oxidant solution.

Stoichiometric Oxidations. The practical details of stoichiometric oxidations can be found in [2 to 7].

Catalytic Oxidations. Catalytic oxidations have been conducted at both atmospheric pressure and under low pressures of the gaseous substrate. Atmospheric pressure reactions are usually carried out in all-glass apparatus consisting of a flask with attached stirrer, condenser and dropping funnel. Two basic procedures are used, firstly the mixture of oxidant, catalyst and substrate is made up in the flask and the reaction allowed to proceed with cooling if necessary [3, 8, 9, 10]. In the second variant, either the oxidant and catalyst or the substrate and catalyst is placed in the flask and the other component run in dropwise from a dropping funnel [11 to 15]. All of the reactants are normally dissolved in a single liquid phase either aqueous or organic, but occasionally a two-phase system has been used, such as water-carbon tetrachloride [13].

A wide range of compounds have been used as secondary oxidants including hydrogen peroxide, persulphates, chlorates, bromates, periodates, perpropionic acid, sodium and calcium hypochlorites, sodium chlorite, tert. butyl hydroperoxide, N-methylmorpholine oxide, triethylamine oxide, and triethanolamine oxide. Starting salts for the catalysts have been varied and examples of these together with secondary oxidant and solvent are to be found in the following table.

catalyst precursor	secondary oxidant	solvent	Ref.
$RuCl_3$	persulphate	water	[3, 8]
	NaOCl	substrate	[13]
	NaOCl	CCl_4-H_2O	[13]
RuO_2	NaOCl	substrate	[13]
	NaOCl	water	[15]

catalyst precursor	secondary oxidant	solvent	Ref.
Ru metal	NaOCl	heptane	[13]
	$NaClO_2$	—	[13]
Ru carbonate	$Ca(OCl)_2$	—	[13]
Ru sulphide	NaOCl	—	[13]
Ru formate	$Ca(OCl)_2$	—	[13]
$RuBr_3$	NaOCl	—	[13]
$OsCl_3$	perpropionic acid	glacial propionic acid	[10]
OsO_4	t-butylhydroperoxide	water	[14]
	N-methylmorpholine oxide	t-butanol	[9]
	triethylamine oxide	t-butanol	[9]
	triethanolamine oxide	t-butanol	[9, 12]
	NaOCl	water	[15]

Catalyst to substrate ratios of between 1:3 [10] and 1:2900 [14] have been used to effect oxidations, but 1:25 to 1:50 is more common.

Oxidations with gaseous substrates are normally conducted in low pressure autoclaves, such as the Parr hydrogenation apparatus, at pressures up to about 60 psi (~ 4 kg/cm^2) [11].

Phase Transfer Catalysis. Reaction in two-phase media can be improved by the addition of an ammonium or phosphonium salt or an ether. These materials, known as transfer agents, aid in the transfer of the active species across the phase boundary increasing the reaction rate and, by modifying the concentration of active species in the organic phase, drive the reaction closer to completion. The theory and mechanism of phase transfer catalysed processes including oxidation by osmium and ruthenium tetroxides have been reviewed [16]. Oxidations with these two reagents are conducted with the substrate and phase transfer agent dissolved in the organic phase and the oxidation catalyst and secondary oxidant dissolved in the aqueous layer. The catalyst to substrate ratio is maintained within the same range as for two-phase oxidation, namely 1:100. Fiftyfold increases in rate of oxidation have been found for osmium tetroxide catalysed reactions in the presence of quaternary ammonium salts or trialkylamines as transfer agents [16, pp. 307/9]. Practical details of oxidations with phase transfer reagents present have been published [15].

Oxidations with Electrochemically Regenerated Secondary Oxidant. In catalytic oxidations with ruthenium and osmium the secondary oxidant is reduced to some lower valent state. For example, periodic acid is reduced to iodic acid, $RuO_2+2HIO_4 \rightarrow RuO_4+2HIO_3$; $OsO_2+2HIO_4 \rightarrow OsO_4+2HIO_3$.

The regeneration of periodic acid as an oxidising agent has been accomplished using an electrochemical cell, hence using much lower levels of secondary oxidant than previously where the secondary oxidant had been consumed [17]. The eletrochemical regeneration system may be operated for both osmium and ruthenium catalysed systems in single or two-phase systems with or without phase transfer agents being present [18]. Similarly osmium-tetroxide catalysed oxidations of olefins using electrochemically regenerated secondary oxidant have been carried out. In this case the secondary oxidant was potassium ferricyanide, which was reduced to the ferrocyanide during the reaction. The regeneration is accomplished at an oxygen-depolarised cathode, $4Fe(CN)_6^{4-}+O_2+2H_2O \rightarrow 4Fe(CN)_6^{3-}+4OH^-$ [19].

References:

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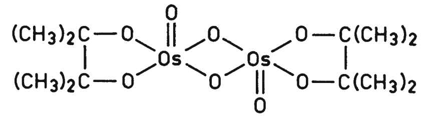
Reactions

Stoichiometric Oxidation. Stoichiometric oxidation of organic functions by ruthenium tetroxide and osmium tetroxide have been reviewed exhaustively in [1] and [2] and partially in [4, 5, 6].

The mechanism by which oxidation takes place is only fully understood for osmium tetroxide oxidation of carbon-carbon double bonds where the intermediates, oxo-osmium(VI) ester complexes can frequently be isolated. The products obtained by reacting alkenes with osmium tetroxide, and alkenes and acetylene with osmium tetroxide in the presence of pyridine have been examined. With alkenes dimeric monoester(I) and monomeric diester(II) complexes are formed which on hydrolysis with sodium sulphate give the cis diol and the complex $Na[Os(SO_3)_3]\cdot 6H_2O$ [7].



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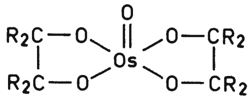
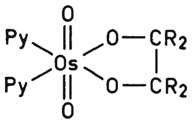
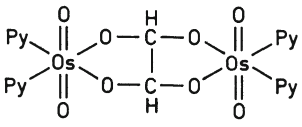


II

Tertiary amines have long been known to promote the rate of formation of osmium ester complexes [8]. The most common tertiary amine used is pyridine and using this amine it has been shown that alkenes and acetylenes react with osmium tetroxide to give cyclic esters of the type $[OsO_2Py_2(O_2R)]$ (III) with alkenes and osmyl complexes $[Os_2O_4Py_4(O_4C_2H_2)]$ (IV) with acetylene.



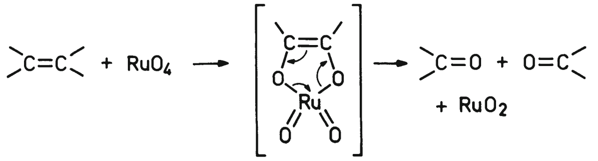
III



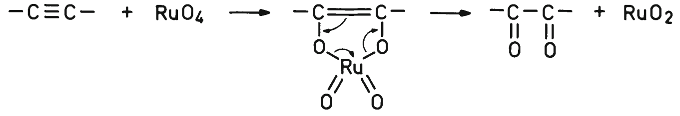
IV

Again these complexes may be hydrolysed with sodium sulphite to form the cis-diol and the complex osmium sulphite [7].

Ruthenium oxidations are proposed to follow the same intermediate ester type compounds route as osmium, but because of the relative instability of Ru^{VI} compared to Os^{VI} the ruthenium esters are only formed as transient species. Cleavage at the double bond takes place with alkenes to give ketones or aldehydes:



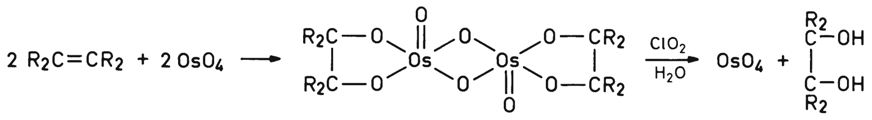
With acetylenes the diketone is formed:



Aldehydes may be further oxidised to give carboxylic acids with ruthenium tetroxide [1].

Oxidation rates of alkenes with ruthenium are directly dependent on the concentration of both the oxidant and the alkene. The introduction of electron-withdrawing groups, such as fluoride, into the alkene structure decreases the rate of reaction. Reactions of osmium tetroxide with alkenes and acetylenes are tabulated in [2].

Catalytic Oxidations. Osmium tetroxide, ruthenium tetroxide and ruthenate/perruthenate oxidations can all be made to operate catalytically, a small quantity of the primary oxidant being regenerated from the metal reduction products by a secondary oxidising reagent. The same mechanism is assumed to operate with catalytic reactions as with the stoichiometric reactions, osmium and ruthenium ester complexes forming. The secondary oxidant reacts with the osmate ester complex to give the cis-diol and osmium tetroxide and with the ruthenium dioxide, formed by ester decomposition, to give the tetroxide [5].



Catalytic oxidations with osmium [2, 9] and ruthenium [1, 10, 11, 12] in aqueous media have been reviewed, as have the use of osmium and ruthenium tetroxides as catalytic agents in phase transfer oxidations [13].

Analytical Uses. The catalytic properties of osmium tetroxide are used as a means of detecting trace quantities of osmium, by converting the osmium trace compound to OsO_4 and using this to catalyse the oxidation of hydroquinone to quinone with hydrogen peroxide at pH = 10.5 or 3.3′-dimethylnaphthidine and potassium chlorate at pH = 2.3 [14]. The reduction of Fe^{III} salts by $SnCl_2$ is catalysed by osmium tetroxide and this reaction has been used as a means of detecting osmium [15]. Titration methods for sulphite, sulphide, thiosulphate and dithionate based on oxidation by catalytic amounts of osmium tetroxide with ferricyanide as secondary oxidant have been proposed [16], while potassium chlorate and cerisulphate titrations for the estimation of Sb^{3+} were improved by the addition of OsO_4 as catalyst [17]. Quantitative estimations of ethanol and methanol have been accomplished by oxidation with excess periodic acid ruthenium tetroxide as catalyst and back titration of the excess periodic acid using ferrous ion [18].

Oxidation of Cyclo-alkanes. Cyclo-alkanes were oxidised by ruthenium tetroxide to a mixture of the cyclic ketone and the aliphatic dicarboxylic acid. The secondary oxidants used were sodium hypochlorite and sodium periodate with a catalyst to substrate ratio of 1:400. The following table shows the substrates used and the product spectrum obtained [19].

cyclo-alkane	products	yield (%)	time
cyclopentane	cyclopentanone	18	7 d
	glutaric acid	63	
cyclohexane	cyclohexanone	26	8 d
	adipic acid	58	
cycloheptane	cycloheptanone	68	2 d
	pimelic acid	20	
cyclo-octane	cyclo-octanone	55	1 d
	suberic acid	23	

Owing to the immiscibility of the cyclo-alkane in water the system is two-phase, with ruthenium tetroxide migrating to the hydrocarbon layer, oxidising the cyclo-alkane and the reduction product migrating to the aqueous layer to be reoxidised. It is noticeable that five- and six-membered rings are more easily cleaved than seven- or eight-membered rings [19].

Oxidation of Alkenes. The oxidation of alkenes by ruthenium tetroxide has been reviewed [1, 11, 12]. The general consensus is that the double bond is cleaved to give aldehydes, ketones or carboxylic acids by ruthenium when used in catalytic amounts. When the double bond is tetrasubstituted then oxidation with RuO_4 always gives ketones, when the double bond has less that four substituents then at least one of the products must be an aldehyde or carboxylic acid.

In contrast osmium tetroxide, when used catalytically does not cleave double bonds but gives rise to cis-hydroxylated products. Reviews have been published of oxidations with osmium and a variety of secondary oxidising agents [2, 9]. The results of oxidising 37 alkenes with osmium tetroxide have been tabulated in [2]. Terminal alkenes give aldehydes, while internal double bonds give cis-diols.

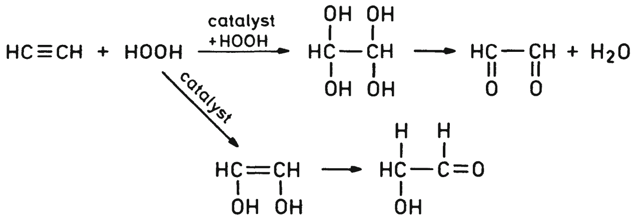
A variety of secondary oxidising agents have been employed. Thus sodium chlorate has been used as a secondary oxidising agent with osmium as catalyst in the preparation of optically active 3,4-dihydroxy adipic acid from hexenediol acid [20]. Studies have been conducted on the oxidation of ethylene, propylene, pentene, indenopinene, diphenylethane, cyclohexene, 1,2-dimethylcyclohexene, anethole, camphene and 2-octalin in methanol, ethanol, ether, ethylacetate and benzene solvents with osmium tetroxide catalyst and potassium chlorate, hydrogen peroxide and tetralin peroxide secondary oxidising agents. Oxidations proceeded faster in methanol and ethanol than in other solvents. Both methanol and ethanol were stable to OsO_4 up to 130 to 140°C, when slow oxidation to aldehydes etc. took place. In all cases either an aldehyde or diol was formed as reaction product with the substrates. Oxidation of 1-decene with sodium periodate-osmium tetroxide gave the aldehyde in water-dioxane solvent [22]. Hydrogen peroxide in t-butanol has been used for the oxidation of 2-methyl-2-butene and cyclohexene and the Diels-Alder adducts of furan, 2-methylfuran, 2-acetoxyfuran and 2-bromofuran [23, 24]. In each case the diols were obtained. Excess hydrogen peroxide caused carbon-carbon cleavage to the carbonyl compounds formed with methylbutene and cyclohexene. Oxidation of unsaturated aldehydes with air-osmium tetroxide caused oxidation of the double bond to give dihydroxy aldehydes and unsaturated acid. Addition of a saturated aldehyde to the reaction mixture caused an increase in the yield of dihydroxy aldehyde compared to unsaturated acid. Unusual oxidation products were obtained when an olefin was oxidised by sodium hypochlorite-osmium tetroxide in the presence of an aryl sulphonamide. The hypochlorite and aryl sulphonamide react to give chloramine-T, which in turn, with osmium tetroxide catalyst, adds across the double bond to give a vicinal hydroxy aryl sulphonamide. For example with p-toluenesulphonamide the product is the vicinal hydroxy-p-toluenesulphonamide. The products formed with this reagent and nineteen olefins are tabulated in [23].

Oxidations of olefins with catalytic quantities of ruthenate ion, unlike ruthenium tetroxide, do not cleave the carbon-carbon double bond exclusively. With some unsaturated compounds such as cinnamyl alcohol attack is confined to the carbinol function and the product is cinnamic acid [24, 25]. The kinetics of ruthenate-catalysed oxidation of unsaturated compounds have been published [26].

1-octene has been oxidised with osmium and ruthenium tetroxides regenerated electrolytically. With osmium the main product was heptaldehyde, while with ruthenium the product was the corresponding carboxylic acid [27].

Oxidation of Alkynes. Oxidation of alkynes by ruthenium and osmium tetroxides gives α-diketones when the alkyne is internal and carboxylic acids, with the loss of one carbon atom, with terminal alkynes [1, 2, 11, 12, 24]. With acetylene osmium gives the aldehydic acid, glyoxalic acid [2]. In an early patent the products are given as hydroxy aldehydes and/or hydroxy acids with osmium and ruthenium, when hydrogen peroxide is the secondary oxidising agent [28]. Thus with acetylene,

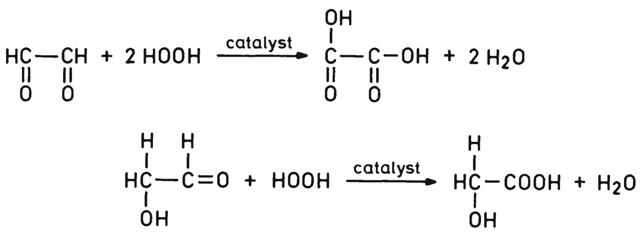
a)



$$\mathrm{HC{\equiv}CH + HOOH \xrightarrow[]{\text{catalyst} \atop \text{+HOOH}} (HO)_2HC{-}CH(OH)_2 \longrightarrow OHC{-}CHO + H_2O}$$

$$\mathrm{HC{\equiv}CH + HOOH \xrightarrow{\text{catalyst}} HOHC{=}CHOH \longrightarrow HOH_2C{-}CHO}$$

b)

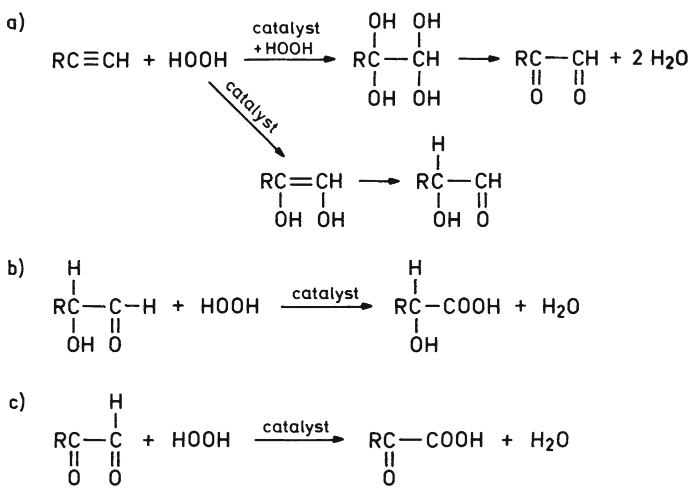


$$\mathrm{OHC{-}CHO + 2\,HOOH \xrightarrow{\text{catalyst}} HOOC{-}COOH + 2\,H_2O}$$

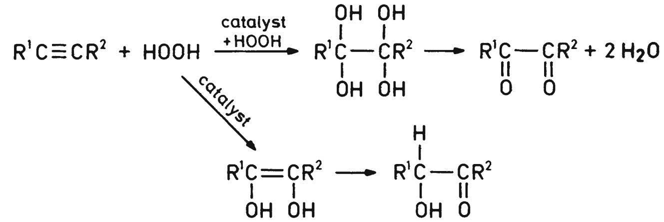
$$\mathrm{HOH_2C{-}CHO + HOOH \xrightarrow{\text{catalyst}} HOH_2C{-}COOH + H_2O}$$

Monosubstituted and disubstituted acetylenes react as follows:

monosubstituted acetylene



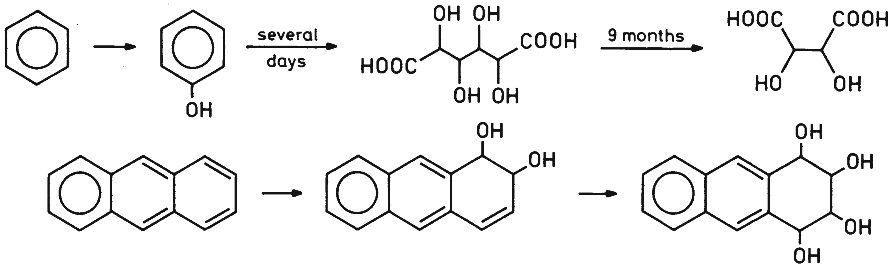
disubstituted acetylene



Oxidation of Aromatics. Ruthenium-catalysed oxidations of the aromatic rings can proceed in three ways:

(I) alkyl side chains on the phenyl ring can be converted to carboxylic acid; (II) the phenyl ring can be cleaved from R-Ph to form R-COOH; (III) the phenyl ring can be degraded to give a dicarboxylic acid [12].

Several authors [1, 12, 24] have reviewed oxidations with ruthenium tetroxide and ruthenate ion of the aromatic ring. Ruthenate ion oxidations do not generally degrade the aromatic ring, although the degree of attack is dependent on time and the secondary oxidant being used.



Osmium catalysed oxidations of aromatics have been reviewed [2, 9].

Oxidation of Alcohols. Ruthenium catalysed oxidations of alcohols give products which are dependent on whether the alcohol is primary, secondary or tertiary. Tertiary alcohols are unattacked, while secondary alcohols yield ketones and primary alcohols give carboxylic acids [1, 11, 12, 24, 25]. Diols yield α-diketones and some cleavage products [1].

The oxidation of alcohol by osmium tetroxide is appreciably slower than that of alkenes with the same catalyst or with ruthenium catalysed oxidations. When oxidation with osmium is practised on unsaturated alcohols, the carbon-carbon double bond is hydroxylated in preference to attack on the carbinol function. Hence allyl alcohol yields glycerol in 98% yield. Where diols are attacked carboxylic acids usually result [2]. The effect of ruthenate ion as a catalyst in alcohol oxidation has been examined and it has been found that primary alcohols yield acids and secondary alcohols give ketones [29]. The yield of carboxylic acids, in the case of primary alcohols, was usually over 90%. The kinetics and mechanism of 2-propanol and 1-propanol oxidation with alkaline osmium tetroxide and ferricyanide ion as secondary oxidant have been studied as well as the kinetics of methanol and ethanol oxidation with the same catalyst [31].

Oxidation of Aldehydes and Ketones. Ruthenium oxidises aldehydes to carboxylic acids and cleaves diketones to give a mixture of acids [12, 24, 25]. The oxidation of acetone and methylethylketone with osmium tetroxide catalyst and ferricyanide ion as secondary oxidant have been studied and both ketones were oxidised to oxalic acid via the ketoacid. With acetone the product spectrum was 80% oxalic acid, 20% acetic acid [32].

Oxidation of Ethers. The preferred catalyst for ether oxidation is ruthenium. Thus ruthenium tetroxide will convert tetrahydrofuran almost quantitatively into γ-butyrolactone, and n-butylether to butylbutyrate in excellent yield. Generally aliphatic ethers are converted to esters, while cyclic ethers are oxidised to lactones [1, 12]. Primary methylethers yield methyl esters, secondary methyl ethers undergo cleavage and give ketones. Benzyl ethers $PhCH_2OR$ give esters PhCOOR in good yield [12].

Oxidation of Sulphur Compounds. Organic sulphides can be oxidised by ruthenium tetroxide to a mixture of sulphoxide and sulphone [1, 12]. For example diphenylsulphide is oxidised to a mixture of diphenylsulphoxide (32%) and diphenylsulphone (43%). Triphenylmethylphenylsulphide gave as its major product triphenylcarbinol [1].

Sulphones and sulphoxides have been prepared by oxidation with osmium tetroxide using oxygen containing nitrogen oxides as secondary oxidant [33]. The nitrogen oxides act as oxygen carriers. By using another property of the osmium catalyst, its ability to catalyse disproportionation of the sulphoxide, the yield of sulphone can be improved [34].

Oxidation of Nitrogen Compounds. Linear primary amines have been oxidised to nitriles by ruthenium tetroxide. Hydrolysis of the nitrile to give amide can occur simultaneously [12]. Cyclic amines are oxidised to the lactams or the imides [1, 12]. Amides are converted to the imides [1].

Amino acids have been deaminated by osmium tetroxide with air as secondary oxidant. A number of amines have been oxidised with ruthenate ion (persulphate secondary oxidant) and acids, aldehydes, amides and nitriles obtained [35].

Phase Transfer Catalysis. The rate of osmium tetroxide-periodic acid oxidations of 1-octene were increased fiftyfold by the addition of tridodecylamine or tetradodecylammonium chloride to the reaction mixture as transfer agents. The improved rate was achieved at the expense of selectivity, up to 13% acid being produced with the quaternary ammonium salt.

Conversions of between 94 an 98% were obtained. Similar improvements with ruthenium tetroxide-periodic acid oxidations of 1-octene were obtained except that the carboxylic acids were the preferred product, 94 to 99% yields of acid were obtained with quaternary ammonium and phosphonium salts as transfer agents [13].

Tetraethylammonium hydroxide has proved an effective transfer agent in the osmium tetroxide-t-butylhydroperoxide oxidation of 1-decene, 1-octene, oleic acid, cyclohexene and α-methylstyrene. The product in each case was the dihydroxy compound [37].

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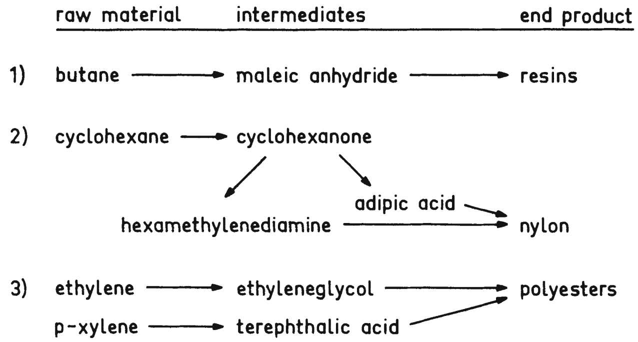
Oxidations with Ruthenium and Osmium Tetroxides for Producing Chemical Intermediates

An intermediate has been defined as "a material that occurs somewhere in a chemical manufacturing process between the introduction of the basic raw materials and the creation of the final end product" [1].

The petrochemical industry takes its basic raw materials from the petroleum refining industry, mainly in the form of hydrocarbons. These can be saturated such as butane and cyclohexane, unsaturated like ethylene and butadiene or aromatic, exemplified by benzene, toluene and xylene. The end products are resins, plastics etc. which are produced by routes such as shown below.



These procedures require that the intermediates be produced by the insertion of oxygen into the starting molecule. Although these oxidations are presently carried out over base metal catalysts, attempts have been made to use ruthenium and osmium tetroxides as catalysts for this purpose. So far none have been commercially successful [1].

It has been suggested that ruthenium tetroxide may be a suitable catalyst for oxygen insertion into alkanes, even though very few reactions are known for this system [2]. Also despite the secondary oxidising agents, such as sodium hypochlorite (household bleach), being inexpensive in absolute terms, they are surprisingly expensive when compared to the cost of the product material. The only cheap oxidising agent suitable for the large scale manufacture of petrochemicals from alkanes is air [3].

The oxidation of alkenes to useful products can be accomplished more easily than is the case with alkanes. Ethylene has been hydroxylated to give excellent yields (88 to 97%) of ethylene glycol, a polyester intermediate [4].

A thorough investigation of the oxidation of propylene with osmium tetroxide-hydrogen peroxide has been made, but were no better than 33% propylene glycol, the main product being acetol (hydroxyacetone) [5, 6]. In the oxidation of ethylene using osmium tetroxide-air osmium reoxidation and hydroxylation took place in a narrow pH window centred at $pH = 9.5$. The rate of reaction was good at first, but declined with time, due to the formation of a complex between osmium tetroxide and ethylene glycol. Operation at elevated pressures gave higher activities and also allowed a greater glycol concentration to accumulate before catalyst activity fell to unacceptably low levels [7]. The only other serious attempt to produce a glycol by osmium tetroxide used the oxidation couple osmium tetroxide-ferricyanide ion to oxidise propylene to propylene glycol. It was proposed to regenerate the secondary oxidant electrochemically. Although selectivity based on glycol formed per unit of ferricyanide consumed was high (96 to 99%), the conversion per unit of propylene passed through the reactor was low [8].

Osmium tetroxide-vanadium pentoxide catalyst in aqueous nitric acid has been used to oxidise cyclohexene to adipic acid in yields up to 88%. Cyclohexene is, however, a relatively expensive feedstock compared to cyclohexane, thus preventing commercial exploitation [9].

Ruthenium tetroxide-hydrogen peroxide was investigated as an oxidant for converting acrolein in methanol to methyl acrylate. Yields of the required plastics precursor were low at 39% [10].

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Ruthenium Tetroxide Catalysed Pollution Control

Catalytic removal of pollutants from gas streams, derived either from industrial processes or automobiles, has become accepted practice and attempts are now being made to widen the concept of catalytic pollution control to areas previously thought to be unamenable to this mode of treatment, such as removal of sulphur compounds from gas streams and fuels and waste water treatment. The use of ruthenium oxidation catalysis in this technology has been reviewed [1].

Wet scrubbing of waste gas streams has long been used to reduce air pollution, but tightening controls on sulphur emissions has led to the incorporation of oxidising agents in the scrubbing liquid, notably potassium permanganate. Some sulphur compounds found in waste gas streams, however, are resistant to potassium permanganate oxidation and have proved a problem. It has been shown that thiophene is only slowly oxidised by the scrubbing liquor, while it is oxidised about 100 times faster by ruthenium tetroxide-sodium hypochlorite making wet scrubbing a practical proposition for these pollutants [2]. Another gas-phase pollutant which can be treated with Ru^{VIII} is vinylchloride. Passage of a gas stream containing >5000 ppm vinylchloride in air over an 0.5% ruthenium-on-alumina catalyst at 376°C was reduced to 2 ppm [3].

Treatments of pollutants in the liquid phase has also been tried. Treating petroleum fractions to be used as fuels with ruthenium tetroxide-sodium hypochlorite to remove sulphur compounds has been suggested. Thus a 500 ppm sulphur level was lowered to 50 ppm by such a treatment in about 4 h [4]. Waste water containing ammonia has been treated at 270°C and 220 psi (~14.8 kg/cm^2) with a 1.1 M equivalent of oxygen (based on the oxidisable constituents) over a 2% ruthenium-on-alumina catalyst. Operation over a 2 week period gave treated waste water pollution contents, NH_3 and $NO_2 + N_2O_3$, of 0.9 to 4.9 and 3.2 to 7 mg/l, respectively. With a conventional treatment the levels were 1.8 to 62 and 4 to 67 mg/l, respectively [5]. Mono-, di- and pentachlorophenols in aqueous solution have been treated with ruthenium tetroxide. Complete fragmentation occurs at 30°C to give carbon dioxide and hydrogen chloride. Polychlorodibenzodioxins can similarly be destroyed by ruthenium tetroxide [6, 7].

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Oxidation Reactions in the Fine Chemicals Industry

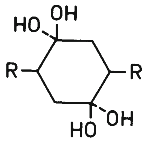
The products of the Fine Chemicals Industry are substances, often of high purity with high added value, but manufactured in relatively small quantities, including solvents, cosmetic constituents and pharmaceuticals. Many are produced from biological material although an increasing number are synthesised particularly when, as is the case with glycerol, the natural source is insufficient to cover the demand. Where the finished product has a high added value compared to the raw materials, attempts to use the selective oxidising powers of ruthenium and osmium tetroxide have been successful and commercial processes flourish; with lower added value products attempts to use these catalysts have proved a failure.

Solvents. The added value of these materials is low and no commercial processes exist, but some patents aimed at the manufacture of butyrolactone, a small scale solvent, and sulphones for solvents, dyestuffs and pharmaceuticals have been granted. Ruthenium tetroxide has been proposed as a catalyst in the oxidation of tetrahydrofuran to butyrolactone. The yield was almost quantitative [1]. In the conversion of sulphoxides to sulphones, yields of 50 to 70% have been obtained, depending on the conditions and sulphoxide being used, with osmium tetroxide as catalyst [2].

Cosmetic Constituents. The only cosmetic constituent in which consistent attempts have been made to apply osmium tetroxide catalysis to its manufacture is glycerol. No commercial process has resulted simply because a cheaper catalyst exists, namely titanium salts. Two compounds have been suggested as raw materials, acrolein and allyl alcohol. The former gives a two stage process, acrolein being oxidised to glyceraldehyde, and the carbonyl function is then hydrogenated to carbinol [3, 4]. The single step route starting with alcohol is the one used today, with a titanium salt and hydrogen peroxide secondary oxidant, to manufacture glycerol commercially. Patents exist, however, for the same process with osmium tetroxide catalyst and as secondary oxidising agents, hydrogen peroxide [4, 5], sodium chlorate [6], sodium hypochlorite [7, 8] and t-butyl hydroperoxide [9]. Ruthenium tetroxide-hydrogen peroxide has been patented as a means of purifying glycerol from molasses [27].

Pharmaceuticals. Both drugs and hormones (steroids) have been prepared commercially using either ruthenium tetroxide or osmium tetroxide as specific oxidation catalysts. The tetroxide of ruthenium has been used principally for forming the steroidal carboxylic acid lactones from the steroidal alcohols having pregnane nuclei [10, 11, 12]. Osmium tetroxide has been used to oxidise pregnenes [13, 14], pregnadienes [15], cyanopregnenes [16, 17], pregnene-ones, pregnadiene-ones and pregnadiene-diones. Pregnadienes were converted, by addition of two hydroxy units across one double bond into the dihydroxypregnenes [13, 18, 19, 20].

Osmium tetroxide has also been used in the preparation of potential antiprotozoal agents, antibacterial agents and antitumour agents. Compounds of the general formula



were prepared from 1,4-dimethylene cyclohexane (R = H) or its trans-2,5-dihydroxyderivative (R = OH). Tests of these compounds as antitumour agents proved negative [21]. 2-carbonyl-5-nitro-imidazoles were made by oxidising nitro-imidazoles in which the 2 position was substituted by an aldehyde, lower alkanoyl or aroyl radicle by osmium tetroxide/sodium periodate [22, 23].

Recovery of Osmium from Catalytic Solutions. Osmium was recovered from the residues of cortisone production by oxidising the Os^{IV} to osmium tetroxide with 1.1 g chromium trioxide, 1.6 ml conc. sulphuric acid and 0.3 g conc. nitric acid per gram of "osmium cake". The osmium tetroxide was distilled away from the organics. Between 85 and 100% of the osmium was recovered depending on scale of operation [24]. Os was also recovered in a similar manner, but using hydrogen peroxide as oxidising agent [25]. It has also been recovered by absorbing the osmium complex in organic form from the solution to be recovered onto alumina, separated this from the remaining aqueous organics by filtration. The osmium containing alumina was then treated with an oxidising agent such as hydrogen peroxide, Ce^{IV} ion, permanganate ion, or hypochlorite ion, and the resulting osmium tetroxide was recovered as a solution in water [26].

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4.4.5.1.4 Oxides as Electrocatalysts

Platinum-group metal oxides were first patented in Holland in 1957, and later (1958) in the UK [1 to 4]. These patents led directly to the ruthenised dimensionally stabilised anodes (DSA) for chlorine production, which have steadily captured the market from the earlier consumable graphite electrodes, until today more than 50% of chlorine produced in the world is manufactured over DSA's. An equally early ICI patent [5] gave rise to a parallel family of electrodes [6, 7, 8] based on platinum or platinum-iridium oxide deposited on titanium which have found use mainly in the manufacture of sodium chlorate and in cathodic protection, although some use is made of these coatings in chlorine manufacture [9]. Small use is made of ruthenium coated DSA's in pinacol manufacture [10], while an iridium dioxide-tantalum pentoxide coating for oxygen evolution has been patented and base metal platinates have been proposed for anode coatings in chlorine and sodium chlorate cells [12]. Recently platinum-iridium oxide coatings have become more widely used in sodium hypochlorite production tending to displace some platinum-titanium anodes [13]. Asahi have patented and are commercialising a palladium oxide anode material [14]. Ruthenium dioxide coated anodes have even been used in the electrowinning of cobalt in Sweden.

The history of DSA's and a review of their application in electrochemical processing has recently been published [15]. At the same time reviews of inorganic electrochemical processing [16], organic electrochemical processing [17], progress in the electrochemical application of platinum metal oxides [9], and of platinum metal oxides as anode materials for the chloralkali industry [18, 19] have appeared.

In all industrial electrochemical processes the price of electricity is the major cost item, forming some 70% of the cost of manufacturing chlorine.

It is not surprising, therefore, that strenuous research and development efforts have been made to reduce power losses within electrochemical cells. Some of this has been achieved by improved cell designs, but by far the greatest savings have accrued through the change from graphite to catalytic platinum metal oxide electrodes. By making the anode catalytic the overvoltage for chlorine evolution may be reduced as can be seen in **Fig. 33** [20].

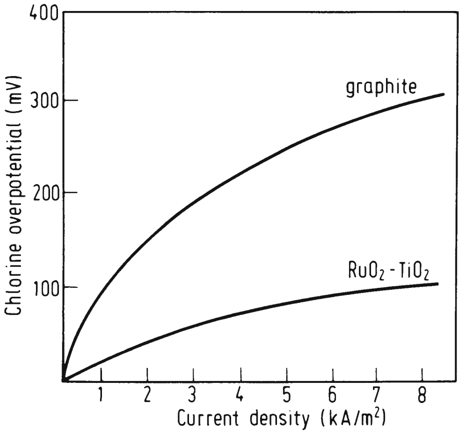

Fig. 33. Chlorine overpotential on graphite and ruthenised titanium anode coatings.

It is, however, essential to ensure that the oxygen overvoltage remains high so that oxygen contamination of the chlorine cell gas is minimal. As oxygen overvoltage is a function of the ruthenium oxide content of the anode coating, a ruthenium content is utilised (usually 35% RuO_2) which has a low chlorine overvoltage at the operating current density with a high oxygen overvoltage. **Fig. 34** shows the relationship between ruthenium content of the anode coating, oxygen overvoltage and cell gas oxygen content.

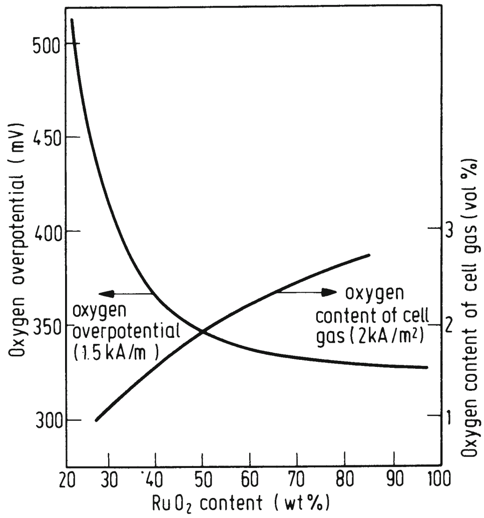

Fig. 34. Effect of RuO_2 content of the anode coating on oxygen overvoltage and cell gas oxygen content [20].

Similar relationships exist for other electrochemical processes and the anode coating is invariably a compromise.

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Preparation and Structure

The preparation of platinum metal oxide anode coatings is deceptively simple, consisting of an application of a solution of the metal salt to the metal anode followed by a heat treatment. Etching of the metal anode, and the addition of adhesion agents, are frequently used to promote bonding of the oxide coat to the metal substrate.

Platinum-Iridium Oxide Anodes. The normal composition of platinum-iridium oxide coatings is 70% Pt – 30% Ir and this is usually made up as a "paint" solution by dissolving the two metal halides in organic solvents to which natural oils have been added. The paint is applied by brushing, rolling, dipping or spraying, usually as a number of thin coatings, each of which is heat-treated between applications. During application and heat-treating some of the titanium is converted to the oxide and appears in the final coating as rutile, anatase or both, normally in a concentration of a few percent [1]. Detailed structures have been described, heat treatment being a major variable in the structure obtained. The iridium is predominantly found as the dioxide dispersed in a platinum metal matrix. A small amount of iridium metal is dissolved in the platinum. Chlorine evolution takes place at the active iridium dioxide centres, which are in the form of iridium dioxide coated platinum particles. Heat treatment appears to change the platinum particle size, the oxide thickness remaining constant [2].

Ruthenium-Titanium Oxide Coatings. The paint solution for ruthenised dimensionally stabilised anodes is usually an aqueous solution of a ruthenium salt and a titanium halide, made acid to prevent hydrolysis of the titanium component. The paint solution is applied by brush, roller or spraying as a series of thin coats, each coat being applied, dried and heat-treated. Rarely alcohol is used as a solvent for the paint, identical coatings being obtained from both aqueous and alcoholic paints. Heat treatment temperatures are normally between 400 and 650°C. Both metal components are present as the dioxides in solid solution with each other, titanium dioxide being present as rutile. The development of the crystal structure commences at 400°C and increases in crystallinity up to ~700°C. Above this temperature the oxide solid solution separates into two distinct phases. The formation of the rutile phase is catalysed by the presence of the normal rutile oxide on the oxidised titanium surface. This layer also helps to minimise the stresses present across the metal-metal coating boundary, promoting adhesion. Although the mixed oxide coating is crystalline it is imperfectly so, increasing the surface area of the coating. The high degree of crystalline disorder raises the electrical conductivity of the coating and provides sites of high catalytic activity. Detailed structures of these coatings depend on the type of cell in which they are to be used [1, 3].

Platinate Coatings. The alkali metal platinates are prepared by heating platinum dioxide (made by the Adams method) in molten lithium chloride-potassium chloride (60:40) to a temperature of 480°C for 5 h followed by 12 h at 600°C. After cooling the soluble chlorides are leached from the insoluble platinate, which is then treated with water, dilute hydrochloric acid and finally boiled with aqua regia. The blue-black powder is then washed with water, dried and ground to a fine powder, analysing as $Li_{0.51\text{ to }0.57}Pt_3O_4$. The platinate is mixed with a low melting glass (4 platinate : 1 glass) and suspended in methanol. This is then applied to a titanium sheet and fired at 600°C for 30 min in an argon atmosphere. The process is then repeated to give an anode with a loading of 4 mg platinate per cm^2 anode surface. Pretreatment of the titanium sheet anode in the vapours of boiling 20% sulphuric acid for 40 min is considered necessary to ensure good adhesion of the coating [4].

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Performance

The performance of platinum metal oxide anodes depends upon a large number of variables including cell design, electrolyte flow, electrolyte concentration, pH, temperature, current loading, impurities etc. With so many variables only examination under laboratory conditions can evaluate differences among various anodes, but commercial operation for extended periods over about a decade have revealed generalised features for each anode type.

Platinum-Iridium Oxide. Changes occur in the coating with time causing variations in its electrochemical behaviour. In the so-called active phase of operation, platinum is slowly and preferentially dissolved from the coating while its operating potential remains constant. Passification of the platinum by operation at high current densities and using anode coating loadings below the critical loading of 4 to 5 g/m^2, inactivates the whole coating. When used as anodes in chlorate production, current densities up to 6 kA/m^2 at minimum coating loadings of 7 to 10 g/m^2 are common. Under these conditions the rate of wear is less than 45 mg per t chlorate. Operation of these coatings in chlorine manufacture from brine has been severely constrained by their high cost and the dissolution of platinum during operation. The high oxygen overpotential results in a high hydroxyl concentration, which on reaction with chlorine gives rise to chlorate production, rather than oxygen contamination of the chlorine product stream. Platinum/iridium coatings have also been used for sodium hypochlorite production from weak brine solutions. Their current efficiency for hypochlorite production is high, but they do exhibit high wear rates, as high as 0.3 μ/Ah although these are lower than those for pure platinum metal coatings [1].

Ruthenium-Titanium Oxides. The use of ruthenium-titanium coatings in chlorine production results in not only energy savings of ~20%, but, because of the enhanced lifetime of the electrodes compared to graphite, of a reduction in the labour requirements of the cell. Operation at low current densities at 1.5 kA/m^2, typical of diaphragm cells, gives an anode coating life of 10 or more years, while operation at 10 kA/m^2 in mercury cells shows a life of ~2 years. The shorter lifetime in mercury cells is to a large extent the result of the narrow electrode spacing of 3 mm, and coating failure is almost certainly due to wear caused by local short circuits. Under the more ideal conditions prevailing in diaphragm and membrane cells coating lifetime is a function of the slow dissolution of ruthenium from the anode coating resulting in passivation of the electrode [1].

Hypochlorite production with these coatings is satisfactory only with high-strength brines containing 30 g/l or more. With lower-strength brines oxygen evolution at the anode predominates. High-strength brines operated at anode current densities of 1.5 kA/m^2, average 8 to 10% oxygen evolution and have an electrode coating lifetime of 1 to 2 years. Some use is made of ruthenium-valve metal oxides as coatings for anodes in the electrowinning of metals from aqueous solutions [1].

Palladium Oxide. Published data for palladium oxide anode coatings are all for experimental cells and no commercial performance details have so far been released.

Palladium oxide coatings have lower chlorine, and higher oxygen overvoltages than ruthenium dioxide coatings and have produced chlorine gas with very low oxygen contents (0.12%). In an accelerated life test, palladium oxide coatings had more than twice the durability of ruthenium-titanium dioxide coatings [2].

Platinate Coatings. Platinate coatings have achieved some small use in chlorine manufacture and in sodium chlorate production. These materials are reported to be extremely stable with operating lifetimes of 3 to 5 years in diaphragm chlorine cells and 2 to 4 years in chlorate cells. Lifetime in mercury chlorine cells is only slightly shorter than in diaphragm cells [1].

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4.4.5.2 Chalcogenides

All six platinum metals form compounds with the group VIb elements sulphur, selenium and tellurium. At present some 56 platinum metal binary chalcogenides have been reported, and a large number of ternary compounds are known to exist in which either part of the platinum metal content is replaced by a base metal or part of the sulphur, selenium or tellurium is replaced by another nonmetal such as antimony, arsenic etc. A list of the binary chalcogenides of the platinum metals is given in the table below.

Most of the compounds are formed at high temperature and/or high pressure, and the catalytic properties have been explored for only a small number of the compounds, such as the disulphides. However, as with the oxides, the precise stoichiometry of the catalytic species under reaction conditions remains unknown, although it may be conjectured that non-stoichiometry plays an important part at least in the catalytic properties of the sulphides.

Phase diagrams have been published for only four of the eighteen families of platinum metal chalcogenides. They are for platinum-sulphur [1], platinum-tellurium [1, 11], rhodium-sulphur [1] and rhodium-selenium [1]. The phase diagrams for all but platinum-sulphur are complex, containing much compound overlap, which may be a reflection on the paucity of data.

Binary chalcogenides of the platinum-group metals:

$Rh_{0.7}S_2$
Rh_2S_3
Rh_3S_4
$Rh_{17}S_{15}$
$Rh_{0.7}Se_2$
Rh_3Se_8
$RhSe_2$
$RhSe_{1.95}$
Rh_2Se_3
Rh_3Se_4
$RhSe$
$Rh_{0.7}Te_2$
$RhTe_2$
Rh_3Te_4
$RhTe$
Rh_3Te_2

$Ir_{0.7}S$
IrS_2
Ir_2S_3
$IrSe_3$
$Ir_{0.7}Se_2$
$IrSe_2$
$Ir_{0.7}Te_2$
Ir_3Te_8
$IrTe_2$
$IrTe$

PdS_2
PdS
$Pd_{2.2}S$
Pd_3S
Pd_4S
$PdSe_2$
$PdSe$
$Pd_{17}Se_{15}$
Pd_3Se
Pd_4Se
$PdTe_2$
$PdTe$
Pd_2Te
Pd_5Te_2
Pd_3Te
Pd_4Te

PtS_2
PtS
$PtSe_2$
Pt_5Se_4
$PtTe_2$
Pt_2Te_3
Pt_3Te_4
$PtTe$

RuS_2
$RuSe_2$
$RuTe_2$

OsS_2
$OsSe_2$
$OsTe_2$

Phase diagrams for ternary and higher order systems do not exist, although a bibliography to multicomponent alloys has been published which lists about 150 ternary, 32 quaternary, 6 quinary and 2 senary compounds containing platinum metals and the chalcogenide elements [2, 3].

A review of the high chalcogenides of the platinum metals was published in 1971 [4] and an extensive review of the chalcogenides of the transition elements which contains a section dealing with the platinum-group metals has appeared more recently [5]. Four binary platinum metal chalcogenide systems have been investigated in depth, palladium-sulphur [6], palladium-selenium [6], palladium-tellurium [6] and rhodium-selenium [7] and published accounts of the properties of individual binary compounds exist, such as platinum disulphide [8], platinum diselenide [8], platinum ditelluride [8], ruthenium disulphide [9], ruthenium ditelluride [9], osmium disulphide [9], osmium ditelluride [9], osmium diselenide [10], ruthenium diselenide [10], and palladium ditelluride [8].

Some of the ternary systems that have been described include compounds such as the sulpho-spinels [12], the seleno and telluro spinels [13] and the system $OsTe_{2-x}Sb_x$ [14]. The crystallography of the ternary compound $Cd_2Pd_3S_4$ has been published [15].

Catalytically the most important of the platinum metal chalcogenides are the sulphides and they have found application mainly in reactions utilising hydrogen atmospheres. This raises the problem of stability which has been addressed by [16, 17]. The latter of these authors introduces simplifying assumptions into the thermodynamic argument which allow the calculation of the free energy change of a reaction at any temperature from the standard heats of formation of the compounds at 298 K. These heats are shown below.

$$\text{Reaction: solid} \left\{\begin{array}{c}\text{oxide}\\ \text{nitride}\\ \text{sulphide}\end{array}\right\} \rightleftharpoons \text{metal} + \text{diatomic gas}; \quad \Delta S^{\circ}_{298} = 22\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

Standard heats of formation of platinum-group metal sulphides in kcal/g-atom nonmetal at 298 K:

RuS	54.5	Rh_2S_3	36.3	PdS	32.3
RuS_2	40			PdS_2	24.8
OsS	40.9	Ir_2S_3	32.1	PtS	38.3
OsS_2	33.0	IrS_2	31.3	PtS_2	28.6

From this data it can be calculated that platinum metal will form PtS at 600 K in an environment which contains a sulphur partial pressure as low as 10^{-16} atm. This pressure can arise from diatomic sulphur itself or from sulphur containing compounds such as hydrogen sulphide etc. The critical factor is the ratio of the partial pressure of hydrogen sulphide to hydrogen in the system, because the pressure is the result of the equilibrium $H_2S \rightleftharpoons H_2 + \frac{1}{2}S_2$.

Calculated virtual pressures of S_2 for various H_2S/H_2 ratios are shown below.

H_2S/H_2	400 K	600 K	800 K
1	7.26×10^{-19}	2.86×10^{-11}	2.14×10^{-7}
10^{-2}	7.26×10^{-23}	2.86×10^{-15}	2.14×10^{-11}
10^{-4}	7.26×10^{-27}	2.86×10^{-19}	2.14×10^{-15}
10^{-6}	7.26×10^{-31}	2.86×10^{-23}	2.14×10^{-19}

It can be seen that at 600 K platinum will form PtS in a gas stream containing between 0.1 and 1.0% hydrogen sulphide in hydrogen (corresponding to $P_{S_2} = 10^{-16}$ atm). Similar data may be calculated for any of the compounds shown in the table on p. 281. Partial pressures of diatomic sulphur over the platinum metal sulphides have been calculated from the data given in [17] and are tabulated in the table below for 400 K (127°C), 500 K (227°C), 600 K (337°C) and 800 K (537°C).

Partial pressures of diatomic sulphur over platinum-group metal sulphides:

sulphide	P_{S_2} (atm) 400 K	500 K	600 K	800 K
RuS	2×10^{-50}	2×10^{-38}	1×10^{-30}	9×10^{-21}
RuS_2	1×10^{-34}	6×10^{-26}	4×10^{-20}	7×10^{-13}
Rh_2S_3	1×10^{-30}	1×10^{-22}	2×10^{-17}	7×10^{-11}
PdS	3×10^{-26}	3×10^{-19}	1×10^{-14}	1×10^{-8}
PdS_2	4×10^{-18}	1×10^{-12}	4×10^{-9}	1×10^{-4}
OsS	1×10^{-35}	1×10^{-26}	9×10^{-21}	2×10^{-13}
OsS_2	5×10^{-27}	8×10^{-20}	5×10^{-15}	4×10^{-9}
Ir_2S_3	5×10^{-26}	5×10^{-19}	2×10^{-14}	1×10^{-8}
IrS_2	4×10^{-25}	2×10^{-18}	8×10^{-14}	4×10^{-9}
PtS	9×10^{-33}	2×10^{-24}	7×10^{-19}	6×10^{-12}
PtS_2	3×10^{-22}	5×10^{-16}	7×10^{-12}	1×10^{-6}

Comparison of the partial pressures over platinum-group metal sulphides with the virtual pressures of diatomic sulphur shows that for practical H_2S/H_2 gas ratios (0 to 1%) all of the sulphides are stable at 800 K except perhaps PdS_2 and PtS_2. At lower temperatures only PdS_2 appears unstable. It is important to remember that the data applies to bulk sulphides, surface sulphide layers may have very different stabilities [18, 19, 20]. Early data for the decomposition $PtS_2 \rightarrow PtS$ suggests that the critical temperature is 960 K, while for $PtS \rightarrow Pt$ it is ~1700 K [21].

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4.4.5.2.1 Preparation

Unlike their base metal counterparts [1, 2], natural platinum-group metal chalcogenides are never used for catalytic purposes, only synthetic material is ever utilised. With most of the platinum metal chalcogenides preparative techniques are used that ensure good crystal growth and, because these compounds have only low surface areas per unit weight, they are of low catalytic activity. Such material is suitable for single crystal work, but is of doubtful value for other than academic study. Even polycrystalline material prepared by these techniques has very low catalytic activity, and it is not until microcrystalline and poorly crystalline or amorphous material is used that activities suitable for commercial exploitation are obtained.

The chalcogens are easily oxidised by air at relatively low temperatures and therefore, preparations much above ambient temperature must be conducted in a vacuum or inert/reducing atmosphere. Even at ambient temperatures, the stability of precipitated platinum metal sulphides is in some doubt, as adsorbed hydrogen sulphide may be oxidised by aerial oxygen, to deposit sulphur on the catalyst surface. The sulphide surface may also be oxidised by air with consequent loss of catalytic activity [3].

The bulk of the information available on the preparation of platinum metal chalcogenide catalysts, refers to the sulphides, the selenides and tellurides being more poorly covered. In general the methods of preparation mimic those of their base metal counterparts, such as precipitation with hydrogen sulphide and sulphiding with hydrogen/hydrogen sulphide mixtures, but some of the preparations are unique to the platinum metals, especially those methods that produce only superficial sulphide coatings. The subject of sulphide catalyst preparation has been reviewed [4, 5], the latter reference containing information on the thermodynamic stability of the platinum metal sulfides under reducing (hydrogen) conditions with/without hydrogen sulphide. Early work on the preparation of platinum metal chalcogenides has been reviewed [6, 7].

As with the platinum metal oxides, the chalcogenides are used in three different applications: (I) unsupported catalysts, (II) supported catalysts, (III) as precursors to platinum metal catalysts, and each application is described separately in the next three sections.

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Unsupported Catalysts

Unsupported platinum metal chalcogenides are made by four main routes: (I) heating together a platinum-group metal and the chalcogenide element/elements, (II) heating together a platinum-group metal compound with the chalcogenide element, (III) precipitation by a chalcogen hydride or alkali metal chalcogenide from aqueous solution of the platinum metal chlorides, (IV) reduction of a mixture of the chalcogen oxide and a platinum metal salt.

Combination of the Elements. This method has been used for the preparation of polycrystalline material for crystallographic work, although it may also be used for highly defined low-activity catalysts. Stoichiometric quantities of the platinum-group metal and chalcogen, in powder form, were intimately mixed, loaded into a Pyrex, vycor or fused silica ampoule, evacuated and sealed. The closed ampoules were then heated at temperatures between 500 and 1000°C. In many preparations the firing would be completed in two stages, for example 600 and 800°C, with the sample being ground and removed under nitrogen between firings. Sometimes the powders would be pressed into pellets to improve particle contact and promote diffusion. Depending on the composition required the ampoules were either quenched in iced water or slowly cooled in an annealing furnace.

Platinum metal chalcogenides formed by combination of the elements:

compounds	Ref.	compounds	Ref.	compounds	Ref.
$RuSe_2$, $RuTe_2$	[1]	$PtSe_2$	[2]	Pd selenides	[6]
$OsSe_2$, $OsTe_2$	[1]	$PtTe_2$	[2]	Pd tellurides	[6]
$PdTe_2$	[2]	Rh selenides	[4]	$OsTe_{2-x}Sb_x$	[7]
IrS_2	[3]	Pt tellurides	[5]	MRh_2Se_4	[8]
PtS_2	[2]	Pd sulphides	[6]	MRh_2Te_4	[8]

Single crystal material can be prepared for some of the platinum metal chalcogenides by a variation of the technique outlined above, and employing a chemical transport agent. The use of chemical transport systems has been reviewed [9, 10]. Platinum disulphide and platinum ditelluride single crystals have been prepared by this method using chlorine as a transport agent [11].

Platinum Metal Compound and Chalcogen. Ruthenium disulphide has been prepared by heating "Ru_9S_8" with the stoichiometric quantity of sulphur in an evacuated quartz ampoule at 950°C for 15 h [1]. A similar technique was used for the preparation of palladium disulphide, palladium diselenide and palladium ditelluride. The monochalcogenide was heated at 600°C for several days in a sealed evacuated silica tube, then annealed at a temperature between 250 to 650°C before being slowly cooled to ambient temperature [6]. Palladium disulphide has also been made by heating palladous chloride with sulphur at 450°C for 4 d in an evacuated quartz tube [12].

Precipitation from Aqueous Solution by Chalcogen Hydride or Alkali Chalcogenide. The precipitation of platinum metal chalcogenides by the action of a chalcogen hydride or alkali metal chalcogenide has long been used (see [6] and [7], Section 4.4.5.2.1, p. 283) and is a primary method of forming microcrystalline and amorphous material for catalytic purposes today. In industrial practice hydrogen sulphide from hydrodesulphurisation reactions is frequently used for making sulphides, but may be contaminated with other materials. Hydrogen selenide and telluride are usually made by reacting aluminium and selenium or tellurium to form aluminium selenide or telluride, which is then finely ground and reacted with water [13].

The use of aqueous solutions of the alkali metal and ammonium chalcogenides is frequently practised, but they are highly alkaline and may contaminate the final material with hydrated oxide [16]. The solubility is to be found in [14, 15].

Chalcogen hydrides have been used to prepare catalytic platinum sulphide [17], palladium disulphide, rhodium sulphide, iridium sulphide [18], and the selenides and tellurides of the six platinum metals [13]. Osmium disulphide has been prepared by treating osmium tetroxide dissolved in sodium hydroxide with sodium sulphide [18].

Reduction of Chalcogen Oxide and Platinum Metal Salt. This is the least frequently used method for preparing unsupported catalysts, rhodium selenide, iridium selenide, ruthenium telluride, rhodium telluride, palladium telluride and platinum telluride. To a solution of rhodium trichloride in dilute (1:1) nitric acid was added a solution of selenium in aqua regia. This solution was then added slowly to a boiling solution of hydrazine dihydrochloride in dilute ammonia. Rhodium selenide precipitated over a period of 1.5 h [18].

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Supported Chalcogenide Catalysts

The majority of platinum metal chalcogenide catalysts are supported on carbon, alumina or silica gel, although other supports such as zeolites or magnesium oxide are occasionally used. Very little information is available on the physical characterisation of supported chalcogenide catalysts. Very few supported selenide or telluride catalysts have been used commercially, sulphide catalysts accounting for the vast majority of production and use.

Preparation of chalcogenide catalysts can be divided into three broad groups: (I) precipitation of the PGM chalcogenide in the presence of the support, (II) treatment of a preformed metal catalyst in situ in the reaction mixture, (III) treatment of a preformed metal catalyst before use.

Only with the first group can the formation of a bulk chalcogenide be ensured; with the other two groups of preparation superficial coatings of the metal crystallites with the chalcogenide occur, after only partial coverage of the metal surface.

Precipitation of the PGM Chalcogenide in the Presence of a Support. A ruthenium sulphide-on-charcoal catalyst was made by dissolving sodium sulphide ($Na_2S \cdot 9H_2O$) in water, raising the temperature to 90°C and adding the charcoal. Ruthenium trichloride solution was added dropwise over a period of 5 min at 90°C. The charcoal catalyst slurry was then filtered and washed with five separate portions of water. Rhodium, palladium, osmium, iridium and platinum sulphide catalysts were made in the same way [1].

The precipitation of platinum metal sulphides in the presence of alumina has been used as a method of preparation since the inception of sulphide reforming catalysts [2]. Catalysts for reductive alkylation have been made by adding chloroplatinic acid and alkali to a carbon slurry, heating to 70 to 100°C and gassing with hydrogen sulphide [3]. Active hydrodesulphurisation catalysts have been made by precipitating one of the platinum-group metals onto a carrier with an alkali metal or amine salt of chalcogen hydride in a non-aqueous solvent [4, 5].

Treatment of a Preformed Metal Catalyst in situ in the Reaction Mixture. A sulphided hydrocracking catalyst has been made by treating a platinum metal catalyst in situ in the reactor with hydrogen-hydrogen sulphide feed gas in the presence of the substrate. It was necessary to maintain the hydrogen sulphide in the feed gas during reaction at 0.2 to 0.5 mmol/mol H_2 when hydrocracking for jet or diesel fuel [6]. The need for the maintenance of sulphiding gas is removed with sealed batch reactors, where the sulphiding agent may be added to the reaction mixture in a measured dose at the start of the reaction. For instance, platinum-on-carbon catalysts have been sulphided by adding dimethylsulphoxide to the reaction mixture prior to hydrogenation in the preparation of phenylhydroxylamine and p-aminophenol [6, 7].

Treatment of Preformed Metal Catalyst before Use. One of the first, and one of the easiest methods of sulphiding is by contacting the catalyst with hydrogen sulphide [8, 9]. Because the preformed metal catalyst is usually covered with a layer of oxygen, giving rise to oxidation of hydrogen sulphide and the formation of sulphur, such methods cannot be relied upon to provide uniformly sulphided catalysts. A simple, but effective advance in sulphiding was accomplished by treating the catalyst with hydrogen and so removing the oxygen layer before treatment with hydrogen sulphide [10 to 14]. The use of ammonium or alkali metal sulphides or hydrosulphides in place of hydrogen sulphide is also permissible. Sulphiding platinum-group metal catalysts with organic sulphides has also been practised without hydrogen pretreatment [15], and with hydrogen pretreatment at high pressure [16]. Dimethylsulphoxide may be used to sulphide platinum-on-carbon catalysts providing a reducing agent, such as hydrazine is added to the catalyst slurry. The advantage of this method is that the catalyst slurry does not need to be blanketed in an inert/reducing atmosphere during treatment [17]. Inorganic oxosulphur compounds such as sulphur dioxide and sulphites, hydrogen sulphites, thiosulphates, metabisulphites, dithionates, etc., of the alkali metals and ammonium, have been used after a hydrogen pretreatment to sulphide platinum-on-carbon catalysts in dilute sulphuric acid slurry. Hydroxylamine salts have been used in place of hydrogen [17 to 19].

Methods for the preparation of supported platinum metal selenides and tellurides are rare. One which may be used for both chalcogens, particularly the high metal tellurides (Pd_4Te) supported on carbon, is to impregnate the carbon with a solution of palladous chloride and tellurium dioxide in aqueous hydrochloric acid, dry the material and then reduce it with hydrogen in nitrogen or in the liquid phase with hydrazine [20].

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Sulphides as Precursors to Supported Platinum Metal Catalysts

Platinum metal catalysts are sometimes prepared via a sulphide intermediate. With monometallic catalysts this technique is resorted to when chloride-free catalysts are needed, and with multimetallic catalysts it is used when one of the components is to be in the sulphide form and the other/others to be metallic.

Chloride-free platinum-on-alumina catalysts have been prepared by reacting chloroplatinic acid solution with ammonium polysulphide to give a solution of a platinum sulphide. This was added to a slurry of alumina and the impregnated support was dried at 185°F (85°C) for 32 h, then at 350°F (~177°C) for 3 h. After grinding and pelleting the final catalyst was fired at 900°F (~482°C) in air for 3 h [1].

In the preparation of a rhenium/platinum catalyst in which the rhenium component is in the sulphided form, but the platinum is present as the metal, the preformed catalyst is subjected to sulphiding treatment which converts much of the platinum to the sulphide form. The catalyst is then subjected to a sulphur-stripping step at a temperature of 700°F (~371°C) and a hydrogen pressure of 300 to 500 psi (~20 to 34 kg/cm^2) in which the platinum is converted to the metal, the rhenium sulphide remaining unreduced [2].

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4.4.5.2.2 Reactions

The major industrial uses of platinum metal sulphide catalysts are in the refining of crude oil, the manufacture of chemical intermediates for the plastics and resins industry and in the production of fine chemicals for pharmaceutical, pesticide and antioxidant markets. These uses are based on a series of organic hydrogen reactions which are more selectively performed over sulphide catalysts than metal catalysts and which also have enhanced useful lifetimes compared to their metallic counterparts [1, 2, 3].

Platinum-group metal sulphide catalysts are very selective for the conversion of polyolefins to mono-olefins [1, 4], the hydrogenation of nitro compounds to amines [4] or the partially hydrogenated hydroxylamine $RNO_2 \xrightarrow{+2H_2} RNHOH \rightarrow RNH_2$ depending on the reaction conditions [5]. Unsaturated nitro compounds may be hydrogenated over ruthenium disulphide to the corresponding unsaturated amines [3], while aromatic halo-nitro compounds can be hydrogenated without dehalogenation to aromatic halo-amines [4, 6].

Aromatic nuclei, ketones, nitriles and esters are not hydrogenated over platinum metal sulphides generally, a fact which is made use of in the reductive alkylation of amines [6, 7]. Acetylenes can be converted completely to olefins over platinum sulphide and cyclic dienes to cyclic monoenes over palladium sulphide catalysts. Condensed aromatic ring systems can be partially hydrogenated, thus, naphthalene can be hydrogenated to tetralin over platinum sulphide [2]. Platinum metal sulphides are also active in the hydrodesulphurisation of heterocyclic sulphur compounds although they have not been used commercially for this reaction [1, 2, 3]. Sulphided platinum metals are, however, predominantly used for reforming, a series of reactions including dehydrogenation of cyclohexanes, dehydrocyclisation of paraffins and olefins to aromatic hydrocarbons and the isomerisation of hydrocarbons [3]. The original reforming catalyst was platinum sulphide [3], but recently sulphided platinum-rhenium and platinum-iridium have been used [2, 3] and palladium sulphide, rhodium sulphide, palladium-rhenium sulphide and rhodium-rhenium sulphide have been tested [1, 2, 3].

The next three sections describe the use of platinum-group metal sulphides in the refining, intermediate and fine chemical industries in greater detail.

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Sulphided Platinum Metal Catalysts in the Petroleum Refining Industry

The petroleum refining industry exists by converting crude oil into fuels and lubricants for mobile and stationary engines, space heating, steam raising etc., and petrochemical feedstocks for processing into chemicals, plastics, rubbers and resins, pharmaceuticals, pesticides etc. Fuels form by far the largest segment of the refining industries production comprising some 70% of the product from a barrel of oil.

The refining of crude oil begins with its distillation into fractions having different boiling ranges. This is accomplished by heating the crude oil to temperatures of 370 to 430°C and separating it into five or six product streams, each of different boiling range, on a fractionating column, see the following table.

The light naphtha fraction, after purification to remove undesirable impurities, is usually of sufficiently high octane number to be used without further refining as a component of motor fuel (gasoline). The heavy naphtha fraction is used as a petrochemical feedstock and as a source of higher octane blending stock via catalytic reforming. Kerosene and light oil are used in the production of jet fuel, diesel fuel, kerosene and furnace oils. The heavy gas oil fraction is used as a diesel fuel for low and medium speed stationary engines. Much of the heavy gas oil and residual oil, however, is converted by catalytic cracking into gasolines by a number of processes, many of which use sulphided platinum-group metal catalysts. In others the platinum metal sulphides have been suggested as useful catalysts although they may not have been used commercially [1].

fractionated stream		boiling range in °C
light naphtha		<100
heavy naphtha		100 to 200
kerosene	middle distillates	200 to 250
light gas oil		200 to 300
heavy gas oil		300 to 400
residual oils		>400

Hydrogenation. Hydrogenation is used to remove unwanted aliphatic unsaturation from gasoline and aromatic petrochemical streams. The presence of dienes in gasoline blending stock is undesirable because they are unstable and polymerise to gums etc. Aromatics and aliphatic olefins, however, both raise the octane rating and therefore it is desirable to retain them. Hydrogenation with platinum metal catalysts tends to hydrogenate the whole aliphatic and some of the aromatic unsaturation. Platinum metal sulphides which are more selectice in the hydrogenation converting dienes to olefins and leaving aromatics untouched have been used. Palladium sulphide has been used to remove dienes from a pyrolysis condensate and improve the octane number [2]. The feedstock contained 38.8% paraffins, 29.6% olefins and 16.4% dienes and was hydrogenated at 20 to 80°C, 30 atm pressure and a liquid space velocity of 2 h^{-1}. Both platinum sulphide and palladium sulphide have been used to remove unwanted unsaturation from low-octane gasoline fractions destined for the production of aromatics for petrochemicals. Because the reaction now removes all aliphatic unsaturation the reaction conditions are more demanding. Thus with the platinum sulphide-on-alumina catalyst (0.75% Pt) the reaction was conducted at 800 to 950°F (425 to 510°C), 400 to 800 psi (~27 to 54 kg/cm^2) pressure and a hydrogen recirculation rate of 1000 to 3000 ft^3/bbl (~178000 to 534000 cm^3/l). The palladium sulphide catalysts supported on alumina (0.5% Pd) required 200°C and 40 atm and gas recirculation of 0.6 m^3 H_2 per l feedstock [3].

Hydrocracking. Hydrocracking is used in the manufacture of gasoline and furnace oils. The process consists of the cracking of long-chain hydrocarbons to smaller molecules in the heavier fractions such as gas oils and residual oils. It is flexible in that the ratio of gasoline to furnace oil may be varied so as to produce mainly gasoline with little furnace oil or vice versa. The catalysts are dual function, with acidic cracking sites provided by the aluminosilicate or zeolite component and hydrogenation provided by the metal sulphide. When gasolines are the required products high acidity with mild hydrogenating power is needed. When gas oils are cracked to jet fuels milder acidity is coupled with stronger hydrogenating capacity. The hydrogenating component of hydrocracking catalysts is included to prevent the build-up of olefins which can lead to carbon deposition on the catalyst (coking) [5].

Early catalysts consisted of base metal sulphides on aluminosilicate supports. Later rhodium sulphide and palladium sulphide were tried and also palladium sulphide promoted molybdenum sulphide [6]. The most common platinum metal sulphide utilised for hydrocracking is palladium sulphide. It has been used when supported on alumina-silica (0.5 to 1.0% Pd) to process fuel oil into gasoline at temperatures of 550 to 750°F (285 to 400°C), 750 to 1500 psi (~50 to 100 kg/cm^2) H_2 pressure, a liquid space velocity of 0.5 to 3.0 h^{-1} and a hydrogen flow of 6000 to 10000 ft^3/bbl (~178 cm^3/l). The iso-normal ratio was greatly improved over the sulphided catalyst compared to unsulphided material, particularly when an addition of an organic sulphur compound was made to the feed stream [7]. Gas oil was processed over palladium sulphide at 600°F (315°C), 1000 psi (~67.4 kg/cm^2) a liquid space velocity of 1 h^{-1} and a hydrogen gas flow of 10000 ft^3/bbl (~1.780000 m^3/l) [8]. Gas oil was also processed at 400 to 750°F (205 to 400°C), 400 to 2500 psi (~27 to 169 kg/cm^2) in a hydrogen stream containing hydrogen sulphide. If gasoline was required the H_2S content was maintained at 0.2 to 0.5 mmol/mol H_2 whereas when processing for jet or diesel fuel it was held at <0.01 mmol/mol H_2 [9].

Rhodium sulphide supported on silica-alumina has been proposed for the hydrocracking of heavy gas oil and middle distillate/gas oil fractions. The rhodium content of the catalyst was 0.1 to 5% with a rhodium: sulphur ratio of 0.6 to 0.8. The feed contained 0.02 to 0.3% sulphur which was 90% converted to hydrogen sulphide. Catalyst ageing was indicated by the daily temperature increase required to maintain a constant reaction rate. With heavy gas oil and a H_2S:H ratio of 10^{-3} the catalyst required a daily temperature increase of 1.22°C per day [10].

All feedstocks hydrocracked over alumina-silicazeolite supported palladium sulphide catalysts require to be low in nitrogen content. In an attempt to overcome this, alumina-silica catalysts containing both palladium sulphide (1.5 wt%) and molybdenum sulphide (MoS 13%) have been used to hydrocrack hydrogen containing (574 ppm N) feedstocks. In this case the molybdenum sulphide provides the hydrodenitrification capacity. Conditions were 785°F (420°C), 1200 psi (~81 kg/cm^2) pressure, liquid hourly space velocity 1.5. The product contained 1.2 ppm N after 100 h and 7.4 ppm after 400 h with a conversion of 55% and a middle distillate: gasoline ratio of 1.4:1.

Reforming. The reforming process is made up of a number of basic reactions, including isomerisation, dehydrocyclisation, dehydrogenation, and in some cases hydrocracking. The feedstock is usually a straight-run petroleum naphtha boiling within the normal gasoline range, having a large proportion of straight chain (unbranched) alkanes and an octane number <50. These alkanes are rearranged into hydrocarbons of higher octane number. Alkanes are both cracked to give homologues of lower carbon number, skeletally isomerised then converted to naphthenes by dehydrocyclisation. Cyclic components undergo skeletal and positional isomerisation and dehydrogenation to give aromatics of high octane number which may remain in the gasoline or be extracted as petrochemical feedstocks. The main difference between reforming and hydrocracking is that with hydrocracking there is an overall consumption of hydrogen, while with reforming hydrogen is both produced (dehydrogenation) and consumed (hydrogenation) giving zero consumption. Another feature of reforming is that there are only low losses of carbon as gases (methane, etc.). In both processes the catalyst is dual function [6].

The use of sulphided platinum metal catalysts in reforming has been reviewed twice [6, 11]. The following examples, taken from the patent literature, illustrate the process. A Mid-continent straight-run naphtha of octane number 34.8 was reformed over a platinum sulphide catalyst (9.3% Pt) at 455°C and a pressure of 500 psi (~34 kg/cm^2) hydrogen with a hydrogen: hydrocarbon flow rate of 3:1 and a liquid hourly space velocity of 2. The product had an octane number of 80.5 to 82.5. Catalytic cracking was controlled by varying the amount of fluorine chemically bound to the alumina support surface [12].

Although it has been claimed that sulphur has a harmful effect on platinum-rhenium reforming catalysts, it is now general practice to sulphide all platinum-rhenium reforming catalysts [13]. It would appear that the problem with platinum-rhenium catalysts is to fully sulphide the rhenium component, leaving the platinum substantially, but not completely sulphur-free. When tested in comparison with an unsulphided catalyst, the sulphided catalyst had a substantially better activity. The charge fed to the reactor had an octane number of 35.6, a sulphur content of 0.2%, and a composition of paraffins 67.4, naphthenes 23.1, and aromatics of 9.5 vol%. The reaction conditions were 300 psi (~21 kg/cm^2) H_2, liquid hourly space velocity 3.0 h^{-1}, and a recycle gas : oil ratio of 5 : 1 [14].

Isomerisation. Isomerisation converts straight-chain hydrocarbons into branched-chain hydrocarbons of the same molecular weight. When carried out under hydrogen pressure the process is known as hydro-isomerisation. The catalysts used are normally dual function catalysts, the acid function being supplied by the support, e.g., alumina-silica, halogenated alumina etc. Rhodium, platinum and palladium sulphides have been used to supply the hydrogenation/dehydrogenation function. In Europe and USA the favoured catalyst is platinum sulphide on alumina-silica [15] although rhodium sulphide has been suggested [16]. In the Eastern bloc countries, because of the greater availability of palladium, a considerable effort has been made to explore the use of palladium sulphide in isomerisation catalysis. Thus, C_9, C_{10}, C_{12}, C_{16} and C_{18} paraffins were individually isomerised over palladium sulphide on alumina catalyst (0.001 to 5.0% Pd) at 380 to 420°C and 40 atm pressure. The yield of isoparaffins increased with increasing palladium content [17]. Normal heptane was isomerised over promoted palladium sulphide on alumina catalysts. Promoters included iron, cobalt, nickel, copper and zinc, the most effective being copper [18]. When C_9 to C_{18} alkanes were isomerised over palladium sulphide on alumina catalysts the ratio of di- to mono-methyl substituted products passed through a maximum with C_{12} to C_{16} alkanes [19].

Hydrodesulphurisation. This is the process in which sulphur compounds present in petroleum fractions are hydrogenolysed to give hydrocarbons and hydrogen sulphide. Hydrodesulphurisation is most important as a means of protecting platinum reforming catalysts from excessive exposure to sulphur compounds and preventing loss of catalyst activity and poisoning. The normal catalyst is molybdenum sulphide promoted with nickel or cobalt, but the platinum metal sulphides have also been proposed as hydrodesulphurisation catalysts. The physical properties of the catalyst, such as pore size distribution, are of equal importance to the hydrogenolysis properties with these catalysts [11]. Petroleum fractions contain a large number of sulphur compounds of varying reactivity, and in technical treatments the most reactive are removed first, leaving the more intractable in the product. Two of the less reactive compounds found in petroleum products are benzothiophen and dibenzothiophen, and RuS_2, OsS_2, IrS_2, PtS_2, PdS, PtS and Rh_2S_3 both supported and unsupported were active in the desulphurisation of these compounds at 350°C and 32 atm pressure [20, 21]. Naphthalene has been commercially desulphurised in toluene solvent over a palladium sulphide-on-alumina catalyst [22, 23].

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Platinum Metal Chalcogenides in the Manufacture of Intermediates

Intermediates may be defined as organic and inorganic chemicals produced on a large scale and used in the manufacture of plastics, resins, rubbers etc. The use of platinum metal sulphides in the production of intermediates is principally in hydrogenation reactions, firstly for gas clean-up, e.g. acetylene removal from ethylene, and secondly for the manufacture of chemicals such as cyclohexane from benzene and hydroxylamine from nitric oxide. Some use, however, has been made of platinum metal sulphides in hydrodealkylation reactions mainly for the preparation of benzene from toluene.

Gas Clean-up. Ethylene is manufactured by the thermal dehydrogenation of ethane or the pyrolysis of naphtha and is normally contaminated with acetylene. For most petrochemical and polymerisation applications the level of acetylene is required to be below 5 ppm and this is achieved by the selective hydrogenation of acetylene to ethylene. The hydrogenation presents no difficulty, occurring at temperatures well below 200°C at 1 atm pressure. Platinum sulphide supported on alumina has been used for this reaction with a conversion of 100% at a selectivity of 75% [1].

Hydrogenation. Cyclohexane and hydroxylamine are both intermediates in the manufacture of nylon by the caprolactam route, and each can be produced by hydrogenation over platinum metal sulphides. Hydroxylamine is manufactured by the reduction of nitric oxide with hydrogen in the presence of a sulphided platinum-on-carbon catalyst suspended in dilute sulphuric acid solution [2, 3]. Conditions for the reduction are quite mild, atmospheric pressure and 25 to 40°C. Various sulphiding agents have been used (see table below) and a comparison of their performance in hydroxylamine manufacture is shown in the table on p. 293.

designation of catalyst	addition	mg addition per 100 g catalyst	at.% S referred to Pt	reaction time (h)
K_1	$Na_2S_2O_4 \cdot H_2O$	75	15.3	0.5
K_2	$Na_2S_2O_4 \cdot H_2O$	150	30.6	0.5
K_3	$Na_2S_2O_4 \cdot H_2O$	300	61.2	1

designation of catalyst	addition	mg addition per 100 g catalyst	at.% S referred to Pt	reaction time (h)
K_4	$Na_2S_2O_4 \cdot H_2O$	490	100	14
K_5	$Na_2S_2O_3 \cdot 5H_2O$	196	30.6	1
K_6	Na_2SO_3	198.5	30.6	
		for comparison		
K_0		without addition		
K_7	$Na_2S_2O_4 \cdot H_2O$	15.0	3.06	1

designation of catalyst	mol NO introduced per hour	conversion of nitric oxide in %	selectivity $\frac{(NH_3OH)_2SO_4}{(NH_4)_2SO_4}$	yield in %		
				$(NH_3OH)_2SO_4$	$(NH_4)_2SO_4$	N_2O/N_2
K_1	1.12	77.6	4.55	69.0	15.0	16.0
K_2	1.1	75.5	7.3	79.3	10.9	9.8
K_3	1.08	82.2	6.88	78.9	11.5	9.6
K_4	1.06	77.7	22.4	91.6	4.1	4.3
K_5	1.1	72.7	6.81	79.4	11.7	8.9
K_6	1.14	77.4	6.4	83.0	13.2	3.8
			for comparison			
K_0	1.08	70.5	1.09	42.8	39.4	17.8
K_7	1.1	72.5	0.5	27.4	55.0	17.6

Cyclohexane is manufactured by the hydrogenation of benzene over nickel or platinum metal catalysts. However, platinum sulphide on alumina, promoted by treatment with aluminium triethyl, has been suggested as a suitable catalyst. Reaction conditions were 150°C at 600 psi (~40 kg/cm^2) hydrogen pressure, reduction was linear reaching 77.5% in 3 h, cyclohexane being the only product [4].

Dealkylation. Dealkylation is used to manufacture benzene from toluene. Toluene was contacted with a commercial platinum on alumina which had been sulphided at temperatures between 800 and 1150°F (~427 to 621°C) with a contact time of 2.5 s at a pressure of 24 psi (~1.7 kg/cm^2) hydrogen.

Hydrodealkylation of toluene over platinum sulphide on alumina catalyst [5]:

temperature		% yield benzene	
°F	°C	sulphided catalyst	unsulphided catalyst
800	427	0	51
950	510	—	43
1000	538	85	37
1050	566	86	37
1100	593	84	27
1150	621	82	24

Oxidation. Butadiene has been acetoxylated over a palladium telluride (Pd_4Te) on carbon catalyst. The only product was 1,4-butenediol which on hydrogenation gives 1,4-butanediol, a valuable intermediate in the production of polyester plastics for engineering [6].

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Platinum-Group Metal Chalcogenides in the Fine Chemicals Industry

Platinum metal chalcogenides have been used for a wide variety of reactions in the Fine Chemicals Industry, among them being hydrogenation, reductive alkylation and oxidations. The largest group of reactions are hydrogenations, where organic functions as different as carbon-carbon double bonds in aliphatics and aromatics, carbon-nitrogen double bonds in heterocyclics and aromatics, may be easily reduced. Somewhat more difficult is the hydrogenation of aromatic sulphides to mercaptans. Reductive alkylations, in which a nitro compound is first reduced to the amine, and then coupled with a ketone to produce an imine which is finally reduced to a secondary amine are the second largest group of reactions, but are probably economically more important than hydrogenations. Oxidation reactions with platinum metal chalcogenides are rare.

Hydrogenation. Platinum metal sulphides have been investigated as hydrogenation catalysts for butadiene, with the aim of obtaining selective conversion of the feedstock to butenes. Platinum sulphide and palladium sulphides supported on alumina and ruthenium sulphide supported on carbon gave selectivities of 100% for butene formation, but only with platinum sulphide on alumina was the conversion commercially interesting at 73%. The other catalysts gave conversions of 7 to 19%. Pressure and temperature in the platinum sulphide catalysed reaction were 100 psi (~7 kg/cm^2) and 221 to 232°C [1]. Hydrogenation of the aromatic nucleus over platinum sulphide required high pressure as well as high temperature. Thus naphthalene can be hydrogenated to tetralin over platinum sulphide on carbon at 275°C and 95 atm pressure [2]. Essentially the same conditions were required to hydrogenate anthracene to 9,20-dihydroanthracene, indene to indan, acenaphthylene to acenaphthene and coumarin to dihydrocoumarin [3]. Unsupported palladium sulphide (PdS_2), rhodium sulphide (RhS_2) iridium sulphide (Ir_2S_3) and osmium sulphide (OsS_2) were active for the hydrogenation of nitrobenzene to aniline at 180°C and 1500 psi (~105 kg/cm^2) [4]. In the reduction of nitrobenzene and m-nitrobenzene sulphonic acid the most active catalyst was platinum sulphide for nitrobenzene and rhodium sulphide for nitrobenzene sulphonic acid [5]. The reduction of pyridine to piperidine required temperatures of 250 to 320°C and pressures of 90 to 120 atm [6, 7]. Substituted phenylpyridines required equally exacting conditions when reduced over platinum or palladium sulphides [8]. The reduction of organic sulphides to the corresponding mercaptans has been accomplished with unsupported ruthenium sulphide [9] and rhodium sulphide supported on carbon; the rhodium catalyst reduction of phenyldisulphide to thiophenol required 130°C and a pressure of 1070 to 1450 psi (~72 to 98 kg/cm^2) [10].

The use of platinum metal chalcogenides in the selective hydrogenation of nitro functions in the presence of other hydrogenable organic functions has become a notable feature of their application. The hydrogenation of a nitro group in the presence of an aromatic ring and a carbon-sulphur linkage is well illustrated by the reduction of 4,4-dinitrodiphenylsulphide over a rhodium sulphide-on-carbon catalyst at 1200 to 1400 psi and 140°C [7, 10, 11]. No hydrogenolysis of the thioether linkage or hydrogenation of the aromatic nucleus was experienced. Hydrogenolysis, however, did occur when N-nitroso-p-nitrodiphenylamine and N-nitrosodiphenylamine were hydrogenated over platinum sulphide and rhodium sulphide on carbon [10]. The products were p-aminodiphenylamine and diphenylamine, respectively. Pressure in both cases was ~1300 psi (~88 kg/cm^2) with a temperature of 120 to 180°C. The reduction of a nitro group in the presence of carbon-carbon unsaturation is almost impossible over metallic catalysts, but platinum metal sulphides, particularly ruthenium disulphide, have been successfully used. Dinitrostilbene sulphonic acid has been hydrogenated to the corresponding diamino compound at 150 atm pressure and 100°C with ruthenium sulphide-on-carbon catalyst. Only traces of 4,4′-diaminodibenzyl-2,2′-disulphonic acid and 4-aminotoluene-2-sulphonic acid being formed. The catalyst was re-used a further four times with only a marginal change in performance [12, 13].

Nitrocinnamic acid and 2-nitro-N-alkylaniline have been reduced over 5% platinum sulphide on carbon catalyst to the corresponding amino compound at 100 to 130 atm H_2 pressure and 75 to 80°C. Impurities were not found in the product [13]. Lower temperatures and pressures are used when the unsaturation is acetylenic. Thus 3-nitrophenylacetylene and various 3-nitrophenylacetylenic alcohols have been reduced over ruthenium disulphide catalysts at 100°C and 25 to 70 atm to yield 75 to 85% acetylenic amine [14, 15].

In theory nitroso, hydroxylamine, azo and hydrazo products may be formed as partial hydrogenation products of nitro group reductions; commercially only hydroxylamine is of interest principally because, in acid solution, phenylhydroxylamine will rearrange to give p-aminophenol: $C_6H_5NO_2 + 2H_2 \rightarrow C_6H_5NHOH + H_2O$; $C_6H_5NHOH \rightarrow$ p-$HOC_6H_4NH_2$. The first stage of this reaction has been investigated with sulphided platinum catalysts in neutral solution [16, 17], and it has been shown that high yields of phenylhydroxylamine may be obtained. Platinum-on-carbon catalysts containing either sulphur or selenium will also hydrogenate nitromethane to N-methylhydroxylamine with 89.5 to 93% selectivity at 35 to 40°C [18].

When nitrobenzene is reduced over platinum sulphide catalyst, either supported or not, the product is p-aminophenol. Unsupported sulphided platinum blacks reduced nitrobenzene in dilute sulphuric acid at ambient temperature and atmospheric pressure to give a 59.4% yield of aminophenols, of which 62% was the para isomer and 38% the ortho isomer [19]. The reduction of nitrobenzene has been shown to be first order in hydrogen and zero order in nitrobenzene over unsupported platinum sulphide at low pressure [20]. Preparation of p-aminophenol from nitrobenzene at higher pressure has been successfully accomplished over platinum sulphide catalysts [21, 22]. The investigators in [21] used hydrogen pressures of 60 to 150 psi (~4 to 10 kg/cm^2) while those in [22] used higher pressures from 150 to 500 psi (~10 to 34 kg/cm^2). By using alcoholic sulphuric acid solutions, compounds of the type $ROC_6H_4NH_2$ (R = alkyl) can be made [23].

The reduction of nitrobenzenes when the aromatic ring is also substituted by a halogen, to yield aromatic halo-amines is a particularly difficult problem. Early attempts to use catalytic hydrogenation with metal catalysts usually gave rise to substantial dehalogenation. When platinum metal sulphides were employed as catalyst the degree of dehalogenation fell considerably [1, 11, 24 to 26] as can be seen from the following table.

Reduction of halonitrobenzenes to halo-anilines [1]:

	$X\text{-}C_6H_4\text{-}NO_2$		catalyst			temp.	pressure	time	mol%
X	weight (g)	mol	type	weight (g)	concentration (g/l)	(°C)	in psi (kg/cm²)	(min)	dehalogenation[a]
p-Cl [b]	315	2.0	Pd[c]	1.58	1	20 to 30	100 to 400 (6.7 to 27)	140	43
[d]	17.0	0.108	Pd sulfide[e]	0.325	5	145	500 to 800	150	0
[d]	17.0	0.108	Pt sulfide[c]	0.325	5	145	500 to 800 (33.7 to 54)	195	0
o-Cl [b]	315	2.0	Pd[c]	1.58	1	20 to 30	100 to 400 (6.7 to 27)	40	11
[f]	78.3	0.5	Pt sulfide[c]	1.5	5	145	500 to 800	70	0
[f]	78.3	0.5	Rh sulfide[c]	1.5	5	100 to 145	500 to 800	15	0
[f]	78.3	0.5	Ru sulfide[c]	1.5	5	140 to 150	500 to 800 (33.7 to 54)	45	0
p-Br [d]	28.1	0.108	Pd sulfide[e]	0.325	5	140 to 150	500 to 800	45	64
[f]	101	0.5	Pt sulfide[c]	1.5	5	130	500 to 800	400	0
[f]	101	0.5	Rh sulfide[c]	1.5	5	105	500 to 800 (33.7 to 54)	135	trace

[a] Yields determined by quantitative GLC analyses. No nitro compound detected in any experiment. The halo-aniline was the only product detected in the absence of dehalogenation. – [b] Experiment run in 1-gallon stirred autoclave with 1260 ml methanol. – [c] 5 wt% metal on carbon. Obtained from Engelhard Industries. –[d] Experiment run in 170-ml Magne-Dash autoclave with 52 ml methanol. – [e] Bulk palladium sulfide prepared by passing H_2S into solution of palladium chloride in aqueous HCl. – [f] Experiment run in 600-ml Magne-Dash autoclave with 240 ml methanol.

With platinum metal sulphides pressures and temperatures of operation have to be raised compared to those for metal catalysts to obtain comparable activity. Dichloro and dibromo nitrobenzenes with the halogen in the 2 and 4 positions can be reduced to the corresponding halo-amines. When the halogen is bromine, then platinum, rhodium or ruthenium sulphides may be used, when it is chlorine then platinum, rhodium, ruthenium and palladium sulphides are suitable [26]. Using these catalysts yields of dihalo-amines as high as 99.5% may be obtained. Attempts to improve the activity and life of the catalyst have centered around supporting the catalyst on carbon and lowering the sulphur content of the metal [27 to 32].

A recent discovery is that platinum-group metal sulphides supported on titanium dioxide can hydrogenate mononitro-aromatics to amines using hydrogen sulphide as reducing agent at atmospheric pressure and 200 to 400°C. The results of trials with platinum metal sulphides and base metal sulphides together with measurements of the activity of the support is shown in the following table [33].

Reduction of nitrobenzene with TiO_2 based catalysts:

catalyst*)	time on stream in min	products (mol%)	
		aniline	nitrobenzene
RuS_x on TiO_2	180	100.0	—
	260	56.1	43.3
RhS_x on TiO_2	90	100.0	—
	180	82.2	17.7
	225(a)	100.0	—
	360(a)	100.0	—
IrS_x on TiO_2	40	100.0	—
	170	53.5	45.8
	220(a)	78.9	20.4
OsS_x on TiO_2	85	100.0	—
	180	73.3	26.7
	270(a)	100.0	—
PdS_x on TiO_2	180	100.0	—
	270	86.2	13.7
	330(a)	100.0	—
PtS_x on TiO_2	45	100.0	—
	180	48.1	51.9
	285(a)	83.8	16.2
0.2% RuS_x on TiO_2	205	100.0	—
	300	97.7	2.259
0.02% RuS_x on TiO_2	315	100.0	—
	300	94.7	5.3

*) Unless otherwise designated all catalysts were wet impregnated with chloride or nitrate salts to yield 2.5% metal on Harshaw TiO_2-0.404 support 10 g samples of each catalyst were heat treated at 500°C, then sulphided at 400°C prior to testing.

(a) After treating the catalyst with an N_2 stream at 400°C for 45 min.

Reductive Alkylation. This is a reaction with a number of selectivity problems which make it fascinating from a catalyst chemist's point of view. The general reaction is $R_1NO_2 \rightarrow R_1NH_2 + R_2R_3CO \rightleftharpoons R_1N=CR_2R_3 \rightarrow R_1NHCHR_2R_3$. The commercial reaction is a batch process and it is established practice to place the catalyst, the nitro body and the ketone in the reactor, pressurise with hydrogen at the reaction temperature and to continue hydrogenation until hydrogen uptake ceases. The hydrogenation of the nitro compound usually presents no difficulty, but is complicated by the possible hydrogenation of the ketone to alcohol. The second problem is in ensuring that the equilibrium of the coupling reaction to produce the imine is established well to the right thus removing ketone from the reaction zone. The last stage of hydrogenation, the reduction of the imine is usually more exacting than the reduction of the nitro compound and frequently requires a higher pressure thus increasing the probability of ketone hydrogenation and introducing the possibility of hydrogenating the aromatic nucleus. Early catalysts for this reaction included Raney nickel and carbon-supported platinum metals. It was not until the mid 1960s that platinum metal sulphides were used, but once shown to be effective they were soon accepted as the best solution to the problem. Early work on the use of platinum metal sulphides as catalysts has been reviewed [34, 35]. The sulphides of all platinum metals are active for the reaction, with the catalyst in either a supported or unsupported form [7, 10]. The conditions used depend upon the metal sulphide being used as catalyst and the compound being hydrogenated, but vary around 120 to 185°C at 1200 to 1400 psi ($\sim$81 to 94 kg/cm^2). Hydrogen sulphide was frequently added to maintain the integrity of the sulphide catalyst. The nitro compounds utilised in this reaction are usually mono or dinitro aromatics, while the ketone is normally aliphatic such as acetone, methylethylketone, methylisobutylketone etc. [7, 10, 36]. However, polycyclic aromatic amines [37], N,N'-disubstituted p-phenylenediamines [38] and diaryl secondary amines [39] have been used, as have cyclohexanone [37] and aromatic ketones [10]. Trialkylamines and tertiary aromatic amines have been prepared by reductive alkylation over platinum, rhodium, palladium and ruthenium sulphides supported on carbon [39, 40]. Platinum metal selenides and tellurides have also been used successfully for reductive alkylation.

Other Reactions. Butadiene has been converted by acetoxylation over palladium telluride (Pd_4Te) on carbon with acetic acid and oxygen, to yield 1,4-butylene diacetate [42]. Platinum sulphide has been used to synthesise silanes from the elements silicon and hydrogen. By controlling the hydrogen pressure SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10} or Si_5H_{12} can be prepared selectively [43]. Palladium sulphide has been used as catalyst in the reaction $UO_2SO_4 + HCOOH + H_2SO_4 \rightarrow U(SO_4)_2 + CO_2 + 2H_2O$. The degree of conversion increased with the amount of catalyst used and was dependent on the pH of the solution, being optimum at a sulphuric acid concentration of 50 to 70 g/l. The catalyst could be separated from the reduced solution and used repeatedly [44].

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4.4.6 Platinum-Group Metal Compounds with Halogens

Catalytically active halo compounds of the platinum-group metals:

simple binary halides	complex halides	complex halide ions
$RuCl_3$, $OsCl_3$, $OsCl_4$, $RhCl_3$, $RhBr_3$, $IrCl_3$, $IrCl_4$, $PdCl_2$, $PtCl_2$, $PtCl_4$	K_2RuCl_5, $(NH_4)_2RuCl_6$, H_2RuCl_5OH, K_2OsCl_6	$[Rh(H_2O)Cl_5]^{2-}$, $[Rh(H_2O)_2Cl_4]^-$, $[RhCl_6]^{3-}$
	H_3RhCl_6, $Rh(NH_3)_3I_3$	
hydrated salts of $RuCl_3$, $RhCl_3$, $IrCl_3$ and $OsCl_3$.	H_2IrCl_6, $(NH_4)_2IrCl_6$, K_2IrCl_6	$[RuCl_5OH]^{2-}$ $[IrCl_6]^{2-}$
	H_2PdCl_4, Li_2PdCl_4, Na_2PdCl_4, K_2PdCl_4	
	H_2PdBr_4, K_2PdBr_4,	
	K_2PdCl_6	
	Na_2PtCl_4, K_2PtCl_4	
	H_2PtCl_6, Na_2PtCl_6	

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4.4.6.1 Preparation

Details of the preparation of the individual compounds used as catalysts is best obtained from the relevant literature references listed in Section 4.4.6.2, and in references [1, 2, 3] of this section. Details of preparing solutions of catalysts are to be found in the references to Section 4.4.6.2.

Supported binary halides and complex halide salts are best prepared by dissolving the metal salt in water, slurrying it with the support and evaporating the whole to dryness at about 100°C. If necessary any remaining water may be removed by heating catalyst at 120°C in a vacuum for 5 to 20 h [4, 7, 8]. The most common supports used for this purpose are charcoal, alumina, silica gel, diatomaceons earth etc. Solutions of platinum metal halides have also been supported on silica [5]. A solution of rhodium trichloride dissolved in ethyleneglycol was added to a slurry of silica powder in methanol. The methanol was then evaporated from the mixture to leave a solution of rhodium trichloride in ethyleneglycol within the pore system of the silica. The resulting catalyst was a free flowing powder which could be used at temperatures to within 100°C of the boiling point of ethyleneglycol. Higher temperatures than this could be obtained by using solvents of higher boiling point. In some applications the finely divided halide is suspended in a liquid in which it is insoluble and the suspension used without further preparation [6].

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[1] J. H. Canterford, R. Colton (Halides of the Transition Elements: Halides of the Second and Third Row Transition Metals, Wiley-Interscience, London 1968). – [2] S. E. Livingstone (in: A. F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, Pergamon, Oxford 1973, pp. 1163/370). – [3] G. Brauer (Handbook of Preparative Inorganic Chemistry, 2nd. Ed., Vol. 2, Academic, New York 1965). – [4] F. Konrad, Ethyl Corp. (U.S. 2765350 [1956]). – [5] G. C. Bond, J. A. Dawson, Johnson Matthey & Co. (Brit. 1116943 [1965]).

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4.4.6.2 Reactions

The halides of the platinum metals have been used for a wide spectrum of catalytic reactions including hydrogenation, oxidation, chlorination etc. Some have been exploited on an industrial scale.

Hydrogenation. When the subject of homogeneous activation of hydrogen in solution was first reviewed in 1956 the only platinum metal salt known to activate hydrogen was ethylene platinous chloride [1]. This material hydrogenated ethylene to ethane at −10°C without deposition of metallic platinum. The proposed mechanism for the reaction was given as $(PtCl_2C_2H_4)_2 + 2\,C_2H_4 \rightleftharpoons 2\,PtCl_2(C_2H_4)_2$; $2\,PtCl_2(C_2H_4)_2 + 2\,H_2 \rightarrow (PtCl_2C_2H_4)_2 + 2\,C_2H_6$ [2].

For the catalytic activation of hydrogen in the presence of the chloropalladate(II) ion in aqueous solution, the rate law was found to be $-d[H_2]/dt = k[H_2][PdCl_4^{2-}]$ with $k = 6.6 \times 10^{11}$ exp $(2 \times 10^4/RT)$ $l \cdot mol^{-1} \cdot s^{-1}$ [3].

In the rhodium chloride catalysed reduction of ferric to ferrous ion the rate expression was found to be similar: $-d[H_2]/dt = K[H_2][Rh^{III}]$ and $k = 2.3 \times 10^{15}$ exp $(25200/RT$ $l \cdot mol^{-1} \cdot s^{-1}$.

The reaction was independent of ferric ion, hydrochloric acid and added electrolyte ion concentration. The reaction was thought to involve $[RhCl_6]^{3-}$ and possibly $[RhCl_5(H_2O)]^{2-}$

species, but no direct evidence was adduced. The rate-determining step was thought to be hydrogen cleavage to form the hydride complex $[HRhCl_5]^{3-}$ [4]. Further work on this reaction using the anionic complexes $[RhCl_6]^{3-}$, $[RhCl_5(H_2O)]^{2-}$ and $[RhCl_4(H_2O)_2]^-$ revealed that all of them activate dihydrogen for Fe^{3+} reduction [5].

The rate of reduction increased with the number of chloride ligands present. Neutral and cationic chloroaquorhodium(III) complexes were not active for this reaction. None of the chloro complexes were active for hydrogenation of the olefinic bond of maleic acid in aqueous solution, but in dimethylacetamide solution $RhCl_3$ was a catalyst for maleic acid hydrogenation, the reaction proceeding via a Rh^I-maleic acid complex [5].

The Russians had studied the activation of hydrogen for the reduction of dichromate ion by simple and complex halides of Ru^{IV}, Rh^{III}, Pd^{II}, Os^{IV}, Ir^{IV} and Pt^{IV}. The concentration of H^+ in solution was found to be important and the most active catalysts were those with metal-metal bonds and unfilled orbitals with a high d character [6].

Stannous chloride was found to promote the co-ordination of ethylene to platinum [7], and platinum-tin complexes have been used to hydrogenate unsaturated olefins and soyabean oil [8], and methyl linolenate [9]. The unsaturated olefins were hydrogenated at 20°C, 1 atm pressure in acetic acid solvent, while soyabean oil required 60°C and 4 atm pressure with the same solvent. The product of soyabean oil hydrogenation was a mixture of C_{16} and C_{18} saturated and unsaturated fatty acids having an iodine number of 79.4 and a trans isomer content of 60%. When methyllinolenate in methanol-benzene mixture was hydrogenated with a platinum-tin complex containing phenylphosphines and phenylarsines, the main product was a mixture of dienes and monoenes. No fully saturated stearate was formed. If the platinum-tin complex was used without phosphines or arsines the product was temperature-dependent. At 30°C considerable conjugation of the unsaturated bonds in linolenate occurred, while at 40°C the catalyst was selective for diene formation. The reaction was thought to proceed through a first formed platinum-tin triene adduct, where conjugation occurs. Subsequent hydrogenation gives rise to a mixture of isomeric dienes and monoenes [8, 9].

Soluble iridium complexes have been used to reduce cyclohexanones, with isopropanol acting both as solvent and hydrogen transfer agent [10]. In the presence of water and methylsulphoxide or using an iridium methylsulphoxide complex, 66 to 78% axial alcohols were formed. Without dimethylsulphoxide only 28 to 30% axial alcohols were formed with $(NH_4)_2IrCl_6$. In anhydrous isopropanol only cyclohexanone ethers were formed, predominantly axial in configuration.

Reduction with Carbon Monoxide. The reduction of quinones [11, 12, 14] and inorganic metal ions [13, 15] in aqueous solution has been extensively studied by the Russians. In the reduction of quinones it was found that with Pd^{2+} and $PdCl_4^{2-}$, precipitation of palladium occurred towards the end of the reduction if the concentration of hydrochloric acid was below 5%. Between 5 and 16.9% hydrochloric acid, palladium remained in solution, but above 16.9% hydrochloric acid the reduction of quinone ceased. In a set of experiments with H_2PdCl_4, H_3RhCl_3 and H_2PtCl_6, it was found that a plot of reaction rate versus hydrochloric acid concentration increased rapidly to a maximum, then declined asymptotically.

On the initial rising part of the curve n, defined as $n\ (\text{for CO}) = \log(W_1/W_2)/\log(P_1/P_2)$ where W = reaction rate and P = CO partial pressure was ~1 for hydrochloric acid concentrations <2% but rose to $n = 2$ for concentrations >2%.

In water-dioxane mixture (3:7), HNO_3, H_2SO_4 and $HClO_4$ increased the rate of reaction as well as HCl. The reaction rate increased linearly with carbon monoxide partial pressure. At high partial pressure of carbon monoxide the reaction rate increased as hydrochloric acid concentration fell. In a large excess of hydrochloric acid, the reaction rates for Pd, Rh and Pt compounds were about the same.

The kinetics of reduction of $Cr_2O_7^{2-}$, IO_2^-, $[Fe(CN)_6]^{3-}$, Fe^{3+}, Sn^{4+} and Cu^{2+} in aqueous solution by carbon monoxide were studied using Pd^{2+}, Rh^{3+} and Pt^{4+} catalysts. The rate of reaction to the amount of catalyst was independent of catalyst concentration at low concentrations. At high concentrations of Na_2PdCl_4 the reaction rate approaches a constant value. In the reduction of ferric ion, log reaction rate versus 1/T was a linear function, but for $Cr_2O_7^{2-}$ the reaction rate increased more rapidly as the temperature rose from 5 to 80°C. The pH of the solution did not affect ferric ion reduction rate, but with $Cr_2O_7^{2-}$, the rate of reaction passed through two maxima.

The most active catalyst was $PdBr_4^{2-}$. Addition of chloride ion to this catalyst decreased the reaction rate, but addition of bromide ion increased it. Increasing the carbon monoxide partial pressure increased the rate of reaction. Catalytic activity was in the order $Pd^{2+} \gg Rh^{3+} \gg Pt^{4+}$.

The reaction mechanism appears to operate through the coordination of carbon monoxide to the catalytic metal ion to form a carbonyl complex. This then hydrolyses to a zero-valent complex, which is then oxidised by the inorganic oxidising agent. The latter is reduced to a lower oxidation state.

Experiments with 64 metal ions as catalysts for the reduction of $Cr_2O_7^{2-}$, Fe^{3+} and Cu^{2+}, showed that only a small number of metals were active for the reaction. Activities for $Cr_2O_7^{2-}$ reduction, expressed in ml CO oxidised per min, are shown in the table below.

ion	compound	activity (ml CO/min)
Cu^{2+}	$CuBr_2$	0.1
	$Cu(CH_3COO)_2$	0.1
Mn^{7+}	$KMnO_4$	0.39
Ru^{4+}	H_2RuCl_5OH	0.25
Rh^{3+}	H_3RhCl_6	0.1/0.33
Pd^{2+}	H_2PdBr_4	19.6
	H_2PdCl_4	8.4
Pd^{2+}	$K_2Pd(NO_2)_4$	2.94
Os^{4+}	K_3OsCl_6	0.06
Ir^{4+}	K_3IrCl_6	0.06
Pt^{4+}	H_2PtCl_6	0.15
Au^{3+}	$HAuCl_4$	0.85
Ce^{4+}	—	low
Hg^{2+}	—	low

Dehydrogenation. Rhodium trichloride has been shown to dehydrogenate isopropanol to give acetone, at the same time rhodium metal was precipitated [16]. If the complex between rhodium trichloride and stannous chloride was used, then dehydrogenation took place without rhodium metal being precipitated [17]. Other platinum-group metal halides in combination with stannous chloride have been shown to be dehydrogenation catalysts, see following table [18].

Dehydrogenation of secondary alcohols by platinum-group metal-tin chloride complexes:

	substrate	product	rate of H_2 evolution
0.58 M HCl 0.093 M LiCl 0.045 M $SnCl_2$ 0.01 M $RhCl_3$	isopropanol	acetone	1.4×10^{-3} mol/h (31.4 cm^3/h)

	substrate	product	rate of H_2 evolution
0.045 M $SnCl_2$ 0.01 M $RhCl_3$	isopropanol	acetone	0.8×10^{-3} mol/h (17.9 cm^3/h)
0.58 M HCl 0.093 M LiCl 0.045 M $SnCl_2$ 0.01 M $RuCl_3$	isopropanol	acetone	0.7×10^{-3} mol/h (15.7 cm^3/h)
0.58 M HCl 0.093 M LiCl 0.045 M $SnCl_2$ 0.01 M H_3IrCl_6	isopropanol	acetone	2.8×10^{-3} mol/h (62.8 cm^3/h)
0.0005 M Li_3IrCl_6 0.003 M $SnCl_2$ 0.03 M HCl	ethanol	acetaldehyde	0.0054 mol in 72 h
0.094 M LiCl 0.029 M $SnCl_2$ 0.0072 M $RhCl_3$	isobutanol	isobutyraldehyde	2×10^{-3} mol/h (44.8 cm^3/h)
0.58 M HCl 0.093 M LiCl 0.045 M $SnCl_2$ 0.01 M $RhCl_3$	isobutanol	methylethylketone	—
0.047 M LiCl 0.00054 M $SnCl_2$ 0.00144 M $RhCl_3$	cyclohexanol	cyclohexanone	0.022 mol/h (493 cm^3/h)

Hydrochlorination. Vinylchloride has been prepared from acetylene and hydrogen chloride with platinum or palladium chloride and gold chloride in molar ratios Pt or Pd : Au = 0.1 to 10. Acetylene and hydrogen chloride (HCl : CH≡CH (molar) = 1.2) at a space velocity of 50 h^{-1} when passed through an aqueous solution (1000 parts) containing platinum chloride (2 parts) and gold chloride (2 parts) at 79°C gave vinylchloride. The conversion was 54% with a selectivity >99%. No solid polymers were formed [19].

Chlorination of Hydrocarbons. Olefins can be chlorinated almost exclusively to the dichloroalkanes over the chlorides of palladium, iridium, rhodium and platinum. Thus, propene was chlorinated to 1,2-dichloropropane in 94.4% yield, cyclo-octene to 1,2-dichloro-cyclooctane (conversion 69%, selectivity 85.2%), styrene to α,β-dichloroethylbenzene (conversion 79%, selectivity 89%). Propylchloride was chlorinated to 1,2,3-trichloropropane (83% yield). Palladous chloride was considered the best catalyst, although iridium trichloride and rhodium trichloride were both acceptable catalysts. In all cases the catalysts were supported on silica gel or alumina and the reactions were conducted in the vapour phase [20].

Benzene has been chlorinated over iridium trichloride on alumina at 150 to 180°C to give p-dichlorobenzene with small amounts of monochlorobenzene and hexachlorobenzene. At 300°C over either iridium, trichloride or rhodium trichloride on alumina, hexachlorobenzene was formed exclusively; p-xylene when chlorinated over rhodium trichloride on alumina at 120 to 130°C gave a 90% yield of 2,3,5,6-tetrachloro-p-xylene. Alkanes, when chlorinated over either rhodium trichloride on alumina or sodium chloroplatinate on silica gave very high yields of the monochloro-alkanes. Thus cyclohexane over rhodium trichloride at 120°C gave cyclohexylchloride, while hexane over sodium chloroplatinate gave hexylchloride at 200°C. Clorination of cyclohexane over rhodium trichloride on alumina at 130 to 150°C gave tetrachloro-cyclohexanone. Over iridium tetrachloride on alumina at 100°C a product was formed which consisted of both tetrachloro-cyclohexanone and hexachloro-cyclohexanone [21].

A 1.5% palladium chloride on alumina catalyst when used to chlorinate benzene at 180 to 200°C gave a mixture of monochlorobenzene, p-dichlorobenzene (main product), o-dichlorobenzene, and 1,2,4-trichlorobenzene. Similarly prepared were hexyl- and cyclohexylchlorides. Palladium chloride can be replaced by iridium or rhodium trichlorides [22].

Oxychlorination. Olefins have been brominated and chlorinated by passing a mixture of the olefin and oxygen (air) over a catalyst consisting of 5% Cu, 1% Pt and 3% Ce as the chlorides, supported on alumina. Reaction temperature was between 250 to 550°C and atmospheric pressure. Thus with ethylene, equal amounts of 1,2-dichloroethane and vinylchloride were formed together with smaller amounts of carbon monoxide, carbon dioxide, hydrogen chloride and water [23].

Dehydrochlorination. 1,1-dichloroethane has been dehydrochlorinated over palladium and platinum salts such as palladous chloride and platinous chloride supported on activated alumina. Yields of vinylchloride were over 60% at reaction temperatures of 250 to 500°C. This is an unusual product from 1,1-dichloroethane, thermal cracking usually gives only 5 to 10% vinylchloride [24].

Hydration. Rhodium(III) chloride and ruthenium(III) chloride have been used to hydrate acetylene to produce aldehydes and ketones. The hydration of acetylene by a 0.0125 M solution of rhodium trichloride in 3 M hydrochloric acid at 60°C produced acetaldehyde at a rate of 2.3×10^{-5} mol/s. Varying the rhodium concentration between 0.0125 and 0.0375 mol and the acetylene concentration between 3.8×10^{-3} and 2.17×10^{-2} mol showed that the reaction was first order in each reactant with the rate law being $-d[C_2H_2]/dt=k[C_2H_2][Rh^{III}]$; k varied between 7.3×10^{-2} and 11.3×10^{-2} mol/s.

Phenylpropionic acid on hydration in the presence of rhodium trichloride produced a β-keto acid which decomposed to acetophenone and carbon dioxide. The active catalytic species was thought to be $[Rh(H_2O)Cl_5]^{2-}$. Solutions containing $[RhCl_6]^{3-}$ showed only about one third the activity of the pentachloroaquo-containing solutions [25].

When ruthenium trichloride was used the products were essentially the same, but the rate of hydration was slower. Thus with acetylene, rhodium was three times more active than ruthenium under the same conditions. Again an aquo-chloro species was thought to be the active catalyst, but no single aquo ion could be identified [26].

Water Gas Shift Reaction. The water gas shift reaction in which carbon monoxide is reacted with water to give hydrogen and carbon dioxide is normally conducted at temperatures of 400 to 500°C. Recently, however, it has been found possible to obtain satisfactory yields of hydrogen when the reaction is conducted at 100 to 400°C in the presence of a platinum-group metal chloride and a water liquid phase. The salts which may be used as catalysts are iridium trichloride, rhodium trichloride, iridium tetrachloride and platinum oxide. The aqueous phase must be alkaline preferably by incorporating ammonia or an organic amine into the liquid phase although sodium hydroxide may also be used. Standard conditions were 200°C with pressures of 100 to 800 psi (~6.7 to 54 kg/cm²). Under these conditions pure carbon monoxide atmospheres were converted to hydrogen-carbon monoxide-carbon dioxide atmospheres containing up to 54% hydrogen [27].

Oxidation. Unsaturated hydrocarbons have been oxidised with palladous chloride, ruthenium trichloride, potassium chlororuthenite, ammonium chlororuthenate, osmium tetrachloride, iridium trichloride and sodium chloro-iridate catalysts and oxygen or air to give a variety of products.

Cyclohexene when shaken with air in the presence of ruthenium trichloride, potassium chlororuthenite or ammonium chlororuthenate was converted to 2-cyclohexanone. Thus 10 ml cyclohexene and 0.226 g K_2RuCl_5 were shaken at 50°C with oxygen; 600 ml O_2 were absorbed in 286 min and 895 ml O_2 in 727 min. With tetrahydronaphthalene and the same catalyst at 100°C, a mixture of ketonic compounds were formed [28].

Ethylene has been oxidised in the vapour phase to give acetic acid. An α-alumina catalyst containing 0.2 wt% $PdCl_2$ and 9.5 wt% V_2O_5 was contained in a reactor at 209°C. 53.2 l air/h, 1.52 l C_2H_4/h and 93.6 l/h steam were passed at a space velocity of 37 l/h, 81.8% of the ethylene was converted to acetic acid with a selectivity of 45.4 mol% [29]. Similarly over the same catalyst 3% C_2H_4, 8% O_2 and 3.2% H_2O vapour was passed at a total pressure of 10.5 to 21 atm to give acetic acid in high yield [30].

Acetophenone was oxidised in the presence of iridium trichloride to benzylalcohol and phenol. 0.3 g $IrCl_3$ with 30 g acetophenone was shaken with 150 ml O_2 per min at 195°C for 3 h. 13.2% of the acetophenone was converted to 2.9 g benzylalcohol and 0.3 g phenol [31].

When cyclohexene was oxidised over palladous chloride with p-benzoquinone as oxidising agent the product was cyclohexanone. $C_6H_{10} + H_2 + C_6H_4O_2 \rightarrow C_6H_{10}O + C_6H_4(OH)_2$.

The reaction was first order with respect to cyclohexene and palladous chloride, even at conversions of 95 to 98% [32].

Toluene was oxidised by di-isopropylperoxydicarbonate in the presence of osmium tetrachloride, ruthenium trichloride or sodium chloroiridate and acetonitrile solvent to yield tolylisopropylcarbonate [33].

In the analytical determination of ruthenium, o-dianisidine was oxidised by potassium periodate, the ruthenium ion acting as catalyst [34].

Decomposition of Hydrogen Peroxide. The catalytic effectiveness of palladium(II) complexes in the decomposition of hydrogen peroxide has been investigated. Some complexes were found to be inactive in this reaction including $K_2Pd(CN)_4$, $K_2Pd(SCN)_4$, $Pd(en)_2Cl_2$, cis- and trans-$Pd(NH_3)_2Cl_2$ and $Pd(NH_3)_4Cl_2$. Both potassium chloropalladite and bromopalladite were catalytically active for the decomposition. When the catalyst concentration was low the reaction was first order in catalyst, but zero order when high. The activation energy was 14.9 kcal/mol for the chloro and 15 kcal/mol for the bromo complex. The suggested mechanism was the replacement of one halide ion by HO_2^-. In agreement with this, the rate of decomposition increased with increasing pH [35].

Isomerisation. When aliphatic olefins of chain length greater than C_4 are heated in the presence of platinum-group metal homogeneous catalysts, two reactions may occur which collectively are known as isomerisation. Firstly the carbon-carbon double bond may change its position in the carbon chain (positional isomerisation) and secondly an internal double bond may assume a cis- or trans-configuration (geometrical isomerisation). This is assumed to be the result of the making and breaking of olefin-metal bonds, and may occur with or without simultaneous hydrogenation.

The isomerisation of olefins with platinum, palladium, rhodium and iridium catalysts has been studied in the absence of hydrogenation. All of the catalysts were found to require co-catalysts, such as an aliphatic alcohol, to induce isomerisation. Olefins isomerised include hexanes and heptanes [36].

Isomerisation of pentenes in nitrogen has been accomplished by passing l-pentene over a catalyst made by soaking a porous support with a solution of rhodium trichloride trihydrate in an organic compound of low volatility containing OH functions, such as ethylene glycol.

A 40 ml/min flow of nitrogen saturated with pentene-1 was passed through the catalyst at 60°C. The product consisted of pentene-1, 27.2%, cis-pentene-2, 29.3%, and trans-pentene-2, 43.5% [31, 38, 40].

Hydrogenation of pentene-1 over platinum(II)-tin(II) complexes gave unusually high levels of trans-pentene-2. The isomerisation occurs at room temperature to a mixture of pentene-2 isomers in which the trans isomer predominates (~85%). The rate of hydrogenation, which was slow, is proportional to pentene-1 concentration, cis-pentene-2 being virtually unhydrogenated. The rate of hydrogenation (and isomerisation) was a maximum at a Pt:Sn ratio of 1:12 [39].

Dimerisation and Hydrodimerisation. Ethylene, propylene and acetylene may be dimerised by passing into solutions of palladous chloride, platinous chloride, platinic chloride, chloroplatinic acid or bromoplatinic acid at 60 to 150°C. The results with acetylene are reproduced in the following table [41].

compound	solvent	reaction temp. in °C	% conversion to vinylacetylene	% conversion to divinylacetylene
$PdCl_2$	dimethyl sulphoxide	120	30.0	0.3
$PdCl_2$	ethylalcohol	80	0.5	0.0
$LiPdCl_3$	propionic acid	120	0.4	0.2
$PtCl_2$	tetrahydrofuran	60	2.4	0.2
$PtCl_4$	nitrobenzene	120	0.7	0.3
$PtCl_4$	dioxane	100	1.5	0.3
H_2PtCl_6	water	100	7.5	1.8
H_2PtCl_6	acetic acid	120	4.0	0.4
H_2PtCl_6	dimethyl sulphoxide	120	50.0	0.0
H_2PtCl_6	dimethyl sulphoxide	150	38.0	0.0
H_2PtBr_6	water	100	12.3	0.1

Acrylonitrile and ethyl acrylate when treated with hydrogen in the presence of group VIII metal halides and optionally Lewis bases such as triphenylphosphine or diphenylamine, give rise to dimerised and hydrodimerised products. Thus acrylonitrile and ethylacrylate when treated with ruthenium trichloridetrihydrate and hydrogen at 25 atm pressure, 100°C, gave adiponitrile, 1,4-dicyanobutenes, diesters and cyanoesters. Acrylonitrile alone with $RuCl_3 \cdot 3H_2O$ catalyst gave 56% 1,4-dicyanobutenes and adiponitrile. The catalyst may be supported on alumina [42, 43].

Polymerisation of Olefins. Rhodium trichloride has been shown to be an excellent catalyst for the selective formation of trans-1,4-polybutadiene from 1,3-butadiene. For example, without rhodium trichloride catalyst the polymerised material contained 65.5% trans, 15.5% cis and 19% vinyl polymers while with rhodium trichloride the respective percentages were 93% trans, 6% cis and <1% vinyl [44]. The yield of trans-polybutadiene was increased to 99% by using ammonium chlororhodate [45]. It has also been found that the rate of polymerisation of 1,3-butadiene to trans-1,4-polybutadiene can be increased with rhodium trichloride, if a small amount of 1,3-cyclohexadiene is added to the polymerisation emulsion [46].

Replacement of Cl by NH_3 in rhodium trichloride gave a decrease in activity. Pyridine behaved in a similar manner. Rhodium trichloride and tribromide were equally active, while $Rh(NH_3)_3I_3$, rhodium acetylacetonate and rhodium trioxalate were of much lower activity [41].

Palladium salts have also been used as catalysts in butadiene polymerisation. The directing influence of the ligands surrounding the metal is shown in the following table [48].

compound	trans-1,4-polymer	1,2-polymer
$PdCl_2$	17%	83%
M_2PdCl_4 ($M = Na^+, K^+, NH_4^+$)	2%	98%
K_2PdCl_6	2%	98%

compound	trans-1,4-polymer	1,2-polymer
$PdBr_2$	9%	91%
PdI_2	85%	15%
$Pd(CN)_2$	78%	22%

Iridium trichloride and ruthenium trichloride have also been used as catalysts for butadiene polymerisation [49], and ruthenium trichloride, osmium trichloride and iridium trichloride for norbornene polymerisation [50, 51].

Other Reactions. Vinyl and alkyl acetates may be converted into vinyl and allyl esters of higher carboxylic acids or to ethylenic ethers using palladium halides, platinum halides or rhodium halides as catalysts. Thus allyl acetate was converted to allyl chloride by reaction with hydrogen chloride in the presence of palladous chloride/cupric chloride catalyst [52], while vinylacetate has been converted to vinylstearate by refluxing it with stearic acid and lithium chloropalladite for 3 h. Lithium chloroplatinate, lithium chlororhodate and sodium chloropalladite have also been used as catalysts in this latter reaction [53].

Ethylenic ethers can be made by contacting a vinyl or allyl ester with a monohydric alcohol and a palladium halide catalyst. When vinylacetate-methanol vapours were passed over lithium chloropalladite supported on charcoal at 120°C, methylvinylether was produced. Vinylisobutylether, allylmethylether, vinylisopropylether, allylisopropylether and methylisopropylether have been produced in this manner [54].

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4.4.6.3 Industrial Processes

Four industrial processes have been based on the palladous chloride-cupric chloride redox couple for the manufacture of acetaldehyde, acetone, allylacetate and vinylacetate. A fifth reaction has been used industrially to produce the esters of higher carboxylic acids from vinylacetate and a carboxylic acid or its sodium salt, utilising palladous chloride as catalyst. This latter process has been given the name "transvinylation".

Acetaldehyde. In this procees ethylene is oxidised to acetaldehyde using oxygen or air as an indirect oxidant: $C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO$.

The reaction takes place in two steps. Firstly the olefin is rapidly oxidised by the palladium catalyst: $CH_2{=}CH_2 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$, then the palladium metal formed is reoxidised in a slower rate-determining step: $Pd + 2CuCl_2 \rightleftharpoons PdCl_2 + Cu_2Cl_2$ and $Cu_2Cl_2 + \frac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$. A small amount of palladous chloride can be made catalytic by working with a large excess of cupric chloride.

The system used is two-phase (gas-liquid), and operated in a titanium or lined bubble column reactor. Two process variants exist, a single step process in which both reaction and regeneration take place in the same reactor, and a two step process in which reaction and regeneration occur in separate reactors. The single step process operates at ~3 atm and 120 to 130°C with pure oxygen. The conversion is ~35 to 45% based on the ethylene fed to the reactor. The heat of reaction, ~58 kcal/mol, is used to distill off the acetaldehyde. With the two-step process ethylene is converted almost completely by the catalyst solution at 10 atm pressure and 105 to 110°C. After reducing pressure and distilling off the acetaldehyde, the palladium catalyst solution is regenerated in the second reactor using air at 10 atm pressure and 100°C. Since the oxygen content of the air fed to the regenerator is almost completely depleted, the nitrogen can be bled off and used as an inert gas in other parts of the plant. Selectivities in both processes are ~94%.

Although once an important process step in the manufacture of acetic acid, with the inception of the route via the carbonylation of methanol, it has become of only marginal importance.

Acetone. Acetone may be manufactured by the direct oxidation of propylene: $CH_3CH{=}CH_2 + \frac{1}{2}O_2 \rightarrow CH_3COCH_3$.

The process operated in the liquid phase at 10 to 14 atm pressure and 110 to 120°C. Propylene conversion is over 99% with selectivities of 92% for acetone and 2 to 4% for propionaldehyde. As with acetaldehyde manufacture, two process variants are possible, although the two-step variant is favoured economically because it is able to treat propylene/propane mixtures from cracking processes. The process is important in Japan, but not elsewhere; n-butene may be converted to methylethyl ketone using this route.

Allyl and Vinyl Acetates. Ethylene at 30 to 40 atm pressure and 110 to 130°C in the presence of palladous chloride-cupric chloride redox catalyst and acetic acid can be converted into vinylacetate. By modifying the operating conditions some ethylene can be oxidised to acetaldehyde and then acetic acid, so that the process may be made to supply its own acetic acid. The vinylacetate selectivity reaches 93% based on acetic acid.

A gas phase process was developed in parallel with the liquid phase ethylene acetoxylation process, using palladium acetate and cupric acetate, which has completely displaced the liquid phase process. By substituting propylene for ethylene, allylacetate may be manufactured by this route.

Transvinylation. The manufacture of vinylesters of the higher carboxylic acids has been undertaken industrially by refluxing vinylacetate with the higher carboxylic acid or its sodium salt in the presence of palladous chloride catalyst. The esters of the higher carboxylic acids are used mainly as co-monomers in the modification of homopolymers for paint manufacture. Yields of up to 97 to 98% are to be expected.

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4.4.7 Homogeneous Catalysis

Although the subject of catalysts with transition metal compounds in solution is not new, the advent of renewed interest in the inorganic chemistry of the transition metals, with ligands such as carbon monoxide, organo-sulphur and organo-phosphorous compounds, has led to new interest in their use as solution catalysts. This revival has given rise to a large amount of academic work which, in its turn, has inspired a number of industrial processes, the large majority of which have been based on the catalytic chemistry of the platinum-group metals with sulphur, nitrogen and phosphorus ligands. This section deals with the solution (homogeneous) catalyst chemistry of the platinum metals in reactions such as hydroformylation, carbonylation, hydrogenation, hydrosilation, oligomerisation, telemerisation etc. [1, 2].

Operations in which the catalyst, dissolved in a solvent, operates on gaseous or liquid substrates to give products in solution have always been accompanied by separation problems. This has restricted the catalysis to reactions in which the products are volatile and are distilled from the pseudo-equilibrium mixture in the reactor, leaving the non-volatile and expensive catalyst behind. More sophisticated solutions, in which the catalyst is bonded to an organic polymer or functionalised inorganic supports such as silica, have not been successful. During the catalytic reaction part of the catalytic compound becomes solubilised and is leached from the support, frequently to contaminate the product. Until such problems can be solved the industrial application of homogeneous processes is likely to remain significant, but narrow [3 to 9].

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4.4.7.1 Hydroformylation

Hydroformylation, also referred to as the Oxo Reaction, is one of the oldest and largest applications of homogeneous catalysis. In 1938 while investigating catalysts for the Fischer-Tropsch process it was found that aldehydes were produced through the reaction of synthesis gas with an alkene in the presence of a cobalt catalyst [1, 2].

A commercial process for the production of detergent alcohols using cobalt carbonyl catalyst was developed in the 1940s. Subsequently a tributylphosphine modified cobalt system was developed [1].

Although a number of rhodium species were being investigated as catalysts in the 1950's there was poor selectivity to the desired n-aldehyde. It was not until the late 1960's that it was shown that the presence of phosphines such as triphenylphosphine, gave catalysts that were highly reactive and selective for the Oxo Reaction [4].

Subsequently, the rhodium LPO (low pressure Oxo) process for the hydroformylation of light olefins was developed. This resulted in a commercial plant using ethylene feedstock being commissioned in 1975 and one using propylene becoming operational in 1976 [5].

A number of reviews have described the relative merits of these processes and a comparison of these three processes for the hydroformylation of propylene [5 to 11], see the following table.

catalyst	$[CoH(CO)_4]$	$[CoH(CO)_3(PBu_3)]$	$[RhH(CO)_2(PPh_3)_2]$
pressure (MPa)	20 to 30	5 to 10	2 to 3
temperature (°C)	140 to 180	180	90 to 120
selectivity to butanols (%)	90	80*)	93
selectivity to n-butanol (%)	67	67*)	84

*) aldehyde + alcohol

It shows that the rhodium process has major benefits, in that it operates with lower temperature and pressure, and gives significantly higher selectivities. The LPO process also operates with low concentrations of rhodium, typically 50 to 100 ppm and at phosphine to rhodium levels of ~75. When the reaction has reached equilibrium the butanols and byproducts are volatilised at their rate of production thus minimising catalyst losses. As rhodium is present at low concentrations an important contribution towards the commercialisation of the LPO process has been the development of a purification system for the synthesis gas and propylene in order to overcome poisoning problems.

The aldehyde products are chemical intermediates and they are converted to alcohols via hydrogenation or aldolisation. In the case of butanols both isomers can be converted to the corresponding alcohols: $CH_3(CH_2)_2CHO + H_2 \rightarrow CH_3(CH_2)_3OH$.

However, 60% of the market for butanols is in the production of 2-ethylhexanol, a plasticiser alcohol, which can only be prepared via aldolisation of the n-isomer, and consequently this product is at a high premium: $2CH_3(CH_2)_2CHO \rightarrow CH_3CH_2CH_2CH{=}C(CH_2CH_3)CHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2CH(CH_2CH_3)CHO$.

Currently there are six LPO plants in operation and a further six under construction. When all these plants are operational the rhodium process will account for one third of the world's production of butyraldehyde. The financial benefits of the LPO process are such that the investment in converting from a cobalt process will be recouped in less than three years. At present the industrial application of rhodium catalyst systems is limited to low molecular weight alkenes although systems under development may result in an extension of rhodium systems to detergent range alkenes [5].

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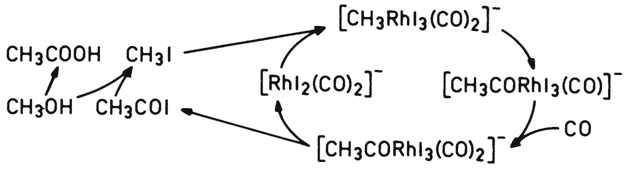
4.4.7.2 Carbonylation

Carbonylation of Methanol. Manufacture of Acetic Acid. Acetic acid has been a major organic chemical for many years. The original process for its manufacture was based on fermentation. Subsequently alternative processes have been developed using alternative feedstocks. In the 1950's a process for the oxidation of butane using cobalt or manganese catalysts was commercialised as was a process for the oxidation of acetaldehyde, acetaldehyde being produced via the palladium catalysed oxidation of ethylene (see Section 4.4.6.3). The trend towards low-energy feedstocks is reflected in the more recent processes for acetic acid manufacture based on methanol feedstocks, where the overall reaction is $CH_3OH + CO \rightarrow CH_3CO_2H$.

In 1965 an iodine/cobalt based catalyst was developed and in the early 1970's commercialisation of a process using a rhodium/iodine catalyst system started. The rhodium system shows considerable advantage over cobalt as it operates at lower temperatures and pressures. Moreover the precious metal system gives selectivities to acetic acid of greater than 99%. The presence of hydrogen has no effect on by-product formation [1, 2].

In the rhodium process a variety of rhodium and iodine sources can be used. The presence of alkali metal salts, however, has a detrimental effect on the reaction. The reaction is first order in both rhodium and iodine. The key step in this process is the formation of a carbon-carbon bond, the probable catalytic cycle is given below [1, 2].



A recent review on the mechanism of rhodium and iridium catalysed carbonylation of methanol has been published [3], and other general reviews are available [4, 5].

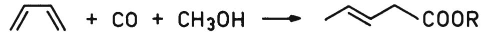
Carbonylation of Methanol. Manufacture of Vinyl Acetate and Acetic Anhydride. In 1960 virtually all vinyl acetate processes were based on acetylene. Subsequently the ready availability of ethylene resulted in the development of a process for the production of vinyl acetate from ethylene and acetic acid. In the 1970's ethylene became more expensive and a number of companies have turned to the use of carbon monoxide as a principal chemical feedstock in the expectation that much more carbon monoxide will be available in the 1990's. This reasoning has led to the development processes for the production of vinylacetate and acetic anhydride from methanol. The process route for vinylacetate is illustrated below.

$$\begin{aligned}
&CH_3OH + CO \longrightarrow CH_3CO_2H\\
&CH_3CO_2H + CH_2OH \longrightarrow CH_3CO_2CH_3\\
&CH_3CO_2CH_3 + CH_3CHO \longrightarrow CH_3CH(O_2CCH_3)_2\\
&CH_3CH(O_2CCH_3)_2 \longrightarrow CH_2{=}CHO_2CCH_3 + CH_3CO_2H
\end{aligned}$$

The first commercial plant for this acetic anhydride route has been built and was started up in 1983 [6].

The catalyst systems for these processes are very similar to those employed in acetic acid production. Rhodium complexes are used in solution with iodides and lithium, calcium or aluminium species as promoters. In addition organophosphorus or organitrogen compounds may be used as co-promotors at 125 to 250°C and 5 to 2000 psi (~0.4 to 140 kg/cm²) CO [7].

Hydrocarboxylation. Palladium and platinum catalysts may be used for hydrocarboxylation reactions, which has application in fine organic chemicals custom synthesis. For example, H_2PtCl_6-$SnCl_2$ systems catalyse the reaction of L-olefins with carbon monoxide and methanol to give linear methylesters and palladium chloride can be used to catalyse the carboxymethylation of butadiene.



Palladium salts may also find minor applications in the carbonylation of aryl halides [8].

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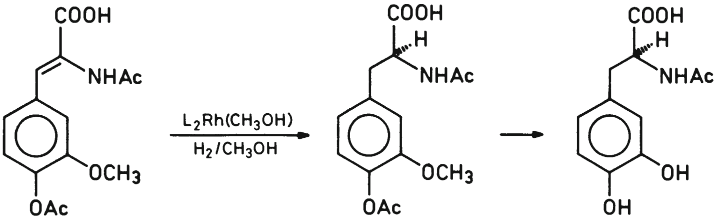
4.4.7.3 Homogeneous Hydrogenation

The first report of a homogeneous hydrogenation catalyst was in 1938 when it was found that a solution of copper acetate in quinoline was capable of reducing benzoquinone to quinhydrone under 1 atm of hydrogen [1]. Progress in this area was slow until the early 1960's when a number of active homogeneous hydrogenation catalysts containing platinum-group metals were reported: chlororuthenate [1, 2], platinum-tin chloride complex [3], $[RhCl(PPh_3)_3]$ [4, 5] and $[RuCl(H)(PPh_3)_3]$ [6]. Since then a vast amount of work has been carried out on homogeneous hydrogenation catalysts, principally based upon platinum-group metals. The literature up to 1971 has been reviewed updated [8, 9].

General treatments of homogeneous hydrogenation are found in [10 to 12]. A review [13] and a book [14] deal with homogeneous hydrogenation reactions in organic chemistry. The chemistry and catalytic activity of Wilkinson's catalyst $[RhCl(PPh_3)_3]$, perhaps the most studied homogeneous hydrogenation catalyst, has been reviewed [15].

The often excellent selectivity and reactivity of platinum-group metal homogeneous hydrogenation catalysts is frequently outweighed by the difficulty of separating the expensive catalyst from the product. Attempts have been made to overcome this problem by immobilising the catalyst on a polymer [16] or inorganic support [17], removal by membrane filtration [18] or use of biphasic systems [19].

The only process which has been commercialised and uses a homogeneous platinum-group metal catalyst is the Monsanto synthesis of l-DOPA, a drug valuable in the treatment of Parkinson's disease. The rhodium complex with a chiral phosphine ligand is used to hydrogenate the precursor under mild conditions. As the environment about the rhodium centre is chiral the reaction proceeds through diastereomeric transition states leading to an excess of one enantiomer of the product. In practice optical yields for the l-isomer of up to 90% are obtained. The scale of this reaction is comparatively small and rhodium is recovered from the solvent after removal of the product [20].



Asymmetric hydrogenation has been covered in recent reviews [21, 22].

To date, no other commercial process uses homogeneous platinum-group metal hydrogenation catalysts. There are, however, several areas where the high selectivity of some of these catalysts could be appropriate if the problems of product/catalyst separation and catalyst recycle could be alleviated. Thus platinum complexes are very selective in edible oil hydrogenations giving almost exclusively monoenes for trienes and dienes with little subsequent hydrogenation of the monoenes [23].

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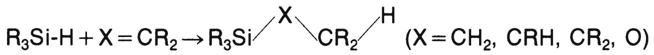
4.4.7.4 Hydrosilation

The hydrosilylation reaction may be illustrated in its most general form by the equation below where a Si-H unit adds across a double bond.



$$R_3Si\text{-}H + X{=}CR_2 \rightarrow R_3Si\text{-}X\text{-}CR_2\text{-}H \quad (X{=}CH_2,\ CRH,\ CR_2,\ O)$$

The earliest examples were reported in the late 1940s and were uncatalysed, occurring in a free radical mechanism under thermal activation. In 1953 heterogeneous platinum catalysts for the addition of trichlorosilane to olefins were reported and from 1957 papers described a range of group VIII metal chloro complexes which, in alcoholic solution, were very active homogeneous hydrosilation catalysts [1]. The most widely used of these catalysts to date is a solution of H_2PtCl_6. The activity of this catalyst is indicated by the reaction of trichlorosilane with ethylene where addition of 10^{-7} mol catalyst per mol substrate at ambient temperature rapidly gives a quantitative yield of ethyltrichlorosilane.

A recent review covers the hydrosilation reactions of a wide range of olefins and silanes catalysed by H_2PtCl_6 and a number of other group VIII metal complexes [2]. The mechanism of the reaction, as rationalised involves oxidative addition of R_3SiH to a low-valent Pt olefin complex as a first step, followed by reversible olefin insertion into the Pt-H bond and irreversible reductive elimination of alkyl silane [3].

The reaction is applied commercially in the preparation of monomers for silicone production, the crosslinking (curing) of silicone elastomers and resins and the joining of silicone and organic polymers to give graft copolymers. The homogeneous platinum catalyst is not used exclusively in industrial hydrosilation as platinum metal on inorganic or carbon supports will also catalyse the reaction, although at a slower rate.

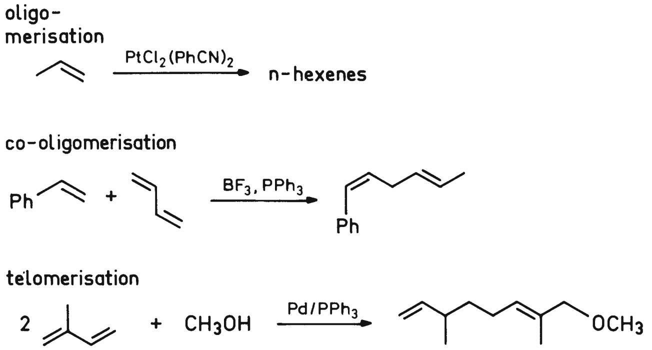
A general review of silicone chemistry gives details of the preparation and uses of specific monomers as well as a discussion of the methods of crosslinking and the properties of the resulting elastomers and resins. An important application for hydrosilation catalysts is the curing of two-component room temperature vulcanising silicone rubbers where a mixture of platinum catalyst and a vinyl-functional polymer forms one component. The other being a hydride-functional curing agent. Mixing initiates the hydrosilation reaction which is usually complete after a few hours at room temperature. Where a longer life for the mixed but uncured product is required, then hydrosilation inhibitors such as acetylenic compounds may be incorporated. These inhibitors are volatile at high temperatures and so may be removed when the hydrosilation is required to take place, allowing the curing reaction to be precisely controlled and completed within minutes at the appropriate temperature. Elastomers cured by hydrosilation are widely used for moulding applications as well as bonding, sealing and electrical insulation [4].

References:

[1] J. L. Speier, J. A. Webster, G. H. Barnes (J. Am. Chem. Soc. **79** [1957] 974/9). – [2] J. L. Speier (Advan. Organometal. Chem. **17** [1979] 407/47). – [3] A. J. Chalk, J. F. Harrod (J. Am. Chem. Soc. **87** [1964] 16/21). – [4] F. O. Stark, J. R. Falender, A. P. Wright (in: G. Wilkinson, F. G. A. Stone, E. W. Abel, Comprehensive Organometallic Chemistry Vol. 2, Pergamon, Oxford 1982, p. 305).

4.4.7.5 Olefin Oligomerisation and Telomerisation

Olefin oligomerisation may be defined as the polymerisation of olefinic monomers to give products consisting of a few monomer units. The starting materials may be pure olefins, in which case dimers, trimers etc. will result, or mixtures of two or more monomers in which highly specific co-oligomerisation may result. Telomerisation is essentially an oligomerisation reaction in which a nucleophile adds to the oligomer metal complex to give a functionalised oligomer. Illustrative examples of specific reactions catalysed by palladium complexes are given below.



A recent review gives a comprehensive survey of this area [1]. The scope of these reactions is enormous, but to date only one oligomerisation process using a platinum-group metal homogeneous catalyst is in commercial use. This is the co-oligomerisation of ethylene and butadiene to give trans-hexa-1,4-diene which is produced on a scale of ~2000 t a year for use as a crosslinking agent in EPDM (ethylene-propylene-diene monomer) rubbers. The trans isomer is favoured for this application and can now be produced with very high selectivity. This codimerisation reaction was discovered in 1961, and used as catalyst an ethanolic solution of rhodium trichloride at 50°C and low pressure [2]. The same catalyst precursor, possibly with the addition of donor ligands, is now used commercially, giving over 80% selectivity to trans-hexa-1,4-diene. The mechanism of the reactions and the reasons for its high selectivity have been elucidated. It proposed a crotyl rhodium(III) complex as a key intermediate to which ethylene adds by insertion to give a hexyl complex, followed by β-elimination to give trans-hexa-1,4-diene and a rhodium(III) hydride complex [3]. Mechanistic work and the effects of various added ligands on the reaction have been reviewed [4].

References:

[1] W. Keim, A. Behr, M. Roper (in: G. Wilkinson, F. G. A. Stone, E. W. Abel, Comprehensive Organometallic Chemistry Vol. 8, Pergamon, Oxford 1982, p. 371). – [2] T. Alderson (U.S. 3013066 [1961]). – [3] R. Cramer (J. Am. Chem. Soc. **89** [1967] 1633/9). – [4] A. C. L. Su (Advan. Organometal. Chem. **17** [1979] 269/318).

4.4.7.6 Developments in Homogeneous Catalysis

A number of reactions involving homogeneous platinum-group metal catalysts have been developed on a laboratory or pilot plant scale which, because of the unusual selectivity or reactivity of these systems, may have large-scale industrial application.

The field of syngas chemistry has received a vast amount of effort. This feedstock is readily available from any natural carbon source and will be of increasing significance in the future. A number of routes to specific petrochemical intermediates have been developed. Thus ethylene glycol has been produced directly from syngas using a rhodium cluster catalyst [1, 2] or a ruthenium carbonyl based catalyst [3]; methanol has been converted to ethanol [4] and short chain carboxylic acids have been homologated [5, 6]. The last of these shows the most promise for immediate application.

The catalytic activation of C-H bonds has also generated a considerable amount of interest, mainly in academic circles. The reaction is widely applied in heterogeneously catalysed hydrocarbon processing, although there is a need for more selective operations which homogeneous catalysts may provide. A number of different systems have been investigated for C-H activation [7 to 9].

The photolysis of water to produce hydrogen and oxygen is a further popular area of research and systems incorporating soluble ruthenium bipyridyl complexes have shown particular promise [10]. Recent reviews in this area have appeared [11, 12].

In conclusion, the successful commercialisation of a number of large scale homogeneous catalytic processes during recent years has to some extent overcome the chemical industry's traditional reluctance to use soluble catalysts, especially those containing platinum-group metals. In the future we can anticipate further homogeneous processes being operated in areas where high selectivity is critical.

References:

[1] C. Masters (Advan. Organometal. Chem. **17** [1979] 61/103, 80). – [2] Union Carbide Corp. (U.S. 4162261 [1979]). – [3] B. D. Dombek (ACS Symp. Ser. No. 152 [1981] 213). – [4] G. Braca, G. Sbrana, G. Velentini, G. Andrich, G. Gregorio (Fundam. Res. Homogeneous Catal. **3** [1979] 221). – [5] J. F. Knifton (ACS Symp. Ser. No. 152 [1981] 225).

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5 Medical Use of Cytostatic Platinum Compounds

5.1 Detection of the Biological Activity of Platinum Compounds

The knowledge of the biological activity of platinum coordination compounds is an outcome of the last twenty years. The main representative of the cytostatic platinum compounds, cis-diamminedichloroplatinum(II), the so-called "cisplatin", is known as a chemical compound since more than a century. It was firstly prepared and characterized by M. Peyrone in 1844 ("Peyrone's chloride") [1].

In 1964, the biological activity of the platinum complexes was detected accidentally by B. Rosenberg who was investigating the influence of electric fields upon Escherichia coli cells cultured in vitro. Using platinum electrodes and a nutritive medium containing ammonium chloride as a nitrogen source, he observed that the bacterial cells failed to divide but continued to grow forming elongated, filamentous giant cells [2]. During the following years, it was demonstrated that the observed induction of the filamentous growth in bacteria was caused by the presence of minimum amounts of cis-diamminedichloroplatinum(II), cis-$(NH_3)_2PtCl_2$, and of cis-diamminetetrachloroplatinum(IV), cis-$(NH_3)_2PtCl_4$, which were formed electrochemically from the Pt electrodes and NH_4Cl [3 to 5].

The biological effectivity was not limited to bacteria, but the platinum complexes were also able to affect mammalian cells and exhibited strong antitumor properties against various experimental systems [6, 7].

The event of the detection of the cytostatic activity of cis-$(NH_3)_2PtCl_2$ and other platinum complexes has opened an era of inorganic cytostatic drugs. Up to now, cis-$(NH_3)_2PtCl_2$ is the most intensely investigated and the clinically most important representative of the platinum compounds; therefore, it will be mainly considered in the following sections.

References:

[1] M. Peyrone (Liebigs Ann. Chem. **51** [1844] 1/29). – [2] B. Rosenberg, L. VanCamp, T. Krigas (Nature **205** [1965] 698/9). – [3] B. Rosenberg, E. Renshaw, L. VanCamp, J. Hartwick, J. Drobnik (J. Bacteriol. **93** [1967] 716/21). – [4] B. Rosenberg, L. VanCamp, E. B. Grimley, A. Y. Thomson (J. Biol. Chem. **242** [1967] 1347/52). – [5] E. Renshaw, A. J. Thomson (J. Bacteriol. **94** [1967] 1915/8).

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5.2 Antitumor Effect of cis-Diamminedichloroplatinum(II) in Animals

cis-$(NH_3)_2PtCl_2$ was the first noble metal complex which was tested against a broad spectrum of experimental tumor systems growing as ascitic, solid or disseminated tumors in animals.

The following table summarizes the best results obtained in the course of experimental antitumor studies. It is obvious that cis-$(NH_3)_2PtCl_2$ exhibits antitumor activity against numerous transplantable tumors growing in rodents [1 to 9], against chemically induced primary tumors of rats and mice [10, 11, 12], as well as against the virally induced Rous sarcoma of chickens [4]. In some cases, the drug is apparently able to induce complete tumor regression and to cure the animals.

Antitumor Activity of cis-$(NH_3)_2PtCl_2$ as Single Agent against Experimental Tumor Systems.

tumor system	results[a]	Ref.
transplantable animal tumors		
leukemia L1210	ILS 60 to 90%	[1, 2]
leukemia P388	ILS 125%	[2]
leukemia RBA-Le	ILS 38%	[6]
dunning ascites leukemia	100% cures	[5]
myeloma MOPA 104E	100% survivors	[7]
sarcoma 180 (ascitic)	ILS 63%	[4]
sarcoma 180 (solid)	T/C 2 to 20%	[1]
	100% cures	[3]
Ehrlich ascites tumors (fluid)	100% cures	[8]
Ehrlich ascites tumors (solid)	T/C 20%	[9]
Walker 256 carcinosarcoma	100% cures	[5]
Lewis lung carcinoma	ILS 20 to 55%	[2]
	100% inhibition	[4]
B16 melanoma	ILS 80 to 280%	[2, 4]
ependymoblastoma	ILS 30 bis 140%	[2, 4]
reticulum cell sarcoma	ILS 141%	[4]
chemically induced animal tumors		
ICI 42, 464 – induced lymphatic or myeloid leukemias[b]	ILS 300%	[12]
DMBA – induced mammary carcinoma[c]	20 to 35% cures	[10]
FANFT – induced bladder carcinoma[d]	ILS 40 to 70%	[11]
virally induced animal tumors		
Rous sarcoma	65% cures	[4]

[a] ILS = increase in lifespan of treated over control animals;

$$T/C = \frac{\text{tumor mass in treated animals}}{\text{tumor mass in control animals}} \times 100;$$

[b] ICI 42,464 = 2γ-chloro-β-isopropylamine ethylnaphthalene hydrochloride.

[c] DMBA = 7,12-dimethylbenz[α]anthracene;

[d] FANFT = N-[4-(5-nitro-2-furyl)-2-thiazolyl]formamide.

These results indicate that (I) cis-$(NH_3)_2PtCl_2$ is active against a series of quite different tumors including ascitic, solid and disseminated tumor sytems, (II) the activity is independent of schedules and routes of administration, and (III) there is no evidence of animal specificity.

References:

[1] B. Rosenberg, L. VanCamp, J. E. Trosko, V. H. Mansour (Nature **222** [1969] 385/6). – [2] M. K. Wolpert-DeFilippes (Cancer Treat. Rept. **63** [1979] 1453/8). – [3] B. Rosenberg, L. VanCamp (Cancer Res. **30** [1970] 1799/802). – [4] B. Rosenberg (Naturwissenschaften **60** [1973] 399/406). – [5] R. J. Kociba, S. D. Sleight, B. Rosenberg (Cancer Chemother. Rept. I **54** [1970] 325/8).

[6] J. Kovařík, F. Švec, D. Zemanová (Neoplasma **24** [1977] 475/86). – [7] V. K. Ghanta, M. T. Jones, D. A. Woodard, J. R. Durant, R. N. Hiramoto (Cancer Res. **37** [1977] 771/4). – [8] P. Köpf-Maier, B. Hesse, H. Köpf (J. Cancer Res. Clin. Oncol. **96** [1980] 43/51). – [9] P. Köpf-Maier, W. Wagner, B. Hesse, H. Köpf (Eur. J. Cancer **17** [1981] 665/9). – [10] C. W. Welsch (J. Natl. Cancer Inst. **47** [1971] 1071/8).

[11] M. S. Soloway (Cancer Res. **37** [1977] 2918/29). – [12] B. J. Leonhard, E. Eccleston, D. Jones, P. Todd, A. Walpole (Nature **234** [1971] 43/5).

5.3 Clinical Trials with cis-Diamminedichloroplatinum(II)

Clinical experience with cis-$(NH_3)_2PtCl_2$ has been gathered since 1971. The most extensively and successfully investigated tumors have been genito-urinary as well as tumors of the head and neck [1 to 10]. Nowadays, clinical application of cis-$(NH_3)_2PtCl_2$ as a cytostatic drug represents the main practical use of platinum with respect to its biological activity.

In this section, the clinical information classified by tumor type is briefly discussed. The results obtained by treatment with cis-$(NH_3)_2PtCl_2$ as single agent are summarized in the table on p. 323.

References:

[1] J. A. Gottlieb, B. Drewinko (Cancer Chemother. Rept. I **59** [1975] 621/8). – [2] F. K. V. Leh, W. Wolf (J. Pharm. Sci. **65** [1976] 315/28). – [3] M. Rozencweig, D. D. Von Hoff, M. Slavik, F. M. Muggia (Ann. Intern. Med. **86** [1977] 803/12). – [4] J. H. Burchenal (Biochimie **60** [1978] 915/23). – [5] E. Wiltshaw (Biochimie **60** [1978] 925/9).

[6] D. D. Von Hoff, M. Rozencweig (Advan. Pharm. Chemother. **16** [1979] 273/98). – [7] M. Rozencweig, D. D. Von Hoff, R. Abele, F. M. Muggia (in: H. M. Pinedo, Cancer Chemotherapy 1979: The EORTC Cancer Chemotherapy Annual 1, Excerpta Med., Amsterdam 1979, pp. 107/25). – [8] D. C. Ash (J. Clin. Hematol. Oncol. **10** [1980] 55/62). – [9] A. W. Prestayko, S. T. Crooke, S. K. Carter (Cisplatin: Current Status and New Developments, Academic, New York 1980). – [10] M. L. Gutierrez, S. T. Crooke (Cancer Treat. Rev. **6** [1979] 153/64).

5.3.1 Genito-Urinary Tumors

Testicular Tumors. Testicular neoplasms have proved to be those human tumors which are most sensible to the treatment with cis-$(NH_3)_2PtCl_2$. The results of the administration against seminomas as well as against non-seminomas (i.e., embryonal carcinomas, teratocarcinomas, choriocarcinomas) of the testis demonstrate a remarkable cytostatic activity of the inorganic drug against these neoplasms. The substance induces partial and complete remissions even when it is applied to patients with advanced stages of testicular tumors [1 to 12]. The response rates vary between 30 and 90% (mean value 58%; table on p. 323), the duration of remissions after single agent therapy amounts from several months up to some years. In comparison to other cytostatic drugs, these results qualify cis-$(NH_3)_2PtCl_2$ to be the most active cytostatic drug against testicular neoplasms.

When the compound is incorporated into combination regimens with other drugs (e.g., vinblastine and bleomycin), the therapeutic effectiveness against human testicular tumors increases highly up to a 100% response rate [13 to 22]; the remissions often last several years, ~60% of the patients are apparently cured. Many of the responding tumors in these studies have been refractory to other cytostatic drugs.

Prostatic Carcinomas. The activity of cis-$(NH_3)_2PtCl_2$ as single agent against carcinomas of the prostate has been documented in several studies [4, 12, 23 to 26]. The drug shows an overall response rate of 30% (table on p. 323) ranging from 12% up to 50%. The responses last between 2 and 16 months and lead to a significant increase of the survival time; in contrast to testicular tumors, however, long-lasting regressions occur only rarely.

Penile Carcinomas. The epidermoid penile carcinomas – even in advanced stages – also show objective responses to the treatment with cis-$(NH_3)_2PtCl_2$ [4, 27, 28] (table on p. 323). Although the duration of remissions only amounts to some months, cis-$(NH_3)_2PtCl_2$ has to be considered as one of the more active agents in the treatment of penile carcinomas.

Ovarian Carcinomas. In analogy to the high activity of cis-$(NH_3)_2PtCl_2$ against testicular tumors, the drug also shows marked efficacy against the corresponding female neoplasms, i.e., the tumors of the ovary. Even in patients who were intensively pretreated by surgery, radiotherapy or by other chemotherapeutic drugs (mostly by alkylating agents), cis-$(NH_3)_2PtCl_2$ given as single agent induces remission of 20 to 50% (mean value 33%; table on p. 323). The duration of remissions, however, is short (3 to 15 months).

Combination with other chemotherapeutic drugs (e.g., adriamycin, cyclophosphamide) results in a further increase of the response rate and in a prolongation of the remission phase up to 2 years [33, 40, 43]. In the case of advanced ovarian carcinomas, the best results have been obtained by the combination of a cis-$(NH_3)_2PtCl_2$ based chemotherapy with prior cytoreductive surgery. This combination leads to response rates of 60 to 70% and to the survival of some of the responders of more than 3 years; single patients are obviously cured [44 to 46].

Today, cis-$(NH_3)_2PtCl_2$ is one of the most useful drugs in the treatment of the highly malignant ovarian carcinomas. In combination with other cytostatic drugs and with surgical removal of the primary tumor, cis-$(NH_3)_2PtCl_2$ leads to high response rates in contrast to the poor results with standard single drugs and combinations without cis-$(NH_3)_2PtCl_2$.

Uterine Carcinomas. The treatment of advanced, inoperable carcinomas of the uterine cervix with cis-$(NH_3)_2PtCl_2$ is of established, but limited value. The drug induces response rates of 20 to 90% (mean value 38%; table on p. 323), the duration of remissions, however, is short and lasts only 2 to 5 months. In the case of the carcinomas of the endometrium, cis-$(NH_3)_2PtCl_2$ does not appear to be active.

Bladder Carcinomas. Against bladder carcinomas, mainly against transitional cell carcinomas even in advanced, metastatic stages, cis-$(NH_3)_2PtCl_2$ exhibits a remarkable degree of effectiveness. The drug applied as single agent induces partial remissions (duration 1 to 13 months) in 31% of the treated patients (table on p. 323) and causes a significant prolongation of life span. The comparison with the effect of other cytostatic drugs shows that cis-$(NH_3)_2PtCl_2$ is at present one of the more active agents against bladder carcinomas [4, 12, 52 to 62].

Local application (intravesical instillation) of cis-$(NH_3)_2PtCl_2$ [4, 63], however, seems to be ineffective in controlling superficial bladder carcinomas.

5.3.2 Carcinomas of the Head and Neck

The tumors of the head and neck, mainly the adenoid cystic carcinomas of the salivary glands and the epidermoid carcinomas, represent another important group of tumors which are sensitive to the treatment with cis-$(NH_3)_2PtCl_2$ as single agent [3, 64 to 72] or in combination whith other cytostatic drugs (e.g., methotrexate, 5-fluorouracil) [73, 74, 75]. The overall response rate with the single agent in a pooled series of patients is 44% (table on p. 323) whereby the optimum values reach 75% [69]. If a combination therapy is applied, the response rates increase up to 50 to 90% [73, 74, 75] with a duration of remissions of 1 to 18 months. The disease-free interval can be prolonged up to several years by the combination of a cis-$(NH_3)_2PtCl_2$-based chemotherapy with radical surgery or with radiotherapy [68, 76, 77].

5.3.3 Bronchogenic Tumors

In the case of bronchogenic tumors ("lung tumors"), monotherapy with cis-$(NH_3)_2PtCl_2$ as single agent [78 to 93] does not appear to be of significant benefit since objective responses do not occur with the same frequency as those observed in genito-urinary or head and neck tumors. Only in some studies [83, 90, 92] a distinct effectiveness could be shown for cis-$(NH_3)_2PtCl_2$ as single agent against carcinomas of the lung.

When the substance is combined with other cytostatic agents, a significant improvement in the response rate occurs against small cell and non-small cell carcinomas of the lung in comparison to standard protocols, the duration of remissions, however, only lasts 2 to 14 months [94 to 100].

5.3.4 Miscellaneous Tumors

Among **skin tumors**, the highly malignant melanomas are most frequent. Treatment of melanomas with cis-$(NH_3)_2PtCl_2$ as single agent [101 to 104] or in combination with other cytostatic drugs [105 to 109] apparently offers only limited therapeutic advantage.

Investigations of the last few years have shown that cis-$(NH_3)_2PtCl_2$ exhibits cytostatic activity against various histologic types of primary and metastatic **brain tumors** [110 to 113]. This observation has been quite unexpected because the compound does obviously not pass the intact blood-brain-barrier (see Section 5.4, pp. 327/8).

In the case of **gastrointestinal tumors**, cis-$(NH_3)_2PtCl_2$ seems to have some effect against carcinomas of the esophagus and the stomach [114 to 118]. Against human colorectal carcinomas, however, no activity has been demonstrated for the substance up to now [119].

Human **lymphomas**, i.e., Hodgkin lymphomas as well as non-Hodgkin lymphomas, are characterized by some sensibility to cis-$(NH_3)_2PtCl_2$ therapy [120 to 127], which induces short-lasting responses in 6 to 50% (mean value 28%; table on p. 323) of the treated patients.

Taking in account the therapeutic results of cis-$(NH_3)_2PtCl_2$ against divers **pediatric tumors** [128 to 138], the drug has also to be considered as an active agent in childhood tumors, especially in osteosarcoma and neuroblastoma.

Against **leukemias** of children or of adults, finally, the substance does not seem to have any activity [139, 140].

Clinical Activity of cis-$(NH_3)_2PtCl_2$ as Single Agent against Various Human Tumors in Advanced Stages.

tumor type	mean response rate[a)]		Ref.
genito-urinary tumors			
testicular tumors	91/156	(58%)	[1 to 12]
prostatic carcinomas	54/182	(30%)	[4, 12, 23 to 26]
penile carcinomas	8/15	(53%)	[4, 27, 28]
ovarian carcinomas	104/318	(33%)	[3, 8, 12, 29 to 39]
carcinomas of the uterine cervix	40/104	(38%)	[3, 12, 39, 47 to 49]
carcinomas of the uterine endometrium	14/55	(25%)	[3, 50, 51]
bladder carcinomas	106/338	(31%)	[4, 12, 52 to 62]
carcinomas of the head and neck	77/174	(44%)	[3, 64 to 72]
bronchogenic tumors	88/587	(15%)	[78 to 93]
skin tumors	8/34	(24%)	[101 to 104]
brain tumors	17/43	(40%)	[110 to 113]
gastrointestinal tumors			
esophageal carcinomas	6/30	(20%)	[114, 115, 116]
gastric carcinomas	6/29	(21%)	[115, 117, 118]
colorectal carcinomas	0/32	(0%)	[119]
lymphomas	29/103	(28%)	[120 to 127]
pediatric tumors	52/256	(20%)	[128 to 138]

[a)] Response = 50 to 100% regression of measurable tumor masses; response rate = number of responders related to the total of treated patients; a mean response rate is given which was averaged over the single response rates given by the authors.

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5.4 Organ Distribution and Pharmacokinetics of cis-Diamminedichloroplatinum(II)

Studies on the organ distribution of platinum after application of cis-$(NH_3)_2PtCl_2$ to animals or to men [1 to 5] have revealed a pronounced uptake of platinum into the liver, the intestine, and – in even higher concentrations – into the kidneys where platinum remains accumulated more than in other organs for at least 12 days after drug application. The platinum levels also remain elevated in the skin, in the uterus and in the ovary for a long time after treatment; the accumulation in these organs is of significance in the light of the cytostatic activity of cis-$(NH_3)_2PtCl_2$ in melanomas and in uterine and ovarian carcinomas (cf. Section 5.3). There is apparently no preferential uptake of platinum into tumors [4].

No penetration of cis-$(NH_3)_2PtCl_2$ or other platinum-containing species into the central nervous system (brain and spinal cord) can be observed [3, 6, 7, 8]. Similarly, only minimum amounts of platinum are detectable within the embryonal compartment after treatment of pregnant mice with cis-$(NH_3)_2PtCl_2$ during early organogenesis [9]. These uncommon results are explainable by the obvious inability of the platinum compound to pass the blood-brain-barrier as well as, at early stages of pregnancy, the placental barrier. In the case of most brain tumors, however, the blood-brain-barrier is apparently violated so that the platinum species enters the brain compartment and is even enriched within the intracerebral tumors [8, 10] – an effect which may explain the antitumor activity of cis-$(NH_3)_2PtCl_2$ against divers brain tumors (cf. Section 5.3).

The plasma levels of platinum after cis-$(NH_3)_2PtCl_2$ application to a variety of animal species and man demonstrate a biphasic clearance of platinum with an initial rapid phase (half-life values: overall $t_{1/2}$ = 20 to 70 min; in man $t_{1/2}$ = 25 to 50 min) followed by a slow phase (overall $t_{1/2}$ = 2 to 10 d; in man $t_{1/2}$ = 58 to 73 h) [1 to 4, 11, 19]. This means that even up to 2 weeks after drug application, platinum is still recognizable in the blood. In tissue samples, platinum is detectable as long as 4 months after administration [12].

After intravenous injection of cis-$(NH_3)_2PtCl_2$, the platinum-containing species is rapidly bound to blood cells and to plasma proteins. Already 1 h after injection and during the following 3 days, a portion of only 5 to 0.2% of the total platinum in the blood is present as non-bound, filtrable platinum species [13].

Portions of ~70 to 90% of the filtrable platinum in the plasma are present as chemically unchanged cis-$(NH_3)_2PtCl_2$ [14]. This confirms the assumption that the hydrolytic reactions giving rise to, inter alia, aquated or hydroxo diammineplatinum(II) complexes as well as to hydroxo-bridged dinuclear and trinuclear species, do not occur in the extracellular space [15, 16, 17].

The elimination of cis-$(NH_3)_2PtCl_2$ from the organism is mainly (80 to 90%) accomplished by the kidneys [4, 18], whereby platinum enters the urine predominantly by glomerular filtration [11, 19], but also by active tubular excretion [19]. Only small amounts of platinum are eliminated via the bile [18, 20].

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5.5 Side Effects and Toxicity of cis-Diamminedichloroplatinum(II)

The organs which are mainly injured by cis-$(NH_3)_2PtCl_2$ are the kidneys and the intestine, whereas the bone marrow is affected to a markedly less extent [1, 2]. This pattern of toxicity is quite unlike to that caused by other cytostatic drugs and shows signs of heavy-metal promoted symptoms.

Nephrotoxicity. The principal target for the toxic action of cis-$(NH_3)_2PtCl_2$ is the kidney [1, 2]. Although several regimens have been developed to reduce renal toxicity, e.g., intravenous hydration along with induction of forced diuresis by mannitol or furosemide [3, 5], the severe nephrotoxicity of cis-$(NH_3)_2PtCl_2$ is still a factor which often limits the therapeutic usefulness of this drug [3].

The cis-$(NH_3)_2PtCl_2$ induced histological findings in the kidney are mainly characterized by degenerative and necrotic alterations of the tubular epithelial cells; a majority of authors found the proximal convoluted tubules to be more extensively affected than the distal ones [3, 6 to 11].

The functional renal disturbances after treatment consist of changes in intrarenal blood flow and in a reduction of glomerular filtration rate which manifests in the elevation of blood retention values, i.e., of blood urea nitrogen (BUN) and of creatinine content [2, 3, 7, 8, 9, 11, 12];

in extreme cases, an uremic status may develop [2, 3]. On the other hand, because of tubular damage, the reabsorption of water, K^+, Ca^{++}, and Mg^{++} is diminished; this results in polyuria, hypokalemia, hypomagnesemia, and hypocalcemia, see **Fig. 35** [3, 13, 14, 15]. As a clinical complication of hypocalcemia and hypomagnesemia, the occurrence of tetanic symptoms has been reported [16].

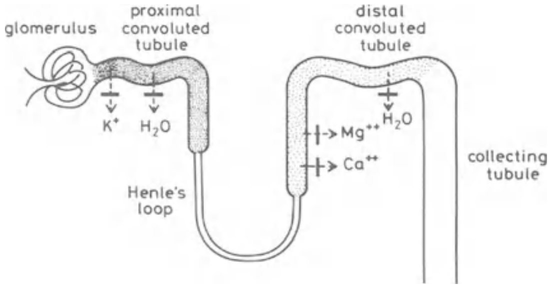

Fig. 35. Nephrotoxicity of cis-$(NH_3)_2PtCl_2$. Disturbances of the reabsorption of water and different ions as a consequence of structural damages in the proximal and in the distal convoluted tubules of the kidney (schematic representation).

Concerning the reasons for the severe nephrotoxicity of cis-$(NH_3)_2PtCl_2$, similar mechanisms as have been described for other heavy-metal compounds seem to be of significance [3, 12]. One important intracellular event may be the reaction with protein SH groups [17] leading to functional aberrations of enzymes [18, 19, 20] and, later on, to structural lesions of the tubular cells. This development is favoured by pharmacokinetic conditions given by the complex renal excretion of the platinum compound which involves glomerular filtration as well as tubular excretion and tubular reabsorption [21].

Gastrointestinal Toxicity. In the intestine, cis-$(NH_3)_2PtCl_2$ induces the inhibition of proliferative activity [22] and the occurrence of histologic injuries, especially of the crypt cells in the small intestine [23]. The corresponding clinical symptoms are nausea, vomiting, and, occasionally, diarrhea [24]. These side-effects can be troublesome and disagreeable in a manner that withdrawal of the treatment may be necessary. It should be pointed out that, on exposure to other heavy metals (e.g., mercury or lead) in elemental or chemically bound form, severe gastrointestinal affection is also a major toxic effect.

Hematologic Toxicity. Compared to other cytostatic drugs, the toxic influence of cis-$(NH_3)_2PtCl_2$ upon bone marrow is not very pronounced. Most investigators described a mild affection of the three blood cell types resulting in transient and moderate leukopenia, thrombocytopenia, and anemia [2, 24].

Neurotoxicity. The neurotoxic influence of cis-$(NH_3)_2PtCl_2$ manifests (I) by damaging and destroying the outer hair cells in the organ of Corti in the inner ear [25, 26, 27], and (II) by demyelination and axonal degeneration in peripheral nerves [24, 28]. The resulting symptoms are (I) tinnitus, hearing loss and deafness especially for higher frequencies [2, 24, 29], and (II) distal sensory disturbances described as peripheral neuropathies of the "glove and stocking" type [24, 28, 30, 31].

It is striking that these neurologic symptoms resemble the neurotoxic phenomena caused by other heavy-metal compounds, e.g., of lead, mercury, or thallium [31].

Allergic Reactions. Allergic reactions after cis-$(NH_3)_2PtCl_2$ application have been reported occasionally. Skin rash and, more often, anaphylactic reactions such as facial edema, tachycardia or hypotension occurred [24, 32].

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5.6 Structure-Activity Relation and Cytostatic Platinum Complexes of the “Second Generation”

Structure-Activity Relation

The detection of the antitumor activity [1] of cis-diamminedichloroplatinum(II), cis-$(NH_3)_2PtCl_2$, has prompted the synthesis and the testing of many related platinum complexes [2 to 9, 28]. From these studies, the structure-activity relation described below has been deduced [2 to 9, 28].

Role of Configuration and Coordination. The antitumor activity of platinum complexes L_2PtX_2 is apparently confined to complexes with cis configuration, whereas the corresponding trans compounds, though chemically more reactive, turned out to be cytostatically inactive. Examples investigated in this respect are the cis and trans isomers of $(NH_3)_2PtBr_2$ and L_2PtCl_2 with L being ammonia, methylamine, ethylamine, pyrrolidine, or cyclohexylamine [7, 28]. It must be supposed that this unique activity of cis isomers is caused by particular reactions with the intracellular target molecules [11].

It is likely that the DNA is the intracellular target for cytostatic platinum compounds [29 to 33], whereby the formation of interstrand as well as intrastrand cross-links by the platinum moiety within the DNA could be established [34 to 37]. In consideration of the high specificity of the cis-configurated complexes, however, the formation of intrastrand chelates has been postulated to be the critical molecular interaction of cytostatic platinum compounds with DNA [11, 37 to 40]. Two types of intrastrand linkages have revealed to be most probable: (I) the chelation of a L_2Pt^{2+} moiety between two adjacent guanine bases at their N7 sites [37, 39, 41, 42]; (II) the chelation of L_2Pt^{2+} within one guanine base at the N7 and the O6 sites [11, 37, 43 to 45], see **Fig. 36**. Recent results especially stress the biological importance of the guanine-guanine linkage within the same strand of DNA.

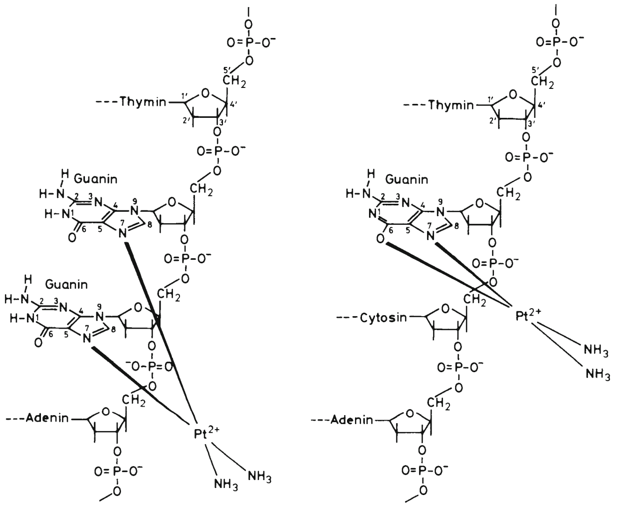


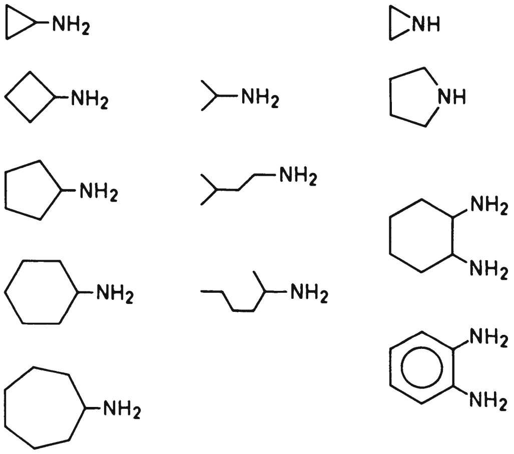
Fig. 36 Two postulated types of intrastrand cross-links in the reaction products of cis-$(NH_3)_2PtCl_2$ with DNA according to [43].

The geometry of the cytostatically active complexes is either planar or octahedral; the planar complexes L_2PtX_2 contain platinum in the +2 oxidation state, whereas Pt^{IV} is present in the octahedral complexes L_2PtX_4 [11].

Only neutral platinum complexes are known to be active; charged Pt^{II} complexes investigated have exhibited no antitumor activity. This phenomenon is possibly connected with the problem of drug transport through cell membranes [5, 6].

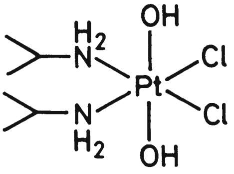
Role of the Leaving Groups X in cis-L_2PtX_2. The chemistry of all cytostatic platinum complexes is dominated by the ability of some of their ligands to exchange quickly. For these anionic leaving groups X, either two monodentate ligands in cis position or one bidentate ligand are required. They must be moderately strong Lewis bases and the rate of exchange of the leaving groups should, at least in the case of monodentate ligands, fall into a restricted "window of lability". The following ligands X have shown to be most suitable: (I) the monodentate ligands Cl^- and Br^-; (II) the bidentate ligands sulphate, oxalate, malonate, and divers substituted malonates. A special advantage of the bidentate ligands is that they enhance the water solubility of the platinum complexes [2 to 9].

Role of the Non-Labile Groups L in cis-L_2PtX_2. The donors L in trans position to the leaving groups X are always strongly bonded, relatively inert amine groups of either monodentate or bidentate neutral ligand molecules. Although they are expected to have only a secondary effect on the reactivity of the complexes they probably act as carrier ligands and, therefore, are important for the cytostatic properties of the complexes. By variation of the amine ligands L, the toxicity of the complexes can be widely influenced and, as a consequence, the therapeutic index can be considerably increased. Whereas substitution of the hydrogen atoms in ammonia by alkyl groups mostly diminishes antitumor activity, the introduction of heterocyclic or alicyclic and, in some cases, also of aromatic amines causes a marked increase of the therapeutic index which is mainly due to decreased toxicity. The following ligands L have turned out to be most advantageous [2 to 9]:



Platinum Complexes of the "Second Generation"

Among the numerous platinum compounds for which cytostatic activity has been reported, only a choice of about twelve representatives (see p. 333) has been selected as strong candidates for a second drug generation to substitute or supply cis-$(NH_3)_2PtCl_2$ in the future [8, 12 to 19]. Compared with cis-$(NH_3)_2PtCl_2$, many of them have differing chemical and physical properties, especially the solubility in aqueous systems is enhanced [12, 20, 21]. At the experimental stage, most of the platinum complexes of the second generation have shown improved antitumor activity [12, 14 to 19], decreased renal toxicity [14, 15, 19] and lack of cross-resistance to cis-$(NH_3)_2PtCl_2$ [13, 15].



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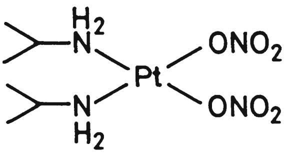

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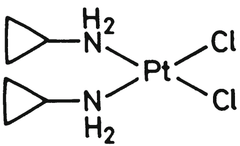

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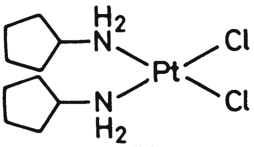

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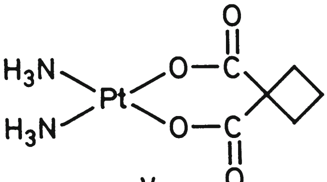

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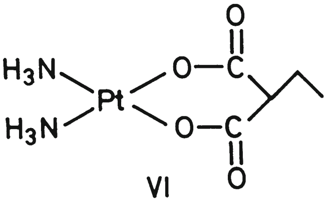

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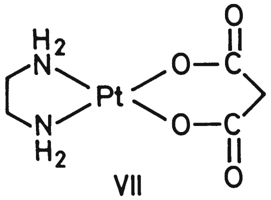

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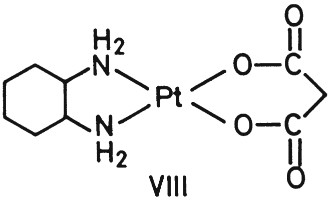

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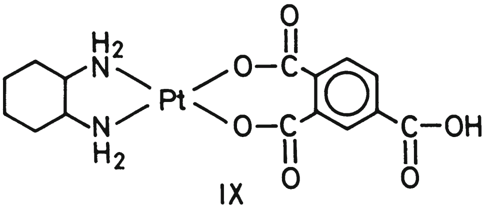

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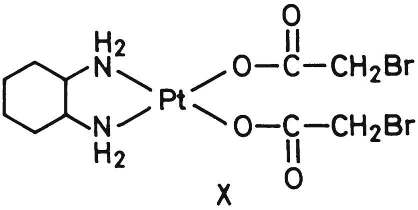

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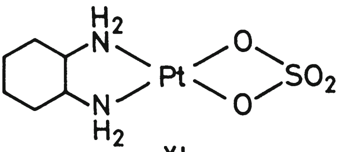

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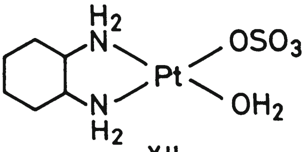


XII

Platinum complexes of the “second generation”:

I bis(isopropylamine)-cis-dichloro-trans-dihydroxoplatinum(IV);
II cis-bis(isopropylamine)dinitratoplatinum(II);
III cis-bis(cyclopropylamine)dichloroplatinum(II);
IV cis-bis(cyclopentylamine)dichloroplatinum(II);
V diammine(cyclobutane-1,1-dicarboxylato)platinum(II);
VI diammine(ethylmalonato)platinum(II);
VII ethylenediamine(malonato)platinum(II);
VIII 1,2-diaminocyclohexane(malonato)platinum(II);
IX 1,2-diaminocyclohexane(4-carboxyphthalato)platinum(II);
X 1,2-diaminocyclohexanebis(bromoacetato)platinum(II);
XI 1,2-diaminocyclohexane(sulphato)platinum(II);
XII 1,2-diaminocyclohexaneaquo(sulphato)platinum(II).

Some of these compounds have been tested in clinical trials. Whereas early investigations did not establish superior clinical properties of the platinum complexes of the "second generation" in men [10, 20, 21], recent studies have shown reduced toxicity, mainly reduced nephrotoxicity in men compared with cis-$(NH_3)_2PtCl_2$ [46, 47] and indicated antitumor activity against ovarian carcinoma and small cell lung cancer [47]. At present, the most promising "second generation" platinum complexes are apparently compounds I ("CHIP", "iproplatin") and V ("CBDCA", "carboplatin"); see pp. 332/3.

Other New-Developed Cytostatic Platinum Compounds

Platinum-Pyrimidine Complexes. The di-aquo hydrolysis product of cis-$(NH_3)_2PtCl_2$ reacts slowly with thymine, uracil, and related pyrimidine derivatives to give water-soluble, deeply coloured complexes, the so-called platinum-pyrimidine blues [22]. The platinum blues are considered to be oligomeric or polymeric cationic species containing platinum ions in "mixed" oxidation states, partial Pt-Pt bonding and amidate (deprotonated amide) ligands bridging the Pt atoms [8, 23, 24]. This structural suggestion has been deduced from X-ray crystallographic data of the model complex shown in **Fig. 37**.

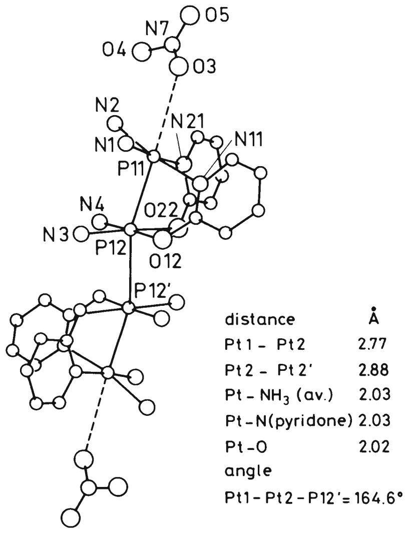
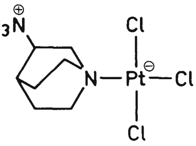


Fig. 37. Structure of the tetranuclear cation of the α-pyridine complex $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5 \cdot H_2O$. Hydrogen atoms and non-associated nitrate ions are omitted [24].

For the platinum-pyrimidine blues, promising antitumor activity and minor nephrotoxic side effects compared with cis-$(NH_3)_2PtCl_2$ have been derived from animal experiments [4, 22]. Preparations of platinum uracil blues were tested in thirteen patients; however, the clinical study was interrupted because of a fatal cardiopulmonary arrest and ineffectiveness in other patients [20].

Trichloroplatinum(II) Complexes. Another type of potential cytostatic compounds has been designed in several new platinum(II) complexes having the general formula $LPtCl_3$ where L is a ligand which bears a formal positive charge and which is bonded via a nitrogen atom (L = monoprotonated diamine) or an olefinic double bond (L = protonated amino-olefin) to platinum [25, 26, 27]. The complexes exhibit cytostatic activity in some in vitro and in vivo systems; the best antitumor activity comparable to that of cis-$(NH_3)_2PtCl_2$ could be shown for 3-aminoquinuclidinium-trichloroplatinum(II):



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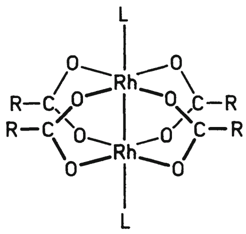
5.7 Cytostatic Complexes of Platinum Metals Other than Platinum

Palladium Complexes. Complexes of palladium, the lighter homologue of platinum, have been screened for cytostatic activity at early stages after the discovery of the tumor-inhibiting properties of cis-diamminedichloroplatinum(II).

There are only few reports on good antitumor properties of palladium(II) and palladium(IV) complexes such as cis-$(NH_3)_2PdCl_2$, cis-$(NH_3)_2PdCl_4$, $[(\pi\text{-}C_3H_5)PdCl]_2$ [1] or (diaminocyclohexane)Pd(malonate) [29]. In contrast to these results, most authors observed only marginal or even no biological activity of palladium complexes; this could be confirmed for palladium compounds which are structurally analogous to antitumor platinum complexes [2, 3], as well as for those which contain ligands cytostatically active by themselves, e.g., antimetabolites [4] or thiosemicarbazone derivatives [5].

It has been supposed that the apparent cytostatic ineffectiveness of palladium complexes compared to platinum complexes is explainable by the enhanced lability and reactivity of the regarded palladium compounds [6].

Rhodium and Iridium Complexes. The rhodium(II) carboxylates (see formula below) have been found to reveal strong tumor-inhibiting properties against various experimental tumor systems [7 to 11].



Among the divers carboxylates investigated ($R = CH_3$, CH_2CH_3, $CH_2CH_2CH_3$, CH_2OCH_3; $L = H_2O$), rhodium(II) butyrate ($R = CH_2CH_2CH_3$), followed by rhodium(II) propionate ($R = CH_2CH_3$), are the most potent inhibitors of tumor growth [8].

With regard to the molecular mechanism of action, the rhodium(II) carboxylates markedly inhibit DNA synthesis [8, 12, 13]. This effect is probably mediated by the inhibition of enzymes involved in DNA synthesis [13, 14].

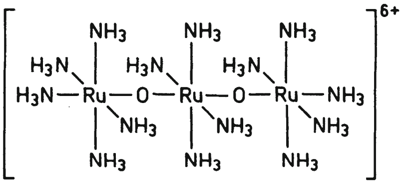
In the series of tested rhodium(III) compounds, antitumor activity has been found mainly in species of the octahedral type mer-L_3RhX_3 ($L = NH_3$ or another monodentate amine, or L_3 = tridentate diethylenetriamine; X = anionic ligand), the activity being most pronounced for the complex with $L = NH_3$ and X = Cl [15]. Another octahedral, cationic complex type, trans-$[L_4RhX_2]X$ ($L = NH_3$ or pyridine or L_2 = ethylenediamine) exhibited marginal cytostatic activity. The corresponding iridium(III) amine complexes are cytostatically inactive [15].

In the case of rhodium(I) and iridium(I) complexes, weak antitumor activity has been reported for some complexes containing the square planar d^8 system [16, 17]: (I) for some rhodium(I) cyclo-octadiene complexes [16], e.g., $COD(NH_3)RhCl$ or COD(piperidine)RhCl (COD = cis, cis-1,5-cyclooctadiene); (II) for dimeric rhodium(I) compounds, e.g., $[(COD)RhCl]_2$; (III) for the rhodium(I) and iridium(I) acetylacetonate derivatives (NBD)Rh(acac) and for (COD)Ir(acac) (NBD = bicyclo(2,2,1)hepta-2,5-diene, acac = acetylacetonate) [17].

Ruthenium Complexes. Numerous octahedral complexes of ruthenium(II) and ruthenium(III) are characterised by antitumor activity [18, 19]. The main representatives are: (I) the neutral Ru^{III} complex $(NH_3)_3RuCl_3$ (mixture of mer and fac isomers); (II) the cationic Ru^{III} complexes cis-$[(NH_3)_4RuCl_2]Cl$ and $[(NH_3)_5RuCH_3CH_2COO](ClO_4)_2$; (III) the bi-ionic Ru^{III} complex $[(en)_2RuC_2O_4][(en)Ru(C_2O_4)_2]$ (en = ethylenediamine) [19]; (IV) the neutral Ru^{II} complex cis-$(DMSO)_4RuCl_2$ (DMSO = dimethylsulfoxide) [18].

With respect to the molecular mode of action of these complexes, there is experimental support that cellular DNA is the target site and that the inhibition of DNA synthesis leads to the cytostatic activity [3, 18 to 23].

Another ruthenium complex, the so-called "ruthenium red" containing the trinuclear cation $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]_5^{6+}$ (see formula below), which serves as selective stain for mucopolysaccharides in microscopy, also exhibits good antitumor activity against various experimental tumor systems [24, 25, 26].



$$[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$$

The molecular mode of action of ruthenium red differs principally from that of the other known platinum-metal containing cytostatic compounds. Ruthenium red inhibits specifically the cell membrane Ca^{2+}-ATPase [27] and impairs the Ca^{2+} transport at the mitochondrial and cellular membrane [28]. Moreover, it is apparently accumulated in tumors [24].

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5.8 Outlook

The development of the merely inorganic compound cis-diamminedichloroplatinum(II) to a clinically approved cytostatic drug has fertilized the field of bio-inorganic chemistry and stimulated experimental studies on biological properties of other inorganic compounds. In the mean time, antitumor activity has also been detected for some non-platinum metal or other inorganic compounds: (I) for early transition-metal compounds, namely the metallocene dihalides [1, 2]; (II) for main-group element compounds, e.g., gallium salts [3, 4] or diorganotin complexes [5]; (III) for some cyclophosphazene derivatives [6].

It can be expected that the near future will bring further information concerning biological properties of inorganic compounds and that the significance of inorganic compounds will increase with respect to their application in medicine.

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Table of Conversion Factors

Following the notation in Landolt-Börnstein [7], values which have been fixed by convention are indicated by a bold-face last digit. The conversion factor between calorie and Joule that is given here is based on the thermochemical calorie, $\mathrm{cal}_{\mathrm{th\,ch}}$, and is defined as 4.184**0** J/cal. However, for the conversion of the "Internationale Tafelkalorie", $\mathrm{cal}_{\mathrm{IT}}$, into Joule, the factor 4.1868 J/cal is to be used [1, p. 147]. For the conversion factor for the British thermal unit, the Steam Table Btu, $\mathrm{BTU}_{\mathrm{ST}}$, is used [1, p. 95].

Force	N	dyn	kp
1 N (Newton)	1	10^5	0.1019716
1 dyn	10^{-5}	1	1.019716×10^{-6}
1 kp	$9.8066\mathbf{5}$	$9.8066\mathbf{5} \times 10^5$	1

Pressure	Pa	bar	kp/m²	at	atm	Torr	lb/in²
1 Pa (Pascal) = 1 N/m²	1	10^{-5}	1.019716×10^{-1}	1.019716×10^{-5}	0.986923×10^{-5}	0.750062×10^{-2}	145.0378×10^{-6}
1 bar = 10^6 dyn/cm²	10^5	1	10.19716×10^3	1.019716	0.986923	750.062	14.50378
1 kp/m² = 1 mm H_2O	$9.8066\mathbf{5}$	$0.98066\mathbf{5} \times 10^{-4}$	1	10^{-4}	0.967841×10^{-4}	0.735559×10^{-1}	1.422335×10^{-3}
1 at = 1 kp/cm²	$0.98066\mathbf{5} \times 10^5$	$0.98066\mathbf{5}$	10^4	1	0.967841	735.559	14.22335
1 atm = 76**0** Torr	$1.0132\mathbf{5} \times 10^5$	$1.0132\mathbf{5}$	1.033227×10^4	1.033227	1	760	14.69595
1 Torr = 1 mm Hg	133.3224	1.333224×10^{-3}	13.59510	1.359510×10^{-3}	1.315789×10^{-3}	1	19.33678×10^{-3}
1 lb/in² = 1 psi	6.89476×10^3	68.9476×10^{-3}	703.069	70.3069×10^{-3}	68.0460×10^{-3}	51.7149	1

Work, Energy, Heat	J	kWh	kcal	Btu	MeV
1 J (Joule) = 1 Ws = 1 Nm = 10^7 erg	1	2.778×10^{-7}	2.39006×10^{-4}	9.4781×10^{-4}	6.242×10^{12}
1 kWh	$\mathbf{3.6}\times10^{6}$	1	860.4	3412.14	2.247×10^{19}
1 kcal	4184.**0**	1.1622×10^{-3}	1	3.96566	2.6117×10^{16}
1 Btu (British thermal unit)	1055.06	2.93071×10^{-4}	0.25164	1	6.5858×10^{15}
1 MeV	1.602×10^{-13}	4.450×10^{-20}	3.8289×10^{-17}	1.51840×10^{-16}	1

1 eV $\triangleq$ 23.0578 kcal/mol = 96.473 kJ/mol

Power	kW	PS	kp·m/s	kcal/s
1 kW = 10^{10} erg/s	1	1.35962	101.972	0.239006
1 PS	0.73550	1	**75**	0.17579
1 kp·m/s	$\mathbf{9.80665}\times10^{-3}$	0.01333	1	2.34384×10^{-3}
1 kcal/s	4.184**0**	5.6886	426.650	1

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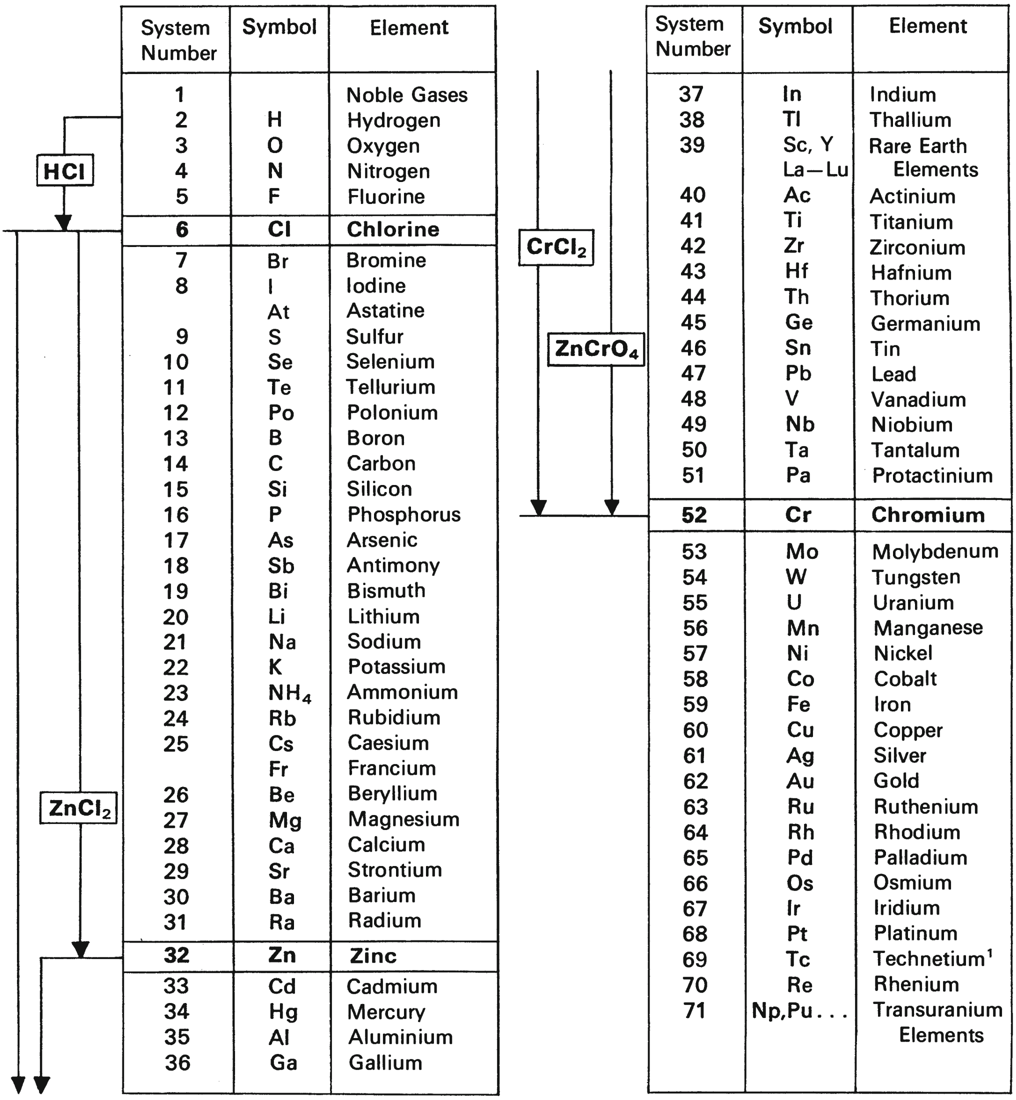
Key to the Gmelin System of Elements and Compounds



System Number	Symbol	Element
1		Noble Gases
2	H	Hydrogen
3	O	Oxygen
4	N	Nitrogen
5	F	Fluorine
6	**Cl**	**Chlorine**
7	Br	Bromine
8	I	Iodine
	At	Astatine
9	S	Sulfur
10	Se	Selenium
11	Te	Tellurium
12	Po	Polonium
13	B	Boron
14	C	Carbon
15	Si	Silicon
16	P	Phosphorus
17	As	Arsenic
18	Sb	Antimony
19	Bi	Bismuth
20	Li	Lithium
21	Na	Sodium
22	K	Potassium
23	NH_4	Ammonium
24	Rb	Rubidium
25	Cs	Caesium
	Fr	Francium
26	Be	Beryllium
27	Mg	Magnesium
28	Ca	Calcium
29	Sr	Strontium
30	Ba	Barium
31	Ra	Radium
32	**Zn**	**Zinc**
33	Cd	Cadmium
34	Hg	Mercury
35	Al	Aluminium
36	Ga	Gallium

System Number	Symbol	Element
37	In	Indium
38	Tl	Thallium
39	Sc, Y La—Lu	Rare Earth Elements
40	Ac	Actinium
41	Ti	Titanium
42	Zr	Zirconium
43	Hf	Hafnium
44	Th	Thorium
45	Ge	Germanium
46	Sn	Tin
47	Pb	Lead
48	V	Vanadium
49	Nb	Niobium
50	Ta	Tantalum
51	Pa	Protactinium
52	**Cr**	**Chromium**
53	Mo	Molybdenum
54	W	Tungsten
55	U	Uranium
56	Mn	Manganese
57	Ni	Nickel
58	Co	Cobalt
59	Fe	Iron
60	Cu	Copper
61	Ag	Silver
62	Au	Gold
63	Ru	Ruthenium
64	Rh	Rhodium
65	Pd	Palladium
66	Os	Osmium
67	Ir	Iridium
68	Pt	Platinum
69	Tc	Technetium[1]
70	Re	Rhenium
71	Np,Pu...	Transuranium Elements

Material presented under each Gmelin System Number includes all information concerning the element(s) listed for that number plus the compounds with elements of lower System Number.

For example, zinc (System Number 32) as well as all zinc compounds with elements numbered from 1 to 31 are classified under number 32.

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[1] A Gmelin volume titled "Masurium" was published with this System Number in 1941.

A Periodic Table of the Elements with the Gmelin System Numbers is given on the Inside Front Cover