MAX-PLANCK-GESELLSCHAFT

Fritz-Haber-Institute, Max-Planck-Society,
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High Temperature Catalysis

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Lecture Series “Modern Methods in Heterogeneous Catalysis”
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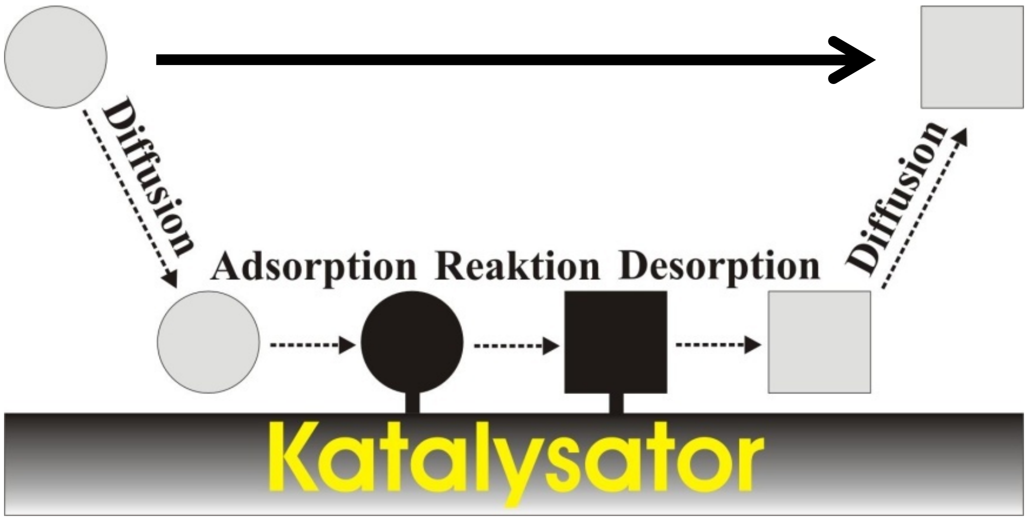
unicat
Unifying Concepts in Catalysis

Emmy Noether-Programm
Deutsche Forschungsgemeinschaft
DFG

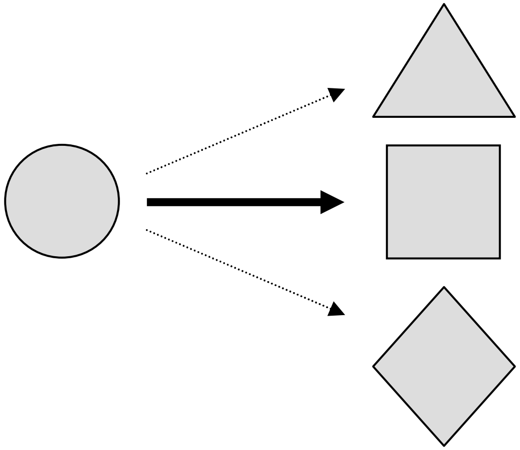
Outline

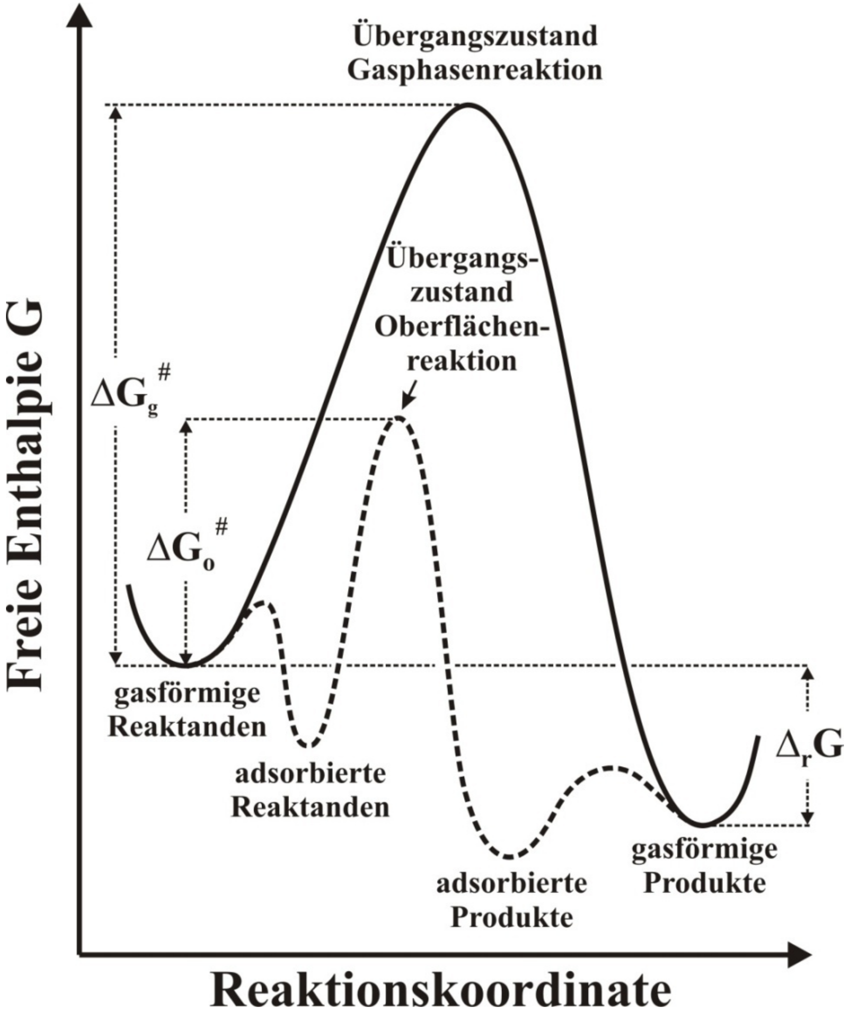
1. What is “High Temperature Catalysis”
2. Why can solid bodies glow and how can I measure their temperature?
3. High Temperature Catalytic Processes in Industry and Research
4. Surface and Gas Phase Reaction Kinetics
5. Physical Transport Processes of Momentum, Heat and Mass
6. Interaction of Chemistry and Transport
7. Numerical Simulation of High Temperature Catalytic Reactions
8. Research Example: Autothermal Methane Oxidation on Rh and Pt

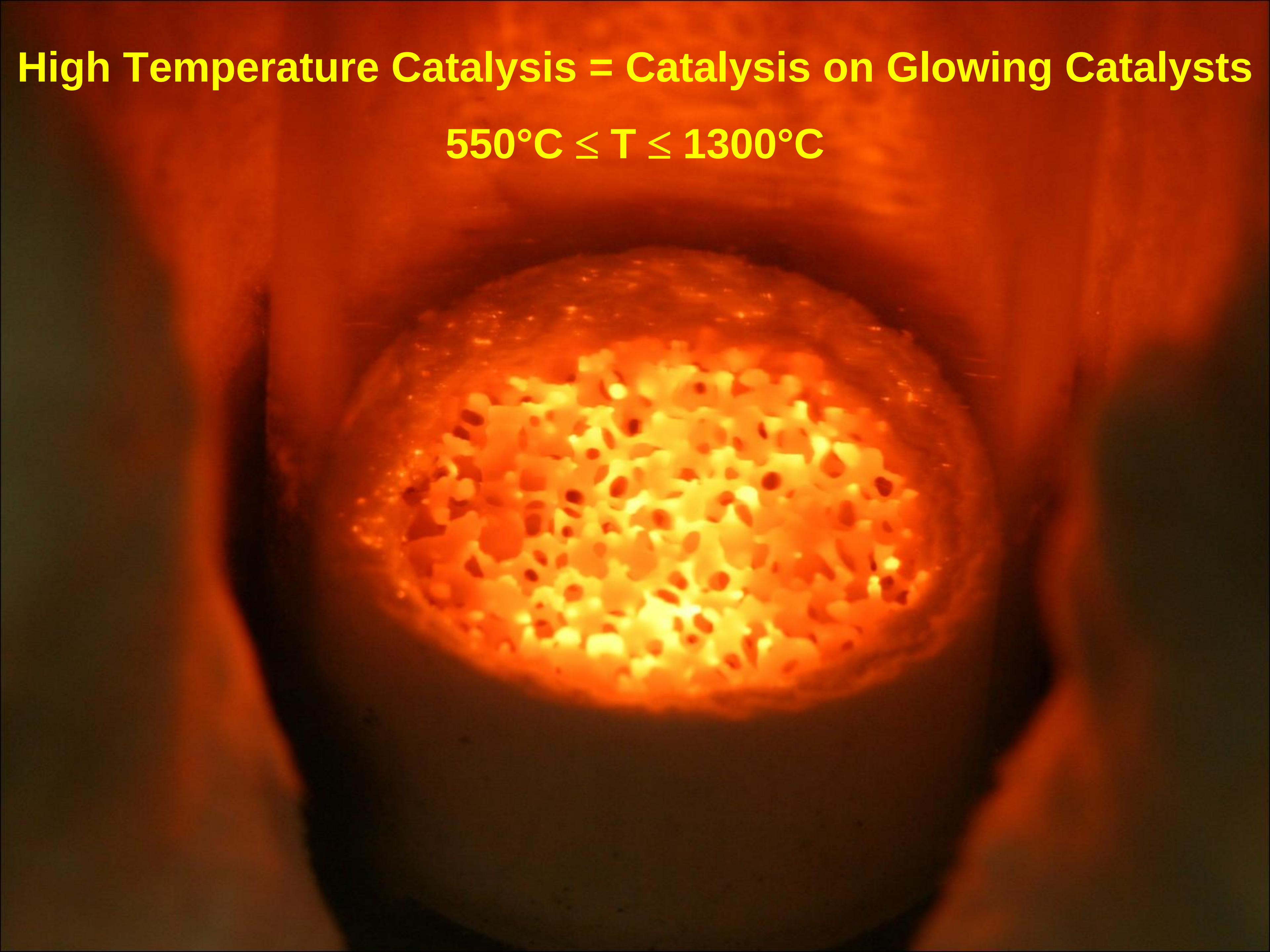
1. What is „High Temperature Catalysis“



$$r \propto e^{-\frac{\Delta G^\#}{RT}} \qquad r_o > r_g$$







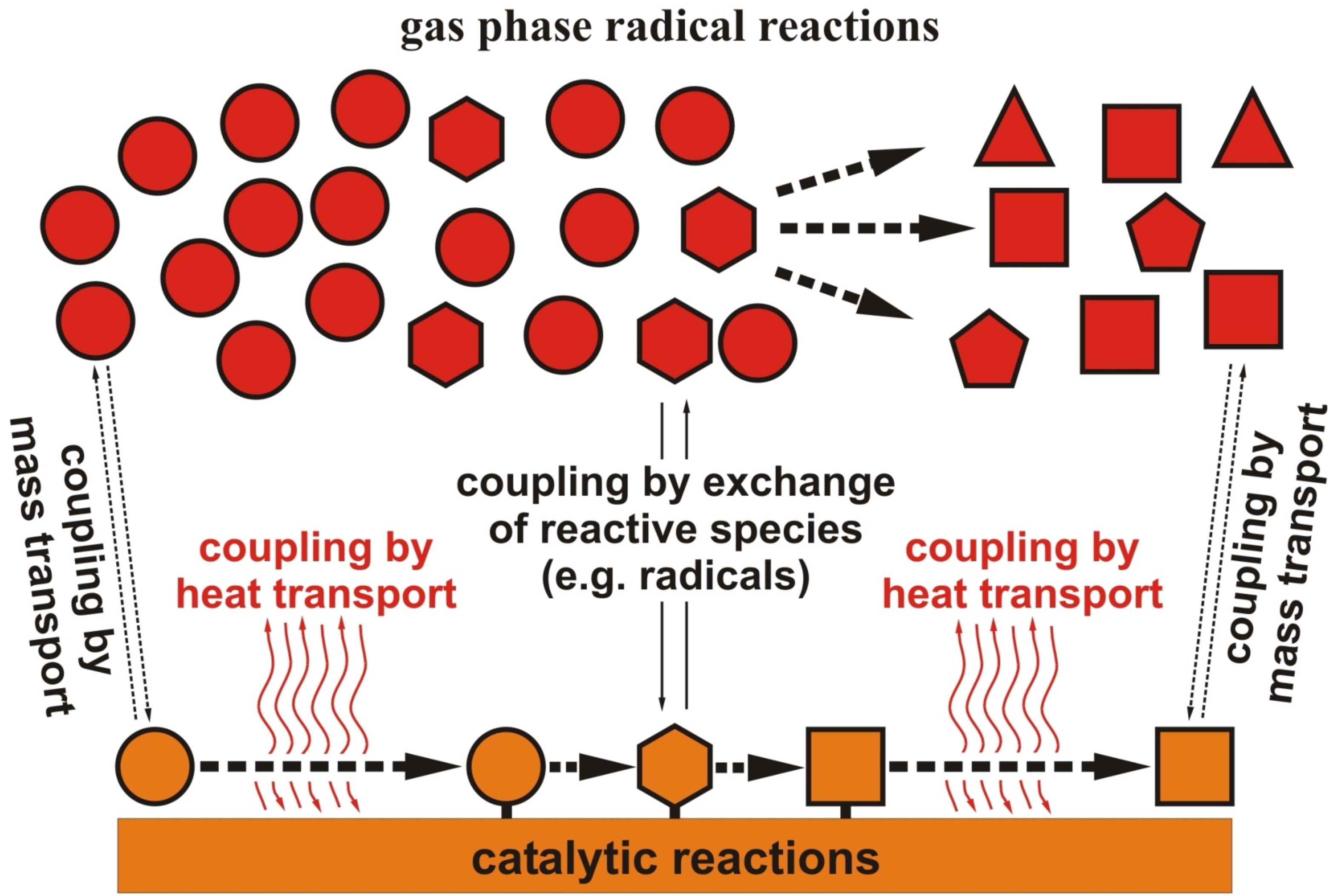
High Temperature Catalysis = Catalysis on Glowing Catalysts

$550°C \leq T \leq 1300°C$

High Temperature Catalysis = Catalysis on Glowing Catalysts

550°C ≤ T ≤ 1300°C

1. What is „High Temperature Catalysis“



2. Why can solid bodies glow ?

- **when a solid body is heated its surface emits radiation of wavelengths in the range 0.1-10µm called thermal radiation**
- **heating raises some of the atoms and molecules of which the solid body consists of to higher energy levels from which they return spontaneously to lower energy states emitting electromagnetic radiation**
- **electromagnetic radiation can be either thought off as waves with a wavelength $\lambda=c/\nu$ or as a bunch of photons with an energy $\varepsilon=h\nu$**
- **absorptivity and emissivity of an (opaque) body are defined as follows:**

$$a_\nu = \frac{q_\nu^{(a)}}{q_\nu^{(i)}} \qquad e_\nu = \frac{q_\nu^{(e)}}{q_{b\nu}^{(i)}}$$

- **$q_\nu^{(a)}d\nu$ and $q_\nu^{(i)}d\nu$ are the absorbed and incident radiation energy per unit area per unit time in the frequency range ν to $\nu+d\nu$**

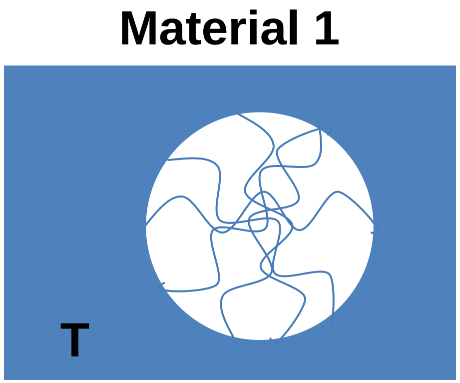
2. Why can solid bodies glow ?

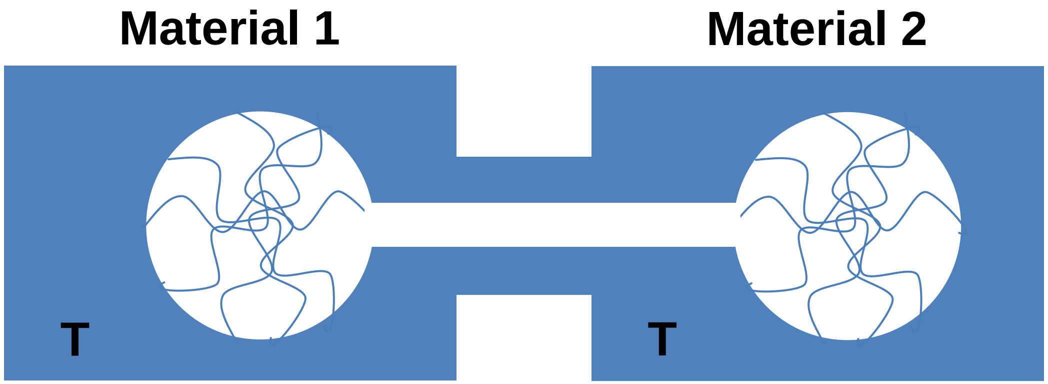
$$a_\nu = \frac{q_\nu^{(a)}}{q_\nu^{(i)}} \qquad e_\nu = \frac{q_\nu^{(e)}}{q_{b\nu}^{(i)}}$$

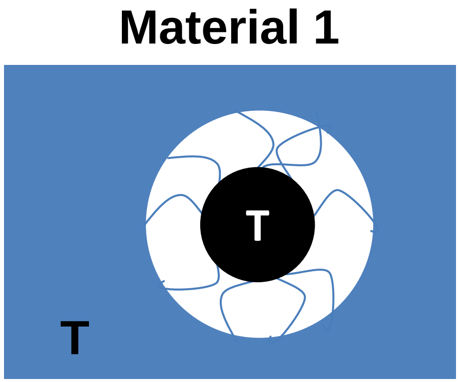
Some comments on that:

- **for any real body, a_ν will be less than unity and will vary considerably with ν and temperature**
- **a hypothetical body for which a_ν will be less than unity but independent of ν and temperature is called a gray body**
- **the limiting case of a gray body with a_ν=1 defines a black body**
- **the emissivity e_ν is also a quantity less than unity for real, non-fluorescing surfaces and is equal to unity for black bodies**

2. Why can solid bodies glow ?







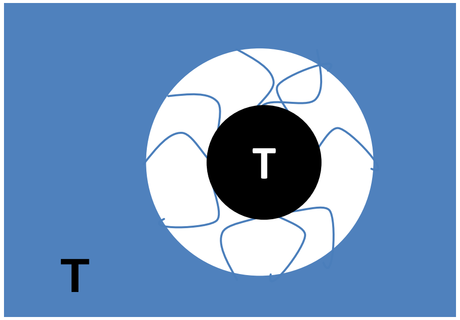
$$q^{(cav)} = q_b^{(e)}$$

2. Why can solid bodies glow ?

number of modes inside a cavity of volume V

$$N(\nu)=\frac{8\pi\nu^3}{3c_n^3}V \Rightarrow p_\nu=\frac{1}{V}\frac{dN}{d\nu}=\frac{8\pi\nu^2}{c_n^3}$$

Material 1



$$q^{(cav)}=q_b^{(e)}$$

Traditional Physics (Rayleigh-Jeans 1905)

$$\langle E\rangle=\frac{\int_0^\infty E\cdot\exp[-(E/kT)]dE}{\int_0^\infty \exp[-(E/kT)]dE}=kT$$

$$\rho_\nu=p_\nu\langle E\rangle=\frac{1}{V}\frac{dN}{d\nu}=\frac{8\pi\nu^2}{c_n^3}kT$$

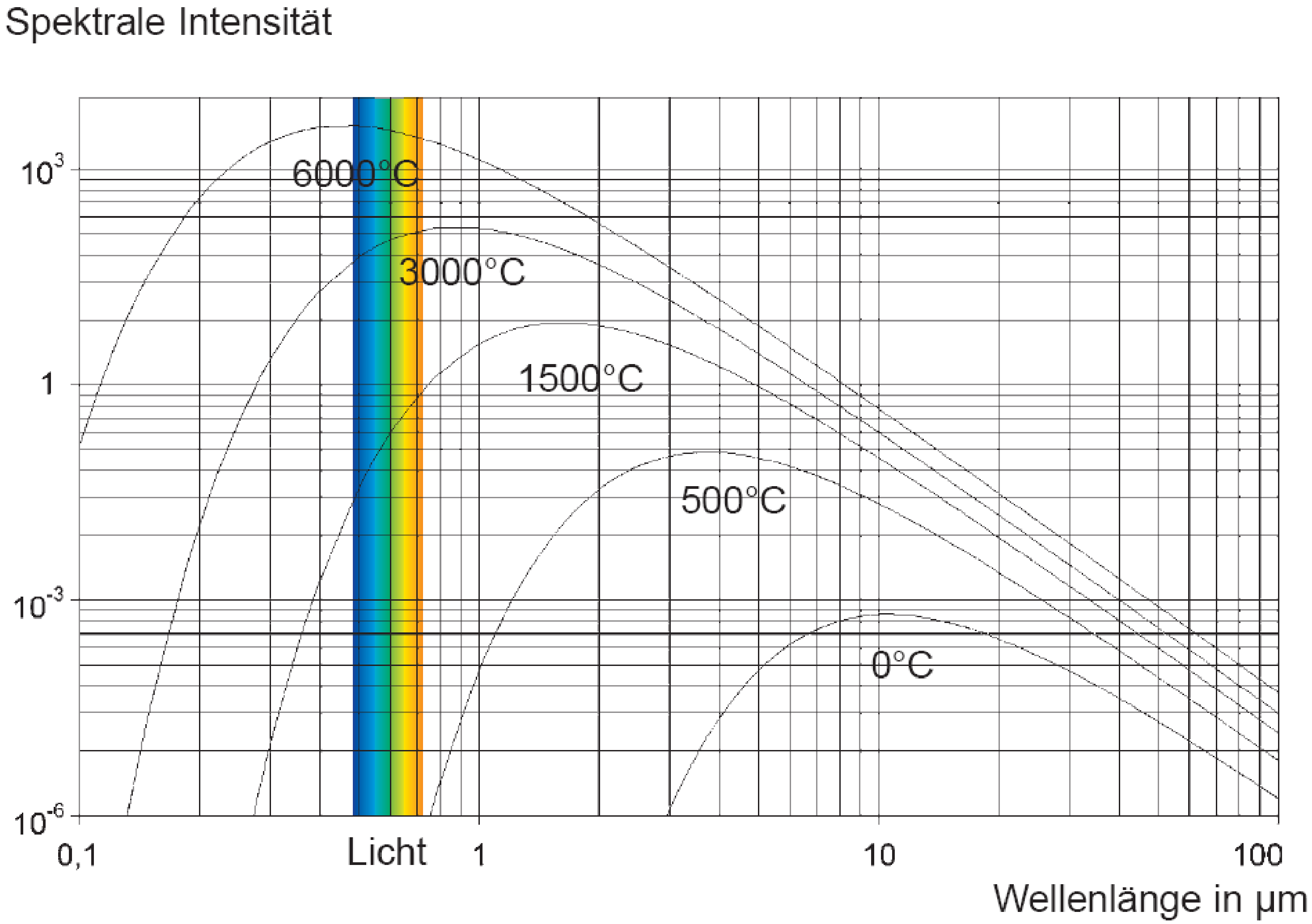
Ultraviolet-Catastrophe

Quantum Physics Max Planck 1900

$$\langle E\rangle=\frac{\sum_{n=0}^\infty nh\nu\cdot\exp[-(nh\nu/kT)]}{\sum_{n=0}^\infty \exp[-(nh\nu/kT)]}=\frac{h\nu}{\exp(h\nu/kT)-1}$$

$$\rho_\nu=p_\nu\langle E\rangle=\frac{1}{V}\frac{dN}{d\nu}=\frac{8\pi\nu^2}{c_n^3}\frac{h\nu}{\exp(h\nu/kT)-1}$$

2. Why can solid bodies glow ?

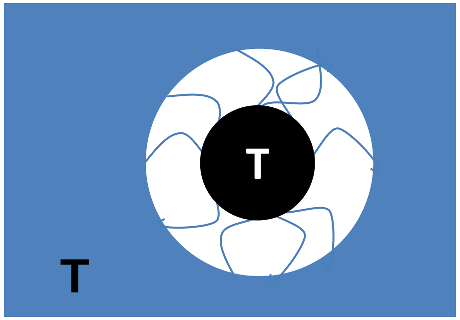


Wien‘s Displacement Law: $\lambda_{\max} T = 0.2884 \cdot cm \cdot K$

Stefan-Boltzmann Law: $q_b^{(e)} = \sigma \cdot A \cdot T^4 = 5.67 \cdot 10^{-8} \cdot A \cdot \frac{W}{m^2 K^4} \cdot T^4$

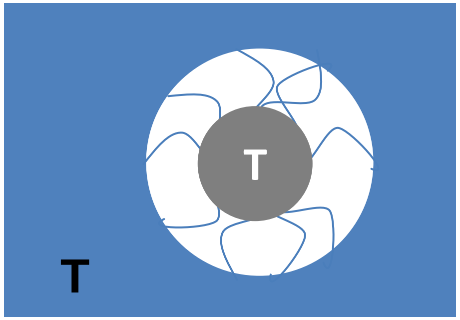
2. Temperature Measurement by Pyrometrie

Material 1



$$q^{(cav)} = q_b^{(e)}$$

Material 1



$$aq^{(cav)} = q^{(e)} \Rightarrow a = \frac{q^{(e)}}{q_b^{(e)}} = e$$

emissivities of different materials

Material	Spektralbereich 0,7 ... 1,15 µm	Spektralbereich 1,4 ... 1,8 µm	Spektralbereich 2 ... 2,5 µm	Spektralbereich 4,9 ... 5,5 µm	Spektralbereich 8 ... 14 µm
Stahl, blank	0,40 ... 0,45	0,30 ... 0,40	0,20 ... 0,35	0,10 ... 0,30	0,10 ... 0,30
Stahl, gewalzt	0,45 ... 0,55	0,35 ... 0,50	0,25 ... 0,40	0,20 ... 0,30	0,20 ... 0,30
Stahl, angelassen	0,70 ... 0,80	0,70 ... 0,85	0,45 ... 0,70	0,30 ... 0,60	0,30 ... 0,60
Stahl, oxidiert	0,80 ... 0,90	0,80 ... 0,90	0,75 ... 0,85	0,70 ... 0,90	0,60 ... 0,80
Kupfer, blank	0,06 ... 0,20	0,06 ... 0,20	0,06 ... 0,10	0,05 ... 0,10	0,03 ... 0,10
Kupfer, oxidiert	0,50 ... 0,80	0,40 ... 0,80	0,40 ... 0,80	0,20 ... 0,70	0,20 ... 0,70
Aluminium, blank	0,05 ... 0,25	0,05 ... 0,25	0,04 ... 0,20	0,03 ... 0,15	0,02 ... 0,15
Aluminium, oxidiert	0,20 ... 0,40	0,10 ... 0,40	0,10 ... 0,40	0,10 ... 0,40	0,95
NiCr, blank	0,20 ... 0,40	0,20 ... 0,40	0,20 ... 0,40	0,20 ... 0,40	0,10 ... 0,30
NiCr, oxidiert	0,65 ... 0,90	0,65 ... 0,80	0,65 ... 0,80	0,65 ... 0,80	0,50 ... 0,80
Kohle, Graphit	0,70 ... 0,95	0,70 ... 0,95	0,70 ... 0,95	0,70 ... 0,95	0,70 ... 0,95
Steine, Erde, Keramik	0,40 ... 0,70	0,40 ... 0,70	0,40 ... 0,70	0,50 ... 0,80	0,80 ... 0,95
Lacke, Farben	—	—	—	0,60 ... 0,90	0,70 ... 0,95

2. Temperature Measurement by Pyrometrie

Radiance of a black body

$$P(T) = \sigma \cdot A \cdot T^4$$

Radiance of a real body

$$P(T) = \varepsilon(\lambda) \cdot \sigma \cdot A \cdot T^4$$

Two-color pyrometer

$$\frac{P_1}{P_2} = \frac{\varepsilon(\lambda_1) \cdot \sigma \cdot A \cdot T^4}{\varepsilon(\lambda_2) \cdot \sigma \cdot A \cdot T^4}$$

$$k = \frac{\varepsilon(\lambda_1)}{\varepsilon(\lambda_2)}$$

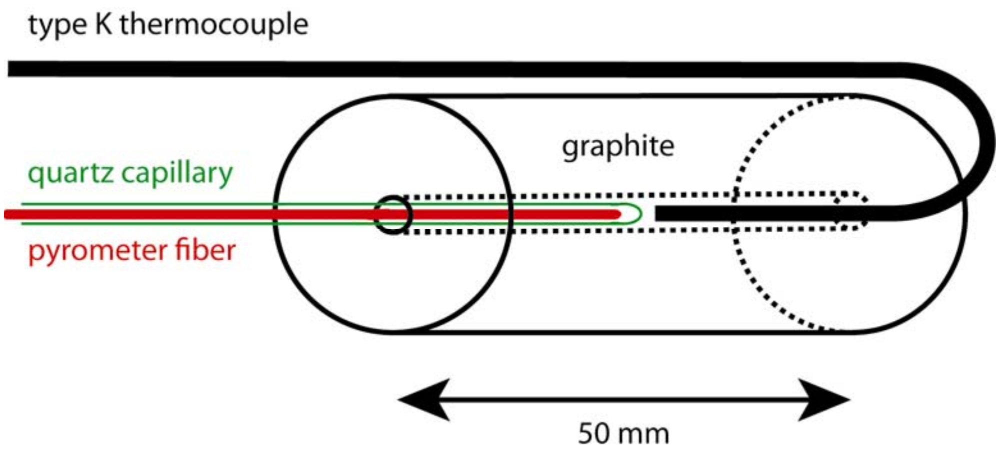
P ... total power of energy radiated from an object

ε ... emissivity

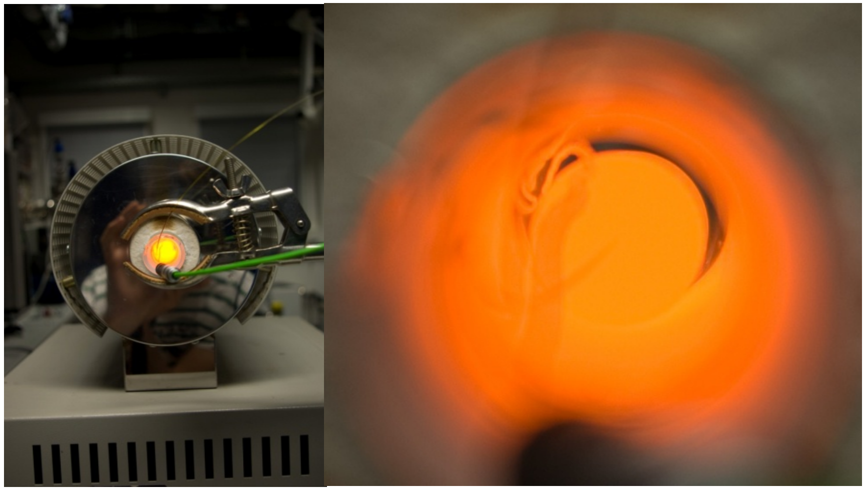
σ ... Stefan-Boltzmann constant

A ... surface area observed

T ... absolute temperature

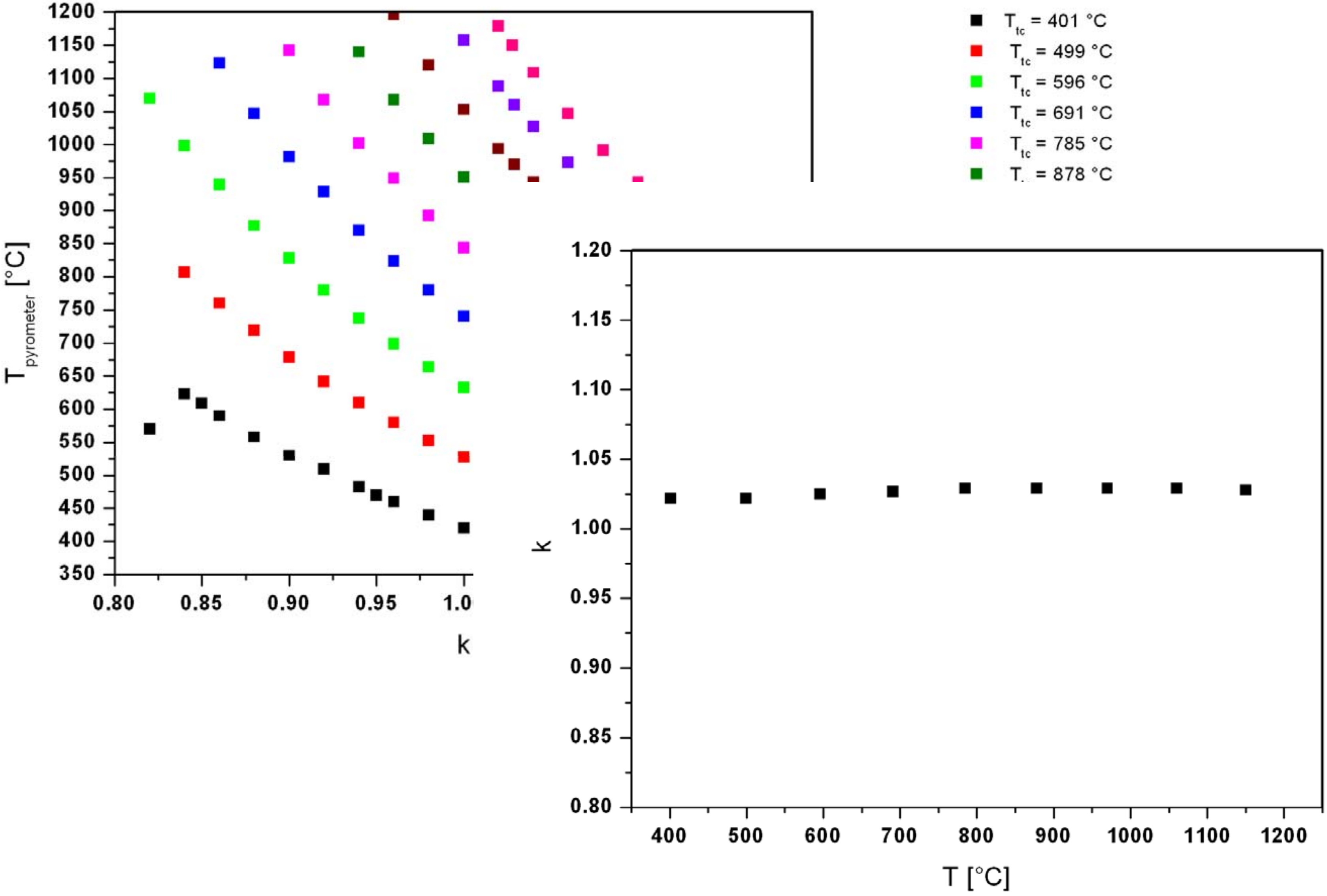


cylindrical graphite body (cavity) yielding homogeneous temperature distribution (black body)



carbon calibration body @ 1060 °C

2. Temperature Measurment by Pyrometrie



3. High Temperature Catalytic Processes in Industry and Research

- high temperature catalysis plays an important role in industry

industrial high temperature processes

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (900°C, Pt/Rh)

$NH_3 + CH_4 + 1.5O_2 \rightarrow HCN + 3H_2O$ (1200°C, Pt/Rh)

$NH_3 + CH_4 \rightarrow HCN + 3H_2$ (1200°C, Pt/Rh)

$CH_4 + H_2O \rightarrow CO + 3H_2$ (700-1100°C, Ni)

$CH_3OH + ½ O_2 \rightarrow HCHO + H_2O$ (600-720°C, Ag)

catalytic combustion (noble metals)

fuel reforming (noble metals)

solid oxide fuel cells (800-1000°C, Ni cermet / YSZ / (La,Sr)MnO_3)

3. High Temperature Catalytic Processes in Industry and Research

high temperature processes at the research stage

$CH_4 + ½\ O_2 \rightarrow CO + 2H_2$ (>1000°C, e.g. Rh)

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$ (600-800°C, e.g. Li/MgO)

$CH_4 + ½\ O_2 \rightarrow HCHO + H_2O$ (>600°C, e.g. VO_x)

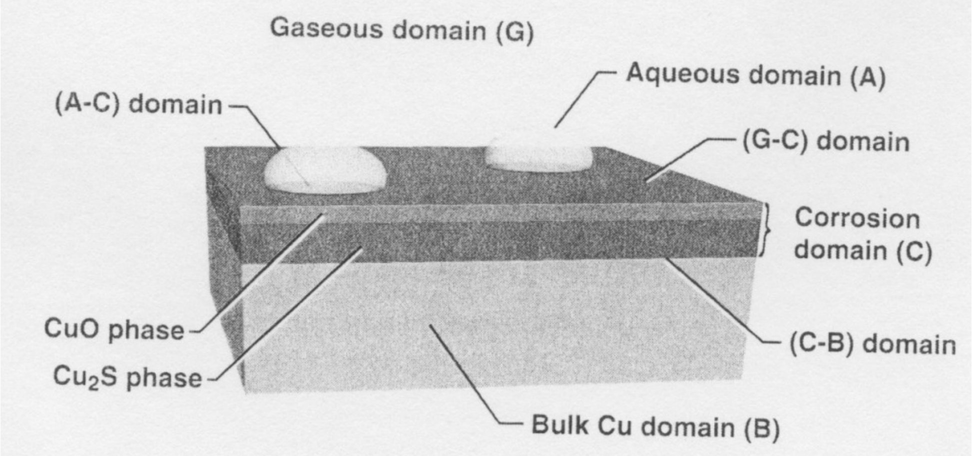
$C_2H_6 + ½\ O_2 \rightarrow C_2H_4 + H_2O$ (700-1100°C, e.g. Pt/Sn)

$C_2H_6 + ½\ O_2 \rightarrow CH_3CHO + H_2O$ (>500°C, VO_x)

4. Surface and Gas Phase Reaction Kinetics

3.1 „Bookkeeping“

example: corrosion of copper



<u>domains:</u>
e.g. gaseous domain (3D), bulk domain (3D), interphase domain (2D)

<u>phases:</u>

- **gas phase (usually 1 per domain)**
- **surface phase (1 or more per domain e.g. steps, terraces…)**
- **bulk phase (1 or more per domain, e.g. CuO, Cu$_2$S)**

<u>species:</u>

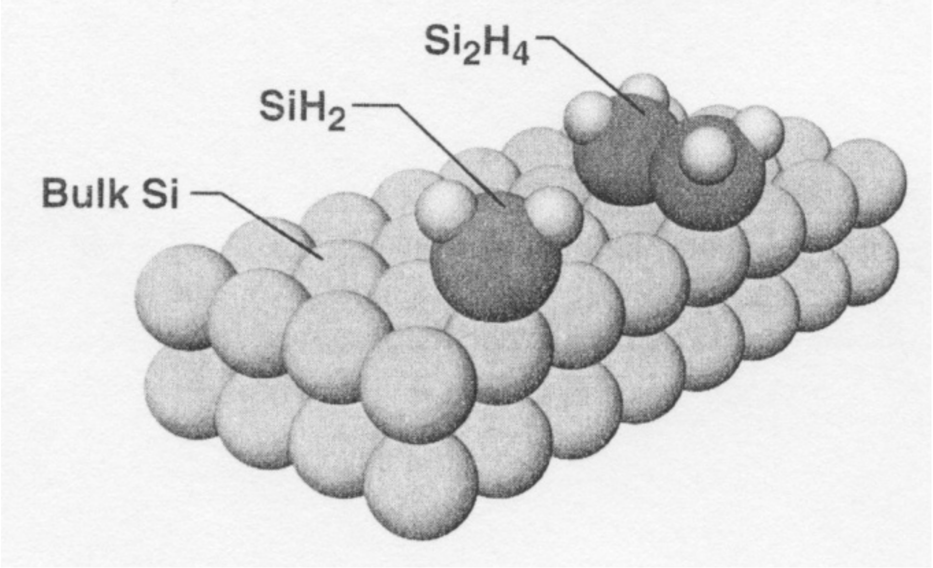
- **gas species K_g^f - K_g^l, surface species $K_s^f(n)$-$K_s^l(n)$, bulk species $K_b^f(n)$-$K_b^l(n)$**

4. Surface and Gas Phase Reaction Kinetics

4.2 Concentration within phases important for catalysis:

o for gas phase species (3D domain) the molar concentration is written

$$[X_k] = \frac{Y_k \rho}{W_k} \quad (k = K_g^f, \ldots K_g^l) \quad \text{in } \frac{mol}{m^3}$$



o the composition of surface phases is usually specified in terms of site fractions

$$\sum_{k=K_s^f(n)}^{K_s^l(n)} Z_k(n) = 1 \quad (n = N_s^f, \ldots, N_s^l)$$

o for kinetics we need the surface molar concentration of a species

$$[X_k] = \frac{Z_k(n)\Gamma_n}{\sigma_k(n)} \quad \text{in } \frac{mol}{m^2}$$

4. Surface and Gas Phase Reaction Kinetics

4.3 Surface reaction kinetics:

o **classic expressions for adsorption (Langmuir adsorption, competitive adsorption, dissociative adsorption) and surface reaction rates (Langmuir Hinshelwood Hougen Watson) can be used to describe surface kinetics in high temperature catalytic reactions**

o **these type of rate expressions are comparably ease to determine experimentally but every catalyst will have a unique rate expression**

o **for example, Pt on alumina catalysts for CO oxidation may have a similar general form of the rate expression by the numerical values of the constants will vary among formulations. Even catalysts with the same composition may have different rate expressions due to differences in the manufacturing method**

o **if the mechanism changes with experimental conditions, e.g. change of rate limiting step at changing temperatures, the general form of the rate law might change**

o **elementary step mechanisms do not have these drawbacks but are difficult to determine**

4. Surface and Gas Phase Reaction Kinetics

example 1: Langmuir adsorption isotherm for a single component A

o **the usual form of the Langmuir adsorption isotherm is**

$$\theta_A = \frac{bp_A}{1+bp_A}$$

o **this general form is readily derived from an elementary step mechanism applying mass action kinetics**

$$A + O(s) \xleftrightarrow{k_1, k_{-1}} A(s)$$

$$\frac{d[A(s)]}{dt} = 0 = k_1[A][O(s)] - k_{-1}[A(s)]$$

$$[O(s)] = \Gamma - [A(s)]$$

$$k_1[A]\Gamma = (k_{-1} + k_1[A])[A(s)]$$

$$\theta_A = \frac{[A(s)]}{\Gamma} = \frac{k_1[A]}{(k_{-1} + k_1[A])} = \frac{K_c[A]}{1 + K_c[A]}$$

$$\theta_A = \frac{K_p(p^0/RT)^{-1}\cdot(p_a/RT)}{1 + K_p(p^0/RT)^{-1}\cdot(p_a/RT)} = \frac{K_p(p_A/p^0)}{1 + K_p(p_A/p^0)}$$

4. Surface and Gas Phase Reaction Kinetics

example 2: competitive adsorption of two species A and B

o **empirical expression**

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \qquad \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

o **an analogues treatment of the following elementary step mechanism using mass action kinetics as for the Langmuir adsorption leads to**

$$A + O(s) \xleftrightarrow{k_1, k_{-1}} A(s)$$

$$B + O(s) \xleftrightarrow{k_2, k_{-2}} B(s)$$

$$\theta_A = \frac{K_{c,1}[A]}{1 + K_{c,1}[A] + K_{c,2}[B]} = \frac{K_{p,1}(p_A / p^0)}{1 + K_{p,1}(p_A / p^0) + K_{p,2}(p_B / p^0)}$$

$$\theta_B = \frac{K_{c,2}[B]}{1 + K_{c,1}[A] + K_{c,2}[B]} = \frac{K_{p,2}(p_B / p^0)}{1 + K_{p,1}(p_A / p^0) + K_{p,2}(p_B / p^0)}$$

4. Surface and Gas Phase Reaction Kinetics

example 3: Langmuir-Hinshelwood Rate Expressions

o **Langmuir-Hinshelwood (Hougen Watson) rate expressions are often used to describe surface reactions such as e.g. A(s)+B(s)→C(s)**

o **in this mechanism it is assumed that A and B adsorb competitively onto the surface and undergo a bimolecular surface reaction to C**

$$A + O(s) \xleftrightarrow{k_1, k_{-1}} A(s)$$

$$B + O(s) \xleftrightarrow{k_2, k_{-2}} B(s)$$

$$A(s) + B(s) \xrightarrow{k_{rxn}} C + 2O(s)$$

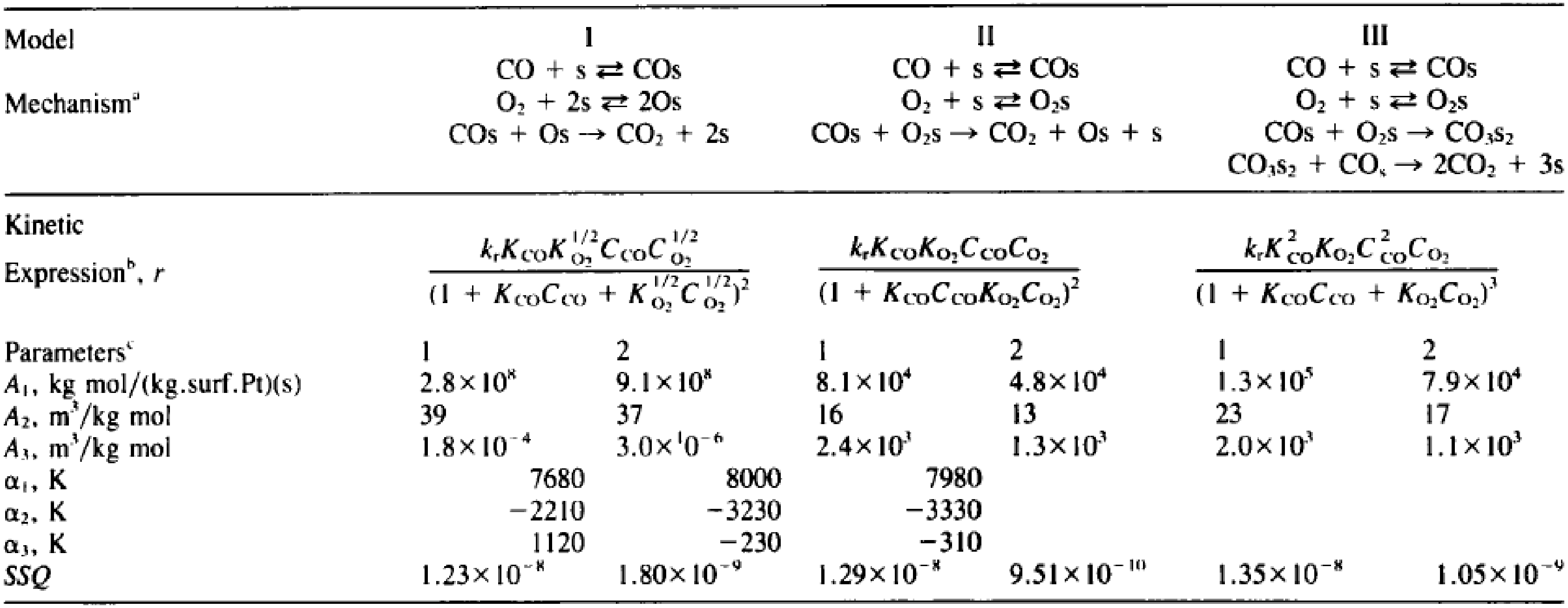
$$[A(s)] = \theta_A \cdot \Gamma = \frac{K_{c,1}\Gamma[A]}{1 + K_{c,1}[A] + K_{c,2}[B]}$$

$$[B(s)] = \theta_B \cdot \Gamma = \frac{K_{c,2}\Gamma[B]}{1 + K_{c,1}[A] + K_{c,2}[B]}$$

$$\frac{d[C]}{dt} = k_{rxn}[A(s)][B(s)] = \frac{k_{rxn}K_{c,1}K_{c,2}\Gamma^2[A][B]}{(1 + K_{c,1}[A] + K_{c,2}[B])^2}$$

4. Surface and Gas Phase Reaction Kinetics

example 3: literature results on CO oxidation on supported Pt catalysts



Model	1		II		III	
Mechanism[a]	$CO + s \rightleftarrows COs$ $O_2 + 2s \rightleftarrows 2Os$ $COs + Os \rightarrow CO_2 + 2s$		$CO + s \rightleftarrows COs$ $O_2 + s \rightleftarrows O_2s$ $COs + O_2s \rightarrow CO_2 + Os + s$		$CO + s \rightleftarrows COs$ $O_2 + s \rightleftarrows O_2s$ $COs + O_2s \rightarrow CO_3s_2$ $CO_3s_2 + CO_s \rightarrow 2CO_2 + 3s$	
Kinetic Expression[b], r	$\frac{k_r K_{CO} K_{O_2}^{1/2} C_{CO} C_{O_2}^{1/2}}{(1 + K_{CO}C_{CO} + K_{O_2}^{1/2} C_{O_2}^{1/2})^2}$		$\frac{k_r K_{CO} K_{O_2} C_{CO} C_{O_2}}{(1 + K_{CO}C_{CO}K_{O_2}C_{O_2})^2}$		$\frac{k_r K_{CO}^2 K_{O_2} C_{CO}^2 C_{O_2}}{(1 + K_{CO}C_{CO} + K_{O_2}C_{O_2})^3}$	
Parameters[c]	1	2	1	2	1	2
A_1, kg mol/(kg.surf.Pt)(s)	2.8×10^{8}	9.1×10^{8}	8.1×10^{4}	4.8×10^{4}	1.3×10^{5}	7.9×10^{4}
A_2, m^3/kg mol	39	37	16	13	23	17
A_3, m^3/kg mol	1.8×10^{-4}	$3.0\times{}^{1}0^{-6}$	2.4×10^{3}	1.3×10^{3}	2.0×10^{3}	1.1×10^{3}
α_1, K	7680	8000	7980			
α_2, K	−2210	−3230	−3330			
α_3, K	1120	−230	−310			
SSQ	1.23×10^{-8}	1.80×10^{-9}	1.29×10^{-8}	9.51×10^{-10}	1.35×10^{-8}	1.05×10^{-9}

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4. Surface and Gas Phase Reaction Kinetics

example 4: elementary step kinetic model:

$$q_i = k_i \prod_{k=1}^{K} [X_k]^{\nu'_{ki}}$$

$$k_i = A_i T^{\beta_i} \exp\left(-\frac{E_i}{RT}\right)$$

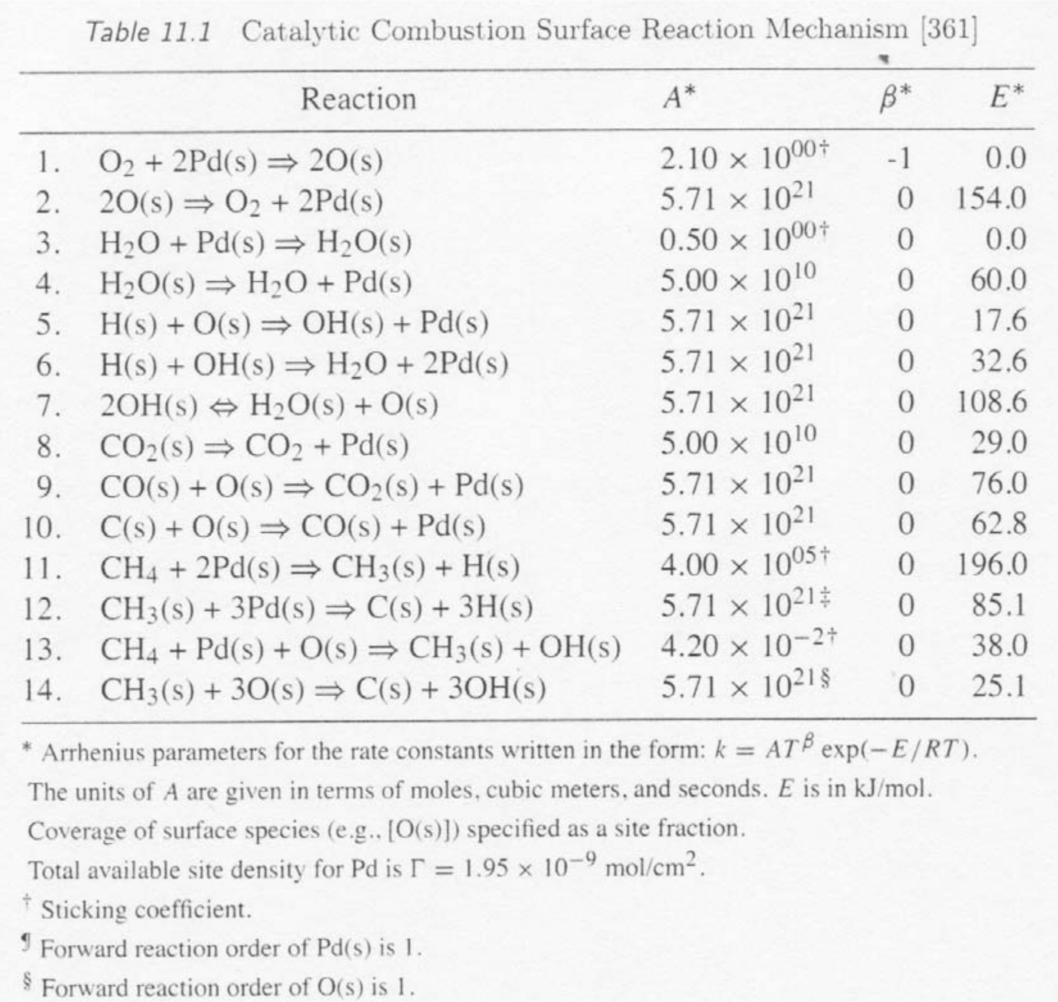


Table 11.1 Catalytic Combustion Surface Reaction Mechanism [361]

	Reaction	A^*	β^*	E^*
1.	$O_2 + 2Pd(s) \Rightarrow 2O(s)$	$2.10 \times 10^{00\dagger}$	-1	0.0
2.	$2O(s) \Rightarrow O_2 + 2Pd(s)$	5.71×10^{21}	0	154.0
3.	$H_2O + Pd(s) \Rightarrow H_2O(s)$	$0.50 \times 10^{00\dagger}$	0	0.0
4.	$H_2O(s) \Rightarrow H_2O + Pd(s)$	5.00×10^{10}	0	60.0
5.	$H(s) + O(s) \Rightarrow OH(s) + Pd(s)$	5.71×10^{21}	0	17.6
6.	$H(s) + OH(s) \Rightarrow H_2O + 2Pd(s)$	5.71×10^{21}	0	32.6
7.	$2OH(s) \Leftrightarrow H_2O(s) + O(s)$	5.71×10^{21}	0	108.6
8.	$CO_2(s) \Rightarrow CO_2 + Pd(s)$	5.00×10^{10}	0	29.0
9.	$CO(s) + O(s) \Rightarrow CO_2(s) + Pd(s)$	5.71×10^{21}	0	76.0
10.	$C(s) + O(s) \Rightarrow CO(s) + Pd(s)$	5.71×10^{21}	0	62.8
11.	$CH_4 + 2Pd(s) \Rightarrow CH_3(s) + H(s)$	$4.00 \times 10^{05\dagger}$	0	196.0
12.	$CH_3(s) + 3Pd(s) \Rightarrow C(s) + 3H(s)$	$5.71 \times 10^{21\ddagger}$	0	85.1
13.	$CH_4 + Pd(s) + O(s) \Rightarrow CH_3(s) + OH(s)$	$4.20 \times 10^{-2\dagger}$	0	38.0
14.	$CH_3(s) + 3O(s) \Rightarrow C(s) + 3OH(s)$	$5.71 \times 10^{21\S}$	0	25.1

* Arrhenius parameters for the rate constants written in the form: $k = AT^{\beta}\exp(-E/RT)$.
The units of A are given in terms of moles, cubic meters, and seconds. E is in kJ/mol.
Coverage of surface species (e.g., [O(s)]) specified as a site fraction.
Total available site density for Pd is $\Gamma = 1.95 \times 10^{-9}$ mol/cm^2.

† Sticking coefficient.

¶ Forward reaction order of Pd(s) is 1.

§ Forward reaction order of O(s) is 1.

4. Surface and Gas Phase Reaction Kinetics

4.4 Gas phase reaction kinetics:

o gas phase reactions proceed via radicals, often in chain reactions

o radical chain reactions consist of initiation, branching and termination reactions

o gas phase reactions are typically strongly pressure dependent and the kinetics are highly nonliner

example: $H_2 + O_2 \rightarrow H_2O$

Initiation

$$H_2 + O_2 \leftrightarrow H\cdot + HO_2\cdot$$

Propagation

$$H\cdot + O_2 + M \leftrightarrow HO_2\cdot + M$$

Branching

$$H\cdot + O_2 \leftrightarrow O\cdot + OH\cdot$$

$$O\cdot + H_2 \leftrightarrow H\cdot + OH\cdot$$

$$O\cdot + H_2O \leftrightarrow OH\cdot + OH\cdot$$

$$OH\cdot + H_2 \leftrightarrow H_2O + H\cdot$$

Termination

$$H\cdot + O_2 + M \leftrightarrow HO_2\cdot + M$$

$$HO_2\cdot + OH\cdot \leftrightarrow H_2O + O_2$$

$$HO_2\cdot + HO_2\cdot \leftrightarrow H_2O_2 + O_2$$

$$H\cdot, O\cdot, OH\cdot, HO_2\cdot \xrightarrow{wall} inert$$

o gas phase reactions are typically strongly pressure dependent and the kinetics are highly nonliner

4. Surface and Gas Phase Reaction Kinetics

Pressure dependence of gas phase reactions:

o for surface reactions k is a function of T

o for gas phase reactions, k can be a function of T and p

o a simple explaination follows from the Lindemann mechanism (Frederick Lindemann 1921)

$$A + B \rightarrow C$$

$$A + B \xleftrightarrow{k_1, k_{-1}} C^*$$

$$C^* + M \xleftrightarrow{k_2, k_{-2}} C + M$$

$$\frac{d\left[C^*\right]}{dt} = 0 = k_1[A][B] - k_{-1}\left[C^*\right] - k_2\left[C^*\right][M]$$

$$\left[C^*\right] = \frac{k_1[A][B]}{k_2[M] + k_{-1}}$$

$$\frac{d[C]}{dt} = k_2\left[C^*\right][M] = \frac{k_2 k_1 [A][B][M]}{k_2[M] + k_{-1}} \equiv k_{observed}[A][B]$$

$$k_{observed} = \frac{k_2 k_1 [M]}{k_2[M] + k_{-1}} \Rightarrow k = f(M \sim p)$$

4. Surface and Gas Phase Reaction Kinetics

$$k_{observed} = \frac{k_2 k_1 [M]}{k_2 [M] + k_{-1}} \Rightarrow k = f(M \sim p)$$

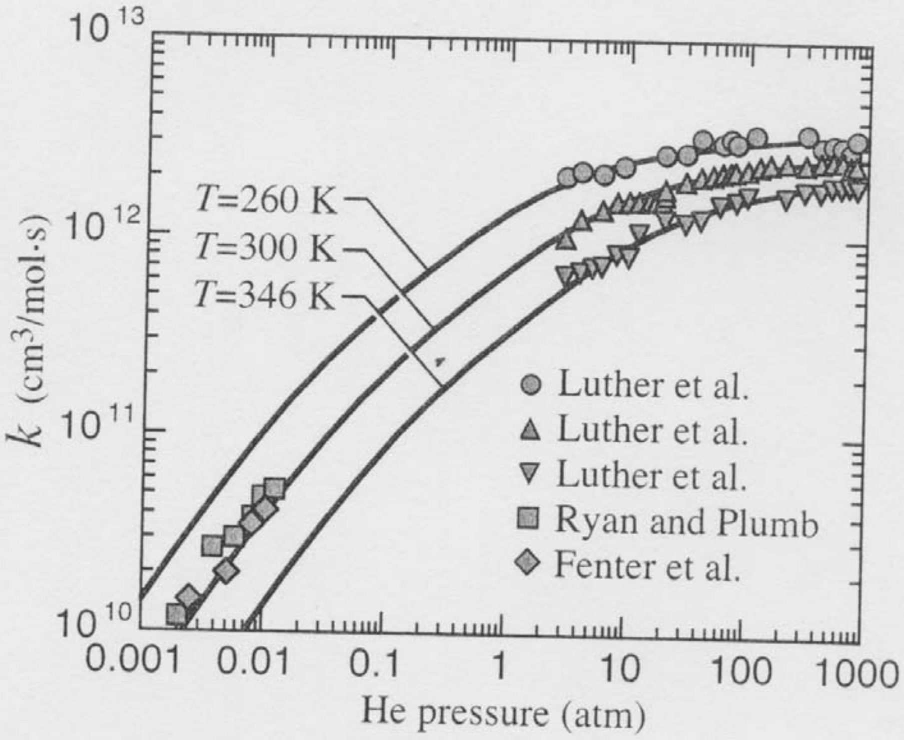
Limiting cases:

$$k_{observed} = k_1 \quad \text{for} \quad [M] \rightarrow \infty$$

$$k_{observed} = \frac{k_2 k_1 [M]}{k_{-1}} \quad \text{for} \quad [M] \rightarrow 0$$

Example: rate constant for the association reaction

$CCl_3 + O_2 \rightarrow CCl_2O_2$



4. Surface and Gas Phase Reaction Kinetics

example for non-linear behaviour and pressure dependence of gas phase reactions

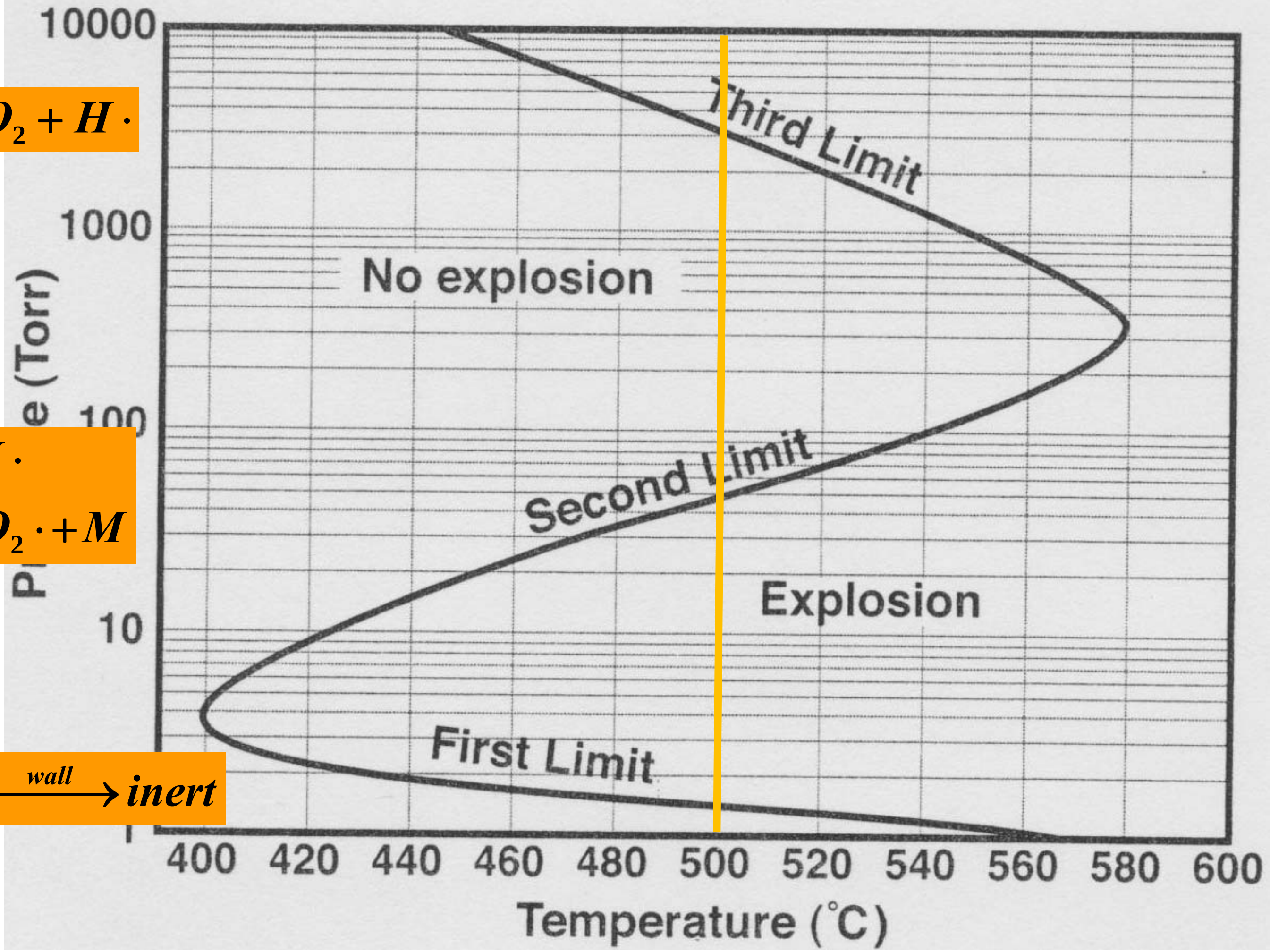
explosion diagram for H_2/O_2 system

$HO_2\cdot + H_2 \rightarrow H_2O_2 + H\cdot$

$H\cdot + O_2 \rightarrow O\cdot + OH\cdot$

$H\cdot + O_2 + M \rightarrow HO_2\cdot + M$

$H\cdot, O\cdot, OH\cdot, HO_2\cdot \xrightarrow{wall} inert$



5. Physical Transport Processes of Momentum, Heat and Mass

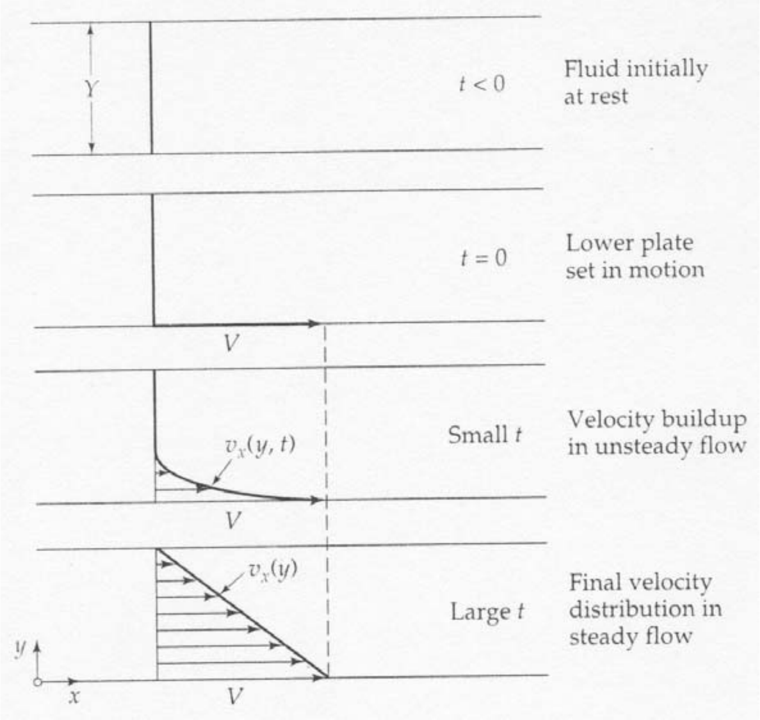
5.1 Momentum transport

- o pair of parralel plates in rest with area A separated by distance Y
- o t=0 lower plate is set in motion in positive x direction with V=constant

$$F = \mu \frac{V}{Y} A$$

$$\frac{F}{A} = \tau_{yx} = -\mu \frac{dv_x}{dy}$$

Newton‘s law of viscosity



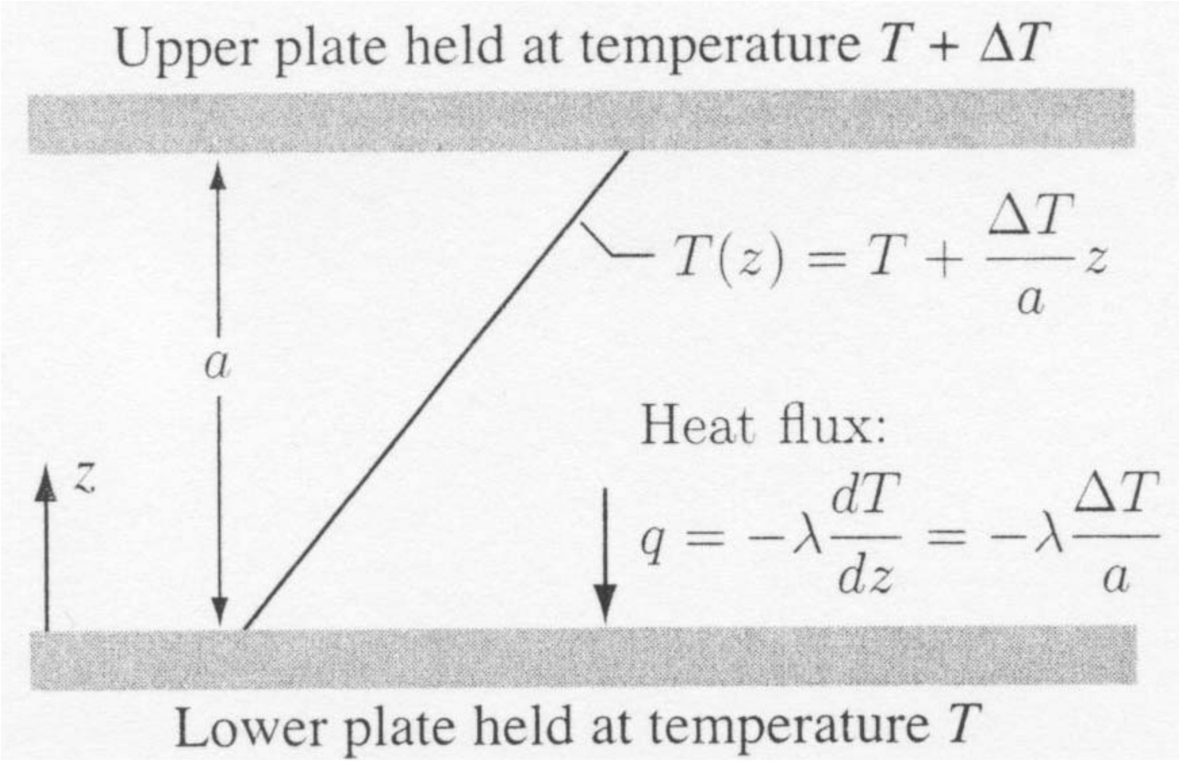
τ_{yx}=flux of x momentum in y direction in (kg·m/s)/m²/s=N/m²

- o the x-momentum flows from a region of high momentum to a region of low momentum (similar to heat and mass)
- o the proportionality constant μ is called the (dynamic) viscosity, has the unit Pa·s=kg/m/s and is material specific (air 1.8E-5 Pa·s, glycerol 1 Pa·s)

5. Physical Transport Processes of Momentum, Heat and Mass

5.2 Heat transport:

Fourier‘s law of heat conduction

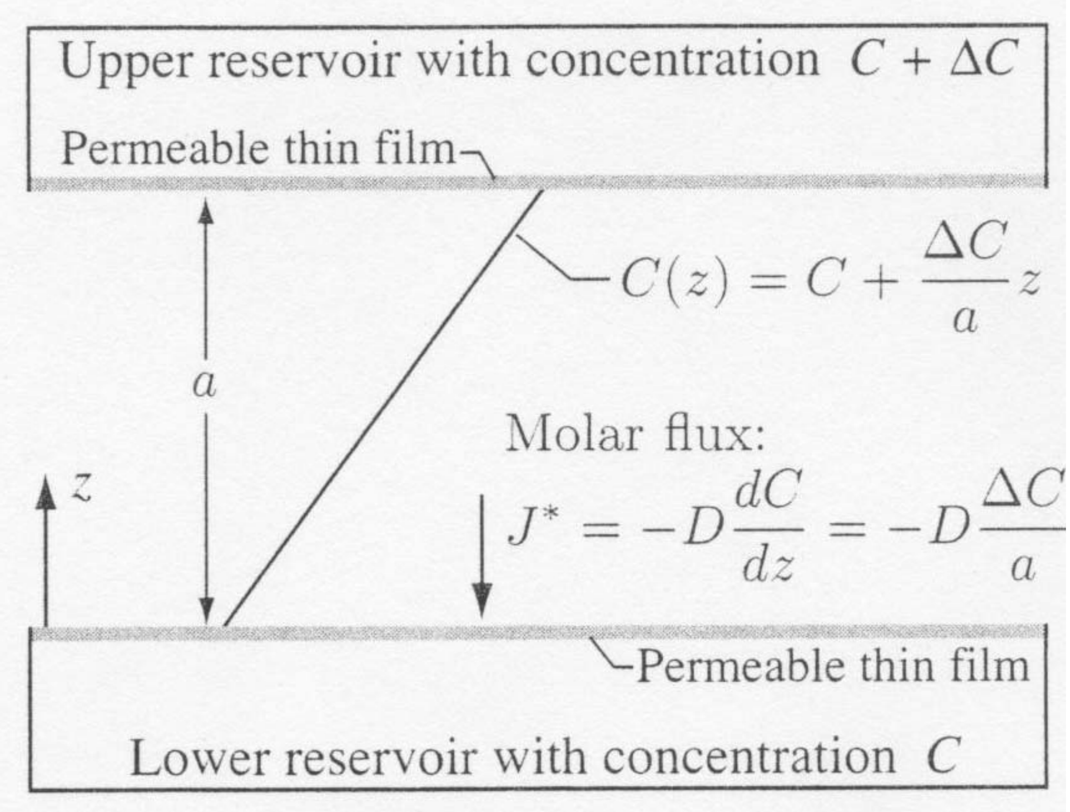


- q=heat flux in z direction in J/m²/s
- heat flows from a region of high temperature to low temperature
- the proportionality constant λ is called the thermal conductivity, has the unit W/m/s and is material specific (air=0.025, stainless steel=16, Al=250)

5. Physical Transport Processes of Momentum, Heat and Mass

5.3 Mass transport:

Fick‘s law of diffusion

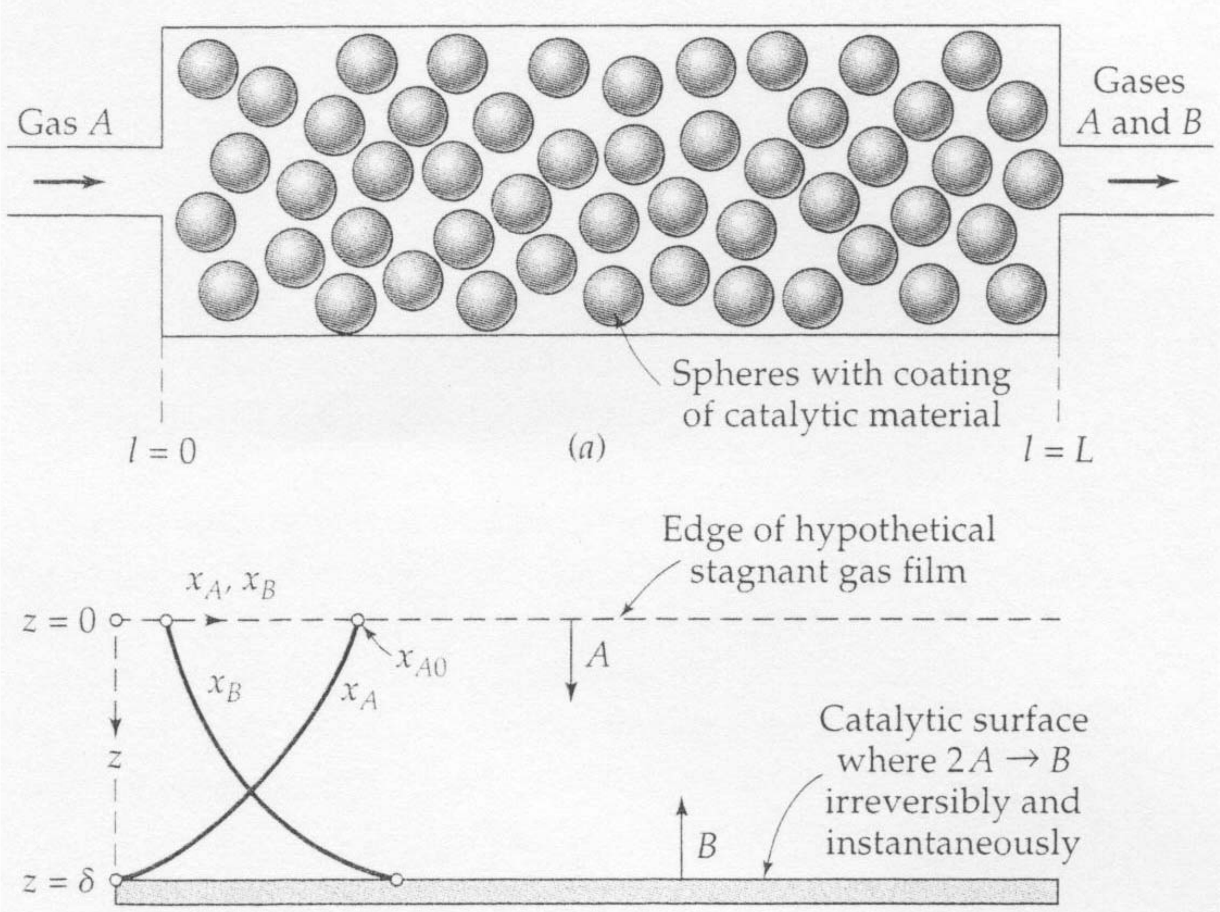


- J=molar flux in z direction in mol/m²/s
- mass (atoms, molecules) flow from a region with high concentration to a region with low concentration
- the proportionality constant D is called the diffusion coefficient, has the unit m²/s and is material specific (H_2 in N_2=7.79E-5)

6. Interaction of Chemistry and Transport

Example: instantaneous reaction 2A → B (e.g. dimerization)

- **catalyst surrounded by a stagnant film through which A has to diffuse to reach the catalyst surface**
- **at the surface, 2A → B react instanteneously**



6. Interaction of Chemistry and Transport

$$\text{combined molar flux}: N_{Az} = \frac{r}{2} = -cD_{AB}\frac{dx_A}{dz} + x_A\left(N_{Az} + N_{Bz}\right)$$

$$\text{steady state and stoichiometry require}: N_{Bz} = -\frac{1}{2}N_{Az}$$

$$\text{inserting into the combined molar flux gives}: \mathrm{N}_{Az} = -\frac{cD_{AB}}{\left(1-\frac{1}{2}x_A\right)}\frac{dx_A}{dz}$$

$$\text{mass balance on A over a thin slab gives}: \frac{dN_{Az}}{dz} = 0$$

$$\Rightarrow \frac{d}{dz}\left(\frac{1}{1-\frac{1}{2}x_a}\frac{dx_A}{dz}\right) = 0 \Rightarrow -2\ln\left(1-\frac{1}{2}x_A\right) = C_1 z + C_2 = -2\ln K_1 z - 2\ln K_2$$

$$\text{boundary condition 1}: \text{at } z = 0 \quad x_A = x_{A0}$$

$$\text{boundary condition 2}: \text{at } z = \delta \quad x_A = 0$$

$$\Rightarrow \left(1-\frac{1}{2}x_A\right) = \left(1-\frac{1}{2}x_{A0}\right)^{1-(z/\delta)} \Rightarrow \boxed{N_{Az} = \frac{r}{2} = \frac{2cD_{AB}}{\delta}\ln\left(\frac{1}{1-\frac{1}{2}x_{A0}}\right)}$$

7. Numerical Simulation of High Temperature Catalytic Reactions

- **Gas (Surface) Species Thermodynamics**

$$k_{ri} = \frac{k_{fi}}{\boxed{K_{ci}}}$$

- **Gas Species Transport Data**
- **Kinetic Model of Surface Chemistry**
- **Kinetic Model of Gas Phase Chemistry**
- **Mathematical Model of Momentum, Heat and Mass Transport (Reactor Model)**

7. Numerical Simulation of High Temperature Catalytic Reactions

Example: Plug Flow Model – Species Balance

$$\rho u A_c \frac{dY_k}{dz} = A_c \boxed{\dot{\omega}_k} W_k + P' \boxed{\dot{s}_k} W_k$$

Example: Plug Flow Model – Energy Balance

$$\rho u A_c c_p \frac{dT}{dz} = -A_c \sum_{k=1}^{K_g} \boxed{\dot{\omega}_k} W_k h_k - P' \sum_{k=1}^{K_g} \boxed{\dot{s}_k} W_k h_k + \hat{h} P \left(T_w - T\right)$$

system of coupled differential – algebraic equations since in catalysis

$\dot{s}_k = 0$ and $\sum_{k=1}^{K_s} Z_k = 1$

7. Numerical Simulation of High Temperature Catalytic Reactions

- gas-phase and surface chemical rate expressions:

$$\sum_{k=1}^{K} \nu'_{ki} \chi_k \Leftrightarrow \sum_{k=1}^{K} \nu''_{ki} \chi_k \quad (\mathrm{i} = 1,\ldots,\mathrm{I})$$

$$\nu_{ki} = \nu''_{ki} - \nu'_{ki}$$

gas concentration (mol/m³)

$$\dot{\omega}_k = \sum_{i=1}^{I} \nu_{ki} q_i \quad q_i = k_{fi} \prod_{k=1}^{K} [X_k]^{\nu'_{ki}} - k_{ri} \prod_{k=1}^{K} [X_k]^{\nu''_{ki}}$$

surface concentration (mol/m²)

$$\dot{s}_k = \sum_{i=1}^{I} \nu_{ki} q_i \quad q_i = k_{fi} \prod_{k=1}^{K} [X_k]^{\nu'_{ki}} - k_{ri} \prod_{k=1}^{K} [X_k]^{\nu''_{ki}}$$

7. Numerical Simulation of High Temperature Catalytic Reactions

- typical Arrhenius expression for the forward rate constant:

$$k_{fi} = A_i T^{\beta_i} \exp\left(\frac{-E_i}{RT}\right)$$

- modification for coverage dependent rate constants possible

$$k_{fi} = A_i T^{\beta_i} \exp\left(\frac{-E_i}{RT}\right) \cdot f\left(\theta_1, \theta_2 \ldots\ldots \theta_k\right)$$

- rate constants for adsorption reactions are calculated from sticking coefficients

$$k_{fi} = \frac{\gamma_i}{\left(\Gamma_{tot}\right)^m} \sqrt{\frac{RT}{2\pi W_k}}$$

7. Numerical Simulation of High Temperature Catalytic Reactions

o **in first approximation thermodynamic properties of species (regardless of phase) are functions of temperature only**

o **thermodynamic data are neeeded to calculate the reverse rate constant for gas phase reactions even if no energy balance is solved**

$$C_{pk}^{0} = \sum_{m=1}^{M} a_{mk} T_k^{(m-1)}$$

$$H_k^{0} = \int_0^{T_k} C_{pk}^{0}\,dT + H_k^{0}(0) \Rightarrow \frac{H_k^{0}}{RT_k} = \sum_{m=1}^{M} \frac{a_{mk} T_k^{(m-1)}}{m} + \frac{a_{M+1,k}}{T_k}$$

$$S_k^{0} = \int_{298}^{T_k} \frac{C_{pk}^{0}}{T}\,dT + S_k^{0}(0) \Rightarrow \frac{S_k^{0}}{R} = a_{1k} \ln T_k + \sum_{m=2}^{M} \frac{a_{mk} T_k^{(m-1)}}{(m-1)} + a_{M+2,k}$$

7. Numerical Simulation of High Temperature Catalytic Reactions

calculation of the reverse rate constant from the forward rate constant and the equilibrium constant

$$\frac{\Delta S_i^0}{R} = \sum_{k=1}^{K} \nu_{ki} \frac{S_k^0}{R} \qquad \frac{\Delta H_i^0}{RT} = \sum_{k=1}^{K} \nu_{ki} \frac{H_k^0}{RT}$$

$$K_{pi} = \exp\left(\frac{\Delta S_i^0}{R} - \frac{\Delta H_i^0}{RT} \right)$$

$$K_{ci} = K_{pi} \left(\frac{p_{atm}}{RT} \right)^{\sum_{k=1}^{K} \nu_{ki}}$$

$$k_{ri} = \frac{k_{fi}}{K_{ci}}$$

if thermodynamic information for surface species are not available (which is usually the case), reverse rate parameters have to be specified

Glowing Thanks For Your Attention !!!