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Preface

A hundred years of Tafel's Equation: 1905–2005

It could be regarded as odd to punctuate the centennial of the work of Julius Tafel through a special edition of *Corrosion Science*, for Tafel was not a corrosion scientist, and his research did not involve corrosion—at least not overtly. Tafel's work in electrochemistry clearly did involve the electrochemistry of metal surfaces, and he could thereby be deemed to have been approaching the area of corrosion science. However, this is not the reason for the centennial mark. Julius Tafel contributed enormously (and probably unknowingly) to the science and technology of corrosion through establishment of his equation: it is right and proper that the centenary of the first publication of Tafel's equation should be marked by this special issue of Corrosion Science. The equation itself is not only a remarkable achievement: it is a remarkable equation.

The year 2005 has been widely celebrated as the centenary of the year in which Albert Einstein published for the first time his special theory of relativity. In the deservedly wide acclaim accorded to Einstein's work, anniversaries of the great achievements of other scientists have been completely eclipsed, even amongst the specialist communities in which their work has a major impact. Among those is the work of Adolf Fick. Who knows that 2005 is the sesquicentenary of the first publication of Fick's law of diffusion [1]? In the absence of this issue of *Corrosion Science*, the centennial of the first publication of Tafel's equation might also be forgotten.

Although Julius Tafel's work is far less known, the fields of corrosion, and of electrochemistry more generally, owe much to Tafel's "Law" relating current density to electrochemical potential (or overpotential). Tafel's Law thereby merits the centenary celebration accorded to the great work that it is. Using Tafel's own symbols, his equation is written as

$$\varepsilon = a + b \log J$$

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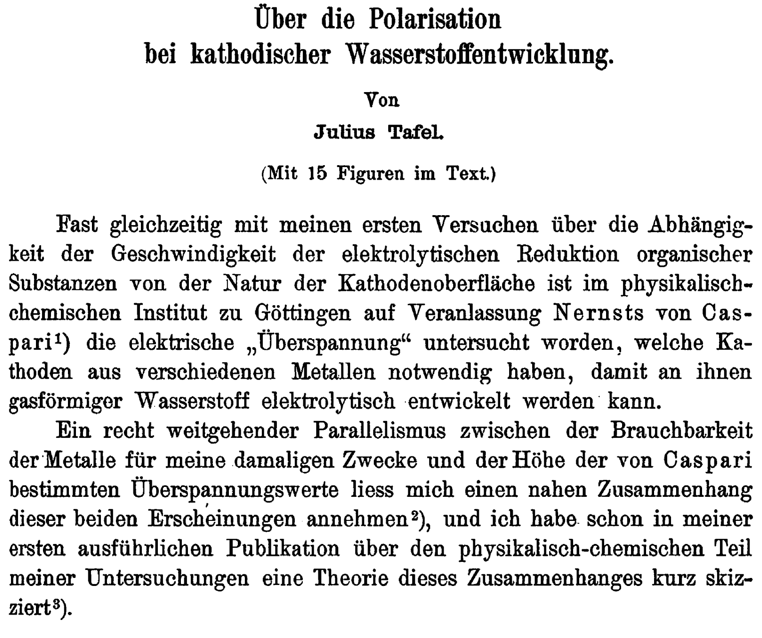
where ε is the potential (overpotential) and J the current density. (In Tafel's original paper, the potential is written with the sign convention opposite to what we would use today, with increasingly cathodic potentials becoming increasingly positive. This was a convention at that time.) Tafel noted his empirical constants a and b, the latter now so well known as the "Tafel slope". The naming of an equation after its originator is in fact quite common. But to have a *slope* in one's own name must be rare indeed.

[It is this writer's opinion that, since Tafel slopes are most frequently expressed in V per decade of current (rather than simply V, were the natural log interval used) it would be appropriate to name the volt-per-decade-of-current unit itself after Tafel, i.e. 1 tafel = 1 V per decade of current, with symbol Ta. Thus 1 Ta = 2.3026 V. This would remove all ambiguity from cited Tafel slopes: the unit of V would then apply only to those measured over the natural log interval, and the unit Ta would apply only to the decadic log interval. The issue is not trivial because the decade of current is itself dimensionless, but numerically different from the (dimensionless) natural log interval.]

There can be few people, if any, in the fields of electrochemistry and corrosion who are not fully familiar with Tafel's equation, first published in an article entitled "Über die Polarisation bei kathodischer Wasserstoffentwicklung" (Concerning the polarisation during cathodic evolution of hydrogen) in 1905 [2]. A facsimile of the title page of Tafel's paper is shown below in Fig. 1.

A detailed and sensitively written biographical article entitled "Who was Tafel?" by Klaus Müller marked the 50th anniversary of Tafel's death: this was published in 1969 [3]. It is not the intention to try to emulate Müller's excellent biography here, and readers are referred to it. Apart from Müller's article however, full details of the life of Tafel are hard to come by. Julius Tafel was born in Choindez in Switzerland on 2 June 1862. To those who reckon that people have done their best work before the age of 40, Tafel was already over that age when he published the Tafel equation, and most of his electrochemistry appeared in publication after that. In common with so many researchers today, Tafel also underwent a change in his field, although he did not stray too far. Originally he was an organic chemist, a tough field in those days, with much opportunity to be original, but very little notion of health and safety; this latter issue probably led to the subsequent decline of Tafel's health. Indeed, his work in electrochemistry, all the more remarkable because his field was organic chemistry, stemmed from his desire to synthesise organic compounds which he regarded as impossible to synthesise by conventional homogeneous reaction chemistry. This itself must be regarded as having been a significantly original idea in those early days. Tafel came to electrochemistry as an organic chemist, and worked at electrochemical reduction of strychnine. His desire to carry out reduction of organic compounds, originally through conventional organic routes, led him to examine the response of some compounds to a cathodically imposed overpotential. He determined, probably uniquely in those days, that some organic compounds could be reduced only by these electrochemical means, having attempted unsuccessfully to carry out the same reductions by conventional routes. His work on strychnine was seminal: [4] his report of the strychnine reaction appears to have been Tafel's first



Über die Polarisation bei kathodischer Wasserstoffentwicklung.

Von

Julius Tafel.

(Mit 15 Figuren im Text.)

Fast gleichzeitig mit meinen ersten Versuchen über die Abhängigkeit der Geschwindigkeit der elektrolytischen Reduktion organischer Substanzen von der Natur der Kathodenoberfläche ist im physikalisch-chemischen Institut zu Göttingen auf Veranlassung Nernsts von Caspari1) die elektrische „Überspannung“ untersucht worden, welche Kathoden aus verschiedenen Metallen notwendig haben, damit an ihnen gasförmiger Wasserstoff elektrolytisch entwickelt werden kann.

Ein recht weitgehender Parallelismus zwischen der Brauchbarkeit der Metalle für meine damaligen Zwecke und der Höhe der von Caspari bestimmten Überspannungswerte liess mich einen nahen Zusammenhang dieser beiden Erscheinungen annehmen2), und ich habe schon in meiner ersten ausführlichen Publikation über den physikalisch-chemischen Teil meiner Untersuchungen eine Theorie dieses Zusammenhanges kurz skizziert3).

Fig. 1. The title page of Tafel's paper announcing the Tafel equation, published in [2]. Reproduced with permission of the publishers.

publication in electrochemistry. In it he determined that he could reduce *both* of the oxygen atoms within the structure *cathodically*, a process he found impossible by other, non-electrochemical methods. His subsequent papers show he carried out many organic reduction reactions using electrochemistry at metal cathodes. His cathodes were generally lead, sometimes mercury. He tried many other cathodes too, and found them less satisfactory; in fact his studies in this area were to constitute an early and remarkably incisive examination of electrocatalysis. His success in reducing organic compounds on lead (and mercury) was indubitably due to its high overpotential for hydrogen evolution, at least in major part. He effectively determined that if the hydrogen overpotential on the cathode was low (as on platinum), then the required reduction reaction of the organic compound under study was impeded. Thus lead and mercury, with high hydrogen overpotentials, were good for the reduction of organic compounds because the competing hydrogen evolution reaction was more difficult. Platinum is a poor cathode for the same organic reduction reactions because it is such a good hydrogen evolution electrocatalyst.

He made some remarkably astute observations about the identity, purity, etc. of the cathode electrocatalyst, and it is surprising that at least some of this early electrochemical synthesis did not become more widely known. For example, he determined that if platinum was used as the *anode* during his reduction reactions, then the efficiency of the reduction reaction on the lead *cathode* could be impaired; he drew the correct conclusion that platinum could dissolve when functioning as an anode, and its subsequent deposition onto the cathode affected cathode behaviour. (This knowledge *should* have become more widely known. Müller commented in 1969 (*loc cit*) that it has gone unheeded for six decades; even now, ten decades later, it seems at times to be neglected.) He also determined that the purity of the electrolyte affected his results, and showed that pre-electrolysis of the electrolyte improved the performance of the cathode material as well. He could be regarded as one of the founders of pre-electrolysis as a method of purifying the electrolyte. Electrochemical reduction at lead cathodes formed a significant part of Tafel's subsequent work. With it, and with many other observations he made in the field, Tafel showed himself to be a pioneer of electrocatalysis. He also reported the difference in the reaction overpotentials on different metals, and used this information in subsequent work to display the properties of cathodic electrocatalysts towards reduction of organic compounds using his knowledge of electrocatalysis to develop electro-organic synthesis: again, it was electrocatalysis that he championed.

Tafel worked with Emil Fischer, an organic chemist, at the University of Erlangen over a lengthy period starting in 1882 when Tafel was still a student. Tafel was thereby an organic chemist. Tafel's tasks were mainly organic syntheses and organic transformations; the field of electrochemistry was relatively young then, despite the early prominence of some aspects, such as Grove's fuel pile (the origin of the fuel cell). He studied reduction reactions, particularly reduction of carbohydrates: these reactions were part of the origin of Fischer's Nobel Prize in chemistry in 1902. Apart from the carbohydrate work, in which Tafel and Fischer first synthesised hexose, Tafel also worked extensively on heterocyclic compounds, on the strychnine/brucine class of compounds. From what can be seen in the literature of those days, the names of the research students who were involved with the work were not always attached to the publication, a most regrettable fact, certainly for the students involved, but also for the public readership since it renders difficulty in tracing the history of these sciences. In the days of that tough regime, it must have been so much more difficult for the student or more junior researcher to make his/her name, as would be expected these days, if the supervisor of that work became the sole author and took all the credit. The same is true of course, of Tafel's own papers, many of which are published under his sole authorship despite the fact that students and other young researchers must inevitably have been involved. The Müller article (loc cit), which also carries an extensive bibliography of Tafel's published works, describes that phenomenon, and most admirably tries to remedy it.

Tafel led a rather tragic life. His later illness, which by all accounts was severe and relentlessly progressive, has been attributed to his exposure to toxic chemicals: it dogged his working life. (It appears that Tafel's earlier supervisor and mentor, Emil Fischer, may also have suffered the effects of exposure to organic toxins.) Irrespective of the causes of his illness, it is a sad fact that Julius Tafel's life ended with suicide in 1918 and the world of electrochemistry indubitably suffered as a consequence. It is probably also to the detriment of electrochemistry that Tafel did not continue with pure electrochemistry, but worked in his last years in the field which would now be called electro-organic chemistry, in which he carried out electrochemical reductions of many complex organic compounds.

Despite the fact that TAFEL was chiefly as organic, or electro-organic chemist, the fundamental nature of Tafel's Law in corrosion science and engineering is clear. Quite apart from its basis in the theory of electrochemical polarisation, it finds wide application to interpreting polarisation curves mechanistically, determining corrosion rates from linear polarisation and impedance methods, measuring the efficacy of corrosion inhibitors and a very wide range of other electrochemical phenomena. But it is worth mentioning also the further impact of this equation at that time.

It must have come as a surprise, or even a shock, to scientists of the day, to find that potential relates linearly to log current, all the more since Tafel's publication of his equation came so long after Georg Simon OHM had first published the familiar Ohm's Law (78 years earlier in 1827) in which current and voltage are related linearly. The idea that current could increase exponentially with potential must have appeared very odd indeed. A full derivation of Tafel's Law, starting from the Arrhenius rate equation, in fact generates a hyperbolic sine expression between the current density and the overpotential because the reverse reaction must also be considered. The hyperbolic sine expression reduces to Ohm's Law for the special case of the limited range of low overpotential (where the quantity within the hyperbolic sine is $\ll 1$), and to Tafel's Law the special case in the bigger range of high overpotentials (where the quantity within the hyperbolic sine $\gg 1$). It is the large numerical value of Faraday's constant (F) that makes the transition between the two limiting cases of the hyperbolic sine expression occur at so low an overpotential. It is doubtful however, that TAFEL could have realised these phenomena in 1905. The low-overpotential ohmic relationship can be used to determine the polarisation resistance and the exchange current density: it is also of course, analogous to the origin of the Stern–Geary equation (derived decades later) defining the *corrosion* resistance and its association with the *corrosion* current density. TAFEL himself could hardly have understood the full implications of his remarkable discovery, although how much he did understand (but did not publish) is not at all clear.

Tafel's equation is all the more remarkable because of the values of the parameters that it generates. What I personally always find astonishing is the small numerical value of the Tafel slope: the fact that the current density can rise by an order of magnitude for a potential increase of only around 0.1 V must be a truly amazing phenomenon for anyone who has studied or measured Tafel slopes. Indeed, Tafel slopes as low as 28–40 mV per decade of current density are not uncommon and are now readily interpretable mechanistically. This fact means that, unlike any other field of chemical reaction, the electrochemist can have the reaction control at his/her fingertips over many orders of magnitude, and really in a very simple way. Of course, the fact again reaches back to the large numerical value of the Faraday constant, F, and FARADAY himself must take some credit for this. Nevertheless, it is the logarithmic nature of Tafel's relationship that gives rise to such a massive effect of overpotential on reaction rate.

Much mechanistic information arising from measuring electrochemical kinetics is due to interpretation of the Tafel slope. It is the fact that the Tafel slope involves a combination of the transfer coefficient and the electron number of the reaction that allows such close mechanistic interpretation, albeit that interpretation of the measured kinetics force the Tafel relationship to be complicated by the fact that it becomes effectively a diophantine equation. TAFEL could not have realised this aspect of his equation through his lifetime because such interpretation remained to be derived subsequently by others. The original publication of TAFEL in 1905 nevertheless carried much information. TAFEL studied hydrogen evolution on a number of metals: Pt, Ni, Cu, Au, Bi, Sn, Hg and others. The original diagram (polarisation curve) of TAFEL is shown in facsimile below in Fig. 2: surprisingly, although he proposed his famous equation for the data, the graph was plotted using a *linear* current density scale, as shown.

He reported not only the Tafel slope (in tabular form), but measured the temperature dependence for mercury of the Tafel slope, *b*, and the hydrogen overpotential. This temperature dependence was surprisingly sensitively and accurately measured. TAFEL measured his Tafel slopes as a differential quantity, and showed that although this slope was independent of the applied current density at low current density, there was a deviation to higher Tafel slopes at high current density: it is likely that he was experiencing the ohmic potential drop in the cell electrolyte here. What readers may find interesting is Tafel's treatment of his experimental data. TAFEL tabulated the data for the evolution of hydrogen on mercury (Table 4, loc cit, p. 272) shown in facsimile in Fig. 3. That table lists both the potential and the Tafel slope, *b*, due to hydrogen evolution as a function of the applied current density as well as the temperature. Inspection of that table shows that at low current density, the Tafel slope *b*, is constant, but appears to rise at current densities $\geqslant 0.01\ \mathrm{A\,cm^{-2}}$. For current densities higher than this, the Tafel slopes were not even listed in Tafel's table. It is not clear why TAFEL did this. In fact the Tafel slopes appear from that table (Tafel's Table 4) to be constant over only one order of magnitude of current density (in *apparent* contrast to Tafel's stated two orders of magnitude). If we take the mean of Tafel's *tabulated* differential values over only one order of magnitude, we get exactly Tafel's stated mean values (see Fig. 3). If however, we take the mean of *all* Tafel's tabulated values, we get values slightly greater than Tafel's reported mean values. At first sight, Julius TAFEL *may* have made an error in reporting this range over which his mean was apparently taken. Tafel's tabulated data (in his Table 4) in fact appear to show a small *rise* of *b* with current density for current densities $\geqslant 0.01\ \mathrm{A\,cm^{-2}}$. He did not plot these Tafel slopes. However, if *we* now plot Tafel's full table of measured *potentials* for hydrogen evolution on mercury (again from his Table 4) as Tafel plots in the form in which we would now plot it, the graph does indeed demonstrate that Tafel's equation is fully applicable over the full range of current density stated in his paper. TAFEL may have been rather modest in his assertions here. The graph of Tafel's Table 4 data plotted by the present author is shown below in Fig. 4. Moreover, if we regress the data in Fig. 4 for current densities $\leqslant 0.04\ \mathrm{A\,cm^{-2}}$, we get exactly the mean values listed by TAFEL (this time covering two orders of magnitude in current density, as he reported).

TAFEL showed remarkable insight into his studies of electrochemical reduction reactions, particularly the hydrogen evolution reaction. He recognised already very early on that the cathodic evolution of hydrogen was probably a multiple step electrochemical reaction, and suggested its mechanism. The proposal [5] that

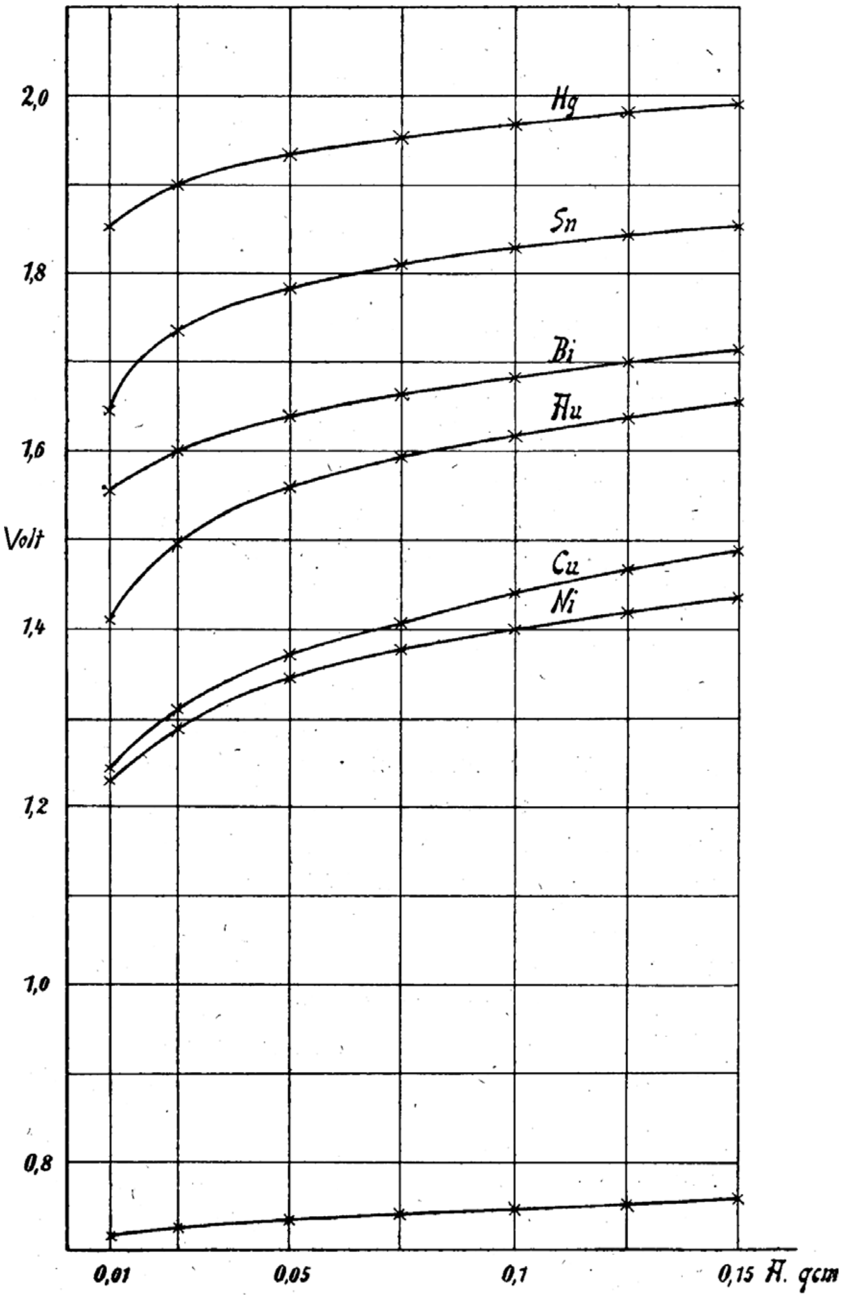


Fig. 2. The original "Tafel plots" describing the evolution of hydrogen on various metal cathodes in 2 N sulphuric acid (N = normal) presented by Julius Tafel as Fig. 15, as published in [2]. Note that the plot was presented on a *linear* current density scale. Reproduced with permission of the publishers.

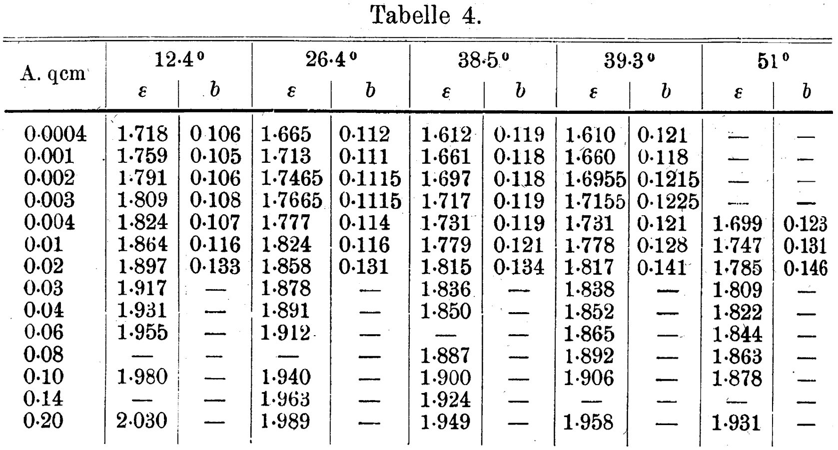


Tabelle 4.

A. qcm	12·4°		26·4°		38·5°		39·3°		51°	
	ε	b	ε	b	ε	b	ε	b	ε	b
0·0004	1·718	0·106	1·665	0·112	1·612	0·119	1·610	0·121	—	—
0·001	1·759	0·105	1·713	0·111	1·661	0·118	1·660	0·118	—	—
0·002	1·791	0·106	1·7465	0·1115	1·697	0·118	1·6955	0·1215	—	—
0·003	1·809	0·108	1·7665	0·1115	1·717	0·119	1·7155	0·1225	—	—
0·004	1·824	0·107	1·777	0·114	1·731	0·119	1·731	0·121	1·699	0·123
0·01	1·864	0·116	1·824	0·116	1·779	0·121	1·778	0·128	1·747	0·131
0·02	1·897	0·133	1·858	0·131	1·815	0·134	1·817	0·141	1·785	0·146
0·03	1·917	—	1·878	—	1·836	—	1·838	—	1·809	—
0·04	1·931	—	1·891	—	1·850	—	1·852	—	1·822	—
0·06	1·955	—	1·912	—	—	—	1·865	—	1·844	—
0·08	—	—	—	—	1·887	—	1·892	—	1·863	—
0·10	1·980	—	1·940	—	1·900	—	1·906	—	1·878	—
0·14	—	—	1·963	—	1·924	—	—	—	—	—
0·20	2·030	—	1·989	—	1·949	—	1·958	—	1·931	—

Fig. 3. Tafel's recorded data for cathodic evolution of hydrogen on mercury in 2 N (N = "normal") sulphuric acid at different temperatures. The table is a facsimile of Table 4 from his paper (loc cit). Reproduced with permission of the publishers.

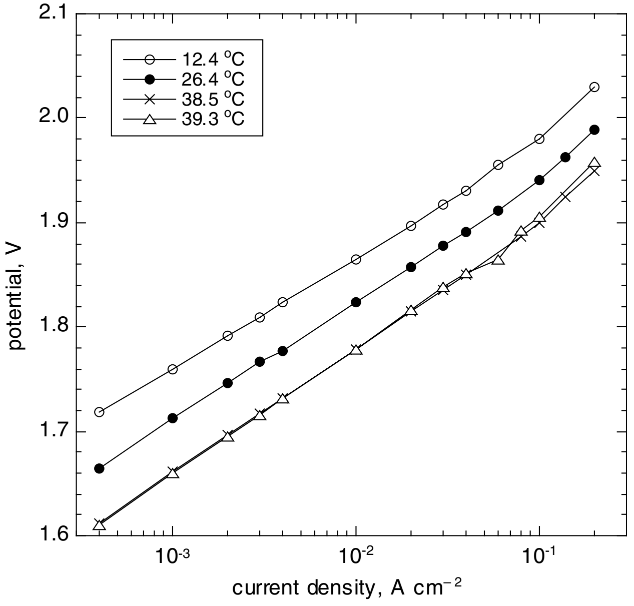


Fig. 4. Tafel plots (prepared by the present author) describing the cathodic evolution of hydrogen on mercury in 2 N sulphuric acid from Tafel's own data given in Table 4 of his original paper (loc cit). The potentials were measured as a function of applied current density and as a function of temperature. The key in the inset shows the temperature in °C.

"Wahrscheinlich ist diese Reaktion eine zusammengesetzte und besteht aus den folgenden Reaktionsstufen $2H^{\cdot} = 2H + 2e$ und $2H = H_2$" was published before

Tafel's equation had appeared, and long before it had been interpreted mechanistically. Thus Tafel had already argued for atomic hydrogen on the metal surface more than 100 years ago. We now regard the basis of this two-step mechanism for cathodic hydrogen evolution from water, in addition to one or two others, as fundamental, and its basis in stimulating hydrogen embrittlement of embrittlable metals during stress corrosion or corrosion fatigue crack formation is widely postulated and accepted today (although we may today quibble about the sign of the electron charge used by Tafel). Tafel had no means of proving this mechanism, but his proposal turned out to be right: the mechanistic interpretations of Tafel's equation were to come many years later. Perhaps had Tafel concentrated on the electrochemistry of his processes rather than the organic compounds he was producing, he would have made more progress into the mechanisms which we are now able to glean from his kinetic equation.

Tafel's reduction reactions took him into organometallic chemistry as well, a field in which he made significant contributions, showing for example, that lead and mercury alkyls could be generated during cathodic reduction of acetone or butanone [6]. Tafel held his ground here, when in 1912 he published (probably his last publication) a refutation of work reported elsewhere by Law, when he (Tafel) states "Die von Law am Schluß der erstzitierten Arbeit aufgestellte Behauptung, daß am Quecksilberkathoden im Gegensatz zum Blei nie metallorganische Verbindungen entstehen, ist, wie ich längst und ausführlich gezeigt habe, falsch" (Law's...conclusion that mercury cannot form organometallic compounds, in contrast to lead, is, as I have for so long and so exhaustively shown, wrong) [7].

It is perhaps a sobering thought for the person adopting the mantle of a titled equation, a titled theory or a new announcement, to look at the history of Tafel's Law. The basis of the logarithmic relationship between current and potential, now known as Tafel's Law (more correctly this should be Tafel's equation) had already been published some considerable time before Tafel himself published it. That matter is not widely known. Two publications had already appeared in 1895 and 1898, the former some 10 years before Tafel's publication. Jahn and Schönrock published both a derivation of this relationship and some experimental evidence for it [8]. Even Haber had his say on the subject [9], also before Tafel's publication in 1905. All of these earlier works associated the remarkable kinetic equation (at that stage, of course, not yet associated with Tafel) with *equilibrium* thermodynamics, particularly the equations of Nernst. These earlier works thereby made the link with equilibrium thermodynamics inextricable. Tafel nevertheless argued that this logarithmic relationship between potential and current exists for electrochemical reactions which are not necessarily reversible, and in doing so provided the much needed separation of the kinetics from the thermodynamics. Indeed, it can be argued that rationalising electrochemical kinetics through arguments based on the equilibrium state is itself irrational. Electrochemical (or indeed chemical) equilibrium must be a special case of reaction kinetics where there is zero net reaction, and therefore arguing the other way round inevitably must be inductive: Tafel was therefore probably right in his defence of his own originality, certainly from the viewpoint of logic. Whether Julius Tafel can really be regarded as the originator of what we now refer to as Tafel's equation, is nevertheless a moot point and will remain so. More modern discussions of Tafel's Law lay the theoretical origins with BUTLER [10] and ERDEY-GRUZ and VOLMER [11]: sometimes the equation when written in its mechanistically interpreted form, is termed the Butler–Volmer equation. Of particular note in mention of the derivation was the remarkably early paper of GURNEY, who derived Tafel's form of equation using quantum mechanics [12]. It is interesting to read Gurney's paper, where he comments (already in 1932): "Although the problem is more than 40 years old, and experimental papers on the subject are poured out every year...". It appears that despite the many papers dealing with what we now call the Tafel equation, it really was quite difficult to provide a full theoretical foundation to it in the early years of the twentieth century. The mechanistic origins of the Tafel Equation also lay the foundation stones of the equation relating the current through an oxide film under the application of an electric field first demonstrated by GÜNTHERSCHULTZE and BETZ [13] and subsequently interpreted by many. The relationship of GÜNTHERSCHULTZE and BETZ shows a linear correspondence between the log of the current density through the oxide film and the electric field across it.

In the century since Tafel's publication, theoretical interpretations of Tafel's law abound, and some articles in this issue of *Corrosion Science* address the matter. The equation and its interpretations must be regarded as fundamental to the interpretation, understanding and quantification of much corrosion science and engineering today, specifically of course, the electrochemistry of corrosion associated with electrolyte solutions. But for this early work of TAFEL, the electrochemical nature of these processes would not be readily interpretable, or even usefully applicable. It is through this, that people like EVANS were able to write so pre-eminently their large works on corrosion in electrolytic solutions, and HOAR (under Evans' supervision) was able to write his Ph.D. thesis entitled "On the Mechanism of Metallic Corrosion" [14].

It is perhaps, ironical, that TAFEL did not work in the field of corrosion, nor of metal dissolution, even though the field of corrosion now values his equation so highly. Most of Tafel's electrochemical work was in fact cathodic: in reading Tafel's publications, the anode seemed to be simply the necessary current carrier. That is perhaps the most curious feature of his work, and it is indeed curious. Sometimes TAFEL found the anode a nuisance since it contaminated the electrolyte, affecting his cathodic reactions. The fact that he found platinum anodes could contaminate his electrolyte (by anodic dissolution) and affect his cathodic reduction reactions could have led him to studying the corrosion of platinum (or at least its anodic dissolution). Perhaps he simply had no interest in the anodic side of electrochemistry because of the compounds he was trying to synthesise by reduction. The anode would of course have produced oxidised products instead of reduced products. That explanation is most unlikely. TAFEL did indeed have a direct interest in organic oxidation reactions and carried out many non-electrochemical oxidation procedures as an organic chemist with several publications in the area (e.g., a paper in 1893 [15] in which he described non-electrochemical oxidation of strychnine). Alternatively, perhaps he did try the anodic side and found it to be uninteresting, or even unintelligible (and therefore unpublishable): we shall never know. Certainly, had TAFEL tried to *oxidise* organic compounds on lead (the metal he found so useful as a cathode), he would have found the interesting competing reactions of oxide growth or simply anodic dissolution (depending on the electrolyte): this could indeed have led him into corrosion science, but it would also have concomitantly hampered his organic oxidation reactions. Perhaps he did indeed try it, but dismissed it because of corrosion. Perhaps TAFEL may have become more interested in anodic processes generally, were the potentiostat then in existence: it was to be another 43 years before HICKLING published details of the first "electronic" potentiostat [16]. Another very curious feature of Tafel's work is that many of his electrochemical reduction processes (and there were indeed many of them published) were reported as syntheses, without any presentation of the current/potential relationships, or any real electrochemical kinetics. For example in his detailed description of forming alkyl lead compounds cathodically no such relationships are shown, although this particular work [17] was published some 6 years after the presentation of Tafel's equation. By that time, TAFEL must have had some notion of the impact that his equation might develop, but his electro-organic synthesis papers kept fairly rigidly to his apparent quest for reduction syntheses, rather than interpretations of electrochemical kinetics or physical electrochemistry. Although again, one can comment on the lack of electronic potentiostats in those days, Tafel's Equation was itself discovered also many years before the advent of the potentiostat. It is hard to believe that he would have found this area uninteresting. Alternatively, perhaps he was so full of ideas for his organic reduction syntheses (which indeed he had), that he simply did not have time to indulge theoretical or physical electrochemistry to any great extent. It nevertheless remains surprising that Julius TAFEL did not pursue in more detail the equation that now bears his name.

Tafel's major sojourn into electrochemistry occurred as a consequence of his organic chemistry, and he really never ceased being an organic chemist. Indeed, his papers on what we might now call physical electrochemistry were few, and associated mainly with the hydrogen evolution reaction. Tafel's work in electrochemistry remained chiefly associated with organic reduction transformations as a synthetic route. (Although he worked mainly on reduction reactions, there is some evidence that he was well aware of the implications for anodic reactions as well.) Although MÜLLER ascribes this predomination of organic chemistry to the fact that physical chemistry (and hence electrochemistry by implication) was not so fashionable in those days, this is unlikely to be the case. MÜLLER seems to have regarded TAFEL as having been quite adventurous in adopting physical chemistry ("by no means then a field represented widely by chairs at Universities"). In point of fact, physical chemistry was a well-established and well-respected profession throughout Tafel's professional lifetime, particularly in Europe: his venture into electrochemistry was certainly no *ad*venture. Evidence for this comes of course, from the fact that there were already journals devoted to physical chemistry (e.g. *Zeit. Physik. Chem.*) and the volume numbers of some of these were already quite high when TAFEL was submitting his papers for publication. Indeed, there was in Germany at the time, a journal already devoted to electrochemistry (*Zeit. Elektrochem.*, for which Volume 1 was published in 1894), and this would certainly have made the fields very firm and respected. Even The Electrochemical Society produced its first volume of *Transactions* (the predecessor to *J. Electrochem. Soc.*) in 1902. There was also an abundance of very widely respected physical chemists and electrochemists who were working prior to or contemporaneously with TAFEL: the names of NERNST, HELMHOLTZ, OSTWALD, ARRHENIUS and HABER (not to mention FARADAY) spring to mind, whose work must have been very familiar to TAFEL (although it must be said that many of these names were in fact involved in many areas of science: it seems that in those days, the boundaries of the subjects of physics, chemistry and physiology were very blurred, and scientists routinely indulged in more than one of them). TAFEL was certainly not alone in his field. In fact, although TAFEL did adopt electrochemistry, and did so successfully, he did this mainly though his organic syntheses, and never really ventured far from that. So one must conclude that Tafel's publications in electrochemistry were chiefly as a consequence of his interests in organic reactions, syntheses and mechanisms, rather than in electrochemistry per se. This should be quite a revelation and an encouragement for those young scientists today, who may feel that real progress in a subject must require a lifetime's work or devotion to a single subject. It is perhaps an irony, that Tafel's name should now have become so widely known in a subject which was not his core subject (physical electrochemistry and corrosion science), at least as we would classify them today. It is also a curiosity that TAFEL made significant advances in his core subject of organic chemistry, particularly electro-organic chemistry, for which he is in fact, relatively speaking, poorly known today.

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A full bibliography of Tafel's published work was presented in the excellent biographical article (loc cit) written by Professor Klaus MÜLLER. Professor MÜLLER also kindly supplied the photograph of TAFEL illustrated as the frontispiece of this issue of *Corrosion Science*. Permission from the publishers of *Zeit. Physik. Chem.* to reproduce parts of Tafel's original paper is gratefully acknowledged.

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