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The centenary of Tafel's equation

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The year 2005 has several historical scientific connotations notably the anniversaries for the equations of Einstein (1905) and Maxwell (1855). However, for electrochemical scientists Tafel has an anniversary of special note: the centenary of his famous equation.

Who was Tafel?

This is the question that was posed in 1969 by Klaus Muller[1] who had been long familiar with the equation that bears his name but who was regretting the lack of good historical sources for electrochemistry. To some extent this ignorance arises because he was a contemporary of great German electrochemists (Ostwald, Nernst and Haber) who all made bigger marks through being awarded Nobel Prizes but also because unlike them he was essentially a self-effacing man who struggled for years with terminal ill health. Thus the 10-year argument between Ostwald and Nernst over where the zero of potential should be placed was apparently of no interest (see Ref. 2 for details).

Julius Tafel was born in Switzerland on 2 June 1862 but was educated first at high schools in Stuttgart and Nuremburg, and then from 1880 at Zurich, Munich and Erlangen Universities. At Erlangen he became assistant to Emil Fischer completing his dissertation in 1884 on isomerism of indazole. Inevitably he became an organic chemist and as a vital experimentalist followed Fischer to Wurzburg in 1885 taking his doctorate in 1888. By 1895 he had over 40 publications on topics concerning carbohydrate and heterocyclic organic chemistry, thereby helping to lay the base for Fischer's Nobel Prize in 1902.

In 1892 he made the first of two strategic decisions: this was to remain in Wurzburg when Fischer went to Berlin. The second was in 1894–1895 when he decided to explore organic electrochemistry by taking sabbatical leave in Leipzig with Wilhelm Ostwald (NL 1909) and then returning to Wurzburg, which was fast becoming an international centre for research (University colleagues included Kohlrausch, Rontgen, Wien and Fick). From 1895 Tafel was using electrodes as electrocatalysts for organic oxidation and reduction (he had previously been using peroxide and hydrazine), so commencing in 1896, a new stream of research papers can be seen in parallel with his continuing synthesis work on pyrrolidine, strychnine, caffeine and their derivatives. In this work he used several metals as electrodes and quickly identified different behaviour with the common metals in a review paper of 1899 'On the course of electrolytic reductions'. During the next five years he accumulated much experimental data and in 1905 published two papers summarising the considerable data and showing that a logarithmic relationship between overpotential η and current I was obeyed[3,4]

$$\eta = a \pm b \ln I \qquad (1)$$

where a and b were characterising constants and '$\pm$' sign depended on cathodic or anodic action. The biggest problem was separating the organic oxidation/reduction with electrode 'catalytic' influences but he did list the metals he studied according to their *disturbing* effects

$$Pt > Ag > Sn > Cu > Hg > Zn > Fe$$

Several separate outcomes of this work were apparent:[5]
 (i) the special positions of lead as an oxidant cathode and mercury as a liquid cathode
 (ii) second the vital need for electrode pre-treatment prior to use
 (iii) the importance of platinum which had been promoted earlier by Nernst's group because of its inertness and reversibility
 (iv) the cathode competition between organic reduction and hydrogen evolution reactions.

It soon became apparent that while Tafel was not the first to note the logarithmic relationship (Jahn and Schonrock in 1895 and 1898, Haber in 1900 and Haber and Russ in 1904), he was the first to systematise the data and to recognise the possibility of something fundamental. However, when he first presented his work in 1902 at a German Electrochemical Society Symposium it was scorned by Ostwald, Nernst, Haber, van't Hoff and others. He also upset Le Blanc, who was the great protagonist of decomposition potentials, by identifying *overpotential* as the critical unit for measurement. In this battle of giants one cannot but help sympathising with Tafel who was clearly very honest, his most endearing characteristic being to recognise and support his own students as co-authors, which was uncommon in the academic culture of those times.

By 1909 a further 20 papers were published on electrochemistry alongside another 20 on organic topics. But then Tafel's health deteriorated such that after this date only seven papers were published. In 1910 he retired at the age of 48 on grounds of ill health and from his bedroom produced over 60 book reviews for *Zeitschrift für Elektrochemie*, worked spasmodically on

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the general textbook that he had long planned but never actually progressed. On 2 September 1918 he took his own life ending years of fever and insomnia. His bequest is 108 scientific papers and over 30 doctoral graduates amongst whom were professors in chemistry, medicine and pharmacy. His heritage is much greater because, although he recognised the need to be able to lay his equation on a theoretical base of rate theory, he was unable to do so and it was not until 1930 that Butler, Volmer and others could achieve that aim.

Tafel's equation

The equation now named after Tafel (equation 1), was obtained from large quantities of experimental data, using mainly organic chemicals in aqueous solutions and a range of metal electrode surfaces. However, the aqueous solutions ensured that hydrogen and oxygen evolution were studied too and recognised as competitive electrode reactions. It had relatively recently been agreed that the zero of potential was set at the potential for the reduction of hydrogen at 25°C and 760 mm pressure but decomposition potential, or cell voltage in modern terms, was still being promoted and recorded as fundamental by Le Blanc and others. Thus the terms for Tafel's data depended on assuming that overpotential was an acceptable concept.

Because of the logarithmic nature of the relationship it was probably not appreciated that the Tafel equation does not apply to the first 10–15 mV of overpotential and at high overpotentials a departure could be seen but was not explored except in the context of Nernst's theory for limiting (diffusion) currents. The use of current density rather than current had become more accepted and was not too controversial. The Tafel coefficients a and b were tabulated and a value of $b = 0.107$ but increasing with temperature was recorded for Hg, Pb and Cd. By extending the curves to $\eta = 0$ the exchange current density could be determined.

Butler, Volmer and their co-workers based their theoretical analyses on the Arrhenius concept of the activated state and an activation energy, which enabled forward and reverse reactions to be calculated for what we now term charge-transfer electrode reactions. A general equation is then derived for the forward and reverse rates the difference being the nett forward current

$$j = j_{\mathrm{fd}} - j_{\mathrm{rev}} = j_0 \exp\left(\frac{\alpha z \eta F}{RT}\right) - j_0 \exp\left(\frac{-(1-\alpha)z\eta F}{RT}\right) \quad (2)$$

where j_{fd} and j_{rev} represent the forward and reverse current density, j_0 the exchange current density, z, R and F the number of electrons, the gas constant and the Faraday constant, respectively, and T the thermodynamic temperature; α is an activation energy curve symmetry factor or transmission coefficient, which is assumed to be 0·5, such that j_{forward} and $\alpha_{\mathrm{reverse}}$ add up to unity.

Various assumptions can be made about the overpotential value in order to simplify this equation. The Tafel assumption is for a reaction to be irreversible and the overpotential to be approximately 15–300 mV below which is a resistive region and above which charge-transfer ceases to be rate-controlling when diffusion (limiting current) effects dominate. In this case the

reverse reaction is neglected and

$$j = j_0 \exp\left(\frac{\alpha z \eta F}{RT}\right) \quad (3)$$

or

$$\ln j = \ln j_0 + \frac{\alpha z \eta F}{RT} \quad (4)$$

On rearranging to separate overpotential η we can obtain

$$\eta = -\left(\frac{RT}{\alpha z F}\right)\ln j_0 + \frac{RT}{\alpha z F \ln j} \quad (5)$$

Because the exchange current density is essentially constant, this is the Tafel equation

$$\eta = a + b \log j \quad (6)$$

where $a = 2\cdot303\{RT/\alpha zF\}\log j_0$ and $b = 2\cdot303\{RT/\alpha zF\}$. It is now clear that plotting overpotential η against $\log j$ gives a straight line of slope b and intercept a, both parameters being characteristic of the electrode process and the factors affecting those parameters have become obvious and Tafel's concept has become fundamental.

Values of Tafel parameters have been tabulated in many textbooks. Because they characterise the reaction it is necessary to distinguish carefully between the electrode surface and the reaction. Table 1 lists some typical values. Figure 1 shows a series of Tafel plots.

Experimentalists sometimes ask how can one rely on seeing a Tafel regime when carrying out experimental work. In practice some general guide-rules can be applied:
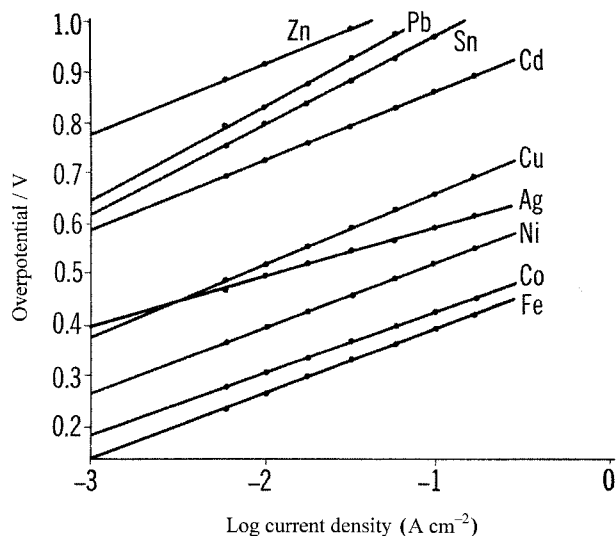
(i)   Tafel behaviour can be expected for 20–100 mV overpotential but individual reactions may be sluggish at reaching equilibrium and because of other simultaneous reactions that range may be curtailed or extended, e.g. 15–200 mV may often occur

(ii) reliable Tafel slopes depend upon having a good straight line graph ideally over at least one decade of current

(iii) the units of Tafel slope are usually expressed as mV per decade of current, i.e. $\Delta(\log \text{current}) = 1$.

The heritage of Tafel

The heritage of Tafel's equation is considerable because it represents the commonest range of overpotential and

Table 1 Some Tafel parameter values for the hydrogen evolution reaction

Metal	Solution	b / mV decade^{-1}	$-\log j_0$ / A cm^{-2}
Ag	1 M HCl	130	3·7
	1 M NaOH	120	6·5
Cu	0·1 M HCl	114	6·84
	0·01 M NaOH	107	6·09
Fe	0·01 M HCl	118	6·29
	0·1 M NaOH	120	6·06
Hg	0·1 M HCl	116	12
Pb	2 M H$_2$SO$_4$	120	12·7
Pt	0·1 M H$_2$SO$_4$	30	3·53
	0·5 M NaOH	117	4·06
Zn	2 M H$_2$SO$_4$	120	10·8

1 Typical Tafel plots for hydrogen evolution from 6 M NaOH at 25°C (after Lyons[6])

2 An Evans diagram for a bimetallic electrode system showing of anodic and cathodic branches and identification of corrosion current and potential

current densities employed in many electrochemical engineering situations. Three examples will be used to illustrate the way in which it has been used.

Reaction mechanisms

Tafel undoubtedly recognised that the parameters a and b had fundamental significance. He was able to see that metal behaviour changed and that the catalytic behaviour of platinum was characterised by a different value of b. He therefore offered possible mechanisms and for the hydrogen evolution reaction the critical mechanism step can be simply construed as follows

Catalytic evolution/reduction

$$M-H+M-H=2M+H_2 \tag{7}$$
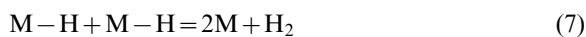
$$b=0.03 \text{ mV}$$

Two − step discharge

$$H_3O^+ + \varepsilon = H_{ads} + H_2O \tag{8}$$

$$2H_{ads} = H_2 \tag{9}$$
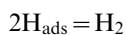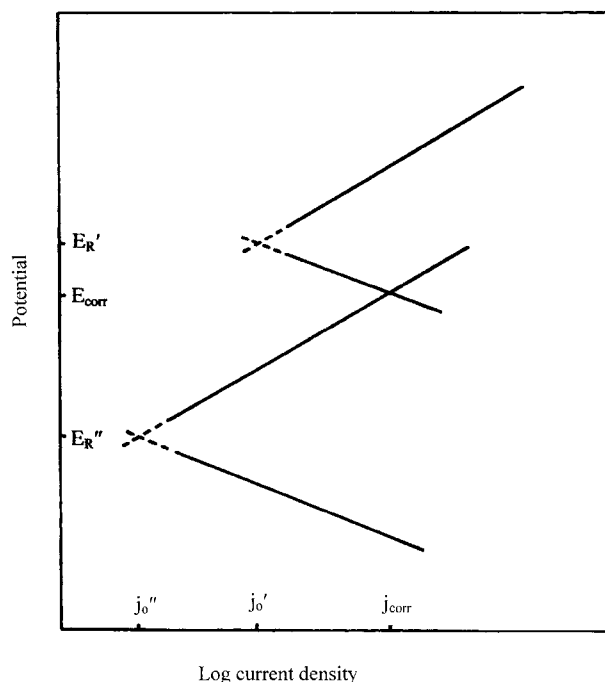
$$b=118 \text{ mV}$$

Tafel invoked a passive layer of hydride or oxide that resisted or disrupted hydroger evolution and which concerned him particularly in the behaviour of lead electrodes.

Departures from the exact value of $b=118$ mV were assumed by Tafel to be due to experimental error or temperature variation (he actually found $b=107$ mV) but once the significance of b in Butler–Volmer theory was seen it is obvious that if the symmetry factor α is not 0·5 the value can vary significantly. Similarly the value of a was considered to be characteristic of the electrode and solution but Butler–Volmer theory showed that it was really a normalised exchange current density.

A number of electrochemical reaction mechanisms have been studied in this way, notably that of corroding iron and reactions on lead where values of $b\approx80$ mV have been noted.

Evans polarisation diagrams

The idea for polarisation diagrams to explain galvanic or bimetallic behaviour under corrosion conditions is attributed to Evans during the 1920s and its origin can be seen in his books and papers of that period. It was formalised and developed by Hoar[7] specifically for metallic coatings since when the details have been refined by many authors. In its original form it assumed simple straight line relationships (E versus log j) for the dynamic corrosion anode and cathode reactions without too much concern for lower and higher potential ranges. It was intent on showing that two reaction systems were involved and the corrosion potential and current arose at the point of intersection of the anode branch of the base metal with the cathode branch of the noble metal (see Fig. 2). For schematic understanding this was sufficient. But two shortcomings were quickly recognised. First, if oxygen reduction is the cathode reaction, because the oxygen solubility is so low it is inevitably under diffusion control at its limiting current so the Tafel region is no longer appropriate (see Fig. 3). Second, once the exchange current density is deemed to be a characteristic parameter, being essentially Tafel's constant a, experimentalists wanted to calculate it from experimental data.

The exchange current density is of course the current density value at zero overpotential η or where the anode and cathode branches intersect. However, the Evans diagram disregards the initial linear E versus j region. Thus there is the convenient j_0 value (the Tafel line intercept) and the true j_0 (the intercept at zero overpotential for the true and polarisation values). As experimentalists know only too well, the true values at $0<\eta<20$ mV are very slow to reach equilibrium and attaining the true j_0 value is frustrating. Nevertheless, the use of Tafel concepts has been hugely beneficial in
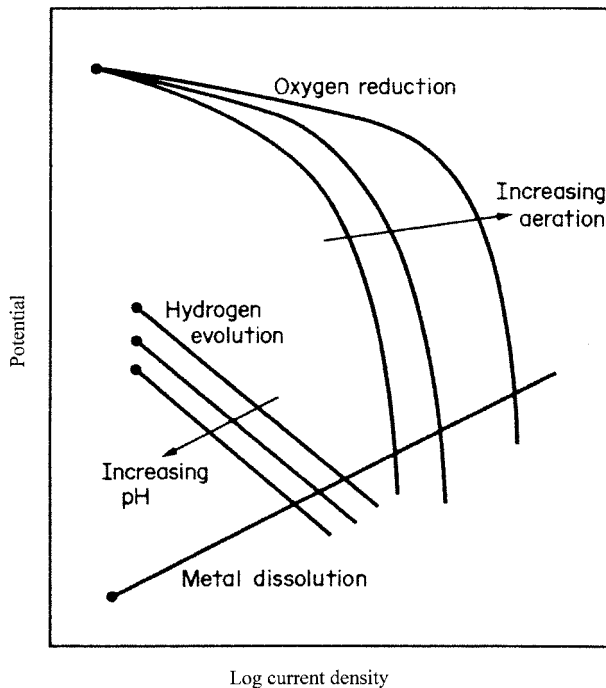
3 An Evans diagram for bimetallic corrosion where the rate-controlling reaction is diffusion-controlled oxygen evolution and the cathode reaction is pH dependent

understanding bimetallic corrosion and especially how the corrosion potential and corrosion current arise.

Polarisation resistance techniques

Electrochemical techniques for measuring corrosion currents and thereby corrosion rates have always been regarded as the ultimate challenge. Direct measurements are rarely satisfactory because of the circuit resistance which can be significantly affected by the imposition of a meter and thus affect the current passing. In 1957 Milton Stern[8] recognised that most corrosion occurs under Tafel conditions and by means of Evans diagrams derived a relationship both analytically and geometrically for the so-called 'polarisation resistance' and corrosion current

$$I_{corr} = \left(\frac{b_a b_c}{2 \cdot 3 (b_a + b_c)} \right) \frac{\Delta I}{\Delta E} \tag{10}$$

Where b is the Tafel slope for anodic and cathodic reactions and $\Delta E / \Delta I$ is the polarisation resistance (*PR*). The Tafel parameters are measured for the reactions concerned in a preliminary experiment (typically they are between $0 \cdot 03$ and $0 \cdot 3$ V decade^{-1} whence i_{corr} is

calculated from a measure of ΔI when an overpotential of 5–10 mV (i.e. ΔE) is applied to the corroding sample. The proportionality constant is often from 10 to 30 and is constant even outside strictly Tafel conditions but this must be proved before the test can be regarded as safe.

In practice the relation

$$i_{corr} = \frac{K}{PR} \tag{11}$$

is found to be reasonably accurate outside strict Tafel conditions, where K is a constant which can be approximated to $b_a / 2 \cdot 303$. Instruments are commercially available and much literature can be found recommending the usage and listing values of b for practical conditions.[9] More detailed and precise derivations have been made by several workers, notably Mansfeld, but the ultimate accolade is that it works. The name is of course a misnomer because it is not a resistance at all but happens to have the units of resistance, i.e. *V/I*. The reciprocal alternative of polarisation conductance is little better so purists can call it the Stern–Geary technique after its originators. However, the technique works even if the title remains!

Conclusions

The name Tafel ranks highly in the annals of applied electrochemistry. Although not receiving the acclaim of his peers during his lifetime, for practical value he ranks as high as Nernst and possibly higher than Ostwald. This centenary note may therefore provide a better profile of the man than has hitherto been apparent. More extensive biographical details may be found in Ref. 1 and for further reading see Refs. 10 and 11.

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