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Electrode kinetics

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Editor's foreword

The migration of an electron from an electrode to an electrolyte solution is an important part of an electrochemical process. We know roughly how ions behave in a bulk solution and we know roughly how electrons behave in a bulk metal electrode: in the present volume we are concerned with the problem of the interface. In the study of the kinetics of processes at electrodes we are able to explore the nature of the solution in the vicinity of the electrode and to construct models of its behaviour. Whereas temperature changes are the lever with which conventional chemical reactants are lifted over potential barriers, in electrode kinetics we possess a new, powerful, easily controlled lever: the potential of the electrode. Our control of this potential gives us power to speed or slow reactions over an enormous range of velocities. The transfer of an electron is a fundamental chemical process: electron transfer between molecules is a fundamental step of a variety of chemical reactions in solution, and both analysis and synthesis benefit from a knowledge of its rate and mechanism.

The behaviour of ions in bulk solution is described by Robbins in *Ions in solution* (2): *an introduction to electrochemistry* (OCS 2), and their chemical behaviour is described by Pass in *Ions in solution* (3): *inorganic properties* (OCS 7). The basic theory of chemical rate processes, on which much of the discussion in the present book hinges, is described in Pilling's *Reaction kinetics* (OCS 22), and the chemical thermodynamics, particularly the concepts of free energy and chemical potential, are to be found in Smith's *Basic chemical thermodynamics* (OCS 8). The statistical mechanical concepts are introduced in Gasser and Richard's *Entropy and energy levels* (OCS 19). Surfaces are of immense technological importance in industry, and apart from the obvious connexion of the material of this book with electrochemical syntheses and power generation from fuel cells, there is a deeper connexion with the general theory of catalysis: see Bond's *Heterogeneous catalysis: principles and applications* (OCS 18).

P.W.A.

Preface

DISTASTE and disgust are the predominant emotions that the normal student feels for electrochemistry. The Pogendorff potentiometer, the normal calomel electrode, liquid junction potentials, reversible and irreversible cells, all seem to him to have been invented by the Holy Office for the torturing of innocent students. As the train of old bearded electrochemists passes on its way, muttering of Galvani potentials and murmuring orisons for Guggenheim, the student escapes from cells without transference and relaxes with a little spin-orbit coupling.

This is a pity. Fig. 0.1 depicts the Ptolemaic view of electrode kinetics. (For the sake of clarity we have omitted the complicated system of epicycles which enable most chemists to remain in perpetual orbit around the subject.) There are many important applications for which an understanding of electrode kinetics is essential: they include corrosion, fuel cells, new batteries for electric cars, and analytical techniques for measuring pollution. But particularly important in view of the depletion of fossil fuels is the contribution that electrochemistry can, and must, make to energy storage and conversion. Photo-electrochemical cells should be capable of collecting solar energy; its storage and utilization will require better and more efficient batteries. As nuclear power replaces fossil fuels industrial processes will be carried out most efficiently by the sequence:



However despite the importance of these applications this book is concerned with the top half of Fig. 0.1 rather than the bottom half. This is because I am most concerned to show how electrode kinetics is linked to other more familiar topics. It is easier and I hope more rewarding to get to, and study, Clapham Junction rather than travel to the end of a picturesque but deserted branch line. Thus I hope that, after reading this book, students will not in future regard electrode kinetics as a remote and difficult subject but will see it more as a link between many different topics in thermodynamics, kinetics, photochemistry, inorganic redox systems, and physical organic chemistry.

Given a book of this length, I had to choose between attempting an aerial survey of the whole of electrode kinetics or working through in more detail some of the more important lines of argument. I have chosen to do the latter since the descriptive approach may 'tell it how it is' but must always be authoritarian. The student has to accept my word that it is so. The more detailed approach allows one to share the argument. Many of these arguments are mathematical in nature and indeed on first impression this book may seem

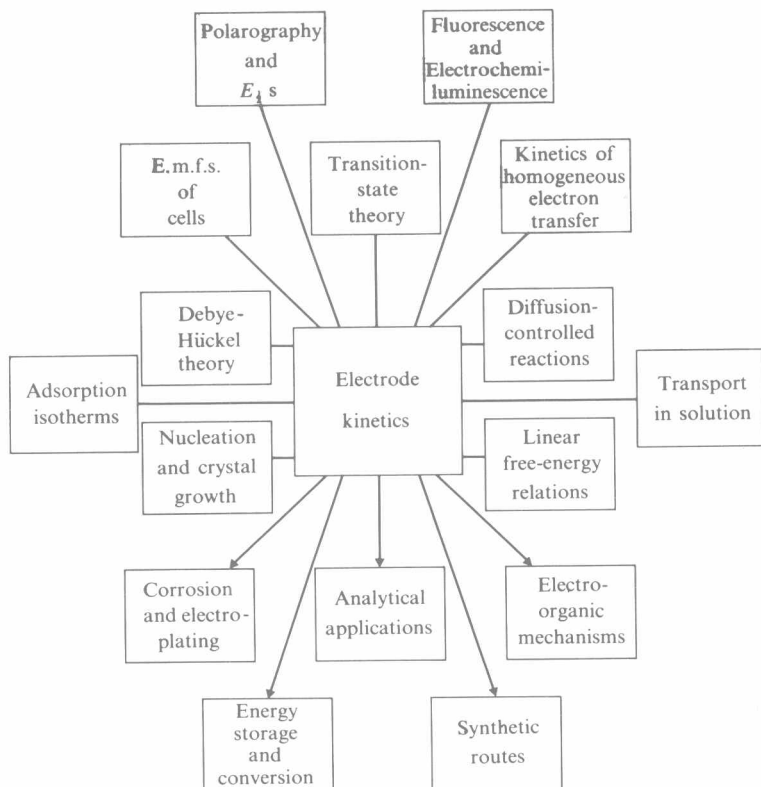


FIG. 0.1. The Ptolemaic view of electrode kinetics.

to have a large number of equations. It has, and the reason is that there is nothing more infuriating than to be told that 'it can easily be shown that' and to find that 'easily' means two days, a ream of foolscap, and the help of a member of the department of mathematics. I hope that I have included enough lines in the argument and enough appendices for the mathematics to be reasonably easy to follow. Certainly no great mathematical skills are required. Providing you can integrate you can cope. If you can't, there are still nearly as many pictures as equations.

Chapters 1, 3, and 5 are the main line of the argument and on a first reading Chapters 2 and 4 could well be omitted. Indeed, having written Chapter 2, I almost left it out myself, but the theory of the double layer is closely connected with Debye-Hückel theory; it is easier to think of the electrode and its ionic atmosphere than the mutual effect of one ion upon another. Also

double layers are important not only in electrode kinetics, but also in colloids and biological interfaces. Hence on general grounds the chapter has remained. Chapter 4 describes a simplified view of the Marcus and Levich theories of electron transfer reactions. This is an important class of reactions firstly because they are the means by which oxidation states are changed and secondly because they lie mid-way between other reactions studied in chemical kinetics and electronic transitions studied in spectroscopy.

I apologize to my electrochemical brethren for not including their favourite branch line or describing in detail their own wayside halt. In particular I have said almost nothing about adsorption, corrosion, fused salts, or electrocrystallization. This is not to say that these topics are unimportant. But the mechanisms involved are more complicated than those described in this book. Thus they will have to wait for another book and another author, more knowledgeable than I.

I wish to thank my pupils and students and in particular Alan Davis and Jon Hadgraft for their helpful comments, Peter Atkins as editor of the series for combining aggressive patience with tempered criticism, and above all Mrs. Elizabeth Price who, without the aid of the Rosetta stone, managed to type the manuscript.

This book is dedicated to my tutor, Professor R. P. Bell, F.R.S. Following the success of his *magnum opus*, I was tempted to call it *The electron in chemistry*, but perhaps that might have led to prosecution under the Trade Descriptions Act.

University College, Oxford

W.J.A.

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1. Potential-dependent rate constants

Introduction

WE start by considering the electrode-solution interface, for electrode kinetics is the study of the rates of reaction of charged particles at the interface between a solid and a liquid solution. Traditionally the solid has been a metal. A metal has the great advantage that it offers only a low resistance to the current caused by the flow of charged particles at the interface. The liquid is usually an ionic solution since again the current must flow through the solution. In this book we shall concentrate on water as the solvent since more work has been carried out in water than in other solvents or in molten salts. Hence we confine ourselves to a metal electrode in contact with an aqueous solution. There are now two types of charged particle that may cross the interface:

- (1) a metal ion;
- (2) an electron.

Sugar/tea system

Let us consider first the metal ion and imagine that as in Fig. 1.1 we have a silver electrode connected to earth in contact with a solution containing Ag^+ . For comparison there is also a mug of sweet tea with a sugar lump connected to nothing.

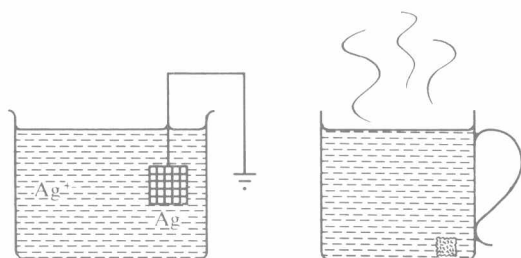


FIG. 1.1. A silver electrode and a sweet cup of tea.

Now in the case of the sugar at the interface some molecules will be leaving the sugar lump and some will be being deposited on it from the solution. So we may write:

$$j = k'_0 - k'_1 [\text{sugar}]_0 \quad (1.1)$$

2 Potential-dependent rate constants

where

j is the flux of sugar from the lump into the tea

k'_0 is a rate constant describing the dissolution process

k'_1 is a rate constant describing the deposition of the sugar

and

$[\text{sugar}]_0$ is the concentration of sugar in the solution at the surface of the lump measured in mol m^{-3} .

The flux j is the number of moles passing through unit area in unit time and for our purposes is measured in $\text{mol m}^{-2} \text{s}^{-1}$. The rate constant k'_0 must have the same dimensions. The rate constants are primed to show that they describe processes happening on a surface and to distinguish them from the familiar unprimed k used to describe reactions occurring in the bulk of the solution. The rate constant k'_1 has the rather peculiar dimensions of m s^{-1} . This is because we have to relate a flux per unit area in terms of a concentration per unit volume. This is also the reason why we shall describe concentrations in terms of mol m^{-3} rather than the more usual units of mol dm^{-3} ; for the old-fashioned 1 mol m^{-3} is the same as 1 mM (millimolar).

Strictly speaking we should include an activity coefficient in eqn (1.1). However the inclusion of γ s, f s, or curly brackets, although pleasing to the purist, makes the equations appear more complicated. Since the inclusion is not essential for our understanding of the fundamentals of electrode kinetics we will deal only with the simpler equations which describe ideal behaviour.

Finally we include a subscript of 0 on $[\text{sugar}]_0$ since the rate depends on the concentration of sugar at the surface of the lump. This concentration may not be the same as the concentration in the bulk of the solution designated $[\text{sugar}]_\infty$. For instance if the lump has just been added to fresh tea then

$$[\text{sugar}]_0 > [\text{sugar}]_\infty = 0.$$

The sugar will be diffusing (before the tea is stirred) from the lump into the rest of the tea.

If enough sugar is added, eventually the tea becomes saturated. Then the flux at the surface of the lump will be zero and the sugar concentration is uniform:

$$[\text{sugar}]_0 = [\text{sugar}]_\infty = k'_0/k'_1. \quad (1.2)$$

The term k'_0/k'_1 describes the solubility of the sugar at whatever temperature the tea has now reached.

Ag^+/Ag system

Now let us see what happens when we turn to the Ag^+ . The sugar can exist either in the lattice of the lump or in the tea. Similarly Ag^+ can exist either in the metallic lattice where it is said to be surrounded by a 'sea of delocalized electrons' or it can exist as a solvated ion surrounded by a sea of water molecules. Thus we can write eqn (1.3) which is the exact counterpart of (1.1).

$$j_{\text{Ag}^+} = k'_0 - k'_1[\text{Ag}^+]_0. \quad (1.3)$$

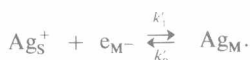
But the difference between Ag^+ and sugar is that the Ag^+ is charged while the sugar is neutral. Thus the potential difference between the metal and solution will affect the rates at which Ag^+ crosses the interface. The more negative the potential of the solution with respect to that of the metal the faster the Ag^+ will move from the metal to the solution and at the same time the harder it will be for the Ag^+ to be incorporated into the metal lattice from the solution. Qualitatively we can therefore write:†

$$(E_{\text{soln}} - E_{\text{metal}}) \downarrow \quad \text{or} \quad (E_{\text{metal}} - E_{\text{soln}}) \uparrow, \quad k'_0 \uparrow \text{ and } k'_1 \downarrow.$$

No such considerations arise in the case of the sugar system. That is why electrode kinetics is concerned with the movement of charged particles across the interface. Although the charge on the particles increases the complexity of the problem, the fact that the rate constants depend on the potential difference at the interface and can therefore be altered by twiddling a knob is an essential distinguishing feature of electrode kinetics.

Effect of potential on rate constants

We now move from a qualitative description to a more quantitative one. Consider the system,



The subscripts S and M indicate solution and metal respectively. Like any other reaction as the Ag^+ transfers from the solution to the lattice and vice versa it will have to surmount a free energy barrier. When the ion is in neither the electronic nor the aqueous 'sea' its free energy is larger. Fig. 1.2 shows a

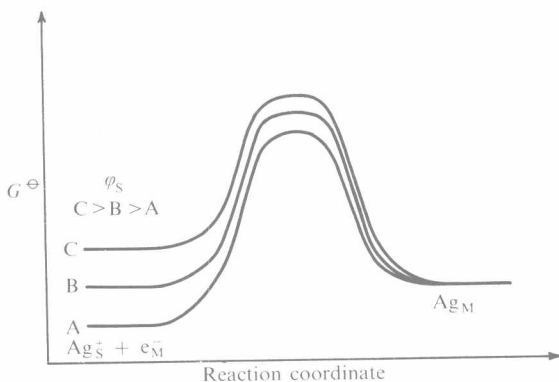


FIG. 1.2. Plot of free energy barriers against reaction coordinate for $\text{Ag}_{\text{S}}^+ + e_{\text{M}}^- \rightleftharpoons \text{Ag}_{\text{M}}$ at three different potentials, showing three slices of Fig. 1.3.

† See Robbins, *Ions in solution (2): an introduction to electrochemistry* (OCS2) for a discussion of the electrode potentials and the significance of their sign.

we move from left to right in Fig. 1.2 the surfaces converge; they are well separated on the left hand side of the diagram and on top of each other on the right hand side. Thus the transition state is less sensitive to changes in potential than the Ag_S^+ . We can write

$$G_\ddagger^\ominus = \text{constant} + \beta n F \phi_\text{S} \quad (1.5)$$

where $n = +1$ for Ag^+ . The parameter β is called the *transfer coefficient*; it is often approximately equal to $\frac{1}{2}$, which corresponds to the gradient of TS being half way between the gradients of OP and QR.

Now in ordinary chemical kinetics one writes from transition-state theory† that

$$k = \frac{k_\text{B} T}{h} \exp \left(-\frac{\Delta G_\ddagger}{RT} \right)$$

or

$$\ln k = \ln \left(\frac{k_\text{B} T}{h} \right) - \frac{\Delta G_\ddagger}{RT},$$

where k_B is the Boltzmann constant with subscript B to distinguish it from k , a rate constant.

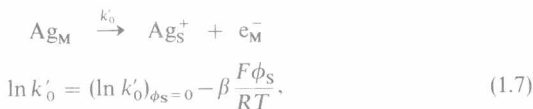
So by exactly the same arguments we write for the heterogeneous rate constants k' :

$$k' = Z' \exp \left(-\frac{\Delta G_\ddagger}{RT} \right)$$

or

$$\ln k' = \ln Z' - \frac{\Delta G_\ddagger}{RT}. \quad (1.6)$$

The frequency factor Z' is different since it has to describe the reactions of molecules with a plane surface and has dimensions of m s^{-1} . We will discuss it at a later stage. For the moment combining (1.5) with (1.6) we obtain for the process



and for the process

$$\begin{aligned} \text{e}_\text{M}^- + \text{Ag}_\text{S}^+ &\xrightarrow{k'_1} \text{Ag}_\text{M} \\ \ln k'_1 &= (\ln k'_1)_{\phi_\text{S}=0} + \frac{F \phi_\text{S}}{RT} - \beta \frac{F \phi_\text{S}}{RT} \\ &= (\ln k'_1)_{\phi_\text{S}=0} + (1 - \beta) \frac{F \phi_\text{S}}{RT} \\ &= (\ln k'_1)_{\phi_\text{S}=0} + \alpha \frac{F \phi_\text{S}}{RT}. \end{aligned} \quad (1.8)$$

† See Pilling, *loc. cit.*

6 Potential-dependent rate constants

While β is the transfer coefficient for an oxidation, it is helpful to define as well α the transfer coefficient for a reduction. For a single electron-transfer reaction,

$$\alpha + \beta = 1.$$

In eqn (1.7) the reactant is unaffected by changes in ϕ_S (the metal is earthed) and the term β describes the effect on the transition state. In eqn (1.8) again the β term refers to the transition state; the $F\phi_S/RT$ term describes the effect of the potential on the free energy of the reactant.

In order to simplify the discussion we have so far kept $\phi_M = 0$ by connecting the electrode to earth. This special condition can now be removed and we can write that in general:

$$\ln k'_0 = (\ln k'_0)_{\phi_S = \phi_M} + \frac{\beta n F (\phi_M - \phi_S)}{RT} \quad (1.9)$$

and

$$\ln k'_1 = (\ln k'_1)_{\phi_S = \phi_M} - \frac{(1 - \beta) n F (\phi_M - \phi_S)}{RT}. \quad (1.10)$$

Eqns (1.9) and (1.10) reduce to (1.7) and (1.8) when $\phi_M = 0$ and $n = 1$. The crucial potential is the potential *difference* at the interface. If both ϕ_M and ϕ_S are increased by one volt then there will be no difference to Fig. 1.3 since while Ag^+ will be less stable the electron will be more stable. Substitution in eqn (1.3) gives

$$j = (k'_0)_{\phi_S = \phi_M} \exp \left[\frac{\beta F (\phi_M - \phi_S)}{RT} \right] - (k'_1)_{\phi_S = \phi_M} \exp \left[\frac{(1 - \beta) F (\phi_M - \phi_S)}{RT} \right] [\text{Ag}^+]_0$$

Nernst equation

When no current flows at the electrode $j = 0$ and

$$[\text{Ag}^+]_0 = [\text{Ag}^+]_\infty = \left(\frac{k'_0}{k'_1} \right)_{\phi_S = \phi_M} \exp \left[\frac{F (\phi_M - \phi_S)}{RT} \right]. \quad (1.11)$$

This equation may be compared with (1.2) for the sugar in the tea. The essential difference is that the 'solubility' of the Ag^+ depends upon the potential difference at the interface. Furthermore we can rearrange eqn (1.11) to obtain,

$$\phi_M - \phi_S = (\phi_M - \phi_S)_{[\text{Ag}^+]_\infty = 1} + \frac{RT}{F} \ln [\text{Ag}^+]_\infty. \quad (1.12)$$

This is just the Nernst Equation for the Ag^+/Ag half cell.† Notice that (1.11) and (1.12) do not contain the parameter α . When we put $j = 0$ we stopped the net transfer of Ag^+ , abandoned the heady regions of kinetics, and descended

† See Robbins, *loc. cit.*, p. 66.

to the more mundane realm of thermodynamics. The parameter α described a property of the transition state, at the top of the free-energy barrier, and therefore has no place in the thermodynamic results (1.11) and (1.12). The Nernst equation can be derived without describing the kinetics. In order to describe the rate processes the kinetic model has to be more detailed and complicated. Thus kinetic derivations are no substitute for an understanding of thermodynamics. However it is of course necessary that the results from the special case of $j = 0$ in the kinetic argument should agree with those of thermodynamics.

$\text{Fe}^{3+}/\text{Fe}^{2+}$ system

We now turn to the second type of electrode process in which an electron and not an ion is transferred across the interface. In this case no atoms are transferred across the interface and the material of the electrode is insoluble in the solution phase. The electrode acts as a source or sink for electrons; it is made of an inert metal, usually platinum. We begin with the simplest example, in which the electrode reaction is a single electron transfer; for example:



Fig. 1.4 shows schematically the levels available to the electrons both in the metal and in the solution. In the metal the electronic energy levels are closely spaced; the valence electrons are delocalized over the whole lattice and to a first approximation they can be considered as a 'gas' of electrons con-

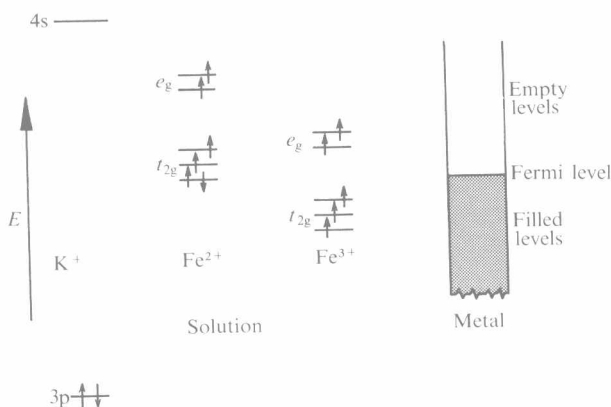


FIG. 1.4. Energy diagram (not to scale) of energy level for electrons in the metal and on ions in the solution.