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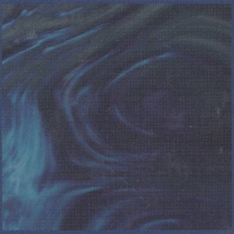

ANALYTICAL AND PHYSICAL ELECTROCHEMISTRY

Hubert H. Girault

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Hubert H. Girault

Translated by Magnus Parsons

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ANALYTICAL
AND PHYSICAL
ELECTROCHEMISTRY

To Freya-Merret, Jan-Torben and Jördis

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PREFACE

This book is a translation of a textbook entitled 'Electrochimie Physique et Analytique' (Presses Polytechniques Universitaires Romandes, 2001). The original goal was to gather in a single book the physical bases of electroanalytical techniques, including electrophoretic methods. Indeed, most of the textbooks dedicated to electrochemistry cover either the physical or the analytical aspects.

As science becomes more and more interdisciplinary, a thorough comprehension of the fundamental aspects becomes more important. The book is therefore intended to provide in a rigorous manner an introduction to the concepts underlying the electrochemical methods of separation (capillary electrophoresis, gel electrophoresis, ion chromatography, etc.) and of analysis (potentiometry, conductometry and amperometry).

My first thanks go to Magnus Parsons (Isle of Sky, Scotland) who did the translation. The present text has been thoroughly reviewed again by Prof. Roger Parsons (FRS), and I wish to thank most sincerely Roger for his support over all these years.

My thanks also go to the reading committee composed of Drs. Henrik Jensen, Jean-Pierre Abid, Maurizio Caragno, Debi Pant and Jördis Tietje-Girault.

I also thank all the team at Fontis Media (Lausanne, Switzerland) for producing this book, and in particular Thierry Lenzin for his patience and meticulous editing.

PREFACE TO THE ORIGINAL FRENCH VERSION

"ELECTROCHIMIE PHYSIQUE ET ANALYTIQUE"

For historical reasons, physical electrochemistry and analytical electrochemistry are often taught separately. The purpose of this course book is to bring these two subjects together in a single volume, so as to bridge the fundamental physical aspects to the analytical applications of electrochemistry.

The philosophy of this book has been to publish *in extenso* all the mathematical derivations in a rigorous and detailed manner, in such a way that the readers can understand rather then accept the physical origins of the main electroanalytical principles.

By publishing this book, I express my thanks to all those who have taught me the way through electrochemistry:

- From my early years in France, I wish to thank all the teachers from the Ecole Nationale d'Electrochimie et d'Electrométallurgie de Grenoble (ENSEEG) for developing my interest in electrochemistry, and of course I thank my parents for their financial and moral support.
- From my years in England, my most profound gratitude goes to Sir Graham Hills for both his scientific and political approach to Science, as well as to Lady Mary Hills for her friendship from the very beginning of my thesis. My admiration goes to Professor Martin Fleischmann (FRS), whose creative force has always been a source of inspiration, and to Professor Roger Parsons (FRS) whose intellectual rigor and mastery of thermodynamics can be found, I hope, in these pages. I would not forget Professor David Schiffrin who has taught me so much and with whom I spent several fruitful years. Thanks to them, I acquired during these years in Southampton a certain comprehension of classical physical electrochemistry.
- From my years in Scotland begins the period of my interest in analytical electrochemistry. I owe much to Drs Graham Heath and Lesley Yellowlees who helped me discover another type of electrochemistry, and I insist on expressing my sincere admiration to Professor John Knox (FRS) for his very scientific approach to chromatography and capillary electrophoresis.
- From my years in Switzerland, I thank Professor Michael Grätzel for his support when I arrived in Lausanne.

As a textbook, this work has been tried and tested on a series of undergraduate classes, and I thank all those students and teaching assistants who helped me with their comments to smooth out the difficulties. In particular I would like to thank Dr. Rosaria Ferrigno for her constructive criticisms; Dr. Pierre-François Brevet, Dr. Frédéric Reymond, Dr. David Fermin and Dr. Joël Rossier for their advice; and Dr. Olivier Bagel for having carried out the experiments whose results have served to illustrate several of the methods described here.

A detailed review of the work was carried out by Professors Jean-Paul Diard (ENSEEG, France) and Roger Parsons (Southampton, UK), and I thank them for their work. For the preparation of the original French version of this text, I thank the PPUR for their work in a collaboration that was both cordial and fruitful.

Finally, more than thanks must go to Dr. Jördis Tietje-Girault for her infallible support over the course of the years ever since our first meeting in the laboratory of Professor Graham Hills.

TABLE OF CONTENTS

PREFACE vii

PREFACE TO THE ORIGINAL FRENCH VERSION viii

CHAPTER 1 ELECTROCHEMICAL POTENTIAL 1
- 1.1 Electrochemical potential of ions 1
- 1.2 Electrochemical potential of electrons 23

CHAPTER 2 ELECTROCHEMICAL EQUILIBRIA 33
- 2.1 Redox reactions at metallic electrodes 33
- 2.2 Cells and accumulators 50
- 2.3 Pourbaix diagrams 54
- 2.4 Electrochemical equilibria at the interface between two electrolytes 57
- 2.5 Analytical applications of potentiometry 63
- 2.6 Ion exchange membranes 78
- Appendix : The respiratory chain 82

CHAPTER 3 ELECTROLYTE SOLUTIONS 83
- 3.1 Liquids 83
- 3.2 Thermodynamic aspects of solvation 85
- 3.3 Structural aspects of ionic solvation 100
- 3.4 Ion-ion interactions 105
- 3.5 Ion pairs 123
- 3.6 Computational methods 129
- Appendix 131

CHAPTER 4 TRANSPORT IN SOLUTION 133
- 4.1 Transport in electrolyte solutions 133
- 4.2 Conductivity of electrolyte solutions 138
- 4.3 Influence of concentration on conductivity 145
- 4.4 Dielectric friction 152
- 4.5 Thermodynamics of irreversible systems 160
- 4.6 Statistical aspects of diffusion 163
- Appendix: Elements of fluid mechanics 171

CHAPTER 5 ELECTRIFIED INTERFACES 177
5.1 Interfacial tension 177
5.2 Interfacial thermodynamics 180
5.3 Thermodynamics of electrified interfaces 184
5.4 Spatial distribution of polarisation charges 194
5.5 Structure of electrochemical interfaces 215

CHAPTER 6 ELECTROKINETIC PHENOMENA AND ELECTROCHEMICAL SEPARATION METHODS 221
6.1 Electrokinetic phenomena 221
6.2 Capillary electrophoresis 229
6.3 Electrophoretic methods of analytical separation 239
6.4 Electrophoretic separation of biopolymers 244
6.5 Ion chromatography 256
6.6 Industrial methods of electrochemical separation 261

CHAPTER 7 STEADY STATE AMPEROMETRY 265
7.1 Electrochemical kinetics 265
7.2 Current controlled by the kinetics of the redox reactions 268
7.3 Reversible systems: Current limited by diffusion 275
7.4 Electrodes with a diffusion layer of controlled thickness 280
7.5 Quasi-reversible systems: Current limited by kinetics and diffusion 288
7.6 Irreversible systems: Current limited by kinetics and diffusion 294
7.7 Quasi-reversible systems: Current limited by diffusion, migration and kinetics 295
7.8 Experimental aspects of amperometry 296

CHAPTER 8 PULSE VOLTAMMETRY 301
8.1 Chronoamperometry following a potential step 301
8.2 Polarography 311
8.3 Square wave voltammetry 319
8.4 Stripping voltammetry
8.5 Thin layer voltammetry 333
8.6 Amperometric detectors for chromatograpy 337

CHAPTER 9 ELECTROCHEMICAL IMPEDANCE 339
9.1 Transfer function 339
9.2 Elementary circuits 343
9.3 Impedance of an electrochemical system 351
9.4 AC voltammetry 368

CHAPTER 10 CYCLIC VOLTAMMETRY 375
10.1 Electrochemically reversible reactions with semi-infinite linear diffusion 375
10.2 Influence of the kinetics 382
10.3 EC reactions 385

10.4 Electron transfer at liquid | liquid interfaces 396
10.5 Assisted ion transfer at liquid | liquid interfaces 399
10.6 Surface reactions 402
10.7 Hemi-spherical diffusion 404
10.8 Voltabsorptometry 407
10.9 Semi-integration 408

ANNEX A VECTOR ANALYSIS 411
1. Coordinate systems 411
2. Circulation of the field vector 412
3. The vector gradient 413
4 Flux of the field vector 414
5 The Green-Ostrogradski theorem 414

ANNEX B Work functions and standard redox potentials 417

SYMBOLS 425

INDEX 429

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CHAPTER 1

ELECTROCHEMICAL POTENTIAL

1.1 ELECTROCHEMICAL POTENTIAL OF IONS

The chemical potential is the main thermodynamic tool used to treat chemical equilibria. It allows us to predict whether a reaction can happen spontaneously, or to predict the composition of reactants and products at equilibrium. In this book, we shall consider electrochemical reactions that involve charged species, such as electrons and ions. In order to be able to call on the thermochemical methodology, it is convenient to define first of all the notion of electrochemical potential, which will be the essential tool used for characterising the reactions at electrodes as well as the partition equilibria between phases. To do this, let us recall first of all, what a chemical potential is, and in particular the chemical potential of a species in solution.

1.1.1 Chemical potential

Thermodynamic definition

Let us consider a phase composed of chemical species j. By adding to this phase one mole of a chemical species i whilst keeping the extensive properties of the phase constant, i.e. the properties linked to its dimensions (V, S, n_j), we increase the internal energy U of the phase. In effect, we are adding the kinetic energy E_{trans}, the rotational energy E_{rot} and the vibrational energy E_{vib} if i is a molecule, the interaction energy between the species E_{int}, perhaps the electronic energy E_{el} if we have excited electronic states and the energy linked to the atomic mass of the atoms E_{mass} if we consider radiochemical aspects, such that:

$$U \quad = \quad E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{int}} + E_{\text{mass}} \tag{1.1}$$

Thus, we define the ***chemical potential*** of the species i as being the increase in internal energy due to the addition of this species

$$\mu_i \quad = \quad \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}} \tag{1.2}$$

In general, the variation in internal energy can be written in the form of a differential:

$$dU = -p\,dV + T\,dS + \sum_i \mu_i\,dn_i \tag{1.3}$$

Having defined the Gibbs energy G as a function of the internal energy

$$G = U + pV - TS \tag{1.4}$$

we can see, by taking the differential of each term of this equation and by replacing dU by the equation (1.3), that

$$dG = V\,dp - S\,dT + \sum_i \mu_i\,dn_i \tag{1.5}$$

This expression gives a definition of the chemical potential, which is in fact easier to use experimentally

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \overline{G}_i \tag{1.6}$$

In other words, the chemical potential μ_i is equal to the work which must be supplied keeping T & p constant in order to transfer one mole of the species i from a vacuum to a phase, except for the volume work. By definition, it represents the partial molar Gibbs energy $\overline{G}_i$. In the case of a pure gas, the chemical potential is in fact the molar Gibbs energy

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = G_m = \frac{G}{n} \tag{1.7}$$

Before treating the chemical potential of a species in the gas phase, let's look, by way of an example, at the influence of pressure on the molar Gibbs energy.

EXAMPLE

Let us calculate the variation in Gibbs energy associated with the isothermal compression from 1 to 2 bars ($T = 298$ K) of (1) water treated as an incompressible liquid and (2) vapour treated as an ideal gas.
Considering one mole, we have the molar quantities

$$\Delta G_m = \int V_m\,dp$$

For water as a liquid, the molar volume ($V_m = 18$ cm^3·mol^{-1}) is constant if we use the hypothesis that liquid water is incompressible. Thus we have:

$$\Delta G_m = V_m \Delta p = 18\cdot 10^{-6}(\mathrm{m^3\cdot mol^{-1}})\times 10^5(\mathrm{Pa}) = 1.8\ \mathrm{J\cdot mol^{-1}}$$

For water as vapour, considered as an ideal gas, the molar volume depends on the pressure,

$V_m = RT/p$

from which we get

$$\Delta G_m = \int_{p_1}^{p_2} V_m \, \mathrm{d}p = RT \int_{p_1}^{p_2} \frac{\mathrm{d}p}{p} = RT \ln\left(\frac{p_2}{p_1}\right) = 1.7 \text{ kJ} \cdot \text{mol}^{-1}$$

which is a thousand times greater.

Chemical potential in the gas phase

For an ideal gas ($pV = nRT$), we express the chemical potential μ for a given temperature with respect to a ***standard pressure*** value defined when the pressure has the standard value $p^{\ominus}$ of 1 bar (=100kPa). Thus by integration, the chemical potential for a given pressure p is linked to the standard chemical potential by:

$$\mu(T) - \mu^{\ominus}(T) = \int_{p^{\ominus}}^{p} V\mathrm{d}p = \int_{p^{\ominus}}^{p} \frac{RT}{p}\mathrm{d}p \tag{1.8}$$

that is

$$\mu(T) = \mu^{\ominus}(T) + RT \ln\left(\frac{p}{p^{\ominus}}\right) \tag{1.9}$$

Remember that an ideal gas is one in which the molecules do not have any interaction energy, and consequently a real gas can only be considered in this manner at low pressures. The chemical potential tends towards negative infinity when the pressure tends to zero because the entropy tends to infinity and because $\mu = G_m = H_m - TS_m$.

When the pressure is sufficiently high, the interactions between the gas molecules can no longer be ignored. These are attractive at medium pressures and the chemical potential of the real gas is therefore below what it would be if the gas behaved as an ideal one. On the other hand, at high pressures, the interactions are mostly repulsive, and in this case the chemical potential of a real gas is higher than it would be if it behaved as an ideal one.

These deviations of the behaviour of a real gas with respect to an ideal gas are taken into account by adding a correcting factor to the expression (1.9) for the chemical potential:

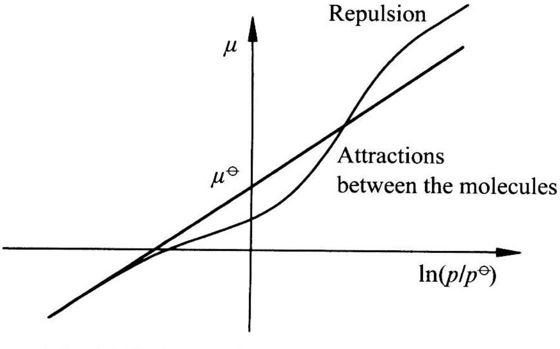

Fig. 1.1 Variation of chemical potential with pressure.

$$\mu(T) \;=\; \mu^{\ominus}(T) + RT\ln\left(\frac{p}{p^{\ominus}}\right) + RT\ln\varphi \;=\; \mu^{\ominus}(T) + RT\ln\left(\frac{f}{p^{\ominus}}\right) \qquad (1.10)$$

where φ is called the ***fugacity coefficient*** (dimensionless) and $f = \varphi p$ is the ***fugacity***.

The term $RT\ln\varphi$ represents the energy of interaction between the molecules. Given that gases tend towards behaving ideally at low pressures, we can see that $\varphi \to 1$ when $p \to 0$.

The reasoning developed above for a pure gas can be applied equally to ideal mixtures of ideal gases. The chemical potential of the constituent i of an ideal mixture of gases is therefore given by

$$\mu_i(T) \;=\; \mu_i^{\ominus}(T) + RT\ln\left(\frac{p_i}{p^{\ominus}}\right) \;=\; \mu_i^{\ominus}(T) + RT\ln\frac{p}{p^{\ominus}} + RT\ln y_i \qquad (1.11)$$

with p_i being the partial pressure of the constituent i and y_i the mole fraction. The standard state of a constituent i corresponds to the pure gas i considered as ideal and at the standard pressure of 1 bar.

Chemical potential in the liquid phase

In a liquid phase, the molecules are too close to one another to allow the hypothesis used in the case of ideal gases, i.e. that the intermolecular forces can be neglected. We define an ideal solution as a solution in which the molecules of the various constituents are so similar that a molecule of one constituent may be replaced by a molecule of another without altering the spatial structure of the solution (e.g. the volume) or the average interaction energy. In the case of a binary mixture A and B, this means that A and B have approximately the same size, and that the energy of the interactions A-A, A-B and B-B are almost equal (for example a benzene-toluene mixture).

When there is an equilibrium between a liquid phase and its vapour, the chemical potential of all the constituents is the same in both phases. If the solution is ideal, its constituents obey Raoult's Law $p_i = x_i\, p_i^*$ with p_i being the partial pressure of the constituent i and p_i^* the saturation vapour pressure of the pure liquid. By analogy with ideal gases, we define a solution as ideal if the chemical potential of its constituents can be written as a function of the mole fraction x_i in the liquid

$$\mu_i(T) \;=\; \mu_i^{\ominus,ideal}(T) + RT\ln x_i \qquad (1.12)$$

The equality of the chemical potentials between the vapour phase and the liquid phase leads to

$$\mu_i^{\ominus,ideal}(T) \;=\; \mu_i^{\ominus}(T) + RT\ln\left(\frac{p_i^*}{p^{\ominus}}\right) \qquad (1.13)$$

In the case of the benzene-toluene mixture, Raoult's law is obeyed for all values of the mole fractions (ideal solution).

Other types of ideal solutions are the binary mixtures A-B in which the molecules are not identical but, where one constituent is present in a much greater quantity than the other. If A is in the majority, it becomes the solvent and B the solute. Such a solution is ideal in as much as the replacement of a molecule of A by one of B or vice-versa has little effect on the properties of the solution, given the dilution of B in A. We call this particular type of ideal solution an ideally dilute solution.

Mole fraction scale

At the molecular level, we can say that in an ideally dilute solution, the solute molecules do not interact with each other, but only interact with the molecules of the solvent that surrounds them. Here again, we have the analogy with the ideal gases. In an ideally dilute solution, that is to say that when $x_A \to 1$, the solvent obeys Raoult's law. The chemical potential of the solvent A is then written as

$$\mu_A(T) = \mu_A^{\ominus,ideal}(T) + RT \ln x_A \tag{1.14}$$

The deviation from the ideal behaviour (for example when the concentration of B is no longer negligible in relation to that of A) can be taken into account by adding a correction term to the expression for the chemical potential

$$\mu_A(T) = \mu_A^{\ominus,ideal}(T) + RT \ln x_A + RT \ln \gamma_A \tag{1.15}$$

Since solutions become ideal when $x_A \to 1$, we can see that at this limit $\gamma_A \to 1$.

As far as the solute is concerned, it obeys Henry's law $p_B = x_B K_B$, where p_B is the partial pressure of the solute B, x_B the mole fraction of B in the liquid and K_B the Henry constant which has the dimension of a pressure.

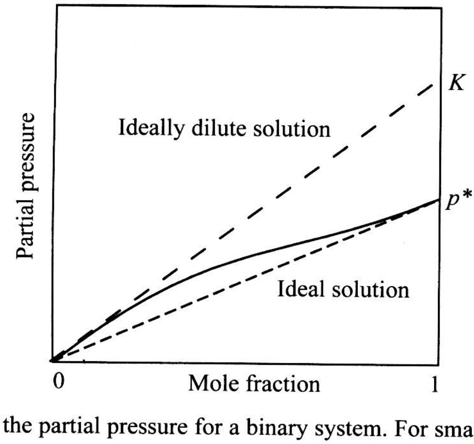

Fig. 1.2 Diagram of the partial pressure for a binary system. For small mole fractions (solute), the partial pressure is proportional to the mole fraction (Henry's law). For mole fractions approaching unity (solvent), the partial pressure is proportional to the mole fraction (Raoult's law).

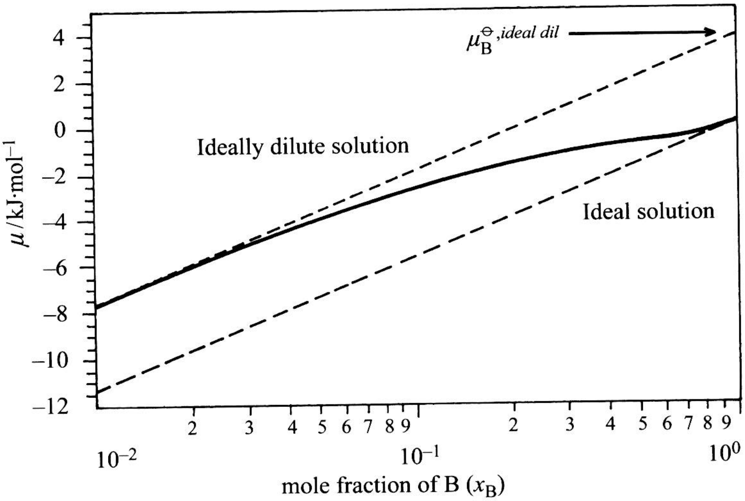

Fig. 1.3 Variation of the chemical potential and the definition of the standard chemical potential at 25°C on the scale of mole fractions for an ideally dilute solution.

The chemical potential of the solute is then written as

$$\mu_B(T) = \mu_B^{\ominus,ideal\ dil}(T) + RT\ln x_B \tag{1.16}$$

with $\mu_B^{\ominus,ideal\ dil}$ being the standard chemical potential on the mole fraction scale for ideally dilute solutions. It is important to note that the standard state is an imaginary state which we would have at the limit $x_B \to 1$, that is to say an extrapolation of the chemical potential of the solute from the infinitely dilute case to its pure state. In other words, the standard state is a pure solution of B that would behave like an ideally dilute solution, i.e. a pure solution in which the molecules do not interact. The equality of the chemical potentials of B between the vapour phase and the liquid phase gives

$$\mu_B^{\ominus,ideal\ dil}(T) = \mu_B^{\ominus}(T) + RT\ln\left(\frac{K_B}{p^{\ominus}}\right) \tag{1.17}$$

The deviations from the ideal behaviour can also be taken into account by adding a correction term to the chemical potential.

$$\mu_B(T) = \mu_B^{\ominus,ideal\ dil}(T) + RT\ln x_B + RT\ln\gamma_B \tag{1.18}$$

The term $RT\ln\gamma_B$ then represents the work of interaction of the solute molecules among themselves. If the solute is a salt, the predominant energy of interaction will be the electrostatic one. We will show later on in this book that it is possible to model this interaction energy using statistical mechanics (see §3.4.2, the Debye-Hückel theory).

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