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THE PRINCIPLES OF APPLIED ELECTROCHEMISTRY

BY

A. J. ALLMAND

M.C., D.Sc., F.I.C., F.R.S.

PROFESSOR OF CHEMISTRY, KING'S COLLEGE, LONDON

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BY THE AUTHOR AND

H. J. T. ELLINGHAM

A.R.C.S., Ph.D., A.M.I.CHEM.E.

LECTURER IN PHYSICAL CHEMISTRY, IMPERIAL COLLEGE
OF SCIENCE AND TECHNOLOGY



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PREFACE TO SECOND EDITION

THE general plan and scope of this book remain as outlined in the preface to the first (1912) edition, and it is hoped that it will still continue to appeal both to students and to those already engaged in industry. There are two main changes to note. When first written, the elements of physical chemistry were by no means universally known or appreciated in technical circles, and short chapters dealing in a very elementary way with such subjects as equilibrium and osmotic pressure were accordingly introduced. Their necessity was criticised by some at the time, and it is certain that they would serve no useful purpose to-day. They have therefore been suppressed, and replaced in Part I, which remains of about the same length as before, by a more detailed treatment of irreversible electrode phenomena. In this connection, we have found it necessary frequently to acknowledge our indebtedness to the recent revised edition of Professor Fritz Foerster's *Elektrochemie wässriger Lösungen*.

Part II, on the other hand, has been considerably enlarged. This was inevitable, if the character of the book were to remain unchanged. Twelve years would, in any case, have made a difference. The twelve years under notice comprised the war period, during which electrochemical and electrometallurgical methods more than maintained their ground in the enormous industrial expansion which then took place. Apart from minor processes, this expansion finds expression in the present volume in the appearance of new and important electrolytic methods for copper and zinc extraction, in much new detail in the chapter dealing with alkali-chlorine cells, and in the complete rewriting of the section on electrothermal metallurgy. We fully realise that our choice of new matter for inclusion is somewhat arbitrary. Thus whilst, as before, we mention the subject of quartz fusion, we say nothing of the incipient use of electric furnaces in the glass industry. The heat treatment of steel is dealt with briefly, whilst the applications of endosmosis and cataphoresis, and a treatment of electrostatic fume precipitation are not included. It was necessary, however, to draw a line somewhere, and the limits of the subject are not too well defined. It may be added that special attention has been given to one or two chapters which were, with justice, criticised in the first edition as being inadequate. Any suggestions or corrections on points of detail will, as before, be gratefully received.

Cordial thanks are due to the following for providing information on,

or criticising, points of which they have special knowledge: Mr. W. J. A. Butterfield; Mr. D. F. Campbell; Professor C. H. Desch, F.R.S.; Professor James Rice; Mr. E. L. Joseph; The Boving Engineering Works, Ltd.; The Chloride Electrical Storage Company, Ltd.; Ernest Scott & Co., Ltd.; The Morgan Crucible Company, Ltd.; The Society of Chemical Industry in Basle; The Tudor Accumulator Company, Ltd.; Watsons (Metallurgists), Ltd.

The undersigned finally would wish, in particular, to pay a warm tribute to Mr. H. J. T. Ellingham, his colleague in this University and collaborator in the rewriting of this book. It is no exaggeration to say that, without Mr. Ellingham's help, a fully revised edition, as this claims to be, could not have appeared. Mr. Ellingham has not only searched through practically the whole of the literature from 1911 to 1923, but has also taken on himself the rewriting of the great bulk of Part I and several important chapters of Part II. To this work he has brought a combination of qualities as nearly ideal from his collaborator's point of view as could well be imagined.

A. J. ALLMAND.

UNIVERSITY OF LONDON,
KING'S COLLEGE,

LIST OF ABBREVIATIONS

<i>Abhand. Bunsen Ges.</i>	Abhandlungen der Deutschen Bunsen Gesellschaft.
<i>Amer. Chem. Jour.</i>	American Chemical Journal.
<i>Ann. Chim. Phys.</i>	Annales de Chimie et de Physique.
<i>Ber.</i>	Berichte der Deutschen Chemischen Gesellschaft.
<i>Berg- und Hütten. Zeit.</i>	Berg- und hüttenmännische Zeitung.
<i>Blast Furn. Steel Plant</i>	Blast Furnace and Steel Plant.
<i>Bull. Soc. Chim.</i>	Bulletin de la Société Chimique de Paris.
<i>Can. Chem. Jour.</i>	Canadian Chemical Journal.
<i>Can. Chem. and Met.</i>	Canadian Chemistry and Metallurgy.
<i>Chem. Abst.</i>	Chemical Abstracts.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>Chem. Met. Eng.</i>	Chemical and Metallurgical Engineering.
<i>Chem. Trade Jour.</i>	Chemical Trade Journal.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Compt. Rend.</i>	Comptes Rendus des Séances de l'Académie des Sciences.
<i>Ding. Poly. Jour.</i>	Dinglers Polytechnisches Journal.
<i>Drud. Ann.</i>	Annalen der Physik (Fourth Series).
<i>Elect. Rev.</i>	Electrical Review.
<i>Elect. World</i>	Electrical World.
<i>Electr.</i>	Electrician.
<i>Electrochem. Ind.</i>	Electrochemical and Metallurgical Industry.
<i>Electrochem. and Metall.</i>	Electrochemist and Metallurgist.
<i>Elektrochem. Zeitsch.</i>	Elektrochemische Zeitschrift.
<i>Elektrotech. Zeitsch.</i>	Elektrotechnische Zeitschrift.
<i>Engin.</i>	Engineering.
<i>Eng. Mining Jour.</i>	Engineering and Mining Journal.
<i>Eng. Mining Jour. Press</i>	Engineering and Mining Journal Press.
<i>Eng. Mining World</i>	Engineering and Mining World.
<i>Found. Trade Jour.</i>	Foundry Trade Journal.
<i>Gazz. Chim. Ital.</i>	Gazzetta Chimica Italiana.
<i>Gen. Elec. Rev.</i>	General Electric Review.
<i>Giorn. Chim. Indus. Appl.</i>	Giornale di Chimica Industriale ed Applicata.
<i>Helv. Chim. Acta</i>	Helvetica Chimica Acta.
<i>Jahrb. Elektrochem.</i>	Jahrbuch der Elektrochemie.
<i>Jahrb. der Rad.</i>	Jahrbuch der Radioaktivität und Elektronik.
<i>Jour. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>Jour. Amer. Inst. Elect. Eng.</i>	Journal of the American Institute of Electrical Engineers.
<i>Jour. Chim. Phys.</i>	Journal de Chimie Physique.
<i>Jour. Four Elect.</i>	Journal du Four Electrique.
<i>Jour. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>Jour. Iron and Steel Inst.</i>	Journal of the Iron and Steel Institute.

<i>Jour. Phys. Chem.</i>	Journal of Physical Chemistry.
<i>Jour. Prakt. Chem.</i>	Journal für praktische Chemie.
<i>Jour. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>Koll. Zeitsch.</i>	Kolloid Zeitschrift.
<i>Lieb. Ann.</i>	Annalen der Chemie.
<i>Manch. Mem.</i>	Memoirs of the Manchester Literary and Philosophical Society.
<i>Metall.</i>	Metallurgie.
<i>Met. Chem. Eng.</i>	Metallurgical and Chemical Engineering.
<i>Metal Ind.</i>	Metal Industry (New York).
<i>Mining Sci. Press</i>	Mining and Science Press.
<i>Philos. Mag.</i>	Philosophical Magazine.
<i>Proc. Acad. Sci. Amsterdam</i>	Proceedings of the Section of Sciences, Royal Academy of Amsterdam.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Rev. Electrochim.</i>	Revue d'Electrochimie.
<i>Rev. Mét.</i>	Revue de Metallurgie.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Amer. Inst. Chem. Eng.</i>	Transactions of the American Institute of Chemical Engineers.
<i>Trans. Amer. Inst. Elect. Eng.</i>	Transactions of the American Institute of Electrical Engineers.
<i>Trans. Amer. Inst. Min. Eng.</i>	Transactions of the American Institute of Mining Engineers.
<i>Trans. Amer. Inst. Min. Met. Eng.</i>	Transactions of the American Institute of Mining and Metallurgical Engineers.
<i>Trans. Can. Min. Inst.</i>	Transactions of the Canadian Mining Institute.
<i>Trans. Chem. Soc.</i>	Transactions of the Chemical Society.
<i>Trans. Farad. Soc.</i>	Transactions of the Faraday Society.
<i>Trans. Inst. Mining Met.</i>	Transactions of the Institution of Mining and Metallurgy.
<i>Wied. Ann.</i>	Annalen der Physik (Third Series).
<i>Zeitsch. Angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. Anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Elektrochem.</i>	Zeitschrift für Elektrochemie.
<i>Zeitsch. Metallkunde</i>	Zeitschrift für Metallkunde.
<i>Zeitsch. Phys. Chem.</i>	Zeitschrift für physikalische Chemie.

LIST OF SYMBOLS USED

A	'Free energy' decrease.
C	Concentration; molecular heat.
C_p, C_v	Molecular heats of gases at constant pressure and constant volume.
Cal.	Large (kilo-) calorie.
E	Potential, voltage.
E.M.F.	Electromotive force.
F	Valence charge (96500 coulombs).
I	Current.
K	Constant: particularly equilibrium constant.
L	Latent heat of change of state; coefficient of self-induction.
M	Molecular weight.
Mol.	Gram molecule.
P	Osmotic pressure.
Q	Quantity of heat.
R	Resistance; gas constant.
S.G.	Specific gravity.
T	Absolute temperature.
U	'Total energy' decrease.
V	Velocity.
a	Area; ionic activity; work done by a system.
c	Specific heat; concentration in gram mols or gram ions per litre. (Concentration of species XY in gram mols or gram ions per litre is expressed by [XY]).
$cal.$	Small (gram-) calorie.
e	Single electrode potential.
e_o	Electrolytic potential.
i	van't Hoff factor.
k	Constant; velocity constant; specific thermal conductivity.
l	Length.
l_c, l_λ	Equivalent ionic conductivity.
m	Mass.
n	Transport number; ions per molecule of salt; valency of ion; frequency.
p	Pressure.
q	Heat effect in reversible process.
r	Specific resistance.
t	Time.
u_c, u_λ	Ionic mobility (velocity under gradient of 1 volt/cm).
v	Volume.
α	Degree of dissociation.
δ	Specific gravity.
η	Viscosity; concentration in gram equivalents per c.c.
Φ	Thermodynamic potential.
κ	Specific conductivity.
Λ	Equivalent conductivity.
π	Electrolytic solution pressure.
θ	Temperature in degrees C.
$\cos \phi$	Power factor.

- (a) One ton is taken as 1000 kilos, unless otherwise expressly stated.
 (b) A H.P. year is taken as 8760 H.P.H.

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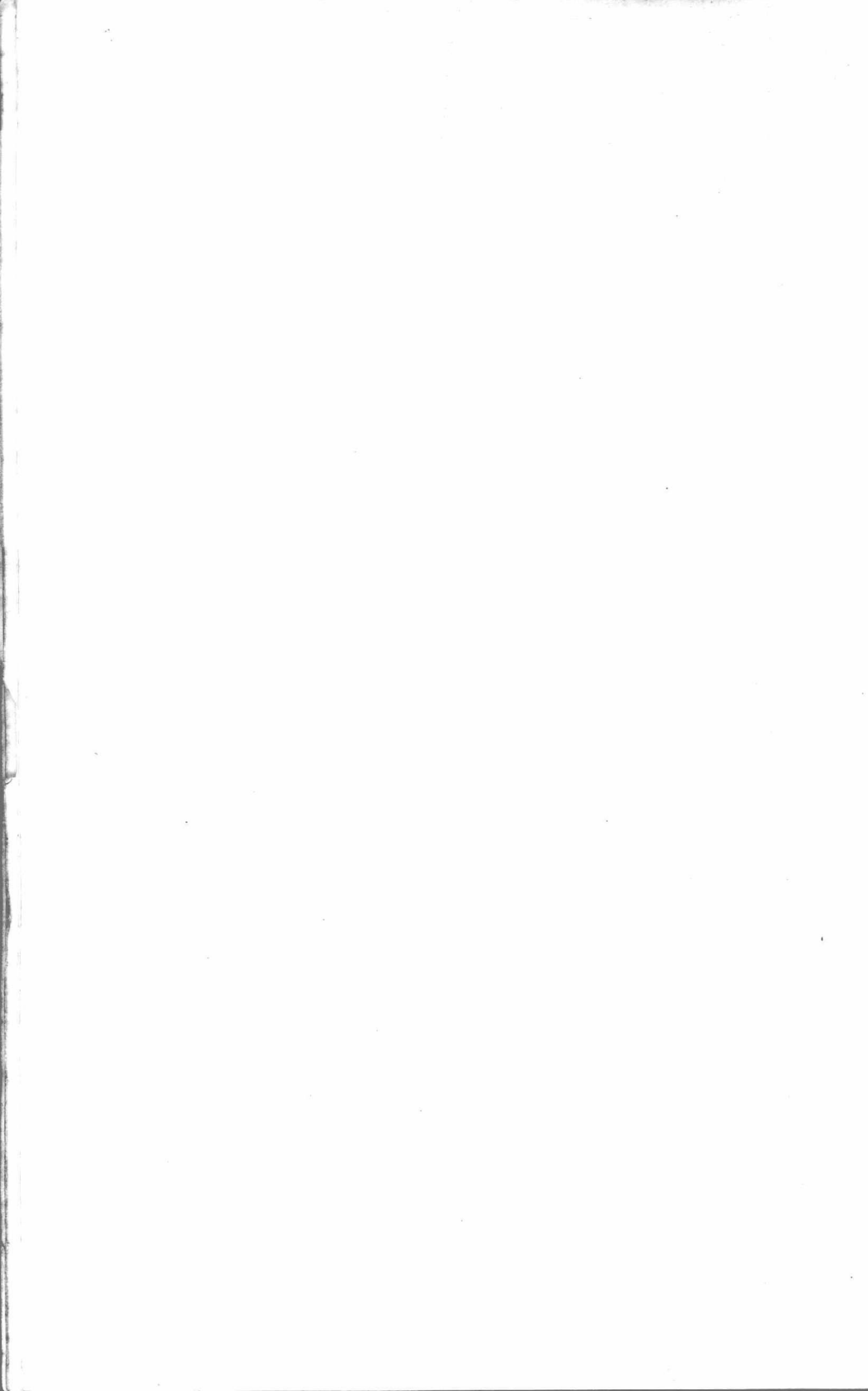
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PART I
GENERAL AND THEORETICAL



CHAPTER I

INTRODUCTORY—POWER

1. Chemical and Electrochemical Methods compared

CHEMICAL reactions can be divided into two classes—those which give out energy (usually in the form of heat), and those which absorb energy, whilst they are taking place. Examples of the former class are the combustion of fuels, the Goldschmidt Thermite processes, the slaking of lime. To the latter class belong the reduction of metals from their ores, and the formation from their elements of oxides of nitrogen or metallic carbides.

Electrochemical reactions can be similarly divided. Those which proceed with liberation of energy are not so important practically as those of the second kind, and will occupy little space in this book. The reaction being electrochemical, the liberated energy appears as electrical energy, and the systems in which the reaction takes place are known as **primary cells**. The Daniell cell is an example. The corresponding reaction is



and, when allowed to take place chemically, liberates its energy as heat.

On the other hand, electrochemical processes of the second kind—those which take place with absorption of electrical energy—have achieved very considerable technical significance, frequently supplanting a purely chemical process, and in some cases furnishing new products which could hardly be obtained in any other way. Thus copper is now chiefly refined electrochemically; the bulk of the world's chlorate production is made electrochemically; the electrochemical production of caustic alkali and bleach becomes continually more important; whilst the manufacture of aluminium, of CaC_2 (and hence acetylene), and of nitrates from the air could not have reached their present proportions without the introduction of electrochemical methods.

In chemical processes, the necessary supply of energy is usually introduced as heat. This often results in considerable wear and tear of plant, and in products rendered impure by the fuel used. Further, it often happens that the simplest and most direct (on paper) of purely chemical methods for reaching a certain result cannot be used, owing to great reaction resistances, or to the impossibility of converting heat

energy into chemical energy under the given conditions. And consequently several successive reactions have to replace a single direct one. Thus, to obtain aluminium from alumina, the old chemical process consisted of preparing AlCl_3 by passing chlorine gas over a mixture of the alumina with carbon, forming a double salt of AlCl_3 with NaCl , and reducing this double salt by heating with metallic sodium.

Electrochemical processes differ in the following respects :—

(a) the energy needed is frequently introduced as electrical energy, not as heat ;

(b) when introduced as heat, the heat is produced from electrical energy just where it is needed, not by means of furnaces or flue gases ;

(c) the processes are generally simpler and more direct than the corresponding chemical processes ;

(d) in consequence of (a) and (b) the products are usually purer ;

(e) the wear and tear of plant is generally less.

On the question of the relative costs of chemical and electrochemical processes, it is impossible to generalise. Sometimes one is the cheaper, sometimes the other. It is a matter decided by numerous factors which vary with each separate case, such as the local power charges, their cost compared with that of raw material, the relative charges for labour and maintenance of plant, the purity of product required, etc. Sometimes the electrochemical method is more expensive, but gives a purer product and is therefore preferably used.

Electrochemical processes should always be of as simple a nature as possible. This statement of course holds good of any kind of technical chemical operation, but particularly of electrochemical ones. They cannot 'stand such hard knocks' as chemical processes can, and generally only work satisfactorily when run under constant conditions. Simplicity is therefore of importance. The raw materials used should also be as pure as possible. When once impurities begin to accumulate, the efficiency of an electrochemical process usually decreases very rapidly. The most successful electrochemical processes are those in which a constant supply of a raw material of high purity and constant composition is assured. If impure, it will usually pay to subject it to a preliminary chemical purification.

2. Electrical Units

Electrical energy, like all other kinds of energy, can be divided into two factors, the *quantity factor* and the *intensity factor*. The possibility of a change taking place in the energy content of a system is determined by the intensity factor only, the extent of the change by both factors. Whether or not a quantity of water can move spontaneously from one level to another is determined in the first instance by the relative heights of the two levels. If movement does take place, the change of potential energy is expressed by the product of the weight of water which has flowed down into the difference in height between the two positions. Here difference in height is the intensity factor, weight of water the quantity factor. A possible transference of heat energy from one part

of a system to another is decided by the difference in temperature between the two regions—the intensity factor of the heat energy. Excluding the effect of passive resistances, it is the affinity of a chemical reaction which decides whether it will set in or not; whilst the amount of chemical energy transferred in such a reaction is given by the product of the affinity of the reaction and the quantity of matter which has been transformed.

Similarly, electrical energy has its intensity factor, **potential difference** (E), and its quantity factor, **quantity of electricity**. The former determines the direction of transference of electrical energy, the product of the two quantities determines the magnitude of the change.

From these fundamental conceptions we can directly pass on to others. When the energy content of a system is increasing or decreasing (*i.e.* when work is being done on or by the system), the change of energy per unit time (the rate of consumption or production of work) is termed the **power**. In the same way, when a transference of electricity takes place across a certain point, the quantity which passes per unit of time is termed the **current**¹ (I). Finally, the rate at which electricity can pass between two points at different electrical potentials is directly proportional to the magnitude of this potential difference, and also depends on the nature of the path along which the current travels.

The relation may be expressed in the form

$$I = \frac{E}{R}$$

where R is called the **resistance** of the conductor (Ohm's Law). If the resistance be great, the current passing for a given difference of potential will be small, and *vice versa*.

In deciding on the units² to serve for the measurement of these magnitudes, it has been found most convenient to define first the units of resistance and current, and to deduce from these the units of potential, energy, power and quantity of electricity. The first primary unit is that of resistance, the **ohm**, which is defined as the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, the column to be 14.4521 grams in weight, of a constant cross-sectional area, and of a length of 106.300 cm. The second primary unit is that of current, the **ampere**. As we shall see later,³ when electricity is passed through a solution of a metallic salt in water, the salt is decomposed, and in many cases the metal is deposited in the free state. It has been found that the phenomenon is a quantitative one, and the ampere is defined as the unvarying electric current, which,

¹ The current flowing across any point, divided by the area of the conductor at that point at right angles to the direction of the current, is called the **current density**.

² The units here defined were specified by the International Conference on Electrical Units and Standards, 1908. They are known as the *international* units. Ohms and volts of slightly lesser magnitude were used some years back, but need no further mention here.

³ P. 12.