Experimental Approach to Electrochemistry

N. J. Selley

54·24
S467

Experimental Approach to Electrochemistry

N. J. Selley M.A., B.Sc.

Senior Lecturer, Kingston Polytechnic (Gipsy Hill Centre).

图书館藏

Edward Arnold

5505582

© N. J. Selley 1977

First published 1977
by Edward Arnold (Publishers) Ltd.
25 Hill Street, London W1X 8LL

ISBN: 0 7131 2540 3 Boards edition
ISBN: 0 7131 2541 1 Paper edition

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of Edward Arnold (Publishers) Ltd.

To H. G. Andrew

Type set by Cotswold Typesetting Ltd, Gloucester,
and printed in Great Britain by Unwin Bros. Ltd. Woking and London

Preface

This book treats a well-established subject in a new way. The content matter corresponds approximately to the basic electrochemistry component of an ordinary degree course in chemistry, but the style of treatment will be seen to be more expansive and less mathematical than the usual student text. (No more than O-level maths is presupposed.)

The first two chapters are devoted to a closer look at topics first met with at O-level, with the intention of revealing aspects which the now more mature reader will appreciate. It is hoped that this critical approach to elementary material will be of particular interest to (present or prospective) science teachers.

After what may serve as a revision of earlier work, the book proceeds (in Chapters 3 to 6) to examine the concepts and principles shown on the diagram overleaf. The aim is full understanding rather than rapid coverage, and the practical work and exercises are designed to assist in this. The practical work does not require elaborate or expensive apparatus, and it should be possible to carry out most of it in a very modestly equipped laboratory. The book may be used either with an organized course or for private study, and in the latter case the student will benefit from the fuller 'Answers', which include indications as to the method of working the exercises.

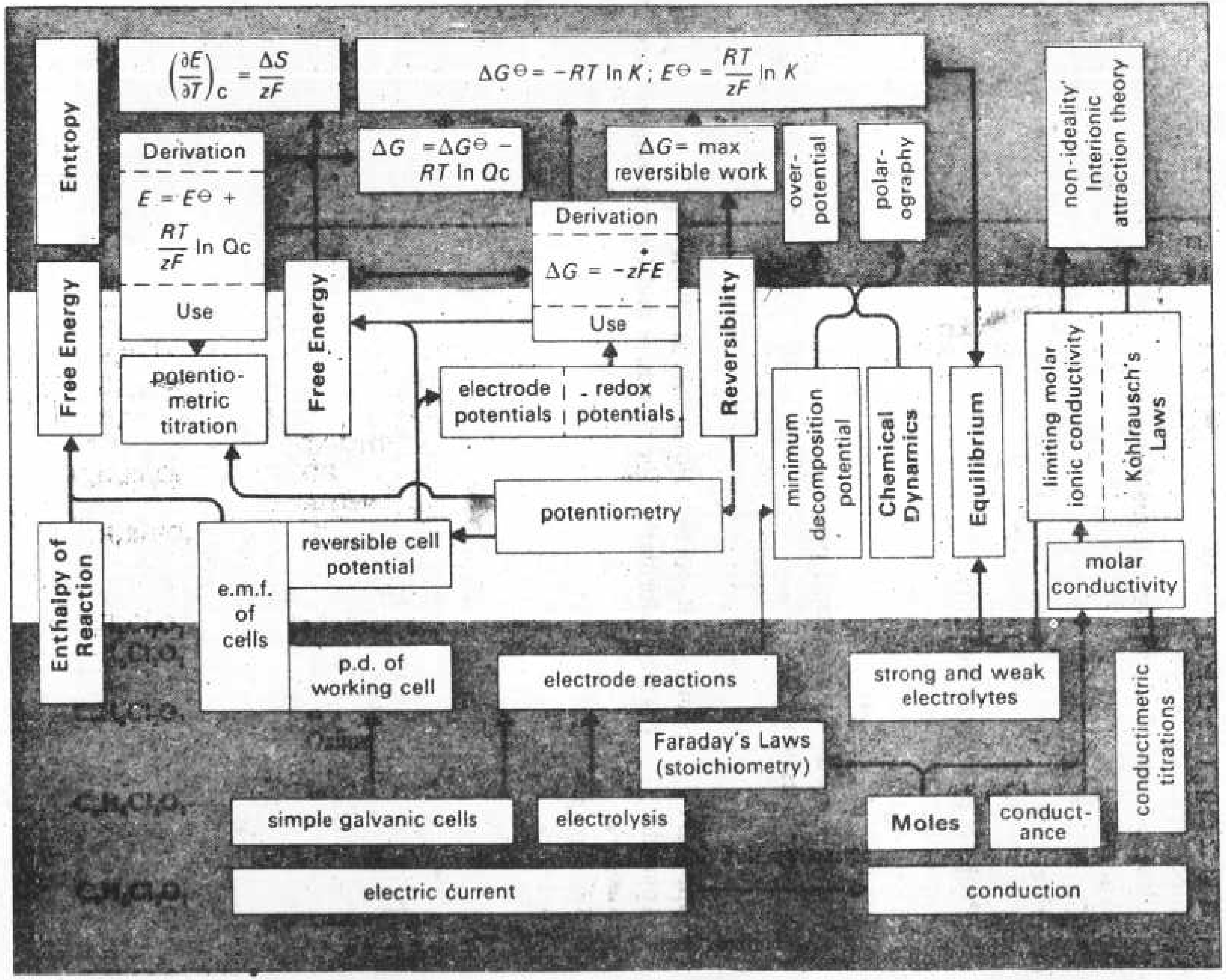
Chapters 7 and 8 continue with an account of some analytical and technical applications of electrochemistry. The intention here is to illustrate the principles and point to the variety of their practical applications, not to give full working instructions for the techniques.

An unusual feature of the book is that the last chapter is entirely devoted to suggestions for individual research or further study projects, over a range of levels of difficulty corresponding to the rest of the book (and in some cases a little beyond). I hope that this chapter will assist lecturers who wish to develop courses based in the laboratory rather than the lecture theatre, and I believe that electrochemistry—a comparatively safe, clean and manageable subject—is a suitable area for experiments along these lines. In schools, too, there may be teachers who reject the view that the need to 'cover the syllabus' (of, say, two or three A-levels) precludes a more searching study of any one topic. They may find that this book enables their students to work individually for a couple of months, each at his own pace, pursuing the study to the point where it becomes a real intellectual challenge.

My thanks are due to the following, for their kind assistance and advice: H. G. Andrew, Esq., Professors J. O'M. Bockris, D. J. G. Ives and A. J. B. Robertson, and Dr T. J. Stone. I am also grateful to the copyright holders for permission to reproduce certain illustrations (as acknowledged in the respective captions).

1976 N. J. Selley

此为试读,需要完整PDF请访问: www.ertongbook.com


Entropy
$\left(\frac{\partial E}{\partial T}\right)_c = \frac{\Delta S}{zF}$
$\Delta G^\ominus = -RT \ln K;\ E^\ominus = \frac{RT}{zF} \ln K$
non-ideality
Interionic attraction theory
Derivation
$E = E^\ominus + \frac{RT}{zF} \ln Qc$
Use
$\Delta G = \Delta G^\ominus - RT \ln Qc$
ΔG = max reversible work
over-potential
polar-ography
Free Energy
Derivation
$\Delta G = -zFE$
Use
Reversibility
Free Energy
potentio-metric titration
electrode potentials
redox potentials
minimum decomposition potential
Chemical Dynamics
Equilibrium
limiting molar ionic conductivity
Kohlrausch's Laws
potentiometry
Enthalpy of Reaction
e.m.f. of cells
reversible cell potential
molar conductivity
p.d. of working cell
electrode reactions
strong and weak electrolytes
conductimetric titrations
Faraday's Laws (stoichiometry)
simple galvanic cells
electrolysis
Moles
conduct-ance
electric current
conduction

An analysis of the relations between the concepts of basic electrochemistry

On this diagram the concepts have been placed at the level where full understanding becomes possible. Many of the concepts can be *used* in routine situations at a much lower level. This applies particularly to the two equations which lie across the boundary between central and upper sections.

The boundaries are arbitrary, and correspond roughly to years of a three-year course. The lower section contains ideas first met in 'O' level and mastered by lower VI; the central area contains ideas which are normally dealt with in some depth for 'A' level; while the upper areas show concepts which, though closely associated with or even fundamental to the others on the diagram, are generally regarded as college or university level.

Contents

Preface (iii)

1 Some Basic Facts
1.1 Conduction 1
1.2 Ionic theory 3
1.3 Chemical changes in electrolysis 7
1.4 Summary 11
1.5 Exercises 12

2 Electrode Reactions
2.1 Redox half-equations 13
2.2 The stoichiometry of electrolysis (Faraday's Laws) 15
2.3 Practical work on simple electrolysis 18
2.4 Concentration changes in aqueous electrolysis 20
2.5 Galvanic cells 21
2.6 Electrode potentials 24
2.7 The electrochemical series 24
2.8 Practical cells 27
2.9 Summary 32
2.10 Exercises 33

3 Electrolytic Conduction
3.1 Introduction 35
3.2 Measuring conductances by d.c. with non-polarizable electrodes 37
3.3 Simple a.c. conductance measurements 39
3.4 The Wheatstone bridge 39
3.5 Molar conductivity 41
3.6 Variation of molar conductivity with concentration 43
3.7 Transport numbers 48
3.8 Interionic attraction theory 49
3.9 The ionic conductivity of aqueous H^+ and OH^- 51

3.10 Practical work 53
3.11 Summary 57
3.12 Exercises 58

4 Galvanic Cells

4.1 Potentiometric cells 61
4.2 Reversible conditions 61
4.3 The potentiometer 64
4.4 Standard cell potentials 66
4.5 The Standard Hydrogen Electrode 68
4.6 Reduction potentials (electrode potentials) 70
4.7 Potentials and free energy 73
4.8 Thermodynamics of cells 76
4.9 Combining redox potentials 81
4.10 Variation of cell potential with temperature 83
4.11 Summary 84
4.12 Exercises 84

5 Cell Potential and Reaction Feasibility

5.1 The variation of cell potential with concentration 87
5.2 Concentration cells and the Nernst equation 89
5.3 Activity cofficients 93
5.4 The liquid junction potential 95
5.5 Use of cell potentials for predicting reactions 96
5.6 Variation of redox potentials with H^+ concentration 99
5.7 Kinetic considerations 101
5.8 Practical investigations (reaction feasibility) 104
5.9 Summary 106
5.10 Exercises 106

6 Electrolysis

6.1 Minimum decomposition potentials 108
6.2 Overpotential 112
6.3 Overpotential and activation energy 117
6.4 Simultaneous electrode processes 120
6.5 Anodic oxidations 123
6.6 Cathodic reductions 127
6.7 Organic electrolysis 129
6.8 Summary 132
6.9 Exercises 132

7 Electro-analytical Methods

7.1 Electrogravimetry 136
7.2 Coulometry 136

7.3 Conductimetry and conductimetric titrations 140
7.4 Potentiometry and potentiometric titrations 141
7.5 Electrodes reversible to the hydrogen ion 147
7.6 Ion-selective electrodes 153
7.7 Polarography and polarographic (amperometric) titrations 153
7.8 Summary 159
7.9 Exercises 159

8 Some Technological Applications
8.1 Metal extraction and refining 163
8.2 Electroplating 164
8.3 Electrochemical polishing and machining 167
8.4 Anodizing 168
8.5 Corrosion of iron 169
8.6 Fuel cells 171

9 Projects in Electrochemistry
Introduction 176
The projects 177
Historical projects 184
Miscellaneous non-practical projects 186
Extended essays 188

Appendix I Standard Reduction Potentials at 298 K 189
Appendix II Further Information for Teachers and Course Supervisors 194
Answers 202
Bibliography 207
Index 209

1

Some Basic Facts

1.1 Conduction

Most simple systems which conduct electricity obey Ohm's Law, though electrolytes with direct current may need a 'minimum decomposition potential' (§4.2) of up to 2 volts before significant current passes. Ohm's Law states that the current I is proportional to the potential difference E across any conductor, so:

$$E = IR \quad \text{or} \quad I = EG$$

where the constants of proportionality are called the resistance R and the conductance G. If E is measured in volts and I in amperes, R will have the unit volts per ampere, named the ohm and given the symbol Ω. Since conductance is the reciprocal of resistance, G will have the unit Ω^{-1}, at one time called the mho. Electricians, but not often chemists, refer to the reciprocal ohm as the siemens.

The resistance of a particular body is usually proportional to the length l of the path of the current, and inversely proportional to the cross-sectional area a. Therefore in order to eliminate the geometry of the particular sample, and to obtain the *resistivity* of the substance, the resistance is multiplied by (area/length). The common unit of resistivity is Ω cm.

Similarly, *conductivity* κ (kappa) is obtained by the relationship

$$\kappa = \frac{l}{a} G \quad \text{or} \quad I = \kappa E \frac{a}{l}$$

Conductivities of various substances may be compared, roughly, by means of a circuit consisting of a 6 V supply, an ammeter, a pair of copper plates, and a variable resistor (rheostat) of about 20 Ω, adjusted to give full-scale deflection on the meter when the copper plates are in contact. The 'ohms' range of any multi-range meter will serve the same purpose. For solids, similarly sized samples are pressed between the plates; and for liquids, the plates are immersed to some standard depth. More careful methods of measurement will be discussed in Chapter 3.

In the case of metallic (electronic) conductors and semiconductors, no chemical change results from the passage of the electric current, but when a current passes through an electrolyte there is invariably chemical reaction at the electrodes (for alternating current see §3.3). The electrodes are the points of contact where the

5505582

Table 1.1 Results of Conductivity Tests

		Examples
(i) Very good conductors	All metals (solid* or molten)	Fe, Pb, Na, Hg
(ii) Good conductors	Some compounds (electrolytes) when molten, but not solid.	NaOH, $PbBr_2$
	Some aqueous solutions of salts, acids and bases (electrolytic solutions)	NaOH, H_2SO_4, $CuCl_2$
	Graphite	C(gr)
(iii) Poor conductors	A few solid compounds (solid electrolytes)	AgCl
	Solutions of weak (slightly dissociated) electrolytes	CH_3COOH(aq), NH_3(aq)
(iv) Very poor conductors†	A few pure liquids (slightly ionized)	pure H_2SO_4, H_2O
(v) Non-conductors	Non-metal elements (solid or liquid)	S, Br_2, C (diamond)
	Molecular compounds (non-electrolytes)	CCl_4, C_6H_6, PCl_5
	Some aqueous solutions (non-electrolytes)	$C_{12}H_{22}O_{11}$, $CO(NH_2)_2$ sucrose urea
Gases conduct only at low pressures and with high potential differences.		

* *Powdered* metals may appear to conduct badly because of poor contact between particles.

† These very weak electrolytes show a misleadingly high conductivity unless specially purified.

current enters or leaves the electrolyte, that is, where there is a change from electronic to electrolytic conduction.

An interesting difference between metallic and electrolytic conductors is the effect of temperature on conductance. The conductance of metals decreases with rise in temperature, though the effect is not very pronounced; but the conductance of electrolytes increases markedly with increasing temperature—it may increase by a factor of five from 10°C to 80°C. (Graphite is anomolous in that it is an electronic conductor which increases its conductance on heating: carbon filament lamps exploit this property.)

The explanation of this difference is that since the conduction in electrolytes is due to the movement of ions (electrically charged atoms or molecules), there is considerable friction or viscosity within the electrolyte; so an increase in temperature, and freer movement of the particles, reduces this friction. In metals, however,

此为试读，需要完整PDF请访问：www.ertongbook.com

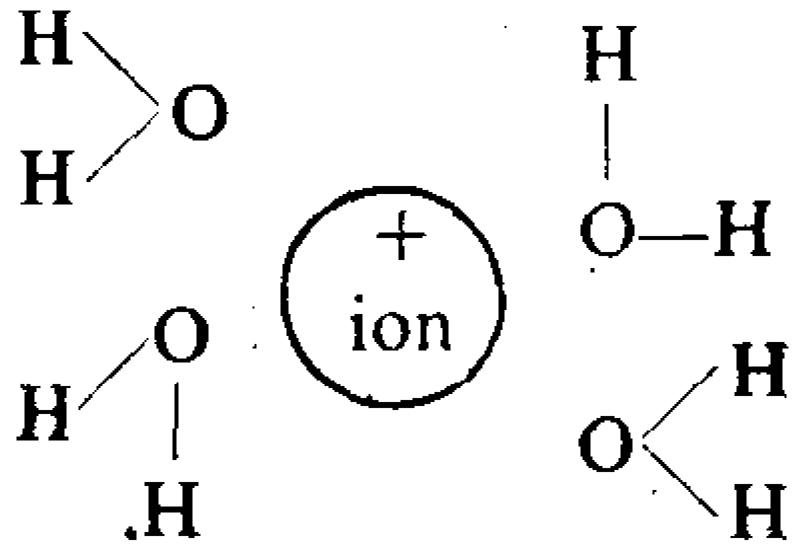
conduction is due to the movement of electrons, which may be pictured as small and fast-moving compared to atoms; a rise in temperature causes an increase in the space between the atoms, which hinders the electron flow.

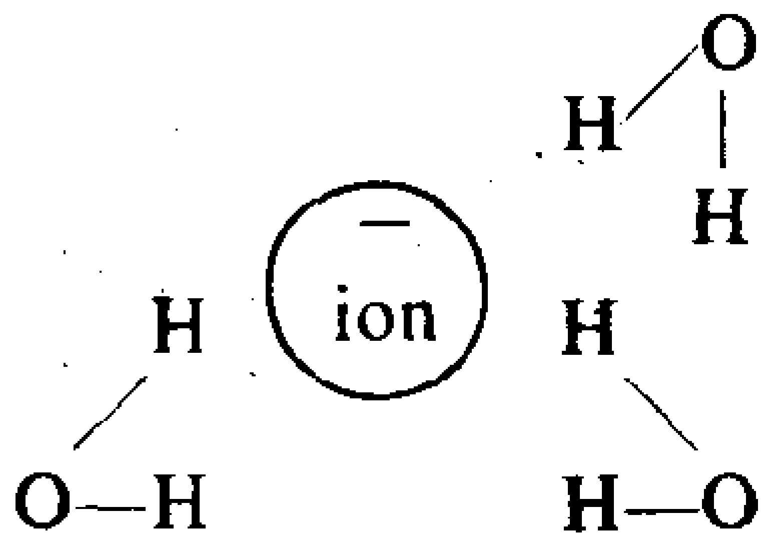
1.2 Ionic theory

X-ray crystallography shows that solids consist of regular crystal lattices, but while some solids have the same unit (the molecule) at all lattice points, others (the 'ionic' solids) have two (or more) different types of unit. In the ionic crystal, any one ion is surrounded by several (often 6) oppositely-charged ions, all equally distant. No ion is connected to any other particular ion: there are no ion-pairs such as Na–Cl or Ca–SO_4 in the solid (though they are predominant in the vapour).

Molecular solids melt and boil at relatively low temperatures, showing that although the bonds within molecules are strong, the forces between molecules are weak. In contrast, ionic solids melt at high temperatures, showing the strong forces between the particles—forces which are interpreted as attractions between oppositely-charged ions.

The modern theory of electrolyte solutions is due to Arrhenius, who announced it in 1883 although it was not generally accepted until 20 years later. The theory is that all solutions of 'strong' electrolytes consist entirely of ions, now known to be 'hydrated' by association with a number of solvent molecules.[1] Thus aqueous sodium chloride solution is $Na^+(aq) + Cl^-(aq)$, with no NaCl molecules; and aqueous H_2SO_4 is almost entirely $H^+(aq)$, $HSO_4^-(aq)$ and $SO_4^{2-}(aq)$.





Chemists in 1890 found this hard to accept because they did not understand the important difference between ions and atoms. Since sodium and chlorine combine so vigorously to form sodium chloride, it was difficult to believe that merely dissolving the salt in water could separate the sodium and chlorine. They were happier with an earlier theory of dynamic equilibrium between dissolved molecules and a *small proportion* of ions, since this would not require so much 'energy of ionization'.

---

[1] The manner and extent of hydration of aqueous ions are not properly understood, and only recently have techniques such as the effect of high pressure on conductivity begun to provide answers. There is little doubt, though, that the hydration arises from electrostatic attraction between the ion and either the partly negative O or the positive H atoms of appropriately oriented H_2O molecules. The energy of hydration (and hence the number of molecules held) is a function of the charge density on the ion (which increases with smaller size and higher charge).

Fortunately van't Hoff had provided evidence of a non-electrochemical kind: his vapour pressure measurements on aqueous solutions only made sense if the electrolyte solutions contained a number of particles twice or three times as great as that of these supposed 'molecules' of the electrolytes. The depression of the vapour pressure of 1 dm^3 of water by 1 mole of $CaCl_2$ approached a value three times as great as that caused by 1 mole of the non-electrolyte urea; that is, the van't Hoff factor i was approximately 3.

However, conductivity and vapour pressure measurements on solutions of some acids and bases showed that they existed largely as molecules with only a small proportion of 'dissociation' into ions. These were the 'weak electrolytes',[2] for example ethanoic (acetic) acid, hydrocyanic (prussic) acid, or ammonia solution.

The ionic theory for strong electrolytes gained further support from the X-ray crystallography results mentioned at the start of this section. If salts are fully ionized in the solid state, it was argued, then no energy will be required to ionize them when they dissolve. This point is not so sound as it seemed at the time, and the objections are (i) the dissolution of a salt in water *is* accompanied by an energy change, which is sometimes so great an absorption of energy as to make the salt insoluble: (ii) some electrolyte solutions are formed by the dissolution of ***molecular*** solids or liquids (e.g. H_2SO_4, $AlCl_3$), yet these processes are often exothermic, despite the supposed 'energy of ionization'. The misunderstanding lay in supposing that the energy of ionization would be simply that for the splitting of the molecule into fragments, with the breaking of bonds; but in fact this energy is more or less regained when the anhydrous ions combine with water to give hydrated ions. This is shown in Fig. 1.1, which displays diagramatically the energy (enthalpy) changes which would accompany a *hypothetical* route from solute to solution via free gaseous anhydrous ions. It is not suggested that these free ions are actually formed as intermediates in the process of dissolution, but such an analysis helps to explain differences in the solubilities of different electrolytes.

The ionic theory readily explains the conductance of electricity through the bulk of the molten or dissolved electrolytes, since in these states the ions are free to move, and those with positive charge (the cations) will move towards the negative electrode, while the negative ions (anions) drift towards the positive electrode. But what happens when the ions reach the electrode is another matter; there must be a change from electrolytic to electronic conductance. Therefore there must be a discharge or creation of ions and an absorption or release of electrons. Fig. 1.2 shows the movement and discharge of ions during the electrolysis of ZnI_2 solution.

Practical work

A simple but convincing demonstration of the movement of ions (electrophoresis) is given by the electrolysis of copper(II) dichromate(VI) solution in a U-tube, with dilute sulphuric acid in the two limbs (Fig. 1.3). As the current passes, a blue colour

[2] Note that since 'weak' and 'strong' are used to indicate partial and complete dissociation, these words should not be used to mean 'dilute' and 'concentrated'.

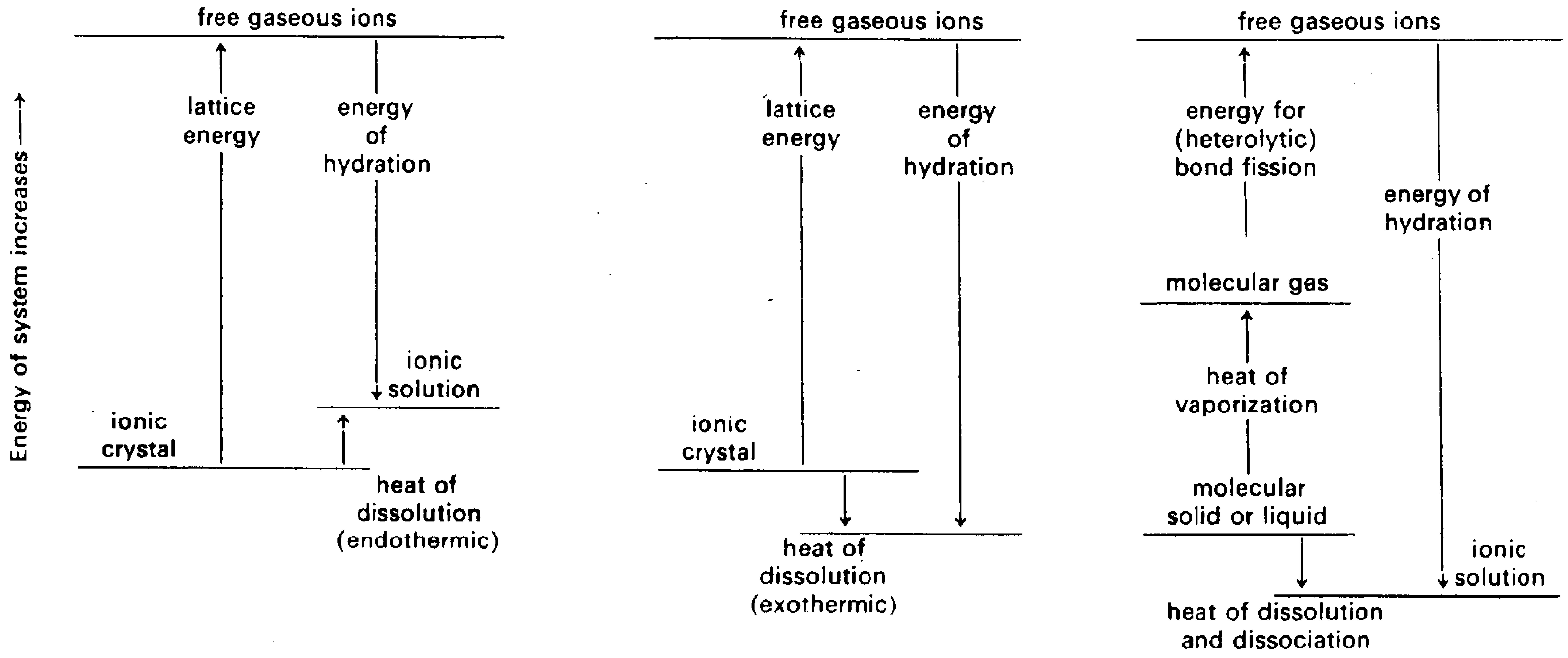

Energy of system increases
free gaseous ions
lattice energy
energy of hydration
ionic solution
ionic crystal
heat of dissolution (endothermic)
free gaseous ions
lattice energy
energy of hydration
ionic crystal
heat of dissolution (exothermic)
free gaseous ions
energy for (heterolytic) bond fission
energy of hydration
molecular gas
heat of vaporization
molecular solid or liquid
ionic solution
heat of dissolution and dissociation

Fig. 1.1 Analysis of energy changes for hypothetical routes (thermochemical cycles) for the formation of electrolytic solutions

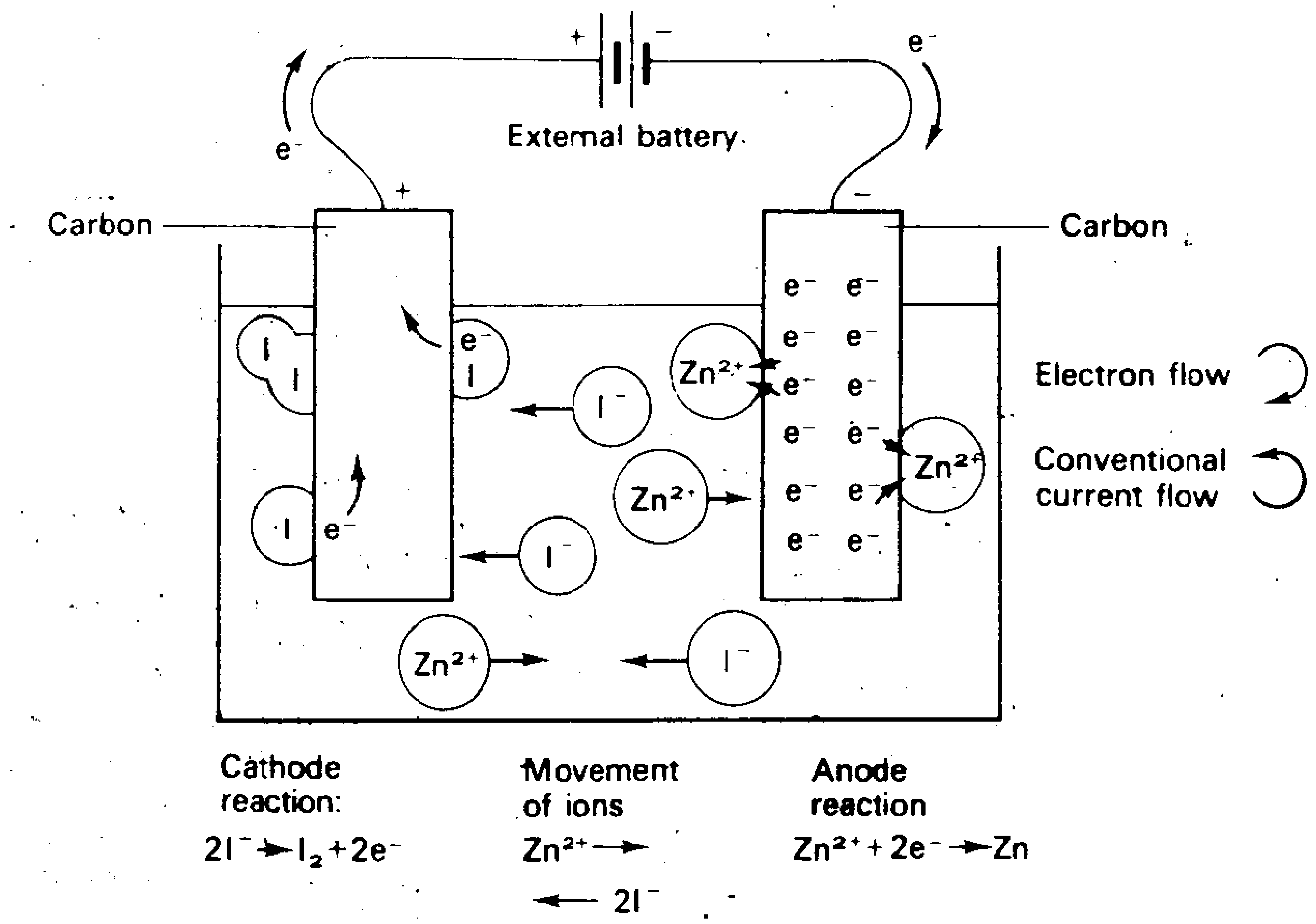

External battery
+
−
e⁻
e⁻
Carbon
Carbon
Zn²⁺
I⁻
Electron flow
Conventional current flow
Cathode reaction:
2I⁻ → I₂ + 2e⁻
Movement of ions
Zn²⁺ →
← 2I⁻
Anode reaction
Zn²⁺ + 2e⁻ → Zn

Fig. 1.2 Electrolysis. The processes comprising the electrolysis of aqueous zinc iodide solution

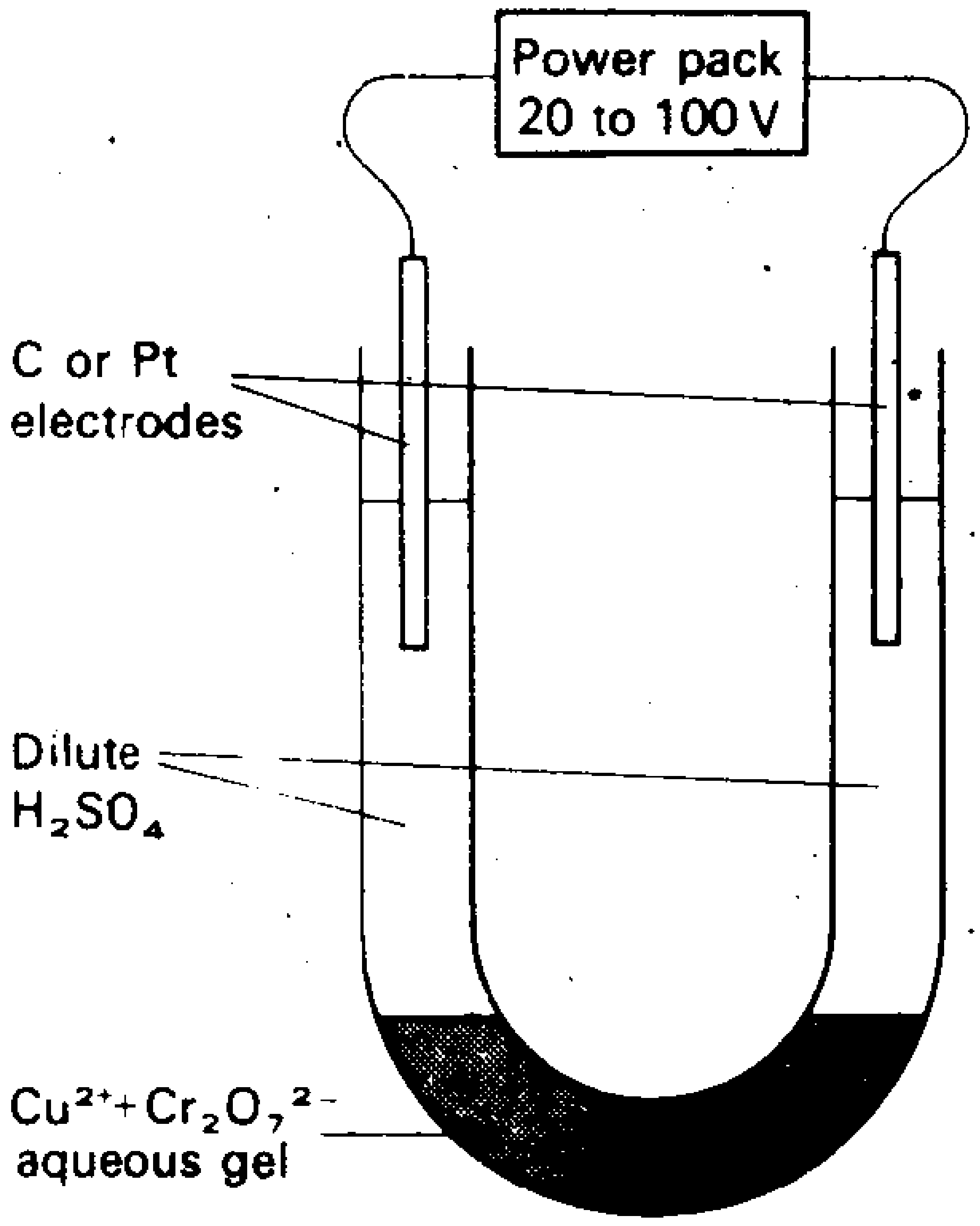

Power pack 20 to 100 V
C or Pt electrodes
Dilute H₂SO₄
Cu²⁺+Cr₂O₇²⁻ aqueous gel

Fig. 1.3 Demonstration of the movement of ions during electrolysis

appears in the acid in which the negative electrode is placed, due to the migration of Cu^{2+}(aq) ions. Simultaneously, orange $Cr_2O_7^{2-}$(aq) ions migrate towards the positive electrode. Even with a potential difference of 20 V, about 15 minutes is required to give clearly visible colours in the limbs of the U-tube, which gives an impression of the slowness of the drift of ions. Practical details for setting up this demonstration, and also a version for individual work, are given in Appendix *II* (p. 194).

A similar but quicker demonstration is provided by the migration of MnO_4^- when electrodes with a potential difference (p.d.) of about 100 V d.c. are placed each side of a single crystal of potassium manganate(VII) on a filter paper moistened with dilute sulphuric acid. An elongated purple stain grows out from the crystal, on one side only.

The use of electrophoresis to separate ions for the purpose of qualitative analysis is the subject of a Project in Chapter 9.

1.3 Chemical changes in electrolysis

Unlike electronic conduction, electrolytic conduction is always accompanied by chemical changes at the electrodes. In some cases the electrodes are attacked, but in other cases they are inert, and then the chemical changes involve only the electrolyte. Despite the variety of possibilities, certain rules are obeyed in all electrolyses:

(1) At the negative electrode, electrons are forced to leave the metallic (or carbon) electrode and take part in an electron-absorbing reaction, most commonly the discharge of a metal ion or hydrogen ion. This results in the formation of a metal plating on the electrode, or the production of hydrogen gas.

(2) At the positive electrode, the externally imposed potential difference causes a deficiency of electrons, thereby encouraging any electron-releasing reaction such as the dissolution of the metal electrode in the form of positive ions, or the discharge of negative ions to produce oxygen, chlorine or another non-metal.

(3) The sum total of these 'half-reactions' at the two electrodes is a complete chemical reaction, but one which would not have occurred without the supply of electrical energy. It is often the exact reverse of a spontaneously occurring reaction.

The examples which follow will illustrate these general rules.

Examples of electrolysis

1. Molten lead bromide with inert electrodes

This experiment illustrates an electrolysis of no industrial importance, but one which provides a good introduction to the theory of electrolysis because the results can be interpreted unambiguously. It is best shown as a lecture demonstration, preferably in a fume cupboard, because of the poisonous nature of the lead bromide fumes and bromine vapour (see Appendix II). Routine eye protection is recommended.

About 5 g dry powdered lead(II) bromide is placed in a porcelain 'boat' or crucible, supported on a drilled asbestos board. Two carbon electrodes, fixed in holes in a wooden bar, are clamped in place, touching the compound at points 1 to 3 cm apart (Fig. 1.4). The d.c. supply (about 12 to 20 V) with a rheostat and lamp in series, is switched on. No current passes.

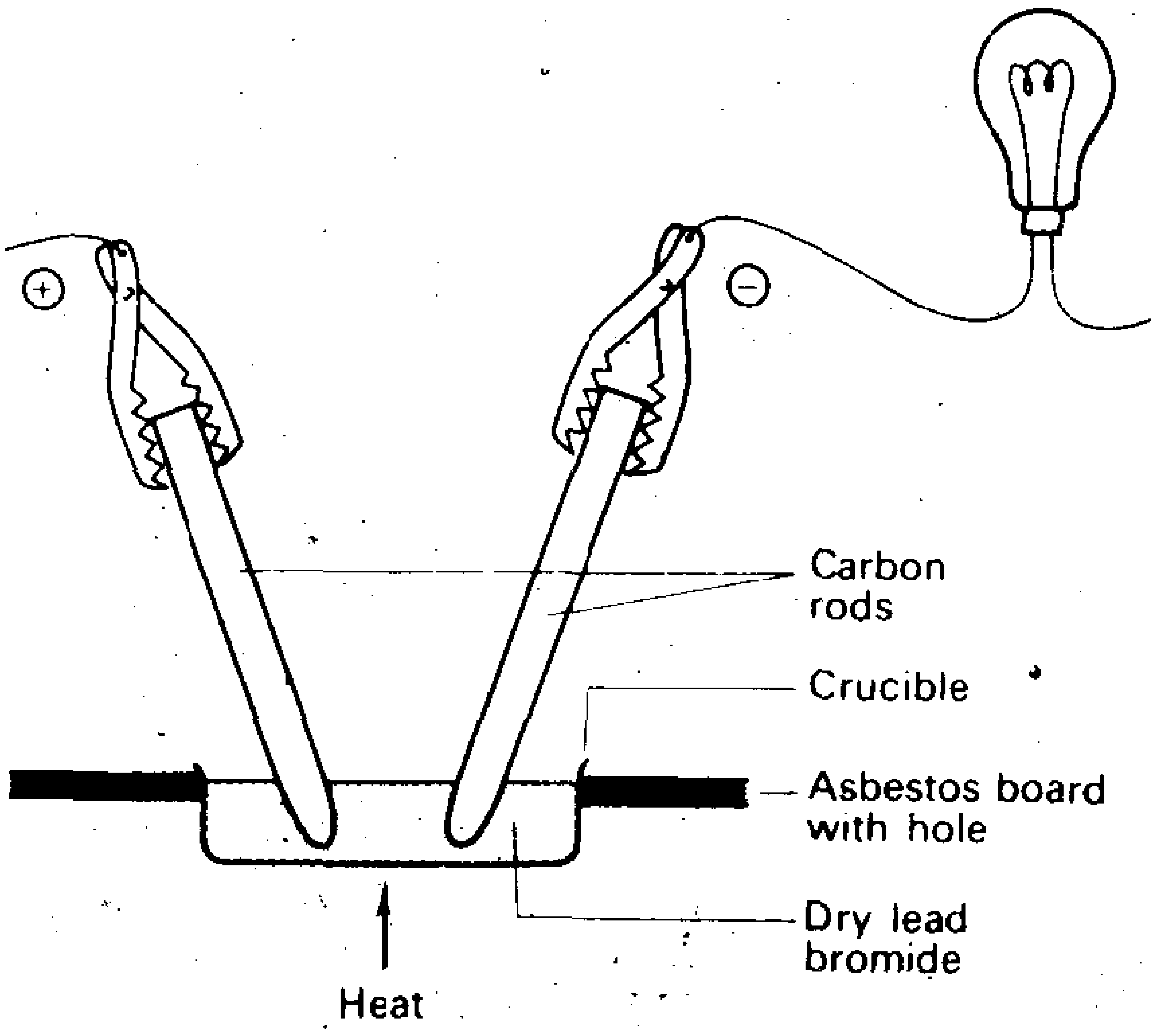


Fig. 1.4 Electrolysis of molten lead bromide

The crucible is heated with a bunsen flame; suddenly the lead bromide melts, and the lamp lights up. After this the heating effect of the current is often sufficient to keep the electrolyte molten. To confirm the point that solid lead bromide does not conduct even when in one piece, with good contact with the electrodes, the current is switched off until the melt solidifies, and then switched on again, no current passes until the solid is remelted.

The current is left on for 5 to 10 minutes. Brown fumes of bromine gas are seen at the positive electrode, and may be tested with starch-iodide paper. Silvery globules of molten lead may sometimes be seen during the electrolysis, but in any case the lead is easily found, after cooling, by dissolving away the residual lead bromide in boiling water.

Assuming that, since they appear to be unchanged, the carbon electrodes do not react, there is only one possible pair of electrode reactions:

At positive anode: Br^- ions arrive and are discharged: $2Br^- \rightarrow Br_2 + 2e^-$

At negative cathode: Pb^{2+} ions arrive and are discharged: $Pb^{2+} + 2e^- \rightarrow Pb$

此为试读，需要完整PDF请访问：www.ertongbook.com