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Teaching and learning difficulties in electrochemistry.

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Example 1

Calculate E° cell for the following cell reactions.

(a) $2Ag^{+}(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}$

(b) $Zn^{2+}(aq) + Ni(s) \longrightarrow Ni^{2+}(aq) + Zn(s)$

Which reaction is spontaneous under standard conditions as written ?

Solution

In (a) the silver ions are reduced to silver atoms

$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$ $\quad E^{\circ}$ red = 0,80 V

while copper atoms are oxidised to copper ions

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$ $\quad E^{\circ}$ ox = -0,34 V

E° cell = E° red + E° ox

= 0,80 + (- 0,34) = 0,46 V Spontaneous

Notice that in combining half-reaction equations to form an overall redox reaction equation, the number of electrons in the oxidation half-reaction must equal those in the reduction half-reaction. However, this does not affect the calculation of E° cell because this is an intensive property (V = J /C).

In (b) zinc ions are reduced to zinc atoms

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ $\quad E^\circ$ red $= - 0,76$ V

Nickel atoms are oxidised to nickel ions

$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$ $\quad E^\circ$ ox $= + 0,24$ V

E° cell $= - 0.76 + 0,24 = -0,52$ V Non-spontaneous

Example 2

For the following half-reactions, write the equation for the combined reaction which would occur spontaneously.

(i) $Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$ E°red = 1,06 V

(ii) $Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$ $\quad E^\circ$ red $= 0,82$ V

As written above, the two half-reactions are reductions whereas, during reaction, one of them must occur as an oxidation half-reaction. The values of the reduction potentials indicate that (i) has a higher tendency to occur as written and so (ii) will have to occur in the opposite direction as an oxidation half-reaction.

Reduction half-reaction

$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$ $\quad E^0$ red = 1,06 V

Oxidation half-reaction

$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$ $\quad E^\circ$ox $= - 0,82$ V

E° cell $= 1,06 + (- 0,82) = 0,24$ V for the overall cell reaction

$$Hg(l) + Br_2(l) \longrightarrow Hg^{2+}(aq) + 2Br^-(aq)$$

4.9 FACTORS DETERMINING THE SIZE OF THE CELL POTENTIAL

The factors that determine the size of E are the same as those that determine the value of the Gibbs function change, ΔG, for a chemical system.

These include (i) the nature of the substances involved in the electrode reactions; (ii) the concentration or pressure of the substances involved in the electrode reactions and (iii) the temperature.

(a) The nature of the substances: As already mentioned in section 4.5, the tendency to accept or transfer electrons is greater for some substances than others .

Example

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \qquad E^\circ \text{ red} = -0,24 \text{ V}$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^\circ \text{ red} = +0,34 \text{ V}$$

$Cu^{2+}(aq)$ accepts electrons more readily than $Ni^{2+}(aq)$.

(b) The concentration of the reacting substances : Consider the following cell reaction

$$2Ag^+(aq) + Zn(s) \longrightarrow 2Ag(s) + Zn^{2+}(aq)$$

$E^\circ = +1,56$ V

The above value indicates the thermodynamic driving force when $[Ag^+] = [Zn^{2+}] = 1$ mol dm^{-3}. If the cell reaction proceeds from here, $[Ag^+]$ decreases and $[Zn^{2+}]$ increases and the thermodynamic driving force clearly must decrease. Indeed it does, and this is observed as a decrease in the cell emf. Eventually, chemical equilibrium will be reached, at which point there is no thermodynamic driving force ($\Delta G = 0$) and the cell emf also equals zero. If one started with $[Ag^+] > 1,0$ mol dm^{-3}, or with $[Zn^{2+}] < 1,0$ mol dm^{-3} the initial driving force would be greater and so would E° cell.

4.10 AGAINST THE THERMODYNAMIC DRIVING FORCE

The reactions which occur in galvanic cells can be reversed in direction if an opposing potential difference larger than the cell emf is applied. For example, in the case of the cell discussed in section 4.5, by applying an opposing potential difference greater than 0,46 V the non-spontaneous cell reaction

$$2Ag(s) + Cu^{2+}(aq) \longrightarrow 2Ag^+(aq) + Cu(s)$$

can be made to occur. In this way a galvanic cell can be converted into an electrolytic cell.

4.11 RELATIONSHIP BETWEEN ΔG and E

Both the Gibbs function change associated with a reaction and the E for a cell reaction, can be used as criteria for spontaneity. Clearly this suggests that the E is related to the Gibbs function change for the overall reaction. The actual relationship is given by

$$\Delta G = - nFE \quad \text{---------- 4.1}$$

where n = the number of moles of electrons transferred from one electrode to another in the external circuit per mole of the cell reaction

E = the emf of the cell expressed in volts,

F = the Faraday constant, 96 500 C / mol.

ΔG is numerically equal to the maximum useful work which a chemical system can do on its surroundings

$$\Delta G = - W_{max} = - nFE \quad \text{----------4.2}$$

The maximum work that can be obtained per mole of reaction is thus the product of the charge transferred in the external circuit between the two electrodes and the cell potential.

Work = Cell potential x Charge ---------- 4.3

Joules Volts Coulombs

The standard cell potential for a Daniell cell

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ is

+1,10V. This implies that for every 1 coulomb of charge that passes round the external circuit the cell (i.e.the

chemical reactions at the electrodes) provides 1,1 joule of energy. This corresponds to 96,5 kJ per mole of e^-.

When one mole of Zn atoms are oxidised and one mole of Cu^{2+} ions are reduced, 2 mole of electrons pass around the external circuit. The maximum work this electricity can do is

$$1{,}10\ V \times 2mol \times 9{,}65 \times 10^4\ C/mol$$
$$= 2{,}12 \times 10^5\ VC$$
$$= 2{,}12 \times 10^5\ J$$

Calculation of E from ΔG

Using equation 4.1 we can calculate ΔG from E and vice versa.

Example

For the reaction represented by $Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$

(a) calculate E^σ cell (b) calculate G^σ for the cell reaction

Solution

Reduction half reactions

i. $Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$ E° red = -0,28V

ii. $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ E° red = - 0,23V

In the above given redox reaction, Co atoms are oxidised while the Ni^{2+} ions are reduced. The relevant half-reaction equations and their corresponding potentials are

$$Co(s) \longrightarrow Co^{2+}(aq) + 2e^- \quad E^\circ \text{ ox} = 0,28 \text{ V}$$

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \quad E^\circ \text{ red} = -0,23 \text{ V}$$

$$E^\circ \text{ cell} = E^\circ \text{ reduction} + E^\circ \text{ oxidation}$$

$$= -0,23 + 0,28$$

$$= 0,05 \text{ V}$$

(b) $\Delta G^\circ = -nFE^\circ$

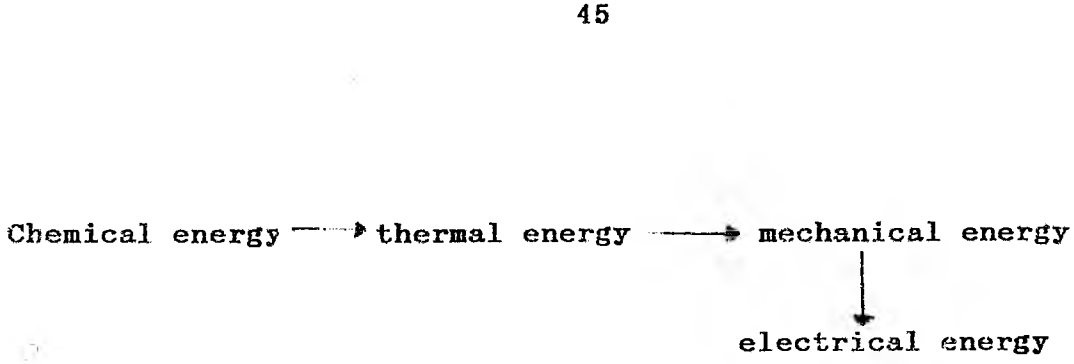
n = 2 mole of electrons per mole of reaction.

F = 96 500 C / mol.

$$\Delta G = -\frac{2 \text{ mol } e^-}{\text{mol}} \times \frac{96\,500 \text{ C} \times 0,05 \text{ V}}{\text{mol } e^-}$$

$$= -10 \text{ kJ / mol}$$

4.12 <u>FUEL CELLS AS ENERGY DEVICES</u> : The conversion of the chemical energy of fuels and oxygen into electrical energy normally consists of burning the fuel and using the thermal energy to produce steam for spinning turbines coupled to electricity generators.



This process is thermodynamically inefficient with less than 40 % of the available chemical energy being converted to electrical energy.

Fuel cells are a special type of galvanic cell which convert chemical energy directly to electrical energy. In these cells, reactants are continuously fed into the cell and products are removed from it. This process is far more efficient than normal fuel combustion with 75 % of the available chemical energy being converted into electrical energy.

A reaction that has successfully been incorporated into a fuel cell is that between gaseous hydrogen and oxygen. This reaction requires a continuous flow of both gases and is run at a temperature of 250° C and a pressure of 25 atm.

<u>The half-reactions are</u> :

anode : $2H_2(g) \longrightarrow 4H^+(aq) + 4e^-$

cathode : $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O\ (aq)$

overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (aq)$

The direct reaction between hydrogen and oxygen releases a lot of energy but has to be initiated because of the high activation energy. When it does occur it goes explosively. To overcome these problems in the practical design of fuel cells using this reaction, each half- reaction has to be carefully controlled. This is done such that each half-reaction is catalysed and a low activation energy is achieved. The carbon electrodes used are impregnated with catalysts.

WORKSHEET 5

MICROSCOPIC PROCESSES OCCURING IN ELECTROCHEMICAL CELLS

L.G. 3.36

5.1 KEY CONCEPTS

(a) Electronic conductors are paths for electrons and undergo no detectable physical or chemical change as a consequence of conduction.

(b) Electrical current in an operating cell occurs as a movement of electrons in the electrodes and as a movement of ions in the electrolyte.

(c) Electrons are transferred between the ions of the electrolyte and atoms of the electrodes at the electrode-electrolyte interface and result in chemical changes.

(d) Overall electrical neutrality is preserved at all times in the electrodes and also in the electrolyte.

5.2 OBJECTIVES By the end of this worksheet you should be able to:

(a) define electronic and ionic conduction and distinguish between the two.

(b) describe the electrode processes which occur when galvanic and electrolytic cells operate.

(c) define electrical neutrality and explain how it is maintained in operating cells.

5.3 INTRODUCTION

In worksheet 2 we looked at the components essential for electrochemical cells to function. In this worksheet we will examine some of the microscopic processes which occur in each component when electrochemical cells operate. We will consider what occurs in the external wires and electrodes during electronic conduction, what occurs in the electrolyte during ionic conduction and the processes which occur during electron transfer at the electrodes.

The emphasis here is that electronic and ionic conduction are continuous in electrochemical cells and the electron transfer reactions at the two electrodes link these two mechanisms of conduction.

The first requirement for electrical conduction is charge carriers that can move through the conducting medium or material. There are three distinct processes by which an electric charge is transported in an electrochemical cell.

(a) Electronic conduction - This involves electron movement and occurs in the electrodes and the metal wires connected to them only. During electronic conduction, no physical or chemical changes occur to the conductor. The temperature may increase due to the electrical resistance.

(b) Ionic conduction - This involves the movement of positive and negative ions in the electrolyte, and also in the salt bridge in the case of galvanic cells.

(c) Electrode processes - These involve electron transfer reactions at the interface of each electrode and the electrolyte. The ionic conduction mechanism in the electrolyte is coupled with the electron conduction mechanism in the electrodes, at the interface of the electrode surface and electrolyte.

All the three processes above must take place simultaneously or current would not flow in the circuit containing the cell.

5.4 ELECTRONIC CONDUCTION

The free or delocalised electrons in solid conductors are in a state of rapid motion. In the absence of a potential difference, as many electrons move in one direction as in the opposite direction with the same speed. There is

therefore no net flow of charge and so no current in the conductor.

If the electrodes of a galvanic cell are connected to opposite ends of the conductor a potential difference is created between the two ends of that conductor. The electrons thus acquire a slow but definite drift in one direction. The drift of these electrons constitutes an electric current. The current will continue as long as there is a potential difference between the two ends of the conductor. Electronic conductors undergo no physical or chemical change as a result of the current.

5.5 IONIC CONDUCTION

Ionic conduction involves the movement of ions in the electrolyte and this is accompanied by chemical changes at the electrode surface.

Consider first the example of an electrolytic cell.

Example

The electrolysis of molten sodium iodide with inert electrodes

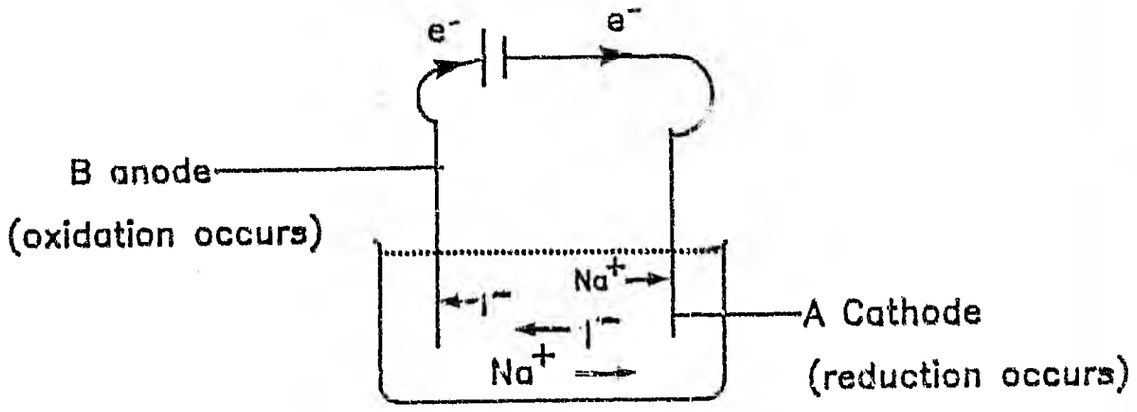


Figure 5.1

As described in worksheet 2, the battery forces a non-spontaneous reaction to occur. Electrons move from one end of the battery to electrode A. At this electrode, electrons are transferred from the electrode surface to sodium ions at the surface of the electrode. Reduction occurs and neutral sodium atoms are formed.

$Na^+(l) + e^- \longrightarrow Na(s)$ ----------5.1

from the electrolyte	on the surface of electrode A	forms on the surface of electrode A

The Na^+ ions which have reacted at A are replaced by more Na^+ ions from the bulk of the electrolyte. There is thus a movement of Na^+ ions towards electrode A as shown in figure 5.1.

Simultaneously, at electrode B, the iodide ions at the electrode surface give up electrons to the electrode, becoming neutral iodine atoms.

Pairs of these combine rapidly to form iodine molecules.

$I^-(l) \longrightarrow I + e^-$

in solution at electrode surface	at electrode surface	on electrode B

followed by

$I + I \longrightarrow I_2(g)$

overall $2I^-(l) \longrightarrow I_2(g) + 2e^-$ -------- 5.2

Oxidation thus occurs at the surface of electrode B. More iodide ions move towards the surface of electrode B to replace those that have reacted.

Thus in the rest of the electrolyte, there will be a general movement of cations towards electrode A (cathode) and negative ions (anions) towards electrode B (anode).

The movement of positive and negative ions in opposite directions constitutes the electric current in the electrolyte. (Note: both positive and negative charges (cations and anions) move here whereas in electronic conduction only negative charges (electrons) move).

5.6 ELECTRICAL NEUTRALITY IN ELECTROCHEMICAL CELLS

One of the important ideas in chemistry is that of the electrical neutrality of chemical systems, i.e. positive and negative charges exist in equal numbers within a system. This principle also applies to electrochemical cells where at any one time, in both galvanic and electrolytic cells , the number of negative and positive charges must be equal. This is true for the external circuit, the electrodes and in all regions of the electrolyte.

In any piece of metal, the total number of electrons equals the total number of protons and, not only is the whole piece electrically neutral but, each atom in it is neutral. In the

electrolyte also the anions must be balanced by the cations. For example, the electrical neutrality condition for aqueous KCl is as follows:

ionic species in solution K^+ , Cl^-, H^+, OH^-.

electrical neutrality : $K^+ + H^+ = Cl^- + OH^-$

It is important to note that electrical neutrality involves a balance of charges rather than ions. For example, in an aqueous solution of copper nitrate $Cu(NO_3)_2$ (Cu^{2+} , $2NO_3^-$), the numbers of ions are not equal but the numbers of positive and negative charges are equal.

5.6.1 Maintaining Electrical Neutrality in Electrolytic Cells

During the time an electric current is flowing through the cell, electrical neutrality is maintained. For each electron picked up by a species from the cathode, an electron must be lost by a species at the anode.

Similarly in any region of the electrolyte, for each anion that migrates towards the anode, a cation must migrate towards the cathode. Negative and positive charges never accumulate in electrochemical cells.

5.6.2 Maintaining Electrical Neutrality in Galvanic Cells

Consider the half -cells X and Y in the galvanic cell shown below :

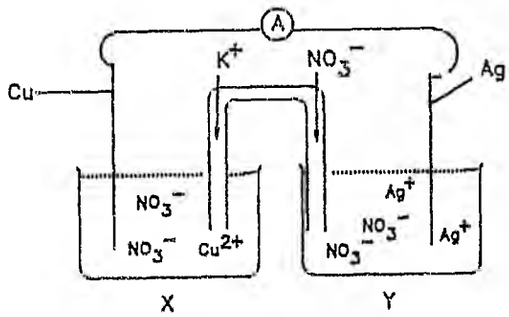


Figure 5.2

When the cell operates, additional $Cu^{2+}(aq)$ ions are introduced into the half-cell X due to the oxidation half-reaction: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$. In half-cell Y, $Ag^+(aq)$ ions are depleted due to the reduction half-reaction: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

In half-cell X two things could happen to balance the additional, excess positive charges (see figure 5.3):

(i) $Cu^{2+}(aq)$ ions can move out of the half-cell X into the salt-bridge;

(ii) Negative ions, in this case NO_3^- (aq), can move from the salt bridge to balance the excess positive charge.

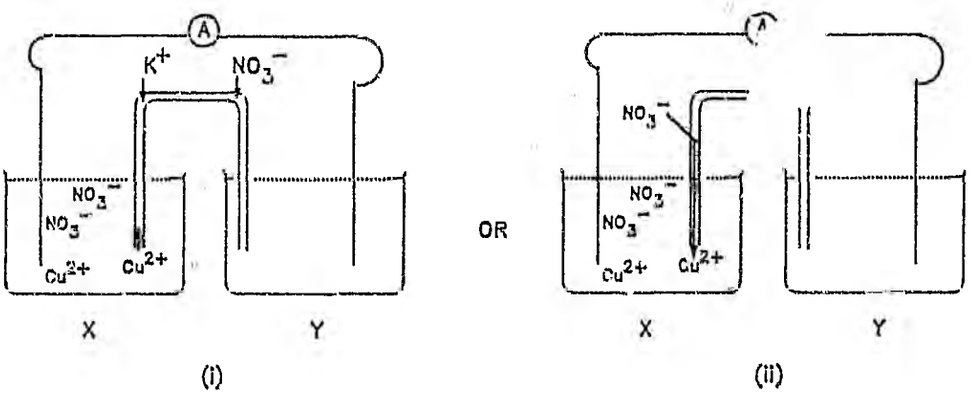


Figure 5.3

(Ions are not shown in half-cell Y so as to focus attention on the salt bridge and half-cell X)

In half-cell Y, where there is a deficiency of positive charges, charge balance can be achieved (figure 5.4) by:

(iii) Some of the negative ions, NO_3^-, moving out of this half-cell Y into the salt bridge;

(iv) Movement of positive ions (K^+ in this case) from the salt bridge to replace the Ag^+ ions which have been reduced.

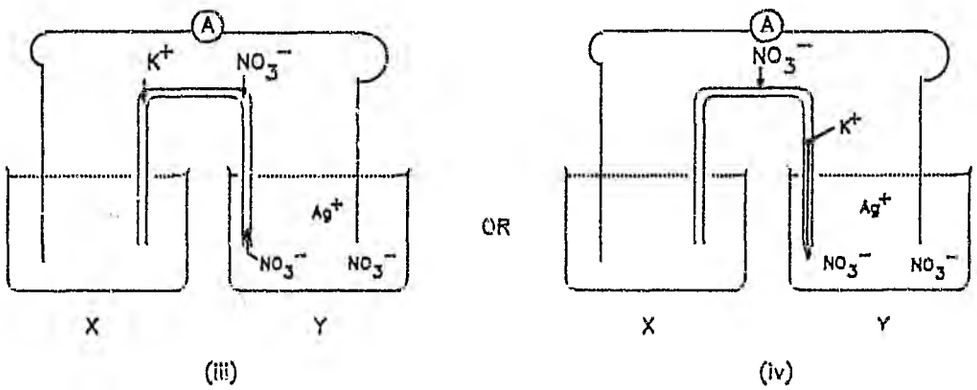


Figure 5.4

(Ions are not shown in half-cell X so as to focus attention on the salt-bridge and half-cell Y.)

During the operation of the galvanic cell all the four processes (i - iv) occur simultaneously so that cations will move from the half-cell X to Y and anions will move from Y to X. Each half-cell has no nett charge at any time (see figure 5.5).

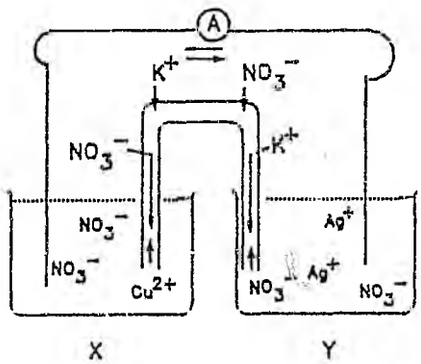


Figure 5.5

nett movement of cations

nett movement of anions

The movement of ions across the salt bridge is very slow and extensive mixing of the two solutions does not occur

5.7 ELECTROLYSIS OF AQUEOUS SOLUTIONS

The products from the electrolysis of an aqueous solution of a salt may differ from those from the electrolysis of the molten salt. The electrolysis of molten electrolytes usually just involves reduction of the cation at the cathode and oxidation of the anion at the anode.

In aqueous solutions, however, water, in addition to the ions of the electrolyte can react at the electrodes. The possible reactions are as follows :

At the anode:

(a) oxidation of the anion and/or cation

(b) oxidation of water molecules

At the cathodes

(a) reduction of cations.

(b) reduction of water molecules.

In general, the species with the highest (most positive) oxidation potential should be preferentially oxidised at the anode while the species with the highest (most positive) reduction potential should be preferentially reduced at the

cathode. Experimentally it is found that other factors such as the concentration of ions in solution as well as the type of electrode can determine which reaction occurs at the electrode surface.

The following standard reduction potentials will be useful in considering examples 1, 2 and 3 below :

	E° red/V
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	-0,41
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2,71
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	+2.01
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+0,82
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1,36

Example 1

Electrolysis of aqueous 1 mol dm^{-3} Na_2SO_4 with platinum electrodes.

Possible oxidation half-reactions	E°ox/V
1. $SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$	-2,01
2. $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 2e^-$	-0,82

Possible reduction half-reactions	E^{o} red/V
3. $Na^{+}(aq) + e^{-} \longrightarrow Na(s)$	-2,71
4. $2H_2O(l) + 2e^{-} \longrightarrow H_2(g) + 2OH^{-}(aq)$	-0,41

The half-reactions which should occur would be 2 at the anode and 4 at the cathode.

Example 2

Electrolysis of aqueous NaCl with platinum electrodes

Possible oxidation half-reactions	E^{o} ox/V
5. $2H_2O(l) \longrightarrow O_2(g) + 4H^{+}(aq) + 4e^{-}$	-0,82
6. $2Cl^{-}(aq) \longrightarrow Cl_2(g) + 2e^{-}$	-1,36

Possible reduction half-reactions	E^{o} red/V
7. $Na^{+}(aq) + e^{-} \longrightarrow Na(s)$	-2,71
8. $2H_2O(l) + 2e^{-} \longrightarrow H_2(g) + 2OH^{-}(aq)$	-0,41

The expected half-reactions would again be oxidation of water at the anode and reduction of water at the cathode. Experimentally, however, it is found that chlorine is formed at the electrode surface instead of oxygen, in spite of the oxidation potentials showing that oxidation of water molecules should be preferred to oxidation of chloride ions. In this case, the oxidation potentials of the two competing

reactions lead to an incorrect prediction because half-reaction 5 has a much larger activation energy than 6. To cause half-reaction 5 to occur requires a higher applied potential than the oxidation potential: in fact the applied potential has to be so high that it is enough to cause half-reaction 6. As mentioned earlier, the half-reaction potentials indicate the thermodynamic tendency of the half-reaction to occur and not the rate at which it can occur.

Example 3

Electrolysis of aqueous $CuSO_4$ with copper electrodes.

In this case where the electrode may be chemically active, at the anode three half-reactions are possible.

Possible oxidation half-reactions	E° ox/ V
9. $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$	-0,34
10. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2e^-$	0,82
11. $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$	-2,01

Possible reduction half- reactions	E° red/ V
12. $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0,34
13. $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0,41

Comparison of the oxidation half-reaction potentials indicates that the copper metal should be preferentially

oxidized. Therefore, equation 9 represents the oxidation half-reaction. At the cathode, reduction of copper ions to copper atoms should be preferred to reduction of water, and therefore equation 12 represents the half-reaction at the cathode.

The cell discussed in example 3 is characteristic of many electroplating cells. In these cells the object to be plated is made the cathode and a piece of the plating metal is made the anode and the solution contains a soluble salt of the plating metal.

APPENDIX I

INSTRUCTORS' NOTES - PHASE IV

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PREFACE

1.1 INTRODUCTION

The worksheets address the electrochemistry defined by the learning goals in the Chemistry 1 course. They have been designed taking into account major difficulties and misconceptions students possess in relation to the topic of electrochemistry. Our investigations on student difficulties in this topic revealed that students often manipulate reaction equations and quantities such as the standard reduction potentials for half-reactions without grasping the underlying concepts. The problem areas identified relate to:

(i) the terminology used in connection with electrode processes.

(ii) misinterpreting electrode processes and half-reaction equations.

(iii) failure to apply the principles of chemical equilibrium.

(iv) the lack of qualitative knowledge regarding the microscopic processes which occur in the different components when the cell functions.

Electrochemistry is a multifaceted topic and can be conceptually demanding. It requires understanding of several pre-requisite concepts some of which have been identified as

problematic to beginners in chemistry. A course in electrochemistry usually assumes that the student has the appropriate pre-requisite knowledge on electrical properties as well as an adequate understanding of chemical concepts such as chemical equilibrium, stoichiometry and ionic equations. It is important therefore, to establish at the outset how much the students understand of these pre-requisite concepts in order to provide the basis for later discussions. The pre-test on page seven tests the students knowledge on these concepts before the lectures on electrochemistry commence. This test deserves attention and should be administered by the lecturer concerned.

1.2 THE CONTENT OF THE WORKSHEETS

The teaching approach adopted here was designed largely on the basis of student misconceptions identified during interviews. It emphasizes the microscopic processes which occur in electrochemical cells and highlights the misconceptions identified. An attempt is made to take these into account and hence alleviate the difficulties in understanding this important topic. Each worksheet contains a set of key concepts, objectives, and an introduction as well as basic scientific information on the area of concern.

1.1.1 Key Concepts

These are simply statements of important scientific ideas that are addressed in the worksheet.

1.1.2 The Objectives

These are meant to delineate clearly to the students what they are expected to know and be able to do when they complete each worksheet.

1.1.3 Introduction

These are introductory remarks on the content to be addressed in the worksheet.

1.1.4 Basic Scientific Information

This appears under various sections depending on the content of the worksheet. A deliberate attempt is made to highlight possible misconceptions and explicitly clarify possible areas of confusion. Preliminary questions and/or predictions are also presented to the students as a way of introducing a particular section where appropriate. The questions and predictions will/can stimulate discussion among the students and create an opportunity to be actively involved in addressing and confronting their pre- conceptions.

A brief overview of the subject matter of each of the five worksheets is as follows:

In worksheet one, the relation between current electricity and chemical reactions is presented as well as the terminology used in connection with redox reactions. Worksheet 2 serves

as an advance organiser for subsequent worksheets. It gives an overview of the material to be covered in worksheets three, four and five. Emphasis in this worksheet is placed on the similarity and differences between the reaction which takes place in the beaker and that which takes place in the electrochemical cell (see worksheet 1 fig 1.0 and 1.1). Both are redox reactions and have the same stoichiometry, Gibbs energy change, ΔG and equilibrium constant. The difference is in their rates because of the physical arrangement of the cell.

The reaction which takes place in the electrochemical cell is discussed in greater detail in this worksheet. Aspects such as the relationship between electrical measurements of current and potential difference and the rate, stoichiometry and Gibbs energy change of a reaction are introduced. These are developed further in worksheets 3 and 4.

Worksheet 3 for example, deals with electrochemical stoichiometry (including stoichiometry in fuel cells) and the rates of cell reactions while worksheet 4 is concerned with the cell emf (potential difference) and how it relates to the thermodynamic driving force of the reaction as well as the work that can be obtained from these reactions. Fuel cells and their importance as energy devices are also discussed in worksheet 4.

The physical arrangement and the necessary components for a galvanic cell to function are also introduced in worksheet 2. These are discussed further in worksheet 5 which deals with the microscopic events which occur in electrochemical cells when they operate.

1.2 THE CONTENT OF THE INSTRUCTORS NOTES

These contain notes on the worksheets and each set of notes is divided into three main sections as follows :

1.2.1 Key Concepts

These are identical to the ones in the student worksheets.

1.2.2 Predominant Misconceptions/Difficulties

These are a list of the common misconceptions identified during our research and those identified by other researchers.

1.2.3 General Teaching Approach and Suggested Methods of Alleviating Misconceptions

This section contains some general remarks on how to approach the teaching of specific aspects in a particular worksheet and what distinctions have to be emphasized. Methods of alleviating the predominant misconceptions are also suggested. In most cases this is done by perfoming a demonstration. These demonstrations can be more interesting and effective if students

are allowed to predict the outcome first and their predictions are tested by experiment. If their predictions are not correct, they become forcefully aware of their erroneous pre-conceptions and can ask appropriate questions. The answers to these questions can help alleviate their difficulties. Some of the demonstrations are not suitable to be carried out in a lecture. It is suggested that these be done during tutorial sessions.

1.3 PRE-REQUISITE CONCEPTS IN ELECTROCHEMISTRY

CONCEPT	KNOWLEDGE REQUIRED
1. Electrical Quantities	i. Explain what an ammeter and voltmeter indicate in a circuit.
2. Chemical Reaction Stoichiometry	i. Know that charge and atoms are conserved in a chemical reaction . ii. State the charge/mole relationship.
3. Electrolytes	i. Write a balanced net ionic equation. ii. Explain how current is conducted in solutions of electrolytes and in molten electrolytes.
4. Metallic Bonding and Electronic Conduction	i. Explain how an electrical current is conducted in metals. ii. Know that electrical conductivity is high in metals and is due to the movement of electrons.
5. Chemical Equilibrium	i. Define what is meant by chemical equilibrium in a chemical system.

ii. State the effect on the equilibrium position of:

a. adding a solid reactant.
b. decreasing or increasing the concentration of a reactant.

iii. Explain the dynamic nature of chemical equilibrium.

iv. Relate the equilibrium constant to ΔG

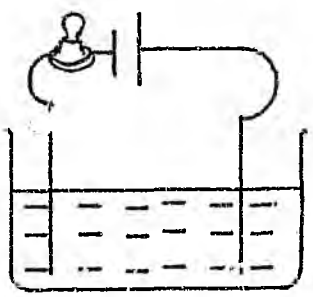
6. Reaction Rate

i. Know the factors that affect the rate of a reaction.

1.4 PRE-TEST ON PRE-REQUISITE CONCEPTS

INSTRUCTIONS : Answer all questions in sections A and B.

1. In the circuit represented in the diagram below, suppose the bulb was glowing brightly, the beaker could contain :



(i) potassium sulphate dissolved in water
(ii) sugar dissolved in pure water
(iii) molten sugar
(iv) dilute sulphuric acid
(v) molten potassium bromide

(a) (i) or (iv) only

(b) (i), (iv) or (v) only

(c) (ii) or (iii) only

(d) (i) or (v) only

(e) (i) or (ii) only

2. When a chemical system is at equilibrium, which of the following statements is true?

(a) the reagents and the products always have the same mass

(b) the forward and reverse reactions occur simultaneously at the same rate

(c) the forward and reverse reactions both stop

(d) the concentration of the reagents is zero

(e) the ratio of the concentration of the products to the concentration of the reagents is never greater than one.

3. The mechanism of electrical conduction in metals is :

(a) the same as in solid electrolytes

(b) the same as in molten electrolytes

(c) dependent on the movement of ions

(d) dependent on the movement of valence electrons

(e) dependent on the movement of atoms

4. The net ionic equation for the reaction which occurs when solutions of sodium hydroxide and hydrochloric acid are mixed is:

(a) $Na^+(aq) + OH^-(aq) + Cl^-(aq) + H_3O^+(aq) \longrightarrow NaCl(aq) + 2H_2O\ (l)$

(b) $NaOH\ (aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O\ (l)$

(c) $Na^+(aq) + Cl^-(aq) \longrightarrow NaCl(s)$

(d) $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

(e) $Na^+(aq) + OH^-(aq) + H_3O^+(aq) \longrightarrow$

$Na^+(aq) + 2H_2O(l)$

5. The following reaction

$Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Ag(s) + Fe^{3+}(aq)$

has reached equilibrium. What can be done to decrease the amount of silver formed ?

(a) stir the solution.

(b) increase the pressure of the solution.

(c) add $Fe^{2+}(aq)$

(d) add $Fe^{3+}(aq)$

(e) add iron filings.

SECTION B

Write your answers in the spaces provided.

6. Questions (i) and (ii) below refer to the reaction shown in question 5 above.

(i). What effect would addition of silver have on the position of equilibrium ? ----------

(ii). What effect would increasing the concentration of silver ions have on the position of equilibrium ----------

---

7. What is the mass of one mole of

(a) Cu^{2+} _____

(b) KCl _____

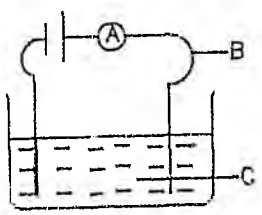
(c) Cl_2 _____

(d) Br^- _____

(e) SO_4^{2-} _____

8. If one mole of hydrogen ions carries a charge of 96 500 coulombs, what is the charge on one hydrogen ion ----------

9. In the circuit shown below:



(a) What quantity does the ammeter show ? _____

(When we talk of an electric current, what is actually moving in B ? _____

in C ? _____

(c) What causes an electric current to flow in the external circuit ?

_____

(d) What quantity would a voltmeter in the circuit show ?

_____

1.5 NOTES ON WORKSHEETS

1.5.1 WORKSHEET 1

KEY CONCEPTS:

(a) When an atom, molecule or ion undergoes oxidation, it loses one or more electrons to some other species which undergoes reduction.

(b) Oxidation and reduction are half-reactions that always occur together and the overall reaction is often called a redox reaction.

(c) Oxidising agents (oxidants) take up electrons and are consequently reduced while reducing agents (reductants) give up electrons and are oxidised.

DIFFICULTIES

(a) Failure to distinguish oxidation and reduction half-reaction equations.

(b) Failure to recognise the oxidant and the reductant in a given redox reaction equation.

GENERAL TEACHING APPROACH AND SUGGESTED METHODS OF ALLEVIATING THE MISCONCEPTIONS

1 Terminology

The basic terminology used in connection with electrochemical processes is introduced. One of the major difficulties is that

students confuse the terms oxidising and reducing agent and fail to identify the substances being oxidised or reduced in a given redox reaction equation.

One other area of confusion is that while oxidation is defined as a loss of electrons there is a gain in oxidation number. One possible solution to this is to get the students to concentrate on the fact that when reduction of a species occurs, its oxidation number is reduced because of a gain of negative charges (electrons). The species being reduced is therefore an oxidising agent.

It is also important to emphasize that oxidising and reducing agents are relative terms and an oxidising agent in one reaction could be a reducing agent in another, depending on how readily the reactants accept or lose electrons. This aspect is discussed in more detail in worksheet 4.

1.5.2 WORKSHEET 2

KEY CONCEPTS:

(a) Reactions which take place in ordinary chemical systems (e.g in a beaker), are the same as those which take place in electrochemical cells. They have the same stoichiometry, Gibbs function change and equilibrium constant. The only difference is in the rate because of the physical arrangement of the cell.

(b) Spontaneous redox reactions take place in galvanic cells. Energy from the chemical reactions is converted to electrical energy.

(c) Galvanic cells consist of chemical components that are initially not at equilibrium and proceed to equilibrium by electron transfer. The electrical energy generated can do work.

(d) Non-spontaneous redox reactions take place in electrolytic cells. Energy is provided by a source of potential difference - often a battery of galvanic cells - forcing the formation of higher energy products.

DIFFICULTIES :

(a) Failure to recognise that redox reactions can take place in ordinary chemical systems e.g in a beaker.

(b) Misunderstanding of the role of components of electrochemical cells.

GENERAL TEACHING APPROACH AND SUGGESTED METHODS OF ALLEVIATING MISCONCEPTIONS

1. Redox Reactions in Electrochemical Cells and in Beakers

Students failed to recognise that redox reactions do not have to take place in electrochemical cells only. When zinc metal was placed in $CuSO_4$ solution, for example, and the students were asked what type of reaction this was only a few recognised it as a redox reaction. This however, was not the case when the students were presented with a galvanic cell arrangement (fig.1.1 Worksheet 1). They immediately recognised this as a redox reaction.

It is important to emphasize that the reactions which take place in the two arrangements shown in figures 1.0 and 1.1 are the same. The difference is that in fig. 1.0 electrons are transferred directly between the reacting species on atomic contact while in fig 1.1 the electrons are transferred through the external wires. Demonstration 2.1 serves to alleviate this misconception. The following can be noted about this demonstration :

(a) The students should be able to recognise that experiments 2.1A and 2.1B are the same (i.e. hydrogen gas is formed in both). The difference is that in 2.1A, chemical energy is converted to heat energy while in 2.1B, chemical energy is converted to electrical energy. (Note: the students should be made to feel that the beaker used in 2.1A gets warmer).

(b) In 2.1A, electron transfer is direct between the zinc atoms and the H^+ ions while in 2.1B, electrons released by the zinc atoms, move through the external circuit. In the first case, heating up of the mixture implies that chemical is converted to thermal energy. The glowing of the bulb in 2.1B, is evidence of an electric current and implies the conversion of chemical to electrical energy

2. Essential Components of Electrochemical Cells and Interpretation of Microscopic Processes

It is desirable to discuss the physical requirements necessary for electrochemical cells to function since some alternative conceptions arise as a result of lack of explicit information. For example, lack of knowledge of the role of components such as the voltmeter and the ammeter seems to give rise to a number of misconceptions.

The knowledge of the nature of each component is also a pre-requisite to deeper understanding of the microscopic processes which occur when the cells operate.
The following are examples of difficulties which arise out of inadequate understanding of the nature and role of the components or misinterpretation of microscopic processes.

(a) Students were required to indicate where the electrons in the the half-reaction : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ came from. The common misconception was that they came from the dissociation of the electrolyte by the electric current. Faraday and his contemporaries thought so but Arrhenius and contemporaries showed that it was wrong. The knowledge of the nature of the electrolyte can help circumvent this difficulty.

(b) Many students perceived the function of the ammeter and the voltmeter to be the same. For example, the voltmeter reading was often referred to as an indicator of the cell reaction rate, that is, the higher the voltage the faster the cell reaction. This confusion between current and voltage led to a number of misinterptetations. These are discussed further in section 1.5.3 and 1.5.4.

(c) Most of the misconceptions regarding the electrolytic cell

arose out of misunderstanding the role of the battery. The most common was "the battery stores electrons until they are ready to flow". The fact that a chemical reaction takes place inside the battery when it operates is of prime importance in alleviating this misconception.

It is essential that students understand that a battery consists of galvanic cells connected in series. The chemical components are therefore used up when it operates.

The purpose of the salt bridge can be explained simply as ensuring that each half-cell has no nett electrical charge at all times during the reaction. At this stage, this may be sufficient since the students do not have adequate knowledge to fully understand the exact processes by which electrical neutrality is maintained. Pre-conceptions relating to the salt bridge can be dealt with in greater detail in worksheet 5.

To elicit some of the student misconceptions concerning the components of electrochemical cells, the following key questions could be asked before introducing section 2.5 on galvanic cells.

(a) What do a voltmeter and an ammeter do in the circuit shown in fig. 1.1 ? (see worksheet 1)

(b) What type of substances are electrolytes ?

(c) What is the purpose of the salt bridge in the circuit shown in figure 1.1 (see worksheet 1).

The students'conceptions regarding the role of the battery in the arrangement shown in fig 2.2 can be elicited when introducing section 2.7 on electrolytic cells (see worksheet). The student misconceptions can be addressed at the time the nature and role of each component are presented.

Demonstration 2.1

Electrical Energy from Chemical Energy

A. Add a few pieces of zinc metal to 10 cm^3 of dilute HCl.

i. What do you observe ? ----------

ii. Why do you think the beaker gets warm ?

---

iii. Write a balanced equation for the reaction taking place in the beaker ----------

iv. What type of reaction is this ? ----------

B. Attach a strip of zinc metal and a piece of copper metal to the side of a beaker and connect each metal to a 1.1 volt bulb as shown.

(c) What is the purpose of the salt bridge in the circuit shown in figure 1.1 (see worksheet 1).

The students' conceptions regarding the role of the battery in the arrangement shown in fig 2.2 can be elicited when introducing section 2.7 on electrolytic cells (see worksheet). The student misconceptions can be addressed at the time the nature and role of each component are presented.

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---

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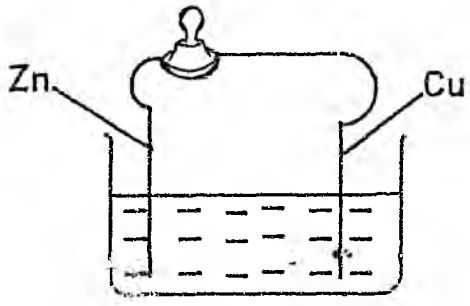
iv. What type of reaction is this ? ----------

B. Attach a strip of zinc metal and a piece of copper metal to the side of a beaker and connect each metal to a 1.1 volt bulb as shown.



Pour dilute HCl into the beaker.

i. What do you observe ? ----------

ii. Does the beaker get warm ? Why ? ----------

---

iii. Write a balanced equation for the overall reaction occuring.----------

iv. Comment on the similarities and differences between experiments A and B.

(iv) Some students believe that electron transfer reactions take place in the electrolyte. This misconception could be

predomin t among students who believe that free electrons are found in solution. It is important for students to understand that electrode reactions take place at the electrode surface. Demonstration 2.2 (electrolysis of aqueous copper chloride with carbon electrodes) serves to alleviate this misconception. One of the key questions to ask could be: "where does the reaction take place?" The formation of chlorine gas (which can be seen on the OHP) and copper at the electrodes, if observed at close range, is evidence of the reaction occuring at the electrodes. The formation of these two products, is also evidence of electrical energy being converted to chemical energy.

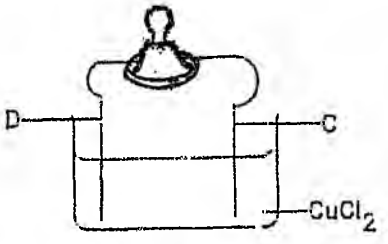
3. <u>The Difference Between a Galvanic and an Electrolytic Cell</u>

The fact that a galvanic cell consists of components which are initially not at equilibrium should be explicitly emphasized. This can be a starting point in later discussions for establishing that the emf of a cell is a measure of the thermodynamic driving force, ΔG of the reaction. As the equilibrium state is approached, the emf decreases and at equilibrium when the driving force is zero, the emf is also zero. (Note: emf = electromotive force. However, this is not a force measurable in Newtons. It is measured in Volt =J/C .

Demonstration 2.2

Chemical Energy from Electrical Energy

A. Make the following cell arrangement

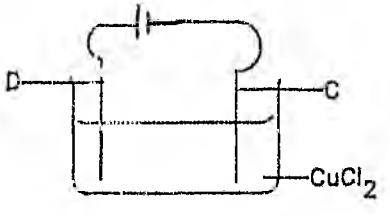


C and D are graphite electrodes

(i) Is there any observable chemical reaction occuring at the electrodes? ----------

(ii) Does the torch light bulb glow? ----------

B. Connect a battery of cells into the circuit as shown below:



C and D are graphite electrod

(i) What do you observe at electrode D? ----------

(ii) Is this reaction spontaneous? Why? ----------

(iii) What evidence is there to show that electrical energy has been converted to chemical energy? ----------

---

1.5.3 WORKSHEET 3

KEY CONCEPTS :

(a) The amount of substance oxidised or reduced at the electrodes is directly proportional to the quantity of charge (electrons) transferred from the anode to the cathode in the external circuit.

(b) The amount of charge which will result in the formation of one mole of univalent atoms will form half a mole of divalent metal atoms. This amount is 1 Faraday = 96 500 Coulombs.

(c) Faraday's laws apply to both galvanic and electrolytic cells.

DIFFICULTIES :

(a) Inadequate understanding of reaction stoichiometry and the mole concept.

(b) Failure to relate the ammeter reading to the rate of the cell reaction.

GENERAL TEACHING APPROACH AND SUGGESTED METHODS OF ALLEVIATING MISCONCEPTIONS

1.Stoichiometry

Research done so far on student difficulties in chemistry indicates that students at different educational levels experience difficulties regarding reaction stoichiometry and the mole concept. Electrochemical stoichiometry is complicated further by the fact that students have to think

in terms of a mole/charge relationship instead of a mass/mole relationship which they are familiar with. Section 2.3 (see worksheet) attempts to explain the relationship between the rate of movement of electrons in the external circuit and the stoichiometry of the cell reaction. This is dealt with further in section 3.2.

2. Current and the Rate of a Cell Reaction

As already indicated in the notes on worksheet 2, students failed to relate electrical measurements of current and voltage to the rate and the Gibbs energy change of the cell reaction respectively. The emphasis on the ammeter as an indicator of the rate (coulombs/second) of movement of electrons in the external circuit is essential.

1.5.4 WORKSHEET 4

KEY CONCEPTS :

(a) The potential difference between two points in a circuit is a measure of the work per unit charge that can be done or energy that can be transferred when electrons move from one point to another in the external circuit. It is measured in Volts and 1 Volt = 1 Joule / Coulomb.

(b) The emf of a cell is a measure of the thermodynamic driving force of the cell reaction. It is measured when negligible or no current flows in the external circuit.

(c) The value of the standard half-reaction potential is independent of the size of the electrode and the volume of the electrolyte.

(d) A galvanic cell can be operated in reverse like an electrolytic cell by applying an opposing voltage greater than the emf of the cell.

(e) The Gibbs function change for a chemical reaction is numerically equal to the maximum work which it can do on its surroundings.

DIFFICULTIES :

(a) Confusion between current and voltage and what the ammeter and voltmeter show.

(b) Failure to apply the principles of chemical equilibrium.

GENERAL TEACHING APPROACH AND SUGGESTED METHODS OF ALLEVIATING MISCONCEPTIONS

1. Interpretation of Half-Reaction Equations

When a metal electrode dissolves, e.g. $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ it is important for students to note that only the cations pass into the electrolyte; the electrons are left behind on the electrode. This oxidation half-reaction is often misinterpreted by students as implying the movement of both the cations and the electrons into the electrolyte solution thus reinforcing the belief in free electrons in solution. There is also confusion because if electrons remain on the electrode it looks as if the metal is reduced (gains electrons) when in fact it is oxidised to cations.

2. The Measurement of Cell Emf

The measurement of cell emf when no current is flowing should be explicitly stated, that is, the need to measure the emf with a high resistance voltmeter. The voltage obtained under such conditions indicates the driving force of the reaction or the thermodynamic tendency of the reaction to occur. The

emf value does not give an indication of how fast a given reaction will occur. A spontaneous reaction may be slow in practice. Emphasize that the voltage measured when significant current is flowing is less than the cell emf since the cell is already doing work on the electrons.

3. Current and Voltage

Many students interviewed did not distinguish between current and voltage and a number of them indicated that a voltmeter shows the electrons flowing in the external circuit.

Demonstration 4.1 is designed to enable students to distinguish between current and voltage. Such a distinction is necessary in explaining why we do not take reaction stoichiometry into account when manipulating E° values.

4. Failure to Apply the Principles of Chemical Equilibrium

Beginners in electrochemistry usually have more experience with homogeneous equilibria than with heterogeneous equilibria. Many students interviewed, failed to recognise that increasing or decreasing the size of the metal electrode should not affect the emf of the cell. This was in spite of being familiar with the fact that in writing the equilibrium constant expression, the value of the solid concentration was a constant. It is

essential to emphasize that the value of the emf is independent of the size of the electrodes and the volume of the electrolytes. The concentration of the electrolyte is relevant of course.

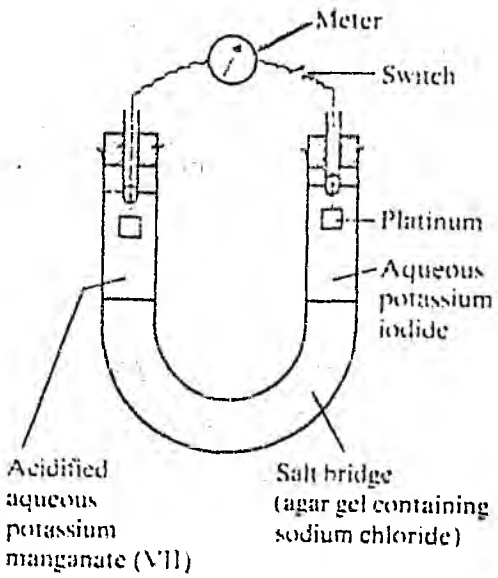
5. The Use of the Term Electrode Potential

It appears that it is customary to refer to an entire half-cell (electrode + electrolyte) as an electrode. For example standard half-reaction potentials are usually referred to as standard electrode potentials. This is misleading and imprecise use of terminology. It seems unwise to define an electrode as both the piece of metal and also the piece of metal plus the electrolyte. It is suggested that the term electrode potential be avoided altogether and rather the terms reduction potential or oxidation potential be used.

Demonstration 4.1

Reduction Potentials and Cell Emf

This experiment summarises some of the most important ideas concerning cell potentials. It also enables the students to interpret half-reaction potential data and cell emf from first principles.



Meter ≡ Potentiometer

Reference: Ainley, D.(1986). An alternative approach to redox potentials. Education in Chemistry, 23: 42-44.

Key Questions

1. What does the deflection of the voltmeter indicate ?
2. What does the deflection of the ammeter indicate ?
3. What does the size of the deflection of the ammeter indicate ?
4. A brown stain is formed around the electrode in the KI solution. What is this due to ?
5. Has this electrode gained or lost electrons from or to the ions in solution ? Is this electrode an anode or a cathode ?
6. Write the half-reaction occuring at this electrode.
7. As the reaction proceeds, the ammeter and voltmeter readings decrease. What does this imply about
   (i) The rate of movement of electrons in the external circuit ?
   (ii) The potential difference/emf of the cell ?

1.5.5 WORKSHEET 5

KEY CONCEPTS :

(a) Electronic conductors are paths for electrons and undergo no detectable physical or chemical change as a consequence of conduction.

(b) Electric current in an operating electrochemical cell occurs as a movement of electrons in the electrodes and as a movement of ions in the electrolyte.

(c) Electrons are transferred between the ions of the electrolyte and atoms of the electrodes at the electrode - electrolyte interface and result in chemical changes.

(d) Overall electrical neutrality is preserved at all times in the electrodes and also in the electrolyte.

PREDOMINANT MISCONCEPTIONS

(a) Conduction through the cell is due to the movement of either free electrons, electrons attached to ions, or electrons moving from ion to ion from one electrode to the other.

(b) The salt bridge provides a pathway for electrons to complete the circuit; these electrons also balance excess positive charge to maintain neutrality in the cell.

(c) The salt bridge makes one half-cell positive and the other negative.

(d) In electrochemical cells ions are attracted to electrodes of opposite charge where they are neutralised by the charge on the electrodes

(e) The anode is the positive electrode and the cathode the negative electrode in both galvanic and electrolytic cells.

GENERAL TEACHING APPROACH AND SUGGESTED METHODS OF ALLEVIATING MISCONCEPTIONS

In this worksheet the microscopic processes occuring when galvanic and electrolytic cells function are discussed. Students were found to have a very poor qualitative understanding of these processes.

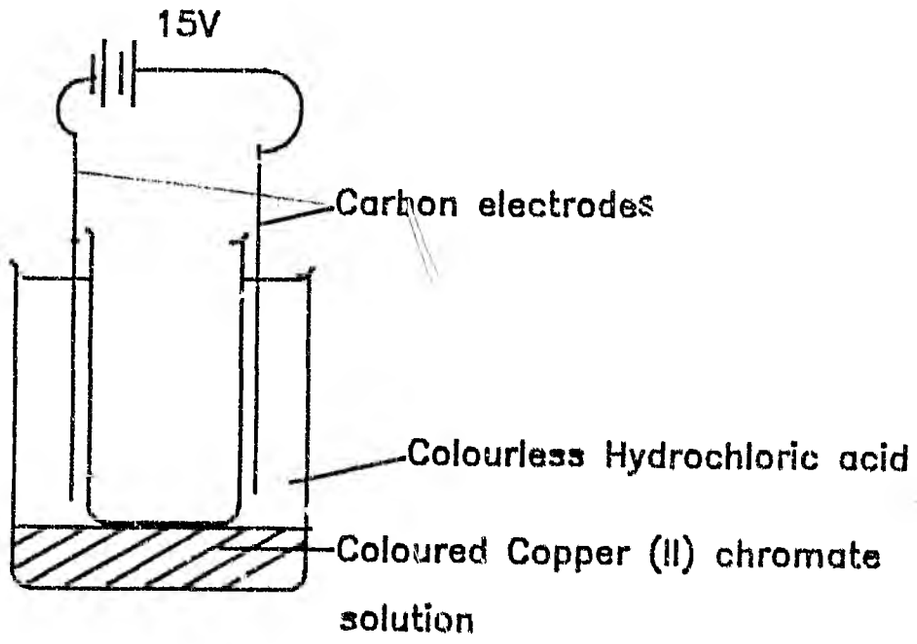
1. Electrolytic and Electronic Conduction

The emphasis here is on distinguishing between a movement of electrons in electronic conductors and the movement of positive and negative ions in the electrolyte. Our research revealed that this is a fundamental problem which can interfere with the comprehension of several concepts such as neutrality. The distinction should be made carefully so that students know that in any cell the movement of free electrons is always through the metallic conductor and never through the electrolyte.

Demonstration 5.1 below shows the movement of ions in the electrolyte and this is evidence that current is due to the movement of ions in opposite directions in the solution.

Demonstration 5.1

Demonstration of movement of ions



Key questions

1. What is the appearance of the U-tube before current is passed through the solution ?
2. What is the appearance of the U-tube after current is passed for thirty minutes ?
3. How can this change in appearance be explained ?
4. What can be said about the nett speed of travel of ions in solution ?

To save time two experiments can be set up. In one the students can be shown the appearance of the tube when no current has been passed through the solution, while in the second one they can be shown the appearance of the tube after 30 minutes.

It is also desirable that the nature of the metal surface be adequately discussed in a qualitative manner and emphasizing that the cations in the metal (sea of electrons model) do not move from one electrode to the other in the external circuit. Many students may make this interpretation due to the confusion arising from the definition of conventional current as a movement of positive charges.

2. Reference to Continuity of Current in the Cell

The reference to the meaning of continuity of current or the electric circuit should be made. In explaining this to the students explicit mention should be made that the continuity of current in circuits containing electrochemical cells is different from that in DC circuits often encountered in physics.

In physics courses current is often implied to be electronic in all parts of the circuit, even if there is a battery. In fact in DC circuits containing a cell, or battery of cells, current is electronic in the wires and ionic in the electrolyte. The electronic current in the wires is continuous with ionic current in the electrolyte.

3. Interpretation of Electrode Processes

(i) In an electrolytic cell the cathode receives electrons from the battery and it is the negative electrode. At the anode, electrons are released from the species undergoing oxidation at the the electrode surface and the anode is called the positive electrode.

Students tend to extend this to galvanic cells so that there is a common misconception that the description anode means a positive electrode and cathode a negative electrode

in both types of cells. In fact in a galvanic cell the anode is described as negative and in an electrolytic cell the anode is described as positive. This is extremely confusing to beginners in electrochemistry. For example, in figure 5.1. in the worksheet, the copper electrode is negative and the silver electrode is positive. If students accept that the copper electrode is negative and the silver electrode is positive, they are likely to become totally confused as to why the Ag^+ ions are "attracted to the positive electrode". As a result of this confusion, some students refer to anions (e.g NO_3^- in this cell) as being reduced at the silver electrode, since "negative ions should be attracted to the positive electrode". One of the most important questions asked by students was:

> " Why then in a Daniell cell do the copper ions move toward the positive copper electrode ? Do not like charges repel ?

ANSWER: The answer to this question is important in understanding the operation of galvanic cells. It must be emphasized that the motion of the ions in the two half-cells is not caused by charge at either electrode. The electrodes are not connected to a battery of cells or a generator : the cell itself generates electricity. The ions thus move due to

the electron transfer reactions at the electrodes and to maintain electrical neutrality.

If we consider the cell in figure 5.2. when the silver ions touching the electrode surface react, this leaves an excess of negative ions near the silver electrode. Other Ag^+ (aq) ions move in to take their place. The diffusion of silver ions from the bulk of the solution is necessary to maintain electrical neutrality.

(ii) Besides causing the confusion discussed above in (i), the convention of designating electrodes as either positive or negative presented other problems in relation to the interpretation of electrode reactions, and also in reinforcing the misconception on electronic conductivity in the electrolyte. Equation 5.2 is an example of a case where neutral iodine atoms are formed at the electrode surface followed by rapid combination to form molecules of I_2 . Several students who focussed their attention on the " charge" on the electrodes misinterpreted this process. The formation of the neutral iodine atoms was accounted for in terms of attraction between the negative iodide ions and the positive electrode. The formation of the neutral atoms was thus interpreted in terms of some reaction between the negative ions (I^-) and the

positive charge on the electrode rather than the loss of an electron by the iodide ion.

One other problem with this type of half-reaction, was failure to recognise that it occurs in two stages :

$$I^- \ (l) \longrightarrow I \qquad e$$

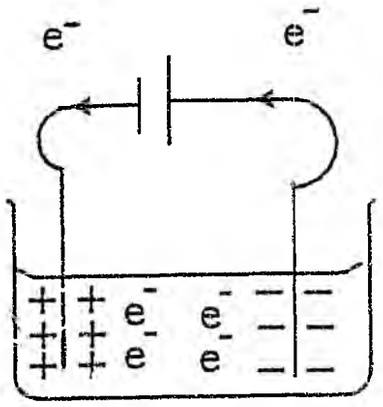
in the melt at electrode surface — on the electrode surface — on the electrode

followed by $I + I \longrightarrow I_2 \ (l)$

Usually only the overall reaction

$2I^- \ (l) \longrightarrow I_2 \ (l) + 2e^-$ is written, suggesting that the half-reaction occurs in one step.

(iii) During our research, some students indicated that "electrons move in the solution and the ions are attracted to the electrodes". Apparently these students thought that the ions are instantaneously attracted to the electrodes, that is, they stick to electrodes of opposite charge such that none remain in the bulk of the solution. We gained the impression that the phrase "attraction of ions to electrodes" evoked the following microscopic picture.



As a result of this supposed instantaneous movement of ions to the electrodes of opposite charge, the movement of electrons then constituted an electric current in the electrolyte.

It is important in explaining this to students to emphasize that the nett movement of ions in solution is slow (in demonstration 5.1 the ions only visibly separate after 15-30 minutes). It is also essential to note that the ions do

not move because of long range attraction between them and a distant electrode but that they diffuse slowly to replace those reacting at the electrode surface.

The confusion of designating electrodes negative and positive can certainly be overcome and some students eventually get it sorted out, but the point is it can be avoided entirely. It seems useful therefore to use the convention applicable to both cells, that is oxidation occurs at the anode and reduction at the cathode in both cells without necessarily referring to electrodes as either positive or negative. Demonstration 5.2 illustrates that it is possible to interpret redox processes from first principles without talking about positive or negative electrodes.

Students should be advised that this policy is being adopted because it may avoid confusion. The existence of the terminology should probably be acknowledged .

(4) Electrical Neutrality

There was widespread uncertainty about how neutrality is maintained in the electrolyte in both types of cells. The problems included :

(i) Disregard for the need for balanced charges in each half-cell.

(ii) Presence of electrons in the electrolyte.

It is important to re-emphasize one of the important ideas which is taught early in school chemistry, that is, positive and negative charges exist in equal numbers within a phase.

One other problem with understanding electrical neutrality seemed to arise from the belief that free electrons are found in the electrolyte. In demonstration 5.2 (investigating galvanic cells), several arrangements are made to confront this misconception. These demonstrations could be conducted during tutorial sessions and should convince the students that no electrons go through the salt bridge and they cannot therefore be found in solution or maintain electrical neutrality.

The investigation can be conducted as follows:

(a) Give students 10-20 minutes to make their predictions and explanations individually.

(b) Discuss the students predictions.

(c) Divide the students into small groups and deliver the apparatus. Let the students make their observations and explanations individually.

(d) Bring students together and let them discuss their observations and explanations. Do not provide the students with any answers; rather guide them to the correct answer.

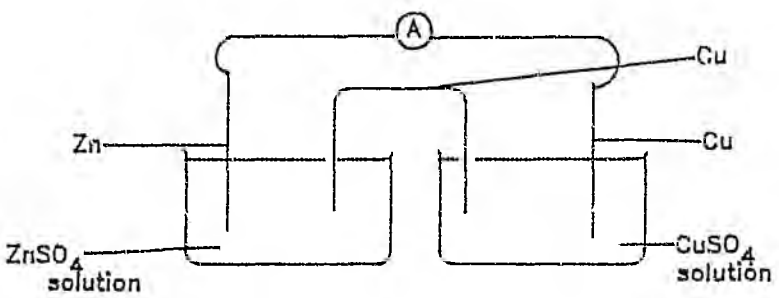
Demonstration 5.2

Investigating Galvanic Cells

Instructions: Predict whether or not a reaction will occur in each of the followin galvanic cell arrangements. Explain your predictions and then make the arrangments with the apparatus provided. Record all your observations and explanations in the table provided.

Cell Arrangements

1



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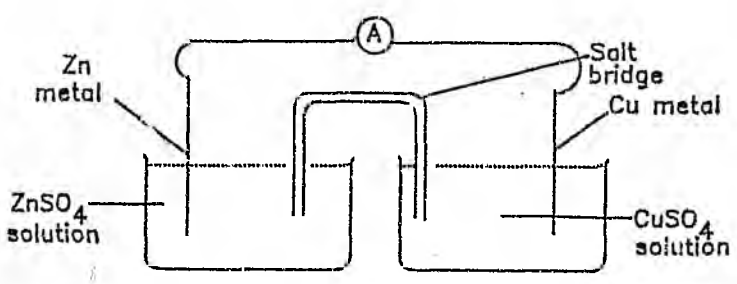

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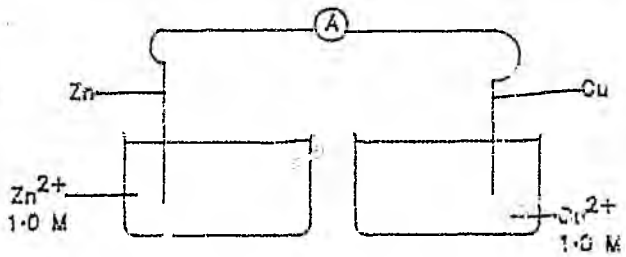

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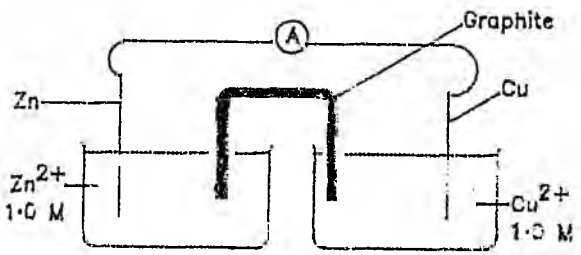

Arrange-ment	prediction reaction/ no reaction	explan-ation	observa-tion rxn/no rxn	exp-lanation
1				
2				
3				
4				
5				

APPENDIX J

SUMMARY OF GROUPS STUDIED

PHASE I

PRELIMINARY INVESTIGATIONS

Subjects	N	Instrument
High School pupils (SG)	4	group interviews
High School pupils (HG)	4	group interviews
College of Education students	10	group interviews/ pencil and paper test
1st year 'slow-stream' chemistry students	9	group interviews/ pencil and paper test.

DETAILED INVESTIGATIONS

Subjects	N	Instrument
1st year 'slow-stream' chemistry students	8	individual interviews

PHASES II AND III

PRELIMINARY INVESTIGATIONS

INSTRUMENT : 10 -item multiple choice questionnaire

Subjects	N	Pre-test/ Posttest
High school pupils (SG)	31	Post-test
High school pupils (HG)	30	Post-test
1st year 'slow-stream' chemistry students	42	Pre- and posttest
Chemistry III students	30	Posttest
HDE (P-G) students		
HDE (I, II)	17	Posttest
HDE (III, IV)	13	Posttest

DETAILED INVESTIGATIONS

INSTRUMENT : 20-item multiple choice questionnaire

Subjects	N	Pretest/Posttest
High school pupils (HG)	30	Posttest
1st year 'slow-stream' chemistry students	40	Pre- and posttest

PHASE IV

INSTRUMENTS : (1) Pre-test on Pre-requisite concepts

(2) 13-item multiple choice questionnaire (Posttest)

Subjects	N	Pretest/Posttest
1st year `slow-stream chemistry students	27	Pre and posttest
Chemistry 100	58	Pre and posttest
Chemistry 101 students	52	Pre and posttest
Chemistry 110	43	Pre and posttest
Chemistry 111	32	Pre and posttest
HDE (F-G) students	30	Pre and posttest (instrument 2 only)

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