Unit title: Physical Chemistry

Unit code: **Y/601/0353**
QCF level: **4**
Credit value: **15**

Aim

This unit gives learners an understanding of concepts and practical techniques in physical chemistry. These include thermodynamics, reaction kinetics, conductivity, electrochemical cells and electrolysis.

Unit abstract

There are certain key concepts in physical chemistry that underpin other strands of chemistry, such as inorganic chemistry, analytical chemistry, organic chemistry and biological processes. Learners will undertake a programme of assignment and related practical work, covering thermodynamics, reaction rate, ionic conductance, electrochemical cells and electrolysis. The emphasis is on being able to use theoretical concepts, interpretation of data and performing calculations. There is the opportunity to research commercial uses of electrolysis.

Learning outcomes

On successful completion of this unit a learner will:

1. Understand the application of the first, second and third laws of thermodynamics to predict the feasibility of reactions
2. Understand the use of rate equations to determine the order of a reaction
3. Understand ionic conductance
4. Understand the application of principles of oxidation and reduction to electrochemical systems.

Unit content

---

1 Understand the application of the first, second and third laws of thermodynamics to predict the feasibility of reactions

Laws of thermodynamics: first, second and third laws

Definition of standard enthalpy changes: enthalpy of combustion; enthalpy of formation; enthalpy of dissociation; mean bond enthalpy; ionisation enthalpy; electron affinity; enthalpy of fusion; enthalpy of vaporisation; enthalpy of sublimation

Calculation of entropy changes: changes of state and heating and cooling of a single substance (including use of molar heat capacity at constant pressure and enthalpies of vaporisation and fusion)

Calculation of ΔH^θ, ΔS^θ: from tables of standard enthalpy changes of formation, ΔH_f^θ of reactants and products and entropies of reactants and products; calculation of ΔH_f^θ from mean bond enthalpies; calculation of enthalpy changes involving standard enthalpy of combustion

Enthalpy changes at different temperatures: use of the Kirchoff equation

Feasibility: Gibbs energy; condition of a negative change in Gibbs energy for a feasible reaction; significance of the signs of ΔH and ΔS; $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$; assumptions made; relationship to equilibrium constants

Changes in enthalpy, entropy, and Gibbs energy: any reaction for which two of these changes may be used to determine the third e.g. for metal/metal salt displacement where ΔH may be found from temperature measurements and ΔG from the appropriate electrochemical cell

2 Understand the use of rate equations to determine the order of a reaction

Methods for following rate of reaction: methods eg spectrophotometry, conductivity, optical rotation, refractive index, dilatometry, measurement of gas pressure, titrimetry of aliquots, problems of fast reactions

Integrated rate equations: zero, first and second order reactions (integration of rate expressions is desirable but not mandatory); units of rate constant; half-life expressions; percentage reaction

Methods for finding reaction order: minimum of two e.g. plotting graphs of functions of concentration versus time in accordance with the integrated rate expressions, use of the general half-life expression for an nth order reaction, use of gradients of two tangents (d[A]/dt) to the reactant concentration versus time plot at concentrations, $[A]_1$ and $[A]_2$, using the method of initial rates for systems involving more than one reactant

Basis: theoretical explanations; relevant equations; assumptions

Determining reaction order from data: a method based on experimental data eg ester hydrolysis, hydrolysis of sucrose, reaction of diazonium salts with water, reaction of crystal violet with hydroxide, iodide/persulfate; tables of concentration/time data

3 Understand ionic conductance

Terms and units commonly used: resistance (Ω); conductance (Ω^{-1}, S, mS, μS); cell constant (m^{-1}, cm^{-1}), conductivity ($\Omega^{-1}\ m^{-1}$, $\Omega^{-1}\ cm^{-1}$, $S\ m^{-1}$, $S\ cm^{-1}$, $mS\ cm^{-1}$, $\mu S\ cm^{-1}$ etc), concentration ($mol\ dm^{-3}$, $mol\ m^{-3}$, $mol\ cm^{-3}$), molar conductivity, □, ($S\ m^2\ mol^{-1}$, $\Omega^{-1}\ m^2\ mol^{-1}$, $S\ cm^2\ mol^{-1}$, $\Omega^{-1}\ cm^2\ mol^{-1}$), limiting molar conductivity, Λ^θ, ionic mobility ($m^2\ s^{-1}\ V^{-1}$, $cm^2\ s^{-1}\ V^{-1}$), ionic charge ($C\ mol^{-1}$)

Constants: shape of molar conductivity versus square root of concentration for weak electrolytes; limiting molar conductivity for strong electrolytes from extrapolation of plot of molar conductivity versus square root of concentration plots; limiting molar conductivity for weak electrolytes from molar conductivities of individual ions; discussion of values of limiting molar conductivities of individual ions with reference to their charge and mobility; acid dissociation constant; solubility; solubility product; assumptions inherent in calculations

Conductivity titrations: strong acid/strong base titration; one other type of titration e.g. weak acid/strong base, strong acid/weak base, weak acid/weak base and precipitation

Conductance experiments: explanation of specific calibration procedures for instruments used; determination of cell constant; variation of molar conductivity with square root of concentration for a strong and a weak electrolyte; determination of acid dissociation constant; determination of solubility product

4 Understand the application of principles of oxidation and reduction to electrochemical systems

Standard cell voltage, E^{θ}_{cell}: oxidation and reduction equations for half-cells; overall cell reaction (redox equation); experimental set-up; redox reactions involving metal/metal ion and platinum/redox couple; use of tables of standard reduction potential to calculate theoretical values of E^{θ}_{cell}; positive standard cell potential, E^{θ}_{cell} for a feasible cell reaction; pictorial representation of apparatus showing electron flow; IUPAC standard cell notation; reference electrodes e.g. standard hydrogen, calomel, silver/silver chloride; liquid junction; salt-bridges; experimental determination of cell voltage for simple cells involving metal/metal ion couple or platimum/redox couple half cells; possible reasons for differences between measured and calculated values e.g. use of concentration rather than activity, liquid junction potential, differences in temperature; $\Delta G = -nFE$ and $\Delta G^\theta = -nFE^\theta$

Nernst equation: relationship between activity and concentration; $E_{cell} = E^{\theta}_{cell} - (RT/nF) \ln Q$ where Q is the product of product activities divided by the product of reactant activities (raised to the powers of the stoichiometric numbers where applicable) for the cell reaction; ability to write a Nernst equation formula for a range of cells; ability to calculate a value for E_{cell} given the half-cells involved, temperature and the activity of relevant ions

Electrolysis: molten salts; aqueous solutions of ions, the role of water; overvoltage; oxidation and reduction equations; products at anode and cathode

Use of Faraday's law: one Faraday equivalent to one mole of electrons flowing in an electrolysis cell; one Faraday = 96485 C mol^{-1}; current = charge/time; calculation of mass of metal plated on cathode given current and time; volume of gas collected at 1 bar pressure and a temperature of 298K in a given electrolysis cell

Commercial applications: electrolytic processes e.g. chlor-alkali industry, Downs cell, Diaphragm cell, membrane cell, Hall-Heroult process, electrorefining, electroplating

Learning outcomes and assessment criteria

Learning outcomes On successful completion of this unit a learner will:	**Assessment criteria for pass** The learner can:
LO1 Understand the application of the first, second and third laws of thermodynamics to predict the feasibility of reactions	1.1 define a range of standard changes in enthalpy 1.2 calculate changes in entropy 1.3 apply thermodynamic data to calculate standard changes in enthalpy and entropy for given reactions 1.4 calculate enthalpy changes at different temperatures 1.5 predict the feasibility of given reactions 1.6 experimentally determine changes in enthalpy, entropy, Gibbs energy, using safe practices
LO2 Understand the use of rate equations to determine the order of a reaction	2.1 review methods for following rate of reaction 2.2 apply calculations using the integrated rate equations 2.3 explain the basis for two methods for determination of reaction order 2.4 use appropriate methods to determine reaction order from data
LO3 Understand ionic conductance	3.1 explain, using appropriate units, terms commonly used in the measurement of electrolytic conductance 3.2 calculate, using conductance measurements, constants for strong and weak electrolytes 3.3 explain the shape of plots from conductivity titrations 3.4 perform appropriate conductance experiments, using safe practices

Learning outcomes On successful completion of this unit a learner will:	**Assessment criteria for pass** The learner can:
LO4 Understand the application of principles of oxidation and reduction to electrochemical systems	4.1 explain reasons for differences between theoretical and experimental values for standard cell voltage, $E0_{cell}$. 4.2 apply the Nernst equation to calculate electrochemical cell potentials at activities other than unity 4.3 apply Faraday’s law to calculate amounts of product in given electrolysis cells 4.4 discuss commercial uses of electrolysis which illustrates the underlying chemical principles

Guidance

Links

This unit has particular links with the following units within this qualification:

- *Unit reference number R/601/0352: Organic Chemistry*
- *Unit reference number R/601/0349: Inorganic Chemistry*
- *Unit reference number H/601/0355: Chemical Laboratory Techniques*
- *Unit reference number J/601/0364: Physical Chemistry of Spectroscopy, Surfaces and Chemical and Phase Equilibria*
- *Unit reference number M/601/0410: Analytical Chemistry.*
- *Unit reference number M/601/0360: Inorganic Chemistry of Crystal Structures and Transition Metal Complexes*
- *Unit reference number A/601/0362: Organic Chemistry of Aromatic and Carbonyl Compounds*

Essential requirements

Delivery

This unit contains a great deal of formal notation and a wide range of quantities and their correct units. An active and experimental approach must be adopted to demonstrate the relevance of the topics to the vocational setting. Tutors must stress the applications of the topics to the chemical process industry and to analytical chemistry.

Tables of thermodynamic data must be used extensively in learning outcome 1. It is envisaged that much of the delivery of this unit will involve building learners' confidence in performing calculations.

Producing an account of methods used in measuring reaction rate should be based on experiments or demonstrations that learners have experienced, for example measuring the volume/pressure of a carbon dioxide in the reaction between calcium carbonate and acid, following the absorbance of a solution of crystal violet and sodium hydroxide, measuring the pH of an acid hydrolysis reaction. Many learners will not have the mathematical background to follow the integration of the differential rate equations. It is then optional whether to integrate the equations or not. However, learners must be able to use the integrated forms of the rate equations to calculate concentrations, reaction times, half-lives and % reaction.

The methods for finding reaction order should be chosen to reflect the mathematical ability of learners. Appropriate equations and manipulations must be used as part of their explanation for why the methods work.

A minimum of two methods for finding reaction order must be used.

The use of conductance symbols and units is difficult for learners to grasp. Learners should build up a glossary of terms and units throughout the delivery of this unit. Experiments which may be carried out include the measurement of conductivity of strong and weak electrolytes (such as potassium sulfate and ethanoic acid) as a function of concentration and the square root of concentration. This introduces the concept of limiting molar conductivity. Learners will appreciate that this may be measured for strong electrolytes but not for weak electrolytes. Learners may calculate the limiting molar conductivity from tables of the limiting molar conductivity of the separate ions involved. The role of mobility and concentration in determining conductivity must be explained. The measurement of conductivity of water samples is used extensively in industry as a measure of the purity of water.

Learners should be familiar with the calculation of standard cell potential. The concepts of half-cell, oxidation, reduction, overall cell reaction, construction of relevant equations, possible experimental set-ups, standard reduction potential, standard conditions and calculation of standard cell potentials must be revised and the concepts of activity, liquid junction and liquid junction potential introduced. Learners must measure cell voltages for simple cells. Appropriate half-cells are Zn^{2+}/Zn, Pb^{2+}/Pg, Cu^{2+}/Cu. Half-cells involving platinum and two ions in solution, e.g. Fe^{3+}, Fe^{2+}/Pt may be used if appropriate. Learners must calculate expected voltages, measure voltages, compare values obtained and suggest reasons for differences.

Learners need to predict products of electrolysis from simple, aqueous ionic solutions and molten ionic substances. They need to write oxidation and reduction equations.

Electrolysis is important industrially. If possible, learners should visit a site where electrolysis takes place to appreciate the scale of the industrial process and the potential environmental implications. There are CD clips that illustrate the processes that use electrolysis.

Assessment

Learning outcome 1 will mainly be assessed through performing a range of straightforward calculations successfully. At least one experiment, relating changes in enthalpy, entropy and Gibb’s energy must be carried out.

For learning outcome 2, learners must review a minimum of three methods for following rate of reaction. The methods of finding reaction order must be tailored to learner ability. At least two data-handling exercises must be used for finding the order of reaction. Two different methods of finding order must be used. At least one experiment should be involved.

Learning outcome 3 is easily assessed through learners making a glossary of terms and performing the indicated conductivity measurements and manipulating the data appropriately.

For learning outcome 4, learners must measure voltages of appropriate electrochemical cells and compare these with calculated values, suggesting reasons for differences. Several Nernst equations must be constructed and at least two evaluated, given appropriate data.

Resources

Learners will need access to appropriate laboratory facilities and technical support.

Employer engagement and vocational contexts

Learners should have the opportunity to observe a commercial electrolytic process in action. Industrial representatives could give presentations on the relevance to process control of thermodynamics and rate of reaction. The industrial relevance of conductivity measurement to the pharmaceutical sector and in environmental management should be addressed. The Nernst equation in relation to biological processes, to electrolysis and to corrosion should be considered.