

## UNIT 2: PHYSICAL CHEMISTRY

**Recommended Prior Knowledge:** Unit 1 (Theoretical Chemistry) should have been studied before this unit.

**Context:** This unit can be studied immediately after Unit 1, or after Unit 4 (Organic Chemistry I). It is recommended that it is studied before Unit 3 (Inorganic Chemistry), however.

**Outline:** The unit looks at enthalpy changes of reactions, bond energies and Hess's law, le Chatelier's principle and aspects of equilibria in gases and in solution ( $K_p$  and  $K_c$ ). The Bronsted-Lowry theory of acids and bases is developed, as are the qualitative aspects of chemical kinetics, including the Boltzmann distribution, catalysis and enzymes.

section	Learning Outcomes	Suggested Teaching Activities	Lesson allocation (approx.%)	Other references
5 (a) 5 (f)	Explain that some chemical reactions are accompanied by energy changes, principally in the form of heat energy. Construct [and interpret] a reaction pathway diagram, in terms of the enthalpy change of the reaction [and of the activation energy] [N.B. leave the contents of the square brackets until later]	Use reaction pathway (enthalpy profile) diagrams to explain the meaning of endo- and exo-thermicity. Practice with profile diagrams for a variety of reactions. (diagrams should include a y-axis labelled <i>enthalpy</i> , an x-axis labelled <i>reaction progress</i> , the molar amounts and state symbols of reactants and products, and an arrow joining them, labelled with $\Delta H$ , going up for an endothermic reaction, and <i>vice versa</i> .) Some important <i>exothermic processes</i> : oxidation of fuels and respiration of glucose + carbohydrates. Some <i>endothermic</i> ones: decomposition of $\text{CaCO}_3$ and photosynthesis.	4	<a href="#">site 5a</a> (Chemical energetics)  <a href="#">site 9</a> (Thermodynamics)  <a href="#">site 11</a> (Thermochemistry)  <a href="#">site 6</a> (Home/AS/ Chemistry/ Chemical Energetics)
5 (c)	Calculate enthalpy changes from appropriate experimental results, including the use of the relationship: $\text{enthalpy change} = mc\Delta T$	Suitable experiments include neutralisation of acids with hydroxides or carbonates (use $1 \text{ mol dm}^{-3}$ or $2 \text{ mol dm}^{-3}$ solutions), powdered metals (e.g. zinc) with solutions of metal salts (e.g. $\text{CuSO}_4(\text{aq})$ ), dissolving salts (e.g. $\text{NH}_4\text{NO}_3$ or $\text{CaCl}_2$ ) in water to make $1 \text{ mol dm}^{-3}$ solutions. Expanded polystyrene coffee cups (supported inside $250 \text{ cm}^3$ beakers to avoid tip-up) make useful insulated calorimeters.	5	<a href="#">site 6</a> (Home/AS/ Chemistry/Chemical Energetics)  CIEX 21, 23

5 (b)	<p>Explain and use the terms: (i) <i>enthalpy change of reaction</i> and <i>standard conditions</i>, with particular reference to: formation; combustion; hydration; solution; neutralisation; atomisation</p> <p>(ii) <i>bond energy</i></p>	<p>Explain that <math>\Delta H^\circ</math> is defined at 298K and 1 atmos (100 kPa), per mole of product or reactant, and producing 1 mol dm<sup>-3</sup> solutions (where relevant) <math>\Delta H^\circ_f</math>, <math>\Delta H^\circ_{at}</math>, <math>\Delta H^\circ_{hyd}</math>, <math>\Delta H^\circ_{sol}</math>, <math>\Delta H^\circ_{neut}</math> are defined in terms of 1 mole of product; <math>\Delta H^\circ_c</math> in terms of 1 mole of reactant. State symbols are important.</p> <p>Give examples of equations showing these enthalpy changes, e.g.</p> $\Delta H^\circ_{at}: \frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ $\Delta H^\circ_f: 2Al(s) + 1\frac{1}{2}O_2(g) \longrightarrow Al_2O_3(s)$ $\Delta H^\circ_c: C_2H_6(g) + 3\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ <p><math>\Delta H</math> for this process is positive, i.e. defined in terms of the <b>breaking</b> of <b>1 mole</b> of bonds. e.g.</p> $E(Cl-Cl): \Delta H^\circ \text{ for } Cl_2(g) \longrightarrow 2Cl(g)$ $E(C-H): \Delta H^\circ \text{ for } \frac{1}{4}CH_4(g) \longrightarrow \frac{1}{4}C(g) + H(g)$	5	<p><a href="#">site 2</a> (AS / Enthalpy calculations)</p> <p><a href="#">site 6</a> (Home/AS/ Chemistry/Chemical Energetics)</p>
5 (e)	<p>Apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:</p> <p>(i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion</p> <p>(ii) average bond energies</p>	<p>A formal definition is useful. Practical work could include finding the <math>\Delta H^\circ</math> for <math>MgSO_4 + 7H_2O(l) \rightarrow MgSO_4 \cdot 7H_2O(s)</math> by dissolving each in water, and measuring the respective temperature changes; or the <math>\Delta H^\circ</math> for <math>CaCO_3(s) \rightarrow CaO(s) + CO_2(g)</math> by dissolving each solid in HCl(aq). Numerical practice with cycles involving combustions of alkenes/alkenes; C(s), H<sub>2</sub>(g) and hydrocarbons <i>or</i> alcohols. Practice with signs of <math>\Delta H</math> and reactions involving different numbers of moles.</p> <p>More cycles involving combustions and decompositions (e.g. H<sub>2</sub>O<sub>2</sub>). Emphasise <i>average</i> bond energies, so not exact in specific cases.</p>	10	<p><a href="#">site 5a</a> (Chemical energetics)</p> <p><a href="#">site 5b</a> (Energy changes)</p> <p><a href="#">site 9</a> (Thermodynamics)</p> <p><a href="#">site 11</a> (Thermochemistry)</p>
8 (a)	<p>Explain and use the terms: <i>rate of reaction</i>; <i>activation energy</i>; <i>catalysis</i></p>	<p>Define rate in terms of mol dm<sup>-3</sup> sec<sup>-1</sup>, but explain that other properties may be proportional to concentrations (e.g. vol. of gas evolved, or mass of reaction mixture remaining). Define catalysis in terms of providing an alternative route of lower activation energy, and define activation energy as the minimum energy reactants need in order to undergo reaction (NOT the energy needed to <i>start</i> a reaction).</p>	3	<p><a href="#">site 5b</a> (Kinetics-definitions only)</p> <p><a href="#">site 9</a> (Reaction kinetics)</p> <p><a href="#">site 11</a> (Kinetics)</p>
8 (b)	<p>Explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction</p>	<p>The greater the concentration, the greater the collision rate. Practical examples could include acid + marble chips (gas syringe or top pan balance); thiosulphate + acid (only [thio] has an effect on rate); acid + metal (gas syringe).</p>	5	<p>CIEX 8, 39</p>
	<p>Show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy</p>	<p>Plotting some Maxwell-Boltzmann data would emphasise that the curve is a <i>histogram</i>. A realistic curve has the most common molecular energy at room temperature at about 8 kJ mol<sup>-1</sup>, whereas a typical <math>E_{act}</math> is over 100 kJ mol<sup>-1</sup>. Emphasise the asymmetry of the curve, starting at <math>E = 0</math> and having a long asymptotic high energy tail.</p>	3	<p><a href="#">site 4</a> (Experiments / Maxwell-Boltzmann)</p>

8 (d)	Explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction	For the same number of molecules, the higher temperature curve should have its maximum at a higher energy, and the high-energy tail should stretch further to the right, but since the two curves enclose the same area under them, the maximum of the higher temperature curve will have a lower y-axis value. For a given $E_{\text{act}}$ , there is a larger number of molecules with $E > E_{\text{act}}$ at the higher temperature.	2	<a href="#">site 4</a> (Experiments > Maxwell-Boltzmann)  CIEX 9, 1, 7
8 (e)	(i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy  (ii) interpret this catalytic effect in terms of the Boltzmann distribution	Heterogeneous catalysts often work by weakening the bonds in the reactants by the process of adsorption. Homogeneous catalysts either enhance the electro- or nucleophilicities of reagents (e.g. $\text{H}^+$ in ester hydrolysis, or $\text{AlCl}_3$ in arene chlorination), or offer an easier redox pathway (e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the $\text{I}^- + \text{S}_2\text{O}_8^{2-}$ reaction). Placing $E_{\text{act}}(\text{catalysed})$ at a lower energy than $E_{\text{act}}$ on the distribution curve shows the larger number of molecules than can now react	4	
9.5 (k)	state examples of catalysis by transition metals and/or their compounds	Some examples are: Fe in the Haber process, $\text{Fe}^{2+}/\text{Fe}^{3+}$ as above, $\text{FeCl}_3$ in Friedel-Crafts, $\text{V}_2\text{O}_5$ in Contact process, Ni in catalytic hydrogenation, Pt in the car exhaust catalytic converter.	2	
8 (f)	describe enzymes as biological catalysts (proteins) which may have specific activity	A brief description of the “lock-and-key” hypothesis, and the idea of an enzyme-substrate complex. Enzymes show characteristics of heterogeneous catalysts (active sites, prior adsorption) and homogeneous catalysts (acid-base or redox reaction mechanisms). Examples could include some proteolytic enzymes with specific activities, e.g. trypsin.	2	
7 (a)	Explain, in terms of rates of the forward and reverse reactions, what is meant by a <i>reversible reaction</i> and <i>dynamic equilibrium</i>	A reversible reaction can take place in either direction. A <i>dynamic equilibrium</i> is characterised by the following: <ul style="list-style-type: none"> <li>• it must occur in a closed system.</li> <li>• forward and backward reactions occur at the same rate.</li> <li>• macroscopic properties are constant.</li> </ul>	2	<a href="#">site 5b</a> (Equilibria)  <a href="#">site 8</a> (Equilibrium)  <a href="#">site 9</a> (Chemical equilibrium)  <a href="#">site 11</a> (Equilibrium)
7 (b)	State Le Chatelier's principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration or pressure, on a system at equilibrium	Emphasise that the principle states that it is the <i>position of equilibrium</i> that changes to <i>oppose</i> ( <b>not</b> cancel) an applied constraint such as a change in temperature or pressure.  Practical examples could include: $\text{BiOCl} + \text{HCl}$ ; $\text{Cr}_2\text{O}_7^{2-} + \text{OH}^-$ ; indicators + $\text{H}^+/\text{OH}^-$ ; $\text{NO}_2/\text{N}_2\text{O}_4$ in syringe in beaker of warm water, or squeezed. There are CD-ROMs that allow Haber process simulations.	8	<a href="#">site 4</a> (Experiments / Le Chatelier's principle)  <a href="#">site 5b</a> (Equilibria)

7 (d)	Deduce expressions for equilibrium constants in terms of concentrations, $K_c$ , and partial pressures, $K_p$	Examples could include esterification, the Haber and Contact processes, and the practical examples given above. Student should be familiar with pressures in Pa or atmospheres. Practical work determining $K_c$ for esterification is possible. [treatment of the relationship between $K_p$ and $K_c$ is not required]	6	<a href="#">site 5b</a> (Equilibria) <a href="#">site 8</a> (Equilibrium) <a href="#">site 9</a> (Chemical equilibrium) <a href="#">site 11</a> (Equilibrium) CIEX 12
7 (c)	Deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction	A distinction should be drawn between the constancy of $K_c$ or $K_p$ during changes in pressure or concentration, and the effect that a change in temperature has on $K_c$ or $K_p$ . Drawing reaction pathway diagrams with and without a catalyst should emphasise that both forward and reverse reactions are speeded up (to the same extent), and hence a catalyst has no effect on the position of equilibrium or the equilibrium constant.	4	
7 (e)	Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data	Practice the calculation of the units of $K_c$ or $K_p$ . Reactions such as the Haber process, or the dimerisation of $\text{NO}_2$ , whose expressions have pressures raised to powers greater than 1, can cause confusion.	3	<a href="#">site 5b</a> (Equilibria) <a href="#">site 9</a> (Equilibrium)
7 (f)	Calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)	The use of the stoichiometric equation is often necessary to solve problems based on the “ $a$ moles of A react with $b$ moles of B giving $c$ moles of C” idea.	4	<a href="#">site 5b</a> (Equilibria)
7 (h)	Show understanding of, and apply the Bronsted-Lowry theory of acids and bases	Acids as proton donors, bases as proton acceptors. The idea of competition between bases for protons. Use of the terminology <i>acid</i> <sub>1</sub> - <i>base</i> <sub>1</sub> and <i>acid</i> <sub>2</sub> - <i>base</i> <sub>2</sub> . Examples such as $\text{HCl} + \text{H}_2\text{O}$ , $\text{NH}_3 + \text{HCl}$ , $\text{NH}_3 + \text{H}_2\text{O}$	4	<a href="#">site 5b</a> (Equilibria) <a href="#">site 6</a> (Acids + bases) <a href="#">site 7</a> (Acids + bases) <a href="#">site 8</a> (Acids + bases) <a href="#">site 9</a> (Acid Base) <a href="#">site 11</a> (Acids + bases)
7 (i)	Explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation	Examples could include $\text{NH}_3(\text{aq})$ , $\text{NaOH}(\text{aq})$ , $\text{CH}_3\text{CO}_2\text{H}(\text{aq})$ , $\text{HCl}(\text{aq})$ . pH and conductivity measurement for equimolar solutions could reinforce the idea of relative extents of dissociation.	4	

7 (g)	Describe and explain the conditions used in the Haber process and Contact process, as examples of the importance of an understanding of chemical equilibrium in the chemical industry	For the Haber process, the idea of the temperature being a <i>compromise</i> between the high rate but low equilibrium yield at high temperatures, and low rate but high yield at low temperatures. Pressure is a compromise between high yield <i>and</i> rate at high pressures, but at high capital and running costs. The importance of recycling $N_2 + H_2$ , so that a high yield is not essential. For the Contact process, the idea that the pressure is not as high as might be expected, because the yield is high enough at low pressures, which are much more economical and safe.	5	<a href="#">site 3</a> (Inorganic/ Industrial Process) <a href="#">site 5b</a> (Equilibria) <a href="#">site 6</a> (Home/AS/ Chemistry/ Industrial Inorganic)
6 (a)	Describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)	OILRIG (oxidation is loss; reduction is gain( of electrons)) is a useful mnemonic. Practice working out oxidation number in molecules, ions and empirical formulae, using the equation $\Sigma(O.N.) = \text{overall charge}$ . Using ionic equations to show the redox reactions occurring in examples such as $Mg + O_2$ ; $Cl_2 + KI$ ; $Cl_2 + FeCl_2$ ; $Zn + CuSO_4$ , all of which could be carried out as practical work.	7	<a href="#">site 1b</a> (Basic Ideas) <a href="#">site 7</a> (Redox reactions) <a href="#">site 8</a> (Reduction and oxidation) <a href="#">site 9</a> (Redox) <a href="#">site 9</a> (Balancing redox)
6 (b)	Explain, including the electrode reactions, the industrial processes of: <i>(i)</i> the electrolysis of brine, using a diaphragm cell <i>(ii)</i> the extraction of aluminium from molten aluminium oxide/cryolite <i>(iii)</i> the electrolytic purification of copper	<i>(i)</i> the overall equation, and also the individual electrode half equations producing $H_2$ and $Cl_2$ . A brief explanation of the production of NaOH through the diffusion of ions through the membrane. <i>(ii)</i> the individual electrode half equations; the use of cryolite to lower the melting point and to increase the conductivity of $Al_2O_3$ ; the need for the continual replacement of the carbon anodes; the environmental aspects of CO and HF emissions. <i>(iii)</i> the individual electrode half equations; how the separation of reactive, easily oxidised, metals (e.g. Zn) and unreactive metals (e.g. Ag) impurities is effected – the former dissolving, but not plating the cathode, and the latter not dissolving at all, but forming anode “sludge”.	8	<a href="#">site 6</a> (Home/AS/ Chemistry/Industrial Inorganic Chem) <a href="#">site 3</a> (Inorganic/ Industrial Processes) <a href="#">site 6</a> (Home/AS/ Chemistry/Extraction of metals) <a href="#">site 11</a> (Electrochemistry)