UNIT 7:   EQUILIBRIA AND KINETICS

Recommended Prior Knowledge: The AS Units 1 and 2 should have been completed before this Unit.

Context: These two Sub-units can be studied on their own, or in conjunction with each other. They can come before or after the other A2 Units.

Outline: Sub-unit 7A covers ionic equilibria involving acids and alkalis, calculation and use of pH, K_a, and K_w, buffers, and solubility products K_{sp}.
Sub-unit 7B builds on the treatment of rates in AS Unit 2. It covers the rate equation, orders of reaction, concentration-time graphs, half-lives of first order reactions and catalysis.

UNIT 7A: EQUILIBRIA

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
7(j)	explain the terms pH; K_a; pK_a; K_w and apply them in calculations	These are best "explained" in terms of the mathematical equations that relate them to concentrations: $pH = -\log_{10}[H^+]$; $K_a = [H^+][A^-]/[HA]$; $pK_a = -\log_{10}K_a$; $K_w = [H^+][OH^-]$. Practice should be given in converting $[H^+]$ into pH (and vice versa), calculating K_a given $[H^+]$ and $[HA]$ (point out that for solutions of weak acids we can always assume $[H^+] = [A^-]$, and $[HA]_{eqm} = [HA]_o$), converting K_a into pK_a (and vice versa), and using K_w to calculate $[H^+]$ in solutions of alkalis.	M 75 C+H 12.5, 12.6 R+N 7.10 P(A2) 7
7(k)	calculate [H+(aq)] and pH values for strong and weak acids and strong bases	Always use the approximation $[H^+] = \sqrt{([HA] \times K_a)}$ for weak acids. Use K_w to convert $[OH^-]$ in a strong alkali into $[H^+]$. Set exemplar and practice problems. Test "predictions" by measuring the pH of various solutions with a pH meter after calculation.	M 75 C+H 12.5 R+N 7.11 P(A2) 5, 6 **site 3** (acids and bases)
7(l)	explain the choice of suitable indicators for acid-base titrations, given appropriate data	Students need to be aware of how the pK_{in} determines the pH range over which the indicator changes colour, and how the pH range for the "end point" of a titration depends on the strengths of the acid and/or alkali. (The two pH ranges must match). No pK_{in} values need to be remembered, but students should know that methyl orange is used for weak alkalis-strong acids, and phenolphthalein for strong alkalis-weak acids. Either can be used for the strong alkali-strong acid case, Get the class to prepare sets of 12 test tubes buffered at pH 1, pH2,... pH12 (one set for each indicator) and mix a few drops of a given indicator in each of the 12 tubes. This gives an instant visual indication of the pH range of the indicator's end point.	M 76 C+H 12.9 R+N 7.12 P(A2) 8

7(m)	describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases	Measuring pH values during titrations and plotting pH-(volume added) curves is an excellent way for students to gain an understanding of end points, and how indicators work. The titration of a weak acid and a weak alkali using bromothymol blue clearly demonstrates the impossibility of using an indicator to determine the exact end point in such a situation. Measuring the pH at regular intervals during the titration of a weak acid with a strong base can be used as a method for calculating the pK_a of the acid, using the equation $pK_a = pH + \log_{10}([HA]/\{A^-\})$.	M 76 C+H 12.9 R+N 7.13 **site 3** (acids and bases) **site 4** (A2: acids and buffers)
7(n)	*(i)* explain how buffer solutions control pH *(ii)* describe and explain their uses, including the role of HCO_3^- in controlling pH in blood	Equations for the reactions between buffer components and added H^+ or OH^- ions should be studied for the systems ($CH_3CO_2H + CH_3CO_2^-$); ($NH_4^+ + NH_3$); and $NH_2CH_2CO_2H$. Remind students that buffers *resist,* rather than totally absorb, changes in pH, and that pH is related to $[H^+]$ or $[OH^-]$. Buffers are only effective when the molar amounts of HA and A^- are significantly greater than the amounts of H^+ or OH^- added. The hydrogen carbonate ion can react with either H^+ or OH^- - the former equilibrium is the one that occurs in blood.	M 75 C+H 12.8 R+N 7.14-7.16 P(A2) 10 **site 8** ionic equilibria)
7(o)	calculate the pH of buffer solutions, given appropriate data	The use of the Henderson-Hasselbach equation, $pH = pK_a + \log_{10}([A^-]/[HA])$, is not essential, but it is an easy one for student to remember and to apply. Its derivation from the expression for the K_a of weak acids (for example) is an easy piece of maths for those familiar with logarithms. One point to emphasise is that although it was assumed that $[H^+] = [A^-]$ in the case of the ionisation of pure weak acids, this is no longer true in buffer solutions, where each can vary independently of the other. If time is available, a useful exercise is for students to be given solutions of a weak acid and its salt (of known concentrations), and be asked to calculate the relative quantities needed to produce a buffer of a target pH. They should then carry out the mixing and compare the pH of the resulting solution with their prediction.	M 75 C+H 12.8 R+N 7.17 **site 4** (A2: acids and buffers)
7(p)	show understanding of, and apply, the concept of solubility product, K_{sp}	The most logical way to extend K_c to solid-solution equilibria is to take the case of $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$, for which $K_c = [M^+(aq)][X^-(aq)]/[MX(s)]$, and point out that since $[MX(s)]$ is a constant, it can be incorporated into K_c (just like $K_w = K_c[H_2O]$). Hence $K_c[MX(s)] = K_{sp} = [M^+(aq)][X^-(aq)]$. The concept should be applied to salts of the form MX_2 and MX_3 as well. Students will need practice in generating K_{sp} expressions, and deriving their units.	M 64 C+H 12.4 R+N 7.18 **site 4** (solubility products) **site 8** (ionic equilibria)
7(q)	calculate K_{sp} from concentrations and *vice versa*	The binary salts are easy! For ternary salts such as MX_2, it has to be remembered that in a saturated solution of MX_2, $[X^-] = \mathbf{2}[M^{2+}]$ at all times. Thus $K_{sp} = [M^{2+}][X^-]^2 = \mathbf{4}[X^-]^3$, and $[X^-] = \sqrt[3]{(K_{sp}/\mathbf{4})}$ The MX_3 case is even more involved. Suitable calculation practice should be given, arriving at solutions to the equation in both directions.	M 64 C+H 12.4 R+N 7.19
7(r)	show understanding of the common ion effect	This is an application of le Chatelier's principle. Nothing quantitative is implied, although a greater understanding can often be achieved if a few simple calculations are done, e.g. calculating the solubility of $AgCl(s)$ in water, and in 0.1 mol dm^{-3} NaCl. For the more able student, practical work with KIO_3 dissolved in KCl solutions of different strengths (titrated with thiosulfate after adding KI(aq) + H^+(aq)) allows the effect to be demonstrated quantitatively.	M 64 C+H 12.4 R+N 7.20 P(A2) 9

UNIT 7B: REACTION KINETICS

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
8(a)	explain and use the terms: *rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step*	Point out that the units of rate are usually concentration/time, although other units, such as pressure/time, can be used. Since the rate equation relates rate, rate constant and concentrations raised to certain powers (orders), the units of the rate constant depend on the overall order of the reaction. Define the half-life as the time taken for the concentration of the (least abundant) reactant to fall to half its initial value, and point out that *all* reactions, not only first order ones, have half lives. But it is only for a first order reaction that successive half-lives are constant. The rate-determining (or rate-limiting) step is the *slowest* in the overall series of elementary reactions leading from reactants to products.	M 77 C+H 11.1, 11.2 R+N 8.9
8(g)	construct and use rate equations of the form rate = $k[A]^m[B]^n$ (limited to simple cases of single step reactions and of multi-step processes with a rate-determining step, for which *m* and *n* are 0, 1 or 2), including: *(i)* deducing the order of a reaction by the initial rates method	Students should practice constructing suitable rate equations that fit in with suggested pathways, including multi-step processes. For each rate equation they should work out the units of *k*. Examples could include general cases (A + 2B $\rightarrow$ C + D etc) and specific ones (e.g. the S_N1 and S_N2 hydrolyses of chloroalkanes; the 2NO + Cl_2 $\rightarrow$ 2NOCl reaction, the iodination of propanone).	M 80 C+H 11.3 R+N 8.14 P(A2) 15, 16 **site 4** (A2: kinetics)
	(v) calculating an initial rate using concentration data [integrated forms of rate equations are not required]	Comparing the initial rates of reaction in two cases where the concentration of just one of the reactants changes allows the order with respect to that reactant to be found. The initial rates will either be given, or the student will be expected to calculate them from concentration-time graphs. Students should be given practice in plotting suitable data, taking tangents at *t* = 0, and using them to calculate the rate of reaction.	R+N 8.13
	(ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs	For a zero order reaction, the concentration-time graph will be a straight line. For a first order reaction it should show a constant half-life (the measurement of the first and second half-lives will suffice)	R+N 8.12
	(iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics *(iv)* predicting the order that would result from a given reaction mechanism (and *vice versa*)	In multi-step reactions, the concentrations of any species involved *after* the rate determining step do *not* appear in the rate equation. Give examples, of both general and specific cases. Students should practice making predictions in both directions: from the mechanism to the orders, and vice versa, using simulated data.	R+N 8.17
8(h)	*(i)* show understanding that the half-life of a first-order reaction is independent of concentration *(ii)* use the half-life of a first-order reaction in calculations	As mentioned above, the first and subsequent half-lives of a first order reaction should be constant. So too should other "half-lives", e.g. the time taken for a reactant concentration to reduce from 80% to 40% of its initial value should be the same as the time from 60% to 30%. Practice with exponential graphs. The main use of half-life in the calculation of rate constants using the relationship $k = 0.693/t_{1/2}$.	M 80 C+H 11.3 R+N 8.11

8(i)	calculate a rate constant using the initial rates method	Once the starting concentrations are known, and the orders have been calculated, the rate constant can be found using the rearranged rate equation $k = $ rate$/[A]^m[B]^n$. Students should be given practice in calculating rate constants in cases where m and n are 0, 1, or 2 (N.B. the sum ($m + n$) will never be greater than 2). In each case, units of k should be calculated.	M 80 C+H 11.3 R+N 8.15
8(j)	devise a suitable experimental technique for studying the rate of a reaction, from given information	The experimental technique will usually involve the measurement of the amount of substance, or a property that is proportional to amount, such as concentration (using a suitable titration), optical density (using a colorimeter), volume of gas (using a gas syringe), total mass (if, for example, a heavy gas such as CO_2 was being evolved), conductivity. Measurement would be taken at known time intervals, and a graph of property/time drawn. Students should be warned that a pH meter should **NOT** be used to measure changes in $[H^+]$: since the relationship is logarithmic, the pH does not change much when $[H^+]$ is at a usefully large concentration.	M 79 C+H 8.2 **site 8** (reaction kinetics)
8(k)	outline the different modes of action of homogeneous and heterogeneous catalysis, including: *(i)* the Haber process *(ii)* the catalytic removal of oxides of nitrogen in the exhaust gases from car engines (see also Section 10.3) *(iii)* the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide *(iv)* the catalytic role of Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction	Short definitions of the words *homogeneous* and *heterogeneous* are useful. Apart from the different states/phases, the major difference between the two is that a homogeneous catalyst always takes part in the reaction ("is used up") in the first step, and is regenerated in a later step. Apart from examples (iii) and (iv) mentioned here, others in the AS/A2 course that could be covered, by way of revision, include: the free radical chlorination of alkanes ($Cl^•$); the addition of HCN to carbonyl compound (CN^-); the halogenation of benzene ($AlCl_3$). Heterogeneous catalysts act by the *adsorption* of reactants onto their surfaces. Other examples include nickel in the catalytic hydrogenation of alkenes, and Al_2O_3 in the dehydration of alcohols. The $I^-/S_2O_8^{2-}$ reaction can be studied in the laboratory, using different transition element ions to see which are effective catalysts, and the results related to $E^ⴱ$ values.	M 78 C+H 8.6 R+N 8.18-8.24 P(A2) 11, 12 **site 8** (reaction kinetics**)**