

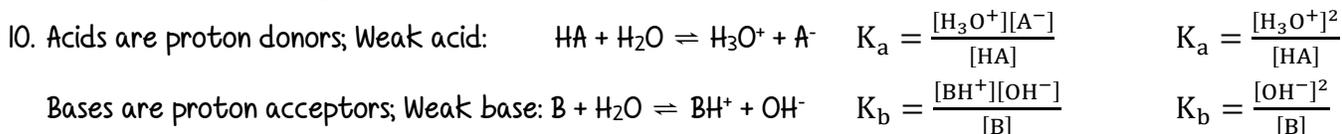
Things to remember in the last hour before the exam: Level 3 EQUILIBRIUM PRINCIPLES IN AQUEOUS SYSTEMS

(This is not a revision sheet – you've done that by now – it's a list of things you might want to remind yourself about...)

- Equation for a sparingly soluble ionic solid AB and AB₂ (or A₂B type). Do NOT write + H₂O in the equation but do use state symbols!
 E.g. AB(s) ⇌ A⁺(aq) + B⁻(aq) OR AB(s) ⇌ A²⁺(aq) + B²⁻(aq); whether ions are 1+ and 1- (e.g. AgCl) or 2+ or 2- (e.g. CuS) requires you to know your ion charges! AB₂(s) ⇌ A²⁺(aq) + 2B⁻(aq). A₂B(s) ⇌ 2A⁺(aq) + B²⁻(aq).
 K_s is the solubility product. Solubility product expressions look like K_s = [A²⁺(aq)][B²⁻(aq)] for AB type OR K_s = [A²⁺(aq)][B⁻(aq)]² for AB₂ type or K_s = [A⁺(aq)]²[B²⁻(aq)] for A₂B type. K_s has no units @ L3.
- Size of K_s. The smaller K_s is, the less soluble the ionic solid is.
- Solubility, s, calculated from K_s is in mol L⁻¹. AB type: $s = \sqrt{K_s}$ and $K_s = s^2$. A₂B / AB₂ type: $s = \sqrt[3]{K_s/4}$ and $K_s = 4s^3$.
- To convert solubility in gL⁻¹ to mol L⁻¹, ÷ M. To turn solubility in mol L⁻¹ to gL⁻¹, x M.
- Solutions already containing one of the ions (a common ion) reduces the solubility of solids e.g. BaSO₄(s) is less soluble in a solution of Na₂SO₄(aq), which contains the common ion, SO₄²⁻. BaSO₄(s) ⇌ Ba²⁺(aq) + SO₄²⁻(aq); presence of SO₄²⁻(aq) from Na₂SO₄(aq) favours back reaction, thereby reducing the solubility of BaSO₄.
- Solubility may be increased due to formation of a complex ion e.g. with ammonia or with NaOH (Question might say at high pH meaning high [OH⁻]). E.g. AgCl(s) ⇌ Ag⁺(aq) + Cl⁻(aq); adding NH₃(aq) which forms complex ion with Ag⁺(aq) reduces the [Ag⁺(aq)], so forward reaction is favoured (to restore equilibrium / minimise the change); more AgCl(s) dissolves / solubility of AgCl(s) increases. Ag⁺(aq) + 2NH₃(aq) → [Ag(NH₃)₂]⁺(aq)
 - Complex ions with excess NH₃ to know (Level 2) are [Ag(NH₃)₂]⁺(aq), [Zn(NH₃)₄]²⁺(aq) & [Cu(NH₃)₄]²⁺(aq)
 - Complex ions with excess NaOH to know (Level 2) are [Zn(OH)₄]²⁻(aq), [Pb(OH)₄]²⁻(aq) & [Al(OH)₄]⁻(aq)
- Solubility may be increased due to reaction of a basic anion with added acid. Question might just say "at low pH" meaning high [H₃O⁺]. E.g. Ca(OH)₂(s) ⇌ Ca²⁺(aq) + 2OH⁻(aq); when H₃O⁺(aq) is added it reacts with OH⁻ to form water, H₃O⁺ + OH⁻ → 2H₂O; reduces OH⁻ concentrations favouring the forward reaction (to restore equilibrium / minimise the change), and Ca(OH)₂ solubility increases.
 CuCO₃(s) + aq ⇌ Cu²⁺(aq) + CO₃²⁻(aq) When H₃O⁺(aq) is added it reacts with CO₃²⁻ to form carbon dioxide and water; reduces CO₃²⁻ concentrations favouring the forward reaction (to restore equilibrium / minimise the change), and CuCO₃ solubility increases. 2H₃O⁺ + CO₃²⁻ → 3H₂O + CO₂
- Predicting precipitation. Calculate Q or IP by substituting actual concentrations once ions are mixed into K_s expression. E.g. for an A₂B substance Q = [A⁺(aq)]²[B²⁻(aq)]. Calculate Q and compare to K_s. If Q > K_s, a ppt forms, if Q = K_s solution will be saturated, if Q < K_s no ppt forms.
 - Mix 10.0 mL 0.300 mol L⁻¹ A with 25.0 mL 0.200 mol L⁻¹ B type calc: conc. of A on mixing is 10/35 x 0.300 mol l⁻¹ and conc. of B on mixing is 25/35 x 0.200 mol L⁻¹. If mixing equal volumes, you can just halve the concentrations.
 - Dissolve 1.00 g of A in 100 mL of 0.400 mol L⁻¹ B type calc.... calculate n(A), calculate C(A) *remember it is dissolving in 100 mL

Acidic and basic solutions - monoprotic acids, bases, salts, and buffers

- From level 2. $\text{pH} = -\log [\text{H}_3\text{O}^+]$ and $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ and $[\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} = K_w$

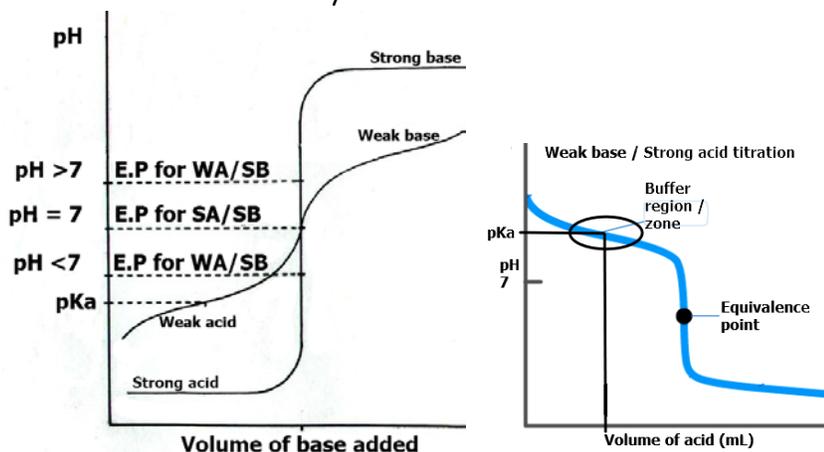


The extent of reaction is small so that the equilibrium concentration of a dissolved weak acid HA or base B can be approximated by the initial concentration of HA or B.

- Acid/base strength. K_a and K_b are dissociation constants and are measures of how completely an acid or base 'dissociates' into ions in water. The smaller the K_a or the larger the pK_a, the weaker the acid. The smaller the K_b or the larger the pK_b, the weaker the base.
- The weaker an acid, the stronger its conjugate base. The stronger an acid (e.g. HCl), the weaker its conjugate base (Cl⁻). Likewise, the weaker the base, the stronger its conjugate acid.

13. $K_a \times K_b = K_w = 1 \times 10^{-14}$. $pK_a + pK_b = pK_w = 14$ $pK_a = -\log K_a$ and $K_a = 10^{-pK_a}$; use the 'same conversion method' for finding pK_b from K_b and vice versa if needed.
14. Acidic salts e.g. ① Dissolve in water $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$ ② An ion reacts with water $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$, so $[H_3O^+] > [OH^-]$. Calculate pH from $[H_3O^+]$ using $K_a = \frac{[H_3O^+]^2}{[\text{acidic salt}]}$
15. Basic salts e.g. ① Dissolve in water $CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$ ② An ion reacts with water $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ so $[OH^-] > [H_3O^+]$. Calculate pH from $[OH^-]$ using $K_b = \frac{[OH^-]^2}{[\text{Basic salt}]}$
16. Buffer solution; Solution which resists change in pH on addition of small amounts of acid or base. The pH of the solution changes very little. Contains weak acid and its conjugate base OR weak base and its conjugate acid
17. Buffer effectiveness: Best when $pH \approx pK_a$ i.e. when $[HA] \approx [A^-]$. When there are significant concentrations of both the weak acid and its conjugate base the solution can resist added acid or base. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other.
- If $pH > pK_a$ (or $[base] > [acid]$) then the buffer will be more efficient at neutralising added strong acid.
 - If $pH < pK_a$ (or $[acid] > [base]$) then the buffer will be more efficient at neutralising added strong base.
 - Diluting a buffer does NOT alter its pH but lowers its effectiveness as the concentrations of both components are now less, and have less capacity to absorb added acid or base.
18. Equations to show how a buffer work to "absorb" addition of small amounts of acid and/or base.
- CH_3COOH/CH_3COO^- buffer. Add H_3O^+ : $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$. Add OH^- : $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$
 - NH_3/NH_4^+ buffer: Add H_3O^+ : $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$. Add OH^- : $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$
19. Buffer calculations. Either use $pH = pK_a + \log \frac{[base]}{[acid]}$. $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ is provided in the Resource sheet BUT here, for acidic buffers, $[A^-]$ is the salt solution and $[HA]$ is the acid. For basic buffers it is necessary to rethink them from the point of $[BH^+]$ (the acidic salt) and $[B]$ (the base), using $K_a(BH^+)$.
20. Species in solution; pH is calculated from $[H_3O^+]$. Electrical conductivity: To conduct a current, a substance requires mobile charged particles / ions. SA, SB and salts completely dissociate to produce high concentrations of ions and are good electrical conductors/electrolytes. In contrast, WA and WB only partially react with water to produce a lower [ions] and are poorer electrical conductors / weaker electrolytes.

21. Titration curves and selection of indicators. You must recognise shape and key features. Note:
WA/WB – NOT assessed.
SA/SB e.g. $HCl + NaOH \rightarrow NaCl + H_2O$ Equivalence point at pH 7.
WA/SB e.g. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$. Equivalence point at $pH > 7$ as CH_3COO^- is a weak base. NOTE; at volume half way to E.P for WA/SB, $pH = pK_a$ of the WA, and around this volume is the 'buffer region/zone'.
SA/WB e.g. $HCl + NH_3 \rightarrow NH_4Cl$ Equivalence point at $pH < 7$ as NH_4^+ is a weak acid.



Calculations of pH at points on the titration curve are beyond the scope of this handout.

22. An indicator is a substance which changes colour according to the pH. Most are weak acids; the acid is one colour and its conjugate base is another colour. The working range (when a colour change is seen) is $pK_a \pm 1$ pH unit e.g. Phenolphthalein has pK_a of 9.3 so changes colour over pH 8.3-10.3. As long as this is in the vertical region of the titration curve it is suitable to indicate equivalence point. pK_a of an indicator is sometimes written as pK_{In} .