

## 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 AB<sub>2</sub> (or A<sub>2</sub>B type). Do NOT write + H<sub>2</sub>O in the equation but do use state symbols!  
 E.g. AB(s) ⇌ A<sup>+</sup>(aq) + B<sup>-</sup>(aq) OR AB(s) ⇌ A<sup>2+</sup>(aq) + B<sup>2-</sup>(aq); whether ions are 1+ and 1- (e.g. AgCl) or 2+ or 2- (e.g. CuS) requires you to know your ion charges! AB<sub>2</sub>(s) ⇌ A<sup>2+</sup>(aq) + 2B<sup>-</sup>(aq). A<sub>2</sub>B(s) ⇌ 2A<sup>+</sup>(aq) + B<sup>2-</sup>(aq).  
 K<sub>s</sub> is the solubility product. Solubility product expressions look like K<sub>s</sub> = [A<sup>2+</sup>(aq)][B<sup>2-</sup>(aq)] for AB type OR K<sub>s</sub> = [A<sup>2+</sup>(aq)][B<sup>-</sup>(aq)]<sup>2</sup> for AB<sub>2</sub> type or K<sub>s</sub> = [A<sup>+</sup>(aq)]<sup>2</sup>[B<sup>2-</sup>(aq)] for A<sub>2</sub>B type. K<sub>s</sub> has no units @ L3.
- Size of K<sub>s</sub>. The smaller K<sub>s</sub> is, the less soluble the ionic solid is.
- Solubility, s, calculated from K<sub>s</sub> is in mol L<sup>-1</sup>. AB type:  $s = \sqrt{K_s}$  and  $K_s = s^2$ . A<sub>2</sub>B / AB<sub>2</sub> type:  $s = \sqrt[3]{K_s/4}$  and  $K_s = 4s^3$ .
- To convert solubility in gL<sup>-1</sup> to mol L<sup>-1</sup>, ÷ M. To turn solubility in mol L<sup>-1</sup> to gL<sup>-1</sup>, x M.
- Solutions already containing one of the ions (a common ion) reduces the solubility of solids e.g. BaSO<sub>4</sub>(s) is less soluble in a solution of Na<sub>2</sub>SO<sub>4</sub>(aq), which contains the common ion, SO<sub>4</sub><sup>2-</sup>. BaSO<sub>4</sub>(s) ⇌ Ba<sup>2+</sup>(aq) + SO<sub>4</sub><sup>2-</sup>(aq); presence of SO<sub>4</sub><sup>2-</sup>(aq) from Na<sub>2</sub>SO<sub>4</sub>(aq) favours back reaction, thereby reducing the solubility of BaSO<sub>4</sub>.
- 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<sup>-</sup>]). E.g. AgCl(s) ⇌ Ag<sup>+</sup>(aq) + Cl<sup>-</sup>(aq); adding NH<sub>3</sub>(aq) which forms complex ion with Ag<sup>+</sup>(aq) reduces the [Ag<sup>+</sup>(aq)], so forward reaction is favoured (to restore equilibrium / minimise the change); more AgCl(s) dissolves / solubility of AgCl(s) increases. Ag<sup>+</sup>(aq) + 2NH<sub>3</sub>(aq) → [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(aq)  
 Knowledge of the following complex ions will be assumed: [Ag(CN)<sub>2</sub>]<sup>-</sup>, [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, [Al(OH)<sub>4</sub>]<sup>-</sup>, [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [Pb(OH)<sub>4</sub>]<sup>2-</sup>, [Zn(OH)<sub>4</sub>]<sup>2-</sup>, [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, and [Ni(CN)<sub>4</sub>]<sup>2-</sup>. This list (formulae only) will be given in the Resource Booklet. Less familiar complex ions may be included in the question resource information.
- Solubility may be increased due to reaction of a basic anion with added acid. Question might just say “at low pH” meaning high [H<sub>3</sub>O<sup>+</sup>]. E.g. Ca(OH)<sub>2</sub>(s) ⇌ Ca<sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq); when H<sub>3</sub>O<sup>+</sup>(aq) is added it reacts with OH<sup>-</sup> to form water, H<sub>3</sub>O<sup>+</sup> + OH<sup>-</sup> → 2H<sub>2</sub>O; reduces OH<sup>-</sup> concentrations favouring the forward reaction (to restore equilibrium / minimise the change), and Ca(OH)<sub>2</sub> solubility increases.  
 CuCO<sub>3</sub>(s) + aq ⇌ Cu<sup>2+</sup>(aq) + CO<sub>3</sub><sup>2-</sup>(aq) When H<sub>3</sub>O<sup>+</sup>(aq) is added it reacts with CO<sub>3</sub><sup>2-</sup> to form carbon dioxide and water; reduces CO<sub>3</sub><sup>2-</sup> concentrations favouring the forward reaction (to restore equilibrium / minimise the change), and CuCO<sub>3</sub> solubility increases. 2H<sub>3</sub>O<sup>+</sup> + CO<sub>3</sub><sup>2-</sup> → 3H<sub>2</sub>O + CO<sub>2</sub>
- Predicting precipitation. Calculate Q or IP by substituting actual concentrations once ions are mixed into K<sub>s</sub> expression. E.g. for an A<sub>2</sub>B substance Q = [A<sup>+</sup>(aq)]<sup>2</sup>[B<sup>2-</sup>(aq)]. Calculate Q and compare to K<sub>s</sub>. If Q > K<sub>s</sub> a ppt forms, if Q = K<sub>s</sub> solution will be saturated, if Q < K<sub>s</sub> no ppt forms.
  - Mix 10.0 mL 0.300 mol L<sup>-1</sup> A with 25.0 mL 0.200 mol L<sup>-1</sup> B type calc: conc. of A on mixing is 10/35 x 0.300 mol l<sup>-1</sup> and conc. of B on mixing is 25/35 x 0.200 mol L<sup>-1</sup>. If mixing equal volumes, you can just halve the concentrations.
  - Dissolve 1.00 g of A in 100 mL of 0.400 mol L<sup>-1</sup> 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

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

10. Acids are proton donors; Weak acid:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$   $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$   $K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]}$   
 Bases are proton acceptors; Weak base:  $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$   $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$   $K_b = \frac{[\text{OH}^-]^2}{[\text{B}]}$

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<sub>a</sub> and K<sub>b</sub> are dissociation constants and are measures of how completely an acid or base ‘dissociates’ into ions in water. The smaller the K<sub>a</sub> or the larger the pK<sub>a</sub>, the weaker the acid. The smaller the K<sub>b</sub> or the larger the pK<sub>b</sub>, the weaker the base.

12. The weaker an acid, the stronger its conjugate base. The stronger an acid (e.g. HCl), the weaker its conjugate base (Cl<sup>-</sup>). 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  $pK_{In}$ .

