ChemFactsheet

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Solubility and Solubility Product

Describing ionic substances as "*soluble in water*" or "*insoluble in water*" is a common occurrence in chemistry. **Fig. 1**

An ionic substance (the *solute*) is usually described as soluble in water (e.g. sodium chloride) if it mixes homogeneously with water (the *solvent*) at a molecular-ionic level to form a transparent mixture, usually referred to as a *solution*. This is often represented by

$$
NaCl(s) + aq \rightarrow Na^{+}(aq) + Cl^{-}(aq)
$$

This implies that the ions from the solid become individual, separate ions in solution with water molecules actually bonded to each ion. The ions are said to be *hydrated* with the water molecules bonded by ion-dipole attractions or coordinate (dative) bonds as seen in fig. 1.

Na⁺ δ - \acute{O} δ + H H H H Cl δ + \bigcirc δ - \bigcirc \bigcirc u $OH₂$ $OH₂$ $OH₂$ $H₂$ $\overline{\text{OH}}_2$ OH₂ $H₂$ O 2+ Ion-dipole attractions Coordinate bonds

Number 233

In contrast, an ionic substance is usually described as *insoluble* if it forms a heterogeneous mixture when added to water. This **appears** to consist of the solid ionic substance and colourless water. However, the liquid phase is in fact a **very dilute solution** of the substance containing separate hydrated ions as before.

This is best represented as an equilibrium process because eventually the rate at which ions leave the surface of the solid to enter the solution equals the rate at which ions are deposited from the solution on to the surface of the solid.

e.g.
$$
BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)
$$

This implies that the very dilute solution is in fact also *saturated* - no more can dissolve at the operating temperature.

It is useful to know which ionic substances are soluble or insoluble. There are a few general rules but, in most cases, it is a matter of learning particular cases. The following summary should help for common ionic compounds.

Q1 Use these rules to complete the following table by deciding whether a precipitate should form, or not, when the indicated compounds are mixed in solution. Answer YES or NO.

Q2 The nitrate of metal M (M^{p+}) is mixed with the sodium salt of anion A (A^{q+}) in aqueous solution. What can be concluded if (a) a precipitate is formed (b) a precipitate is not formed? Explain.

Solubility

The mixing process (*dissolving*) of a "soluble" substance does not carry on indefinitely. All "soluble" ionic substances eventually reach a limit of solubility when the solution is described as *saturated*.

At this point, the process can also be represented as an equilibrium process (as for the $BaSO₄$ example above) because the solid will be in equilibrium with its saturated solution.

$NaCl(s) + aq \rightleftharpoons Na^+(aq,sat) + Cl^-(aq,sat)$

The only difference between water *soluble* and *insoluble* substances is therefore the amount that must dissolve to form a saturated solution. The amount will be relatively high for a soluble substance but relatively low for an insoluble substance. Hence, the use of other phrases such as *sparingly soluble* to describe those substances that are usually considered to be insoluble.

The amount of substance dissolved in a saturated solution (its *solubility*) depends on the actual substance, the pressure and the temperature. In general, solubilities of ionic substances increase with increasing temperature but are usually quoted at 25°C (298K). Pressures have negligible effects but are still quoted at 100kPa.

- Definition : The solubility of a substance is the *maximum* amount (i.e. saturated) (usually measured in g or moles) of that substance that may be dissolved in a specified amount of water (usually 100 or 1000 cm³) at 100kPa and a specified temperature (usually 298K).
	- e.g. (a) Solubility of NaCl = 359 g per 1000cm³ at 298K
	- (b) Solubility of $BaSO_4 = 0.0002448$ g per 100cm³ at 298K
- Q3 Convert each of these solubilities to mol dm-3.

Solubility Products

These are K_{c} type equilibrium constants applied to the equilibrium described earlier for a sparingly soluble solid in equilibrium with its component aqueous ions at constant temperature.

Note: The following ideas **do not** apply to "soluble" substances (e.g. NaCl) because the ion density in such solutions is so high that interactions between ions make the equilibrium law unreliable.

For a general sparingly soluble ionic substance, $M_p A_q$, the equilibrium at constant temperature is: $M_p A_q(s) \Rightarrow pM^{q+}(aq) + qA^p(aq)$

Applying the equilibrium law gives: $Kc = \frac{[M^{q+}(aq)]^p \times [A^p(aq)]^q}{[M!A^p(aq)]^q}$ [$M_p A_q(s)$]

where $[X]$ represents the concentration of substance X measured in mol dm⁻³.

However, the concentration of the solid phase is constant (C). The K_c expression can therefore be rewritten as: K_c × C = [M^{q+}(aq)]^p × [A^{p-}(aq)]^q. $Kc \times C$ is the product of 2 constants which is therefore another constant. This combined constant is labelled K_{sn} and called the **solubility product** of M_pA_q .

Hence,
$$
K_{sp} = [M^{q+}(aq)]^p \times [A^p(aq)]^q
$$

Note: Like ionic product of water (K_{w}) , the word "product" in solubility product refers to the mathematical term, not the chemical term. Mathematically, product means the result of multiplication. Hence, the multiplication of the ion concentrations in the K_{∞} expression.

<u>Note</u>: The **units** of K_{sp} are given by (mol dm⁻³)^{p+q}

Q4 For each of the following sparingly soluble substances

- 1. AgBr 2. PbCl₂ 3. Fe(OH)₃ 4. Ca₃(PO₄)₂
	- (a) write the equation for the equilibrium present in a saturated solution
	- (b) write the expression for K_{sn}
	- (c) deduce the units of K_m

By their very nature, sparingly soluble substances produce saturated solutions with low to extremely low ion concentrations. Hence, when these are substituted into a K_{sp} expression, the values of K_{sp} are generally very low. This and variations can be seen in the data shown in table 1. **Table 1**

- Q5 Use the data in table 1 to complete each of the following statements about solubility trends
	- (a) Down group 2, sulphate solubilities DECREASE / INCREASE
	- (b) Down group 2, hydroxide solubilities DECREASE / INCREASE
	- (c) Down group 2, fluoride solubilities DECREASE / INCREASE
	- (d) Down group 2, carbonate solubilities DECREASE / INCREASE
	- (e) Down group 7, halide solubilities DECREASE / INCREASE

The significance of Ksp values

The values of K_{α} define the conditions necessary for a precipitate of a sparingly soluble substance to form when solutions containing the metal ion and the anion are mixed.

If $[M^{q+}(aq)$ and $[A^p(aq)]$ in **any** solution are substituted into the K_{sp} expression ($[M^{q+}(aq)]^p$ x $[A^p(aq)]^q$) and the value derived is:

- 1. Greater than $K_{\rm sp}$, a precipitate will form
- 2. Less than or equal to $K_{\rm so}$, a precipitate will not form.
- Q6 Using the K_{en} data table, will a precipitate of lead chloride form when 10.0 cm^3 of 0.05 mol dm^3 lead nitrate is mixed with 10.0 m^3 cm3 0.02 mol dm-3 sodium chloride at 298K?
- Q7 Using the $K_{\rm sn}$ data table, will a precipitate of silver chloride form when one drop (assume this is 0.05 cm^3) of 0.10 mol dm^3 silver nitrate is mixed with 10.0 cm^3 0.10 mol dm⁻³ sodium chloride at 298K?

Measuring solubility products

This involves measuring the concentration of one of the component ions in a saturated solution of the salt at constant temperature. The concentration of the other ion can then be deduced from the formula of the salt.

- e.g.1 For PbCl₂, if $[Pb^{2+}]$ is measured at "x" mol dm⁻³, then $[Cl^-] = 2x$
- e.g.2 For Ag_2CrO_4 , if $[\text{Ag}^+]$ is measured at "x" mol dm⁻³, then $[\text{CrO}_4^2]$ $= x/2.$
- Q8 (a) For Fe(OH)₃, if $[Fe^{3+}]$ is measured at "x" mol dm⁻³, what is [OH-]?
	- (b) For Al(OH)₃, if [OH⁻] is measured at "x" mol dm⁻³, what is $[A1^{3+}]$?

The problem with making such measurements is that the concentration to be measured is very low. Hence, very sensitive techniques need to be employed.

Two common methods are colorimetry and electrode potential measurements.

If one of the ions is coloured (e.g. Cu^{2+} or CrO_4^2), comparison of the absorbance by the saturated solution with those of an appropriate range of standard solutions can give the concentration of the coloured ion.

Note: See FactSheet 329 for further details.

Alternatively, electrode potential measurements make use of the Nernst equation to measure the concentration of the metal ion (M^{q+}) in the saturated solution. The general equation is:

$$
E_{M} = E_{M}^{\bullet} + \frac{0.059}{q} \log_{10}[M^{q+}(aq)]
$$

For example if the potential of a silver electrode dipping into a saturated solution of silver chloride relative to a standard hydrogen electrode at 298K is measured (i.e $E_{Ag} = +0.512V$) then using $E_{Ag}^{\circ} = 0.799V$ and $q = 1$ for the Ag⁺ ion, gives $[Ag^+(aq)] = 1.37 \times 10^{-5}$ mol dm⁻³.

Note: See FactSheet 199 for full practical details.

Since Ag⁺ : Cl⁻ = 1 : 1, [Cl⁻(aq)] is also 1.37×10^{-5} mol dm⁻³. \rightarrow K_{sp} [AgCl] = 1.37 × 10⁻⁵ × 1.37 × 10⁻⁵ = 1.88 × 10⁻¹⁰ mol² dm⁻⁶.

Q9 The potential of a copper electrode dipping into a saturated solution of copper hydroxide relative to a standard hydrogen electrode at 298K is +0.149V. Using E_{Cu}° = +0.340V calculate the solubility product of copper(II) hydroxide at 298K.

Converting solubility to solubility product

e.g.1 The solubility of magnesium hydroxide is 0.0065 g dm⁻³ at 298K. Calculate K_{sn} of magnesium hydroxide at 298K. $[Mg(OH)_{2}(aq)] = 0.0065 g dm⁻³$ $= 0.0065 / (24.1 + 2(16+1))$ mol dm⁻³ $= 1.119 \times 10^{-4}$ mol dm⁻³ $Mg(OH)_{2}(s) + aq \rightarrow Mg(OH)_{2}(aq) \rightarrow Mg^{2+}(aq) + 2OH(aq)$ \rightarrow [Mg²⁺(aq)] = 1.119 × 10⁻⁴ mol dm⁻³ and $[OH(aq)] = 2 \times 1.119 \times 10^{-4} = 2.238 \times 10^{-4}$ mol dm⁻³ $\rightarrow K_{sp} = [Mg^{2+}(aq)] [OH^{-}(aq)]^{2}$ $= 1.119 \times 10^{-4} \times (2.238 \times 10^{-4})^2$ $= 5.57 \times 10^{-12}$ mol³ dm⁻⁹ e.g.2 The solubility of calcium phosphate is 7.14×10^{-7} mol dm⁻³ at

- 298K. Calculate K_{sn} of calcium phosphate at 298K. $Ca_3(PO_4)_2(s) + aq \rightarrow Ca_3(PO_4)_2(aq) \rightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ $[Ca₃(PO₄)₂(aq)] = 7.14 \times 10^{-7}$ \rightarrow [Ca²⁺(aq)] = **3** × 7.14 x 10⁻⁷ = 2.142 × 10⁻⁶ mol dm⁻³ and $[PO_4^{3}(aq)] = 2 \times 7.14 \times 10^{-7} = 1.428 \times 10^{-6}$ mol dm⁻³ \rightarrow K_{sp} = [Ca²⁺(aq)]³ [PO₄³⁻(aq)]² $= (2.142 \times 10^{-6})^3 \times (1.428 \times 10^{-6})^2$ $= 2.00 \times 10^{-29}$ mol⁵ dm⁻¹⁵
- Q10 The solubility of chromium hydroxide is 1.293×10^{-6} g dm⁻³ at 298K. Calculate K_{sp} of chromium hydroxide at 298K.

Converting solubility product to solubility

- e.g.1 Calculate the solubility of silver bromide at 298K given its K_{sn} is 5.40×10^{-13} mol² dm⁻⁶ at 298K. Let solubility $AgBr = S$ mol dm⁻³ $AgBr(s) + aq \rightarrow AgBr(aq) \rightarrow Ag^{+}(aq) + Br(aq)$ \rightarrow [Ag⁺(aq)] = S and [Br(aq)] = S \rightarrow K_{sp} = [Ag⁺(aq)] × [Br(aq)] = S × S = 5.40 × 10⁻¹³ \rightarrow S $\stackrel{\text{sp}}{=}$ $\sqrt{(5.4 \times 10^{13})}$ = 7.35 \times 10⁻⁷ mol dm⁻³ $= 7.35 \times 10^{-7} \times (107.9 + 79.9) = 1.38 \times 10^{-4}$ g dm⁻³
- e.g.2 Calculate the solubility of lead iodide at 298K given its K_{m} is 8.50×10^{-9} mol³ dm⁻⁹ at 298K. Let solubility $PbI_2 = S$ mol dm⁻³ $PbI_2(s) + aq \rightarrow PbI_2(aq) \rightarrow Pb^{2+}(aq) + 2I(aq)$ \rightarrow [Pb²⁺(aq)] = S and [I(aq)] = 2S \rightarrow K_{sp} = [Pb²⁺(aq)] × [I⁻(aq)]² = S × (2S)² = 4S³ = 8.50 × 10⁻⁹ \rightarrow S ^{\pm 3} √(8.50 × 10⁻⁹/4) = **1.29** × **10⁻³ mol dm⁻³** $= 1.29 \times 10^{-3} \times (207.2 + 126.9) = 0.431$ g dm⁻³
- Q11 Calculate the solubility of aluminium hydroxide at 298K given its K_{sp} is 3.12×10^{-34} mol³ dm⁻⁹ at 298K.

The common ion effect

This refers to the reduction in the solubility of an ionic precipitate when a soluble compound containing one of the ions of the precipitate is added to the solution in equilibrium with the precipitate.

For example, silver chloride is less soluble in sodium chloride solution than in water because of the presence of the common chloride ion.

It can be applied quantitatively for sparingly soluble substances where K_m is applicable or qualitatively to these and more soluble substances.

e.g. In a previous example, the solubility of silver bromide at 298K was calculated to be 7.35 x 10^{-7} mol dm⁻³ using its K_g as 5.40 x 10-13 mol2 dm-6 at 298K. Calculate the solubility of silver bromide in 0.100 mol dm-3 sodium chloride solution.

Let the new solubility $AgBr = S$ mol dm⁻³ $AgBr(s) + aq \rightarrow AgBr(aq) \rightarrow Ag^{+}(aq) + Br(aq)$ Dissolution of the AgBr produces equal concentrations (S) of Ag⁺ and Br ions but the sodium bromide adds 0.100 mol dm⁻³ of Br. \rightarrow [Ag⁺(aq)] = S and [Br(aq)] = S + 0.100 \rightarrow K_{sp} = [Ag⁺(aq)] × [Br(aq)] = S × (S + 0.100) = 5.40 × 10⁻¹³ But $S \ll 0.100$ \rightarrow S \times 0.100 \approx 5.40 \times 10⁻¹³ $S = 5.40 \times 10^{-12}$ mol dm⁻³

This shows that the solubility of AgBr has been reduced to almost one millionth by the presence of the common Br ion at a relatively low concentration.

Qualitatively this can be predicted using Le Chatelier's principle.

$$
AgBr(s) \Rightarrow Ag^+(aq) + Br(aq)
$$

Addition of bromide ions from the sodium bromide causes the equilibrium to shift to the left in order to reduce the effect of the addition. Hence, silver ions are removed by precipitation of more silver bromide which amounts to the reduction in solubility of the silver bromide.

There are many practical applications of this effect. For example used in areas where drinking water is derived from chalk or limestone rocks. Soluble sodium carbonate is added to the water to reduce the calcium carbonate content and hence, the hardness of the water.

$$
\text{CaCO}_3(\text{s}) \ \Leftrightarrow \ \text{Ca}^{2+}(\text{aq}) \ + \ \text{CO}_3^{2-}(\text{aq})
$$

The common carbonate ion pushes the equilibrium to the left reducing the amount of dissolved calcium ions which is responsible for the hardness. The calcium ions are said to be "salted out".

Q12 The salting out process is also used in the manufacture of soaps which are sodium salts of fatty acids (e.g. $CH_3(CH_2)_{16}COO(Na^+)$ produced by the alkaline hydrolysis of a fat or oil. Using the common ion effect, explain why sodium chloride solution is added to the reaction mixture after hydrolysis.

Answers to Questions

- Q1 $A \rightarrow$ CaCl₂ and NaNO₃ possible both soluble NO $B \rightarrow CaCO₃$ and NaNO₃ possible – CaCO₃ insoluble YES $C \rightarrow BaSO_4$ and NaNO₃ possible – BaSO₄ insoluble YES
	- $D \rightarrow Ba(OH)$ ₂ and NaNO₃ possible both soluble NO
- Q2 (a) The compound of M^{p+} with A^{q-} (i.e. M_qA_p) is insoluble
	- (b) The compound of M^{p+} with A^{q-} (i.e. M_q^T) is soluble. Each mixture will contain Na^+ , NO_3^- , M^{n+} and A^{m-} ions. Possible compounds from this mixture must involve a positive ion combining with a negative ion. According to rule 1, NaNO₃ is always soluble. Hence the experiment tests the solubility of the compound formed from M^{n+} and A^{m} . A precipitate will not form if this compound is soluble but a precipitate will form if this compound is insoluble.
- Q3 (a) Solubility of NaCl = 359 g per 1000cm³ $= 359 / (23.0 + 35.5) = 6.14$ mol dm⁻³
	- (b) Solubility of BaSO₄ = 0.0002448 g per 100cm³ $= 0.0002448 / 233.4$ moles per 100cm³ $= (0.0002448 / 233.4) \times 1000/100$ moles per 1000cm³ $= 1.05 \times 10^{-5}$ mol dm⁻³
- $Q4$ 1. (a) AgBr(s) \Rightarrow Ag⁺(aq) + Br(aq) (b) $K_{sp} = [Ag^+(aq)] [Br(aq)]$ (c) Units of $K_{sp} = (mol \, dm^{-3})^{1+1} = mol^2 \, dm^{-6}$
- 2. (a) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ (b) $K_{sp} = [Pb^{2+}(aq)] [Cl^{-}(aq)]^{2}$ (c) Units of $K_{sp} = (mol \ dm^{-3})^{1+2} = mol^3 \ dm^{-9}$
- 3. (a) $\text{Fe(OH)}_3(s) \Rightarrow \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq)$ (b) $K_{sp} = [Fe^{3+}(aq)] [OH (aq)]^{3}$ (c) Units of $K_{sp} = (mol \text{ dm}^{-3})^{1+3} = mol^4 \text{ dm}^{-12}$
- 4. (a) $Ca_3(PO_4)_2(s) \Rightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ (b) $K_{sp} = [Ca^{2+}(aq)]^3 [PO_4^{3-}(aq)]^2$ (c) Units of $K_{sp} = (mol \text{ dm}^{-3})^{3+2} = mol^5 \text{ dm}^{-15}$
- Q5 (a) -- DECREASE (b) -- INCREASE (c) -- INCREASE (d) -- DECREASE (e) DECREASE
- $Q6$ As a result of dilution during mixing, $[Pb^{2+}]$ after mixing $= 0.05 \times 10/20 = 0.025$ mol dm⁻³ As a result of dilution during mixing, [Cl-] after mixing $= 0.02 \times 10/20 = 0.01$ mol dm⁻³ $K_{sp} = [Pb^{2+}(aq)][Cl^{2}(aq)]^{2} = 1.2 \times 10^{-5}$ mol³ dm⁻⁹ In the mixture, $[Pb^{2+}][C1]$ ² = 0.025 × (0.01)² = 2.5 × 10⁻⁶ This is less than K_{∞} which means a precipitate will not form.
- $Q7$ As a result of dilution during mixing, $[Ag^+]$ after mixing $= 0.10 \times 0.05/10.05 = 4.98 \times 10^{-4}$ mol dm⁻³ As a result of dilution during mixing, [Cl-] after mixing $= 0.10 \times 10/10.05 = 9.95 \times 10^{-2}$ mol dm⁻³ $K_{sp} = [Ag^+(aq)][Cl^-(aq)] = 1.9 \times 10^{-10} \text{ mol}^3 \text{ dm}^3$ In the mixture, $[Ag^*][Cl] = 4.98 \times 10^{-4} \times 9.95 \times 10^{-2} = 4.95 \times 10^{-5}$ This is greater than K_{∞} which means a precipitate will form. Precipitation of AgCl will occur until the remaining [Ag⁺] and [Cl⁻] values satisfy the K_{sp} value.
- Q8 (a) $[OH] = 3x$ (b) $[A]^{3+} = x/3$
- Q9 Substituting into Nernst equation gives $0.149 = 0.340 + (0.059/2) \log_{10}[Cu^{2+}]$ \rightarrow [Cu²⁺] = 3.353 × 10⁻⁷ mol dm⁻³ Also $[OH^-] = 2 \times [Cu^{2+}] = 2 \times 3.353 \times 10^{-7}$ $= 6.706 \times 10^{-7}$ mol dm⁻³ \rightarrow K_{sp} = [Cu²⁺][OH⁻]² = 3.353 x 10⁻⁷ × (6.706 × 10⁻⁷)² $= 1.51 \times 10^{-19}$ mol³ dm⁻⁹
- Q10 [Cr(OH)₃] = [Cr³⁺] = 1.293 × 10⁻⁶ / (52 +3(16+1)) = 1.255 × 10⁻⁸ mol dm⁻³ $Cr(OH)_3 \rightarrow Cr^{3+} + 3OH^{-}$ \rightarrow [OH·] = 3[Cr³⁺] = 3 × 1.255 × 10⁻⁸ = 3.765 × 10⁻⁸ \rightarrow K_{sp} = [Cr³⁺] × [OH⁻]³ = 1.255 x 10⁻⁸ × (3.765 x 10⁻⁸)³ $= 6.698 \times 10^{-31}$ mol⁴ dm⁻¹²
- Q11 Let solubility $Al(OH)_{3} = S \text{ mol dm}^{3}$ $\text{Al(OH)}_{3}(s) + aq \rightarrow \text{Al(OH)}_{3}(aq) \rightarrow \text{Al}^{3+}(aq) + 3\text{OH}^{-}(aq)$ \rightarrow [Al³⁺(aq)] = S and [OH·(aq)] = 3S $\rightarrow K_{\text{sp}} = [\text{Al}^{3+}(\text{aq})] \times [\text{OH}^{\cdot}(\text{aq})]^{3} = S \times (3S)^{3} = 27S^{4} = 3.12 \times 10^{-34}$ \rightarrow S = ⁴ $\sqrt{(3.12 \times 10^{-34}/27)} = 1.84 \times 10^{-9}$ mol dm⁻³ $= 1.84 \times 10^{-9} \times (27.0 + 3(16+1)) = 1.44 \times 10^{-7}$ g dm⁻³
- Q12 Addition of sodium chloride reduces the solubility of the soaps and allows them to be separated more easily. The soaps precipitate due to the presence of the common Na⁺ ion.

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