

CHEM1902/4 Worksheet 11 – Answers to Critical Thinking Questions

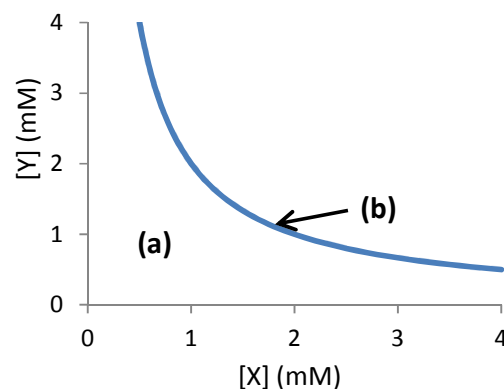
The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

Model 1: The Unit Cell

- Number of Cl atoms = $8 \times \frac{1}{8}$ (atoms on corners) + $6 \times \frac{1}{2}$ (atoms on faces) = 4.
 - Number of Na atoms = $12 \times \frac{1}{4}$ (atoms on edges) + 1 (atom at centre) = 4.
 - Cation : anion = 4 : 4 or 1 : 1. This is consistent with the formula NaCl.
- Number of Ti atoms = 1 (atom at centre).
 - Number of Ca atoms = $8 \times \frac{1}{8}$ (atoms on corners) = 1
 - Number of O atoms = $6 \times \frac{1}{2}$ (atoms on edges) = 3.
 - The formula is $\text{Ca}_1\text{Ti}_1\text{O}_3$ or CaTiO_3 .
 - Calcium always form Ca^{2+} ions. Oxygen always forms O^{2-} ions. To make the charges balance, titanium must be present as Ti^{4+} : $(\text{Ca}^{2+})(\text{Ti}^{4+})(\text{O}^{2-})_3$.

Model 2: The solubility product

- See opposite. The system is only at equilibrium at the concentrations on the line.
 - $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$
 $K_{sp} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)]$
 - $\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)$
 $K_{sp} = [\text{Ag}^+(aq)]^2[\text{SO}_4^{2-}(aq)]$
 - $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$
 $K_{sp} = [\text{Pb}^{2+}(aq)][\text{Cl}^-(aq)]^2$
 - $[\text{Pb}^{2+}(aq)] = x$ and $[\text{Cl}^-(aq)] = 2x$.
 - $K_{sp} = [\text{Pb}^{2+}(aq)][\text{Cl}^-(aq)]^2 = (x)(2x)^2 = 4x^3$
If $4x^3 = 1.6 \times 10^{-5}$, then $x = 1.59 \times 10^{-2}$.
 $[\text{Pb}^{2+}(aq)] = x = 1.59 \times 10^{-2} \text{ M}$ and $[\text{Cl}^-(aq)] = 2x = 3.17 \times 10^{-2} \text{ M}$
 - Molar solubility = $(K_{sp} / 27)^{1/4}$
 - and (d) are salts with 1:1 stoichiometry so molar solubility = $(K_{sp})^{1/2}$
 - and (c) are salts with 1:2 stoichiometry so molar solubility = $(K_{sp} / 4)^{1/3}$
- Hence:
- molar solubility = $(2.8 \times 10^{-7})^{1/2} = 5.3 \times 10^{-4} \text{ M}$
 - molar solubility = $(4.5 \times 10^{-17} / 4)^{1/3} = 2.2 \times 10^{-6} \text{ M}$
 - molar solubility = $(8.7 \times 10^{-9} / 4)^{1/3} = 1.3 \times 10^{-3} \text{ M}$



$$(d) \text{ molar solubility} = (5 \times 10^{-15})^{1/2} = 7 \times 10^{-8} \text{ M}$$

The solubility increases in the order (d) < (b) < (a) < (c).

6. (a) (ii) X_2Y
 (b) (iii) 2×10^{-9}

Model 3: To dissolve or not to dissolve?

1. (a) $[Mg^{2+}(aq)] = 0.050 \text{ M}$ and $[OH^-(aq)] = 0.060 \text{ M}$
 (b) $Q_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2 = (0.050)(0.060)^2 = 1.8 \times 10^{-4}$
 (c) $Q_{sp} > K_{sp}$ so $Mg(OH)_2$ (s) precipitate forms.
2. (a) After mixing, $[Mg^{2+}(aq)] = 0.025 \text{ M}$ and $[F^-(aq)] = 0.0050 \text{ M}$.
 $Q_{sp} = [Mg^{2+}(aq)][F^-(aq)]^2 = (0.025)(0.0050)^2 = 6.3 \times 10^{-7}$
 $Q_{sp} > K_{sp}$ so precipitation will occur.
- (b) After mixing, $[Mg^{2+}(aq)] = 0.025 \text{ M}$ and $[F^-(aq)] = 0.00050 \text{ M}$.
 $Q_{sp} = [Mg^{2+}(aq)][F^-(aq)]^2 = (0.025)(0.00050)^2 = 6.3 \times 10^{-9}$
 $Q_{sp} < K_{sp}$ so no precipitation will occur.

Model 4: Le Châtelier's Principle and Solubility

1. $K_{sp} = [Pb^{2+}(aq)][Cl^-(aq)]^2$
2. Adding Cl^- ions would push the equilibrium in the direction of reactants: the solubility would decrease.
3. With $[Cl^-(aq)] = 0.5 \text{ M}$,
 $[Pb^{2+}(aq)] = K_{sp} / [Cl^-(aq)]^2 = K_{sp} / (0.5)^2 = K_{sp} / 0.25 = 4K_{sp}$
4. Adding extra $PbCl_2(s)$ has *no effect*. As the $[Pb^{2+}(aq)]$ and $[Cl^-(aq)]$ are already such that $[Pb^{2+}(aq)][Cl^-(aq)]^2 = K_{sp}$, the solution is saturated and it is not possible to dissolve more solid.

Model 5: Solubility and pH

1. $K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3$
2. $pOH = 14.000 - 8.179 = 5.821$. As $pOH = -\log[OH^-(aq)]$, $[OH^-(aq)] = 10^{-5.821} \text{ M}$.
3. From Q5, $[Fe^{3+}(aq)] = K_{sp} / [OH^-(aq)]^3 = (1 \times 10^{-39}) / (10^{-5.821})^3 = 2.9 \times 10^{-22}$.
4. If the pH decreases, $[OH^-(aq)]$ will also decrease. It is predicted that the pH of the ocean will fall by about 0.3 pH units over this century. pOH will thus increase by about 0.3 units.

As $[Fe^{3+}(aq)] = K_{sp} / [OH^-(aq)]^3$, this will lead to an increase in $[Fe^{3+}(aq)]$. It is uncertain what the effect of this will be for marine life - see, for example:

<http://www.sciencemag.org/cgi/content/full/327/5966/676>

5. $[Fe^{3+}(free)] \approx 10^{-19} \text{ M}$. Most of the Fe^{3+} is complexed in proteins such as transferrin and ferritin.