7.6 The Solubility Product Constant

- Most salt solutions are very soluble in water.
- Some are weak electrolytes and are only slightly soluble in water.

$\rightarrow$ (aq) $\rightarrow$ 100% dissociates

$\hookrightarrow$ (s) $\rightarrow$ equilib

Biological Application of Solubility

- Proteins and nucleic acids produce toxic nitrogenous wastes when metabolized and different organisms have adapted different methods of dealing with them.
- Aquatic animals eliminate nitrogenous wastes as ammonia since it is highly soluble and can be eliminated via the gills. But ammonia is very toxic to living things and it has to be eliminated immediately.
- Mammals and amphibians convert nitrogenous wastes into urea, which is much less toxic and very soluble. It can be stored in the body until excreted.
- Birds and reptiles convert it to uric acid that is almost non-soluble and less toxic than ammonia.
- Why the difference? Fish have gills and can get rid of ammonia immediately; mammals have bladders and can get rid of the urea when it is convenient; birds lay eggs and they don't want waste products to build up in the egg so uric acid is insoluble and will not poison the chick.

Solubility Product

- Solubility: the concentration of a saturated solution of a solute in a particular solvent at a particular temperature; solubility is a specific maximum concentration.
- Solubility Product Constant (K_{sp}): the value obtained from the equilibrium law applied to a saturated solution. (Ignore units.)

(Undissolved solid) $\quad C_cD_{d(s)} \leftrightarrow cC^+_{(aq)} + dD^-_{(aq)}$ *(ions in solution)*
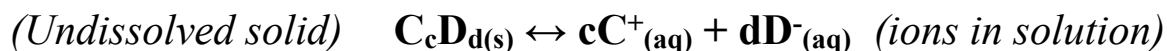
$$K_{sp} = [C]^c[D]^d \quad \textit{(at saturation)}$$

Calculating Solubility Using K_{sp} Values

- E.g. Calculate K_{sp} for magnesium fluoride at 25°C, given a solubility of 0.00172 g/100 mL.

$$\text{mol}/\text{L}$$
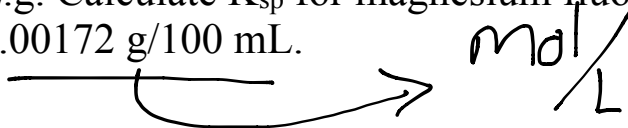
$K_{sp} = [Mg^{2+}_{(aq)}] [F^-_{(aq)}]^2 \qquad$ (remember MgF_2 is a solid)

	$MgF_{2(s)}$	$\leftrightarrow$	$Mg^{2+}_{(aq)}$	+	$2F^-_{(aq)}$
Initial	*		0		0
Change	*		+x		+2x
Equilibrium	*		x		2x

$[Mg^{2+}_{(aq)}] = [MgF_{2(s)}] = 0.00172g/100ml \times 1\ mol/62.31g \times 1000mL/1L$
$\qquad\qquad = 2.8 \times 10^{-4}\ mol/L$

$x = 2.8 \times 10^{-4}\ mol/L$
$[Mg^{2+}_{(aq)}] = x = 2.8 \times 10^{-4}\ mol/L$
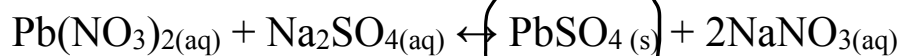$[F^-_{(aq)}] = 2x = 5.5 \times 10^{-4}\ mol/L$

$K_{sp} = [Mg^{2+}_{(aq)}] [F^-_{(aq)}]^2 = (2.8 \times 10^{-4})(5.5 \times 10^{-4})^2 = 8.4 \times 10^{-11}$
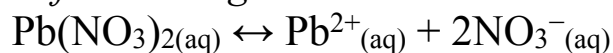
Predict Precipitation

- Trial Ion Product: the reaction quotient applied to the ion concentrations of a slightly soluble salt.
- Calculate the [ ] of the ions involved
- Substitute the concentrations into the Ksp expression = Q
- Compare value to actual Ksp

- E.g. Would a precipitate of lead (II) sulfate, $PbSO_{4(s)}$, ($K_{sp} = 1.8×10^{-8}$) form if 255 mL of 0.00016 mol/L lead(II)nitrate, $Pb(NO_3)_{2(aq)}$, is poured into 456 mL of 0.00023 mol/L sodium sulfate, $Na_2SO_{4(aq)}$?

$Pb(NO_3)_{2(aq)} + Na_2SO_{4(aq)} \leftrightarrow PbSO_{4(s)} + 2NaNO_{3(aq)}$

equilibrium

Before mixing:
$Pb(NO_3)_{2(aq)} \leftrightarrow Pb^{2+}_{(aq)} + 2NO_3^-_{(aq)}$
$[Pb^{2+}_{(aq)}] = Pb(NO_3)_{2(aq)}] = 0.00016$ mol/L

$Na_2SO_{4(aq)} \leftrightarrow 2Na^+_{(aq)} + SO_4^{2-}_{(aq)}$
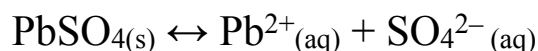$[SO_4^{2-}_{(aq)}] = [Na_2SO_{4(aq)}] = 0.00023$ mol/L

After mixing, there is 255 mL + 456 mL = 711 mL of the solution.

Therefore, the concentrations of the lead(II)and sulfate ions in the mixed solution are calculated as: $C_iV_i=C_fV_f$

$[Pb^{2+}_{(aq)}] = 0.00016$ mol/L $\times \dfrac{255mL}{711mL}$ $= 5.74 \ 10^{-5}$ mol/L

$[SO_4^{2-}_{(aq)}] = 0.00023$ mol/L $\times \dfrac{456 \ mL}{711mL}$ $= 1.48 \ 10^{-4}$ mol/L

$PbSO_{4(s)} \leftrightarrow Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)}$

$Q = [Pb^{2+}_{(aq)}][SO_4^{2-}_{(aq)}] = (5.74×10^{-5})(1.48×10^{-4}) = 8.46×10^{-9}$
$K_{sp} = 1.8×10^{-8}$

$Q < K_{sp}$. Therefore, a precipitate does not form.

- $Q > K_{sp}$ Precipitate will form (supersaturated)
- $Q = K_{sp}$ Precipitate will not form (saturated)
- $Q < K_{sp}$ Precipitate will not form (unsaturated)

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Common Ion Effect page 491

- Chemicals will have lower solubilities in solutions of common ions versus pure water
- Use ICE tables
- The initial ion concentration will be affected by the already present ion
- The unknown "x" is the new solubility of the chemical
- Review example question from calculating K_e notes and how it applies to

Solubility in Solutions With Common Ions

What is the molar solubility of $PbCl_{2(s)}$ in a 0.2 mol/L $NaCl_{(aq)}$ solution at SATP?

In this problem, you are asked to determine the amount of $PbCl_{2(s)}$ that will dissolve into a solution that already contains $Cl^-_{(aq)}$ ions. The two salts have a common ion, $Cl^-_{(aq)}$.
 $NaCl_{(s)}$ (which has high solubility) dissolves completely in water to form $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions.

$$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$
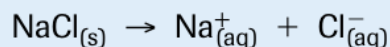
Therefore, before the addition of the lead(II) chloride,

$$[Cl^-_{(aq)}] = [NaCl_{(aq)}] = 0.2\ mol/L$$

We can look up the solubility product constant of $PbCl_{2(s)}$ in a solubility table, for example, the table in Appendix C8. The low K_{sp} value shows that it is only slightly soluble in water. We can therefore say that $PbCl_{2(s)}$ establishes a dynamic equilibrium in solution according to the following equation:

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\ Cl^-_{(aq)} \qquad\qquad K_{sp} = 1.7 \times 10^{-5}\ at\ 25°C$$
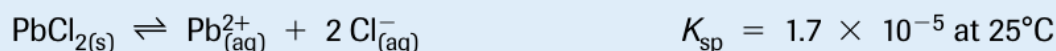
Table 5 ICE Table to Predict the Solubility of $PbCl_{2(s)}$ in a Solution Containing $NaCl_{(aq)}$

	$PbCl_{2(s)}$	$\rightleftharpoons$	$Pb^{2+}_{(aq)}$	+	$2\ Cl^-_{(aq)}$
Initial concentration (mol/L)	—		0		0.2
Change in concentration (mol/L)	—		$+x$		$+2x$
Equilibrium concentration (mol/L)	—		x		$0.2 + 2x$

$K_{sp} = [Pb^{2+}_{(aq)}][Cl^-_{(aq)}]^2 = 1.7 \times 10^{-5}$

$K_{sp} = (x)(0.2 + 2x)^2 = 1.7 \times 10^{-5}$

We can simplify the math in this question by noting that the K_{sp} is very small ($PbCl_2$ has a very low solubility in water). It follows that the value of x and therefore, $2x$ will be exceedingly small. When this very small value is added to 0.2 (a much larger value), the result will essentially remain 0.2. We make the simplifying assumption that

$0.2 + 2x \doteq 0.2$

Therefore,

$K_{sp} \doteq (x)(0.2)^2 = 1.7 \times 10^{-5}$

$x \doteq \dfrac{1.7 \times 10^{-5}}{(0.2)^2}$

$x \doteq 4.2 \times 10^{-4}$

To determine whether the assumption that $0.2 + 2x \doteq 0.2$ is appropriate, we notice that

$2x = 2(4.2 \times 10^{-4})$

$= 8.4 \times 10^{-4}$

which is indeed much smaller than 0.2. We accept the assumption as valid.

The molar solubility of lead(II) chloride in 0.2 mol/L $NaCl_{(aq)}$ solution is 4.2×10^{-4} mol/L.