Lecture 26: Solution Chemistry

Definitions, K_{sp}, Predicting Precipitates

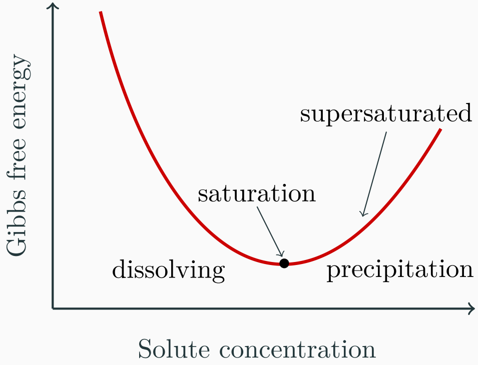
Solution Definitions

Definitions	
Solution:	Mixture composed of two or more substances
Solvent:	Present in the greatest amount, dissolves the solute
Solute:	Not the greatest amount, gets dissolved

Solution chemistry = Equilibrium with fancy terminology

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4{}^{2-}(aq)$$

$$K_{sp} = [Ca^{2+}][SO_4{}^{2-}]$$



Definitions

Saturation point: Max amount of a solute that can dissolve in a solvent $Q_{sp} = K_{sp}$, $\Delta G_{toeq} = 0$

Dissolving: $Q_{sp} < K_{sp}$, $\Delta G_{\text{toeq}} < 0$

Precipitation: $Q_{sp} > K_{sp}$, $\Delta G_{\text{toeq}} > 0$

K_{sp}**:** equilibrium constant for dissolving salt in water

How much insoluble salt dissolves in water?

$$\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

	AgCl	Ag^+	Cl^-
Initial	–	0	0
Change	–	$+x$	$+x$
Equilibrium	–	x	x

$$K_{sp} = x^2 = 1 \times 10^{-10} \implies x = \boxed{1 \times 10^{-5}\,\text{M}}$$

Solubility: mols of salt that can dissolve per liter solvent

Common Ion Effect

What is the solubility of CaF_2 in 0.1 M NaF?

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq) \quad K_{sp} = 1 \times 10^{-12}$$
$$K_{sp} = [Ca^{2+}][F^-]^2$$

	CaF_2	Ca^{2+}	F^-
Initial	–	0	0.1
Change	–	$+x$	$+2x$
Equilibrium	–	x	$0.1 + 2x$

$$K_{sp} = x(0.1 + \cancel{2x})^2 \approx x(0.1)^2$$
$$x = 1 \times 10^{-10}\ \text{M}$$

In water: $x = 6.39 \times 10^{-5}$ M

Common Ion Effect

Decrease in solubility due to presence of a shared ion

Shortcut reminders: Always check afterwards, only for addition since $0.1 \gg x$

Is there a precipitate? Compare Q to K

If 10 mL of 0.001 M Na_2CO_3 and 10 mL of 0.025 M $AgNO_3$ are mixed together, does Ag_2CO_3 ($K_{sp} = 6.2 \times 10^{-12}$) precipitate?

Key Idea: Remember to account for dilution

$$Q = [\mathrm{Ag}^+]^2[\mathrm{CO_3}^{2-}]$$

Dilution: total volume = 20 mL

$$[\mathrm{Ag}^+] = 0.025\,\mathrm{M} \times \frac{10\,\mathrm{mL}}{20\,\mathrm{mL}} = 0.0125\,\mathrm{M}$$

$$[\mathrm{CO_3}^{2-}] = 0.001\,\mathrm{M} \times \frac{10\,\mathrm{mL}}{20\,\mathrm{mL}} = 5.00 \times 10^{-4}\,\mathrm{M}$$

$$Q = 7.81 \times 10^{-8} \implies Q > K \implies \boxed{\text{precipitation occurs}}$$

What concentration will a precipitate form?

NaF(s) is added to 1×10^{-6} M $Ca(NO_3)_2(aq)$. At what concentration of $[F^-]$ will a precipitate form?

$$CaF_2\,(s) \rightleftharpoons Ca^{2+} + 2\,F^-$$

	CaF_2	Ca^{2+}	F^-
Initial	–	1×10^{-6}	0
Change	–	0	$+2x$
Equilibrium	–	1×10^{-6}	$2x$

$$Q_{sp} = 1 \times 10^{-12} = [Ca^{2+}][F^-]^2$$
$$1 \times 10^{-12} = (1 \times 10^{-6})(2x)^2$$
$$x = 5 \times 10^{-4}\ \text{M}$$
$$[F^-] = 2x = \boxed{1 \times 10^{-3}\ \text{M}}$$

$$Q_{sp} = 1 \times 10^{-12} = [Ca^{2+}][F^-]^2$$
$$1 \times 10^{-12} = (1 \times 10^{-6})(x)^2$$
$$x = \boxed{1 \times 10^{-3}\ \text{M}}$$

$$Q_{sp} > K_{sp} \implies [F^-] > 1 \times 10^{-3}\ \text{M}$$

No ICE coeffs if adding from external source

Example: Precipitation Calculations

Na_3PO_4 is added to 0.1 M $Al(NO_3)_3(aq)$ and 0.1 M $Mn(NO_3)_2(aq)$. Which salt precipitates first? $K_{sp}(AlPO_4) = 9.8 \times 10^{-21}$, $K_{sp}(Mn_3(PO_4)_2) = 1 \times 10^{-22}$

$$AlPO_4\,(s) \rightleftharpoons Al^{3+} + PO_4{}^{3-}$$

$$K_{sp} = [Al^{3+}][PO_4{}^{3-}]$$

$$[PO_4{}^{3-}] = \frac{9.8 \times 10^{-21}}{0.1} = 9.8 \times 10^{-20}$$

$$\boxed{AlPO_4 \text{ precipitates first}}$$

$$Mn_3(PO_4)_2\,(s) \rightleftharpoons 3\,Mn^{2+} + 2\,PO_4{}^{3-}$$

$$K_{sp} = [Mn^{2+}]^3[PO_4{}^{3-}]^2$$

$$[PO_4{}^{3-}] = \sqrt{\frac{1 \times 10^{-22}}{(0.1)^3}} = 3.16 \times 10^{-10}$$

Example: Precipitation Calculations

How much $Al(NO_3)_3(aq)$ remains when $Mn_3(PO_4)_2$ begins to precipitate?

From previous result:

$$[PO_4{}^{3-}] = 3.16 \times 10^{-10}$$

For $AlPO_4$:

$$K_{sp} = [Al^{3+}][PO_4{}^{3-}]$$
$$[Al^{3+}][PO_4{}^{3-}] = 9.8 \times 10^{-21}$$
$$[Al^{3+}] = \frac{9.8 \times 10^{-21}}{3.16 \times 10^{-10}} = 3.1 \times 10^{-11}$$
$$\frac{3.1 \times 10^{-11}}{0.1} \times 100\% = \boxed{3.1 \times 10^{-8}\% \text{ remaining from initial}}$$

Essentially all Al^{3+} has precipitated by this point

Equilibrium Hess's Law

Equilibrium Hess's Law

Rule 1: Reversing a reaction inverts the equilibrium constant

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad K$$
$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2 \quad K^{-1}$$

Rule 2: Multiplying a reaction by a factor raises K to that power

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad K$$
$$2\,N_2 + 6\,H_2 \rightleftharpoons 4\,NH_3 \quad K^2$$

Rule 3: Adding reactions multiplies their equilibrium constants

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \quad K_1$$
$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \quad K_2$$
$$N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \quad K_1 \cdot K_2$$

Solubility Rules

1. Salts containing Group I ions (Li^+, Na^+, K^+, Rb^+, Cs^+) are soluble, with few exceptions. Salts containing the ammonium ion ($NH_4{}^+$) are also soluble.
2. Salts containing nitrate ion ($NO_3{}^-$) are generally soluble.
3. Salts containing halide ions (Cl^-, Br^-, I^-) are generally soluble, except with Ag^+, Pb^{2+}, and $Hg_2{}^{2+}$. Thus, $AgCl$, $PbBr_2$, and Hg_2Cl_2 are insoluble.
4. Most silver salts are insoluble, Exceptions: $AgNO_3$ and $AgC_2H_3O_2$, which are soluble.
5. Most sulfate salts are soluble, Exceptions:: $CaSO_4$, $BaSO_4$, $PbSO_4$, $SrSO_4$, and Ag_2SO_4.
6. Most hydroxide salts are only slightly soluble. Hydroxides of Group I elements are soluble. Hydroxides of Group II elements ($Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$) are slightly soluble. Hydroxides of transition metals and Al^{3+} are insoluble, e.g., $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$.
7. Carbonates are frequently insoluble. Group II carbonates such as $CaCO_3$, $SrCO_3$, and $BaCO_3$ are insoluble, as are $FeCO_3$ and $PbCO_3$.
8. Chromates are frequently insoluble, e.g., $PbCrO_4$ and $BaCrO_4$.
9. Phosphates such as $Ca_3(PO_4)_2$ and Ag_3PO_4 are frequently insoluble.
10. Fluorides such as BaF_2, MgF_2, and PbF_2 are frequently insoluble.