Exam 3: Thursday!

Solubility equilibria and the solubility product constant, K_{sp}

Ch 4 : sol. rules   SOL (OR) INSOL.

in reality, everything dissolves (maybe a little/lot)

insol: $< \frac{1g}{1L}$ sol: $> \frac{1g}{L}$

let's be more specific!

Let's meet our final eq^m constant: K_{sp} : solubility product (eq^m) constant.

charges!

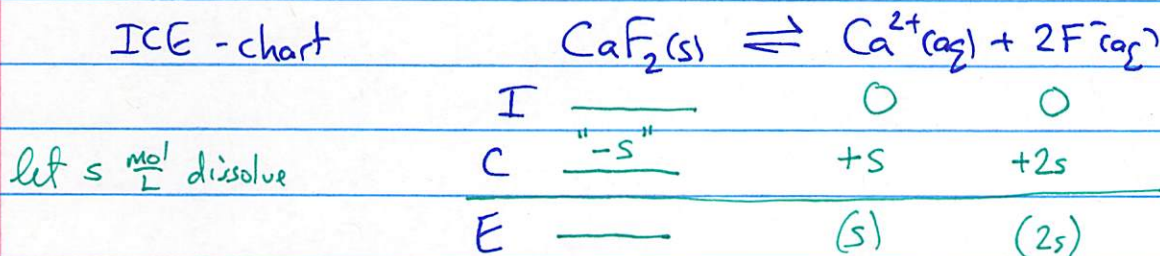rxn: ionic compound (s) $\rightleftharpoons$ dissolved ions (aq)

ex: calcium fluoride : $CaF_2 (s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

K_{sp}

$$K_{sp} = [Ca^{2+}][F^-]^2_{eq}$$ chap/appendix II

$$= 1.46 \times 10^{-10} \quad (25°C, \text{ textbook})$$

let's calculate molar solubility of CaF_2 in water. ⓢ

ICE-chart $CaF_2 (s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

	CaF_2	Ca^{2+}	$2F^-$
I	—	0	0
C	"$-s$"	$+s$	$+2s$
E	—	(s)	$(2s)$

let s $\frac{mol}{L}$ dissolve

$$K_{sp} = [Ca^{2+}][F^-]^2_{eq} \Rightarrow 1.46 \times 10^{-10} = (s)(2s)^2 = 4s^3$$

$4s^2$

TABLE 17.2 Selected Solubility Product Constants (K_{sp}) at 25 °C

Compound	Formula	K_{sp}	Compound	Formula	K_{sp}
Barium fluoride	BaF_2	2.45×10^{-5}	Lead(II) chloride	$PbCl_2$	1.17×10^{-5}
Barium sulfate	$BaSO_4$	1.07×10^{-10}	Lead(II) bromide	$PbBr_2$	4.67×10^{-6}
Calcium carbonate	$CaCO_3$	4.96×10^{-9}	Lead(II) sulfate	$PbSO_4$	1.82×10^{-8}
Calcium fluoride	CaF_2	1.46×10^{-10}	Lead(II) sulfide*	PbS	9.04×10^{-29}
Calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}	Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Calcium sulfate	$CaSO_4$	7.10×10^{-5}	Magnesium hydroxide	$Mg(OH)_2$	2.06×10^{-13}
Copper(II) sulfide*	CuS	1.27×10^{-36}	Silver chloride	$AgCl$	1.77×10^{-10}
Iron(II) carbonate	$FeCO_3$	3.07×10^{-11}	Silver chromate	Ag_2CrO_4	1.12×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver bromide	$AgBr$	5.35×10^{-13}
Iron(II) sulfide*	FeS	3.72×10^{-19}	Silver iodide	AgI	8.51×10^{-17}

*Sulfide equilibrium is of the type: $MS(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$

$$\sqrt[3]{\dfrac{1.46\times10^{-10}}{4}} = \sqrt[3]{\dfrac{4s^3}{4}} \qquad\Rightarrow\qquad s = \sqrt[3]{\dfrac{1.46\times10^{-10}}{4}}$$

$$\sqrt[x]{a} = a^{1/x} \qquad\qquad = 3.32\times10^{-4}\,M$$

$\underset{\text{molar sol. of } CaF_2 \text{ in pure } H_2O}{\underbrace{}}$

@ 25°C

solubility: #g/L

$$sol = \dfrac{3.32\times10^{-4}\,\text{mol } CaF_2}{L} \times \dfrac{78.08g\ CaF_2}{1\ \text{mol } CaF_2}$$

$$= 0.0259g/L$$

Common ion effect

When we dissolve an ionic cpd in a sol^n that contains a common ion (where we already have an ion that is going to dissolve)
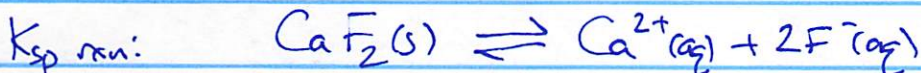
ex: What's molar sol. of CaF_2 in 0.100M $NaF_{(aq)}$?

$$NaF_{(aq)} \xrightarrow{100\%} Na^+_{(aq)} + F^-_{(aq)}$$
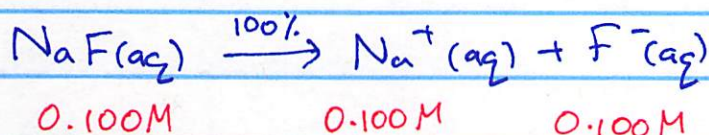
$\phantom{NaF_{(aq)}}$ 0.100M 0.100M 0.100M $\rangle$ a common ion

K_{sp} rxn: $\qquad CaF_2(s) \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$

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

in common!

	CaF_2	Ca^{2+}	F^-
I	——	0	0.100
C	"-s"	+s	+2s
E	——	(s)	(0.100+2s)
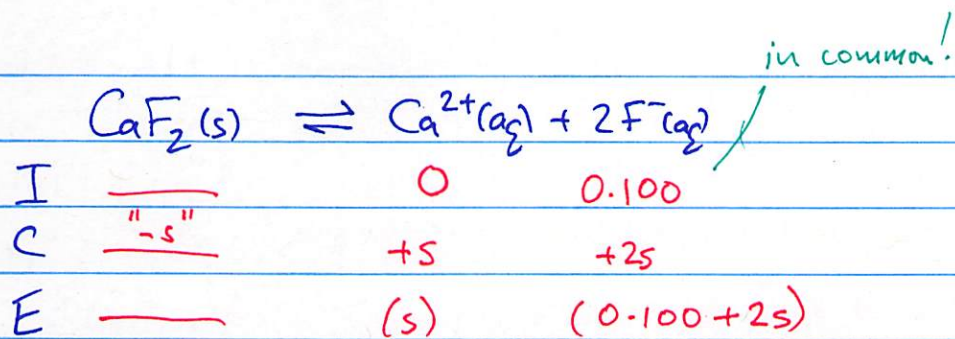
$$K_{sp} = [Ca^{2+}][F^-]^2_{eq} \implies 1.46 \times 10^{-10} = (s)(0.100 + 2s)^2$$
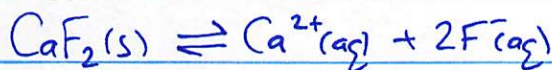
let's assume $2s \ll 0.100$

then: $\quad 1.46 \times 10^{-10} \approx (s)(0.100)^2$

$$s \cong \frac{1.46 \times 10^{-10}}{0.100^2} = 1.46 \times 10^{-8} M$$

safe!
phew!!

What's molar sol of CaF_2 in pure water? $3.32 \times 10^{-4} M$ 20,000× smaller than in pure H_2O!

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

LHS shift ◁ ——————

less dissolved   when it's dissolved in $NaF(aq)$. ($[F^-]\uparrow$)
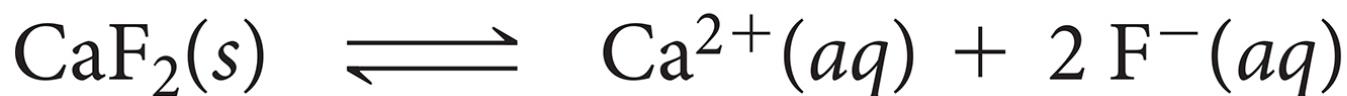
less sol.

ex: In which sol^n is $BaSO_4$ most soluble?

a) $0.10 M$ $Ba(NO_3)_2 (aq)$ — Ba^{2+} in common

b) $0.10 M$ $Na_2SO_4 (aq)$ — SO_4^{2-} in common

(✸) c) $0.10 M$ $NaNO_3 (aq)$ no common ion!?

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

The common ion effect can be qualitatively understood by application of Le Chatelier's principle! The presence of a common ion increases the concentration of one of the RHS species (stress), causing a shift to the LHS (relief) that represents a decrease in solubility (formation of dissolved ions).
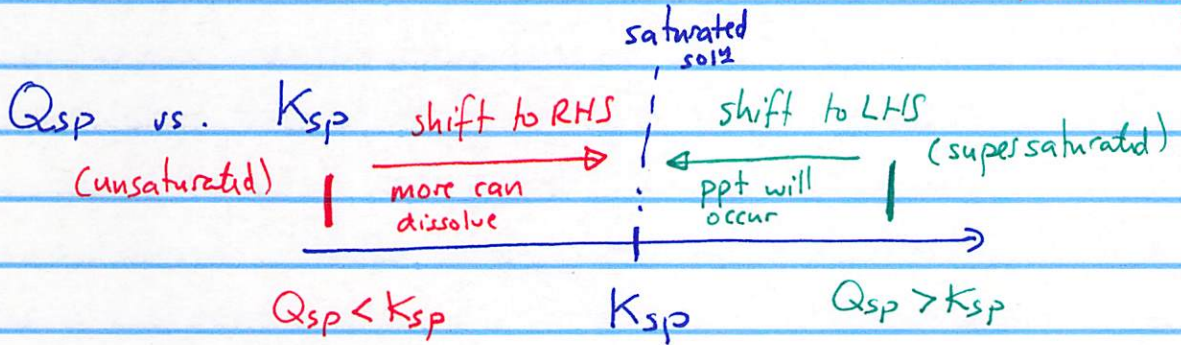
Common ion
0.100 M F⁻(aq)

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

Equilibrium shifts left

Precipitation

ppt* ⟵

K_{sp} rxn: ionic cpd (s) ⇌ ions (aq)

⟶ dissolving

Q_{sp} vs. K_{sp}

saturated soln

shift to RHS | shift to LHS

(unsaturated) ⟵ more can dissolve ⟶ | ppt will occur ⟵ (supersaturated)

$Q_{sp} < K_{sp}$ K_{sp} $Q_{sp} > K_{sp}$

ex: $K_{sp}(CaF_2) = 1.46 \times 10^{-10}$ $CaF_2 (s) \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$
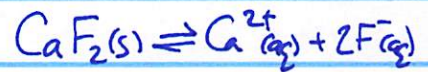
if we mix $Ca(NO_3)_2 (aq) + NaF (aq)$ so that

$$[Ca^{2+}] = 2.5 \times 10^{-3} M$$

$$[F^-] = 2.0 \times 10^{-3} M$$

what will happen?

$$Q_{sp} = [Ca^{2+}][F^-]^2$$
$$= (2.5 \times 10^{-3})(2.0 \times 10^{-3})^2$$
$$= 1.0 \times 10^{-8}$$

$Q_{sp} > K_{sp}$, ⇒ shift to LHS

⇒ PPT!