CHEM 1032 Key **Week 7**

Equilibrium

This worksheet is aimed at practicing the concepts of equilibrium based on their relationship with thermodynamics. It is intended for you to work through it in order. *(Don't skip ahead.)*

$$PbCrO_{4\,(s)} \leftrightarrow Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Write the equilibrium expression for the reaction.

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}]$$

The equilibrium concentrations of aqueous species are listed below. What is the equilibrium constant for the reaction?

$[Pb^{2+}] = 0.1341\ \mu M$ $[CrO_4^{2-}] = 0.1341\ \mu M$

$$0.1341\,\mu M \left| \frac{1\ M}{1\times10^{6}\,\mu M} \right. = 1.34\times10^{-7}\ M$$

$$K_{sp} = (1.34\times10^{-7})(1.34\times10^{-7})$$

$$K_{sp} = 1.80\times10^{-14}$$

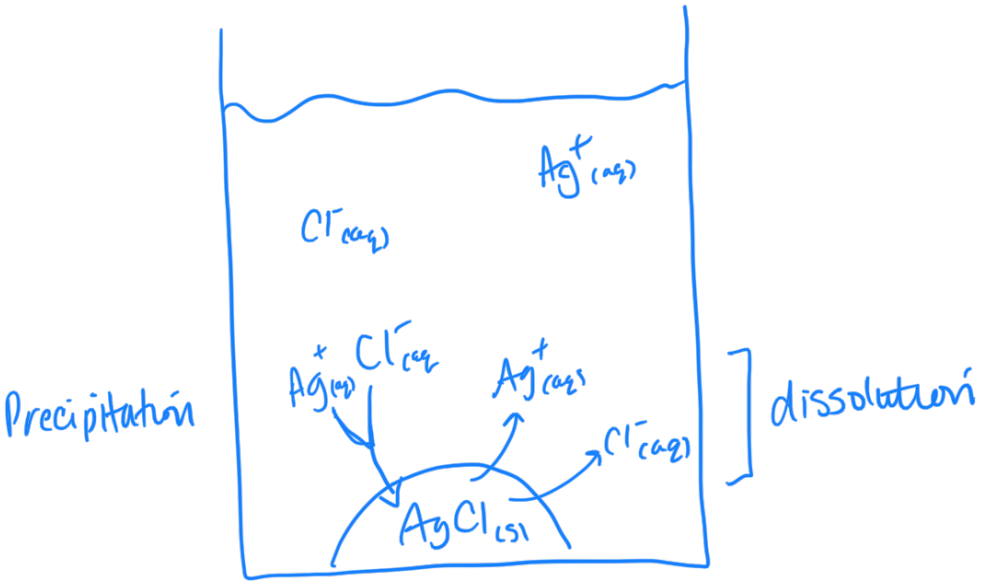
Explain why solids do not appear in equilibrium expressions.

Solids do not appear because equilibrium expressions show concentrations, looking at how they change. Since a solid has a constant concentration, there is no change which could occur. Concentration is constant because moles and volume change together.

Are reactants favored in the reaction or products? Explain based off of your value of K.

Based on the value of K_{sp} the reaction is reactants favored. When $K \ll 1$, the value of the numerator (products) is very small.

Draw a diagram which shows what is occurring on the molecular level in the solution.



Calculate the value of Gibbs Free Energy. Is the reaction spontaneous?

$$\Delta G^\circ = -RT\ln K$$

$$\Delta G^\circ = -(8.314\ J/mol\cdot K)(298\ K)(\ln 1.80\times10^{-14})$$

$$\Delta G^\circ = +78.4\ KJ/mol$$

No, the ΔG° is (+) indicating it is nonspontaneous

If you were to raise the temperature of the system, how would this change the equilibrium?

Solubility generally decreases with increasing temperature. Based on the reaction ΔS°_{rxn} is (+) so ΔH°_{rxn} must also be +.

Therefore these reactions are more spontaneous at higher T.

Consider the spontaneity of the reaction and that products are present in solution. How do you rectify these two phenomena?

The reaction is nonspontaneous but we still see that some products form, this is because spontaneity is telling us the extent that the forward reaction can occur before equilibrium is established. So in this case (+) ΔG° tells us very few products form before the backward reaction occurs.

If a scientist were to mix 50.0 mL of 0.0100 M $Pb(NO_3)_2$ and 50.0 mL of 0.0020 M Na_2CrO_4 in a beaker, what would happen?

Write the full reaction.

$$Pb(NO_3)_{2\,(aq)} + Na_2CrO_{4\,(aq)} \longrightarrow 2\,NaNO_{3\,(aq)} + PbCrO_{4\,(s)}$$

Write the net ionic reaction.

$$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow PbCrO_{4\,(s)}$$

Calculate the concentration of Pb^{2+} and CrO_4^{2-} if no precipitation were to occur. $M_1V_1 = M_2V_2$

50.0 mL
+ 50.0 mL
100.0 mL
total V

Pb^{2+} $(0.0100\,M)(50.0\,mL) = (M_2)(100.0\,mL)$

$M_2 = 0.0050\,M\ Pb^{2+}$

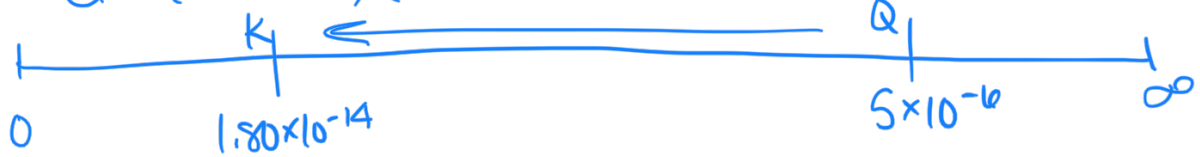
CrO_4^{2-} $(0.0020\,M)(50.0\,mL) = (M_2)(100.0\,mL)$

$M_2 = 0.0010\,M\ CrO_4^{2-}$

Calculate the value of Q. Will a precipitate form? Why. Explain using equilibrium.

$$PbCrO_{4\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

$Q = (0.0050\,M)(0.0010\,M) = 5\times10^{-6}\,M$



Q is much >> K, so backwards (precipitation) must occur.

Calculate the value of ΔG for the reaction under the current conditions. Will a precipitate form?

78.4 kJ/mol × 1000

$\Delta G = \Delta G^\circ + RT \ln Q$

$\Delta G = 78400\ J/mol + (8.314\ J/mol\cdot K)(298\ K)\ln(5\times10^{6})$

$\Delta G = 116\ kJ/mol$ ← represents forward reaction

$-116\ kJ/mol$ ← represents backward reaction, backward very spontaneous.

Continuing with the example from the previous page, what would occur in each of the following examples? Indicate the relationship of Q and K when the change is introduced.

Sodium nitrate ($NaNO_3$) salt is added to the solution?

$NaNO_3$ is comprised of the spectator ions which do occur with the precip of $PbCrO_4$ (no common ion), thus it will not change anything

$Q = K$, because equilibrium not affected

The headspace above the solution is decreased by half?

Volume changes only affect equilibria of gaseous components in the reaction. This equilibrium is in the aqueous phase... so no change.

$Q = K$, because equilibrium unaffected

Potassium chromate (Na_2CrO_4) is added to the solution?

K_2CrO_4

$2K^+$ CrO_4^{2-}

↑ common ion!

$PbCrO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}$

Increasing a product concentration will push the reaction backwards. More precip will occur.

$Q > K$