Models of solution chemistry

Due Date: Wednesday, July 28,

1. Write the expression for the equilibrium constant for each of the following reactions. Write the pressure of a gaseous molecule, X, as $P_X$.

(a) $\text{Cl}_2(g) + 2\text{OH}^-(aq) \rightleftharpoons \text{Cl}^-(aq) + \text{OCl}^-(aq) + \text{H}_2\text{O}(l)$

$$K = \frac{[\text{Cl}^-][\text{OCl}^-]}{[P_{\text{O}_2}][\text{OH}^-]^2}$$

(b) $\text{Hg}(l) + \text{I}_2(g) \rightleftharpoons \text{HgI}_2(s)$

$$K = \frac{1}{P_{\text{I}_2}}$$

2. From the equations $\text{CuN}_3(s) \rightleftharpoons \text{Cu}^+ + \text{N}_3^-$ $K = 4.9 \times 10^{-9}$

$\text{HN}_3 \rightleftharpoons \text{H}^+ + \text{N}_3^-$ $K = 2.2 \times 10^{-5}$

find the value of $K$ for the reaction $\text{Cu}^+ + \text{HN}_3 \rightleftharpoons \text{CuN}_3(s) + \text{H}^+$. All species are aqueous unless otherwise indicated.

Soln:

$$\text{Cu}^+ + \text{N}_3^- \rightleftharpoons \text{CuN}_3(s) \quad K_1 = 1/(4.9 \times 10^{-9}) = 2.04 \times 10^8$$

$$\text{HN}_3 \rightleftharpoons \text{H}^+ + \text{N}_3^- \quad K_2 = 2.2 \times 10^{-5}$$

Summing up:

$$\text{Cu}^+ + \text{HN}_3 \rightleftharpoons \text{CuN}_3(s) + \text{H}^+ \quad K = K_1 K_2 = 2.04 \times 10^8 \times 2.2 \times 10^{-5} = 4.5 \times 10^3$$
3. Suppose that the following reaction has come to equilibrium:
\[ \text{Br}_2(l) + \text{I}_2(s) + 4\text{Cl}^- (aq) \rightleftharpoons 2\text{Br}^- (aq) + 2\text{ICl}_2^- (aq) \]
If more I\(_2\)(s) is added, will the concentration of ICl\(_2^-\) in the aqueous phase increase, decrease, or remain unchanged?

**Soln:**
Concentrations of solids are defined in their pure states and are always unity. Therefore, they are omitted from the equilibrium equation. Iodine is added in solid form and therefore the concentrations of ICl\(_2^-\) will remain unchanged.

4. Find \(\Delta G^\circ\) for the reactions
(a) \(\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \quad K = 6.5 \times 10^{-5}\)
\[
\Delta G^\circ = -RT\ln K = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln(6.5 \times 10^{-5})
\]
\[= 23.9 \text{ kJ/mol} \]
(b) \(\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \quad K = 7.1 \times 10^{-12}\)
\[
\Delta G^\circ = -RT\ln K = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln(7.1 \times 10^{-12})
\]
\[= 63.6 \text{ kJ/mol} \]

5. For the reaction \(\text{Mg}^{2+} + \text{Cu}(s) \rightleftharpoons \text{Mg(s)} + \text{Cu}^{2+}\), \(K = 10^{-92}\) and \(\Delta S^\circ = +18 \text{ J/(K.mol)}\).

(a) Under standard conditions, is \(\Delta G^\circ\) positive or negative? The term "standard conditions" means that reactants and products are in their standard states.
\[
\Delta G^\circ = -RT\ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln(10^{-92}) = 524.8 \text{ kJ/mol}
\]
Therefore, \(\Delta G^\circ\) is positive.

(b) Under standard conditions, is the reaction endothermic or exothermic?
\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]
\[
\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = 524.8 \text{ kJ/mol} + (298 \text{ K})(18 \text{ J K}^{-1} \text{ mol}^{-1})
\]
\[= 524.8 \text{ kJ/mol} + 5.36 \text{ kJ/mol}
\]
\[= 530.2 \text{ kJ/mol} \]
Since \(\Delta H^\circ\) is positive the reaction is endothermic.
6. For the sum of two reactions, we know that $K_3 = K_1 K_2$. Show that this implies that
$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

\[ \begin{align*}
A + B & \rightleftharpoons C + D \quad K_1 \\
D + E & \rightleftharpoons B + F \quad K_2 \\
A + E & \rightleftharpoons C + F \quad K_3
\end{align*} \]

**Soln.**
For the first and second reactions steps, $K_1 = e^{-\frac{\Delta G_1^\circ}{RT}}$ and $K_2 = e^{-\frac{\Delta G_2^\circ}{RT}}$.
Since the third reaction is derived by adding the first and the second reactions, the equilibrium constant for the third reaction can be expressed as the product of the individual equilibrium constants for reaction 1 and 2. Therefore, $K_3 = K_1 K_2$

Representing the total free energy change in the standard state for the third reaction as $\Delta G_3^\circ$,
$K_3 = e^{-\frac{\Delta G_3^\circ}{RT}} = e^{-\frac{\Delta G_1^\circ}{RT}} \times e^{-\frac{\Delta G_2^\circ}{RT}} = e^{-\left(\frac{\Delta G_1^\circ + \Delta G_2^\circ}{RT}\right)}$
Therefore, $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

7. Consider a reaction between gaseous fluorine ($F_2$) and solid graphite ($C$) that produces tetrafluoroethylene;

\[ \begin{align*}
2F_2 (g) + 2C (s) & \rightleftharpoons F_2C=CF_2 (g) \\
\text{Fluorine} & \quad \text{Graphite} \quad \quad \quad \quad \text{Tetrafluoroethylene}
\end{align*} \]

A bacteria called Teflon eats up $C_2F_4$ and make Teflon (shown below) for their cell wall.

Will the reaction shift to the left or right if these bacteria are added? Explain.

**Soln.**
The reaction will shift to the right. This will occur because, according to La Chatelier's principle, if the bacteria eats up $C_2F_4$ (the product of the reaction), the equilibrium will be shifted in a direction such that more product is formed.
MULTIPLE CHOICE QUESTIONS (CHOOSE THE RIGHT ANSWER)

8. The mathematical equation which represents the solubility product when the insoluble compound Mn_2S_3 is dissolved in water is
(a) [Mn^{2+}]^2[S^{2-}]^3 = K_{sp}.
(b) [Mn^{3+}]^3[S^{2-}]^2 = K_{sp}.
(c) [Mn^{3+}]^2[S^{2-}]^3 = K_{sp}
(d) [Mn^{2+}]^3[S^{2-}]^2 = K_{sp}.

9. Given that the solubility product for La(IO_3)_3 is 1.0 x 10^{-11}, what is the concentration of La^{3+} in a saturated solution of lanthanum iodate?
   (a) 7.8 x 10^{-4} molar
   (b) 1.0 x 10^{-3} molar
   (c) 7.18 x 10^{-5} molar

10. If a 0.100 M solution of NaOH is added to a solution containing 0.200 M Ni^{2+}, 0.200 M Ce^{3+}, and 0.200 M Cu^{2+}, which metal hydroxide will precipitate first? K_{sp} for Ni(OH)_2 = 6.0 x 10^{-16}, K_{sp} for Ce(OH)_3 = 6.0 x 10^{-25}, and K_{sp} for Cu(OH)_2 = 4.8 x 10^{-20}.
   (a) Ni(OH)_2
   (b) Ce(OH)_3
   (c) Cu(OH)_2

11. What is the lead concentration of a saturated solution of lead(II) sulfate containing 0.020 molar Na_2SO_4? K_{sp} for PbSO_4 = 6.3 x 10^{-7}.
   (a) 7.9 x 10^{-4} molar
   (b) 5.6 x 10^{-3} molar
   (c) 3.2 x 10^{-5} molar

12. Consider the following equilibria:
   \[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad K_{sp} = 1.8 \times 10^{-10} \]
   \[ \text{AgCl(s)} + \text{Cl}^- \rightleftharpoons \text{AgCl}_2^- \quad K_2 = 1.5 \times 10^{-2} \]
   \[ \text{AgCl}_2^- + \text{Cl}^- \rightleftharpoons \text{AgCl}_3^{2-} \quad K_3 = 0.49 \]
   At equilibrium, if [Ag^+] is 9.00 x 10^{-11} M, then the concentrations of Cl^-, AgCl_2^-, and AgCl_3^{2-}, respectively are
   (a) 0.20 M; 0.0300 M; 0.0294 M
   (b) 0.2 M; 0.00030 M; 0.000294 M
   (c) 2.0 M; 0.0300 M; 0.0294 M

13. The reaction of EDTA with a trivalent metal ion at a pH of 4.0 may be written as:
   (a) M^{3+} + Y^{4+} \rightleftharpoons MY^{-}.
   (b) M^{3+} + H_2Y^{2-} \rightleftharpoons MY^{-} + 2H^+.
   (c) M^{3+} + H_4Y \rightleftharpoons MY^- + 4H^+.
14. Calculate the conditional formation constant $K_f'$ for the formation of an EDTA complex with copper(II) at a pH of 5.00, if $\log K_f = 18.80$.
   (a) $2.3 \times 10^{12}$
   (b) $7.0 \times 10^5$
   (c) $5.9 \times 10^{-26}$

15. Calculate the p$Co^{2+}$ after 12.00 mL of 0.03846 M EDTA in the titration of 25.00 mL of 0.020 M $Co^{2+}$ ($K_f = 2.04 \times 10^{16}$) at pH = 6.00.
   (a) $1.04 \times 10^{-3}$ molar
   (b) 4.415
   (c) 2.983

16. Calculate the p$Co^{2+}$ after 13.00 mL of 0.03846 M EDTA in the titration of 25.00 mL of 0.020 M $Co^{2+}$ ($K_f = 2.04 \times 10^{16}$) at pH = 6.00.
   (a) 9.095
   (b) 6.723
   (c) $1.89 \times 10^{-7}$ molar

17. In the following reaction, identify the conjugate acid-base pair:
    $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-.$
   (a) $NO_2^-$, OH$^-$
   (b) $NO_2^-$, H$_2$O
   (c) $NO_2^-$, HNO$_2$

18. A solution was found to contain $8.26 \times 10^{-4}$ M NaOH. Calculate the pH of the solution.
   (a) 3.08
   (b) 10.9
   (c) 1.00

19. Calculate the hydrogen ion concentration of a 0.100 M solution of methyl amine. $K_a$ for methyl amine hydrochloride = $2.3 \times 10^{-11}$.
   (a) $1.5 \times 10^{-6}$ molar
   (b) $6.9 \times 10^{-3}$ molar
   (c) $1.5 \times 10^{-12}$ molar

20. Find the concentration of phenol and phenolate ion in a 0.0100 M solution of phenol. $K_a$ for phenol = $1.05 \times 10^{-10}$.
   (a) $1.02 \times 10^{-6}$ molar phenol and $1.02 \times 10^{-6}$ molar phenolate ion
   (b) $1.02 \times 10^{-6}$ molar phenol and $1.00 \times 10^{-2}$ molar phenolate ion
   (c) $1.00 \times 10^{-2}$ molar phenol and $1.02 \times 10^{-6}$ molar phenolate ion