1) A 35.0-g sample of ethylene glycol, $HOCH_2CH_2OH$, is dissolved in 500.0 g of water. The vapor pressure of water at 32 °C is 35.7 mm Hg. What is the vapor pressure of the water–ethylene glycol solution at 32 °C? (Ethylene glycol is nonvolatile.) (1 atm = 1.01325 bar)

Moles $HOCH_2CH_2OH = 35.0\,g \times \frac{1\ mol}{62.07\ g} = .564\ mol$

Moles $H_2O = 500\,g \times \frac{1\ mol}{18.0169\ g} = 27.8\ mol$

$$X_{H_2O} = \frac{27.8\ mol}{27.8\ mol + .564\ mol} = 0.980$$

$$P = X_{H_2O} P^\circ = (0.980)(35.7\ mm\ Hg) = \boxed{35.0\ mm\ Hg}$$

2) An aqueous solution contains 3.00% phenylalanine ($C_9H_{11}NO_2$) by mass. (Phenylalanine is nonionic and nonvolatile.) Find the following:

(a) the freezing point of the solution $K_{fp} = -1.86\ °C/m$

Assume 100.0 g solution: 3.00 g $C_9H_{11}NO_2$ and 97.0 g H_2O

Moles $C_9H_{11}NO_2 = 3.00\,g \times \frac{1\ mol}{165.19\ g} = .0182\ mol$

Molality $C_9H_{11}NO_2 = \frac{.0182\ mol}{.0970\ kg} = .188\ m$

$\Delta T_{fp} = K_{fp} m = (-1.86\ °C/m)(.188\ m) = -0.349°C$

$T_{fp} = 0°C - 0.349°C = \boxed{-0.349°C}$ (Exact)

(b) the boiling point of the solution $K_{bp} = 0.5121\ °C/m$

Use molality calculated above

$\Delta T_{bp} = K_{bp} m = (0.5121\ °C/m)(.188\ m) = .0963\ °C$

$T_{bp} = 100°C + .0963°C = \boxed{100.0963°C}$ (Exact)

(c) the osmotic pressure of the solution at 25 °C $P = 1.0\,g/1\,mL$

$V = 100.0\,g \times \frac{1\,mL}{1.0\,g} \times \frac{1\,L}{1000\,mL} = .100\,L$

Molarity $C_9H_{11}NO_2$ $\frac{.0182\ mol}{.100\ L} = .182\ M$

$$\Pi = MRT = .182\ M \times \left(0.08206\ \frac{L\text{-}atm}{mol\text{-}K}\right)(298\ K)$$

$$= \boxed{4.45\ atm}$$

3) An aqueous solution contains 0.180 g of an unknown, nonionic solute in 50.0 g of water. The solution freezes at −0.040 °C. What is the molar mass of the solute? $K_{fp} = -1.86\ °C/m$

Moles of unknown = $\frac{0.180\ g}{MM}$

Molality of unknown = $\frac{0.180\ g}{MM \times 0.0500\ kg} = \frac{3.60}{MM}$

$\Delta T_{fp} = K_{fp}\, m$

$-0.040°C = (-1.86\ °C/m)\left(3.6/MM\right)$ $\quad .00597 = \frac{1}{MM}$ $\quad$ **MM = 167 g/mol**

4) List the following aqueous solutions in order of increasing melting point.
(a) 0.1 *m* sugar (b) 0.1 *m* NaCl
(c) 0.08 *m* $CaCl_2$ (d) 0.04 *m* Na_2SO_4

a) 0.1 m × 1 = 0.1 m
b) 0.1 m × 2 = 0.2 m
c) 0.08 m × 3 = 0.24 m
d) 0.04 m × 3 = 0.12 m

c < b < d < a

5) Data for the reaction $NO(g) + \frac{1}{2}O_2(g)$ n $NO_2(g)$ are given (for a particular temperature) in the table.

Concentration (mol/L)			
Experiment	[NO]	$[O_2]$	Initial Rate (mol NO / (L*h))
1	3.6×10^{-4}	5.2×10^{-3}	3.4×10^{-8}
2	3.6×10^{-4}	1.04×10^{-2}	6.8×10^{-8}
3	1.8×10^{-4}	1.04×10^{-2}	1.7×10^{-8}
4	1.8×10^{-4}	5.2×10^{-3}	?

(a) What is the rate law for this reaction?

To determine order of NO, compare exp. # 2 and 3.
When $[O_2]$ is held constant and [NO] doubles (3 to 2), the rate quadruples. Therefore the order is 2 for NO.
To determine order of O_2, compare exp # 1 and 2.
When [NO] is held constant and $[O_2]$ doubles (1 to 2), the rate also doubles. Therefore the order is 1 for O_2.

$$Rate = k[NO]^2[O_2]$$

(b) What is the rate constant for the reaction?

$$\text{Rate} = k[NO]^2[O_2]$$

Using Experiment #1

$$3.4\times10^{-8}\ M/h = k\left(3.6\times10^{-4}\ M\right)^2\left(5.2\times10^{-2}\ M\right)$$

$$\boxed{k = 50\ M^{-2}/h}$$

(c) What is the initial rate of the reaction in experiment 4?

$$\text{Rate} = 50\ M^{-2}/h\ [NO]^2[O_2]$$
$$= 50\ M^{-2}/h\ \left(1.8\times10^{-9}\ M\right)^2\left(5.2\times10^{-3}\ M\right)$$
$$= \boxed{8.4\times10^{-9}\ \text{mol NO/L}\cdot h}$$

6) Data for the decomposition of dinitrogen monoxide:

$$N_2O(g) \rightarrow N_2(g) + \tfrac{1}{2}O_2(g)$$

on a gold surface at 900 °C are given below. Determine the order of the reaction and the rate constant. Using the rate law and value of *k*, determine the decomposition rate at 900 °C when $[N_2O] = 0.035$ mol/L.

Time (min)	$[N_2O]$ (mol/L)	Zero	First $\ln[N_2O]$	Second $1/[N_2O]$
15.0	0.0835		-2.483	12.0
30.0	0.0680		-2.688	14.7
80.0	0.0350		-3.352	28.6
120.0	0.0220		-3.817	45.5

Only the first order graph ($\ln[N_2O]$ vs. Time(min)) will have a straight line, therefore the reaction is first order

$$\text{rate} = k[N_2O]$$

$$\text{Slope} = \frac{\text{rise}}{\text{run}} = \frac{(-3.817 - -2.483)}{(120.0 - 15.0)} = -.0127$$

$$k = |-.0127| = .0127\ \text{min}^{-1}$$

$$\text{rate} = .0127\ \text{min}^{-1}[N_2O]$$
$$= .0127\ \text{min}^{-1}\ (.035\ \text{mol/L})$$
$$= \boxed{4.4\times10^{-4}\ M/\text{min}}$$

7) Ozone, O_3, in the Earth's upper atmosphere decomposes according to the equation:

$$2\,O_3(g) \rightarrow 3O_2(g)$$

The mechanism of the reaction is thought to proceed through an initial fast, reversible step, follow by a slow, second step.

Step 1: Fast reversible $O_3(g) \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} O_2(g) + O(g)$

Step 2: Slow $O_3(g) + O(g) \xrightarrow{k_2} 2O_2(g)$

(a) Which of the steps is rate-determining?

Step 2

(b) Write the rate equation for the rate-determining step.

$$\text{Rate} = k_2[O_3][O]$$

O is not in the overall reaction and must be removed.

$$\frac{k_1}{k_{-1}} = \frac{[O_2][O]}{[O_3]^2} \qquad [O] = \frac{k_1}{k_{-1}}\frac{[O_3]}{[O_2]}$$

$$\text{Rate} = k_2[O_3]\frac{k_1}{k_{-1}}\frac{[O_3]}{[O_2]} = \boxed{k\,[O_3]^2/[O_2]}$$

8) Carbonyl bromide decomposes to carbon monoxide and bromine:

$$COBr_2(g) \leftrightarrow CO(g) + Br_2(g)$$

K_c is 0.190 at 73 °C. If you place 0.0500 mol of $COBr_2$ in a 2.00-L flask and heat it to 73 °C, what are the equilibrium concentrations of $COBr_2$, CO, and Br_2? What percentage of the original $COBr_2$ decomposed at this temperature?

$$[COBr_2]_i = 0.0500\ \text{mol}/2.00\ \text{L} = .0250\ M$$

	$COBr_{2(g)} \rightleftharpoons$	$CO_{(g)}$	+ $Br_{2(g)}$
I	.0250	0	0
C	$-x$	$+x$	$+x$
E	$.0250-x$	x	x

$$K_c = \frac{[CO][Br_2]}{[COBr_2]} \qquad 0.190 = \frac{x^2}{.0250-x}$$

$$(.0250-x)(0.190) = x^2$$

$$x^2 + 0.190x - .00475 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = .0224$$

$$[COBr_2] = .0250 - .0224 = .0026\ M$$

$$[CO] = [Br_2] = .0224\ M$$

$$\%\ COBr_2\ \text{decomposed} = \frac{.0224}{.0250} \times 100 = 89.6\%$$

9) Calculate K for the reaction

$$SnO_2(s) + 2CO(g) \leftrightarrow Sn(s) + 2CO_2(g)$$

given the following information:

1. $SnO_2(s) + 2H_2(g) \leftrightarrow Sn(s) + 2H_2O(g)$ $K_1 = 8.12$
2. $H_2(g) + CO_2(g) \leftrightarrow H_2O(g) + CO(g)$ $K_2 = 0.771$

Equation 1 is fine as is.
Equation 2 needs to be reversed and doubled

Reversed : Invert K (K^{-1})
Doubled : Square K (K^2)
Reversed and doubled: (K^{-2})

$$K = K_1 \times \frac{1}{K_2^2} = 8.12 \times \frac{1}{(0.771)^2} = \boxed{13.7}$$

10) The reaction of hydrogen and iodine to give hydrogen iodide has an equilibrium constant, K_c, of 56 at 435 °C.

$$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$$

(a) What is the value of K_p?

only gases → $\Delta n = 2 - 2 = 0$

$$K_p = K_c(RT)^{\Delta n} = 56\,(RT)^0 = \boxed{56}$$

(b) Suppose you mix 0.045 mol of H_2 and 0.045 mol of I_2 in a 10.0-L flask at 425 °C. What is the total pressure of the mixture before and after equilibrium is achieved?

$T = 425°C + 273\ K = 698\ K$

$PV = nRT$

$$P_i = \frac{nRT}{V} = \frac{(.045\ mol + .045\ mol)(.08205\ L\text{-}atm/K\text{-}mol)(698\ K)}{10.0\ L} = \boxed{.52\ a}$$

$$P_{H_2} = P_{I_2} = \frac{.52}{2} = .26\ atm$$

	$H_2(g)$	+ $I_2(g)$	⇌ $2HI(g)$
I	.26	.26	0
C	−x	−x	+2x
E	.26−x	.26−x	2x

$$\sqrt{56} = \sqrt{\frac{(2x)^2}{(.26-x)^2}} \qquad 7.48 = \frac{2x}{.26-x} \qquad x = .21$$

$$P_f = 2(.26-x) + 2x = 2(.26-.21) + 2(.21)$$

$$P_f = \boxed{.52\ atm}$$

(c) What is the partial pressure of each gas at equilibrium?

$$P_{H_2} = P_{I_2} = .26 - .21 = .05\ atm$$

$$P_{HI} = 2(.21) = .42\ atm$$

Total pressure remained the same because same number of moles of gas on each side.

11) A 0.015M solution of hydrogen cyanate, HOCN, has a pH of 2.67.
(a) What is the hydronium ion concentration in the solution?

$$[H_3O^+] = 10^{-2.67} = 2.1 \times 10^{-3}\ M$$

(b) What is the ionization constant, K_a, for the acid?

	$HOCN_{(aq)}$	+ $H_2O_{(l)}$	⇌	$OCN^-_{(aq)}$	+ $H_3O^+_{(aq)}$
I	.015	|		0	0
C	−x	|		+x	+x
E	.015−x	|		x	2.1×10^{-3}

$x = 2.1 \times 10^{-3}$,

$$K_a = \frac{[OCN^-][H_3O^+]}{[HOCN]} = \frac{[2.1\times10^{-3}]^2}{(.015 - 2.1\times10^{-3})} = \boxed{3.5\times 10^{-4}}$$

12) What are the equilibrium concentrations of H_3O+, $CN-$, and HCN in a 0.025 M solution of HCN? What is the pH of the solution? (HCN $K_a = 4.0 \times 10^{-10}$)

$HCN_{(aq)}$	+ $H_2O_{(l)}$	⇌	$CN^-_{(aq)}$	+ $H_3O^+_{(aq)}$
.025	|		0	0
−x	|		+x	+x
.025−x	|		x	x

$$K_a = \frac{[CN^-][H_3O^+]}{[HCN]}$$

$$4.0\times 10^{-10} = \frac{x^2}{.025 - x}$$

$$x = 3.2\times 10^{-6}$$

$[CN^-] = [H_3O^+] = 3.2\times 10^{-6}\ M$

$[HCN] = .025\ M$

$pH = -\log [H_3O^+] = 5.50$

13) Sodium cyanide is the salt of the weak acid HCN. Calculate the concentrations of H_3O^+, OH^-, HCN, and Na^+ in a solution prepared by dissolving 10.8 g of NaCN in enough water to make 5.00×10^2 mL of solution at 25 °C. (HCN $K_a = 4.0 \times 10^{-10}$)

$10.8\,g\ NaCN \times \frac{1\ mol\ NaCN}{49.01\ g} = .220\ moles$ $\quad [NaCN] = \frac{.229\ mol}{.500\ L} = .440\ M$

Na^+ is simply a spectator ion because NaCN will fully ionize.

K_b for $CN^- = K_w / K_a$

$= 1 \times 10^{-14} / 4.0 \times 10^{-10}$

$K_b = 2.5 \times 10^{-5}$

	$CN^-_{(aq)}$	+ $H_2O_{(l)}$	$\rightleftharpoons$	$HCN_{(aq)}$	+ $OH^-_{(aq)}$
I	.440			0	0
C	$-x$			$+x$	$+x$
E	$.440-x$			x	x

$K_b = \frac{[HCN][OH^-]}{[CN^-]}$ $\quad 2.5 \times 10^{-5} = \frac{x^2}{.440 - x}$

$x = 3.3 \times 10^{-3}$

$[Na^+] = 0.440\ M$

$[CN^-] = .440 - 3.3 \times 10^{-3} = .437\ M$

$[HCN] = [OH^-] = 3.3 \times 10^{-3}\ M$ $\quad [H_3O^+] = 1 \times 10^{-14} / [OH^-] = 3.0 \times 10^{-12}\ M$

14) What mass of sodium acetate, $NaCH_3CO_2$, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? ($HC_2H_3O_2$ $K_a = 1.8 \times 10^{-5}$)

$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

$pH = pK_a + \log \frac{[base]}{[acid]}$

$4.50 = 4.74 + \log \frac{[base]}{[acid]}$

$-0.24 = \log \frac{[base]}{[acid]}$

$10^{-0.24} = 10^{\log \frac{[base]}{[acid]}}$

$.58 = \frac{[base]}{[acid]}$

$[base] = .58\,[acid]$

$\frac{n_b}{V} = .58\,[acid]$

$n_b = .58\,[acid] \cdot V$

$= .58(.10)(1.00\ L)$

$n_b = .058\ moles$

mass $NaCH_3CO_2$ = moles × MM

$= (.058\ mol)(82.03\ g/mol)$

$= \boxed{4.7\ g}$

15) You titrate 25.0 mL of 0.10 M NH_3 with 0.10 M HCl. (NH_3 $K_b = 1.8 \times 10^{-5}$)

(a) What is the pH of the NH_3 solution before the titration begins?

	$NH_3(aq)$	$+ H_2O(l)$	$\rightleftharpoons NH_4^+(aq)$	$+ OH^-(aq)$
I	0.10		0	0
C	$-x$		$+x$	$+x$
E	$0.10-x$		x	x

$1.8 \times 10^{-5} = \frac{x^2}{.10-x}$

$x = 1.3 \times 10^{-3}$

$[OH^-] = x$

$pOH = -\log(1.3 \times 10^{-3}) = 2.87$ $pH = 14 - pOH = 14 - 2.87 =$ **11.13**

(b) What is the pH at the equivalence point?

moles NH_3 = .10 M x .025 L = .0025 moles

At equivalence point: moles NH_3 = moles HCl

V_{HCl} needed = .0025 mol / 0.10 M = .025 L

Total V = .025 L + .025 L = .050 L

$[NH_4^+]_i = \frac{.0025\ mol}{.050\ L} = .05$ M

NH_4^+ K_a = $1 \times 10^{-14} / 1.8 \times 10^{-5}$ $= 5.6 \times 10^{-10}$

	$NH_4^+(aq)$	$+ H_2O(l) \rightleftharpoons$	$NH_3(aq)$	$+ H_3O^+(aq)$
I	.05		0	0
C	$-x$		$+x$	$+x$
E	$.05-x$		x	x

$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$

$5.6 \times 10^{-10} = \frac{x^2}{.05-x}$

$x = 5.3 \times 10^{-6}$

$[H_3O^+] = x$

$pH = -\log[5.3 \times 10^{-6}]$

$=$ **5.28**

(c) What is the pH at the half equivalence point of the titration?

At half equivalence point

$pOH = pK_b = -\log(1.8 \times 10^{-5}) = 4.74$

$pH = 14 - pOH = 14 - 4.74 =$ **9.26**

(d) Calculate the pH of the solution after adding 5.00, 15.0, 20.0, 22.0, and 30.0 mL of the acid.

25.0 mL is equivalence point. For 5.00, 15.0, 20.0, and 22.0 it is in the buffer region (Use Henderson Hasselbach)

For the 30.0 mL, there is excess HCl

For HH, can use moles instead of [ ] because V cancels in ration since it is the same.

mL .10 M HCl	5.00	15.0	20.0	22.0
n_a moles HCl	.0005	.0015	.0020	.0022
n_b moles NH_3	.0020	.0010	0.005	.0003
pH	9.86	9.08	8.66	8.39

moles HCl $= n_a = .10\ M \times V$

$n_b = .0025 - n_a$

$pH = pK_a + \log\frac{n_b}{n_a}$

$= 9.26 + \log\frac{n_b}{n_a}$

Total V = 55.0 mL) 30.0 mL of acid means 5.0 mL excess of HCl

moles excess HCl = .005 L x .10 M = .0005 moles

$[HCl] = \frac{.0005\ mol}{.055\ L} = .0091\ M = [H_3O^+]$

$pH = -\log(.0091) =$ **2.04**

16) Calculate the molar solubility of silver thiocyanate, AgSCN, in pure water and in water containing 0.010 M NaSCN. ($AgSCN\ K_{sp} = 1.0 \times 10^{-12}$)

Pure Water

$AgSCN_{(s)} \rightleftharpoons Ag^+_{(aq)} + SCN^-_{(aq)}$

I	0	0
C	+x	+x
E	x	x

$K_{sp} = [Ag^+][SCN^-]$

$1.0 \times 10^{-12} = x^2$

$x = 1 \times 10^{-6}$ mol/L

Water containing NaSCN

$AgSCN_{(s)} \rightleftharpoons Ag^+_{(aq)} + SCN^-_{(aq)}$

I	0	.010
C	+x	+x
E	x	.010 + x

$K_{sp} = [Ag^+][SCN^-]$

$1 \times 10^{-12} = x(.010 + x)$

$1 \times 10^{-12} = .010x$

$x = 1 \times 10^{-10}$ mol/L

17) A solution contains Ca^{2+} and Pb^{2+} ions, both at a concentration of 0.010 M. You wish to separate the two ions from each other as completely as possible by precipitating one but not the other using aqueous Na_2SO_4 as the precipitating agent. ($CaSO_4\ K_{sp} = 4.9 \times 10^{-5}$, $PbSO_4\ K_{sp} = 2.5 \times 10^{-8}$)

(a) Which will precipitate first as sodium sulfate is added, $CaSO_4$ or $PbSO_4$?

Since both $CaSO_4$ and $PbSO_4$ have the same general K_{sp} expression for 1:1 salts: $K_{sp} = [M^{2+}][SO_4^{2-}]$ and the cations both have the same concentration (0.010 M), you can just look at K_{sp}. Since $PbSO_4$ has a smaller K_{sp} it will precipitate first.

(b) What will be the concentration of the first ion that precipitates (Ca^{2+} or Pb^{2+}) when the second, more soluble salt begins to precipitate?

The more soluble salt that will precipitate second is $CaSO_4$.

$K_{sp} = [Ca^{2+}][SO_4^{2-}]$ $\quad [SO_4^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{4.9 \times 10^{-5}}{0.010} = 4.9 \times 10^{-3}$ M

The $[SO_4^{2-}]$ for the $PbSO_4$ will be the same

$K_{sp} = [Pb^{2+}][SO_4^{2-}]$ $\quad [Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{2.5 \times 10^{-8}}{4.9 \times 10^{-3}} = 5.1 \times 10^{-6}$ M

Answer Key

Chapter 18: Thermodynamics

Question 18:
Fill in the following table. Assume no two rows are the same

ΔH	ΔS	ΔG	Low Temp	High Temp
-	+	-	spontaneous	spontaneous
-	-	Temp. dependent	spontaneous	Non-spontaneous
+	+	Temp. dependent	non-spontaneous	spontaneous
+	-	+	non-spontaneous	non-spontaneous

Question 19 (18.25):
Heating some metal carbonates, among them magnesium carbonate, leads to their decomposition.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

$\Delta S_f°$ MgO = 26.85 J/mol K
$\Delta S_f°$ CO_2 = 213.74 J/mol K
$\Delta S_f°$ $MgCO_3$ = 65.84 J/mol K

$\Delta H_f°$ MgO = -601.85 kJ/mol
$\Delta H_f°$ CO_2 = -393.51 kJ/mol
$\Delta H_f°$ $MgCO_3$ = -1111.69 kJ/mol

(a) Calculate $\Delta_r G°$ for the reaction.

$\Delta_r G° = \Delta_r H° - T\Delta_r S° = 116.33 \frac{kJ}{mol} - 298.15K \times 0.17475 \frac{kJ}{mol\,K} = \boxed{64.23 \frac{kJ}{mol}}$

$\Delta_r H° = \sum \Delta H_f°(products) - \sum \Delta H_f°(reactants) = -601.85 \frac{kJ}{mol} - 393.51 \frac{kJ}{mol} - (-1111.69 \frac{kJ}{mol}) = 116.33 \frac{kJ}{mol}$

$\Delta_r S° = \sum \Delta S_f°(products) - \sum \Delta S_f°(reactants) = 26.85 \frac{J}{mol\,K} + 213.74 \frac{J}{mol\,K} - 65.84 \frac{J}{mol\,K} = 174.75 \frac{J}{mol\,K}$

(b) Over what temperature range is the reaction predicted to be product-favored at equilibrium?

$\Delta G = 0$ when $T = \frac{\Delta H}{\Delta S} = \frac{116.33 \text{ kJ/mol}}{0.17475 \frac{kJ}{mol\,K}} = 665.7K$

As T increases, ΔG decreases. So $\Delta G < 0$ when $T > 665.7K$

The reaction is product-favored at equilibrium when $\Delta G < 0$, so when $T > 665.7K$

(c) What is the equilibrium constant of the above reaction at T = 500 K? R = 8.314 J/mol K

$\Delta G_f° = -RT\ln(K)$

$-\frac{\Delta G_f°}{RT} = \ln(K)$

$K = e^{\frac{-\Delta G_f°}{RT}} = e^{\frac{-64.87 \text{ kJ/mol}}{0.008314 \frac{kJ}{mol\,K} \times 500K}} = e^{-15.61} \approx 1.67 \times 10^{-7}$

Question 20 (18.31):
For the synthesis of ammonia from its elements at 25 °C, $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$
$\Delta f\ G°\ N_2\ (g) = \Delta f\ G°\ H_2\ (g) = 0$ kJ/mol $\Delta f\ G°\ NH_3\ (g) = -16.37$ kJ/mol

(a) Calculate $\Delta_r\ G°$. Is the reaction product-favored at equilibrium?

$\Delta_r G° = \sum \Delta_r G°_{products} - \sum \Delta_r G°_{reactants} = -16.37 \frac{kJ}{mol} - (0 \frac{kJ}{mol} + 0 \frac{kJ}{mol}) = \mathbf{-32.74} \frac{kJ}{mol}$

(b) Calculate $\Delta_r G$ when the reactants and product are each present at a partial pressure of 0.10 atm and the reaction is at 350 K. Is the reaction spontaneous under these conditions?

$\Delta_r G = \Delta_r G° - RT \ln(Q)$ $Q = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(0.10\ atm)^2}{(0.10\ atm)^4} = 100$

$= -32.74 \frac{kJ}{mol} - 0.008314 \frac{kJ}{mol\ K} \times 350\ K \times \ln(100)$

$= -19.34 \frac{kJ}{mol}$ Yes, it is spontaneous

Question 21 (18.33):
For each set of compounds below, circle the one of highest entropy. Assume that all are at the same temperature. Briefly explain your reasoning.

(a) HF(g) HCl(g) (HBr(g))

Entropy increases with molar mass

(b) $NH_4Cl(s)$ ($NH_4Cl(aq)$)

Solutions have greater entropy than solids

(c) ($C_2H_4(g)$) $N_2(g)$ (same molar mass)

Entropy increases with molecular complexity

(d) NaCl(s) (NaCl(g))

Solids have lower entropy than gases

Chapter 19: Electrochemistry

Question 22 (19.21):

Consider the following half reactions

Half Reaction	E°(V)
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+ 0.34 V
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	- 0.14 V
$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$	- 0.44 V
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$	- 0.76 V
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	- 1.66 V

(a) Based on $E°$ values, which metal is the most easily oxidized?

$Al(s)$

(b) Which metals on this list are capable of reducing $Fe^{2+}(aq)$ to Fe(s)?

$Zn(s)$, $Al(s)$

(c) Write a balanced chemical equation for the reaction of $Fe^{2+}(aq)$ with Sn(s). Is this reaction product- favored or reactant-favored?

$Fe^{2+}(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + Fe(s)$

$E_{cell}^{\circ} = -0.44V - (-0.14V) = -0.30V$

The reaction is reactant favored

(d) Write a balanced chemical equation for the reaction of $Zn^{2+}(aq)$ with Sn(s). Is this reaction product- favored or reactant-favored?

$Zn^{2+}(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + Zn(s)$

$E_{cell}^{\circ} = -0.76V - (-0.14V) = -0.62V$

The reaction is reactant favored

Question 23 (19.33):

One half-cell in a voltaic cell is constructed from a silver wire electrode in a $AgNO_3$ solution of unknown concentration. The other half-cell consists of a zinc electrode in a 1.0 M solution of $Zn(NO_3)_2$. A potential of 1.48 V is measured for this cell. Use this information to calculate the concentration of $Ag^+(aq)$.

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E° = -0.76$ V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad E° = 0.80$ V

Balanced Equation: $2Ag^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

$E_{cell}^{\circ} = 0.80V - (-0.76V) = 1.56V$

$Q = \frac{[Zn^{2+}]}{[Ag^+]^2}$

$E_{cell} = E_{cell}^{\circ} - \frac{0.0257}{n} \ln(Q)$

$\ln(Q) = \left(\frac{n}{0.0257}\right)(E_{cell}^{\circ} - E_{cell})$

$\ln\left(\frac{[Zn^{2+}]}{[Ag^+]^2}\right) = \left(\frac{2}{0.0257}\right)(1.56V - 1.48V) = 6.226$

$\frac{[Zn^{2+}]}{[Ag^+]^2} = e^{6.226} = 505.6$

$\frac{1}{e^{6.226}} = \frac{[Ag^+]^2}{e}$

$[Ag^+] = 0.044$ M

Question 24 (19.37):
Use standard reduction potentials below to calculate the value of K_{sp} for AgBr (s)

- $AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$ 0.0713 V
- $Ag^+(aq) + e^- \rightarrow Ag(s)$ 0.7994 V

Complete Reaction:

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

$E_{cell} = 0.0713\,V - 0.7994\,V$
$= -0.7281\,V$

$E^\circ_{cell} = \frac{0.0257}{n} \ln(K_{sp})$

$\ln(K_{sp}) = \frac{nE^\circ_{cell}}{0.0257}$

$K_{sp} = e^{nE^\circ_{cell}/0.0257} = e^{\frac{-0.7281}{0.0257}} = 4.967 \times 10^{-13}$

Question 25 (19.49):
Electrolysis of a solution of $CuSO_4$ (aq) to give metal Cu (s) is carried out using a current of 0.66 A. How long should electrolysis continue to produce 0.50 g of copper?

$0.50\,g\,Cu \times \frac{1\,mol\,Cu}{63.546\,g\,Cu} \times \frac{2\,mol\,e^-}{1\,mol\,Cu} \times \frac{96485\,C}{1\,mol\,e^-} \times \frac{1\,s}{0.66\,C} = 2300\,s$

molar mass Cu

$Cu^{2+} + 2e^- \rightarrow Cu$

$F = \frac{96485\,C}{1\,mol\,e^-}$

Question 26 (19.3 & 19.5):
Balance the following redox equations. (a) is in acidic solution (b) is in basic solution

(a) $MnO_4^-(aq) + HSO_3^-(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$

$[MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$ $\quad 2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

$[HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^-] \times 5$ $\quad + 5HSO_3^- + 5H_2O \rightarrow 5SO_4^{2-} + 15H^+ + 10e^-$

$2MnO_4^- + 5HSO_3^- + H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

(b) $Fe(OH)_2(s) + CrO_4^{2-}(aq) \rightarrow Fe(OH)_3(s) + [Cr(OH)_4]^-(aq)$

$(OH^-(aq) + Fe(OH)_2(s) \rightarrow Fe(OH)_3(s) + e^-) \times 3$ $\quad 3OH^-(aq) + 3Fe(OH)_2(s) \rightarrow Fe(OH)_3(s) + 3e^-$

$CrO_4^{2-}(aq) + 4H_2O(aq) + 3e^- \rightarrow [Cr(OH)_4]^- + 4OH^-(aq)$ $\quad + CrO_4^{2-}(aq) + 4H_2O(aq) + 3e^- \rightarrow [Cr(OH)_4]^- + 4OH^-(aq)$

$CrO_4^{2-}(aq) + 3Fe(OH)_2(s) + 4H_2O(aq) \rightarrow [Cr(OH)_4]^- + Fe(OH)_3(s) + OH^-(aq)$

Chapter 25: Nuclear Chemistry

Question 27:
Give an example of each of the four types of nuclear reactions (α emission, β emission, positron emission, electron capture) for $^{235}_{92}U$.

α emission $^{235}_{92}U \rightarrow {}^{4}_{2}\alpha + {}^{231}_{90}Th$

β emission $^{235}_{92}U \rightarrow {}^{0}_{-1}\beta + {}^{235}_{93}Np$

positron emission $^{235}_{92}U \rightarrow {}^{0}_{1}\beta + {}^{235}_{91}Pa$

electron capture $^{235}_{92}U + {}^{0}_{-1}e \rightarrow {}^{235}_{91}Pa$

Question 28 (25.15):
The uranium-235 radioactive decay series, beginning with $^{235}_{92}U$ and ending with $^{207}_{82}Pb$, occurs in the following sequence: α, β, α, β, α, α, α, α, β, β, α. Write an equation for each step in this series.

$$^{235}_{92}U \rightarrow {}^{231}_{90}Th + {}^{4}_{2}He \rightarrow {}^{231}_{91}Pa + {}^{0}_{-1}e \rightarrow {}^{227}_{89}Ac + {}^{4}_{2}He \rightarrow {}^{227}_{90}Th + {}^{0}_{-1}e \rightarrow {}^{223}_{88}Ra + {}^{4}_{2}He \rightarrow {}^{219}_{86}Rn + {}^{4}_{2}He \rightarrow {}^{215}_{84}Po + {}^{4}_{2}He \rightarrow {}^{211}_{82}Pb + {}^{4}_{2}He \rightarrow {}^{211}_{83}Bi + {}^{0}_{-1}e \rightarrow {}^{211}_{84}Po + {}^{0}_{-1}e \rightarrow {}^{207}_{82}Pb + {}^{4}_{2}He$$

Question 29 (25.19): Predict the probable mode of decay for each of the following radioactive isotopes, write an equation to show the products of decay, and briefly explain your reasoning.

(a) bromine-80

$^{80}_{35}Br$

35 protons, 45 neutrons

n >> p, beta emission

$^{80}_{35}Br \rightarrow {}^{0}_{-1}\beta + {}^{80}_{36}Kr$

(b) californium-240

$^{240}_{98}Cf$

98 protons, 142 neutrons

protons > 92, alpha emission

$^{240}_{98}Cf \rightarrow {}^{4}_{2}\alpha + {}^{236}_{96}Cm$

(c) cobalt-61

$^{61}_{27}Co$

27 protons, 34 neutrons

n >> p, beta emission

$^{61}_{27}Co \rightarrow {}^{0}_{-1}\beta + {}^{61}_{28}Ni$

(d) carbon-11

$^{11}_{6}C$

6 protons, 5 neutrons

fewer neutrons than protons, positron emission or electron capture

$^{11}_{6}C \rightarrow {}^{11}_{5}B$

Question 30: Given ${}_1^1H = 1.00783\ amu$ ${}_0^1n = 1.00867\ amu$, calculate the binding energy per mole of nucleons for the following.

(a) ^{11}B (11.00931 g/mol)

^{11}B: 11 nucleons, 6 neutrons and 5 protons

$6n + 5p = 6(1.00867\ g/mol) + 5(1.00783\ g/mol)$

$= 11.09117\ g/mol\ B$

$\Delta m = (11.0917 - 11.00931)\ g/mol\ B = 0.0818\ g/mol\ B = 8.186 \times 10^{-5}\ kg/mol\ B$

~~8.186 kg/mol B~~

Binding energy $= \Delta mc^2 = (8.186 \times 10^{-5}\ kg/mol\ B)(3.00 \times 10^8\ m/s)^2 \left(\frac{1\ J}{1\ kg\ m^2 s^{-2}}\right)$

$= 7.367 \times 10^{12}\ J/mol\ B$

$\frac{\text{Binding energy}}{\text{mol nucleon}} = 6.26 \times 10^8\ \frac{J}{mol\ B} \times \frac{1\ mol\ B}{11\ mol\ nucleon} = 6.70 \times 10^8\ \frac{J}{mol\ nucleon}$

(b) ^{40}Ca (39.96259 g/mol)

^{40}Ca: 40 nucleons, 20 neutrons and 20 protons

$20n + 20p = 20(1.00867\ g/mol + 1.00783\ g/mol)$

$= 40.33\ g/mol\ Ca$

$\Delta m = (40.33 - 39.96259)\ g/mol\ Ca = 0.3674\ g/mol\ Ca = 3.674 \times 10^{-4}\ kg/mol\ Ca$

Binding energy $= \Delta mc^2 = (3.674 \times 10^{-4}\ kg/mol\ Ca)(3.00 \times 10^8\ m/s)^2 \left(\frac{1\ J}{1\ kg\ m^2 s^{-2}}\right)$

$= 3.307 \times 10^{13}\ J/mol\ Ca$

$\frac{\text{Binding energy}}{\text{mol nucleon}} = 3.307 \times 10^{13}\ \frac{J}{mol\ Ca} \times \frac{1\ mol\ Ca}{40\ mol\ nucleons} = 8.26 \times 10^8\ \frac{J}{mol\ nucleon}$

(c) ^{16}O (15.99492 g/mol)

^{16}O: 16 nucleons, 8 neutrons and 8 protons

$8n + 8p = 8(1.00867\ g/mol + 1.00783\ g/mol)$

$= 16.132\ g/mol\ O$

$\Delta m = 16.132\ \frac{g}{mol\ O} - 15.9949\ \frac{g}{mol\ O} = 0.13708\ \frac{g}{mol\ O}$

$= 1.3708 \times 10^{-4}\ kg/mol\ O$

Binding energy $= \Delta mc^2 = 1.234 \times 10^{10}\ \frac{J}{mol\ O}$

$\frac{\text{Binding energy}}{\text{mol nucleon}} = 7.70 \times 10^8\ \frac{J}{mol\ nucleon}$

Question 31: Gallium-67 ($t_{1/2}$ = 78.25 hours) is used in the medical diagnosis of certain kinds of tumors. If you ingest a compound containing 0.015 mg of this isotope, what mass (in milligrams) remains in your body after 13 days? (Assume none is excreted.)

Method 1

$13\ days \times \frac{24\ hrs}{day} \times \frac{1\ half\ life}{78.25\ hrs} = 3.987\ half\ lives$

$\text{mass remaining} = 0.015\ mg \times \left(\frac{1}{2}\right)^{3.987}$

$= 0.000946\ mg$

$= 9.46 \times 10^{-4}\ mg$

Method 2

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{78.25\ hr} = 0.00886\ hr^{-1}$

$13\ days \times \frac{24\ hrs}{day} = 312\ hrs = t$

$\ln(mass) = -kt + \ln(mass_0)$

$\ln(mass) = -0.00886\ hr^{-1} \times 312\ hrs + \ln(0.015)$

$\ln(mass) = -6.883$

~~$9.46 \times 10^{-4}\ mg$~~

$mass = 9.46 \times 10^{-4}\ mg$