### Constants

\[
R = 8.314 \text{ J/mol K} = 0.08314 \text{ L bar/K mol}
\]
\[
F = 9.6485 \times 10^4 \text{ C/mol}
\]
\[
h = 6.63 \times 10^{-34} \text{ J s}
\]
\[
h = 1.05 \times 10^{-34} \text{ J s}
\]
\[
k = 1.3806504 \times 10^{-23} \text{ J/K}
\]
1. The phase diagram for carbon, shown below, indicates the extreme conditions that are needed to form diamonds from graphite.
(a) At 2000 K, what is the minimum pressure needed before graphite changes into diamond? (2%)
(b) What is the minimum temperature at which liquid carbon can exist at pressures below 10000 atm? (2%)
(c) Rank the diamond, graphite, and liquid phases in order of increasing density. Justify your answer. (3%)
(d) At what pressure and temperature do the three phases coexist in mutual equilibrium? What is this point called? (3%)

![Phase Diagram](image)

2. A solution prepared by dissolving 0.52 g of polystyrene in 100 cm$^3$ of benzene showed an osmotic pressure of 3.12 Torr at 25 °C.
(a) Calculate the molar mass of the polymer. (3%)
(b) Calculate the freezing-point depression of the solution. The freezing-point constant of benzene is 5.12 K kg mol$^{-1}$, and the density of benzene 0.88 g cm$^3$. (2%)
(c) Osmometry is commonly used to determine the molar mass of polymers and macromolecules, whereas the freezing-point depression is not. Why? (3%)

3. Draw a phase diagram to show where the supercritical fluids would be. Give one of their applications in chemistry. (4%)

4. The temperature-composition diagram for mixtures of acetonitrile and water is shown below. The upper curve in the figure shows the composition of the vapor in equilibrium with the liquid mixture at the boiling point, and the lower the
variation in the boiling point with the composition of the liquid mixture.

(a) What phase(s) exist at points P, Q, and R? (3%)

(b) Determine the composition of the vapor formed when a mixture of acetonitrile and water with $x_{AN} = 0.10$ begins to boil. (2%)

(c) Is the enthalpy of mixing $\Delta H_{\text{mix}}$ in this case positive or negative? Explain your answer. (3%)

(d) From the sign of $\Delta H_{\text{mix}}$, what can you conclude (just qualitatively) about intermolecular interactions in pure acetonitrile and water and in their mixtures? (3%)
5. A chemist needs to prepare the compound \( \text{PH}_3\text{BCl}_3 \) by using the reaction \( \text{PH}_3(\text{g}) + \text{BCl}_3(\text{g}) \rightarrow \text{PH}_3\text{BCl}_3(\text{s}) \) for which \( K = 19.2 \) at 60 °C. (a) Write the expression for \( K \). (b) What is the value of \( K_c \) for this reaction? (c) Some solid \( \text{PH}_3\text{BCl}_3 \) was added to a closed 500-mL vessel at 60 °C that already contains 0.0128 mol \( \text{PH}_3 \). What is the equilibrium concentration of \( \text{PH}_3 \)? (d) At 70 °C, \( K = 26.2 \). Is this reaction endothermic or exothermic? Explain your reasoning. (e) What is the new value of \( K_c \)? (f) Can the reactants in the preceding reaction be classified as acids or bases? Explain your answer. (12%)

6. State whether reactants or products will be favored by an increase in the total pressure (resulting from compression) on the following equilibria. If there is no change, explain why that is so. (6%)

   (a) \( 2 \text{O}_3(\text{g}) = 3 \text{O}_2(\text{g}) \)
   (b) \( \text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) = \text{H}_2(\text{g}) + \text{CO(\text{g})} \)
   (c) \( 2 \text{HD}(\text{g}) = \text{H}_2(\text{g}) + \text{D}_2(\text{g}) \)

7. Predict whether each of the following equilibria will shift toward products or reactants with a temperature decrease: (4%)

   (a) \( \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{CO(\text{g})} + \text{H}_2(\text{g}), \Delta H^\circ = +206 \text{ kJ.} \)
   (b) \( \text{CO(\text{g})} + \text{H}_2\text{O(\text{g})} = \text{CO(\text{g})} + \text{H}_2(\text{g}), \Delta H^\circ = -41 \text{ kJ.} \)

8. Calculate the reaction Gibbs free energy of \( \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g}) \) at 230 °C when the partial pressures of \( \text{PCl}_3, \text{Cl}_2, \) and \( \text{PCl}_5 \) are 0.22 bar, 0.41 bar, and 1.33 bar, respectively. What is the spontaneous direction of change, given that \( K = 49 \) at this temperature. (8%)

9. Describe the functions of hemoglobin (Hb) and myoglobin (Mb) in the body. (3%)
10. A electrochemical cell: C(gr)|Cl\(_2\)(g)|Cl\(^{-}\)(aq)||MnO\(_4^{-}\)(aq),H\(^{+}\)(aq),Mn\(^{2+}\)(aq)|Pt(s).

(a) Write two half reactions and the balanced equation for the cell reaction.
(b) The standard potentials for the couples MnO\(_4^{-}/\)Mn\(^{2+}\) and Cl\(_2/\)Cl\(^{-}\) are +1.51 and +1.36 V, respectively. Calculate the standard emf of this cell.
(c) Write the expression for reaction quotient and calculate the standard reaction Gibbs free energy at 25°C.
(d) If the concentration of chemicals in this cell are prepared as:
\[ \text{C(gr)|Cl}_2(g, 1.0 \text{ bar})|\text{Cl}^{-}(aq, 0.10 \text{ M})||\text{MnO}_4^{-}(aq, 0.010 \text{ M}), \text{H}^{+}(\text{pH} \text{ 4.0}), \text{Mn}^{2+}(aq, x \text{ M})|\text{Pt(s)} \]
and an emf of -0.30 V is measured. What’s the concentration of Mn\(^{2+}\)?
(e) Does the reaction of the cell in question (d) take place spontaneously or not? Is it possible to change the reaction from spontaneous to nonspontaneous (OR from nonspontaneous to spontaneous) by decreasing pH? If your answer were YES, what’s the pH needed to be adjusted to?

11. \( \text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^{+} + 6 \text{ e}^{-} \rightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O} \quad E^\circ = +1.33 \text{ V} \)
\( \text{Cr}^{3+} + \text{ e}^{-} \rightarrow \text{ Cr}^{2+} \quad E^\circ = -0.41 \text{ V} \)
\( \text{Cr}^{2+} + 2 \text{ e}^{-} \rightarrow \text{ Cr} \quad E^\circ = -0.91 \text{ V} \)
Calculate the \( E^\circ \) of the half reaction: \( \text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^{+} + 12 \text{ e}^{-} \rightarrow 2 \text{ Cr} + 7 \text{ H}_2\text{O} \).

12. The cell notation of a commercial nicad battery is written as:
\( \text{Cd(s)|Cd(OH)}_2(s)|\text{KOH(aq)}||\text{Ni(OH)}_3(s)|\text{Ni(OH)}_2(s)|\text{Ni(s)} \). Nickel metal is not involved in the electrode reactions.

(a) Write the anode and cathod reactions.
(b) Why this cell can maintain a stable potential difference at 1.25V?
(c) For a nicad cell that provides energy of 250 J, what’s the mass of \( \text{Ni(OH)}_3 \) has to be loaded in this cell at least?
Solutions:

1. (a) 7.0 GPa  
   (b) 4100 K  
   (c) graphite < diamond < liquid  
   The diamond-graphite boundary has a positive slope, so diamond is denser than graphite. The slope of the diamond-liquid boundary is negative, so diamond is less dense than liquid carbon.  
   (d) At about 14.5 GPa (14~15 GPa) and 4100 K (4000~4200K). (2%) Triple point. (1%)  

2. (a) van’t Hoff equation: \( \Pi = cRT \) (the \( i \) factor is equal to unity because polystyrene is a nonelectrolyte.)  
   \[
   \frac{3.12}{760} = \frac{0.52}{0.100} \times \frac{0.082 \times 298}{M} 
   \]
   \[M = 3.09 \times 10^4 \approx 3.1 \times 10^4 \text{ g mol}^{-1}\]  
   (b) \( \Delta T_f = k_i m = 5.12 \times \frac{0.52 / 3.095 \times 10^4}{100 \times 0.88 \times 10^{-3}} = 9.77 \times 10^{-4} \approx 9.8 \times 10^{-4} \text{ K}\)  
   (c) As estimated in part (b), the freezing-point depression is usually too small to be measured with high accuracy, so osmometry would be the preferred method for determining the molar mass of polymers and macromolecules.  

3. The supercritical fluid has found many applications in chemistry such as environmentally benign solvents for extraction. (2%)
4. (a) P: Vapor, Q: Vapor and liquid, R: Liquid (1% each)
(b) $x_{AN} = 0.55$ (0.53~0.58)
(c) Since the mixture boils at a lower temperature than do the component liquids, the vapor pressure of the mixture is higher than predicted by Raoult’s law (positive deviation). Therefore the mixing process is endothermic, and the enthalpy of mixing $\Delta H_{mix}$ is positive.
(d) $\Delta H_{mix} > 0$ indicates that upon mixing, acetonitrile and water molecules would form less stable molecular structures than in pure solvents. In other words, intermolecular interactions between acetonitrile and water molecules in the binary mixture are unfavorable compared with those among acetonitrile molecules and among water molecules.

5. Ans: (a) $K = 1/P_{PH_3} P_{BCl_3}$ (1%)
(b) $K = K_c (RT)^{\Delta n} = K_c (RT)^{-2};$
   $K_c = 19.2/ (0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}) (333 \text{ K})^{-2} = 1.48 \times 10^4.$ (2%)
(c) $P_{PH_3} = nRT/V = 0.710 \text{ bar.}$ (1%)

\[
\begin{array}{c|c|c}
\text{PH}_3 + \text{BCl}_3 & \text{PH}_3 \text{BCl}_3 \\
0.710 & 0 \\
0.710 + x & x \\
\end{array}
\]

$K = 19.2 = 1/(0.710 + x) x ;$ (1%)

$x = 0.067; P_{PH_3} = 0.710 + 0.067 = 0.777$

$c_{PH_3} = P_{PH_3} / RT = 0.028 \text{ mol L}^{-1}.$ (1%)

(d) $K$ increases as $T$ increases, (favors products) the reaction is endothermic. (2%)
(e) $K_c = K / (RT)^{\Delta n} = 2.13 \times 10^4$ (2%)
(f) PH$_3$ is a Lewis base while BCl$_3$ is a Lewis acid. (2%)
6. Ans: There is a net increase in the amount of gas for both (a) and (b), then applying pressure will shift the reaction toward reactants in order to remove the stress applied by increasing the pressure. (a) reactants; (b) reactants; (c) no change

7. Ans: (a) endothermic reaction, lowering the temperature will tend to shift the reaction toward reactants. (b) favor products.

8. Ans: 
\[ \Delta G_r = \Delta G^\circ_r + RT \ln Q \]
\[ = -RT \ln K + RT \ln Q \]
\[ = -(8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1})(503 \text{ K}) \left[ \ln(49+\ln1.33/(0.22\times0.41)) \right] \]
\[ = -5.0 \text{ kJ mol}^{-1}. \]  
Because \( \Delta G_r \) is negative, the reaction will be spontaneous to form products.

9. Ans: Hb is the major oxygen carrier from lungs to muscle tissues. Mb acts as a reserve only when the Hb oxygen has been used up.

10. (a) half reactions: 
\[ 2 \text{Cl}^{-} (\text{aq}) \rightarrow \text{Cl}_2 (g) + 2 \text{e}^-; \]
\[ \text{MnO}_4^{-} (\text{aq}) + 8 \text{H}^+ (\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4 \text{H}_2\text{O} ; \]
balanced equation:
\[ 2 \text{MnO}_4^{-} (\text{aq}) + 16 \text{H}^+ (\text{aq}) + 10 \text{Cl}^{-} \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 5 \text{Cl}_2 (g) + 8 \text{H}_2\text{O} \]
(b) \[ 1.51-1.36 = 0.15 \text{ (V)} \]
(c) \[ Q = \left[ \text{Mn}^{2+} \right]^2 \left[ \text{Pc}_{12} \right]^5 / \left[ \text{MnO}_4^{-} \right]^2 \left[ \text{H}^+ \right]^{16} \left[ \text{Cl}^- \right]^{10} \]
\[ G_r^\circ = -nFE = -10 \times 96485 \times 0.16 = 154 \times 10^3 \text{ J/mol} \]
(d) \[ E = E^+ - (RT/nF) \ln Q = E^+ - 0.05917/n \log Q \]
\[ \rightarrow -0.30 = 0.15 - 0.05917/10 \log(x^2 \times 10^5 / 0.01^2 \times 10^{-4} \times 0.1^{10}) \]
\[ 76 = \log(x^2 \times 10^{78}) \rightarrow \log x = -1.0 \rightarrow \left[ \text{Mn}^{2+} \right] = 0.10 \text{ M} \]
(e) nonspontaneous; 
Increasing [H\(^+\)] will raise E. When E is raised > 0 V, the reaction takes place spontaneously. 
when \[ E = 0 = 0.15 - 0.05917/10 \log(0.11^2 \times 1^5 / 0.01^2 \times [\text{H}^+]^{16} \times 0.1^{10}) \], pH 0.8
\[ \rightarrow \text{pH} < 0.8, E > 0, \text{ the reaction takes place spontaneously} \]
11. \[ G^\circ = -F \times (6 \times 1.33 - 2 \times 0.41 - 4 \times 0.91) = -F \times 3.52 \]

\[ E^\circ = \frac{G^\circ}{-12F} = +0.29 \text{ (V)} \]

12. (a) anode: Cd(s) + 2 OH\(^{-}\)(aq) \rightarrow Cd(OH)\(_2\)(s) + 2 e\(^{-}\)
cathod: Ni(OH)\(_3\)(s) + e\(^{-}\) \rightarrow Ni(OH)\(_2\)(s) + OH\(^{-}\)(aq)

(b) cell reaction: Cd(s) + 2 Ni(OH)\(_3\)(s) \rightarrow Cd(OH)\(_2\)(s) + 2 Ni(OH)\(_2\)(s)
Cd, Cd(OH)\(_2\), Ni(OH)\(_2\), and Ni(OH)\(_3\) are solid

\( \rightarrow \) the reaction quotient \( Q = 1 \) \( \rightarrow \) a constant potential difference

(c) \[ \frac{250 \text{ W}}{1.25 \text{ V}} = 200 \text{ C} \rightarrow 2.07 \times 10^{-3} \text{ mol} \]

\( \rightarrow (2.07 \times 10^{-3}) \times (58.69 + 51) = 0.23 \text{ (g)} \]