Chemistry 4501

Exam III

December 8, 2017

1) There are 10 multiple choice problems and 2 short derivation problems. Each multiple choice problem is worth 8 points and each short derivation problem is worth 20 points.

2) There is one correct answer to every multiple-choice problem. Circle the letter for the answer you believe to be correct. There is no partial credit. There is no penalty for guessing.

3) Show all of your work on the short derivation problems (use back(s) of pages if necessary). Partial credit will be awarded where appropriate.

4) You should try to go through all the problems once quickly, answering those that seem simple immediately, but saving harder ones for later.

5) A list of useful formulae and other data is provided at the end of the exam. No electronic devices of any sort are allowed. You should not need to do any calculations that are not trivial arithmetic.

6) Feel free to tear off the equations pages. The backs of those pages may also prove useful as scratch paper.
1. For a pure-substance pressure/temperature \((P/T)\) phase diagram, which of the below statements is *not* true when a given \(P/T\) point is on one of the *lines* on the diagram?

(a) The chemical potentials of all phases present are equal  
(b) The molar enthalpies of all phases present are equal  
(c) \(\Delta G_{\text{trs}} = 0\)  
(d) At least two phases are in equilibrium  
(e) The Gibbs phase rule applies  
(f) (not used)

2. A given substance has a 1 bar melting point of 300 K with a molar volume of fusion of 0.2 J mol\(^{-1}\) bar\(^{-1}\) and a molar enthalpy of fusion of 10 kJ mol\(^{-1}\). At what rate does the melting temperature change with pressure at 300 K and, based on that, what would you estimate for the melting point at 1001 bar?

(a) \(-2 \times 10^{-3}\) K bar\(^{-1}\); 302 K  
(b) \(6 \times 10^{-3}\) K bar\(^{-1}\); 306 K  
(c) \(-1.5 \times 10^{-2}\) K bar\(^{-1}\); 285 K  
(d) \(-6 \times 10^{-3}\) K bar\(^{-1}\); 294 K  
(e) \(1.5 \times 10^{-2}\) K bar\(^{-1}\); 315 K  
(f) The melting temperature is independent of pressure and does not change

3. Consider a non-ideal two-component solution. Which of the below statements is/are true in the limit of \(x_2 \to 1\) (mole fraction standard state)?

(a) \(P_1 \to x_1 P_1^*\)  
(b) \(P_1 \to x_2 k_{H,1}\)  
(c) \(P_2 \to x_2 P_2^*\)  
(d) \(P_2 \to x_2 k_{H,2}\)  
(e) \(P_1 \to (1-x_2) k_{H,1}\)  
(f) (c) and (e)
4. The below plot is of the chemical potential as a function of pressure for a pure substance having a positive value of $\Delta V_{\text{fus}}$. Which of the following statements is/are true?

(a) The line marked $A$ is the liquid and the temperature is below the triple point
(b) The line marked $B$ is the solid and the temperature is below the triple point
(c) The dashed lines refer to unstable phases that may persist briefly until the system comes to equilibrium
(d) all of the above
(e) (not used)
(f) (not used)

5. The vapor pressure of component 1 of a solution is given by $P_1 = 100x_1\exp(-2x_2^2)$. Which of the below statements is true?

(a) As $x_1 \to 0$, $P_1$ over the solution obeys Raoult’s Law
(b) The solution is ideal
(c) The solution shows positive deviations from ideality
(d) Molecules of each component have less favorable interaction energies with each other than with themselves
(e) $P_1^* = 100$ and $k_{\text{H}_2\text{O}} = 100e^{-2}$
(f) At $x_1 = 0.5$, $\gamma_1 = e^{0.5}$ (Raoult’s standard state)
6. The above temperature-composition diagram is for a binary mixture of phenol and water. Which of the below statements is true when one mole of water is mixed with one mole of phenol at 60° C?

(a) There is one liquid phase with \( x_{\text{phenol}} = x_{\text{water}} \)

(b) There are two liquid phases each with \( x_{\text{phenol}} = x_{\text{water}} \)

(c) There are two liquid phases, one of pure phenol, and one with \( x_{\text{phenol}} < x_{\text{water}} \)

(d) There are two liquid phases, one of pure water, and one with \( x_{\text{phenol}} > x_{\text{water}} \)

(e) There are two liquid phases, one with \( x_{\text{phenol}} < x_{\text{water}} \), and one with \( x_{\text{phenol}} > x_{\text{water}} \)

(f) The two pure liquid phases layer based on density but do not mix

7. A solute has dissolved in an aqueous solution and the volume of mixing is negative. Which of the below statements is always true?

(a) The molality of the solution is less than the molarity

(b) The enthalpy of mixing is positive

(c) The entropy of mixing is negative

(d) The solution will have a lower boiling point than the pure solvent

(e) The solute Henry’s constant is identical in the molal and molar standard states

(f) Distillation will generate an azeotrope
8. Assuming full dissociation, what is the ionic strength of a solution when 0.1 mol of the strong electrolyte \( \text{CaCl}_2 \) is dissolved into 1 L of solution at 350 K (units of charge squared moles per liter).

(a) 0.0  
(b) 0.2  
(c) 0.3  
(d) 0.6  
(e) 0.8  
(f) 1.0

9. Which of the following statements about \( K_p \) is/are true?

(a) It equals \(-Q_p\) at equilibrium  
(b) It equals \(\exp(\Delta_r G^0/RT)\)  
(c) It is a pressure-dependent quantity  
(d) It is a temperature-dependent quantity  
(e) (a), (b), and (d)  
(f) All of the above

10. \[ \Delta_f H^0 (\text{HBr}) = -200 \text{ kJ mol}^{-1} \quad \Delta_f S^0 (\text{HBr}) = 150 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ \Delta_f S^0 (\text{Br}_2) = 400 \text{ J mol}^{-1} \text{ K}^{-1} \quad \Delta_f S^0 (\text{H}_2) = 200 \text{ J mol}^{-1} \text{ K}^{-1} \]

Given the above standard molar enthalpies and entropies of formation at 400 K and 1 bar, what is the standard molar Gibbs free energy of reaction for the below process with all species as gases at 400 K and 1 bar?

\[ \frac{1}{2} \text{Br}_2 + \frac{1}{2} \text{H}_2 \rightleftharpoons \text{HBr} \]

(a) \(-140 \text{ kJ mol}^{-1}\)  
(b) \(-126 \text{ kJ mol}^{-1}\)  
(c) \(-115 \text{ kJ mol}^{-1}\)  
(d) 0 kJ mol\(^{-1}\)  
(e) 64 kJ mol\(^{-1}\)  
(f) 108 kJ mol\(^{-1}\)
11. (Short answer) What is an azeotrope? What purification can be accomplished for a liquid mixture that is not already at the azeotropic composition (and explain how this purification proceeds)? You may find it helpful in answering this question to create a phase diagram of mole fraction vs temperature, labeling important features appropriately.
12. (Short derivation) Consider the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$. Assuming that you start with 1 mole of $\text{N}_2\text{O}_4$ and 0 moles of $\text{NO}_2$, compute the equilibrium constant $K_p$ if the extent of reaction at equilibrium $\xi_{eq} = 0.2$ for a constant total pressure of $P = 1.5$ bar and a standard state pressure of 1 bar. If the pressure were increased to 3 bar, explain how $K_p$ and/or $\xi_{eq}$ would change (you don’t need to do any new calculations — just give a qualitative explanation).
Mathematical Formulae

\[ e^x = \sum_{j=0}^{\infty} \frac{x^j}{j!}, \quad e^x = \sum_{j=0}^{\infty} \frac{1}{1-x}, \quad |x| < 1 \]
\[ \ln(N!) = N \ln N - N \quad \text{(Stirling’s approx.)} \]

Results from Quantum Mechanics

\[ E = h \nu = h c \omega \quad c = \lambda \nu \quad \hbar = h / 2\pi \quad D_e = D_0 + h \nu / 2 \]

\[ \varepsilon_n = \frac{n^2 \hbar^2}{8ma^2}, \quad n = 1,2,\ldots, \quad g_n = 1 \]

\[ \varepsilon_j = J(J+1)\frac{\hbar^2}{2I}, \quad j = 0,1,2,\ldots, \quad g_j = 2J+1, \quad \Theta_{\text{rot}} = \frac{\hbar^2}{(2Jk_B)} \]

\[ \varepsilon_n = (n + \frac{1}{2})h\nu, \quad n = 0,1,2,\ldots, \quad g_n = 1, \quad \Theta_{\text{vib}} = h\nu / k_B \]

Gases and Equations of State

\[ \text{compressibility factor } Z = \frac{P\bar{V}}{RT} \quad P\bar{V} = RT \quad \text{(ideal gas)} \]
\[ X_R = X / X_c \quad X = P,V,T \]
\[ \left( P + \frac{a}{\bar{V}^2} \right)(\bar{V} - b) = RT \quad \text{(van der Waals)} \]
\[ Z = 1 + B_2P(T) + B_3P(T)P^2 + \cdots \quad \text{(virial } P) \]
\[ Z = 1 + B_2V(T) \frac{1}{\bar{V}} + B_3V(T) \frac{1}{\bar{V}^2} + \cdots \quad \text{(virial } V) \]
\[ B_2V(T) = RTB_2P(T) = \bar{V} - \bar{V}_{\text{ideal}} \]
\[ u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad \text{(Lennard-Jones potential)} \]

Statistical Thermodynamics

\[ Q = \sum_j \text{ states } e^{-E_j / k_B T} \quad Q = \sum_j \text{ levels } g_j e^{-E_j / k_B T} \quad p_j = \frac{g_j e^{-E_j / k_B T}}{Q} \]
\[ Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \quad \text{(ideal gas)} \]
\[ q(V,T) = q_{\text{elec}}(T)q_{\text{trans}}(V,T)q_{\text{rot}}(T)q_{\text{vib}}(T) \]
\[ q_{\text{trans}}(V,T) = \left( \frac{2\pi mk_BT}{\hbar^2} \right)^{3/2} V \quad q_{\text{rot}}(T) = \frac{2I_kB_T}{\sigma h^2} \quad q_{\text{vib}}(T) = \prod_j \frac{\epsilon^{-h\nu_j / k_BT}}{1 - \epsilon^{-h\nu_j / k_BT}} \]
\[ U = \langle E \rangle = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \quad C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V} \]
Chemical Equilibria
Phase Equilibria and Solutions
Thermodynamic Laws

\( dU = \delta q + \delta w \)

\( C_V(T) = \left( \frac{\partial U}{\partial T} \right)_V \)

\( \delta w = -P_{eq} dV \)

\( \Delta U = q + w \)

\( dS \geq \frac{\delta q}{T} \)

\( dS = \frac{\delta q_{rev}}{T} \)

\( H = U + PV \)

\( C_P(T) = \left( \frac{\partial H}{\partial T} \right)_P \)

\( A = U - TS \)

\( G = H - TS \)

\( \left( \frac{\partial G}{\partial T} \right)_P = -S \)

\( \left( \frac{\partial G}{\partial P} \right)_T = V \)

\( \left[ \frac{\partial (\Delta G / T)}{\partial T} \right]_P = -\frac{\Delta H}{T^2} \)

\( G^*(T)_{\text{ideal gas}} = G^o(T) + RT \ln \left( \frac{P}{P^o} \right) \)

\[ \frac{dP}{dT} = \frac{\Delta_{trs} \tilde{H}}{T \Delta_{trs} \tilde{V}} \]

\[ \frac{d(\ln P)}{dT} = \frac{\Delta_{trs} \tilde{H}}{RT^2} \]

\[ \mu_j = \left( \frac{\partial A}{\partial n_j} \right)_{T,V,n_{i\neq j}} \]

\[ \left( \frac{\partial G}{\partial n_j} \right)_{T,P,n_{i\neq j}} \]

\[ G(T,P,\mu_1,\mu_2) = n_1 \mu_1 + n_2 \mu_2 \]

\[ \mu(T,P) = \mu^o(T) + RT \ln \left( \frac{P}{P^o} \right) \]

\[ x_1 d\mu_1 + x_2 d\mu_2 = 0 \]

\[ \mu^s_{ln} = \mu^*_{ln} + RT \ln \frac{P_j}{P^*} \]

\[ P_j = x_j \mu^* \text{(Raoult)} \]

\[ P_j = x_j k_{H,j} \text{(Henry)} \]

\[ a_j = \frac{P_j}{A_j}, A_j = \begin{cases} P^*_1, \text{Raoult} \\ k_{H,x_1}, \text{Henry (mol frac)} \\ k_{H,m_1}, \text{Henry (molal)} \\ k_{H,c_1}, \text{Henry (molar)} \end{cases} \]

\[ a_j = \frac{k_{H,x_1}}{k_{H,m_1} + k_{H,c_1}}, B_j = \frac{m_2}{c_2}, \text{Henry (molal)} \]

\[ \Delta T_{fus} = \nu K_f m \]

\[ \Delta T_{vap} = \nu K_b m \]

\[ \Pi = \nu c v T \]

\[ \ln \gamma_\pm = -\left[ q_+ q_- \right] \frac{\kappa}{8 \pi \epsilon_0 \epsilon_1 k_B T} \]

\[ \kappa^2 = \frac{2 N_A}{\epsilon_0 \epsilon_1 k_B T} I_c \]

\[ I_c = \frac{1}{2} \sum_j c_j q_j^2 \]

Chemical Equilibria

\[ \Delta_r G^*(T) = \Delta_r G^o(T) + RT \ln Q_P \]

\[ \Delta_r G^o(T) = -RT \ln K_P \]

\[ \left\{ \frac{\partial [\ln K_P(T)]}{\partial T} \right\}_P = \frac{\Delta_r H^o}{RT^2} \]

For example reaction: \( aA_{(g)} + bB_{(g)} \rightleftharpoons yY_{(g)} + zZ_{(g)} \)

\[ \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \Delta_r G = \mu_y + \mu_z - a \mu_a - b \mu_b \]

\[ \left( \frac{\partial H}{\partial \xi} \right)_{T,P} = 0 \]

\[ Q_P(T) = \left( \frac{P_Y}{P^o} \right)^y \left( \frac{P_Z}{P^o} \right)^z \]

\[ K_P(T) = \left( \frac{P_Y}{P^o} \right)^y \left( \frac{P_Z}{P^o} \right)^z \]

\[ K_C(T) = \left( \frac{q_A}{V_s^o} \right)^a \left( \frac{q_B}{V_s^o} \right)^b \]

\[ \left( \frac{q_Y}{V_s^o} \right)^y \left( \frac{q_Z}{V_s^o} \right)^z \]