Chemistry 4501

Final Exam

December 20, 2017

1) There are 20 multiple choice problems and 4 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. 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. Their backs may also prove useful as scratch paper.
1. For water (H₂O) in a 1 L box, what will be the relative numbers of different quantized energy levels within an energy window of 10,000 cm⁻¹ above D₀ for the electronic ground state?

(a) translational < rotational < vibrational < electronic
(b) rotational < translational < vibrational < electronic
(c) electronic < vibrational < rotational < translational

(d) translational < vibrational < rotational < electronic
(e) translational < electronic < rotational < vibrational
(f) the same number of all levels will be found

2. A certain gas is well described by the van der Waals equation of state at a certain temperature T. As the molar volume is increased, to what value does the compressibility factor Z converge?

(a) Zero
(b) One
(c) R
(d) kₐ
(e) e
(f) π²

3. For a linear molecule, what is the contribution to the molar constant volume heat capacity from rotation?

(a) (3/2)kₐ
(b) Nₐ
(c) kₐ
(d) 1 cm⁻¹
(e) It depends on the mass
(f) R

4. Which of the following statements about energy levels and states is true at thermal equilibrium?

(a) There can be greater population of a higher energy state compared to a lower energy state
(b) There are always more levels than states
(c) There may be more states than levels
(d) There can be greater population of a higher energy level compared to a lower energy level
(e) (c) and (d)
(f) All of the above
5. The below plot shows the second virial coefficient, $B_{2v}$, as a function of $T$ for 4 different gases. If you have the same number of moles in the same size container for each gas at 300 K, which gas has the lowest pressure, $P$?

(a) He  
(b) N$_2$  
(c) CH$_4$  
(d) CO$_2$  
(e) All pressures will be equal  
(f) (not used)

6. Consider the following empirically developed gas partition function:

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi mk_B T}{h^2}\right)^{3N/2} (V - Nb)^N e^{aN^2/k_BT}$$

where $a$ and $b$ are non-negative empirical constants. If $a$ and $b$ are both greater than zero, what is the pressure for the gas?

(a) $P = \frac{Nk_B T}{V}$  
(b) $P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$  
(c) $P = P_c$  
(d) $P = \frac{Nk_B T}{V - b} - \frac{aN^2}{T^{1/2}V^2}$  
(e) $P = \frac{Nk_B T}{V} + \frac{Nab}{V^2} + \frac{Na^2b^2}{V^3} + \cdots$  
(f) 1 bar
7. The partition function $Q$ for a system of all non-degenerate levels, and having a ground state energy of 0, is equal to 2. What fraction of the population is in the ground state?

(a) 0%  
(b) 11%  
(c) 50%  
(d) 67%  
(e) 75%  
(f) 100%

8. Which of the following are state functions?

(a) Energy $U$  
(b) Gibbs free energy $G$  
(c) Entropy $S$  
(d) Helmholtz free energy $A$  
(e) (a) and (c)  
(f) All of the above

9. One mole of an ideal gas is expanded adiabatically to twice its original volume. What is the net transfer of heat $q$ from the surroundings?

(a) $-(3/2)RT$  
(b) $-2J$  
(c) $0J$  
(d) $(3/2)RT$  
(e) $-w$  
(f) $\Delta U$

10. Consider the reversible, isothermal expansion of an ideal gas from a pressure of 10 bar to 2 bar. Defining the system as the gas and the surroundings as the universe, the change in the entropy of the system at 300 K is $13.4 \text{ J mol}^{-1} \text{ K}^{-1}$. Now, which of the following statements is always true if the same isothermal expansion is carried out, but not reversibly?

(a) The entropy change for the system will be $13.4 \text{ J mol}^{-1} \text{ K}^{-1}$  
(b) The entropy change for the surroundings will be positive  
(c) The total entropy change (sum of system and surroundings) will be larger than in the reversible case  
(d) (a) and (b)  
(e) (a) and (c)  
(f) all of the above
11. To what is \( \left( \frac{\partial S}{\partial P} \right)_T \) equal?

(a) \( \left( \frac{\partial P}{\partial V} \right)_T \)  
(b) \( \left( \frac{\partial A}{\partial T} \right)_V \)  
(c) \( \left( \frac{\partial G}{\partial T} \right)_S \)  
(d) \( \left( \frac{\partial P}{\partial S} \right)_T \)  
(e) \(-\left( \frac{\partial V}{\partial T} \right)_P \)  
(f) \( \left( \frac{\partial P}{\partial T} \right)_V \)

12. The below plot is of the chemical potential as a function of pressure for a pure substance having a negative value of \( \Delta V_{\text{fus}} \). Which of the following statements is false?

(a) The line marked A is the liquid  
(b) The line marked B is the solid  
(c) Raising the temperature would lower line B relative to line A  
(d) The line marked C is the gas  
(e) At no point are all three phases in equilibrium  
(f) The temperature is below the critical point
13. The pressure on an incompressible solid having a molar volume of 0.2 L is increased from 10 bars to 20 bars at a constant temperature 300 K. By how much does the molar free energy of the solid increase? (All answers have units of L-bar/mol, you may assume \( R = 0.1 \) L-bar/K-mol)

(a) 0  
(b) 1  
(c) 2  
(d) 30  
(e) 30 \ln 2  
(f) 60

14. When two liquids having a total number of molecules that sums to one mole are mixed, what is the final volume? In the answers \( V \) is an initial pure volume, \( \bar{V} \) is a partial molar volume, \( n \) is number of moles, and \( x \) is mole fraction.

(a) \( \bar{V}_1 + \bar{V}_2 \)  
(b) \( x_1 V_1 + x_2 V_2 \)  
(c) \( n_1 \bar{V}_1 + n_2 \bar{V}_2 \)  
(d) \( V_1 + V_2 \)  
(e) \( x_1 \bar{V}_1 + x_2 \bar{V}_2 \)  
(f) \( (c) \) and \( (e) \)

15. Consider 0.001 mol of the strong electrolyte Na\(_2\)SO\(_4\) dissolved into 1 L of water at 300 K. Which of the below statements is/are true?

(a) The conductivity of the solution is the same as that measured for pure water  
(b) The mean ionic activity coefficient is less than 1  
(c) The mean ionic activity coefficient is greater than 1  
(d) The freezing point depression is smaller than what would be observed if 0.001 mol CaCl\(_2\) were substituted for Na\(_2\)SO\(_4\)  
(e) The ionic strength of the solution is 0.002 mol L\(^{-1}\)  
(f) The inverse Debye length \( \kappa^{-1} \) will decrease at higher temperatures

16. Given the electrochemical cell reaction \( \text{H}_2(g) + \text{PbSO}_4(s) \rightleftharpoons 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + \text{Pb}(s) \), which of the following changes would not decrease the cell voltage?

(a) Increase in the size of the lead electrode  
(b) Decreased solution pH  
(c) Dissolution of K\(_2\)SO\(_4\)  
(d) Dissolution of HBr  
(e) Decreased pressure of H\(_2\)  
(f) (not used)
17. Consider the below composition diagram. Which of the below statements is/are true for either 1 or 2 as a solute in solution (in the mole fraction Henry’s law standard state)?

(a) \( k_{H,1} = P_1 \)
(b) \( \gamma_1 \) is less than 1 over the range \( 0.2 \leq x_1 \leq 0.8 \)
(c) Molecules of each component have less favorable interaction energies with each other than with themselves
(d) \( k_{H,2} < 200 \) torr
(e) \( \gamma_2 = 1 \) for \( x_1 \sim 0.55 \)
(f) The solution behaves ideally

18. Consider the dissociation of dilithium in the gas phase \( \text{Li}_2 \rightleftharpoons 2\text{Li} \). If we start with 2 moles of dilithium and zero moles of lithium, which of the following equations correctly expresses the equilibrium constant as a function of the extent of reaction \( \xi \) and the total pressure \( P \) assuming ideal behavior of the gases?

(a) \( K_P = \frac{4\xi_{eq}^2}{4 - \xi_{eq}^2} P \)
(b) \( K_P = \frac{4\xi_{eq}^2}{2 - \xi_{eq}} P \)
(c) \( K_P = \frac{2\xi_{eq}^2}{4 - \xi_{eq}^2} P^2 \)
(d) \( K_P = \frac{2\xi_{eq}^2}{4(1 - \xi_{eq})} P \)
(e) \( K_P = \frac{2\xi_{eq}^2}{2 + \xi_{eq}} P \)
(f) \( K_P = \xi_{eq} P^{-1} \)
19. What is the purpose of a salt bridge in an electrochemical cell?

(a) It carries current corresponding to the non-reversible work that can be harvested from the full cell.

(b) It permits the Gibbs-Duhem equation to govern the Debye-Hückel behavior of the ions in solution.

(c) It maintains all electrolyte solutions at unit activity to ensure constant voltage.

(d) It transfers heat efficiently from one half cell to the other so that the temperature remains constant.

(e) It permits transfer of non-redox active ions between half-cells to maintain charge balance during cell operation.

(f) It makes the cell taste much better when sprinkled in sparingly.

20. Standard reduction potentials are shown for 2 half-cells below. What is the standard notation for a full cell constructed from these two half cells, the standard potential for the full cell, and the correct value of \( n \) to be used in relating the potential to free energy?

\[
\begin{align*}
\text{Cd}^{2+}(aq) + 2e^- &\rightarrow \text{Cd(s)} \quad E^o = -0.40 \text{ V} \\
\text{In}^{3+}(aq) + 3e^- &\rightarrow \text{In(s)} \quad E^o = -0.34 \text{ V}
\end{align*}
\]

(a) \( \text{In(s) } | \text{In(NO}_3^3\text{)}(aq) \ || \text{CdCl}_2(aq) \ ) | \text{Cd(s)}, E^o = 0.12 \text{ V}, n = 1

(b) \( \text{In(s) } | \text{In(NO}_3^3\text{)}(aq) \ || \text{CdCl}_2(aq) \ ) | \text{Cd(s)}, E^o = 0.06 \text{ V}, n = 6

(c) \( \text{In(s) } | \text{In(NO}_3^3\text{)}(aq) \ || \text{CdCl}_2(aq) \ ) | \text{Cd(s)}, E^o = 0.01 \text{ V}, n = 6

(d) \( \text{Cd(s) } | \text{CdCl}_2(aq) \ || \text{In(NO}_3^3\text{)}(aq) \ ) | \text{In(s)}, E^o = 0.06 \text{ V}, n = 6

(e) \( \text{In(s) } | \text{In(NO}_3^3\text{)}(aq) \ || \text{CdCl}_2(aq) \ ) | \text{Cd(s), E}^o = 0.06 \text{ V}, n = 1

(f) \( \text{In(s) } | \text{In(NO}_3^3\text{)}(aq) \ || \text{CdCl}_2(aq) \ ) | \text{Cd(s), E}^o = 0.06 \text{ V}, n = 6
21. (short answer) A temperature composition diagram for phenol and water is shown below at right. Describe in words what would be observed in a flask containing one mole of water and one mole of phenol as the temperature is raised from 25 to 80 °C.
22. (short derivation) The coefficient of thermal expansion for a substance, $\alpha$, and its isothermal compressibility, $\kappa$, are defined below. Compare and contrast the values for each of these quantities at 1 bar and 300 K for an ideal gas and a hard-sphere gas, where the latter obeys the equation of state $P(\bar{V} - b) = RT$, and $b$ is a positive constant.

$$\alpha = \frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial T} \right)_p$$ and $$\kappa = -\frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial P} \right)_T$$
23. Sketch a pressure-temperature phase diagram (pressure on y axis, temperature on x axis) showing colligative effects on boiling and melting for a water solution. Label the diagram to make clear how freezing point changes, boiling point changes, liquid vapor pressure changes, and how lines on the diagram relate to adjacent phases.
24. Considering the total differential of the entropy as a function of temperature and pressure, as well as the total differential of the enthalpy expressed in its natural variables (which can be quickly derived using the 1st and 2nd Laws), derive expressions for (i) the constant-pressure temperature dependence of the entropy, and (ii) the constant-temperature pressure dependence of the entropy.
Mathematical Formulae

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

Results from Quantum Mechanics

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

translation (1D):  \quad $$\epsilon_n = \frac{n^2 \hbar^2}{8ma^2}, \quad n = 1,2,..., \quad g_n = 1$$

rot. (1D):  \quad $$\epsilon_j = J(J+1)\frac{\hbar^2}{2I}, \quad J = 0,1,2,..., \quad g_J = 2J+1, \quad \Theta_{\text{rot}} = \hbar^2/(2Jk_B)$$

vib. (1 mode):  \quad $$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar \nu, \quad n = 0,1,2,..., \quad g_n = 1, \quad \Theta_{\text{vib}} = \hbar \nu / k_B$$

Gases and Equations of State

compressibility factor $$Z = \frac{P\tilde{V}}{RT}$$  \quad $$\tilde{P}\tilde{V} = RT \quad \text{(ideal gas)}$$  \quad $$X_R = X / X_c \quad X = P, V, T$$

$$\left(P + \frac{a}{\tilde{V}^2}\right)(\tilde{V} - b) = RT \quad \text{(van der Waals)}$$  \quad $$Z = 1 + B_2P(T)P + B_3P(T)P^2 + \cdots \quad \text{(virial P)}$$

$$Z = 1 + B_2V(T)\frac{1}{\tilde{V}} + B_3V(T)\frac{1}{\tilde{V}^2} + \cdots \quad \text{(virial V)}$$  \quad $$B_2V(T) = RTB_2P(T)\approx \tilde{V} - \tilde{V}_{\text{ideal}}$$

$$u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \quad \text{(Lennard - Jones potential)}$$

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 $$p_j = \frac{g_j e^{-E_j/k_B T}}{Q}$$

$$Q(N,V,T) = \left[ q(V,T) \right]^N \quad \text{(ideal gas)}$$  \quad $$q(V,T) = q_{\text{elec}}(T)q_{\text{trans}}(V,T)q_{\text{rot}}(T)q_{\text{vib}}(T)$$

$$q_{\text{trans}}(V,T) = \left( \frac{2\pi mk_BT}{\hbar^2} \right)^{3/2} V$$  \quad $$q_{\text{rot}}(T) = \frac{2Ik_BT}{\sigma h^2}$$  \quad $$q_{\text{vib}}(T) = \prod_j^{\text{normal modes}} \frac{e^{-\nu_j/k_BT}}{1 - e^{-\nu_j/k_BT}}$$

$$U = \left< E \right> = k_BT^2 \frac{\partial \ln Q}{\partial T} \quad N,V$$  \quad $$P = k_BT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}$$  \quad $$C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V}$$
Thermodynamic Laws

\[
\frac{dU}{dT} = \delta q + \delta w \quad \delta w = -P_{eq} dV \quad \Delta U = q + w
\]

\[
C_V(T) = \frac{\partial U}{\partial T} \quad dS = \frac{\delta q}{T} \quad dS = \frac{\delta q_{rev}}{T}
\]

\[
H = U + PV \quad C_P(T) = \frac{\partial H}{\partial T} \quad A = U - TS
\]

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

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

Phase Equilibria and Solutions

\[
\frac{dP}{dT} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V} \quad \frac{d(\ln P)}{dT} = \frac{\Delta_{\text{trs}} H}{RT^2} \quad \mu_j = \left( \frac{\partial A}{\partial n_j} \right)_{T,V,n_{eq}} \quad \left( \frac{\partial G}{\partial n_j} \right)_{T,P,n_{eq}}
\]

\[
G(T, P, \mu_1, \mu_2) = n_1 \mu_1 + n_2 \mu_2 \quad \mu_j(T, P) = \mu^o_j(T) + RT \ln \left( \frac{P}{P^o} \right)_{eq} \quad x_1 d\mu_1 + x_2 d\mu_2 = 0
\]

\[
\mu_j^{\text{ln}} = \mu_j + RT \ln \left( \frac{P_j}{P^o} \right)_{eq} \quad P_j = x_j P_j^* \quad (\text{Raoult}) \quad P_j = x_j k_{H,j} \quad (\text{Henry})
\]

\[
a_j = \frac{P_j}{A_j} \quad A_j = \begin{cases} \frac{P_j^*}{P^o} \quad \text{Raoult} \\ k_{H,x_2} \quad \text{Henry (mol frac)} \\ k_{H,m_2} \quad \text{Henry (molal)} \\ k_{H,c_2} \quad \text{Henry (molar)} \end{cases} \quad \gamma_j = \frac{a_j}{B_j} \quad B_j = \begin{cases} x_1 \quad \text{Raoult} \\ x_2 \quad \text{Henry (mol frac)} \\ m_2 \quad \text{Henry (molal)} \\ c_2 \quad \text{Henry (molar)} \end{cases}
\]

\[
\Delta T_{\text{fus}} = v K_f m \quad \Delta T_{\text{vap}} = v K_b m \quad \Pi = v c R T
\]

\[
\ln \gamma_{\pm} = -\left[ q_+ q_- \right] \frac{\kappa}{8 \pi \varepsilon_0 \varepsilon_1 k_B T} \quad \kappa^2 = \frac{2 N_A}{\varepsilon_0 \varepsilon_1 k_B T} I_c \quad I_c = \frac{1}{2} \sum_j c_j q_j^2
\]

Chemical Equilibria

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

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

\[
\frac{Q_p(T)}{P_A^o / P^o} = K_p(T) \quad \frac{Q_c(T)}{P_A^o / P^o} = K_c(T)
\]

\[
Q_p(T) = \left( \frac{P_Y}{P^o} \right)^y \left( \frac{P_Z}{P^o} \right)^z \quad K_p(T) = \left[ \left( \frac{P_Y}{P^o} \right)^y \left( \frac{P_Z}{P^o} \right)^z \right]_{eq} \quad K_c(T) = \left[ \left( \frac{Q_Y / V}{P^o} \right)^a \left( \frac{Q_Z / V}{P^o} \right)^b \right]_{eq}
\]
Electrochemistry

For example reaction: $wW + xX \rightleftharpoons yY + zZ$

$$\Delta G = -nFE$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

$$E^0 = E_{\text{red}}^0 + E_{\text{ox}}^0$$

$$E^0 = \frac{RT}{nF} \ln K_a$$