

CH353 – Physical Chemistry I
Spring 2013, Unique 52575

FINAL EXAM

**** This exam will end promptly at 5 pm ****

Name: Key

Always assume ideal gas unless directed otherwise.

You may use any material that does not have a heartbeat and does not connect to the internet or cellular network.

Honor Code:

“The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.”

I certify that the work on this exam is entirely my own.

Signature

Date

1. (60 points) Determine if the following statements are true or false.

a. True False If two van der Waals gasses, both initially at 5.0 atm, are allowed to expand reversibly to a final pressure of 1.0 atm, the gas with the greater van der Waals b constant will do more work.

b. True False If adding 25 J of heat to a 5.6 g block of iron increases its temperature by 10°C , then adding 25 J of heat to a 2.8 g block of iron will increase its temperature by 20°C .

c. True False ΔH is always equal to zero for any adiabatic processes of an ideal gas.

d. True False Raising the temperature of an exothermic reaction shifts equilibrium towards the products.

e. True False In an ideal solution composed of two compounds A and B, if $P_A^* > P_B^*$, then $y_A > x_A$ always.

f. True False In a reversible transformation, the system always returns to its initial state.

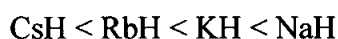
g. True False Dipole-dipole intermolecular interactions are stronger than van der Waals forces.

h. True False A closed system must be surrounded with a perfectly insulating impermeable boundary.

i. True False A system will do the maximum amount of work moving along a reversible path.

j. True False $C_{P,m} > C_{V,m}$ always.

k. True False The molar entropy of the alkali halides increases in the following order:



l. True False A system moves spontaneously to lower chemical potential.

m. True False For any substance, $\Delta H_{\text{sub}} > \Delta H_{\text{vap}}$ always.

n. True False In any binary solution, if one component obeys Raoult's law over all compositions, then the other component must obey Raoult's law over all compositions also.

2. (40 points) Two organic liquids, A and B, form an ideal solution. At 300 K, solution of A and B has a total vapor pressure of 43.3 kPa. The vapor pressures of the pure liquids are $P_A^* = 52.0$ kPa and $P_B^* = 40.0$ kPa.

a) Determine the composition (as mole fractions) of the liquid and vapor phases of this solution.

$$P_{\text{tot}} = X_A P_A^* + X_B P_B^* \quad X_B = 1 - X_A$$

$$P_{\text{tot}} = X_A P_A^* + (1 - X_A) P_B^* = X_A (P_A^* - P_B^*) + P_B^*$$

$$X_A = \frac{P_{\text{tot}} - P_B^*}{P_A^* - P_B^*} = \frac{43.3 \text{ kPa} - 40.0 \text{ kPa}}{52.0 \text{ kPa} - 40.0 \text{ kPa}}$$

$$X_A = 0.275$$

$$X_B = 1 - X_A = 0.725$$

$$Y_A = \frac{P_A}{P_{\text{tot}}} = \frac{X_A P_A^*}{P_{\text{tot}}} = \frac{(0.275)(52.0 \text{ kPa})}{43.3 \text{ kPa}}$$

$$Y_A = 0.33$$

$$Y_B = 1 - Y_A = 0.67$$

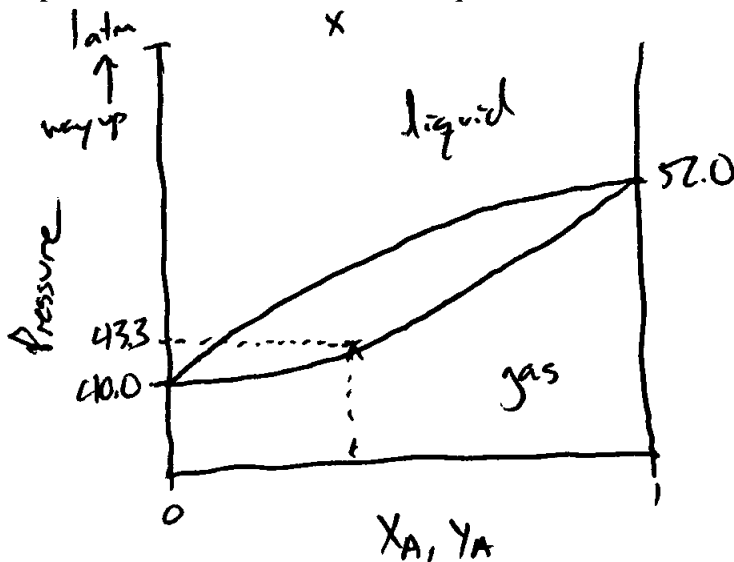
b) In your own words, define Raoult's Law.

Ideal Soln: Intermolecular forces between two different molecules are the same as the pure species

c) An inert gas is added to the headspace above the liquid until the total pressure of the system is 1 atm. Is the solution all liquid, all vapor, or a combination of liquid and vapor?

1 atm = 101 kPa \Rightarrow the soln is all liquid

d) Draw a pressure composition diagram of this solution, and clearly indicate the composition and phase of the solution at external pressures of 43.3 kPa and 1 atm.



3. (30 points) When a gas held at constant temperature is compressed, the change in internal energy of the gas is called the *internal pressure*, π_T :

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$$

Determine the value of π_T for both an ideal gas and a van der Waals gas, and rationalize your answer in clear, comprehensible English.

$$dU = T ds - P dV$$

$$\frac{dU}{dV} = T \left(\frac{ds}{dV} \right) - P$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

ideal: $P = \frac{nRT}{V}$; $\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{nR}{V} \right) - \frac{nRT}{V} = 0$$

This is what we already know; if $\Delta T = 0$, then $\Delta U = 0$ for an ideal gas

vdW: $P = \frac{nRT}{V-nb} - a \left(\frac{n}{V} \right)^2$; $\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V-nb}$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{nR}{V-nb} \right) - \left(\frac{nRT}{V-nb} \right) + a \left(\frac{n}{V} \right)^2$$

$$\left(\frac{\partial U}{\partial V} \right)_T = a \left(\frac{n}{V} \right)^2$$

If the gas is not ideal and has intermolecular interactions, then ΔU will change, even at $\Delta T = 0$. The magnitude of this change is quantified by π_T .

4. (40 points) 1.0 mole of a monatomic ideal gas initially at 300 K and 1.0 atm expands isothermally in two ways:

$$V_i = \frac{nRT}{P_i} = \frac{(1.0 \text{ mol})(0.082 \frac{\text{L atm}}{\text{mol K}})(300 \text{ K})}{1.0 \text{ atm}}$$

a) reversibly to a final pressure of 0.5 atm.

b) against a constant final pressure of 0.5 atm.

$$V_i = 24.6 \text{ L}$$

$$V_f = 49.2 \text{ L}$$

Determine q , w , ΔU , ΔH , ΔS_{sys} , ΔS_{surr} , ΔS_{tot} , and ΔG for both expansion paths.

$$a) w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -(1.0 \text{ mol})(8.314 \text{ J/K mol})(300 \text{ K}) \ln\left(\frac{49.2 \text{ L}}{24.6 \text{ L}}\right)$$

$$\boxed{w = -1.73 \text{ kJ}} \quad \boxed{\Delta U = \Delta H = 0} \quad \boxed{q = -w = 1.73 \text{ kJ}}$$

$$\Delta S_{\text{sys}} = nR \ln\left(\frac{V_f}{V_i}\right) = (1.0 \text{ mol})(8.314 \text{ J/K mol}) \ln\left(\frac{49.2 \text{ L}}{24.6 \text{ L}}\right)$$

$$\boxed{\Delta S_{\text{sys}} = 5.77 \text{ J/K}} \quad \boxed{\Delta S_{\text{tot}} = 0, \Delta S_{\text{surr}} = -5.77 \text{ J/K}}$$

$$b) w = -P\Delta V = -(0.5 \text{ atm})(49.2 \text{ L} - 24.6 \text{ L}) = -12.3 \text{ L atm} \left(\frac{1.01 \times 10^5 \text{ Pa}}{1 \text{ atm}}\right) \left(\frac{1 \text{ m}^3}{1000 \text{ L}}\right)$$

$$\boxed{w = -1.24 \times 10^3 \text{ J}} \quad \boxed{\Delta U = \Delta H = 0}$$

$$\boxed{q = 1.24 \times 10^3 \text{ J}}$$

$$\boxed{\Delta S_{\text{sys}} = 5.77 \text{ J/K}}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-q_{\text{sys}}}{T} = \frac{-1.24 \times 10^3 \text{ J}}{300 \text{ K}}$$

$$\boxed{\Delta S_{\text{surr}} = -4.1 \text{ J/K}}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 5.77 \text{ J/K} - 4.1 \text{ J/K}$$

$$\boxed{\Delta S_{\text{tot}} = 1.7 \text{ J/K}}$$

5. (25 points) Borneol (B) isomerizes to isoborneol (IB) at 500 K with $\Delta G_{\text{rxn}}^0 = 10 \text{ kJ mol}^{-1}$. You mix 0.30 moles of B and no IB at a total pressure of 80 kPa.

a) Is the isomerization of B spontaneous under these conditions?

No

b) What is the equilibrium composition of the system?

$$K_p = \exp\left[\frac{-\Delta G_{\text{rxn}}^0}{RT}\right] = \exp\left[\frac{-10 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/Kmol})(298 \text{ K})}\right] = 0.018 = \text{small} \Rightarrow z_{\text{eq}} \text{ small}$$

B	IB
Initial: 0.30	0
equil: 0.30 - 2z _{eq}	2z _{eq}
n _{TOT} = 0.30 - 2z _{eq} + 2z _{eq} = 0.30	
X _B = $\frac{0.30 - 2z_{\text{eq}}}{0.30}$	$\frac{2z_{\text{eq}}}{0.30}$
P _B = $\frac{(0.30 - 2z_{\text{eq}})P_{\text{TOT}}}{0.30}$	
P _{IB} = $\frac{(2z_{\text{eq}})P_{\text{TOT}}}{0.30}$	
K _p = $\frac{\left[\frac{P_{\text{TOT}} 2z_{\text{eq}}}{0.30}\right]}{\left[\frac{(0.30 - 2z_{\text{eq}})P_{\text{TOT}}}{0.30}\right]} = \frac{2z_{\text{eq}}}{0.30 - 2z_{\text{eq}}}$	

$$0.30 k_p - k_p 2z_{\text{eq}} = 2z_{\text{eq}}$$

$$2z_{\text{eq}}(1 + k_p) = 0.30 k_p$$

$$2z_{\text{eq}} = \frac{0.30 k_p}{1 + k_p} = \frac{(0.30)(0.018)}{1 + 0.018}$$

$$2z_{\text{eq}} = 0.0053$$

$$\text{B: } 0.30 \text{ moles} - n(0.0053) = 0.29 \text{ moles}$$

$$\text{IB: } 0.0053 \text{ moles}$$

c) If you increase the pressure, will that favor reactants or products in this reaction and why?

Increasing pressure will not shift equilibrium in either direction.

Qualitatively, this is because there is 1 mole on both reactant + product side. Quantitatively, P_{TOT} is not in the expression for z_{eq} , so the magnitude of P_{TOT} does not affect z_{eq} .

6. (30 points) A solid compound A decomposes to two gaseous compounds B and C by the following reaction:



A chunk of A is placed into a sealed container that is then evacuated to an initial pressure of 0 atm at very low temperature. The container is then heated to 298 K, causing some of the A to decompose to B and C. What is the final pressure inside the container? The following information might be useful.

compound	ΔG_f° (kJ mol ⁻¹)
A	-10.0
B	0
C	10.0

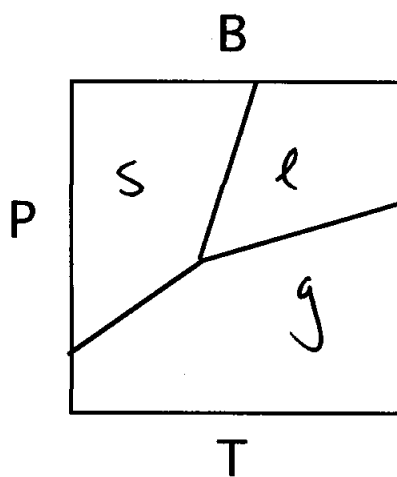
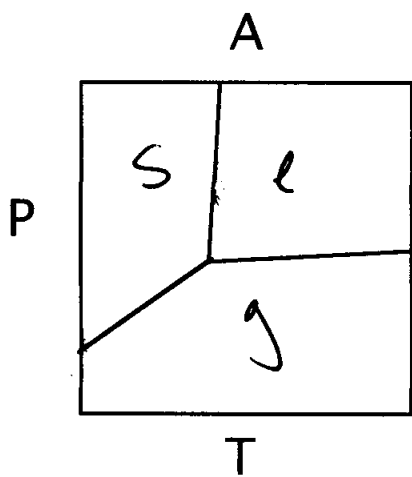
$$\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ(\text{B}) + 3 \Delta G_f^\circ(\text{C}) - 2 \Delta G_f^\circ(\text{A}) = 0 + 3(10 \text{ kJ/mol}) - 2(-10 \text{ kJ/mol})$$

$$\Delta G_{\text{rxn}}^\circ = 50 \text{ kJ/mol} \quad K_p = \exp\left[\frac{-\Delta G_{\text{rxn}}^\circ}{RT}\right] = \exp\left[\frac{-(50 \text{ kJ/mol})}{(8.314 \text{ J/kmol})(298 \text{ K})}\right]$$

$$K_p = 1.7 \times 10^{-9} = \text{small}$$

We could go through the process of finding z_{eq} , then the equilibrium composition. However, K_p is a very small number, so let's just say there is no rxn, and $P_f \approx 0$.

7. (25 points) The phase diagrams of two different substances, A and B, are given below (assume the x and y axes are on the same scale). Which substance has a larger enthalpy of fusion? Explain your reasoning.



$$\frac{dP}{dT} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}} \Delta V_{\text{trans}}}$$

The substance that has the larger ΔH_{fus} will have the steeper slope between solid + liquid phases. Therefore $\Delta H_{\text{fus}}(A) > \Delta H_{\text{fus}}(B)$.

8. (20 points) The kinetic model of gasses assumes the system is in ceaseless random motion in all directions. Describe a situation in which this requirement would be violated.

If the system is biased in some way, molecules can be prevented from moving freely along one or more of the translational directions. This could happen if an electric or magnetic field is applied to the system. This is actually a very common experimental technique.

9. (30 points) The ground state of the hydrogen atom is singly degenerate (1s), and is at energy 0. The first excited state of the atom is quadruply degenerate (2s + 3 2p), and is 2.18×10^{-18} J higher in energy than the ground state. The second excited state is also quadruply degenerate and is 1.7×10^{-18} J higher in energy than the first excited state. From this information, determine the probability of finding a hydrogen atom in the first excited state at 300 K, 1000 K, and 3000 K.

$$P_i = \frac{g_i e^{-E_i/k_B T}}{\sum_j g_j e^{-E_j/k_B T}}$$

$$q = \sum_j g_j e^{-E_j/k_B T}$$

$$q = 1 \cdot e^{-0} + 4e^{-2.18 \times 10^{-18} \text{ J} / k_B T} + 4e^{-\frac{(2.18 + 1.7) \times 10^{-18} \text{ J}}{k_B T}}$$

300k: $P_1 = \frac{4e^{-2.18 \times 10^{-18} \text{ J} / (1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}}{1 + 4 \exp\left[\frac{-2.18 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}\right] + 4 \exp\left[\frac{-(2.18 + 1.7) \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}\right]}$

$$1 + 4 \exp\left[\frac{-2.18 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}\right] + 4 \exp\left[\frac{-(2.18 + 1.7) \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}\right]$$

$$P_1(300k) = \frac{8.23 \times 10^{-229}}{1 + 8.23 \times 10^{-229} + 3.8 \times 10^{-407}} \approx 0$$

≈ 0 very small number

over \rightarrow

9. continued:

$$1000\text{K: } p_i = \frac{4 \exp \left[\frac{-2.18 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(1000 \text{ K})} \right]}{1 + 4 \exp \left[\frac{-2.18 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(1000 \text{ K})} \right] + 4 \exp \left[\frac{-(2.18 + 1.7) \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(1000 \text{ K})} \right]}$$

$$p_i(1000\text{K}) = \frac{9.9 \times 10^{-69}}{1 + 9.9 \times 10^{-69} + 3.13 \times 10^{-102}} = \text{a very small \# still,}$$

but 200 orders of magnitude more likely than at 300K

$$3000\text{K: } p_i = \frac{5.41 \times 10^{-23}}{1 + 5.41 \times 10^{-23} + 7.94 \times 10^{-41}} = \text{small, but 46 orders of magnitude more likely}$$