*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

1. (**10 Points**) For each statement or question in the **left** column, find the appropriate response in the **right** column and place the letter of the response in the blank line provided in the **left** column.

1. In the limit of infinite aqueous dilution of a solute, Henry's Law standard state allows us to consider the activity of the solute as: _____t_____	a. entropy of mixing
	b. ideal
2. The lowering of the chemical potential of a species in an ideal mixture (vapor or liquid) is a consequence of _____a___	c. intensive
	d. 3
3. For a binary (two species) two-phase system, how many degrees of freedom (intensive variables) are possible? _____q____.	e. $\gamma_i = \hat{\phi}_i \dfrac{p}{p^o}$
	f. equal
4. Fugacity is an empirical approach to incorporate _____s_ in the treatment of chemical potential.	g. $\gamma_i = \hat{\phi}_i$
	h. $dA = dw_{total,reversible}$
5. Colligative properties as discussed in this course arise because of _____o_____ contributions to the lowering of free energy in ideal solutions.	i. enthalpy
	j. 4
6. At the azeotropic condition for a binary system (two species, "i" and "j") system, what condition always holds? __n___	k. equilibrium
	l. positive
7. The activity coefficient for a species "i" in a gas mixture with standard state of pure "i" in gas phase at the temperature and pressure of interest is: ___g__.	m. 1
	n. $x_i = y_i$
8. Henry's Law gives the partial pressure of a dilute solute within the approximation that the vapor phase is ___b____.	o. entropic
	p. $a_{solute} = \hat{\phi}_{solute}\gamma_{solute}$
9. The Debye - Hückel model estimates the electrostatic potential around a charged, spherical ion in a molecularly explicit solvent and is formulated for low concentration electrolyte solutions (True or False) _____false_____.	q. 2
	r. continuous
10. The change in Helmholtz Free Energy of a pure fluid during a constant temperature process is equivalent to the total reversible work associated with the process. That is, we can write: ____h_____	s. non-ideality
	t. $a = \dfrac{m}{m^0}$

2. (**10 Points**) Given the following data for the equilibrium vapor pressures and temperatures for the following reaction at equilibrium, estimate the most accurate value for the vaporization enthalpy to the best of your abilities. *Be sure to clearly state any approximations and assumptions you invoke.*

$$butane(liquid) \ = \ butane(gas)$$
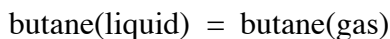
T (Kelvin)	Pressure (Pascal)
187.45	667
195.35	1333
204.25	2666
214.05	5333
220.35	7999
228.95	13332
241.95	26664
256.85	53329

Solution:

For this problem, we use the Clausius-Clapeyron, with the assumptions that the vapor is ideal and the vaporization enthalpy is constant over the temperature range given.

The Clausius-Clapeyron Equation is:

$$\frac{d\ln P}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

Integrating gives:

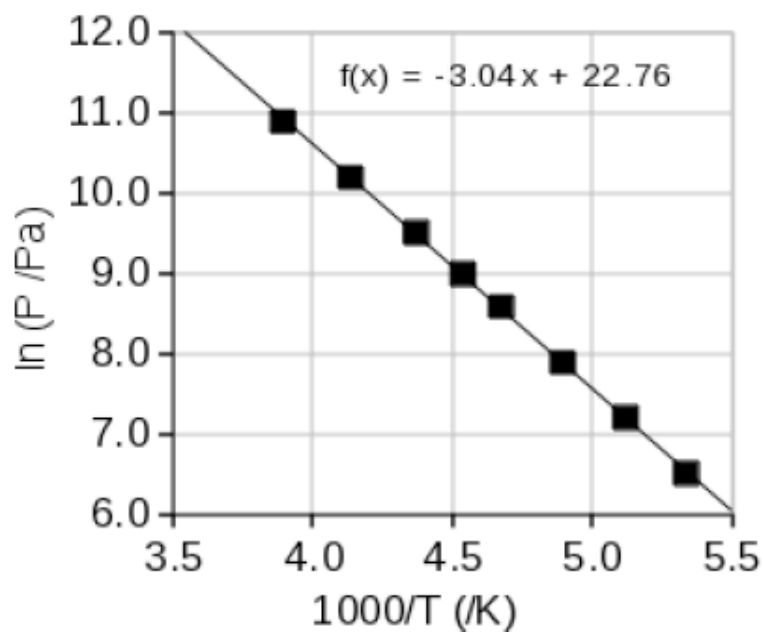$$\ln P = \left(\frac{-\Delta H_{vap}}{R} \right) \frac{1}{T} + C$$

This has the form of a straight line with slope of vaporization enthalpy divided by R when ln(P) is plotted against inverse absolute temperature.

T(K)	P (torr)	P(Pa)	1000/T	ln(P/Pa)
187.45	5.00	667	5.335	6.502
195.35	10.00	1333	5.119	7.195
204.25	20.00	2666	4.896	7.889
214.05	40.00	5333	4.672	8.582
220.35	60.00	7999	4.538	8.987
228.95	100.00	13332	4.368	9.498
241.95	200.0	26664	4.133	10.191
256.85	400.0	53329	3.893	10.884

$\Delta_{vap}H =$ 25.28 kJ/mol

SUMMARY OUTPUT

	Coefficients	Standard Err	t Stat	P-value	Lower 95%	Upper 95%
Intercept	22.76	0.10	225.55	0	22.51	23.01
X Variable	-3.04	0.02	-139.85	0	-3.09	-2.99

$f(x) = -3.04x + 22.76$

Plot of ln (P /Pa) versus 1000/T (/K)

3. (**10 Points**) For each statement or question in the **left** column, find the appropriate response in the **right** column and place the letter of the response in the blank line provided in the **left** column.

1. The entropy change for a reversible process at constant temperature and pressure is always positive (True or False) ___False_____	a. entropy b. U and V c. intensive d. 3 e. Legendre Transform
2. The thermodynamic potentials U, H, A, and G contain _____L___	f. equal g. Le Chatelier h. $dA = dw_{total,reversible}$ i. enthalpy j. 4 k. zero
3. The Gibbs Free Energy is maximized under conditions of constant temperature and pressure (True or False) ___False_____.	l. the same fundamental thermodynamic information m. 1 n. $x_i = y_i$ o. dual p. $a_{solute} = \hat{\phi}_{solute} \gamma_{solute}$
4. Entropy is a function of the natural variables _____B____	q. 2 r. entropic s. non-ideality t. Carnot
5. A powerful tool to allow transformation from one set of independent variables to another is _____E_____	

Score for Page

4. (**10 Points**) Consider that you have been given a phase diagram for a material for which the following behavior is seen for the coexistence lines:

$$0 \; < \; \left(\frac{dP}{dT}\right)_{\text{sublimation}} \; < \; \left(\frac{-dP}{dT}\right)_{\text{fusion}} \; < \; \left(\frac{dP}{dT}\right)_{\text{vaporization}}$$

If this phase diagram is correct, then this fluid has one unusual property and one property that violates one of the laws of thermodynamics, particularly close to the triple point. Using your knowledge of thermodynamics answer the following questions. Keep in mind that the physical reasons you give must be in mathematical terms, not completely in words.

A. What property is unusual and why?

Solution: The property

$$\left(\frac{-dP}{dT}\right)_{\text{fusion}} < 0$$

is unusual as only a few substances such as water, behave in this manner (Si is another such fluid).

B. What law is violated and why?
Solution: Let's consider the Clausius-Clapeyron equation in the form including entropies.

$$\left(\frac{dP}{dT}\right)_{\text{vaporization}} = \frac{S_{gas,molar} - S_{liquid,molar}}{V_{gas,molar}}$$

$$\left(\frac{dP}{dT}\right)_{\text{sublimation}} = \frac{S_{gas,molar} - S_{solid,molar}}{V_{gas,molar}}$$

Let's see what the implications of the given inequalities are:

$$\left(\frac{dP}{dT}\right)_{\text{sublimation}} < \left(\frac{dP}{dT}\right)_{\text{vaporization}}$$

$$\frac{S_{gas,molar} - S_{solid,molar}}{V_{gas,molar}} < \frac{S_{gas,molar} - S_{liquid,molar}}{V_{gas,molar}}$$

$$-S_{solid,molar} < -S_{liquid,molar}$$

$$S_{solid,molar} > S_{liquid,molar}$$

The given information suggests that the entropy of the solid is greater than that of the liquid, which by the second law is impossible.

5. (**10 Points**) Determine the entropy change when one mole of a liquid (normal boiling point = 356K) is heated from 298K up to 428K at constant pressure given the following information (temperature in Kelvin):

C_p of liquid: 45 cal/mole/degree
C_p of vapor: $10.8 + 3.35 \times 10^{-2}\ T + 0.95 \times 10^{-4}\ T^2$ cal/mole/degree
Heat of Vaporization: 4405 cal/mole

Solution:

$$\Delta S = nC_{P,m} \ln\left(\frac{T_b}{T_1}\right) + \frac{\Delta H^{vap}}{T_b} + (10.8)\ln\left(\frac{428}{356}\right) + (0.0335)(428 - 356) - (0.000095)\left(428^2 - 356^2\right)$$

$$= (1mole)(45cal/mol/K)(0.17783724) + 12.373596 + (10.8)(0.16532398)$$

$$+ (0.0335)(72) - (0.000095)\left(428^2 - 356^2\right)$$

$$= (8.00 + 12.373596 + 1.9893 + 2.412 + 2.68)cal/K$$

$$= 27.46 cal/K$$

Score for Page

6. (10 Points) The vapor pressures of tetrachloromethane(1) and trichloroethylene(2) between 76.8 Celsius and 87.2 Celsius are expressed empirically by:

$$\ln\left(P_1^{saturation}\right) = 15.8401 - \frac{2790.78}{t + 226.4}$$

$$\ln\left(P_2^{saturation}\right) = 15.0124 - \frac{2345.4}{t + 192.7}$$

where "t" is the Celsius temperature and saturation pressure is in torr. Assuming that tetrachloromethane and trichloroethylene form an ideal solution between 76.8 Celsius and 87.2 Celsius at all compositions, calculate the values of x_1 and y_1 at 82.0 Celsius (at ambient pressure of 760 torr). The components form a binary, two-phase system with liquid compositions denoted with "x" and vapor compositions denoted with "y".

Solution:
At t = 82 Celsius,

$$\ln\left(P_1^{saturation}\right) = 15.8401 - \frac{2790.78}{82.0 + 226.4} = 6.7919$$

$$P_1^{saturation} = 890torr$$

$$\ln\left(P_2^{saturation}\right) = 15.0124 - \frac{2345.4}{82.0 + 192.7} =$$

$$P_2^{saturation} = 648torr$$

Now let's determine the compositions. The total pressure is 760 torr (ambient pressure).

$$P^{Total} = P_1 + P_2 = x_1 P_1^{saturation} + (1 - x_1) P_2^{saturation}$$

$$x_1 = \frac{P_2^{saturation} - 760torr}{P_2^{saturation} - P_1^{saturation}} = \frac{648torr - 760torr}{648torr - 890torr}$$

$$x_1 = 0.463$$

$$x_2 = 1 - x_1 = 0.537$$

$$y_1 = \frac{x_1 P_1^{saturation}}{760torr} = \frac{(0.463)(890torr)}{760torr}$$

Score for Page

7. (**10 Points**) A solution containing 0.80 grams of a protein in 100 mL of a solution has an osmotic pressure of 2.06 torr at 25.0 Celsius. What is the molecular mass of the protein?

Solution:

$$c = \frac{\Pi}{RT} = \frac{(2.06\,torr)(1\,atm/760\,torr)}{(0.08206\,L-atm-mol^{-1}-K^{-1})(298.15K)}$$

$$= 1.11 \times 10^{-4}\,mol/L$$

$$= 1.11 \times 10^{-5}\,mol/100mL$$

Thus, the molecular mass is:

$$\frac{0.8\,gram}{1.11x10^{-5}\,mole} = 72000\,gram/mole$$

Score for Page

8. (**10 Points**) **A.** Consider an ideal gas that occupies 2.25 L at 1.33 bar. Calculate the work required to compress the gas isothermally to a volume of 1.5 L at a constant pressure of 2.0 bar followed by another isothermal compression to 0.8 L at a constant pressure of 2.5 bar.

Solution:
i. From (2.25 L, 1.33 bar) to (1.5 L, 2.00 bar):

$$w = -\int P_{ext}dV = (-2.0bar)(1.5L - 2.25L)(100\ J\ bar^{-1}dm^3) = 150\ J$$

ii. From (1.5L, 2 bar) to (0.8 L, 2.5 bar)

$$w = -\int P_{ext}dV = (-2.5bar)(0.8L - 1.5L)(100\ J\ bar^{-1}dm^3) = 175\ J$$

Total work involved in the two-step process is +325J

B. What is the work for compressing the gas isothermally and reversibly from 2.25 L to 0.8 L?

Solution:
Reversible process: for ideal gas PV=nRT, so initially,

$$PV = (2.25L)(1.33bar)(100J\ bar^{-1}\ dm^3) = 299.25J = nRT$$

To find the work for isothermal, reversible compression of ideal gas:

$$w = -\int PdV = -nRT\int d\ln(V) = -nRT\ln\left(\frac{V_2}{V_1}\right) = -(299.25J)\ln\left(\frac{0.8}{2.25}\right) = 309J$$

Thus, total work for reversible compression is less than for work at constant external pressure

9. (**10 Points**) Consider the following reaction:

Score for Page

$$N_2(g) \ + \ 3H_2(g) \ = \ 2NH_3(g)$$
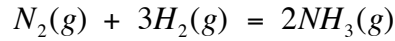
At 1000 Kelvin, $\Delta H^o_{rxn} = -123.77 \ kJ \ mol^{-1}$. What is the enthalpy of formation for NH_3 (gas) at 300 Kelvin? Consider the following molar heat capacities: $C_{p,m} = 3.502R$, $3.466R$, and $4.217R$ for $N_2(g)$, $H_2(g)$, and $NH_3(g)$, respectively. State any approximations you invoke.

Solution:

$$\Delta H^o_{rxn}(300K) = \Delta H^o_{rxn}(1000K) + \int_{1000K}^{300K}\Delta C_P(T)dT$$

Assuming constant heat capacities for all species over this temperature range, we have:

$$\Delta H^o_{rxn}(300K) = -123.77 \ kJ/mol \ + \ \left[2C_{P,m}(NH_3(gas)) - C_{P,m}(N_2(gas)) - 3C_{P,m}(H_2(gas))\right](-700K)$$
$$= -123.77 \ kJ/mol \ + 8.314 Jmol^{-1}K^{-1}\left[(2)(4.217) - 3.502 - (3)(3.466)\right](-700K)$$
$$= -91.96 kJ/mol$$

$$\Delta H^o_{formation}(300K) = (0.5)(\Delta H^o_{rxn}(300K)) = -45.98 kJ/mol$$

Score for Page

10. (10 Points). A. A 17.5 gram mass of ice at 273 Kelvin is added to 125 grams of liquid water at 325 Kelvin at constant pressure. Is the final state of the system ice or water? Take the molar specific heat of liquid water to be 75.3 J K^{-1} mol^{-1}

Solution: This is a first law (energy balance) problem. The final temperature could be at or below the freezing temperature, or it could be above (liquid). Let's first assume that the final temperature is above the freezing temperature. Considering the entire system to be isolated, we have the following working relation (the First Law):

$$\Delta U = q_{water} + q_{ice} = 0$$

Now we independently can write the heat interaction for the ice and water as:

$$q_{water} = n_{water,liquid} C_{P,molar}^{water,liquid} \left(T_f - T_{initial}^{water,liquid} \right)$$

$$q_{ice} = n_{ice} \Delta H_{ice}^{fusion} + n_{ice} C_{P,molar}^{water,liquid} \left(T_f - T_{initial}^{ice} \right)$$

The sum of the previous two equations is zero, allowing us to solve for Tfinal as follows:

$$q_{water} = n_{water,liquid} C_{P,molar}^{water,liquid} \left(T_f - T_{initial}^{water,liquid} \right)$$

$$q_{ice} = n_{ice} \Delta H_{ice}^{fusion} + n_{ice} C_{P,molar}^{water,liquid} \left(T_f - T_{initial}^{ice} \right)$$

$$T_f = \frac{n_{ice} C_{P,molar}^{water,liquid} T_{initial}^{ice} + n_{water,liquid} C_{P,molar}^{water,liquid} T_{initial}^{water,liquid} - n_{ice} \Delta H_{ice}^{fusion}}{n_{ice} C_{P,molar}^{water,liquid} + n_{water,liquid} C_{P,molar}^{water,liquid}}$$

$$= 309 K$$

B. Is the process spontaneous?

Solution:
For this part, we need to determine the total entropy change, of water and ice. Since the total system is isolated, we should find that the entropy change is positive and thus the process is spontaneous.

For the ice:
$$\Delta S_{ice} = \frac{n_{ice} \Delta H_{ice}^{fusion}}{T_{fusion}} + n_{ice} C_{P,molar}^{water,liquid} \ln\left(\frac{T_f}{T_{fusion}} \right)$$

$$= 30.4 \ J/K$$

$$\Delta S_{water,liquid} = n_{water,liquid} C_{P,molar}^{water,liquid} \ln\left(\frac{T_f}{T_{initial}^{water,liquid}} \right)$$

$$= -26.7 \ J/K$$

Since the sum of the entropy changes is positive, the process is indeed spontaneous.

Score for Page

11. (**10 Points)** Addition of 1.52 grams of a substance to 100 grams of camphor lowers the freezing point of camphor by 2.80 Celsius. Estimate the molar mass of the substance.

Solution:
Assume ideality of the solution (as derived in class discussion). For camphor, the value of the freezing point depression constant is given in Table 7.5 as 40 K/molal.

$$\Delta T = K_f m$$

$$m = \frac{\Delta T}{K_f} = \frac{2.80K}{40K/molal} = 0.070 \ molal$$

Small molality, so the assumption of ideality is suitable.

Molar mass:

$$0.070 \frac{mole \ \text{substance}}{kg \ \text{solvent}} = \frac{1.52 gram \ \text{substance}}{0.1 \ kg \ \text{solvent}} = \frac{15.2 gram \ \text{substance}}{kg \ \text{solvent}}$$

$$1 \ mole \ subs \tan ce = 15.2 gram / 0.07 = 217 g / mole$$

Thus, molar mass is 217 g/mole.

Score for Page

12. (**10 Points**) For each statement or question in the **left** column, find the appropriate response in the **right** column and place the letter of the response in the blank line provided in the **left** column.

1. The reversible work needed to compress a gas is _____H___ that needed in an irreversible process affecting the same change.	a. equal to
2. An extensive thermodynamic property is independent of the amount of substance or system size. (True or False?)___False_____	b. amount
3. The Joule-Thomson process is a(n) __F_____ process.	c. volume, and pressure.
4. The Second Law of Thermodynamics allows us to formulate bounds on the amount of internal energy that can be converted to work. (True or False) ___False_____	d. isoenergetic
5. The internal energy of an ideal gas depends on temperature ___g_____.	e. greater than
6. We can write the standard enthalpy of reaction in a general form as: $$\Delta H^0_{reaction}(T) = \sum_{products,i} \nu_i \Delta H^o_{f,i} - \sum_{react,j} \nu_j \Delta H^o_{f,j}$$ because enthalpy has the quality of being a(n) _____i___.	f. isenthalpic g. only h. less than i. state function j. inexact integral k. natural variable

Score for Page

13. Bonus (10 Points) It can be shown that the partition function of an ideal gas of "N" diatomic molecules in an external electric field, ε, is:

$$Q = \left(\frac{[q]^N}{N!}\right) \quad with \quad q = C\left(\frac{k_B T}{\mu\varepsilon}\right) \sinh\left(\frac{\mu\varepsilon}{k_B T}\right)$$

Here, T is temperature, k_B is Boltzmann's constant, μ is the dipole moment of a single molecule, and C is a constant independent of ε. The partition function, Q, relates to the Helmholtz Free Energy through the following equation:

$$A = -k_B T \ln Q = -k_B T \ln\left[\frac{[q]^N}{N!}\right]$$

Using this information along with the Fundamental Thermodynamic Relation for the total derivative of the Helmholtz Free energy:

$$dA = -SdT - PdV - (N\overline{\mu})\, d\varepsilon$$

where $\overline{\mu}$ is the average dipole moment of a molecule in the direction of the external field, ε, show that at constant temperature and volume:

$$\overline{\mu} = \mu\left[\coth\left(\frac{\mu\varepsilon}{k_B T}\right) - \left(\frac{k_B T}{\mu\varepsilon}\right)\right]$$

Solution:

From the fundamental relation for the Helmholtz free energy, we know the following partial derivative:

$$-N\overline{\mu} = \left(\frac{\partial A}{\partial \varepsilon}\right)_{T,V,N}$$

$$\overline{\mu} = \left(\frac{-1}{N}\right)\left(\frac{\partial A}{\partial \varepsilon}\right)_{T,V,N}$$

So we need to use the relation for A to determine the partial derivative at constant T, V, and N.

$$A = -k_BTN\ln(q) + k_BT\ln(N!)$$

$$\left(\frac{\partial A}{\partial \varepsilon}\right)_{T,V,N} = \left(\frac{\partial\left[-k_BTN\ln(q) + k_BT\ln(N!)\right]}{\partial \varepsilon}\right)_{T,V,N} = \left(\frac{\partial\left[-k_BTN\ln(q)\right]}{\partial \varepsilon}\right)_{T,V,N}$$

$$= \frac{-k_BTN}{q}\left(\frac{\partial q}{\partial \varepsilon}\right)_{T,V,N} = \left(\frac{-k_BTN}{C\left(\frac{k_BT}{\mu\varepsilon}\right)\sinh\left(\frac{\mu\varepsilon}{k_BT}\right)}\right)\left(\frac{Ck_BT}{\mu}\left[\left(\frac{\mu\cosh\left(\frac{\mu\varepsilon}{k_BT}\right)}{k_BT\varepsilon}\right) - \left(\frac{\sinh\left(\frac{\mu\varepsilon}{k_BT}\right)}{\varepsilon^2}\right)\right]\right)$$

$$= \left(\frac{-k_BTN}{\sinh\left(\frac{\mu\varepsilon}{k_BT}\right)}\right)\left(\left[\left(\frac{\mu\cosh\left(\frac{\mu\varepsilon}{k_BT}\right)}{k_BT}\right) - \left(\frac{\sinh\left(\frac{\mu\varepsilon}{k_BT}\right)}{\varepsilon}\right)\right]\right)$$

$$= \left(\frac{-k_BTN}{1}\right)\left(\left[\left(\frac{\mu\coth\left(\frac{\mu\varepsilon}{k_BT}\right)}{k_BT}\right) - \left(\frac{1}{\varepsilon}\right)\right]\right)$$

$$= -N\left(\mu\coth\left(\frac{\mu\varepsilon}{k_BT}\right) - \left(\frac{k_BT}{\varepsilon}\right)\right)$$

So the final expression for the average dipole moment is:

$$\overline{\mu} = \left(\frac{-1}{N}\right)\left(\frac{\partial A}{\partial \varepsilon}\right)_{T,V,N} = \left(\frac{-1}{N}\right)\left[-N\left(\mu\coth\left(\frac{\mu\varepsilon}{k_BT}\right) - \left(\frac{k_BT}{\varepsilon}\right)\right)\right]$$

$$= \left(\mu\coth\left(\frac{\mu\varepsilon}{k_BT}\right) - \left(\frac{k_BT}{\varepsilon}\right)\right)$$

as needed.

Score for Page