

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. (20 Points) Complete the sentence in the left column using the answers provided in the right column. Where requested, explicitly write out True or False so as to avoid ambiguity.

1. For a multi-component, multi-region system that allows the transfer of the different components between regions of the system, the _____f__ of an individual species is _____i_____ throughout the entire system at equilibrium.	a. equal to
2. The various Fundamental Equations of Thermodynamics are unrelated and provide different ways of considering the same information. True or False _____FALSE_____	b. fugacity coefficient
3. One measure of the non-ideality of a pure vapor or a mixture of vapors is the _____b_____.	c. spatially-dependent
4. For gas-phase reactions of species described by the following equation of state: $PV = nRT$, the equilibrium constant accounts for the _____e__ contributions to the Gibbs Free Energy of reaction arising from _____g__ of the individual gases.	d. Coefficient of non-ideality, C_{NI}
5. For ideal, dilute solutions, the Henry's Law standard state represents a real, stable state of a pure fluid at the relevant system conditions of temperature, pressure, and composition. True or False _____FALSE_____	e. entropic
	f. chemical potentials
	g. mixing
	h. less than
	i. the same and time-independent

DO NOT WRITE IN THIS SPACE

p. 1 _____/20

p. 2 _____/20

p. 3 _____/20

p. 4 _____/20

p. 5 _____/20

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p. 6 _____/15
(Extra credit)

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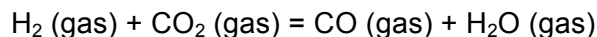
TOTAL PTS

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2. (20 Points) Consider the following reaction at T = 298.15 K and P = 1 bar:



Starting with “a” moles of H₂ (gas) and “b” moles of CO₂ (gas), how many moles of each of the four components are present at equilibrium. Assume ideal gas behavior for each species and standard pressure of 1 bar.

Solution:

	H ₂	CO ₂	H ₂ O	CO	
Initial moles	a	b	0	0	
Moles @ equilibrium	a-n	b-n	n	n	
Mole fraction @ equilibrium	$\frac{a-n}{a+b}$	$\frac{b-n}{a+b}$	$\frac{n}{a+b}$	$\frac{n}{a+b}$	

At equilibrium,

$$\Delta G_{rxn}^{\circ} = -RT \ln K_p$$

The standard molar Gibbs free energy of reaction is given by:

$$\begin{aligned} \Delta G_{rxn}^{\circ} &= \nu_{\text{H}_2} \Delta G_{\text{formation, H}_2}^{\circ} + \nu_{\text{CO}_2} \Delta G_{\text{formation, CO}_2}^{\circ} + \nu_{\text{CO}} \Delta G_{\text{formation, CO}}^{\circ} + \nu_{\text{H}_2\text{O}} \Delta G_{\text{formation, H}_2\text{O}}^{\circ} \\ &= -\Delta G_{\text{formation, H}_2}^{\circ} - \Delta G_{\text{formation, CO}_2}^{\circ} + \Delta G_{\text{formation, CO}}^{\circ} + \Delta G_{\text{formation, H}_2\text{O}}^{\circ} \\ &= 0 - (-94.26 \frac{\text{kcal}}{\text{mol}}) + (-32.81 \frac{\text{kcal}}{\text{mol}}) + (-54.64 \frac{\text{kcal}}{\text{mol}}) \\ &= 6.81 \frac{\text{kcal}}{\text{mol}} = 28.51 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Thus, the dimensionless equilibrium constant is:

$$28510 \frac{\text{J}}{\text{mol}} = -RT \ln K_p$$

$$K_p = e^{\frac{-28510 \frac{\text{J}}{\text{mol}}}{RT}} = e^{-11.50144} = 1.0 \times 10^{-5}$$

At equilibrium (note all exponents are unity, so they are not explicitly included here),

$$K_p = 1.0 \times 10^{-5} = \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{CO}_2}} = \frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{H}_2} x_{\text{CO}_2}} = \frac{n^2}{(a-n)(b-n)}$$

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$$K_p = 1.0 \times 10^{-5} = \frac{P_{CO} P_{H_2O}}{P_{H_2} P_{CO_2}} = \frac{x_{CO} x_{H_2O}}{x_{H_2} x_{CO_2}} = \frac{n^2}{(a-n)(b-n)}$$

$$n^2 = K_p (n^2 - (a+b)n + ab) = K_p n^2 - K_p (a+b)n + K_p ab$$

$$0 = (K_p - 1)n^2 - K_p (a+b)n + K_p ab$$

$$n = \frac{K_p(a+b) \pm \sqrt{K_p^2(a+b)^2 - 4abK_p(K_p - 1)}}{2(K_p - 1)}$$

If a = 1 mol and b = 2 mol,

$$\begin{aligned} n &= \frac{3K_p \pm \sqrt{9K_p^2 - 8K_p(K_p - 1)}}{2(K_p - 1)} \\ &= \frac{3(0.00001) \pm \sqrt{9(0.00001)^2 - 8(0.00001)(0.00001 - 1)}}{2(0.00001 - 1)} \\ &= 0.0045 \text{ mol} \end{aligned}$$

If you forget the quadratic formula, one can consider that K_p is small and make some approximations. With small K_p , "n" will be small. We can retain only certain terms in the quadratic polynomial:

$$K_p = 1.0 \times 10^{-5} = \frac{P_{CO} P_{H_2O}}{P_{H_2} P_{CO_2}} = \frac{x_{CO} x_{H_2O}}{x_{H_2} x_{CO_2}} = \frac{n^2}{(a-n)(b-n)} \approx \frac{n^2}{(a)(b)}$$

$$n^2 \approx abK_p$$

$$n \approx \sqrt{abK_p} = \sqrt{2(0.00001)} = 0.0045 \text{ mol}$$

Thus, small K_p approximation leads to essentially the same final equilibrium moles and the number is quite small as expected for self-consistency.

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3. (20 Points) Determine the enthalpy of vaporization of methanol using the following experimental data for temperature versus equilibrium saturation pressure (vapor pressure) of pure methanol. State any assumptions you make in your solution of this problem.

Pressure (mm Hg)	40	100	400	760	1520	3800	7600	15200	30400	45600
T (Celsius)	5.0	21.2	49.9	64.7	84.0	112.5	138.0	167.8	203.5	224.0

Solution: Use Clausius-Clapeyron equation with assumption of ideal gas and constant vaporization enthalpy (over the given temperature range).

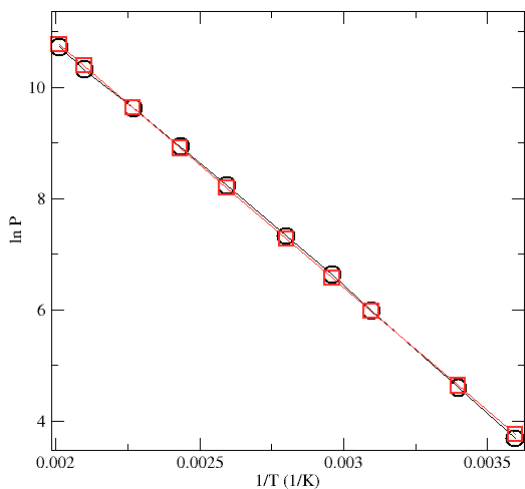
$$\ln P = \left(\frac{-\Delta H_{\text{vap}}}{R} \right) \left(\frac{1}{T} \right) + c$$

Plot $\ln P$ versus inverse temperature and perform linear regression.

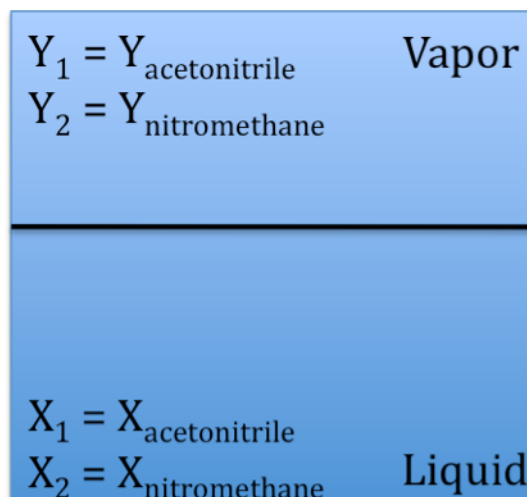
Regression Results:

Number of observations	= 10
Mean of independent variable	= 0.002725033
Mean of dependent variable	= 7.610287
Standard dev. of ind. variable	= 0.0005397251
Standard dev. of dep. variable	= 2.389071
Correlation coefficient	= -0.9997924
Regression coefficient (SLOPE)	= -4425.54
Standard error of coefficient	= 31.8908
t - value for coefficient	= -138.7717
Regression constant (INTERCEPT)	= 19.67003
Standard error of constant	= 0.08842427
t - value for constant	= 222.4506
y = 19.67 - 4425.5 * x	

$\Delta H_{\text{vap}} = (-R)(\text{slope}) = 36.8 \text{ kJ/mol}$ (see figure; circles = data; squares = regression)



4. (20 Points) The binary system acetonitrile(1)/nitromethane(2) is sufficiently well-described as an ideal solution (both vapor and condensed phase are ideal) for considering vapor-liquid equilibrium (VLE) (see figure). For this problem, species 1 is acetonitrile and species 2 is nitromethane. One can thus use Raoult's expression relating the mole fractions of species in the vapor to the condensed phase mole fractions and individual species' saturation vapor pressures. Using this information, along with the following Antoine relations for the temperature dependence of the individual species' saturation pressures, determine the equilibrium liquid and vapor compositions for a temperature of 75 Celsius and $X_1=0.6$.

**Data:**

Antoine equations for the vapor pressures of pure species. **Temperature in Celsius and pressure in kilopascal (kPa).**

$$\ln P_1^{\text{saturation}} = 14.2724 - \frac{2945.47}{T + 224.0}$$

$$\ln P_2^{\text{saturation}} = 14.2043 - \frac{2972.64}{T + 209.0}$$

Solution:

First determine the vapor pressures of the two species at the given temperature, $T=75$ Celsius = 348.15 K.

$$P_1^{\text{saturation}} = e^{\left(14.2724 - \frac{2945.47}{T + 224.0}\right)} = e^{\left(14.2724 - \frac{2945.47}{75 + 224.0}\right)} = 83.2069 \text{ kPa}$$

$$P_2^{\text{saturation}} = e^{14.2043 - \frac{2972.64}{T + 209.0}} = e^{14.2043 - \frac{2972.64}{75 + 209.0}} = 41.9828 \text{ kPa}$$

$$P_{\text{Total}} = x_1 P_1^{\text{saturation}} + x_2 P_2^{\text{saturation}} = (0.6)(83.2069) + (0.4)(41.9828)$$

$$= 49.92414 + 16.79312 = 66.71726$$

$$y_1 = \frac{x_1 P_1^{\text{saturation}}}{x_1 P_1^{\text{saturation}} + x_2 P_2^{\text{saturation}}} = \frac{49.92414}{66.71726} = 0.748$$

$$y_2 = 1 - y_1 = 0.252$$

$$x_1 = 0.6$$

$$x_2 = 0.4$$

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5. (20 Points). State which thermodynamic potential reaches an extremum under the following external constraints on a system; consider no external work other than pressure-volume work is possible for this problem:

A. Temperature, pressure, and system composition **Gibbs Free Energy**

B. Temperature, volume, and system composition **Helmholtz Free Energy**

C. Entropy, volume, and system composition **Internal Energy**

D. Internal energy, volume, and system composition **Entropy**

6. (15 Bonus Points). It can be shown that the partition function of an ideal gas of "N" diatomic molecules in an external electric field, ϵ , is:

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

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:

$$dA = -SdT - PdV - (N\bar{\mu}) d\epsilon$$

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

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

Solution:

From the relation for the total differential of A at constant volume and temperature:

$$dA = -SdT - PdV - (N\bar{\mu}) d\epsilon = -(N\bar{\mu}) d\epsilon$$

thus

$$\left(\frac{\partial A}{\partial \epsilon} \right)_{T,V} = -N\bar{\mu} \quad \Rightarrow \quad \bar{\mu} = \left(\frac{-1}{N} \right) \left(\frac{\partial A}{\partial \epsilon} \right)_{T,V}$$

That's it; simply a matter of doing some differentiation now:

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$$\begin{aligned}\bar{\mu} &= \left(\frac{-1}{N}\right) \left(\frac{\partial A}{\partial \epsilon}\right)_{T,V} = \left(\frac{-1}{N}\right) \left(\frac{\partial(-k_B T \ln Q)}{\partial \epsilon}\right)_{T,V} \\ &= \left(\frac{k_B T}{N}\right) \left(\frac{\partial(\ln Q)}{\partial \epsilon}\right)_{T,V} \\ &= \left(\frac{k_B T}{N}\right) \left(\frac{\partial(N \ln q)}{\partial \epsilon}\right)_{T,V} - \left(\frac{k_B T}{N}\right) \left(\frac{\partial(\ln N!)}{\partial \epsilon}\right)_{T,V}\end{aligned}$$

second term is zero since N! does not depend on electric field

$$\begin{aligned}\bar{\mu} &= \left(\frac{k_B T}{N}\right) \left(\frac{\partial(N \ln q)}{\partial \epsilon}\right)_{T,V} = \left(\frac{N k_B T}{N}\right) \left(\frac{\partial(\ln q)}{\partial \epsilon}\right)_{T,V} = k_B T \left(\frac{\partial(\ln q)}{\partial \epsilon}\right)_{T,V} \\ &= -k_B T \left(\frac{\partial \ln \epsilon}{\partial \epsilon}\right)_{T,V} + k_B T \left(\frac{\partial \ln \left(\sinh\left(\frac{\mu \epsilon}{k_B T}\right)\right)}{\partial \epsilon}\right)_{T,V} \\ &= \frac{-k_B T}{\epsilon} + k_B T \left(\frac{\mu}{k_B T}\right) \coth\left(\frac{\mu \epsilon}{k_B T}\right) \\ &= \mu \left[\coth\left(\frac{\mu \epsilon}{k_B T}\right) - \frac{k_B T}{\mu \epsilon}\right]\end{aligned}$$