

Exam #1

Name Key

Student ID _____

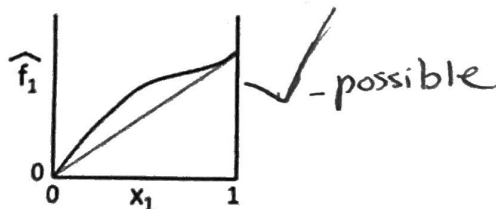
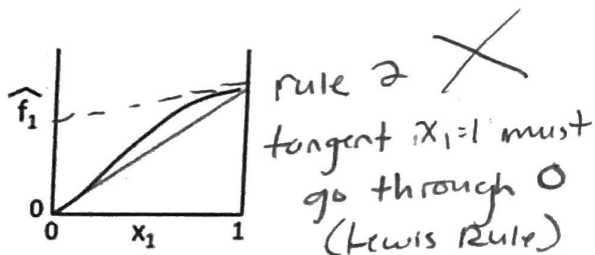
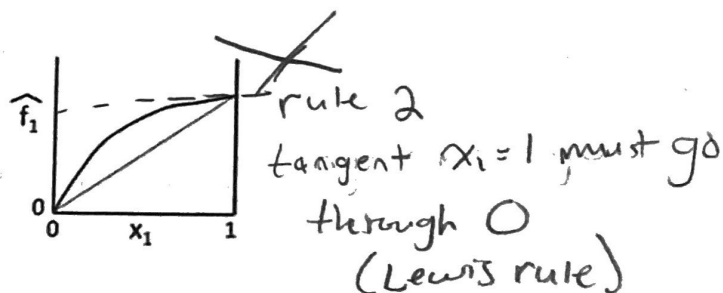
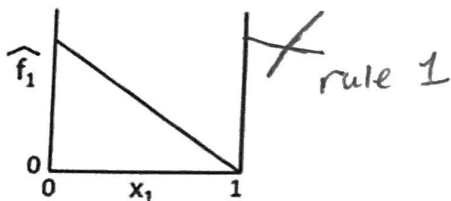
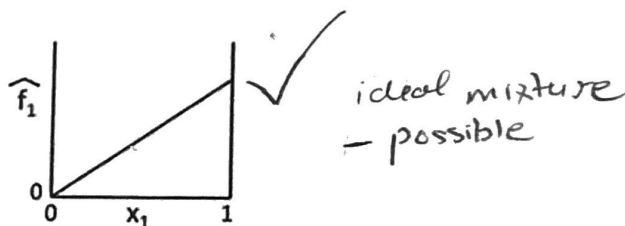
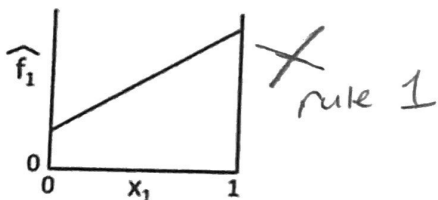
Exam Guidelines:

- Non-graphing calculator and pencil/pens are permitted.
- One 8.5 x 11" sheet of paper with only your own handwriting is allowed (both sides ok).
- No textbook or other resources.
- All other materials, books, and cell phones should be zipped in your backpack.
- Show all your work and provide complete explanations to receive credit.
- Time = 50 minutes
- have access to appendix

Problem	Estimated Time	Score	Possible
1	5 min		15
2	15 min		35
3	25 min		50
Total			100

Extra Space for your work below:

1. Below are fugacity six plots for the fugacity of liquid 1 vs. mole fraction in a binary solution of 1 and 2. Circle the ones which are plausible. For the ones that are not plausible, explain why with one sentence.



2 rules for fugacity plots:

- 1) @ $x_1 = 0$, $\hat{f}_1 = 0$
- 2) @ $x_1 = 1$, $\hat{f}_1 = \hat{f}_1^{\text{ideal}}$ (fugacity line must be tangent to ideal line)
 $x_1 = 0$, $\hat{f}_1 = 0$ (for Lewis-Randall line)

2. Many cars around the world run on compressed natural gas (CNG). It is a hot day, and a driver left their car in a sunny spot. After some time, the temperature inside the CNG tank is 51 °C and the pressure is 69 bar. For the purposes of this exercise, you may assume that the natural gas is a vapor composed of 90% methane and 10% ethane.

- a. Is the Lewis fugacity rule a good way to determine the fugacity of methane under these conditions? Explain your reasoning qualitatively (no equations).

yes. Lewis Randall is good assumption if:

1) species a is in excess ✓

2) species a and b are chemically similar ✓

- b. Is it as good of an assumption for ethane? Why?

No, ethane (relative to methane) is not excess species for Lewis-Randall rule assumption

- c. Calculate the fugacity of methane under these conditions.

lookup values, T_c , P_c , ω , Lee-Kesler

Lewis Randall Rule for methane vapor

$$\hat{f} = \phi_{CH_4} y_{CH_4} P$$

Lee-Kesler correlations needed (high P)

$$T_r = \frac{T}{T_c} = \frac{324 K}{190.6 K} = 1.7$$

$$P_r = \frac{P}{P_c} = \frac{69 \text{ bar}}{46} = 1.5$$

$$\log \phi_{CH_4} = \log \phi^{(0)} + \omega \log \phi^{(1)}$$

solve for ϕ using tables

$$\hat{f} = \phi (0.90) (69 \text{ bar})$$

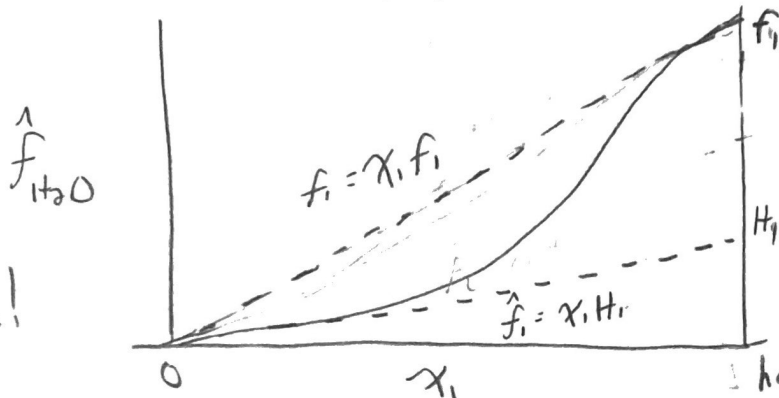
3. The radiator in your car runs on a mixture of water (1) and ethylene glycol (2). The excess thermodynamic properties of water/ethylene glycol mixtures are as follows $g^E = -400x_1x_2$ (J/mol) - fitted from J. Chem. Eng. Data, 1984, 29, 427-429). Assume that the temperature in your radiator is about 130 °C

- a. Are the water-glycol interactions stronger than the water-water and glycol-glycol interactions? Why?

g^E is negative, therefore the mixture is favorable thus unlike interactions are greater

- b. Qualitatively draw a plot of the fugacity of water as a function of its mole fraction, x_1 .

The Lewis Randall
Ideal line
must go
through 0
in the sketch!



H_1 H_1 must be $< f_1^sat$
as unlike interactions
are greater, will
have less tendency to
escape

- c. Label the fugacity of the pure species.
d. Calculate the activity coefficient of water in a 40% water/60% glycol mixture.

$$RT \ln \gamma_1 = A x_2^2$$

$$(8.314 \text{ J/mol}\cdot\text{K})(403 \text{ K}) \ln \gamma_1 = (-400)(0.6)^2$$

$$\boxed{\gamma_1 = 0.96}$$

- e. What is the pressure in your radiator? Assume the gas phase is ideal.

$$f_i = \phi_i x_i P^{sat}$$

$$P_{tot} = P_1 + P_2$$

$$P_{tot} = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

$$P_{tot} = (0.4)(0.96)(P_1^{sat}) + (0.6)(0.98)(P_2^{sat})$$

$$\phi_1 = 1$$

$$\phi_2 = 1$$

$$P_1^{sat} = f_1$$

$$P_2^{sat} = f_2$$

$$\gamma_1 = 0.96$$

$$\gamma_2 = 0.98$$

$$x_1 = 0.4$$

$$x_2 = 0.6$$

Antoine's
Equation

Solve

solving for γ_2

$$(8.314)(403 \text{ K}) \ln \gamma_2 = (-400)(0.4)^2$$

$$\text{J/mol}\cdot\text{K} \quad \rightarrow 0.98$$

Exam #2 (40 pts total)

- Time = 50 minutes
- One 8.5 x 11" sheet of paper with only your own handwriting is allowed
- Show all work and provide complete explanations to receive credit.

1. Gas-phase fugacity: (15 pts)

- a. Calculate the fugacity coefficient of pure acetylene at its saturation pressure at 277K, 29.6 bar. From the Lee-Kesler tables: $\log \Phi^0 = -0.111$, $\log \Phi^1 = -0.053$ and $\omega = 0.184$ (4pts)

$$\log \Phi_1 = \log \Phi^{(0)} + \omega \log \Phi^{(1)}$$

$$\log \Phi_1 = -0.111 + 0.184(-0.053)$$

$$\log \Phi_1 = -0.12 \quad \boxed{\Phi_1 = 0.757}$$

- b. Calculate the fugacity of acetylene vapor that is in equilibrium with a liquid mixture that contains 30 mol% acetylene and 70 mol% acetone at 277K. Assume that the liquid is behaving ideally and that the Lewis Fugacity Rules holds for the gas phase. (6pts)

$$\hat{f}^v = \hat{f}^l$$

$$\hat{\phi}_1 y_1 P = x_1 x_1 P^{\text{sat}}$$

$$\hat{f}^v = \hat{\phi}_1 y_1 P$$

$$= (0.757)(0.30)(29.6 \text{ bar})$$

$$\boxed{\hat{f}^v = 6.73 \text{ bar}}$$

- c. In reality, the mixtures of acetone and acetylene have negative excess Gibbs free energies. Will the pressure be higher or lower than the one you predicted under the previous question? Why? (5 pts)

negative g^E means mixture is favored and unlike interactions greater. Fugacity is tendency for unlike interactions to escape, so \hat{f} must be smaller, meaning pressure is also smaller.

2. Liquid-phase fugacity and VLE of benzene (B) and acetonitrile (A) (25 pts)

- a. The activity coefficient of benzene, γ_B^∞ , in infinite dilution in acetonitrile is 3.2 at 293.15K. Assuming benzene and acetonitrile follow a two-suffix Margules model, calculate the A parameter in J/mol (4 pts)

$$RT \ln \gamma_B^\infty = A x_a^2$$

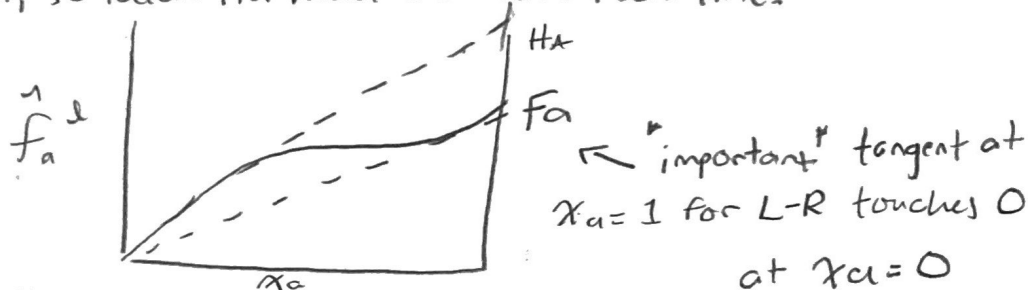
$$\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (293.15 \text{ K}) \ln(3.2) = A (1)^2$$

$$\boxed{A = 2834.8 \text{ J/mol}}$$

$x_a = 1$ if b in infinite dilution

- b. Qualitatively draw a curve of the fugacity of acetonitrile in the liquid as a function of its mole fraction in the liquid phase (x_a) (4pts)

* A is positive, so g^E is also positive! this means unlike interactions and unfavorable, so ideal H_a must be above real line.



- c. Are the like interactions or unlike interactions stronger? Why? (5 pts)

like interactions, see explanation above.

$H_a > F_a$, as per curve. F_a (ideal like interactions) has lower fugacity, less tendency to escape mixture, so must be stronger.

- d. The vapor pressures of acetonitrile and benzene at 293.15K are 9.3 kPa and 12.8 kPa, respectively. Calculate the total pressure above a liquid acetonitrile and benzene mixture, as well as the gas phase composition (y_a and y_b) at equilibrium, if $x_a = 0.35$ and $x_b = 0.65$. (12 pts)

VLE problem,
want to solve gas composition
so this is bubble pt calculation;

Raoult's Law; $P = \sum x_i P_i^{\text{sat}}$

$$P = x_a P_a^{\text{sat}} + x_b P_b^{\text{sat}}$$

$$P_{\text{total}} = (0.35)(9.3 \text{ kPa}) + (0.65)(12.8 \text{ kPa})$$

$$\boxed{P_{\text{total}} = 11.575 \text{ kPa}}$$

$$y_i = \frac{x_i P_i^{\text{sat}}}{P_{\text{total}}}$$

$$y_a = \frac{x_a P_a^{\text{sat}}}{P_{\text{total}}}$$

$$y_b = \frac{x_b P_b^{\text{sat}}}{P_{\text{total}}}$$

$$y_a = \frac{(0.35)(9.3 \text{ kPa})}{(11.575 \text{ kPa})}$$

$$y_b = \frac{(0.65)(12.8 \text{ kPa})}{(11.575 \text{ kPa})}$$

$$\boxed{y_a = 0.28}$$

$$\boxed{y_b = 0.72}$$