

ATOMS, MOLECULES AND RESEARCH

THERMODYNAMICS SPRING QUARTER MID TERM EXAMINATION, 2004

STUDENT NAME

Answer key

ANSWER ALL THE QUESTIONS. PLEASE SHOW ALL WORK.

1. Define the following terms. Please give short answers.

a) "congruent melting point"

The melting point of a "new compound" formed by the stoichiometric combination of two different elements/compounds.

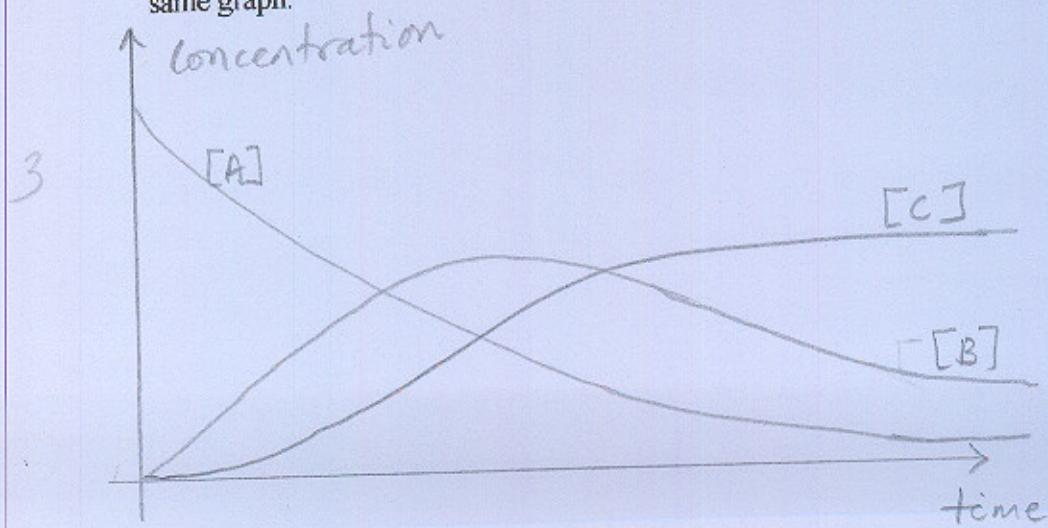
b) "colligative properties" and give two examples

The change in solvent properties due to the presence of a solute
 m.p. depression
 b.p. elevation
 decrease in vapor pressure
 osmotic pressure

c) Half life of a chemical reaction

The time it takes for a reactant to be reduced to half of its original concentration

- d) If you are given two consecutive first order reactions: $A \rightarrow B \rightarrow C$ draw a graph of concentration versus time to show how the concentrations of A, B, and C change with time. Draw all three on the same graph.



2. A solution containing 25.3 mol % benzene and 74.7 mol % toluene boils at 100°C and 1 atm. The liquid obtained by condensing the vapor boils at 94.8°C. Calculate the composition of this liquid assuming ideal behavior. The vapor pressure of pure benzene is 1357 torr at 100°C and 1108 torr at 94.8°C.

$$x_b = 0.253$$

$$x_t = 0.747$$

$$\text{at } 100^\circ\text{C} \quad P_b = \alpha_b P_b^* = (0.253)(1357 \text{ torr})$$

y_b	y_t
11	11
x_b	x_t

$$P_b = 343.3 \text{ torr}$$

$$\text{But } P_b = y_b P_{\text{tot}} \quad \text{since } 100^\circ\text{C and 1 atm; } P_{\text{tot}}$$

$$(343.3 \text{ torr}) = y_b (1 \text{ atm}) \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right)$$

$$\Rightarrow y_b = 0.452 \quad \therefore y_t = 1 - y_b = 0.548$$

$\Rightarrow y_b = 0.452$ y_t
 We take the vapor composed of y_b and y_t and
 $y_t = 0.548$

condense it.
 \therefore Composition of the condensate } $y_b = 0.452, y_t =$
 at $94.8^\circ C$

ndense it.
∴ Composition of the } condensate } $y_b = 0.452$, y_t
at $94.8^\circ C$

$$\therefore \text{Composition of } y \text{ the liquid} \quad y_b = 0.452, \quad y_t = 0.540$$

3. Look at the boiling point diagram given on the next page for a mixture of benzene and toluene, plotted at 1 bar pressure. Using this diagram answer the following questions.

- a) If a solution containing 0.5 mole fraction of benzene was heated, at what temperature will the first bubble of vapor appear. Show work.

91.5°C
 On the diagram, A is when this solution first forms bubbles of vapor. \therefore Temperature is given by point B ($= 91.5^\circ\text{C}$)

- b) What will be the composition of the above vapor? Show work.

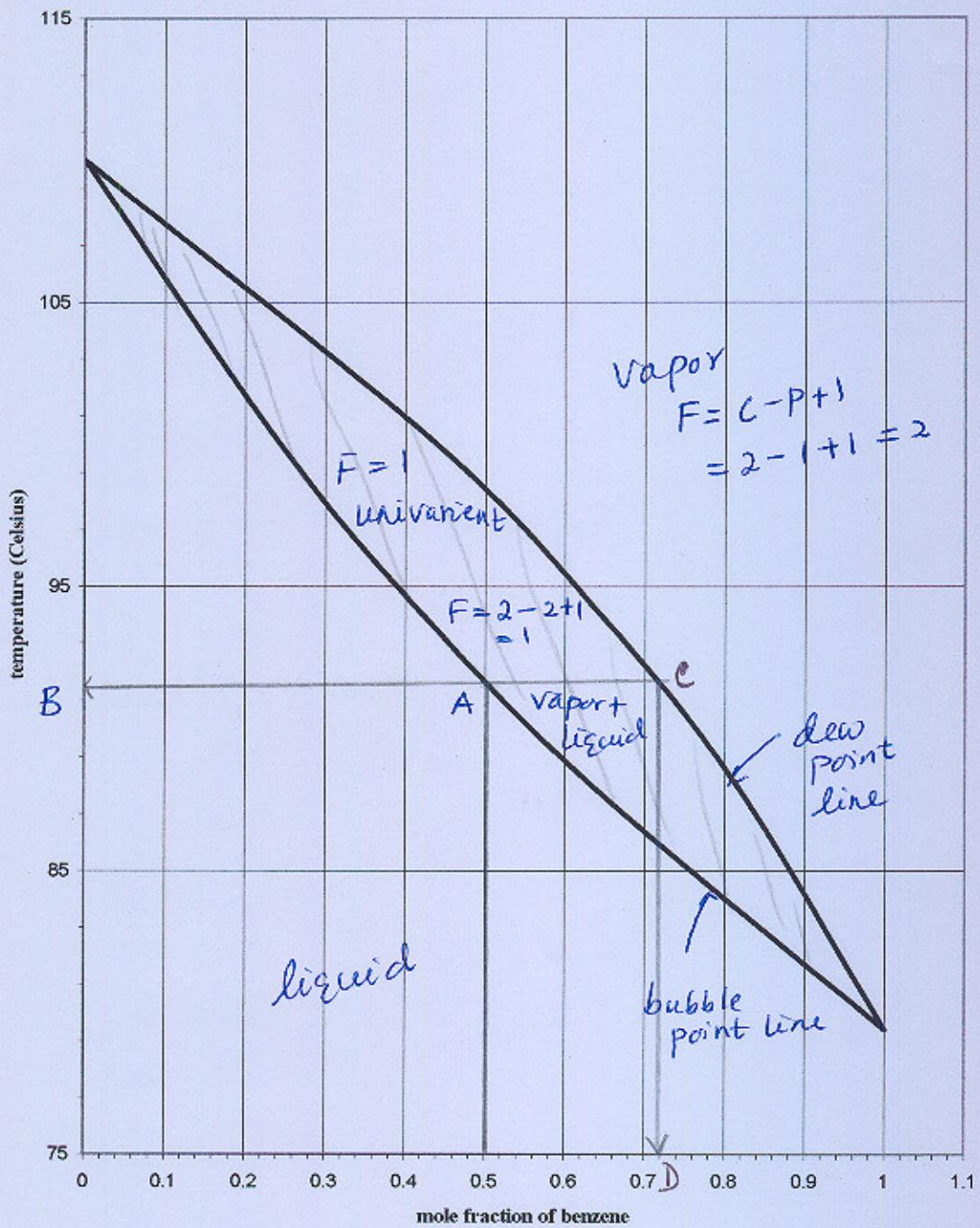
Draw a tie line from A to C. Find the composition at C (which is D) = 0.72 mole fraction benzene
 $= 0.28$ mole fraction toluene

- c) What is the phase rule you use for this diagram and why?

$F = C - P + 1$
 The "normal" rule where $F = C - P + 2$ is changed to
 $F = C - P + 1$ because pressure is held constant.

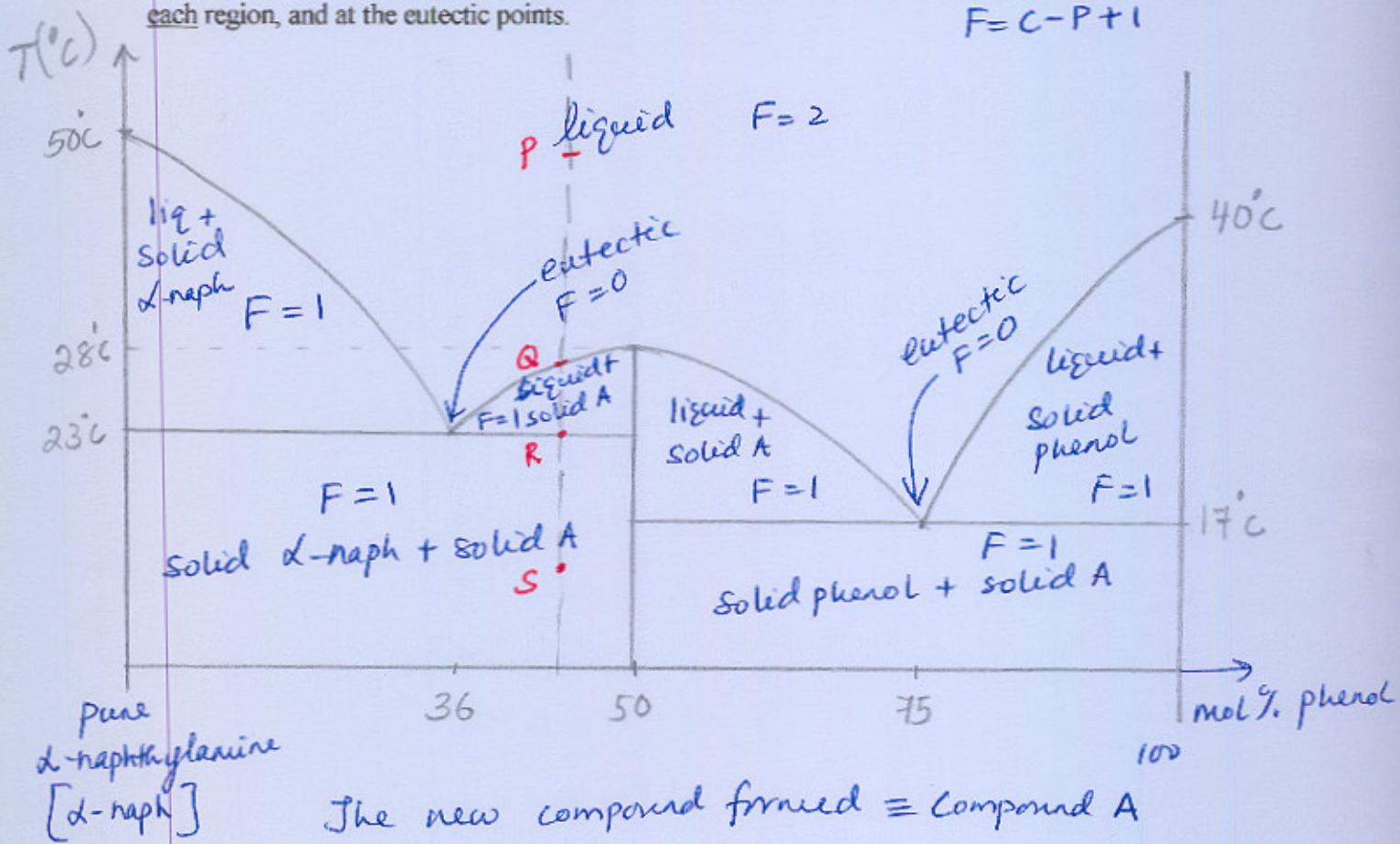
- d) Mark the following on the phase diagram.

- Bubble point curve
- Dew point curve
- An area that is univariant \sim means $F = 1$



4. Phenol melts at 40°C; α -naphthylamine melts at 50°C. In the binary system of phenol and α -naphthylamine, there are eutectics at 75 mol% phenol and 17°C, and 36 mol % phenol and 23°C. A compound is formed at 50 mol% phenol with a melting point of 28°C. All these data are recorded at 1 atm. Sketch a boiling point diagram at 1 atm for this system. Clearly mark the eutectics and the phases present in each region. Determine the number of degrees of freedom in each region, and at the eutectic points.

$$F = C - P + 1$$



Describe clearly what happens if a mixture containing 40 mol% phenol is cooled from 50°C to 10°C.

At point P [40% phenol & 50°C] the system is a homogeneous liquid, which when cooled from P to Q will cool down in the liquid phase. At point Q, solid A crystals will begin to precipitate out. The liquid will become richer in α -naph, as more and more solid A precipitates out with cooling. At point R, all of the liquid will turn into a solid, the last liquid being solidified as solid α -naph. From R to S, the solid mixture (immiscible) will cool down.

5. In an experiment, a diligent student observed that the rate constant of a reaction doubled when the temperature was changed from 25 °C to 33 °C . What is the activation energy of this reaction?

$$k_1 = A e^{-E_a/RT_1} \quad \text{--- (1)} \quad T_1 = 25^\circ\text{C} = 298.15\text{K}$$

$$2k_1 = A e^{-E_a/RT_2} \quad \text{--- (2)} \quad T_2 = 33^\circ\text{C} = 306.15\text{K}$$

$$\frac{(2)}{(1)} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{-\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]}$$

$$\ln 2 = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -\frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$E_a = -R \ln 2 \left[\frac{T_1 T_2}{T_1 - T_2} \right]$$

$$E_a = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(0.693) \left[\frac{(298.15\text{K})(306.15\text{K})}{(298.15\text{K} - 306.15\text{K})} \right]$$

$$= 65.74 \times 10^3 \text{ J mol}^{-1}$$

$$= \underline{\underline{65.7 \text{ kJ mol}^{-1}}}$$

6. For the reaction: $A + B + C \rightarrow D$ the following information is available.

[A]	[B]	[C]	$-d[A]/dt$	
1.0	1.0	1.0	3.2×10^{-3}	①
0.1	1.0	1.0	3.2×10^{-4}	②
1.0	0.1	1.0	3.2×10^{-5}	③
1.0	0.1	0.1	1.0×10^{-5}	④

Determine the rate law and the rate constant from this data.

$$\text{rate law: } \text{rate} = k[A]^\alpha [B]^\beta [C]^\gamma = -\frac{d[A]}{dt}$$

$$\textcircled{1} \Rightarrow \text{rate} = k[1]^\alpha [1]^\beta [1]^\gamma = 3.2 \times 10^{-3} \quad \textcircled{5}$$

$$\textcircled{2} \Rightarrow \text{rate} = k(0.1)^\alpha (1)^\beta (1)^\gamma = 3.2 \times 10^{-4} \quad \textcircled{6}$$

$$\textcircled{3} \Rightarrow \text{rate} = k(1)^\alpha (0.1)^\beta (1)^\gamma = 3.2 \times 10^{-5} \quad \textcircled{7}$$

$$\textcircled{4} \Rightarrow \text{rate} = k(1)^\alpha (0.1)^\beta (0.1)^\gamma = 1.0 \times 10^{-5} \quad \textcircled{8}$$

$$\textcircled{5} \Rightarrow \frac{(0.1)^\alpha}{(1)^\alpha} = \frac{3.2 \times 10^{-4}}{3.2 \times 10^{-3}} \Rightarrow (0.1)^\alpha = 0.1 \Rightarrow \underline{\alpha = 1}$$

$$\textcircled{7} \Rightarrow \frac{(0.1)^\beta}{(1)^\beta} = \frac{3.2 \times 10^{-5}}{3.2 \times 10^{-3}} \Rightarrow (10^{-1})^\beta = (10^{-2}) \Rightarrow \underline{\beta = 2}$$

$$\textcircled{8} \Rightarrow \frac{(0.1)^\gamma}{(1)^\gamma} = \frac{1.0 \times 10^{-5}}{3.2 \times 10^{-5}} \Rightarrow (0.1)^\gamma = 0.3125$$

$$\ln(0.1)^\gamma = \ln(0.3125)$$

$$\gamma \ln(0.1) = \ln(0.3125)$$

$$\Rightarrow \gamma = \frac{\ln(0.3125)}{\ln(0.1)} = 0.5$$

\therefore Rate law:

$$\text{rate} = [A][B]^2[C]^{0.5}$$

$$⑤ \Rightarrow k(1)(1)^2(1)^{0.5} = 3.2 \times 10^{-3}$$

$$k = \underline{\underline{3.2 \times 10^{-3}}}$$

7. Consider the n^{th} order reaction $A \rightarrow \text{Products}$
 Derive the following equation for this reaction.

$$t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{(n-1) k [A]_0^{n-1}}$$

where k = rate constant, $[A]_0$ = initial concentration of A, and $t_{\frac{1}{2}}$ = half life of A

$$\text{rate} = - \frac{d[A]}{dt} = k [A]^n$$

$$\Rightarrow \frac{d[A]}{[A]^n} = -k dt$$

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^n} = - \int_{t=0}^t k dt \Rightarrow \left[\frac{[A]^{-n+1}}{-n+1} \right]_{A_0}^{A_t} = -kt$$

$$\frac{[A_t]^{-n+1} - [A_0]^{-n+1}}{(-n+1)} = -kt$$

$$\frac{1}{(1-n)} \left[\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} \right] = -kt$$

$$\left[\frac{1}{(\frac{[A]_0}{2})^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] = -kt_{\frac{1}{2}}$$

$$\frac{1}{-k(1-n)} \left[\frac{2^{n-1}}{[A_0]^{n-1}} - \frac{1}{[A_0]^{n-1}} \right] = t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{(2^{n-1} - 1)}{(n-1) k [A_0]^{n-1}}$$