

NAME: SOLUTIONS

CHEM 5200 – Physical Chemistry
EXAM #3

6 November 2003

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.

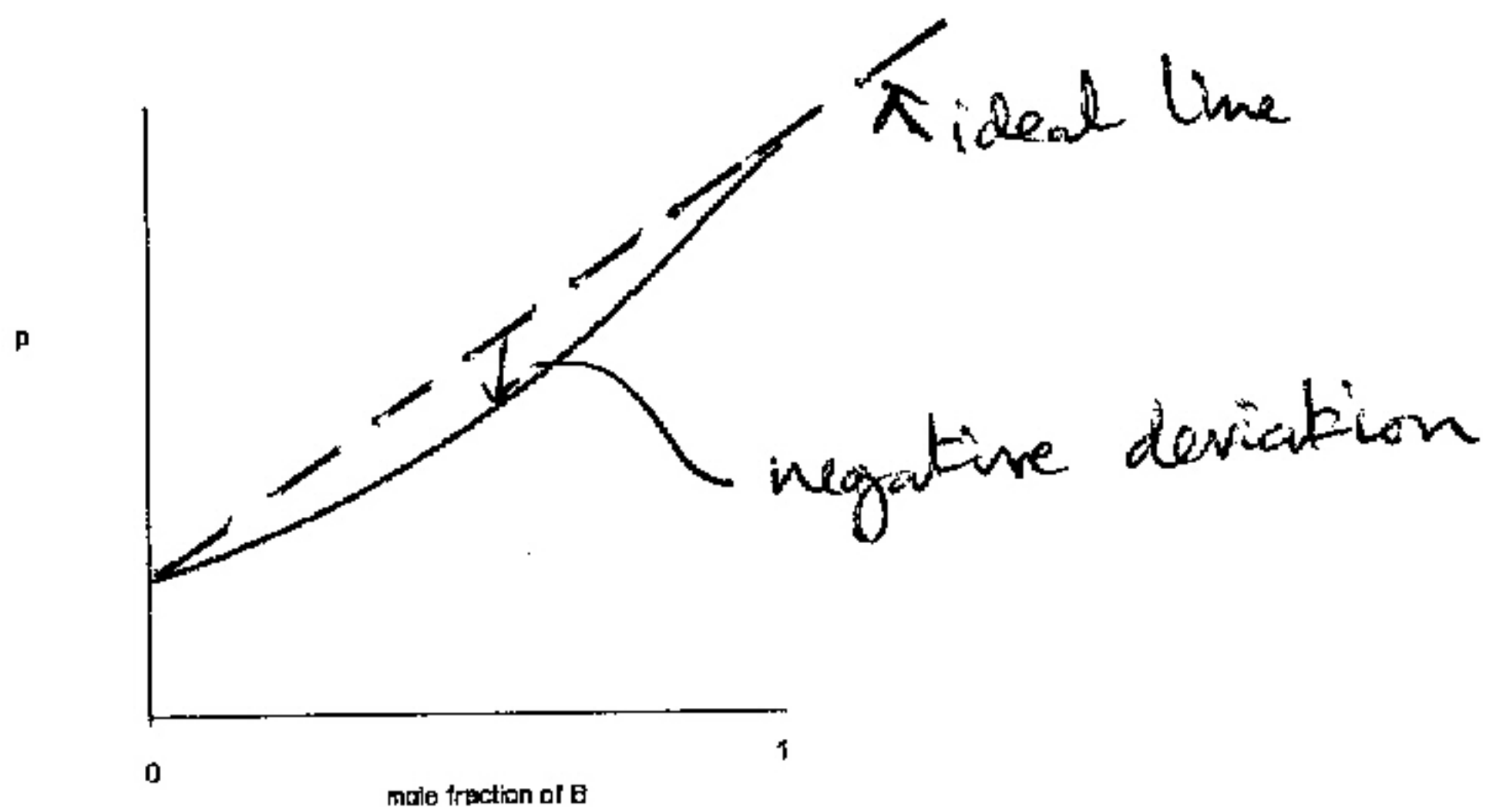
Give units for all quantities!

Some data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ $\gamma = C_p/C_v$
 $C_p - C_v = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$
 $A = U - TS$ Trouton's constant = $85 \text{ J K}^{-1} \text{ mol}^{-1}$

1. 21 points.

Consider the mixture of two liquids A and B. The vapor pressure p of this mixture is plotted as a function of composition below.

- Is this an ideal solution? *Explain very briefly.*
- Does this mixture obey Raoult's Law, or show a positive or negative deviation? *Justify briefly.*
- Comment briefly on the relative intermolecular forces in pure A, pure B, and in the mixture.



- No, there is a non-linear relation between p and x_B .
- No, it shows a negative deviation where p is lower in the mixture than for an ideal mixture.
- A to B forces are stronger (more attractive) than A-A or B-B.

2. 39 points.

a) Starting with an expression for dG , derive the Maxwell relation:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

AND provide AN EXPLANATION FOR EACH STEP. Points will be awarded for a demonstrated UNDERSTANDING of the process. Example:

STEPS:	EXPLANATION
whatever mathematical step	commonly known formula
whatever mathematical step	integrated
whatever mathematical step	because of this-and-that property, X=Y

b) Use this result to evaluate ΔS when the pressure acting on 30 cm^3 liquid methanol is raised isothermally from 10^5 Pa to $2 \times 10^7 \text{ Pa}$. You may assume V is roughly constant. The coefficient of expansion is $\alpha = 0.001 \text{ K}^{-1}$.

$$a) \quad G = H - TS \quad \therefore \quad dG = dH - Tds - SdT$$

$$H = U + pV \quad \therefore \quad dH = dU + pdV + Vdp$$

$$U = q_r + w \quad \therefore \quad dU = dq_r + dw = Tds - pdV$$

$$\text{collecting together: } dG = Tds - pdV + pdV + Vdp - Tds - SdT \\ = Vdp - SdT$$

$$\text{consider } G \text{ as } G(p, T) \text{ so } dG = \left(\frac{\partial G}{\partial p}\right)_T dp = \left(\frac{\partial G}{\partial T}\right)_p dT$$

$$\text{Compare terms in } dG \text{ to see } \left(\frac{\partial G}{\partial p}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p}\right)_T\right)_p = \left(\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T}\right)_p\right)_T \quad \therefore \quad \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$b) \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad \text{so} \quad \left(\frac{\partial V}{\partial T}\right)_p = \alpha V = 0.001 \text{ K}^{-1} \cdot 30 \times 10^{-6} \text{ m}^3 \\ = 3 \times 10^{-8} \text{ m}^3 \text{ K}^{-1}$$

$$\Delta S = \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p}\right)_T dp = - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_p dp = -3 \times 10^{-8} \text{ m}^3 \text{ K}^{-1} (2 \times 10^7 \text{ Pa} - 10^5 \text{ Pa}) \\ = -0.597 \text{ J K}^{-1}$$

3. 40 points.

- (a) Apply the Clapeyron equation $dp/dT = \Delta S/\Delta V$ to the evaporation of a liquid, and with the assumption of ideal gas behavior for the vapor, negligible volume for the liquid, and that $\Delta_{\text{vap}}H$ is independent of temperature, find $\ln(p_2/p_1)$ as function of $\Delta_{\text{vap}}H$, T_1 and T_2 , where p_1 and p_2 are the vapor pressures at temperatures T_1 and T_2 .
- (b) Water boils at 100°C at 10^5 Pa pressure. Use your result to part (a) to find the boiling point of water at high altitude in Boulder, CO, where the atmospheric pressure is $8.7 \times 10^4\text{ Pa}$. $\Delta_{\text{vap}}H$ is 40.7 kJ mol^{-1} .

$$a) \Delta S \approx \frac{\Delta H}{T} \quad \text{and} \quad \Delta V \approx V_{\text{gas}} \approx \frac{RT}{P}$$

$$\text{so} \quad \frac{dp}{dT} = \frac{\Delta H}{T} \cdot \frac{P}{RT} = \frac{P \Delta H}{RT^2} \quad \therefore \quad \frac{dp}{P} = \frac{\Delta H}{R} \cdot \frac{dT}{T^2}$$

Integrate both sides

$$\int_{p_1}^{p_2} \frac{dp}{P} = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \text{so} \quad \ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$b) \quad \ln\left(\frac{8.7 \times 10^4 \text{ Pa}}{10^5 \text{ Pa}}\right) = \frac{-40.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_2} - \frac{1}{373 \text{ K}}\right)$$

which gives $T_2 \approx 369 \text{ K}$

(a drop of 4 K)