

EXAM 3

October 31, 2012

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!

YOUR NAME Solutions

Some data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$$dU = dq + dw \quad dS = dq_{\text{rev}}/T \quad \gamma = C_p/C_v \quad C_p - C_v = nR$$

$$dw = -p_{\text{ex}} dV \quad \text{Heat engine } \varepsilon = (T_h - T_c)/T_h \quad \text{adiabat: } pV^\gamma = \text{const}$$

$$\check{H} = U + pV \quad G = H - TS \quad A = U - TS$$

(1) 30 points

Starting with an expression for dH (HINT: in terms of p , V , T and S), derive the result that $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

$$H = U + pV \quad dU = dq + dw = TdS - pdV$$

$$dH = TdS - pdV + pdV + Vdp \\ = TdS + Vdp$$

Considering H as a function of S and p :

$$dH = \underbrace{\left(\frac{\partial H}{\partial S}\right)_p}_{= T} dS + \underbrace{\left(\frac{\partial H}{\partial p}\right)_S}_{= V} dp$$

Since order of differentiation is irrelevant:

$$\frac{\partial}{\partial p} \left(\left(\frac{\partial H}{\partial S} \right)_p \right)_S = \frac{\partial}{\partial S} \left(\left(\frac{\partial H}{\partial p} \right)_S \right)_p$$

Therefore

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

(2) 30 points

Evaluate the entropy change for the spontaneous evaporation of 1 mole of superheated liquid water (the system) to make steam at 380 K. You may assume the heat capacities do not vary significantly with temperature.

DATA: $\Delta_{\text{vap}}H = 41.00 \text{ kJ mol}^{-1}$ at 373 K, $C_p(\text{water}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_p(\text{steam}) = 33.6 \text{ J K}^{-1} \text{ mol}^{-1}$.

What can you say about the entropy change for the surroundings?

Entropy is a state function, so we can find

$$\Delta S_{\text{sys}} = \Delta S_{\text{cool}} + \Delta S_{\text{vap}} + \Delta S_{\text{warm}}$$

$$\Delta S_{\text{cool}} = C_{p(\text{liq})} \ln\left(\frac{T_f}{T_i}\right) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{373 \text{ K}}{380 \text{ K}}\right) = -1.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{warm}} = C_{p(\text{vap})} \ln\left(\frac{T_f}{T_i}\right) = 33.6 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{380 \text{ K}}{373 \text{ K}}\right) = 0.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} = \frac{4.100 \times 10^4 \text{ J mol}^{-1}}{373 \text{ K}} = 109.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S = -1.4 \text{ J K}^{-1} \text{ mol}^{-1} + 109.9 \text{ J K}^{-1} \text{ mol}^{-1} + 0.6 \text{ J K}^{-1} \text{ mol}^{-1} = 109.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Since change is spontaneous, $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

therefore $\Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$

so $\Delta S_{\text{surr}} > -109.1 \text{ J K}^{-1} \text{ mol}^{-1}$

(3) 30 points

i) Starting from the Clausius-Clapeyron equation for the evaporation of a liquid,

$$dp/dT = \Delta_{\text{vap}}H / (T \Delta_{\text{vap}}V)$$

and the assumption that $\Delta_{\text{vap}}H$ is independent of temperature, deduce one form of the approximate Clapeyron equation, that

$$\ln\left(\frac{p_1}{p_2}\right) = -\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where p_1 and p_2 are the vapor pressures at temperatures T_1 and T_2 .

ii) Water boils at 373 K at 10^5 Pa pressure. Use the result from part (i) to find the water's boiling point in Boulder, CO when $p = 8 \times 10^4$ Pa, given that $\Delta_{\text{vap}}H = 41 \text{ kJ mol}^{-1}$.

i) assume molar ΔH_{vap} $V = \frac{RT}{P}$

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T \left(\frac{RT}{P}\right)} = \frac{\Delta H_{\text{vap}} P}{RT^2}$$

$$\int \frac{dp}{P} = \int \frac{\Delta H_{\text{vap}}}{R} \frac{dT}{T^2} \quad \ln p \Big|_{p_1}^{p_2} = -\frac{\Delta H_{\text{vap}}}{R} T^{-1} \Big|_{T_1}^{T_2}$$

$$\text{so } \ln p_1 - \ln p_2 = \ln\left(\frac{p_1}{p_2}\right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{ii) } \ln\left(\frac{10^5 \text{ Pa}}{8 \times 10^4 \text{ Pa}}\right) = \frac{-41,000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)$$

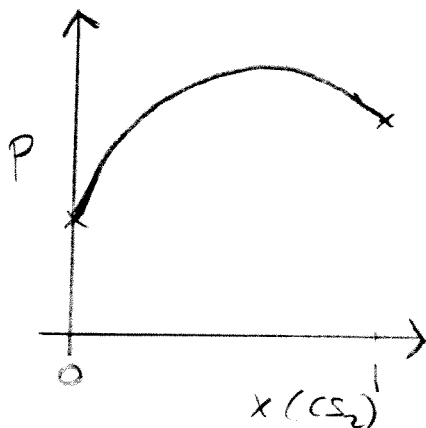
$$\hookrightarrow T_2 = \left(\frac{1}{373 \text{ K}} + \ln\left(\frac{1.0 \times 10^5 \text{ Pa}}{8 \times 10^4 \text{ Pa}}\right) \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{41,000 \text{ J mol}^{-1}}\right)^{-1}$$

$$= 366.8 \text{ K}$$

(4) 10 points

Here is a plot of vapor pressure as function of composition for mixtures of CS_2 and CH_3COCH_3 .

Define an ideal solution. Is the deviation from Raoult's Law positive or negative? **Explain your reasoning briefly.** Interpret this deviation in terms of intermolecular forces in the system.



Positive, because Raoult's Law dictates a linear relationship between mole fraction and partial pressure.

See Chapter 5 for description of intermolecular forces.