

Please budget your time carefully and show all work.

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

(1) (20 pts)

(a) Given that  $S = f(T, P)$ , derive an expression for  $dS$  in terms of  $T$  and  $P$  that is valid for any fluid, i.e., in terms of quantities like  $C_p$ ,  $\alpha$ , and  $\kappa$ .

$$\textcircled{a} \quad dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

$$\uparrow$$

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_p dT}{T} \quad \text{at const } P.$$

$$\Rightarrow \left( \frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T}$$

for  $\left( \frac{\partial S}{\partial P} \right)_T$  a Maxwell relation gives

$$\begin{array}{|c|c|} \hline P & S \\ \hline \downarrow & \downarrow \\ T & V \\ \hline \end{array}$$

$$- \left( \frac{\partial V}{\partial T} \right)_P$$

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$\text{but } \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{so} \quad \left( \frac{\partial V}{\partial T} \right)_P = V \alpha$$

$$\therefore dS = \frac{C_p}{T} dT - V \alpha dP$$

(b) The coefficient of thermal expansion  $\alpha$  of Fe(s) at 25°C is  $355 \times 10^{-7} \text{ K}^{-1}$ . What is the change in molar entropy of iron when the pressure is raised from 1 to 1000 bar at a constant temperature of 25°C? (The density of iron at 25°C is  $7.86 \text{ g cm}^{-3}$  and its molar mass is  $55.85 \text{ g/mol}$ )

$$\textcircled{b} \text{ at const. } T, \quad dS = -V\alpha dP$$

assuming  $V$  and  $\alpha$  are independent of  $P$ ,

$$\Delta S = -V\alpha\Delta P \quad \text{or} \quad \Delta \bar{S} = -\bar{V}\alpha\Delta P$$

$$\begin{aligned} \bar{V} &= \frac{1}{\rho} = \frac{1 \text{ cm}^3}{7.86 \text{ g}} \times \frac{55.847 \text{ g}}{\text{mol}} \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 \\ &= 7.1052 \times 10^{-6} \text{ m}^3/\text{mol} \end{aligned}$$

$$\begin{aligned} \Delta \bar{S} &= -(7.1052 \times 10^{-6}) (355 \times 10^{-7}) (1000 - 1) \times \frac{10^5 \text{ Pa}}{1 \text{ bar}} \\ &= -0.0252 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(2) (10 pts)

Consider the volume dependence of the Gibbs free energy under isothermal conditions. Show that this dependence is equal to  $-\frac{1}{\kappa}$ , where  $\kappa$  is the isothermal compressibility.

$$dG = -SdT + VdP$$

isothermal:  $dG = VdP$

divide by  $dV$  at const.  $T$ :  $\left(\frac{\partial G}{\partial V}\right)_T = V \left(\frac{\partial P}{\partial V}\right)_T$

but  $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

so  $\left(\frac{\partial G}{\partial V}\right)_T = V \left[-\frac{1}{V\kappa}\right] = -\frac{1}{\kappa}$

(3) (20 pts.)

(a) State the two approximations involved in deriving the Clausius-Clapeyron equation,

$$\frac{dP}{P} = \frac{\Delta\bar{H}}{RT^2} dT, \text{ from the Clapeyron equation, } \frac{dP}{dT} = \frac{\Delta\bar{H}_{trans}}{T\Delta\bar{V}_{trans}}$$

$$\Delta\bar{V} = \bar{V}_g - \bar{V}_{l,s} \approx \bar{V}_g$$

$$\bar{V}_g \approx \frac{RT}{P} \quad (\text{ideal gas})$$

(b) The normal boiling point ( $P = 1 \text{ atm}$ ) of ethanol is  $78.3^\circ\text{C}$ , and at this temperature  $\Delta\bar{H}_{vap} = 38.9 \text{ kJ/mol}$ . To what value must  $P$  be reduced if we want to boil ethanol at  $25.0^\circ\text{C}$  in a vacuum distillation?

$$\text{integrated C-C eqn: } \ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln P_2 = \ln(1) - \frac{38.9 \times 10^3}{8.3145} \left( \frac{1}{298.15} - \frac{1}{351.45} \right)$$

$$= -2.3798$$

$$P_2 = 0.093 \text{ atm}$$

(4) (20 pts.) A solution with 25.3 mol% benzene and 74.7% toluene boils at 100°C when the pressure is 1 atm (760 torr).

(a) Assuming the solution is ideal, what would be the composition of the vapor above the boiling solution ( $y_{\text{benzene}}$  and  $y_{\text{toluene}}$ )? Note that  $P_{\text{benzene}}^* = 1357$  torr at 100°C.

$$P_A = X_A P_A^* \quad \text{if ideal}$$

$$\text{so } P_{\text{benzene}} = (0.253)(1357) = 343.3 \text{ torr}$$

$$y_{\text{benzene}} = \frac{P_{\text{benzene}}}{760} = \frac{343.3}{760} = 0.452$$

$$y_{\text{toluene}} = 1 - y_{\text{benzene}} = 0.548$$

(b) When this vapor is condensed, a compositional analysis determines that it is actually 48.2 mol% benzene. What then is the Raoult's law standard state activity and associated activity coefficient of benzene in the original solution?

$$y_{\text{benzene}} = \frac{P_{\text{benzene}}}{X_{\text{benzene}} P_{\text{benzene}}^*}$$

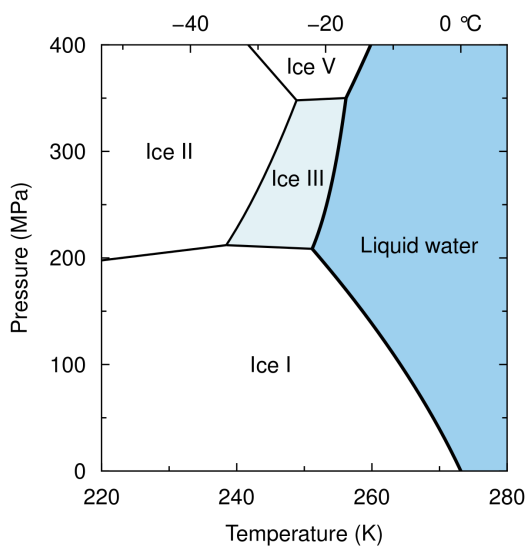
$$P_{\text{benzene}} = (0.482)(760) = 366.3 \text{ torr}$$

$$\gamma = \frac{366.3}{343.3} = 1.07$$

$$a_i = \gamma_i X_i = (1.07)(0.253) = 0.271$$

(5) (10 pts.) At 1 atm, the density of ice is  $0.92 \text{ g/cm}^3$ . Explain why the slope of the phase boundary between liquid water and ice is negative at low pressure, while it is actually positive at high pressure (see the phase diagram on the last page of exam). Show your work.

As seen in the Clapeyron equation (for example, see problem 3 above), the slope of P vs. T is inversely proportional to the change in molar volume between the two phases in equilibrium. At low pressures, the density of Ice I is less than that of liquid water, hence its molar volume is larger. Therefore  $\Delta\bar{V}(\text{Ice I} \rightarrow \text{water})$  is negative at these pressures and so is  $dP/dT$ . At higher pressures, e.g., when Ice III or Ice V is the most stable form of solid water on the liquid-solid coexistence curve, the density of the solid is evidently greater (and its molar volume hence smaller) than that of liquid water and the slope is positive.



(6) Multiple choice (4 pts each)

- (i) The fugacity of a gas represents
- (a) the actual pressure of a real gas.
  - (b) the pressure an ideal gas would have to exert to reproduce the chemical potential of the real gas.
  - (c) the intrinsic reactivity of a real gas.
  - (d) the capability of a real gas to do maximum expansion work.
- (ii) The criterion for equilibrium between two phases  $\alpha$  and  $\beta$  at constant  $T$  and  $P$  are
- (a)  $\Delta G > 0$
  - (b)  $\mu(\alpha) > \mu(\beta)$
  - (c)  $\mu(\alpha) = \mu(\beta)$
  - (d)  $\Delta A < 0$
- (iii) One mole of an ideal gas is expanded isothermally until its volume is doubled. What is  $\Delta G$  for this process?
- (a)  $\ln 2$
  - (b)  $RT/2$
  - (c)  $RT \ln \frac{1}{2}$
  - (d) can not be determined with this information
- (iv) Which of the following does not describe an ideal solution?
- (a) Activity coefficients are defined by a Raoult's law standard state.
  - (b)  $\mu_i = \mu_i^* + RT \ln x_i$
  - (c) All of the intermolecular interactions are nonzero but equivalent.
  - (d)  $P_i = x_i P_i^*$
- (v) The differential of a function  $z$  is found to be  $dz = (2x-2y+2)dx + (4y-2x-4)dy$ . If this is an exact differential, which of the following would have to be true:
- (a)  $(2x-2y+2) = (4y-2x-4)$
  - (b)  $\frac{\partial^2 z}{\partial x^2} = \frac{\partial^2 z}{\partial y^2}$
  - (c)  $\frac{\partial}{\partial y}(2x - 2y + 2) = \frac{\partial}{\partial x}(4y - 2x - 4)$
  - (d)  $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} = 0$