## CHEM352: Physical Chemistry I Homework Set III - due $1^{st}$ of Nov, 5.00 pm

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Lecture: Tue,  $2.10\text{-}3.25~\mathrm{pm}$  & Fri  $2.10\text{-}3.25~\mathrm{pm}$ , C111

Office hours: Wed, 4-6 pm,  $\mathbf{HB}$  -  $\mathbf{1321B}$ 

Problem 1 CH7/5pts

Warm up. Show that:

1.  $P\kappa = 1 - P\left(\frac{\partial \ln z}{\partial P}\right)_T$ , where  $\kappa$  is the isothermal compressibility.

- 2.  $P\beta = 1 + T\left(\frac{\partial \ln z}{\partial T}\right)_P$ , where  $\beta$  is the thermal expansion.
- 3. Show that  $T_c$ ,  $P_c$  and  $V_{m.c}$  in a system described by a van der Waals equation of state depend only on a and b parameters.

Problem 2 CH7/5pts

A 1.0 mole sample of Argon undergoes an isothermal reversible expansion from an initial volume of 1.00 L to a final volume of 50.0 L at 400 K. Calculate the heat transfer and the work done in this process using (1) ideal gas and (2) van der Waals equations of state. What fraction of work in the van der Waals case is due to the attractive term in the potential?  $A_A r = 1.355$  [bar· L² · mol -2],  $b_A r = 0.032$  [L · mol -1],

Problem 3 (P6.6) CH6/5pts

The shells of marine organisms contain calcium carbonate,  $CaCO_3$ , in a crystalline form of calcite., The second crystalline form of  $CaCO_3$  is an aragonite. Their physical and thermodynamic properties at T=298K and P=1 bar are listed below:

| Property                                 | Calcite | Aragonite |
|--|---------|-----------|
| $\Delta H_f^o[kJ \cdot mol^{-1}]$        | -1206.9 | -1207.0   |
| $\Delta G_f^o[kJ \cdot mol^{-1}]$        | -1128.8 | -1127.7   |
| $C_{P.m}^o[J\cdot K^{-1}\cdot mol^{-1}]$ | 81.9    | 81.3      |
| $S^{o}[J \cdot K^{-1} \cdot mol^{-1}]$   | 92.9    | 88.7      |
| $ ho[gmL^{-1}]$                          | 2.710   | 2.930     |

- 1. Would an isolated sample of calcite convert to argonite at T=298 K and P=1 bar? Explain.
- 2. Can you induce this convertion by varying applied pressure (T=298K)? Explain. What would it be the conversion pressure?
- 3. Can you induce this convertion by varying temperature (P=1bar)? Explain. What would it be the conversion temperature?

## Problem 4 (P6.24) CH6/5pts

Following reaction has  $K_p = 3.32 \cdot 10^3$  at 298 K.

$$H_2O_{(l)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

At what temperature the  $K_p = 5.50 \cdot 10^3$ ? Calculate the partial pressures of each gaseous component of the reaction. (Read chapter 6.11 before solving this problem).

CH8/5pts Problem 5

he vapor pressure of a solid and a liquid of the same substance is given by following equations:

$$\ln\left(\frac{P}{Torr}\right) = 22.413 - 2211(K/T)$$

$$\ln\left(\frac{P}{Torr}\right) = 18.352 - 1736(K/T)$$
(1a)

$$\ln\left(\frac{P}{Torr}\right) = 18.352 - 1736(K/T) \tag{1b}$$

- Calculate  $\Delta H_{fusion}$ ,  $\Delta H_{sublimation}$  and  $\Delta H_{vaporization}$ ,.
- Calculate the triple point temperature and pressure.

Hint - look at the formula that relates temperature and pressure of vapors above a liquid/solid and try to identify respective terms.