ROCHESTER

Workshop -3d

Physical Chemistry II

Exercises and Homework Set 8

Conceptional Review

- **i.** Discuss circular processes in pV and TS diagrams, conservation laws (state functions).
- ii. Relation between sense of circulation and work done/heat absorbed.
- **iii.** Evolution of enthalpy, entropy and free energy at phase transitions and inside coexistence region(spinodal).
- iv. Activity of real matter, gases and liquids.

1. Phase Coexistence-Maxwell Construction



The Maxwell Construction of the tie-line pressure (PTL) for a van der Waals model of a real gas at given temperature T relies on the equality of the two hatched areas in the shown p-V diagram. This is equivalent to equality of the pV work w_{FEDCB} done on the vdW gas along the isothermal

path $(F \rightarrow E \rightarrow D \rightarrow C \rightarrow B)$ and the work $w_{FDB} = p_{TL} \cdot (V_I - V_{II})$ required to compress a real gas through the (isothermal) coexistence region $\Delta V = (V_I - V_{II})$. For the evaluation of p_{TL} , it is useful to consider a hypothetical circular process Γ ($F \rightarrow E \rightarrow D \rightarrow C \rightarrow B \rightarrow D \rightarrow F$).

- a) What conditions on the molar free energies define the coexistence end points *F* and *B*?
- **b)** By what amount does the entropy change over the circular process Γ ?
- **c)** Show that the circular path integrals over heat (Q) transfer and work done are equal, i.e., $\oint_{\Gamma} dQ = \oint_{\Gamma} p(T) \cdot dV$.

d) Derive an expression for the tie-line pressure in terms of the width $\Delta V = V_I - V_{II}$ of the coexistence region.

2. Entropy of Pure Liquids

Consider processes involving **N** moles of a pure real liquid for which heat capacity C_p , isothermal compressibility factor κ , and thermal expansion factor α are known. The entropy **S** of the liquid depends on pressure **p** and temperature **T**.

- a) Write down the total differential *dS* in terms of its independent variables *p* and *T* and explicit expressions for the corresponding partial derivatives.
- **b)** Calculate the function S(p,T) for a volume of 1L water (at standard state) at a pressure of p = 10bar and temperature of T = 298K.

Data: $V_m = 18.0 \cdot 10^{-6} \ m^3/mol$; $\alpha = 2.1 \cdot 10^{-4} K^{-1}$

3. Virial Expansion

Assume the van der Waals model for **N** moles of a real gas in a container of volume **V** and fixed temperature **T**, with excluded volume **b** per mole and pressure reduction parameter **a**, i.e., $p = NRT \cdot (V - Nb)^{-1} - a \cdot \rho^2$ where $\rho = N/V$ is the density of the gas.

a) Express its pressure \boldsymbol{p} as a power series in the density ρ , i.e.,

$$p(\rho) = R \cdot T \cdot \rho \cdot \left[1 + B(T) \cdot \rho + C(T) \cdot \rho^{2} + \cdots\right]$$

(**Hint:** Use $\sum_{n=0}^{\infty} x^n = (1-x)^{-1}$ for $x \ll 1$)

b) Derive the viral coefficients **B**(**T**) and **C**(**T**).