ChE 221A Chemical Engineering Thermodynamics

Mid-semester examination (75 points)

1. Answer the following questions:

   a. State the law of corresponding states (3 Points)

   b. How the stability criterion in Helmholtz free energy representation leads to $\kappa_T \geq 0$ and stability criterion in entropy representation leads to $C_V \geq 0$ (6 Points)

   c. Derive Gibbs phase rule from the first principles (6 Points)

   d. On a $P-V$ diagram, show various isotherms, the critical point, a spinodal and a binodal for a region where liquid and vapor phases coexist (4 Points). Show the stable, metastable and unstable region (3 Points). Describe thermodynamic characteristics of the critical point in terms of Helmholtz free energy, pressure, volume, temperature and their derivatives/differentials (5 Points). (Total 12 Points)

2. The throttling process at constant volume requires Euken coefficient ξ, which is defined as $\xi = \left(\frac{\partial T}{\partial \underline{V}}\right)_{\underline{U}}$. Express ξ in terms of measurable properties C_P, κ_T, α, T and/or P (13 Points)

3. Obtain κ_T and α for van der Waals gas (5 points)

4. Two compartments, a and b, of a thermodynamic system enclosed in an isolated chamber respectively obey the following thermal equations of states: $\frac{1}{T_a} = \frac{3N_a R}{2U_a}$ and $\frac{1}{T_b} = \frac{5N_b R}{2U_b}$, where R is a universal gas constant (8.314 kJ/kmol K). System a contains 3 kmol while b contains 2 kmol. Initially both the systems are separated by an insulating wall, such that

system a is at 400 K and system b is at 700 K. At a certain time wall separating both the systems is made diathermal, and both the systems are allowed to reach a state of thermal equilibrium. Determine the final temperature and the values of U_a and U_b after the equilibrium is established. (15 Points)

5. A pure one-phase substance completely fills a closed rigid vessel at fixed temperature. It has been claimed that it is sometimes possible to reduce the system pressure by isothermally adding more material (which also means by adding a number of moles of the substance). In order to verify this claim if we consider a van der Waals fluid, we get that it is indeed possible to fill a rigid cylinder isothermally with more material that results in reduction in pressure under following condition:

$$\frac{\alpha}{\left(\underline{V}^{*}-1\right)} \square 2,$$

where α is positive and is a function of $\underline{V}^{*}$ and T^{*}. By analyzing this problem, you are expected to obtain α and put an appropriate condition: $\leq$, $\geq$, $=$, $<$, or $>$ in the box $\square$. Here superscript * represents suitable dimensionless volume $(\underline{V})$ and temperature (T) by using gas constant R and the parameters of van der Waals equation: a and b as derived in the class (15 Points)