Qualify Examination

Chemical Engineering Thermodynamics

Dec. 27, 2007

Part I. Undergraduate level (50 %)

(1) Values of the virial coefficients B and C [$P\underline{V}/(RT) = 1 + B(T)/\underline{V} + C(T)/\underline{V}^2 + \cdot\cdot\cdot$] at a fixed temperature can be obtained from experimental PVT data by noting that

$$\lim_{P\to 0\ (\underline{V}\to\infty)} [P\underline{V}/(RT)] = 1$$

$$\lim_{P\to 0\ (\underline{V}\to\infty)} \underline{V}[P\underline{V}/(RT) - 1] = B$$

$$\lim_{P\to 0\ (\underline{V}\to\infty)} \underline{V}^2[P\underline{V}/(RT) - 1 - B/\underline{V}] = C$$

Show that the van der Waals equation [$(P + a/\underline{V}^2)(\underline{V} - b) = RT$] leads to the following expressions for the virial coefficients

$B = b - a/(RT)$

$C = b^2$ (25 %)

(2) An adiabatic turbine is operating with an ideal gas working fluid of fixed inlet temperature and pressure, T_1 and P_1, respectively, and a fixed exit pressure P_2. Show that the minimum outlet temperature T_2 occurs when the turbine operates reversibly, that is, when the rate of internal generation of entropy within the system ($\dot{S}_{gen}$) = 0. Determine the maximum work that can be extracted from the turbine. (Hint: starting from mass, energy, and entropy balances.) (25 %)

Part II. Graduate level (50 %)

(3) Based on the knowledge of intermolecular forces, compare qualitatively the molar excess enthalpies for the following four equal-molar mixtures at a given *T*.

Mixture A: n-octane + cyclohexane
Mixture B: *m*-xylene + tetrahydrofuran (C_4H_8O)
Mixture C: water + methanol
Mixture D: 2, 2, 3-trimethylbutane + cyclohexane

Please give a brief explanation to support your answer. (16 %)

(4)

(a) Express γ_2^* in terms of γ_2, where $\gamma_2^* = 1 \ as \ x_2 \to 0$ and $\gamma_2 = 1 \ as \ x_2 \to 1$. (10 %)

(b) Derive ln γ_2^*, if

$$ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$ (4 %)

(5) Explain concisely the following terms:

(a) **Phase space** in Statistic Thermodynamics (5 %)
(b) **Cubic equations of state** (5 %)
(c) **Binary interaction parameter,** *kij*, in a mixing rule (5 %)
(d) **Local composition** concept proposed by Wilson (5 %)