Chapter 6 Assignment
(Answers are in parenthesis)

1. The molar volume (cm^3 mol^1) of a binary liquid mixture at T and P is given by: V = $120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2$ cm^3/mol (a) Find expressions for the partial molar volumes of species 1 and 2 at T and P. (b) (c) Show that these expressions satisfy the Gibbs/Duhem equation. (d) Show that $(d\overline{V}_1/dx_1)_{x_1=1} = (d\overline{V}_2/dx_1)_{x_1=0} = 0$ (e) Calculate V_1, V_2, $\overline{V}_1^{\infty}$, and $\overline{V}_2^{\infty}$. [$\overline{V}_1 = 128 - 2x_1 - 20x_1^2 + 14x_1^3$; $\overline{V}_2 = 70 + x_1^2 + 14x_1^3$; $V_1 = 120; V_2 = 70$ $\overline{V_1^{\infty}} = 128; \overline{V_2^{\infty}} = 84$, all in cm^3/mol]

2. For a ternary solution at constant T and P, the composition dependence of molar property M is given by: $M = x_1M_1 + x_2M_2 + x_3M_3 + x_1x_2x_3C$; where M_1, M_2, and M_3 are the values of M for pure species 1, 2, and 3, and C is a parameter independent of composition. Determine expressions for $\overline{M}_1$, $\overline{M}_2$, and $\overline{M}_3$. As a partial check on your results, verify that they satisfy the summability relation. For this correlating equation, what are the $\overline{M}_i$ at infinite dilution? **[** $\overline{M}_i = M_i + Cx_jx_k(1-2x_i)$ **;** $\overline{M}_i^{\infty} = M_i + Cx_jx_k$ **]**

3. For a particular binary liquid solution at constant T and P, the molar enthalpies of mixtures are represented by the equation: $H = x_1(a_1+b_1x_1) + x_2(a_2+b_2x_2)$; where the a_i and b_i are constants. Since the equation has the form of $H = \Sigma \overline{H}_i x_i$; it might be that $\overline{H}_i = a_i + b_ix_i$. Show whether this is true.

4. Say that for a binary solution the heat (enthalpy of mixing) data is available in the form ΔH_{mix} *vs.* x_1. Show that the partial molar enthalpies are given by the following equations: $\overline{H}_1 - H_1 = \Delta H_{mix} - x_2 \dfrac{d(\Delta H_{mix})}{dx_2}$; and, $\overline{H}_2 - H_2 = \Delta H_{mix} + (1-x_2)\dfrac{d(\Delta H_{mix})}{dx_2}$

5. Show that: $\overline{H}_1 = -x_2^2 \left.\dfrac{\partial(H_{mix}/x_2)}{\partial x_2}\right|_{T,P}$

6. For a ternary system (containing A, B, and C) show that:

   (i) $\overline{M}_A = M + (1-x_A)\left(\dfrac{\partial M}{\partial x_A}\right)_{T,P,x_B} - x_B\left(\dfrac{\partial M}{\partial x_B}\right)_{T,P,x_A}$

   (ii) $\overline{M}_A = M + (1-x_A)\left(\dfrac{\partial M}{\partial x_A}\right)_{T,P,x_C} - x_C\left(\dfrac{\partial M}{\partial x_C}\right)_{T,P,x_A}$

7. Prove the following identities: (a) $\overline{A}_i = \mu_i - P\left(\dfrac{\partial \mu_i}{\partial P}\right)_{T,n}$, (b) $\overline{U}_i = \mu_i - P\left(\dfrac{\partial \mu_i}{\partial P}\right)_{T,n} - T\left(\dfrac{\partial \mu_i}{\partial T}\right)_{P,n}$

$\overline{A}_i$ = partial molar Helmholtz's free energy
$\overline{U}_i$ = partial molar internal energy
μ_i = partial molar Gibss free energy (chemical potential)

8. When one mole of sulphuric acid (1) is added to ‘n’ moles of water at 25^{0}C the heat evolved is calculated according to the equation: $Q(cal) = \frac{17860n}{n+1.7893}$. Assuming that the molar enthalpies of both the components are zero at 25^{0}C, compute the partial molar enthalpies for a mixture containing 1 mole of sulphuric acid and three moles of water. $[\bar{H}_1 = -6981.5 cal/mol; \bar{H}_2 = -1395.0 cal/mol]$

9. The heat of mixing for octanol(1)/decane(2) is given by: $\Delta H_{mix} = x_1 x_2 \left[A + B(x_1 - x_2)\right] J/mol$

   Where, $A = -12974 + 51.05T; B = 8728.8 - 34.13T; T(^{\circ}K)$. (i) Compute the partial molar enthalpies of each component for an equi-molar solution at 300K (assuming pure component enthalpies to be zero). (ii) A mixture containing 20mol% of octanol is mixed with another containing 80mol% octanol in a steady flow isothermal mixer. How much heat needs to be added or removed from the mixer? $[\bar{H}_1 = 917.8 J/mol;\ \bar{H}_2 = 257.7 J/mol; 211.4 J/mol\ of\ mixture]$

10. The Berthelot EOS is given by: $\left(P + \frac{a}{TV^2}\right)(V-b) = RT$; Show that the fugacity coefficient is: $\ln\phi = \frac{b}{V-b} - \frac{2a}{RT^2V} - \ln\left(\frac{V-b}{V}\right) - \ln\left[\frac{V}{V-b} - \frac{a}{RT^2V}\right]$
11. Estimate the fugacity of methane at 32C and 9.28 bar. Use the generalized compressibility factor correlation. **[9.15bar]**
12. Determine the ratio of the fugacity in the final state to that in the initial state for steam undergoing the isothermal change of state: from 9000 kPa and 400 C to 300 kPa. **[0.04]**
13. Estimate the fugacity of n-Pentane at its normal-boiling point temperature and 200 bar. **[2.4bar]**