

**Q.1 Question 1**

Given the van der Waals equation of state (vdW EOS),

$$P = \frac{RT}{V-b} - \frac{a}{V^2},$$

- (a) Show that the vdW EOS can be expressed as a cubic polynomial equation in  $Z$  (compressibility coefficient),

$$Z^3 - (1+B)Z^2 + AZ - AB = 0,$$

with  $B = bP/(RT)$ ,  $A = aP/(RT)^2$  and  $R \left( = 8.314 \times 10^{-5} \frac{\text{bar.m}^3}{\text{mol.K}} \right)$  is the molar gas constant [7 marks]

**Solution:**

[2/7] We can rearrange the vdW EOS,

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \Rightarrow \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RTV} = \frac{1}{1 - \frac{b}{V}} - \frac{a}{RTV}$$

[1/7] Eliminating  $V$  as  $V = ZRT/P$ ,

$$Z = \left( 1 - \frac{bP}{ZRT} \right)^{-1} - \frac{aP}{Z(RT)^2} = \frac{ZRT}{ZRT - bP} - \frac{aP}{Z(RT)^2}$$

[3/7] Manipulating this expression,

$$\begin{aligned} Z^2 R^2 T^2 (ZRT - bP) &= Z^2 (RT)^3 - aP (ZRT - bP) \\ Z^3 - \frac{bP}{RT} Z^2 - Z^2 - \frac{aP}{(RT)^2} Z + ab \frac{P^2}{(RT)^3} &= 0 \end{aligned}$$

[1/7] with  $B = bP/(RT)$ ,  $A = aP/(RT)^2$ ,

$$Z^3 - (1+B)Z^2 + AZ - AB = 0$$

- (b) Calculate the fugacity of gaseous  $\text{CO}_2$  at 310 K and 1.4 MPa using the vdW EOS, with  $a = 0.3658 \text{ Pa.m}^6.\text{mol}^{-2}$ ,  $b = 4.286 \times 10^{-5} \text{ m}^3.\text{mol}^{-1}$ . Given,

$$\ln \left( \frac{f}{P} \right) = -\ln \left( 1 - \frac{b}{V} \right) - \frac{a}{RTV} - \ln Z + (Z-1).$$

Use the largest real root of the cubic polynomial equation in  $Z$  to represent the gaseous phase. [13 marks]

**Solution:**

[5/13] Solving the cubic polynomial in  $Z$ , with  $B = bP/(RT)$  and  $A = aP/(RT)^2$ ,

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \implies A = 7.7095 \times 10^{-2} ; B = 2.3281 \times 10^{-2}$$
$$\implies Z = 0.9436$$

*Now for the fugacity equation, either*

$$\ln \left( \frac{f}{P} \right) = -\ln \left( 1 - \frac{b}{V} \right) - \frac{a}{RTV} - \ln Z + (Z - 1)$$

*or*

$$\ln \left( \frac{f}{P} \right) = -\ln \left( 1 - \frac{B}{Z} \right) - \frac{A}{Z} - \ln Z + (Z - 1)$$

**[8/13]**

*leads to  $f = 1.32 \times 10^6 \text{ Pa}$ .*

**Total Question Marks:20**

**Q.2 Question 2**

In a saturated liquid mixture of benzene and toluene containing 45 mol% of benzene, determine:

- (a) Temperature and composition of the first bubble at 200 kPa. [10 marks]

**Solution:**

[1/10] *The molar constraint of vapour composition is*

$$\sum_{i=1}^2 y_i = y_1 + y_2 = 1,$$

[1/10] *and replacing the Raoult law,  $y_i = \frac{x_i P_i^{\text{sat}}}{P}$ , in the constraint relation,*

$$\begin{aligned} P &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} \\ &= x_1 \exp\left(A_1 - \frac{B_1}{T + C_1}\right) + x_2 \exp\left(A_2 - \frac{B_2}{T + C_2}\right) \end{aligned} \quad (1)$$

[3/10] *Solving this non-linear equation we obtain the bubble temperature of the benzene-toluene mixture as  $T = 391.79 \text{ K}$ . In order to calculate the compositions, we should*  
 [1/10] *use the Raoult's relation with  $P_1^{\text{sat}} = 289.01 \text{ kPa}$ ,*

[4/10] 
$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = 0.6503 \implies y_2 = 0.3497$$

- (b) Pressure and composition of the first bubble at 400 K. [10 marks]

**Solution:**

[1/10] *The molar constraint of vapour composition is*

$$\sum_{i=1}^2 y_i = y_1 + y_2 = 1,$$

[1/10] *and replacing the Raoult law,  $y_i = \frac{x_i P_i^{\text{sat}}}{P}$ , in the constraint relation,*

$$\begin{aligned} P &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} \\ &= x_1 \exp\left(A_1 - \frac{B_1}{T + C_1}\right) + x_2 \exp\left(A_2 - \frac{B_2}{T + C_2}\right) \end{aligned} \quad (2)$$

[3/10] *Solving this equation for  $T = 400 \text{ K}$  results in  $P = 245.28 \text{ kPa}$ . In order to calculate*  
 [1/10] *the compositions, we should use the Raoult's relation with  $P_1^{\text{sat}} = 352.16 \text{ kPa}$ ,*

[4/10] 
$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = 0.6461 \implies y_2 = 0.3539$$

For this problem, benzene and toluene mixtures may be considered as ideal and you should use,

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{T + C}$$

with  $[P] = \text{bar}$ ,  $[T] = \text{K}$ ,  $[B] = \text{K}$  and  $[C] = \text{K}$ .

<b>Species</b>	<b>A</b>	<b>B</b>	<b>C</b>
Benzene (1)	14.1603	2948.78	-44.5633
Toluene (2)	14.2515	3242.38	-47.1806

**Total Question Marks:20**

**Q.3 Question 3**

Consider the following chemical reaction representing the chemical equilibrium between dinitrogen tetroxide,  $N_2O_4(g)$ , and nitrogen dioxide,  $NO_2(g)$  at  $25^\circ C$  and 1 atm,



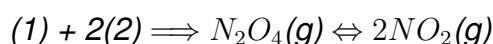
Determine:

- (a) Equilibrium constant of this reaction.

[8 marks]

**Solution:**

The reaction  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  may be obtained by combining reactions (1) and (2), i.e.,



Thus, the standard free Gibbs energy change of the mixture at  $25^\circ C$  can be obtained from the

$$\Delta G_{mix,298}^\circ = \Delta G_{mix,1}^\circ + 2\Delta G_{mix,2}^\circ = 1.07 \text{ kcal.mol}^{-1} = 4479.88 \text{ J.mol}^{-1}$$

The equilibrium constant at  $25^\circ C$  is given by

$$K_{eq,298} = \exp \left[ -\frac{\Delta G_{mix,298}^\circ}{RT} \right] = 0.1641$$

- (b) Equilibrium composition of  $N_2O_4(g)$ .

[12 marks]

**Solution:**

The equilibrium constant can also be obtained as a function of the species' activities,

$$K = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{\left( \frac{\hat{f}_{NO_2}}{f_{NO_2}^\circ} \right)^2}{\left( \frac{\hat{f}_{N_2O_4}}{f_{N_2O_4}^\circ} \right)}$$

Assuming ideal gas behaviour,  $\hat{f}_i = P_i$ ,  $f_i^\circ = P_{NO_2}^\circ = P_{N_2O_4}^\circ = 1 \text{ atm}$ ,

$$K = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{\left( \frac{\hat{f}_{NO_2}}{f_{NO_2}^\circ} \right)^2}{\left( \frac{\hat{f}_{N_2O_4}}{f_{N_2O_4}^\circ} \right)} = \frac{\left( \frac{P_{NO_2}}{P_{NO_2}^\circ} \right)^2}{\left( \frac{P_{N_2O_4}}{P_{N_2O_4}^\circ} \right)} = \frac{\left( \frac{P \cdot y_{NO_2}}{1 \text{ atm}} \right)^2}{\left( \frac{P \cdot y_{N_2O_4}}{1 \text{ atm}} \right)}$$

As  $P = 1 \text{ atm}$ ,

$$K = \frac{\left( \frac{P \cdot y_{NO_2}}{1 \text{ atm}} \right)^2}{\left( \frac{P \cdot y_{N_2O_4}}{1 \text{ atm}} \right)} = \frac{y_{NO_2}^2}{y_{N_2O_4}}$$

During the reaction,

	$N_2O_4$	$NO_2$	Total
Initial	1	0	1
Final	$1 - \xi$	$2\xi$	$1 + \xi$

[2/12] The mole fractions of  $N_2O_4$  and  $NO_2$  can be expressed as

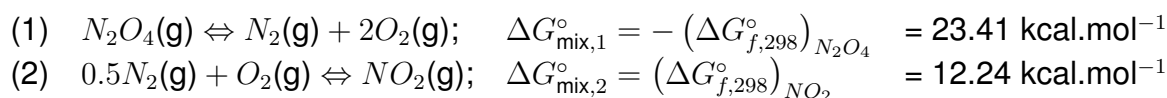
$$y_{N_2O_4} = \frac{1 - \xi}{1 + \xi} \quad \text{and} \quad y_{NO_2} = \frac{2\xi}{1 + \xi}$$

[2/12] and be replaced in the previous equation with  $K_{eq,298} = 0.1641$  (from (a))

$$K = \frac{y_{NO_2}^2}{y_{N_2O_4}} = \frac{\left(\frac{2\xi}{1 + \xi}\right)^2}{\frac{1 - \xi}{1 + \xi}} = 0.1641 \implies \xi = 0.1985$$

[2/12] The equilibrium composition is  $y_{N_2O_4} = 0.6688$  and  $y_{NO_2} = 0.3312$ .

For this problem, you should consider the following reaction data:



where  $G_{f,298}^\circ$  is the standard molar free Gibbs energy of formation. Also, the equilibrium constant at 25°C is given by

$$K_{eq,298} = \exp \left[ -\frac{\Delta G_{mix,298}^\circ}{RT} \right]$$

where  $R \left( = 8.314 \frac{\text{J}}{\text{mol.K}} \right)$  is the molar gas constant and  $\Delta G_{mix,298}^\circ$  is the standard free Gibbs energy change of the mixture. Assume ideal gas behaviour.

**Total Question Marks:20**

**Q.4 Question 4**

- (a) Two litres of an anti-freezing solution is needed for a cooling process. The solution is prepared by mixing 30%-mol of methanol in water. What are the volumes of pure methanol and water at 25°C necessary to prepare solution? Partial molar volumes ( $\bar{V}$ ) for methanol and water in a 30%-mol of methanol solution and their pure species molar volumes ( $V$ ), both at 25°C are: [8 marks]

	$\bar{V}_i$ (cm <sup>3</sup> .mol <sup>-1</sup> )	$V_i$ (cm <sup>3</sup> .mol <sup>-1</sup> )
Methanol (1)	38.6320	40.7270
Water (2)	17.7650	18.0680

**Solution:**

- [2/8] *The molar volume of the 30%-mol of methanol solution is given by,*

$$V = \frac{V^T}{n_T} = \frac{\sum_{i=1}^2 n_i \bar{V}_i}{n_T} = \sum_{i=1}^2 x_i \bar{V}_i = x_1 \bar{V}_1 + x_2 \bar{V}_2$$

$$= (0.3)(38.6320) + (0.7)(17.7650) = 24.0251 \text{ cm}^3.\text{mol}^{-1}$$

- [2/8] *The total number of moles are:*

$$n_T = \frac{V^T}{V} = \frac{2000}{24.0251} = 83.2463 \text{ mol}$$

- [4/8] *The volume of pure methanol and water for the solution are:*

$$V_1^{\text{pure}} = x_1 n_T V_1 = 1017.11 \text{ cm}^3$$

$$V_2^{\text{pure}} = x_2 n_T V_2 = 1052.87 \text{ cm}^3$$

- (b) In generating expressions from  $G^E/RT$  from VLE data, a convenient approach is to plot values of  $G^E/(x_1 x_2 RT)$  vs  $x_1$  and fitting results with an appropriate function. Consider if such data were fit by the expression,

$$\frac{G^E}{x_1 x_2 RT} = A + B x_1^2.$$

From the expression  $G^E/(x_1 x_2 RT)$ , provide equations for the activity coefficient,  $\ln \gamma_i$ , as a function of  $A$ ,  $B$ ,  $x_1$  and  $x_2$ , given [12 marks]

$$\ln \gamma_i = \frac{\bar{G}_i^E}{RT}.$$

**Solution:**

- [2/12] *For a binary mixture:*

$$\overline{M}_1 = M + x_2 \frac{dM}{dx_1} \quad \text{and} \quad \overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

**[3/12]** *thus*

$$\ln \gamma_1 = \frac{\overline{G}_1^E}{RT} = \frac{G^E}{RT} + x_2 \frac{dG^E/RT}{dx_1} \quad \text{and} \quad \ln \gamma_2 = \frac{\overline{G}_2^E}{RT} = \frac{G^E}{RT} + x_1 \frac{dG^E/RT}{dx_2}$$

**[5/12]** *with*

$$\frac{dG^E/RT}{dx_1} = (1 - 2x_1) A + (3 - 4x_1) Bx_1^2$$

**[2/12]** *The activity coefficient is then given by,*

$$\begin{aligned} \ln \gamma_1 &= x_1 (1 - x_1) (A + Bx_1^2) + (1 - x_1) [(1 - 2x_1) A + (3 - 4x_1) Bx_1] \\ \ln \gamma_2 &= x_1 (1 - x_1) (A + Bx_1^2) + x_1 [(1 - 2x_1) A + (3 - 4x_1) Bx_1] \end{aligned}$$

**Total Question Marks:20**



**Q.5 Question 5**

- (i) A concentrated binary solution containing mainly species 2 (though  $x_2 \neq 1$ ) is in equilibrium with a vapour phase containing both species 1 and 2. Pressure and temperature of this two-phase system are 1 bar and 298.15 K. Given  $\mathcal{H}_1 = 200$  bar (Henry constant) and  $P_2^{\text{sat}} = 0.10$  bar, calculate  $x_1$  and  $y_1$ . [10 marks]

**Solution:**

Assuming that at 1 bar the vapour phase behaves as an ideal gas. The vapour phases fugacities are then equal to the partial pressures. Assume the Lewis/Randall rule applies to concentrated species 2 and that Henry's law applies to dilute species 1, therefore,

$$y_1 P = \mathcal{H}_1 x_1; \quad \text{and} \quad y_2 P = x_2 P_2^{\text{sat}}$$

[5/10] with  $x_1 + x_2 = 1$ . Thus  $P = y_1 P + y_2 P$  becomes,

$$P = \mathcal{H}_1 x_1 + (1 - x_1) P_2^{\text{sat}} \implies x_1 = 4.502 \times 10^{-3}$$

[5/10] and  $y_1 = \frac{\mathcal{H}_1 x_1}{P} = 0.9$ .

- (ii) Chemical species A and B are in vapour-liquid equilibrium at 298.15 K. The following conditions are applied to this system:

	$P_i^{\text{sat}}$ (bar)	$\ln \gamma_i$
<b>A</b>	1.24	$1.8 x_B^2$
<b>B</b>	0.89	$1.8 x_A^2$

Assuming that  $y_i P = x_i \gamma_i P_i^{\text{sat}}$  (where  $\gamma_i$  is the activity coefficient of species  $i$ ) is valid, calculate the pressure  $P$  and the vapour mole fraction  $y_A$  for a liquid mole fraction  $x_A = 0.65$ . [10 marks]

**Solution:**

With  $x_A = 0.65$  and  $x_B = 0.35$ , we can calculate the activity coefficients,  $\gamma_A$  and  $\gamma_B$ , and apply in

[5/10] 
$$P = x_A \gamma_A P_A^{\text{sat}} + x_B \gamma_B P_B^{\text{sat}} = 1.671 \text{ bar.}$$

[5/10] The vapour mole fraction is obtained from

$$y_A = \frac{x_A \gamma_A P_A^{\text{sat}}}{P} = 0.6013$$

**Total Question Marks:20**

**END OF PAPER**

**Total Paper Marks:100**

## 1. Fundamentals of Thermodynamics:

$$dU = dQ + dW; \quad dW = -PdV; \quad C_v = \left( \frac{\partial U}{\partial T} \right)_V; \quad C_p = \left( \frac{\partial H}{\partial T} \right)_P;$$

$$C_p - C_v = R; \quad TV^{\gamma-1} = \text{const}; \quad TP^{\frac{1-\gamma}{\gamma}} = \text{const}; \quad PV^\gamma = \text{const}$$

$$dH = dU + d(PV); \quad dS = \frac{dQ}{T}; \quad PV = nRT$$

## 2. Volumetric Properties of Pure Fluids:

$$\Psi = 2 + \mathcal{C} - \mathcal{P} - \mathcal{R}; \quad \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P; \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T; \quad T_r = \frac{T}{T_c}; \quad P_r = \frac{P}{P_c}; \quad PV = ZRT$$

$$Z = 1 + \frac{BP}{RT} = 1 + \frac{BP_c}{RT_c} \frac{P_r}{T_r}; \quad \frac{BP_c}{RT_c} = B^0 + \omega B^1; \quad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}; \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}; \quad a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}; \quad b = \frac{1}{8} \frac{RT_c}{P_c}; \quad [\text{van der Waals (vdW) EOS}]$$

$$P = \frac{RT}{V-b} - \frac{a}{V\sqrt{T}(V+b)}; \quad a = \frac{0.42748R^2 T_c^2}{P_c}; \quad b = \frac{0.08664RT_c}{P_c}; \quad [\text{Redlich-Kwong (RK) EOS}]$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}; \quad a = \frac{0.427R^2 T_c^2}{P_c}; \quad b = \frac{0.08664RT_c}{P_c} \quad \text{and}$$

$$\alpha = \left[ 1 + (0.48508 + 1.55171\omega - 0.15613\omega^2) (1 - \sqrt{T_r}) \right]^2; \quad [\text{Soave-Redlich-Kwong (SRK) EOS}]$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b) + b(V-b)}; \quad a = \frac{0.45274R^2 T_c^2}{P_c}; \quad b = \frac{0.07780RT_c}{P_c}; \quad \text{and}$$

$$\alpha = \left[ 1 + \kappa (1 - \sqrt{T_r}) \right]^2; \quad \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2; \quad [\text{Peng-Robinson (PR) EOS}]$$

$$Z_{\text{vap}} = 1 + \beta - q\beta \frac{Z_{\text{vap}} - \beta}{(Z_{\text{vap}} + \varepsilon\beta)(Z_{\text{vap}} + \sigma\beta)}; \quad [\text{Vapour \& Vapour-like Roots}]$$

$$Z_{\text{liq}} = 1 + \beta + (Z_{\text{liq}} + \varepsilon\beta)(Z_{\text{liq}} + \sigma\beta) \left( \frac{1 + \beta - Z_{\text{liq}}}{q\beta} \right); \quad [\text{Liquid \& Liquid-like Roots}]$$

$$\beta = \Omega \frac{P_r}{T_r}; \quad q = \frac{\Psi\alpha}{\Omega T_r}; \quad \alpha_{\text{SRK}} = \left[ 1 + (0.480 + 1.574\omega - 0.176\omega^2) (1 - \sqrt{T_r}) \right]^2; \quad \text{and}$$

$$\alpha_{\text{PR}} = \left[ 1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) (1 - \sqrt{T_r}) \right]^2$$

EOS	$\alpha$	$\sigma$	$\varepsilon$	$\Omega$	$\Psi$
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{\text{SRK}}$	1	0	0.08664	0.42748
PR	$\alpha_{\text{PR}}$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

Table 1: Parameters for the generic form of cubic equations of state.

$$Z_{\text{vap}}^{(i+1)} = Z_{\text{vap}}^{(i)} - \frac{F(Z_{\text{vap}}^{(i)})}{F'(Z_{\text{vap}}^{(i)})}; \quad (\text{Root-finder expression for the Newton-Raphson method})$$

## 3. Thermodynamic Properties of Pure Fluids:

$$H = U + PV; \quad G = H - TS; \quad A = U - TS;$$

$$dU = TdS - PdV; \quad dH = TdS + VdP; \quad dA = -PdV - SdT; \quad dG = VdP - SdT;$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V; \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P; \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V; \quad \text{and}$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P; \quad (\text{Maxwell relations})$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{\partial H}{\partial S}\right)_P; \quad \left(\frac{\partial U}{\partial V}\right)_S = -P = \left(\frac{\partial A}{\partial V}\right)_T; \quad \left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T; \quad \text{and}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S = \left(\frac{\partial G}{\partial T}\right)_P$$

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP; \quad dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP;$$

$$dU = C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV; \quad dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV;$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT \quad (\text{Generating function});$$

$$M^R = M - M^{\text{ig}}; \quad \frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}; \quad \frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P}; \quad \text{and}$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \quad (\text{Residual properties});$$

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}; \quad \frac{d(\ln P^{\text{sat}})}{dT} = \frac{\Delta H^{\text{fg}}}{RT^2}; \quad (\text{Clapeyron relations})$$

$$x^{(V)} = \frac{M - M^{(L)}}{M^{(V)} - M^{(L)}} \quad (\text{Quality of vapour});$$

## 4. Vapour-Liquid Equilibrium of Mixtures:

$$x_i = \frac{n_i^{(L)}}{n}; \quad y_i = \frac{n_i^{(V)}}{n}; \quad \sum_{i=1}^c x_i = 1; \quad \sum_{i=1}^c y_i = 1 \quad (\text{Molar fraction of liquid and vapour phases});$$

$$\bar{M}_i = \left(\frac{\partial(nM)}{\partial n_i}\right)_{T,P,n_{j \neq i}} \quad (\text{Partial molar property}); \quad M^E = M - M^{\text{id}} \quad (\text{Excess properties})$$

$$\mu_i = \left(\frac{\partial(nG)}{\partial n_i}\right)_{T,P,n_{j \neq i}} = \bar{G}_i; \quad dG = VdP - SdT + \sum_i \mu_i dx_i;$$

$$P_i = y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (\text{Raoult's law}); \quad P = \sum_{i=1}^c P_i = \sum_{i=1}^c y_i P; \quad T_c^t = \sum_{i=1}^c y_i T_{c,i}; \quad P_c^t = \sum_{i=1}^c y_i P_{c,i};$$

$$P_i = y_i P = x_i \mathcal{H}_i \quad (\text{Henry's law});$$

$$K_i = \frac{P_i^{\text{sat}}}{P} = \frac{y_i}{x_i}; \quad F = V + L; \quad Fz_i = x_i L + y_i V; \quad \sum_{i=1}^c \frac{z_i K_i}{1 + V(K_i - 1)} = 1;$$

## 5. Solution Thermodynamics:

$$RT \left( \frac{\partial \ln f}{\partial P} \right)_T = \bar{v}; \quad \lim_{P \rightarrow 0} \frac{f}{P} = 1; \quad RT \ln \left( \frac{\bar{f}_i}{y_i f_i} \right) = \int_0^P (\bar{V}_i - \bar{v}_i) dP$$

$$\bar{f}_i^V = y_i P' \quad \text{and} \quad \bar{f}_i^L = x_i f_i^L \quad (\text{Lewis-Randall relation});$$

$$\mu_i - \mu_i^0 = RT \ln \left( \frac{\bar{f}_i}{f_i^0} \right); \quad a_i = \frac{\bar{f}_i}{f_i^0}; \quad \gamma_i = \frac{a_i}{y_i} = \frac{\bar{f}_i}{x_i f_i};$$

$$\phi_i = \frac{f_i}{P}; \quad G_i^R = G_i - G_i^{\text{ig}} = RT \ln \left( \frac{f_i}{P} \right) = RT \ln \phi_i;$$

$$f_i^L(P) = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[ \frac{V_i^L (P - P_i^{\text{sat}})}{RT} \right]$$

$$\left( \frac{\partial M}{\partial T} \right)_{P,x} dT + \left( \frac{\partial M}{\partial P} \right)_{T,x} dP - \sum_{i=1}^c x_i d\bar{M}_i = 0 \quad (\text{Gibbs-Duhem equation})$$

$$\sum_i x_i d\bar{M}_i = 0; \quad \sum_i x_i \frac{d\bar{M}_i}{dx_j} = 0;$$

$$M^E = M - \sum_i x_i M_i; \quad \bar{M}_1 = M + x_2 \frac{dM}{dx_1}; \quad \bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0; \quad \frac{d\bar{M}_1}{dx_1} = -\frac{x_2}{x_1} \frac{d\bar{M}_2}{dx_1}$$

$$PV^{\text{igm}} = \left( \sum_{i=1}^c n_i \right) RT; \quad \bar{V}_i^{\text{igm}}(T, P, y) = \frac{RT}{P} = \bar{V}_i^{\text{ig}}(T, P); \quad P_i^{\text{igm}} \left( \sum_{i=1}^c n_i, V, T, y \right) = \frac{n_i RT}{V} = P_i^{\text{ig}}(n_i, V, T);$$

$$\bar{U}^{\text{igm}}(T, y) = \sum_{i=1}^c y_i \bar{U}_i^{\text{ig}}(T); \quad \bar{H}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{H}_i^{\text{ig}}(T, P); \quad \bar{V}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{V}_i^{\text{ig}}(T, P)$$

$$\bar{S}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{S}_i^{\text{ig}}(T, P) - R \sum_{i=1}^c y_i \ln y_i; \quad \bar{G}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{G}_i^{\text{ig}}(T, P) + RT \sum_{i=1}^c y_i \ln y_i; \quad \text{and}$$

$$\bar{A}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{A}_i^{\text{ig}}(T, P) + RT \sum_{i=1}^c y_i \ln y_i$$

$$M^{\text{id}} = \sum_i x_i \bar{M}_i^{\text{id}}; \quad V^{\text{id}} = \sum_i x_i V_i; \quad H^{\text{id}} = \sum_i x_i H_i; \quad S^{\text{id}} = \sum_i x_i S_i - R \sum_i x_i \ln x_i \quad \text{and}$$

$$G^{\text{id}} = \sum_i x_i G_i - RT \sum_i x_i \ln x_i;$$

$$d \left( \frac{nG^E}{RT} \right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \ln \gamma_i dn_i; \quad \frac{V^E}{RT} = \left( \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial P} \right)_{T,x}; \quad \frac{H^E}{RT} = -T \left( \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial T} \right)_{P,x};$$

$$\ln \gamma_i = \left( \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial n_i} \right)_{T,P,n_j (n_j \neq n_i)}; \quad \bar{G}_i^E = RT \ln \gamma_i;$$

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]; \quad \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]; \quad (\text{Margules activity model});$$

$$\ln \gamma_1 = B_{12} \left(1 + \frac{B_{12}x_1}{A_{21}x_2}\right)^{-2}; \quad \ln \gamma_2 = B_{21} \left(1 + \frac{B_{21}x_1}{A_{12}x_2}\right)^{-2}; \quad (\text{Van Laar activity model});$$

$$\frac{G^E}{RT} = x_1 \ln(x_1 + x_2 C_{12}) - x_2 \ln(x_2 + x_1 C_{21}) \quad \text{with}$$

$$\ln \gamma_1 = -\ln(x_1 + x_2 C_{12}) + x_2 \left( \frac{C_{12}}{x_1 + x_2 C_{12}} - \frac{C_{21}}{x_2 + x_1 C_{21}} \right) \quad \text{and}$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 C_{21}) + x_1 \left( \frac{C_{12}}{x_1 + x_2 C_{12}} - \frac{C_{21}}{x_2 + x_1 C_{21}} \right);$$

## 6. Chemical Reaction Equilibrium:

$$\sum_{i=1}^C \nu_i A_i = 0; \quad d\epsilon = \frac{dn_i}{\nu_i}; \quad \sum_i n_i = \sum_i n_{i0} + \epsilon \sum_i \nu_i; \quad n = n_0 + \nu\epsilon$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon}$$

$$\sum_i \nu_i G_i = \sum_i \nu_i \mu_i = 0; \quad \prod_i \left( \frac{\bar{f}_i}{f_i^0} \right)^{\nu_i} = \prod_i a_i^{\nu_i} = K = \exp \left( \frac{-\Delta G^0}{RT} \right);$$

$$\Delta H^0 = -RT^2 \frac{d}{dT} (\Delta G^0 / RT) \quad (\text{Standard heat of reaction});$$

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2} \quad (\text{Van't Hoff equation});$$

$$\prod_i (y_i \phi_i)^{\nu_i} = K \left( \frac{P}{P^0} \right)^{-\nu}, \quad \text{where } \nu = \sum_i \nu_i \quad (\text{gas-phase});$$

$$\prod_i (y_i \gamma_i)^{\nu_i} = K \exp \left[ \frac{P^0 - P}{RT} \sum_i (\nu_i V_i) \right]^{-\nu} \quad (\text{liquid-phase});$$

$$\prod_i (y_i)^{\nu_{i,j}} = \left( \frac{P}{P^0} \right)^{-\nu_{i,j}} K_j; \quad (\text{ideal gas multi-reaction})$$

# Appendix A: Physical Constants and Conversion Factors

## PHYSICAL CONSTANTS

Avogadro's number,  $N_A = 6.023 \times 10^{26}$  molecules/kgmole  
 Boltzmann's constant,  $k = 1.381 \times 10^{-23}$  J/(molecule·K)  
 Electron charge,  $e = 1.602 \times 10^{-19}$  C  
 Electron mass,  $m_e = 9.110 \times 10^{-31}$  kg  
 Faraday's constant,  $F = 96,487$  kC/kgmole electrons = 96,487 kJ/(V·kgmole electrons)  
 Gravitational acceleration (standard),  $g = 32.174$  ft/s<sup>2</sup> = 9.807 m/s<sup>2</sup>  
 Gravitational constant,  $k_G = 6.67 \times 10^{-11}$  m<sup>3</sup>/(kg·s<sup>2</sup>)  
 Newton's second law constant,  $g_c = 32.174$  lbm·ft/(lbf·s<sup>2</sup>) = 1.0 kg·m/(N·s<sup>2</sup>)  
 Planck's constant,  $h = 6.626 \times 10^{-34}$  J·s/molecule  
 Stefan-Boltzmann constant,  $\sigma = 0.1714 \times 10^{-8}$  Btu/(h·ft<sup>2</sup>·R<sup>4</sup>) =  $5.670 \times 10^{-8}$  W/(m<sup>2</sup>·K<sup>4</sup>)  
 Universal gas constant  $\mathfrak{R} = 1545.35$  ft·lbf/(lbmole·R) = 8314.3 J/(kgmole·K)  
     = 8.3143 kJ/(kgmole·K) = 1.9858 Btu/(lbmole·R)  
     = 1.9858 kcal/(kgmole·K) = 1.9858 cal/(gmole·K)  
     = 0.08314 bar·m<sup>3</sup>/(kgmole·K) = 82.05 L·atm/(kgmole·K)  
 Velocity of light in a vacuum,  $c = 9.836 \times 10^8$  ft/s =  $2.998 \times 10^8$  m/s

## UNIT DEFINITIONS

1 coulomb (C) = 1 A·s	1 ohm ( $\Omega$ ) = 1 V/A
1 dyne = 1 g·cm/s <sup>2</sup>	1 pascal (Pa) = 1 N/m <sup>2</sup>
1 erg = 1 dyne·cm	1 poundal = 1 lbm·ft/s <sup>2</sup>
1 farad (F) = 1 C/V	1 siemens (S) = 1 A/V
1 henry (H) = 1 Wb/A	1 slug = 1 lbf·s <sup>2</sup> /ft
1 hertz (Hz) = 1 cycle/s	1 tesla (T) = 1 Wb/m <sup>2</sup>
1 joule (J) = 1 N·m	1 volt (V) = 1 W/A
1 lumen = 1 candela·steradian	1 watt (W) = 1 J/s
1 lux = 1 lumen/m <sup>2</sup>	1 weber (Wb) = 1 V·s
1 newton (N) = 1 kg·m/s <sup>2</sup>	

## CONVERSION FACTORS

Length	Energy
1 m = 3.2808 ft = 39.37 in = 10 <sup>2</sup> cm = 10 <sup>10</sup> Å	1 J = 1 N·m = 1 kg·m <sup>2</sup> /s <sup>2</sup> = 9.479 × 10 <sup>-4</sup> Btu
1 cm = 0.0328 ft = 0.394 in = 10 <sup>-2</sup> m = 10 <sup>8</sup> Å	1 kJ = 1000 J = 0.9479 Btu = 238.9 cal
1 mm = 10 <sup>-3</sup> m = 10 <sup>-1</sup> cm	1 Btu = 1055.0 J = 1.055 kJ = 778.16 ft·lbf = 252 cal
1 km = 1000 m = 0.6215 miles = 3281 ft	1 cal = 4.186 J = 3.968 × 10 <sup>-3</sup> Btu
1 in = 2.540 cm = 0.0254 m	1 Cal (in food value) = 1 kcal = 4186 J = 3.968 Btu
1 ft = 12 in = 0.3048 m	1 erg = 1 dyne·cm = 1 g·cm <sup>2</sup> /s <sup>2</sup> = 10 <sup>-7</sup> J
1 mile = 5280 ft = 1609.36 m = 1.609 km	1 eV = 1.602 × 10 <sup>-19</sup> J

(Continued)

**CONVERSION FACTORS** (Continued)**Area**

$$1 \text{ m}^2 = 10^4 \text{ cm}^2 = 10.76 \text{ ft}^2 = 1550 \text{ in}^2$$

$$1 \text{ ft}^2 = 144 \text{ in}^2 = 0.0929 \text{ m}^2 = 929.05 \text{ cm}^2$$

$$1 \text{ cm}^2 = 10^{-4} \text{ m}^2 = 1.0764 \times 10^{-3} \text{ ft}^2 = 0.155 \text{ in}^2$$

$$1 \text{ in}^2 = 6.944 \times 10^{-3} \text{ ft}^2 = 6.4516 \times 10^{-4} \text{ m}^2 = 6.4516 \text{ cm}^2$$

**Volume**

$$1 \text{ m}^3 = 35.313 \text{ ft}^3 = 6.1023 \times 10^4 \text{ in}^3 = 1000 \text{ L} = 264.171 \text{ gal}$$

$$1 \text{ L} = 10^{-3} \text{ m}^3 = 0.0353 \text{ ft}^3 = 61.03 \text{ in}^3 = 0.2642 \text{ gal}$$

$$1 \text{ gal} = 231 \text{ in}^3 = 0.13368 \text{ ft}^3 = 3.785 \times 10^{-3} \text{ m}^3$$

$$1 \text{ ft}^3 = 1728 \text{ in}^3 = 28.3168 \text{ L} = 0.02832 \text{ m}^3 = 7.4805 \text{ gal}$$

$$1 \text{ in}^3 = 16.387 \text{ cm}^3 = 1.6387 \times 10^{-5} \text{ m}^3 = 4.329 \times 10^{-3} \text{ gal}$$

**Mass**

$$1 \text{ kg} = 1000 \text{ g} = 2.2046 \text{ lbm} = 0.0685 \text{ slug}$$

$$1 \text{ lbm} = 453.6 \text{ g} = 0.4536 \text{ kg} = 3.108 \times 10^{-2} \text{ slug}$$

$$1 \text{ slug} = 32.174 \text{ lbm} = 1.459 \times 10^4 \text{ g} = 14.594 \text{ kg}$$

**Force**

$$1 \text{ N} = 10^5 \text{ dyne} = 1 \text{ kg} \cdot \text{m/s}^2 = 0.225 \text{ lbf}$$

$$1 \text{ lbf} = 4.448 \text{ N} = 32.174 \text{ poundals}$$

$$1 \text{ poundal} = 0.138 \text{ N} = 3.108 \times 10^{-2} \text{ lbf}$$

**Power**

$$1 \text{ W} = 1 \text{ J/s} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^3 = 3.412 \text{ Btu/h} = 1.3405 \times 10^{-3} \text{ hp}$$

$$1 \text{ kW} = 1000 \text{ W} = 3412 \text{ Btu/h} = 737.3 \text{ ft} \cdot \text{lbf/s} = 1.3405 \text{ hp}$$

$$1 \text{ Btu/h} = 0.293 \text{ W} = 0.2161 \text{ ft} \cdot \text{lbf/s} = 3.9293 \times 10^{-4} \text{ hp}$$

$$1 \text{ hp} = 550 \text{ ft} \cdot \text{lbf/s} = 33000 \text{ ft} \cdot \text{lbf/min} = 2545 \text{ Btu/h} = 746 \text{ W}$$

**Pressure**

$$1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg}/(\text{m} \cdot \text{s}^2) = 1.4504 \times 10^{-4} \text{ lbf/in}^2$$

$$1 \text{ lbf/in}^2 = 6894.76 \text{ Pa} = 0.068 \text{ atm} = 2.036 \text{ in Hg}$$

$$1 \text{ atm} = 14.696 \text{ lbf/in}^2 = 1.01325 \times 10^5 \text{ Pa}$$

$$= 101.325 \text{ kPa} = 760 \text{ mm Hg}$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 0.987 \text{ atm} = 14.504 \text{ lbf/in}^2$$

$$1 \text{ dyne/cm}^2 = 0.1 \text{ Pa} = 10^{-6} \text{ bar} = 145.04 \times 10^{-7} \text{ lbf/in}^2$$

$$1 \text{ in Hg} = 3376.8 \text{ Pa} = 0.491 \text{ lbf/in}^2$$

$$1 \text{ in H}_2\text{O} = 248.8 \text{ Pa} = 0.0361 \text{ lbf/in}^2$$

**MISCELLANEOUS UNIT CONVERSIONS****Specific Heat Units**

$$1 \text{ Btu}/(\text{lbm} \cdot ^\circ\text{F}) = 1 \text{ Btu}/(\text{lbm} \cdot \text{R})$$

$$1 \text{ kJ}/(\text{kg} \cdot \text{K}) = 0.23884 \text{ Btu}/(\text{lbm} \cdot \text{R}) = 185.8 \text{ ft} \cdot \text{lbf}/(\text{lbm} \cdot \text{R})$$

$$1 \text{ Btu}/(\text{lbm} \cdot \text{R}) = 778.16 \text{ ft} \cdot \text{lbf}/(\text{lbm} \cdot \text{R}) = 4.186 \text{ kJ}/(\text{kg} \cdot \text{K})$$

**Energy Density Units**

$$1 \text{ kJ/kg} = 1000 \text{ m}^2/\text{s}^2 = 0.4299 \text{ Btu/lbm}$$

$$1 \text{ Btu/lbm} = 2.326 \text{ kJ/kg} = 2326 \text{ m}^2/\text{s}^2$$

**Energy Flux**

$$1 \text{ W/m}^2 = 0.317 \text{ Btu}/(\text{h} \cdot \text{ft}^2)$$

$$1 \text{ Btu}/(\text{h} \cdot \text{ft}^2) = 3.154 \text{ W/m}^2$$

**Heat Transfer Coefficient**

$$1 \text{ W}/(\text{m}^2 \cdot \text{K}) = 0.1761 \text{ Btu}/(\text{h} \cdot \text{ft}^2 \cdot \text{R})$$

$$1 \text{ Btu}/(\text{h} \cdot \text{ft}^2 \cdot \text{R}) = 5.679 \text{ W}/(\text{m}^2 \cdot \text{K})$$

**Thermal Conductivity**

$$1 \text{ W}/(\text{m} \cdot \text{K}) = 0.5778 \text{ Btu}/(\text{h} \cdot \text{ft} \cdot \text{R})$$

$$1 \text{ Btu}/(\text{h} \cdot \text{ft} \cdot \text{R}) = 1.731 \text{ W}/(\text{m} \cdot \text{K})$$

**Temperature**

$$T(^{\circ}\text{F}) = \frac{9}{5} T(^{\circ}\text{C}) + 32 = T(\text{R}) - 459.67$$

$$T(^{\circ}\text{C}) = \frac{5}{9} [T(^{\circ}\text{F}) - 32] = T(\text{K}) - 273.15$$

$$T(\text{R}) = \frac{9}{5} T(\text{K}) = (1.8) T(\text{K}) = T(^{\circ}\text{F}) + 459.67$$

$$T(\text{K}) = \frac{5}{9} T(\text{R}) = T(\text{R})/1.8 = T(^{\circ}\text{C}) + 273.15$$

**Density**

$$1 \text{ lbm/ft}^3 = 16.0187 \text{ kg/m}^3$$

$$1 \text{ kg/m}^3 = 0.062427 \text{ lbm/ft}^3 = 10^{-3} \text{ g/cm}^3$$

$$1 \text{ g/cm}^3 = 1 \text{ kg/L} = 62.4 \text{ lbm/ft}^3 = 10^3 \text{ kg/m}^3$$

**Viscosity**

$$1 \text{ Pa} \cdot \text{s} = 1 \text{ N} \cdot \text{s}/\text{m}^2 = 1 \text{ kg}/(\text{m} \cdot \text{s}) = 10 \text{ poise}$$

$$1 \text{ poise} = 1 \text{ dyne} \cdot \text{s}/\text{cm}^2 = 1 \text{ g}/(\text{cm} \cdot \text{s}) = 0.1 \text{ Pa} \cdot \text{s}$$

$$1 \text{ poise} = 2.09 \times 10^{-3} \text{ lbf} \cdot \text{s}/\text{ft}^2 = 6.72 \times 10^{-2} \text{ lbm}/(\text{ft} \cdot \text{s})$$

$$1 \text{ centipoise} = 0.01 \text{ poise} = 10^{-3} \text{ Pa} \cdot \text{s}$$

$$1 \text{ lbf} \cdot \text{s}/\text{ft}^2 = 1 \text{ slug}/(\text{ft} \cdot \text{s}) = 47.9 \text{ Pa} \cdot \text{s} = 479 \text{ poise}$$

$$1 \text{ stoke} = 1 \text{ cm}^2/\text{s} = 10^{-4} \text{ m}^2/\text{s} = 1.076 \times 10^{-3} \text{ ft}^2/\text{s}$$

$$1 \text{ centistoke} = 0.01 \text{ stoke} = 10^{-6} \text{ m}^2/\text{s} = 1.076 \times 10^{-5} \text{ ft}^2/\text{s}$$

$$1 \text{ m}^2/\text{s} = 10^4 \text{ stoke} = 10^6 \text{ centistoke} = 10.76 \text{ ft}^2/\text{s}$$