UNIVERSITY OF ABERDEEN   SESSION 2017–18

EX3029

Degree Examination in EX3029 Chemical Thermodynamics

11ᵗʰ December 2017   14.00–17.00

PLEASE NOTE THE FOLLOWING

(i) You **must not** have in your possession any material other than that expressly permitted in the rules appropriate to this examination. Where this is permitted, such material **must not** be amended, annotated or modified in any way.

(ii) You **must not** have in your possession any material that could be determined as giving you an advantage in the examination.

(iii) You **must not** attempt to communicate with any candidate during the exam, either orally or by passing written material, or by showing material to another candidate, nor must you attempt to view another candidate's work.

(iv) You **must not** take to your examination desk any electronic devices such as mobile phones or other smart devices. The only exception to this rule is an approved calculator.

Failure to comply with the above will be regarded as cheating and may lead to disciplinary action as indicated in the Academic Quality Handbook.

Notes: *(i) Candidates ARE permitted to use an approved calculator.*

(ii) Candidates ARE NOT permitted to use the Engineering Mathematics Handbook.

(iii) Data sheets are attached to the paper.

(iv) Candidates ARE NOT permitted to use GREEN or RED pen in their booklets.

Attempt ALL questions.
Each question is worth 20 marks.

Question 1

In the design of a new process, nitrogen dioxide (NO_2) is produced through the decomposition of nitrogen tetroxide (N_2O_4),

$$N_2O_4(g) \Longleftrightarrow 2NO_2(g),$$
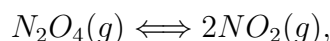
The Gibbs energy of formation at 25°C of both species are:

$$\left(\Delta G^\circ_{f,298}\right)_{N_2O_4} = 97.89 \text{ kJ mol}^{-1} \text{ and } \left(\Delta G^\circ_{f,298}\right)_{NO_2} = 51.31 \text{ kJ mol}^{-1}.$$

The standard enthalpy of this reaction at 25°C is 56.189 kJ mol^{-1}. For such decomposition, three scenarios are considered to assess overall conversion:

A. Decomposition of N_2O_4 at 25°C;

B. Initial dilution with inert N_2 prior to the decomposition of N_2O_4 at 25°C;

C. Decomposition of N_2O_4 at 126.85°C.

Calculate the composition of the species in equilibrium for:

a) Scenario A;   [5 marks]

b) Scenario B, where the initial concentration of N_2O_4 in the $N_2O_4 - N_2$ mixture before the dissociation is 20 mol%. Assume that the equilibrium constant at 25°C is 0.1484;   [5 marks]

c) Scenario C. Assume that the equilibrium constant at 25°C is 0.1484;   [8 marks]

d) Which scenario will lead to larger NO_2 production? Why?   [2 marks]

Given:

$$\Delta M^\circ_r = \sum_{i=1}^{c} \nu_i \Delta M^\circ_{f,i},$$

where $M = \{U, H, G, S, A\}$, ν is the molar stoichiometric coefficient, and

$$\Delta H^\circ_r(T) - \Delta H^\circ_{r,25°C} = \int \Delta C^\circ_p dT \qquad \text{with } \Delta C^\circ_p = \sum_{i=1}^{c} \nu_i C_{p,i},$$

where the molar heat capacity at constant pressure for both gases is expressed in polynomial form as,

$$C_p = a + bT + CT^2 + dT^3, \quad \left(\text{in J mol}^{-1} \text{ K}^{-1}\right)$$

where

	a $\left(\text{J mol}^{-1} \text{ K}^{-1}\right)$	$b \times 10^{-2}$ $\left(\text{J mol}^{-1} \text{ K}^{-2}\right)$	$c \times 10^{-5}$ $\left(\text{J mol}^{-1} \text{ K}^{-3}\right)$	$d \times 10^{-9}$ $\left(\text{J mol}^{-1} \text{ K}^{-4}\right)$
NO_2	22.929	5.711	-3.519	7.866
N_2O_4	33.054	18.661	-11.339	–

Question 2

a) Calculate the molar volume $\left(\text{in m}^3 \text{ mol}^{-1}\right)$ and compressibility factor (Z) for gaseous ammonia at 450 K and 56 atm using the van der Waals (vdW) equation of state. Critical temperature and pressure of ammonia are 405.5 K and 111.3 atm, respectively. [12 marks]

b) Using the definitions of volume expansivity (β) and isothermal compressibility (κ) coefficients,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,$$

and the cyclic rule applied to PVT relations,

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1,$$

show that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}.$$

[3 marks]

c) Using the cyclic rule definition

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1,$$

obtain an algebraic expression for $\left(\frac{\partial V}{\partial T}\right)_P$ for the van der Waals equation of state.

[5 marks]

Question 3

(a) What is the change in entropy when 0.7 m^3 of CO_2 and 0.3 m^3 of N_2 form a gas mixture at 1 bar and 25°C? Assume ideal gases, and given

$$\Delta S = -nR \sum_{i=1}^{n} y_i \ln y_i,$$

where S, n and y are entropy, number of moles and mole fraction, respectively. R is the molar gas constant. [10 marks]

(b) Calculate the bubble point pressure and vapour composition for a liquid mixture of 41.2 mol% of ethanol (1) and n-hexane (2) at 331 K. Given,

$$\ln \gamma_1 = \frac{A}{\left(1 + \dfrac{Ax_1}{Bx_2}\right)^2}, \quad \ln \gamma_2 = \frac{A}{\left(1 + \dfrac{Bx_2}{Ax_1}\right)^2} \text{ and}$$

$$\ln P_i^{sat} = C_i + \frac{D_i}{T + E_i}$$

where

$$\begin{cases} A = 2.409, & B = 1.970 \\ C_1 = 16.1952, & C_2 = 14.0568, \\ D_1 = -3423.53, & D_2 = -2825.42, \\ E_1 = -55.7152, & E_2 = -42.7089 \end{cases}$$

[P] = kPa and [T] = [D_i] = [E_i] = K. [10 marks]

Question 4

a) Figure 1 shows a $P - xy$ phase diagram for an arbitrary binary mixture that is vaporised at constant temperature (M-z). Determine (i) to (ix) from Table 1. [10 marks]
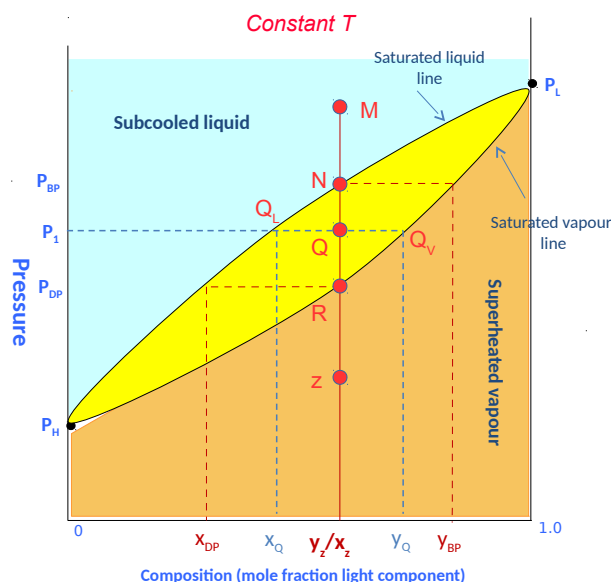

Figure 1: *VLE for binary mixture: P-xy diagram at constant temperature.*

Coordinate	Pressure	Fluid State	x_1	y_1
M	–	subcooled liquid	$x_1 = x_z$	$y_1 = 0$
N	bubble point (P_{BP})	–	(i)	(ii)
Q	–	(iii)	(iv)	(v)
R	(vi)	–	(vii)	(viii)
z	–	(ix)	(x)	–

Table 1: *Properties of $P - xy$ phase diagram*

b) Using the Redlich-Kwong equation of state, develop algebraic expressions for changes in specific entropy $(s_2 - s_1)$ and internal energy $(u_2 - u_1)$ of a gas between two states at the same temperature (*i.e.,* $T_1 = T_2$) and pressures P_1 and P_2.
[10 marks]

Question 5

a) A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is obtained through a single-stage liquid/vapour separator. Equilibrium mole fractions are $x_1 = 0.002$ and $y_1 = 0.950$. Assuming that the modified Raoult's law applies,

$$y_i P = x_i \gamma_i P_i^{\text{sat}},$$

determine T and P for the separator. Activity coefficients for the liquid phase are given by,

$$\ln \gamma_1 = 0.93 x_2^2 \quad \text{and} \quad \ln \gamma_2 = 0.93 x_1^2,$$

and the saturated vapour pressure is given by,

$$\ln P^{\text{sat}} = A - \frac{B}{T} \quad \text{with [P] = bar and [T] = [B] = K,}$$

with $A_1 = 10.08$, $B_1 = 2572.0$, $A_2 = 11.63$ and $B_2 = 6254.0$.   [13 marks]

b) Determine the temperature and composition of the first bubble created from a saturated liquid mixture of benzene and toluene containing 45 mol% percent of benzene at 200 kPa. Benzene and toluene mixtures may be considered as ideal. Given,   [7 marks]

$$\ln P^{sat} = A - \frac{B}{T + C} \quad \text{with [P] = kPa and [T] = [B] = [C] = K,}$$

and

	A	B	C
Benzene	14.1603	2948.78	-44.5633
Toluene	14.2514	3242.38	-47.1806

END OF PAPER

Unit Conversion

1) Gas Contant, R

R	Units $\left(\text{V.P.T}^{-1}\text{n}^{-1}\right)$
8.3145	J.K^{-1}.mol^{-1}
8.3145	kJ.K^{-1}.kmol^{-1}
8.3145	l.kPa.K^{-1}.mol^{-1}
8.3145$\times10^{-3}$	cm^3.kPa.K^{-1}.mol^{-1}
8.3145	m^3.Pa.K^{-1}.mol^{-1}
8.3145$\times10^{-5}$	m^3.bar.K^{-1}.mol^{-1}
8.2057$\times10^{-2}$	l.atm.K^{-1}.mol^{-1}

2) Length

1 m =	3.2808 ft =	39.37 in =	10^2 cm =	10^{10} A
1 mm =	10^{-3} m =	10^{-1} cm =	10^{-6} km	
1 mile =	5280 ft =	1609.36 m =	1.609 km	

3) Area

1 m^2 =	10^4 cm^2 =	10.76 ft^2 =	1550 in^2
1 in^2 =	6.944$\times10^{-3}$ ft^2 =	6.4516$\times10^{-4}$ m^2	

4) Volume

1 m^3 =	35.313 ft^3 =	6.1023$\times10^4$ in^2 =	1000 l = 264.171 gal

5) Mass

1 kg =	1000 g =	2.2046 lbm

6) Force

1 N =	10^5 dyne =	1 kg.m.s^{-2} =	0.225 lbf

7) Energy

1 J =	1 N.m =	1 kg.m^2.s^{-2} =	9.479$\times10^{-4}$ Btu
1 kJ =	1000 J =	0.9479 Btu =	238.9 cal

8) Power

1 W =	1 J.s^{-1} =	1 kg.m^2.s^{-3} =	3.412 Btu.h^{-1} =	1.3405$\times10^{-3}$ hp
1 kW =	1000 W =	3412 Btu.h^{-1} =	737.3 ft.lbf.s^{-1} =	1.3405 hp

9) Pressure

1 Pa =	1 N.m^{-2} =	1 kg.m^{-1}.s^{-2} =	1.4504$\times10^{-4}$ lbf.in^{-2}	
1 atm =	14.696 lbf.in^{-2} =	1.01325$\times10^5$ Pa =	101.325 kPa =	760 mm-Hg
1 dyne.cm^{-2} =	0.1 Pa =	10^{-6} bar =	145.04 lbf.in^{-2}	
1 bar =	10^5 Pa =	0.987 atm =	14.504 lbf.in^{-2}	

10) Temperature

$$\begin{cases} T\left(°F\right) = \dfrac{9}{5}T\left(°C\right) + 32 = T(R) - 459.67 \\ T\left(°C\right) = \dfrac{5}{9}\left[T\left(°F\right) - 32\right] = T(K) - 273.15 \end{cases}$$

11) Viscosty

1 Pa.s =	1 N.s.m^{-2} =	1 kg.m^{-1}.s^{-1} =	10 poise	
1 poise =	1 dyne.s.cm^{-2} =	1 g.cm^{-1}.s^{-1} =	0.1 Pa.s =	6.72×10^{-2} lbm.ft^{-1}.s^{-1}
1 stoke =	1 cm^2.s^{-1} =	10^{-4}cm^2.s^{-1} =	1.076×10^{-3} ft^2.s^{-1}	

Formula Sheet

1) Fundamentals of Thermodynamics:

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

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

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

2) Volumetric Properties of Pure Fluids:

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

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

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

$$P = \frac{RT}{V-b} - \frac{a}{V\sqrt{T}\,(V+b)}; \ \ a = \frac{0.42748R^2T_c^{2.5}}{P_c}; \ \ b = \frac{0.08664RT_c}{P_c}; \ \ \text{[Redlich-Kwong (RK) EOS]}$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V\,(V+b)}; \ \ a = \frac{0.42748R^2T_c^2}{P_c}; \ \ b = \frac{0.08664RT_c}{P_c} \ \ \text{and}$$

$$\alpha = \left[1 + \left(0.480 + 1.574\omega - 0.176\omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2; \ \ \text{[Soave-Redlich-Kwong (SRK) EOS]}$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V\,(V+b) + b\,(V-b)}; \ \ a = \frac{0.45724R^2T_c^2}{P_c}; \ \ b = \frac{0.07780RT_c}{P_c}; \ \ \text{and}$$

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

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

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

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

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

EOS	α	σ	ε	Ω	Ψ
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	α_{SRK}	1	0	0.08664	0.42748
PR	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

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

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

3) Thermodynamic Properties of Pure Fluids:

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

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

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

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

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

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

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

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

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

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

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

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

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

4) Vapour-Liquid Equilibrium of Mixtures:

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

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

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

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

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

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

5) Solution Thermodynamics:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6) Chemical Reaction Equilibrium:

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

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

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

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

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

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

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

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