CH 2010

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CH19B072

ASSIGNMENT - 1

1) We have,

$B_{11} = -625 \text{ cm}^3/\text{mol}$ $\quad$ $B_{22} = -110 \text{ cm}^3/\text{mol}$

$B_{12} = B_{21} = -153 \text{ cm}^3/\text{mol}$

$P = 10$ bar $\quad$ $T = 313.2$ K

mole fraction of butane $= \dfrac{(19+072)}{150} = \underline{\underline{0.61\ \%}}$

ie $\quad y_1 = \underline{\underline{0.0061}}$

$\quad y_2 = \underline{\underline{0.9939}}$

By mixing rule, we have

$$B_{mix} = y_1^2 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2^2 B_{22}$$

$$= y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

$$= (0.0061)^2(-625) + 2(0.0061)(0.9939)(-153) + (0.9939)^2(-110)$$

$$= \underline{\underline{-110.54 \text{ cm}^3/\text{mol}}}$$

(This is very close to B_{22} because mole fraction of 1 is very low) ie the mixture contains mostly CO_2

(a) To find molar volume of the mixture :

(At a moderate pressure like 10 bar, we can use pressure expansion of virial equation upto two terms)

$$Z = 1 + B'P$$

But $B' = \frac{B}{RT}$

$$\Rightarrow Z = 1 + \frac{BP}{RT}$$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{B_{mix}P}{RT}$$

$$\Rightarrow V = B_{mix} + \frac{RT}{P} = -110.54 \frac{cm^3}{mol} + \frac{8.314 \times 313.2}{10 \times 10^5 \times 10^{-6}} \frac{cm^3}{mol}$$

$$\Rightarrow V = 2493.40 \frac{cm^3}{mol}$$ → molar volume of mixture

(b) We can find k_{12} using the formula : (at 313.2K)

$$|B_{12}| = \sqrt{B_{11} B_{22}} (1-k_{12})$$

$$k_{12} = 1 - \frac{|B_{12}|}{\sqrt{B_{11} B_{22}}}$$

$$= 1 - \frac{153}{\sqrt{110 \times 625}}$$

$$\Rightarrow k_{12} = 0.416481$$ → binary interaction parameter

2) $l = 2$ $\Rightarrow$ alkane : C_2H_6 $M_w = 30$ g/mol

$m = 72$ kg $P = 10 + \frac{72}{19} = 13.79$ bar

$T = 273.15 + 2 \times 72 = 417.15$ °C $= 690.3$ K

$n = 72 \times 10^3 / 30 = 2400$ moles

(a) Ideal gas model

$$Pv = RT$$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{2400 \times 8.314 \times 690.3}{13.79 \times 10^5} \text{ m}^3$$

$$V = 9.988 \text{ m}^3$$

(b) Redlich - Kwong EOS

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2} v(v+b)} \rightarrow (1)$$

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c} = 9.882 \left[\frac{J \, m^3 \, k^{1/2}}{mol^2}\right]$$

$$b = \frac{0.08664 RT_c}{P_c} = 4.513 \times 10^{-5} \left[\frac{m^3}{mol}\right]$$

$[T_c = 305.4$ K , $P_c = 48.74$ bar$]$

Now, we can use

$P = 13.79 \times 10^5$ Pa , $T = 690.3$ K , a and b

to find v numerically

I used Newton-Raphson method (not including all the iterations here because of space constraint)

$$V = 0.004143 \ m^3/mol$$

$$\Rightarrow V = Vn = 0.004143 \times 2400 = \underline{\underline{9.9432 \ m^3}}$$

(c) <u>Peng-Robinson EOS</u>

$$P = \frac{RT}{v-b} - \frac{a\,\alpha(T)}{v(v+b)+b(v-b)}$$

where $\alpha = [1 + K(1-\sqrt{T_r})]^2$

$$T_r = \frac{T}{T_c} = \frac{690.3}{305.4} = \underline{\underline{2.2603}}$$

ω of ethane $= 0.099$

$$K = 0.37464 + 1.54226\omega + -0.26992\omega^2$$

$$= \underline{\underline{0.52468}}$$

$$\Rightarrow \alpha = \underline{\underline{0.5415}}$$

~~Substituting~~

$$a = \frac{0.45724(RT_c)^2}{P_c} = 0.6048 \left[\frac{J\,m^3}{mol^2}\right]$$

$$b = \frac{0.07780\,RT_c}{P_c} = 4.053 \times 10^{-5} \left[\frac{m^3}{mol}\right]$$

Now, we use the values of P, T, R, a, b and α in Peng-Robinson EOS to find v numerically

I used Newton-Raphson method

$$v = 0.004149 \ \frac{m^3}{mol}$$

$$\Rightarrow V = v \times n = 0.004149 \times 2400 = \underline{\underline{9.9576 \ m^3}}$$

(d) <u>Compressibility charts</u>

$$T_r = \frac{T}{T_c} = \frac{690.3}{305.4} = 2.2603$$

$$P_r = \frac{P}{P_c} = \frac{13.79}{48.74} = 0.283$$

~~$z^{(0)}$~~

T_r \ P_r	0.25	0.5
2.5	~~0.9987~~	~~0.9977~~
2.75	~~1.0001~~	~~1.0005~~

~~$\Rightarrow z^{(0)} =$~~

$\underline{\underline{z^{(0)}}}$

T_r \ P_r	0.25	0.5
2.25	0.9965	0.9935
2.5	0.9987	0.9977

By double interpolation,

$$z^{(0)} = \underline{\underline{0.9962}}$$

$\underline{\underline{Z^{(1)}}}$

By double interpolation,

T_R \ P_R	0.25	0.5
2.25	0.0181	0.0360
2.5	0.0168	0.0334

$Z^{(1)} = \underline{\underline{0.02}}$

$\omega = 0.099$ for ethane

$$Z = Z^{(0)} + Z^{(1)} \times \omega = \frac{Pv}{RT}$$

$$v = \frac{8.314 \times 690.3}{13.79 \times 10^5} \left[0.9962 + 0.02 \times 0.099 \right]$$

$$v = 0.004154 \ \frac{m^3}{mol}$$

$\Rightarrow V = vn = 0.004154 \times 2400 = \underline{\underline{9.97 \ m^3}}$

All methods - Tabulated

Value of V in m^3

Ideal gas	:	9.988
Redlich - kwong	:	9.9432
Peng- Robinson	:	9.9576
Compressibility charts	:	9.97

3) Berthelot EOS

(a) $$P = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

At critical point, $P = P_c$, $T = T_c$, $v = v_c$

$$\Rightarrow P_c = \frac{RT_c}{v_c - b} - \frac{a}{T_c v_c^2}$$

$$\left(\frac{\partial P}{\partial v}\right)_{@T_c} = \frac{-RT_c}{(v_c-b)^2} + \frac{2a}{T_c v_c^3} = 0 \rightarrow (1)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{T_c v_c^4} = 0 \rightarrow (2)$$

$$\left[\frac{\partial P}{\partial v} \text{ and } \frac{\partial^2 P}{\partial v^2} = 0 \text{ at critical point}\right]$$

~~(1) × 2 + (2) ×~~

(eqn (1)) × 2 + (eqn (2)) × $(v_c - b)$

$$\Rightarrow \frac{4a}{T_c v_c^3} - \frac{6a(v_c-b)}{T_c v_c^4} = 0$$

$$\Rightarrow \boxed{v_c = 3b} \rightarrow (3)$$

Substituting $v_c = 3b$ in eqn (1)

$$\Rightarrow \boxed{a = \frac{9}{8} v_c R T_c^2} \rightarrow (4)$$

Substituting (3) and (4) in

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{T_c V_c^2}$$

$$\Rightarrow P_c = \frac{RT}{3b - b} - \frac{\frac{9}{8} V_c R T_c^2}{T_c V_c^2}$$

$$P_c = \frac{RT}{2b} - \frac{9 R T_c}{8(3b)} = \frac{RT_c}{8P_c}$$

$$\Rightarrow \boxed{b = \frac{RT_c}{8P_c}}$$

$$a = \frac{9}{8} V_c R T_c^2 = \frac{9}{8}(3b) R T_c^2$$

$$= \frac{9}{8} \times \left(3 \times \frac{RT_c}{8P_c}\right) \times RT_c^2$$

$$\boxed{a = \frac{27 R^2 T_c^3}{64 P_c}}$$

(b) We have,

$$V_c = 3b \rightarrow (1)$$

$$a = \frac{27}{64} \frac{R^2 T_c^3}{P_c} \rightarrow (2)$$

$$b = \frac{RT_c}{8P_c} \rightarrow (3)$$

Substituting (1) in Berthelot EOS

$$\Rightarrow P = \frac{RT}{V - \frac{V_c}{3}} - \frac{a}{TV^2}$$

$$\Rightarrow P = \frac{\frac{RT}{V_c}}{\left(\frac{V}{V_c}\right) - \frac{1}{3}} - \frac{a}{TV^2}$$

$$\left(V_R = \frac{V}{V_c} \right)$$

$$\Rightarrow P = \frac{\frac{RT}{b}}{3V_R - 1} - \frac{a}{TV^2}$$

Substituting (3)

$$\Rightarrow P = \frac{\frac{RT}{RT_c} \times 8P_c}{3V_R - 1} - \frac{a}{TV^2}$$

$$\Rightarrow P = \frac{8P_cT_R}{3V_R - 1} - \frac{a}{TV^2} \qquad \left(T_R = \frac{T}{T_c} \right)$$

Substituting (2)

$$\Rightarrow P = \frac{8P_cT_R}{3V_R - 1} - \frac{27 T_c^3 R^2}{64 P_c T V^2}$$

From (3), $R^2 T_c^2 = 64 P_c^2 b^2$

$$\Rightarrow P = \frac{8P_cT_R}{3V_R - 1} - \frac{27 P_c T_c b^2}{TV^2}$$

Now substitute (1)

$$\Rightarrow P = \frac{8 P_c T_r}{3 v_r - 1} - \frac{3 P_c T_c v_c^2}{T \; v^2} \qquad \left(P_r = \frac{P}{P_c}\right)$$

$$\Rightarrow \boxed{P_r = \frac{8 T_r}{3 v_r - 1} - \frac{3}{T_r v_r^2}} \rightarrow \text{reduced form}$$

(c) From (2), we have

$P = 13.79$ bar

$T = 690.3K$

$$a = \frac{27 R^2 T_c^3}{64 P_c} = \underline{\underline{602.347 \ Pa\,K \frac{m^6}{mol^2}}}$$

$$b = \frac{R T_c}{8 P_c} = \underline{\underline{23.016 \times 10^{-5}}} \ \frac{m^3}{mol}$$

Substituting these values in Berthelot EOS:

$$P = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

We can solve v using numerical techniques.

& used Newton-Raphson method

$v = 0.004251 \ m^3/mol$

$V = v \times n = 0.004251 \times 2400 = \underline{\underline{10.2 \ m^3}}$

4) Vanderwaal's parameters

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad \left[\frac{J m^3}{mol^2} \right]$$

$$b = \frac{R T_c}{8 P_c} \quad \left[\frac{m^3}{mol} \right]$$

I choose Benzene (mw = 78 g/mol → condition (1)).

oxygen and propane (oxygen → 0 → condition (2))

Gas	P_c (bar)	T_c (K)	$a = \frac{27 R^2 T_c^2}{64 P_c}$ $\left(\frac{J m^3}{mol^2}\right)$	$b = \frac{R T_c}{8 P_c}$ (m^3/mol)
Benzene	48.94	562.1	1.88	1.19×10^{-4}
Oxygen	50.46	154.6	0.138	3.18×10^{-5}
Propane	42.44	370	0.94	9.06×10^{-5}

a : Benzene > Propane > Oxygen

b : Benzene > Propane > Oxygen

Physical significance

a → affected by attractive interaction

b → affected by size

a

All three of them are non-polar molecules. Therefore, only London dispersion forces are prevalent. Larger and heavier atoms and molecules exhibit stronger dispersion forces than smaller and lighter ones. This is because in larger atom or molecule, the valence electrons are, on average, farther from the nuclei than in a smaller atom or molecule. They are less tightly held and can more easily form temporary dipoles, ie larger molecules have more polarizability. Benzene is largest and heaviest, while O_2 is the smallest

∴ a: Benzene > Propane > Oxygen

b

b is directed depended on size of molecule

~~∴~~ ~~b~~: Benzene is largest and O_2 is smallest.

∴ b: Benzene > Propane > Oxygen

5: Considering mixture of O_2 and propane

For both O_2 and propane, the dipole moments are zero. ($a \rightarrow O_2$ $b \rightarrow C_3H_8$)

$\therefore$ dipole-dipole and induction forces are zero

$\mu_a = \mu_b = 0$

$\therefore$ Only forces is dispersion

$$\Gamma_{aa} = \Gamma_{aa}^{\text{dipole-dipole}} + \Gamma_{aa}^{\text{induction}} + \Gamma_{aa}^{\text{dispersion}}$$

$$\Gamma_{aa}^{\text{dipole-dipole}} \rightarrow -\frac{2}{3}\frac{\mu_a^2\mu_a^2}{kT}\frac{1}{r^6} \rightarrow 0$$

$$\Gamma_{aa}^{\text{induction}} \rightarrow \underbrace{-\frac{\alpha_a\mu_a^2}{r^6} - \frac{\alpha_a\mu_a^2}{r^6}}_{\rightarrow 0}$$

$$\Gamma_{aa}^{\text{dispersion}} \rightarrow -\frac{3}{2}\frac{\alpha_a\alpha_a}{r^6}\frac{I_aI_a}{I_a+I_a}$$

$$\boxed{\Gamma_{aa} = -\frac{3}{4}\frac{\alpha_a^2 I_a}{r^6}}$$

$$\Gamma_{bb} = \Gamma_{bb}^{\text{dipole-dipole}} + \Gamma_{bb}^{\text{induction}} + \Gamma_{bb}^{\text{dispersion}}$$

$$\Gamma_{bb}^{\text{dipole-dipole}} \rightarrow -\frac{2}{3}\frac{\mu_b^2\mu_b^2}{kT}\frac{1}{r^6} \rightarrow 0$$

$$\Gamma_{bb}^{\text{induction}} \rightarrow -\frac{\alpha_b\mu_b^2}{r^6} - \frac{\alpha_b\mu_b^2}{r^6} \rightarrow 0$$

$$\Gamma_{bb}^{\text{dispersion}} \rightarrow -\frac{3}{4}\frac{\alpha_b^2 I_b}{r^6}$$

$$\boxed{\Gamma_{bb} = -\frac{3}{4}\frac{\alpha_b^2 I_b}{r^6}}$$

$$\Gamma_{ab} = \Gamma_{a-b}^{\text{dipole-dipole}} + \Gamma_{a-b}^{\text{induction}} + \Gamma_{a-b}^{\text{dispersion}}$$

$$\Gamma_{a-b}^{\text{dipole-dipole}} \downarrow -\frac{2}{3}\frac{\mu_a^2 \mu_b^2}{kT}\frac{1}{r^6} \downarrow 0$$

$$\Gamma_{a-b}^{\text{induction}} \downarrow -\frac{\alpha_a \mu_b^2}{r^6} - \frac{\alpha_b \mu_a^2}{r^6} \downarrow 0$$

$$\Gamma_{a-b}^{\text{dispersion}} \downarrow -\frac{3}{2}\frac{\alpha_a \alpha_b}{r^6}\frac{I_a I_b}{I_a + I_b}$$

$$\boxed{\Gamma_{ab} = -\frac{3}{2}\frac{\alpha_a \alpha_b}{r^6}\frac{I_a I_b}{I_a + I_b}}$$

Note: the terms became zero because $\mu_a = \mu_b = 0$ (dipole moment is zero for non-polar molecules)

Oxygen (a)

$\alpha_a = 16 \times 10^{-25}\ cm^3$

$I_a = 12.07\ eV$

Propane (b)

$\alpha_b = 62.9 \times 10^{-25}\ cm^3$

$I_b = 10.94\ eV$

Substituting the above values,

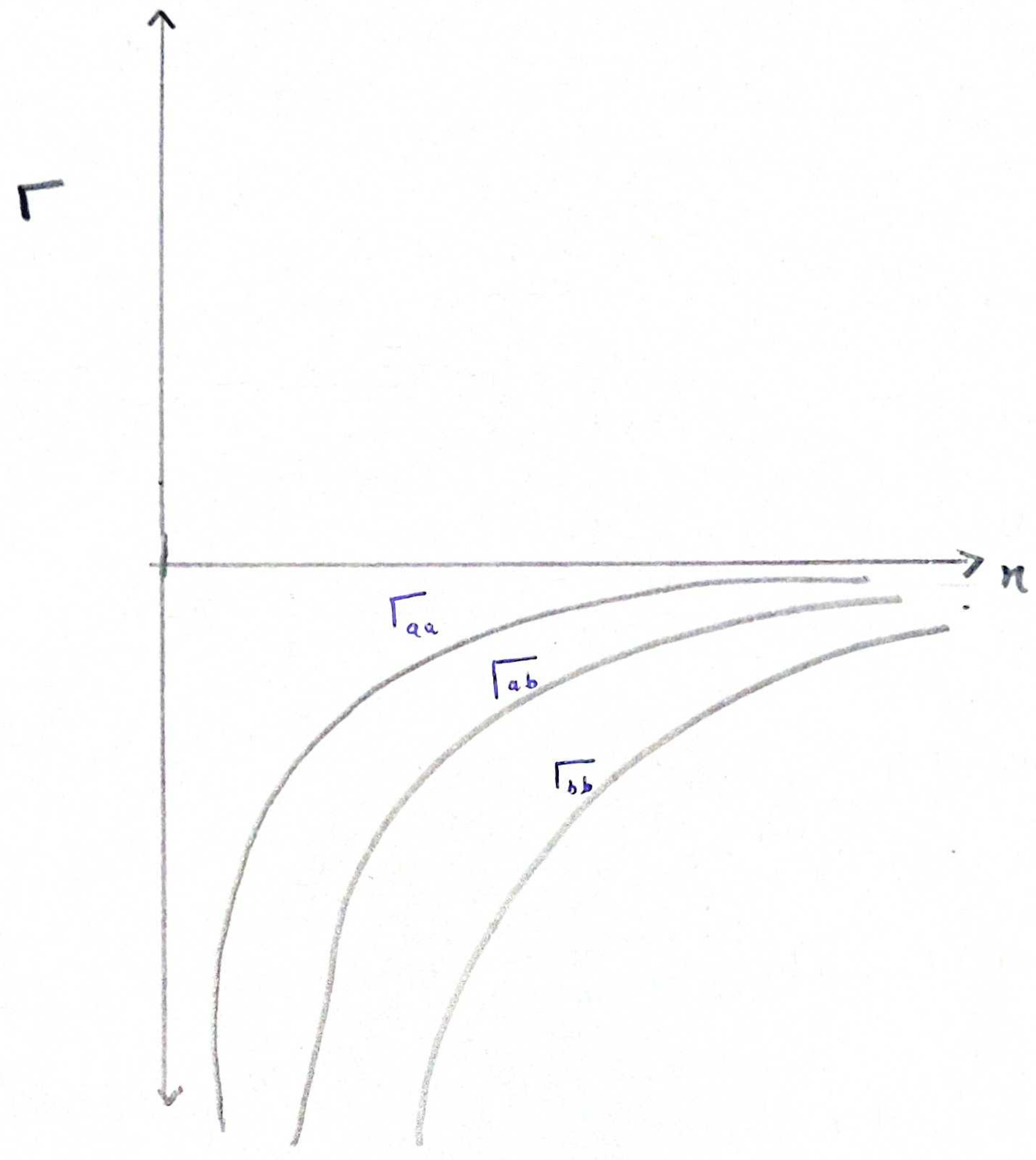
$$\Gamma_{aa} = \frac{-2.317 \times 10^{-47}}{r^6} \ (eV)(cm^6)$$

$$\Gamma_{bb} = \frac{-32.462 \times 10^{-47}}{r^6} \ (eV)(cm^6)$$

$$\Gamma_{ab} = \frac{-8.663 \times 10^{-47}}{r^6} \ (eV)(cm^6)$$

attractive interactions

Qualitative plot of Γ_{aa}, Γ_{ab}, Γ_{bb}



Attractive interactions are maximum when $r \rightarrow 0$