Assignment - 5

~~Cde~~

1. (a) ideal gas law model.

$P\underline{V} = RT$

$\Rightarrow P = \frac{RT}{\underline{V}}$

$\therefore \underline{W} = -\int P d\underline{V}$ [$\underline{W}$ is work done per mole].

$= -\int \frac{RT}{\underline{V}} d\underline{V}$

$= -RT \ln \frac{\underline{V}_2}{\underline{V}_1}$

$= -(8.314)(1000) \ln \left(\frac{1}{10}\right)$

$= 8.314 \times 1000 \times \ln 10$

$= 19143.69$ J/mole.

$\therefore$ Total workdone $= n\underline{W} = 2 \times 19143.69$

$= \boxed{38287.38 \text{ J}}$ or, $\boxed{38.287 \text{ KJ}}$

(b) R-K equation:

$P = \frac{RT}{\underline{V} - b} - \frac{a}{T^{1/2} \underline{V}(\underline{V}+b)}$, $a = 14.24 \frac{J K^{1/2} m^3}{mol^2}$

$b = 2.11 \times 10^{-5} \frac{m^3}{mol}$.

$\underline{V}_{initial} = \frac{10}{2} = 5 \frac{\text{Litre}}{\text{mol}} = 0.005 \frac{m^3}{mol}$

$\underline{V}_{final} = \frac{1}{2} = 0.5 \frac{\text{litre}}{\text{mol}} = 0.0005 \frac{m^3}{mol}$.

$$W = -\int P\,dV$$

$$= -\int_{V_{initial}}^{V_{final}} \frac{RT}{V-b}\,dV + \int_{V_{initial}}^{V_{final}} \frac{a.}{T^{1/2}\,V(V+b)}\,dV$$

$$= -RT\ln\left|\frac{V_{final}-b}{V_{initial}-b}\right| + \frac{a}{T^{1/2}.b}\int_{V_{initial}}^{V_{final}} \frac{(V+b)-V}{V(V+b)}\,dV$$

$$= RT\ln\left|\frac{0.005-2.11\times10^{-5}}{0.0005-2.11\times10^{-5}}\right| + \frac{a}{T^{1/2}\,b}\int_{V_{initial}}^{V_{final}}\frac{dV}{V} - \frac{a}{T^{1/2}b}\int_{V_{initial}}^{V_{final}}\frac{dV}{V+b}$$

$$= 19467.002 + \frac{14.24}{(1000)^{1/2}(2.11\times10^{-5})}\ln\frac{0.0005}{0.005}$$

$$- \frac{14.24}{(1000)^{1/2}(2.11\times10^{-5})}\ln\left|\frac{0.0005+2.11\times10^{-5}}{0.005+2.11\times10^{-5}}\right|$$

$$= 19467.002 - 21341.63\ \ln 10 + 21341.63\,(2.26546)$$

$$= 18674.74\ \text{J/mol}$$

$\therefore$ Total work done $= 2W = 2 * 18674.74$

$= \boxed{37349.484\ \text{J}}$ or $\boxed{37.349\ \text{kJ}}$

(c) From first law of Thermodynamics, $\Delta U = q + W$

$$W = \Delta U - q$$

$$W = \Delta U - T\Delta S \quad \text{(since, Process is reversible)}$$

$$W_{12} = (U_2 - U_1) - T(S_2 - S_1)$$

To use steam tables, we need to know initial and final Pressure.

Let it's calculated using Redlich - Kwong equation of state.

$$\therefore P_{initial} = \frac{RT}{\underline{V}_{initial} - b} - \frac{a}{T^{1/2}\underline{V}_{in}(\underline{V}_{in} + b)}$$

$$= \frac{(8.314)(1000)}{0.005 - 2.11\times10^{-5}} - \frac{14.24}{(1000)^{1/2}(0.005)(0.005 + 2.11\times10^{-5})}$$

$$= 1669846.75 - 17936.64$$

$$= 1651910.11 \text{ Pa.}$$

$$= 1.65 \text{ MPa}$$

Similarly P_{final} can also be calculated using RK EOS by Putting

$$\underline{V} = \underline{V}_{final} = 0.0005$$

$$P_{final} = 15.6 \text{ MPa.}$$

From steam table at $P = 1.65$ MPa and $T = 1000$ K,

$$\underline{u}_1 = 3522.6 \text{ KJ/kg} \qquad \underline{S}_1 = 8.101 \frac{\text{kJ}}{\text{kg K}}.$$

at $P = 15.6$ MPa and $T = 1000$ K.

$$\underline{u}_2 = 3462.2 \frac{\text{kJ}}{\text{kg}} \qquad \underline{S}_2 = 7 \frac{\text{kJ}}{\text{kg K}}$$

$$\therefore \underline{W}_{12} = (3462.2 - 3522.6) - 1000(7 - 8.101)$$

$$= -60.4 + 1101$$

$$= 1040.6 \text{ kJ/kg}.$$

$\therefore$ 2 mol water $\equiv$ 0.036 kg.

$\therefore$ Total work done $= 0.036 * 1040.6$

$$= \boxed{37.462 \text{ kJ}}$$

Part (a) has significant difference from Part (b) and (c).
Hence, Redlich-Kwong EOS or steam table is much accurate.
to calculate work done. Compared to ideal gas law.

2. For oxygen Van der Waal constants are as follows:

$$a = 0.138 \ Pa \cdot \frac{m^6}{mol^2}$$

$$b = 32.6 \times 10^{-6} \ m^3/mol$$

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

For $T_r = 0.95$, $V_{r,l} \doteq 0.68$ and $V_{r,g} \doteq 1.7$

(From figure 9.15)

where, $T_r = \frac{T}{T_c}$; $V_{r,l} = \frac{\underline{V}^l}{V_{cr}}$; $V_{r,g} = \frac{\underline{V}^g}{V_{cr}}$

For Van der Waal, $V_{cr} = 3b$.

$$\therefore \underline{V}^l = (0.68)(3 \times 32.6 \times 10^{-6}) = \cancel{65.28 \times 10^{-6} \ m^3} \ 66.504 \times 10^{-6} \ m^3/mol$$

$$\underline{V}^g = (1.7)(3 \times 32.6 \times 10^{-6}) = 166.26 \times 10^{-6} \ m^3/mol.$$

$$\underline{V} = 200 \ cm^3$$

$$= \frac{200 \times 10^{-6} \ m^3}{2 \ mol} = 10^{-4} \ m^3/mol$$

$$\therefore x = \frac{\underline{V} - \underline{V}_L}{\underline{V}_g - \underline{V}_L} = \frac{10^{-4} - 66.504 \times 10^{-6}}{(166.26 - 66.504) \times 10^{-6}}$$

$$= 0.336$$

n_g = mole number in vapour phase $= 2 * 0.336 = \boxed{0.672 \text{ mole}}$

n_l = mole " " Liquid Phase $= 2 * (1 - 0.336) = \boxed{1.328 \text{ mole}}$

V_g = volume " gas phase $= 0.672 * 166.26 = \boxed{111.73 \ cm^3}$

$\therefore V_l = (200 - 111.73) = \boxed{88.27 \ cm^3}$

3. At triple point all three phases coexist.

$$\therefore\ 24.38 - \frac{3063}{T_{tP}} = 27.92 - \frac{3754}{T_{tP}}$$

$$\Rightarrow \frac{3754 - 3063}{T_{tP}} = 27.92 - 24.38$$

$$\Rightarrow \frac{691}{T_{tP}} = 3.54$$

$$\Rightarrow \boxed{T_{tP} = 195.2\,K}$$

$$\therefore \ln P_{tP} = 24.38 - \frac{3063}{195.2} = 8$$

$$\Rightarrow P_{tP} = 5933.69\ Pa \approx \boxed{5.4\ KPa}$$

Latent heat of Sublimation, $\Delta H_{sg} = 3754\,R = (3754)(8.314)$

$$= \boxed{31210.756\ J/mol}$$

Latent heat of vapourization, $\Delta H_{lg} = 3063\,R = (3063)(8.314)$

$$= \boxed{25465.782\ J/mol}$$

[4] Van der Waals EoS is given as:-

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad , N=1$$

→ One of the physical consequence of thermal stability is

$$k_T > 0$$

As we know;

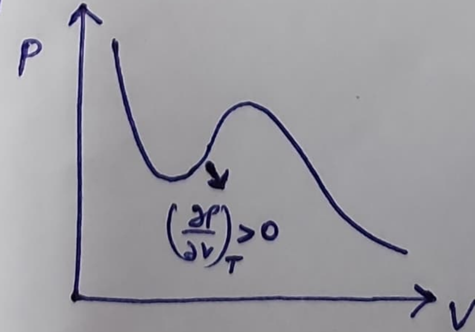
$$k_T = -\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T \quad -①$$

For Van der waal EoS;

$$k_T = \left(-\frac{1}{V}\right)\left[-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\right]$$

$$k_T = \frac{RT}{V(V-b)^2} + \frac{2a}{V^4}$$

→ Now, when $\left(\frac{\partial P}{\partial V}\right)_T > 0 \Rightarrow k_T < 0 \Rightarrow$ This refers to instability



Van der Waals EOS

5. $$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$$

$$\Rightarrow \frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V}-b} - \frac{a}{RT\underline{V}} = \frac{1}{1-\frac{b}{\underline{V}}} - \frac{a}{RT\underline{V}}$$

We know,

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots$$

$$\frac{1}{1-\frac{b}{\underline{V}}} = 1 + \frac{b}{\underline{V}} + \left(\frac{b}{\underline{V}}\right)^2 + \left(\frac{b}{\underline{V}}\right)^3 + \cdots$$

$$\therefore \frac{P\underline{V}}{RT} = 1 + \frac{b - \frac{a}{RT}}{\underline{V}} + \left(\frac{b}{\underline{V}}\right)^2 + \left(\frac{b}{\underline{V}}\right)^3 + \cdots$$

$$= 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \cdots$$

$\therefore$ Second virial coefficient, $B = b - \frac{a}{RT}$

Third virial coefficient, $C = b^2$

~~Alternate~~ Redlich - Kwong EOS

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

$$\Rightarrow \frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V}-b} - \frac{a}{RT^{3/2}(\underline{V}+b)} = \frac{1}{1-\frac{b}{\underline{V}}} - \frac{a/RT^{3/2}}{\underline{V}+b}$$

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots$$

$$1 - \frac{b}{\underline{V}} = 1 + \frac{b}{\underline{V}} + \left(\frac{b}{\underline{V}}\right)^2 + \cdots$$

Second term $= \dfrac{a/RT^{3/2}}{V+b}$

$$= \frac{a}{RT^{3/2}} \cdot \frac{V}{V(V+b)}$$

$$= \frac{a}{RT^{3/2}} \cdot \frac{1}{V} \cdot \frac{1}{\left(1+\frac{b}{V}\right)}$$

$$= \frac{a}{RT^{3/2}} \cdot \frac{1}{V} \cdot \frac{1}{\left\{1-\left(-\frac{b}{V}\right)\right\}}$$

$$\therefore \frac{1}{1+\frac{b}{V}} = 1 - \frac{b}{V} + \left(\frac{b}{V}\right)^2 - \cdots$$

$$\therefore \text{Second term} = \frac{a}{RT^{3/2}} \cdot \frac{1}{V}\left\{1 - \frac{b}{V} + \left(\frac{b}{V}\right)^2 - \cdots\right\}$$

$$= \frac{a}{RT^{3/2}V} - \frac{ab}{RT^{3/2}V^2} + \frac{ab^2}{RT^{3/2}V^3} - \cdots$$

$$\therefore \frac{PV}{RT} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 - \frac{a}{RT^{3/2}V} + \frac{ab}{RT^{3/2}V^2} - \frac{ab^2}{RT^{3/2}V^3} + \cdots$$

$$= 1 + \frac{b - \frac{a}{RT^{3/2}}}{V} + \frac{b^2 - \frac{ab}{RT^{3/2}}}{V^2} + \cdots$$

Second virial coefficient, $B = b - \dfrac{a}{RT^{3/2}}$

$$C = b^2 - \frac{ab}{RT^{3/2}}$$

6. $T = -30^\circ C = 243.15\ K$,

$P = 10.6\ bar = 1.06 \times 10^6\ Pa$.

Critical properties of ethane :-

$T_c = 305.4\ K$ $\quad P_c = 48.84\ bar$ $\quad \omega = 0.099$

$= 48.84 \times 10^5\ Pa$.

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

$$\alpha(T) = \left[1 + \kappa\left(1 - \sqrt{T_r}\right)\right]^2. \qquad T_r = \frac{T}{T_c} = \frac{243.15}{305.4} = 0.796.$$

$$\kappa = 0.37464 + 1.54226\,(0.099) - 0.26992\,(0.099)^2.$$

$$= 0.52468$$

$$\alpha = \left[1 + 0.52468\left(1 - \sqrt{0.796}\right)\right]^2 = 1.116.$$

$$a = \frac{0.45724\,(RT_c)^2}{P_c} = 0.6036\ J.\frac{m^3}{mol}.$$

$$b = \frac{0.0778\,RT_c}{P_c} = 4.045 \times 10^{-5}\ m^3/mol$$

$$P = \frac{RT}{\underline{V} - 4.045 \times 10^{-5}} - \frac{(0.6036)(1.116)}{\underline{V}\left(\underline{V} + 4.045 \times 10^{-5}\right) + 4.045 \times 10^{-5}\left(\underline{V} - b\right)}$$

$$= \frac{2021.549}{\underline{V} - b} - \frac{0.6736}{\underline{V}^2 + 2b\underline{V} - b^2}$$

$$\Rightarrow P = \frac{2021.549(\underline{v}^2 + 2b\underline{v} - b^2) - 0.6736(\underline{v} - b)}{(\underline{v}-b)(\underline{v}^2 + 2b\underline{v} - b^2)}$$

$$\Rightarrow P = \frac{2021.549\,\underline{v}^2 + 0.1635\,\underline{v} - 3.31\times10^{-6} - 0.6736\,\underline{v} + 2.724\times10^{-5}}{(\underline{v}-b)(\underline{v}^2 + 2b\underline{v} - b^2)}$$

$$\Rightarrow P\{\underline{v}^3 + 2b\underline{v}^2 - b^2 v - b\underline{v}^2 - 2b^2\underline{v} + b^3\}$$

$$= 2021.549\,\underline{v}^2 - 0.5101\,\underline{v} + 2.394\times10^{-5}$$

$$\Rightarrow 1.06\times10^{6}\,\underline{v}^3 + 42.877\,\underline{v}^2 - 5.20\times10^{-3}\,\underline{v} + 7.015\times10^{-8}$$

$$= 2021.549\,\underline{v}^2 - 0.5101\,\underline{v} + 2.394\times10^{-5}$$

$$\Rightarrow 1.06\times10^{6}\,\underline{v}^3 - 1978.672\,\underline{v}^2 + 0.5049\,\underline{v} - 2.387\times10^{-5} = 0$$

Using cubic equation solver,

$$\underline{v} = \begin{cases} 6.02e-5 \\ 0.00023 \\ 0.00157 \end{cases}$$

Among these three, the lowest value corresponds to the molar volume of saturated ethane liquid & highest value corresponds to molar volume of saturated ethane vapour.

$\therefore v^L = 6.02\times10^{-5}\ m^3/mol$ $\quad v^g = 0.00157\ m^3/mol$

M.W of ethane = 30 g/mol.

$$\rho^{liq} = \frac{1}{v^l} * M.W_{ethane} \left(\frac{g}{mol}\right) \cdot \left(\frac{mol}{m^3}\right)$$

$$= \frac{1}{6.02 \times 10^{-5}} \times 30 \frac{g}{m^3} \times \frac{1}{10^6} \frac{m^3}{cm^3}$$

$$= 0.498 \ g/cm^3$$

$$\rho^{vap} = \frac{M.W.ethane}{v_g}$$

$$= \frac{30}{0.00157} \times \frac{1}{10^6}$$

$$= 0.019 \ g/cm^3$$

→ The reported values are : $\rho^{Liq} = 0.468$ ~~and~~ g/cm^3

$\rho^{vap} = 0.0193 \ g/cm^3$

using Peng-Robinson equation ρ^{liq} value is 6.4% higher than the reported value, and ρ^{vap} value is ~ 1% lower than the reported value.

7. M.W. of Propane $= 44 \times 10^{-3} \ \frac{kg}{mol}$.

$\therefore$ No. of moles of propane present, $n = \frac{50}{44 \times 10^{-3}}$

$= 1136$ mol

ⓐ ideal gas law.

$$V = \frac{nRT}{P}$$

here, $T = 50^{\circ}C = 323.15$ K, $P = 35$ bar $= 35 \times 10^5$ Pa.

$$V = \frac{1136 \times 8.314 \times 323.15}{35 \times 10^5} = \boxed{0.872 \ m^3}$$

ⓑ Redlich Kwong EOS :-

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

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c}.$$

$$b = \frac{0.08664 RT_c}{P_c}$$

Critical properties of Propane:

$T_c = 370$ K ; $P_c = 42.44$ bar $= 42.44 \times 10^5$ Pa, $\omega = 0.152$.

Putting the values of T_c & P_c

$$a = 18.33 \ \frac{J \cdot m^3 K^{1/2}}{mol^2}$$

$$b = 6.28 \times 10^{-5} \ \frac{m^3}{mol}$$

Now, $\underline{V}$ is calculated using excel solver.

initially guessed value of $\underline{V} = 0.001$

After solving,

$$\underline{V} = 0.0001095 \ m^3/mol$$

$$\therefore V = (1136)(0.0001095) = \boxed{0.1244 \ m^3}$$

(c) Peng Robinson EOS:-

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

$$\alpha = \left[1 + K\left(1-\sqrt{T_r}\right)\right]^2 \qquad T_r = \frac{T}{T_c} = \frac{323.15}{370} = 0.8734$$

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

$$= 0.37464 + 1.54226(0.152) - 0.26992(0.152)^2$$

$$= 0.6028$$

$$\alpha = \left[1 + 0.6028\left(1 - \sqrt{0.8734}\right)\right]^2 = 1.081$$

$\therefore V_2 = 1200 - 111 \ldots$

$$a = \frac{0.45724\,(RT_c)^2}{P_c} = 1.02\ \frac{J.m^3}{mol}.$$

$$b = \frac{0.0778\,RT_c}{P_c} = 5.64\times10^{-5}\ \frac{m^3}{mol}.$$

After solving using excel-solver,

$$\underline{V} = 9.421\times10^{-5}\ m^3/mol.$$

$$\therefore\ V = 1136\ \underline{V} = 1136\times9.421\times10^{-5} = \boxed{0.107\ m^3}$$

(d) Compressibility chart

$$P_r = \frac{P}{P_c} = \frac{35\times10^5}{42.44\times10^5} = 0.8247, \qquad T_r = 0.8734$$

From compressibility chart at $P_r \approx 0.8247$ and $T_r \approx 0.875$;

$$Z \cong 0.13$$

$$\therefore\ V = \frac{Z.nRT}{P} = \frac{0.13\times1136\times8.314\times323.15}{35\times10^5}$$

$$= \boxed{0.113\ m^3}$$