Homework #2 Key

①

Conversions:
760 torr = 1 atm
$1000\ \text{cm}^3 = 1\ \text{L}$

$T = 298\ \text{K}$

$P = 10^{-12}\ \text{torr} \rightarrow 1.3158 \times 10^{-15}\ \text{atm}$

$V = 1.00\ \text{cm}^3 \rightarrow 1 \times 10^{-3}\ \text{L}$

Assume ideal gas ($\downarrow P$)...

$$P\bar{V} = RT$$

$$\bar{V} = \frac{(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K}) \cdot 298\ \text{K}}{1.3158\times10^{-15}\ \text{atm}} = \boxed{1.858\times10^{16}\ \text{L/mol}}$$

$$\left((1.1858\times10^{16})^{-1}\ \text{mol/L}\right) * (1\times10^{-3}\ \text{L}) * \left(6.022\times10^{23}\ \frac{\text{molecules}}{\text{mole}}\right) = \boxed{3.24\times10^{4}\ \text{molecules}}$$

②

M, molar mass units = g/mol

$\bar{V} \Rightarrow \text{L/mol} \qquad \rho = \text{g/L} \quad \therefore \quad M = \bar{V}\rho \quad \text{or} \quad \bar{V} = M/\rho$

use virial expression...

$$\frac{P\bar{V}}{RT} = 1 + \frac{B_{2v}}{\bar{V}} \quad \text{or} \quad \frac{P}{RT}\cdot\frac{M}{\rho} = 1 + B_{2v}\,\rho/M$$

$$\boxed{\frac{P}{\rho} = \frac{RT}{M} + \frac{RTB_{2v}}{M^2}\cdot\rho}$$

$y = mx + b \leftarrow$ plot ρ on x axis
P/ρ on y axis

(see attached)

$b = \frac{RT}{M}, \ M = \frac{RT}{b}$

$b = 0.5656$
$m = -0.0049$

$$M = \frac{(0.08314\ \text{L}\cdot\text{bar/mol}\cdot\text{K})(300\ \text{K})}{0.5656\ \text{bar}\cdot\text{L/g}} = \boxed{44.1\ \text{g/mol}}$$

$ID_{\text{unknown}} = CO_2$

$\frac{RTB_{2v}}{M^2} = m$

use R in bar!

$B_{2v} = mM^2/RT$
$= -0.38\ \text{L/mol}$

③ Propane @ 400 K , $\rho = 10.62\ \mathrm{mol/dm^3}$ $\left[\bar{V} = 0.094162\ \frac{\mathrm{dm^3}}{\mathrm{mol}}\right]$

$R = 0.0831451\ \frac{\mathrm{dm^3 \cdot bar}}{\mathrm{K \cdot mol}}$

a) $P\bar{V} = RT$, $P = \frac{RT}{\bar{V}} = \boxed{353.2\ \mathrm{bar}}$, 11.7% error

b) $a = 9.3919\ \frac{\mathrm{dm^6 \cdot bar}}{\mathrm{mol^2}}$, $b = 0.090494\ \mathrm{dm^3/mol}$

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} = \boxed{8008\ \mathrm{bar}},$$ 1901% error

c) $A = 183.02\ \frac{\mathrm{dm^6 \cdot bar}}{\mathrm{mol^2\ K^{1/2}}}$ $B = 0.062723\ \mathrm{dm^3/mol}$

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} = \boxed{438.4\ \mathrm{bar}},$$ 9.6% error

d) $\alpha = 9.6938\ \frac{\mathrm{L^2 \cdot bar}}{\mathrm{mol^2}}$ $\beta = 0.05632\ \mathrm{L/mol}$ $\mathrm{dm^3} = \mathrm{L}$

$$P = \frac{RT}{\bar{V} - \beta} - \frac{\alpha}{\bar{V}(\bar{V} + \beta) + \beta(\bar{V} - \beta)} = \boxed{284.19\ \mathrm{bar}},$$ 28.95% error

Redlich-Kwong equation gives best results

④ See attached Excel

⑤ $\bar{V} = \frac{RT}{P}$

$$\left(\frac{\partial \bar{V}}{\partial P}\right)_T = -\frac{RT}{P^2}$$

$$K = \frac{-1}{\bar{V}} \cdot \frac{-RT}{P^2} = \frac{P}{RT} \cdot \frac{RT}{P^2} = \frac{1}{P}$$

$$\boxed{K = \frac{1}{P}}$$

⑥

From Table 16.7

$\varepsilon / k_B = 118\ \text{K}$ per molecule

$\varepsilon = 118 k_B \cdot N_A$ per mole

$\varepsilon = 118\ \text{K} \cdot 1.38 \times 10^{-23}\ \text{J/K} \cdot 6.022 \times 10^{23}$ molecules/mole

$\varepsilon = 980\ \text{J/mol}$ or $0.980\ \text{kJ/mol}$

From Table 13.2

$D_0 = 493.6\ \text{kJ/mol}$

The energy to break the O_2 bond (and form two independent O atoms) is much greater than the energy to break the $O_2 \cdots O_2$ Vander Waals interaction (and form two independent O_2 molecules).