Q1: 1

$$F_6S \left\{ \begin{array}{l} T = 75°C = 348.15\,K \\ P = 15\,\text{bar} \\ T_c = 318.7\,K;\ \omega = 0.286 \\ P_c = 37.6\,\text{bar} \end{array} \right.$$

$$\left\{ \begin{array}{l} V: ? \\ Z: ? \end{array} \right.$$

(a) Virial EOS:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad (*)$$

$B = -194\ \text{cm}^3/\text{mol}$

$C = 15300\ \text{cm}^6/\text{mol}^2$

Solving for $\underline{V}$ (calculator, using an interative method) with the initial guess of (ideal gas equation)

$$V^{GUESS} = \frac{RT}{P} = 8.314\frac{J}{molK} \times 348.15K \times \frac{1}{15\,\text{bar}}$$

$$V^{GUESS} = 1929.68\ \text{cm}^3/\text{mol}$$

leads to (from $*$)

$$V = 1722.2698 \text{ cm}^3/\text{mol}$$

Now calculating Z,

$$Z = \frac{PV}{RT} = 0.8925$$

(b) RK EOS:

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}(V+b)V} \qquad (*')$$

with:

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \; ; \; b = 0.08664 \frac{RT_c}{P_c}$$

There are two ways to solve this problem:

(i) Calculating V from Eqn $(*')$ through an iterative method and then obtain $\underline{Z}$ or;

(ii) Using the general form of the cubic EOS to obtain $\underline{Z}$ and then calculate $\underline{V}$:

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)}$$

where: $P_r = 0.3989$; $\Omega = 0.08664$
$T_r = 1.0924$; $\Psi = 0.42748$

$$\alpha = T_r^{-1/2} = 0.9568$$

$$\beta = \Omega \frac{P_r}{T_r} = 3.1637 \times 10^{-2}$$

$$q = \frac{\Psi \alpha}{\Omega T_r} = 4.3215$$

$$\varepsilon = 0 \quad ; \quad \sigma = 1$$

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{Z(Z + \beta)}$$

Using $Z^{GUESS} = 1$

$$Z = 0.8883 \implies V = \frac{ZRT}{P} = 1714.1342 \, \frac{cm^3}{mol}$$

(c) SRK EOS:

Using the same procedure as in (b) with

$P_r = 0.3989$; $\Omega = 0.08664$

$T_r = 1.0924$; $\Psi = 0.42748$

$\alpha = 0.9191$; $\beta = 3.1637 \times 10^{-2}$

Using $Z^{GUESS} = 1$

$q = 4.1512$; $\sigma = 1$; $\varepsilon = 0$

$Z = 0.8949 \Rightarrow V = 1726.8701 \ cm^3/mol$

(d) PR EOS:

Using the same procedure as in (b) with

$P_r = 0.3989$; $\Omega = 0.07780$

$T_r = 1.0924$; $\Psi = 0.45724$

$\alpha = 0.9296$; $\beta = 0.02841$

Using $Z^{GUESS} = 1$

$q = 5.0013$; $\sigma = 1+\sqrt{2}$; $\varepsilon = 1-\sqrt{2}$

$Z = 0.8818 \Rightarrow V = 1701.5913 \ cm^3/mol$

In summary:

F_6S $\left\{ \begin{array}{l} 348.15\,K \\ 15\ bar \end{array} \right.$

	Z	V (cm³/mol)
Virial	0.8925	1722.27
RK	0.8883	1714.13
SRK	0.8949	1726.87
PR	0.8818	1701.59

Q2: N_2 (gas) $\left\{ \begin{array}{l} 175\,K \\ V = 3.75 \times 10^{-3}\ m^3/kg \end{array} \right.$

MW = 28 g/mol

P: ? $P^{exp} = 10^4\ kPa$

(a) Ideal gas EOS

transforming from specific volume to molar volume

$$P = \frac{RT}{V} = 8.314 \frac{J}{\cancel{mol.K}} \times 175 \cancel{K} \times \frac{\cancel{kg}}{3.75 \times 10^{-3} m^3} \times \frac{1000 \cancel{g}}{1 \cancel{kg}} \times \frac{\cancel{mol}}{28 \cancel{g}} \times \frac{1\ N.m}{1 \cancel{J}}$$

[Pa = N/m²]

$P = 1.3857 \times 10^7$ Pa

The error

$$\varepsilon = \frac{|P - P^{exp}|}{P^{exp}} \times 100 = \frac{|1.3857 \times 10^7 - 10^7|}{10^7} \times 100$$

$\varepsilon = 38.57\%$

(b) vdW ($T_c = 126.2\,K$; $P_c = 34$ bar)

$\alpha = 1$; $\Omega = 1/8$; $\Psi = 27/64$

$\varepsilon = 0$; $\sigma = 0$; $T_r = 1.3867$

$P_r = P/P_c \therefore P$?

↳ Thus we <u>can not</u> use the general form of the cubic EOS, thus

$$a = \frac{27}{64}\frac{R^2 T_c^2}{P_c} = \frac{27}{64}\left[8.134\frac{\cancel{J}}{mol.\cancel{K}} \times 126.2\cancel{K} \times \frac{1\,\cancel{Pa}.m^3}{1\cancel{J}}\right]^2 \times \frac{1}{34\,\cancel{bar}} \times \frac{1\,\cancel{bar}}{10^5\,\cancel{Pa}}$$

$[m^6.Pa/Kg^2]$

$$1J \times \frac{1\,Kg\,m^2/s^2}{1J} \times \frac{1\,Pa}{1\,Kg/(m\,s^2)} = \frac{1\,Pa.m^3}{1J}$$

$$1J = 1\,Pa.m^3$$

$$a = 0.1366\,\frac{m^6.Pa}{\cancel{mol}^2} \times \left[\frac{1\,\cancel{mol}}{28\cancel{g}} \times \frac{1000\cancel{g}}{1Kg}\right]^2$$

$$a = 174.2347\,\frac{m^6.Pa}{Kg^2}$$

$$b = \frac{RT_c}{8P_c} = 8.314\frac{\cancel{J}}{\cancel{mol}.\cancel{K}} \times 126.2\cancel{K} \times \frac{1}{8} \times \frac{1}{34\,\cancel{bar}} \times \frac{1\,\cancel{bar}}{10^5\,\cancel{Pa}} \times \frac{1\,\cancel{Pa}.m^3}{1\cancel{J}} \times \frac{1\,\cancel{mol}}{28\cancel{g}} \times \frac{1000\cancel{g}}{1Kg}$$

$[m^3/Kg]$

$$b = 1.3777\times10^{-3}\,m^3/Kg$$

Replacing in

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

$[Pa]$

$$P = \left[8.314 \frac{\cancel{J}}{\cancel{mol}\cdot\cancel{K}} \times 175\cancel{K} \times \frac{1 Pa.m^3}{1\cancel{J}} \times \frac{1\cancel{mol}}{28\cancel{g}} \times \frac{1000\cancel{g}}{1 Kg} \right] \times$$

$$\left[3.75\times10^{-3} \frac{m^3}{Kg} - 1.3777\times10^{-3} \frac{m^3}{Kg} \right]^{-1} +$$

$$- \left[174.2347 \frac{m^6 Pa}{Kg^2} \right] \left[3.75\times10^{-3} m^3/Kg \right]^{-2}$$

$$P = 9.5138\times10^{6}\ Pa$$

$$\mathcal{E} = \frac{|9.5138\times10^{6} - 10^{7}|}{10^{7}} \times 100 = 4.86\%$$

Q3 : $V = 0.0283\ m^3$
$T = 0°C$ (const)
$P_1 = 1\ atm$; $P_2 = 3000\ atm$
$\kappa = 3.9\times10^{-6} - 0.1\times10^{-9}P$ [P]: atm; [κ]: atm^{-1}

} Hg

Assuming that the volume of liquid mercury remains constant during the compression,

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

with

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \therefore dV = -\kappa V\,dP$$

replacing in the expression for work,

$$W = -\int P\Big[-\underbrace{(a+bP)}_{\kappa}V\Big]dP$$

$a = 3.9\times10^{-6}\ atm^{-1}$
$b = -0.1\times10^{-9}\ atm^{-2}$

$$W = V\left[\int aP\,dP + \int bP^2\,dP\right] = V\left[\frac{aP^2}{2}\Bigg|_{P_1}^{P_2} + \frac{bP^3}{3}\Bigg|_{P_1}^{P_2}\right]$$

constant

$$W = 0.4712\ m^3.atm = 47.7438\ kJ$$

Q4: Liquid water $\quad T_1 = 25°C \quad P_1 = 1\,bar$

$T_2 = 50°C$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = 36.2 \times 10^{-5}\,K^{-1}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = 4.42 \times 10^{-5}\,bar^{-1}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\frac{dV}{V} = \beta\, dT - \kappa\, dP$$

Assuming β & κ are constant during the process, we can easily integrate this equation

$$\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

The vessel is rigid $\rightarrow$ V constant $(V_2 = V_1)$

$$P_2 = \frac{\beta(T_2 - T_1)}{\kappa} + P_1 = 205.75\,bar$$