THERMODYNAMICS AND MOLECULAR PHYSICS

2.1 EQUATION OF THE GAS STATE • PROCESSES

2.1 Let m_1 and m_2 be the masses of the gas in the vessel before and after the gas is released. Hence mass of the gas released,

$$\Delta m = m_1 - m_2$$

Now from ideal gas equation

$$p_1 V = m_1 \frac{R}{M} T_0 \text{ and } p_2 V = m_2 \frac{R}{M} T_0$$

as V and T are same before and after the release of the gas.

so,
$$(p_1 - p_2) V = (m_1 - m_2) \frac{R}{M} T_0 = \Delta m \frac{R}{M} T_0$$

or,
$$\Delta m = \frac{(p_1 - p_2) V M}{R T_0} = \frac{\Delta p V M}{R T_0} \tag{1}$$

We also know $p = \rho \dfrac{R}{M} T$ so, $\dfrac{M}{R T_0} = \dfrac{\rho}{p_0}$ $\tag{2}$

(where $p_0 = $ standard atmospheric pressure and $T_0 = 273$ K)

From Eqs. (1) and (2) we get

$$\Delta m = \rho V \frac{\Delta p}{p_0} = 1 \cdot 3 \times 30 \times \frac{0 \cdot 78}{1} = 30 \text{ g}$$

2.2 Let m_1 be the mass of the gas enclosed.

Then,
$$p_1 V = \nu_1 R T_1$$

When heated, some gas, passes into the evacuated vessel till pressure difference becomes Δp. Let p'_1 and p'_2 be the pressure on the two sides of the valve. Then $p'_1 V = \nu'_1 R T_2$ and

$$p'_2 V = \nu'_2 R T_2 = (\nu_1 - \nu'_1) R T_2$$

$$p'_2 V = \left(\frac{p_1 V}{R T_1} - \frac{p'_1 V}{R T_2}\right) \quad \text{or} \quad p'_2 = \left(\frac{p_1}{T_1} - \frac{p'_1}{T_2}\right) T_2$$

But,
$$p'_1 - p'_2 = \Delta p$$

So,
$$p'_2 = \left(\frac{p_1}{T_1} - \frac{p'_2 + \Delta p}{T_2}\right) T_2$$

$$= \frac{p_1 T_2}{T_1} - p'_2 - \Delta p$$

or,
$$p_2' = \frac{1}{2}\left(\frac{p_1 T_2}{T_1} - \Delta p\right) = 0.08 \text{ atm}$$

2.3 Let the mixture contain ν_1 and ν_2 moles of H_2 and H_e respectively. If molecular weights of H_2 and H_e are M_1 and M_2, then respective masses in the mixture are equal to

$$m_1 = \nu_1 M_1 \quad \text{and} \quad m_2 = \nu_2 M_2$$

Therefore, for the total mass of the mixture we get,

$$m = m_1 + m_2 \quad \text{or} \quad m = \nu_1 M_1 + \nu_2 M_2 \tag{1}$$

Also, if ν is the total number of moles of the mixture in the vessels, then we know,

$$\nu = \nu_1 + \nu_2 \tag{2}$$

Solving (1) and (2) for ν_1 and ν_2, we get,

$$\nu_1 = \frac{(\nu M_2 - m)}{M_2 - M_1}, \qquad \nu_2 = \frac{m - \nu M_1}{M_2 - M_1}$$

Therefore, we get $m_1 = M_1 \cdot \dfrac{(\nu M_2 - m)}{M_2 - M_1}$ and $m_2 = M_2 \dfrac{(m - \nu M_1)}{M_2 - M_1}$

or,
$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \frac{(\nu M_2 - m)}{(m - \nu M_1)}$$

One can also express the above result in terms of the effective molecular weight M of the mixture, defined as,

$$M = \frac{m}{\nu} = m \frac{R T}{p V}$$

Thus,
$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \cdot \frac{M_2 - M}{M - M_1} = \frac{1 - M/M_2}{M/M_1 - 1}$$

Using the data and table, we get :

$$M = 3.0 \text{ g and, } \frac{m_1}{m_2} = 0.50$$

2.4 We know, for the mixture, N_2 and CO_2 (being regarded as ideal gases, their mixture too behaves like an ideal gas)

$$pV = vRT, \quad \text{so} \quad p_0 V = vRT$$

where, v is the total number of moles of the gases (mixture) present and V is the volume of the vessel. If v_1 and v_2 are number of moles of N_2 and CO_2 respectively present in the mixture, then

$$v = v_1 + v_2$$

Now number of moles of N_2 and CO_2 is, by definition, given by

$$v_1 = \frac{m_1}{M_1} \quad \text{and,} \quad v_2 = \frac{m_2}{M_2}$$

where, m_1 is the mass of N_2 (Moleculer weight $= M_1$) in the mixture and m_2 is the mass of CO_2 (Molecular weight $= M_2$) in the mixture.

Therefore density of the mixture is given by

$$\rho = \frac{m_1 + m_2}{V} = \frac{m_1 + m_2}{(vRT/P_0)}$$

$$= \frac{p_0}{RT} \cdot \frac{m_1 + m_2}{v_1 + v_2} = \frac{p_0 (m_1 + m_2) M_1 M_2}{RT (m_1 M_2 + m_2 M_1)}$$

$$= 1 \cdot 5 \text{ kg/m}^3 \text{ on substitution}$$

2.5 (a) The mixture contains v_1, v_2 and v_3 moles of O_2, N_2 and CO_2 respectively. Then the total number of moles of the mixture

$$v = v_1 + v_2 + v_3$$

We know, ideal gas equation for the mixture

$$pV = vRT \quad \text{or} \quad p = \frac{vRT}{V}$$

or,
$$p = \frac{(v_1 + v_2 + v_3) RT}{V} = 1 \cdot 968 \text{ atm on substitution}$$

(b) Mass of oxygen (O_2) present in the mixture : $m_1 = v_1 M_1$

Mass of nitrogen (N_2) present in the mixture : $m_2 = v_2 M_2$

Mass of carbon dioxide (CO_2) present in the mixture : $m_3 = v_3 M_3$

So, mass of the mixture

$$m = m_1 + m_2 + m_3 = v_1 M_1 + v_2 M_2 + v_3 M_3$$

Moleculer mass of the mixture : $M = \dfrac{\text{mass of the mixture}}{\text{total number of moles}}$

$$= \frac{v_1 M_1 + v_2 M_2 + v_3 M_3}{v_1 + v_2 + v_3} = 36 \cdot 7 \text{ g/mol. on substitution}$$

2.6 Let p_1 and p_2 be the pressure in the upper and lower part of the cylinder respectively at temperature T_0. At the equilibrium position for the piston :

$$p_1 S + mg = p_2 S \quad \text{or,} \quad p_1 + \frac{mg}{S} = p_2 \ (m \text{ is the mass of the piston.})$$

But $p_1 = \dfrac{R T_0}{\eta V_0}$ (where V_0 is the initial volume of the lower part)

So, $$\frac{RT_o}{\eta V_0} + \frac{mg}{S} = \frac{RT_0}{V_0} \quad \text{or,} \quad \frac{mg}{S} = \frac{RT_0}{V_0}\left(1 - \frac{1}{\eta}\right) \tag{1}$$

Let T be the sought temperature and at this temperature the volume of the lower part becomes V', then according to the problem the volume of the upper part becomes $\eta' V'$

Hence, $$\frac{mg}{S} = \frac{RT}{V'}\left(1 - \frac{1}{\eta'}\right) \tag{2}$$

From (1) and (2).

$$\frac{RT_0}{V_0}\left(1 - \frac{1}{\eta}\right) = \frac{RT}{V'}\left(1 - \frac{1}{\eta'}\right) \quad \text{or,} \quad T = \frac{T_0\left(1 - \dfrac{1}{\eta}\right) V'}{V_0\left(1 - \dfrac{1}{\eta'}\right)}$$

As, the total volume must be constant,

$$V_0(1 + \eta) = V'(1 + \eta') \quad \text{or,} \quad V' = \frac{V_0(1 + \eta)}{(1 + \eta')}$$

Putting the value of V' in Eq. (3), we get

$$T = \frac{T_0\left(1 - \dfrac{1}{\eta}\right) V_0 \dfrac{(1 + \eta)}{(1 + \eta')}}{V_0\left(1 - \dfrac{1}{\eta'}\right)}$$

$$= \frac{T_0(\eta^2 - 1)\eta'}{(\eta'^2 - 1)\eta} = 0.42 \text{ k K}$$

2.7 Let ρ_1 be the density after the first stroke. The the mass remains constant

$$V\rho = (V + \Delta V)\rho_1, \quad \text{or,} \quad \rho_1 = \frac{V\rho}{(V + \Delta V)}$$

Similarly, if ρ_2 is the density after second stroke

$$V\rho_1 = (V + \Delta V)\rho_2 \quad \text{or,} \quad \rho_2 = \left(\frac{V}{V + \Delta V}\right)\rho_1 = \left(\frac{V}{V + \Delta V}\right)^2 \rho_0$$

In this way after nth stroke.

$$\rho_n = \left(\frac{V}{V + \Delta V}\right)^n \rho_0$$

Since pressure α density,

$$p_n = \left(\frac{V}{V + \Delta V}\right)^n p_0 \quad \text{(because temperature is constant.)}$$

It is required by $\dfrac{p_n}{p_0}$ to be $\dfrac{1}{\eta}$

so, $$\frac{1}{\eta} = \left(\frac{V}{V + \Delta V}\right)^n \quad \text{or,} \quad \eta = \left(\frac{V + \Delta V}{V}\right)^n$$

Hence $$n = \frac{\ln \eta}{\ln\left(1 + \dfrac{\Delta V}{V}\right)}$$

2.8 From the ideal gas equation $p = \dfrac{m}{M}\dfrac{RT}{V}$

$$\frac{dp}{dt} = \frac{RT}{MV}\frac{dm}{dt} \tag{1}$$

In each stroke, volume v of the gas is ejected, where v is given by

$$v = \frac{V}{m_N}\left[m_{N-1} - m_N\right]$$

In case of continuous ejection, if (m_{N-1}) corresponds to mass of gas in the vessel at time t, then m_N is the mass at time $t + \Delta t$, where Δt, is the time in which volume v of the gas has come out. The rate of evacuation is therefore $\dfrac{v}{\Delta t}$ i.e.

$$C = \frac{v}{\Delta t} = -\frac{V}{m(t + \Delta t)} \cdot \frac{m(t + \Delta t) - m(t)}{\Delta t}$$

In the limit $\Delta t \to 0$, we get

$$C = \frac{V}{m}\frac{dm}{dt} \tag{2}$$

From (1) and (2)

$$\frac{dp}{dt} = -\frac{C}{V}\frac{mRT}{MV} = -\frac{C}{V}p \quad \text{or} \quad \frac{dp}{p} = -\frac{C}{V}dt$$

Integrating $$\int_{p}^{p_0} \frac{dp}{p} = -\frac{C}{V}\int_{t}^{0} dt \quad \text{or} \quad \ln\frac{p}{p_0} = -\frac{C}{V}t$$

Thus $$p = p_0 e^{-Ct/V}$$

2.9 Let ρ be the instantaneous density, then instantaneous mass $= V\rho$. In a short interval dt the volume is increased by $C dt$.

So, $$V\rho = (V + C dt)(\rho + d\rho)$$

(because mass remains constant in a short interval dt)

so,
$$\frac{d\rho}{\rho} = -\frac{C}{V} dt$$

Since pressure α density $\quad \frac{dp}{p} = -\frac{C}{V} dt$

or
$$\int_{p_1}^{p_2} -\frac{dp}{p} = \frac{C}{V} t,$$

or
$$t = \frac{V}{C} \ln \frac{p_1}{p_2} = \frac{V}{C} \ln \frac{1}{\eta} \cdot 1.0 \text{ min}$$

2.10 The physical system consists of one mole of gas confined in the smooth vertical tube. Let m_1 and m_2 be the masses of upper and lower pistons and S_1 and S_2 are their respective areas.

For the lower piston
$$p S_2 + m_2 g = p_0 S_2 + T,$$

or, $\quad T = (p - p_0) S_2 + m_2 g \qquad (1)$

Similarly for the upper piston
$$p_0 S_1 + T + m_1 g = p S_1,$$

or, $\quad T = (p - p_0) S_1 - m_1 g \qquad (2)$

From (1) and (2)
$$(p - p_0)(S_1 - S_2) = (m_1 + m_2) g$$
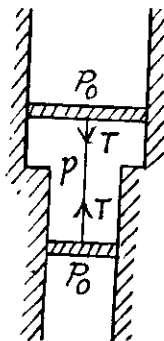
or, $\quad (p - p_0) \Delta S = mg$

so, $\quad p = \dfrac{mg}{\Delta S} + p_0 = \text{constant}$

From the gas law, $p V = \nu R T$
$$p \Delta V = \nu R \Delta T \text{ (because } p \text{ is constant)}$$

So,
$$\left(p_0 + \frac{mg}{\Delta S}\right) \Delta S \, l = R \Delta T,$$

Hence,
$$\Delta T = \frac{1}{R}(p_0 \Delta S + mg) l = 0.9 \text{ K}$$

2.11 (a) $p = p_0 - \alpha V^2 = p_0 - \alpha \left(\dfrac{RT}{p}\right)^2$

$\qquad\qquad$ (as, $V = RT/p$ for one mole of gas)

Thus, $\qquad T = \dfrac{1}{R\sqrt{\alpha}} p \sqrt{p_0 - p} = \dfrac{1}{R\sqrt{\alpha}} \sqrt{p_0 p^2 - p^3} \qquad (1)$

For T_{max}, $\quad \dfrac{d}{dp}\left(p_0 p^2 - p^3\right)$ must be zero

which yields,
$$p = \frac{2}{3} P_0 \qquad (2)$$

Hence, $T_{max} = \frac{1}{R\sqrt{\alpha}} \cdot \frac{2}{3} P_0 \sqrt{P_0 - \frac{2}{3} P_0} = \frac{2}{3} \left(\frac{P_0}{R}\right) \sqrt{\frac{P_0}{3\alpha}}$

(b) $p = P_0 e^{-\beta V} = P_0 e^{-\beta RT/p}$

so
$$\frac{\beta RT}{p} = \ln \frac{P_o}{p}, \quad \text{and } T = \frac{p}{\beta R} \ln \frac{P_0}{p} \qquad (1)$$

For T_{max} the condition is $\frac{dT}{dp} = 0$, which yields

$$p = \frac{P_0}{e}$$

Hence using this value of p in Eq. (1), we get

$$T_{max} = \frac{P_o}{e \beta R}$$

2.12 $T = T_0 + \alpha V^2 = T_0 + \alpha \frac{R^2 T^2}{p^2}$

(as, $V = RT/p$ for one mole of gas)

So,
$$p = \sqrt{\alpha} \, RT \, (T - T_0)^{1/2} \qquad (1)$$

For
$$P_{min}, \quad \frac{dp}{dT} = 0, \text{ which gives}$$

$$T = 2 T_0 \qquad (2)$$

From (1) and (2), we get,
$$P_{min} = \sqrt{\alpha} \, R \, 2T_0 \, (2T_0 - T_0)^{-1/2} = 2 R \sqrt{\alpha T_0}$$

2.13 Consider a thin layer at a height h and thickness dh. Let p and $dp + p$ be the pressure on the two sides of the layer. The mass of the layer is $Sdh\rho$. Equating vertical downward force to the upward force acting on the layer.
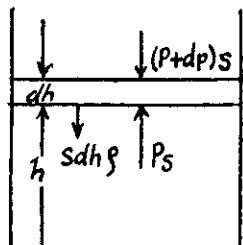
$$Sdh \, \rho \, g + (p + dp) \, S = p \, S$$

So, $\frac{dp}{dh} = -\rho g \qquad (1)$

But, $p = \frac{\rho}{M} RT$, we have $dp = \frac{\rho R}{M} dT$,

or, $-\frac{\rho R}{M} dT = \rho g \, dh$

So, $\frac{dT}{dh} = -\frac{gM}{R} = -34 \text{ K/km}$

That means, temperature of air drops by 34°C at a height of 1 km above bottom.

2.14 We have, $\dfrac{dp}{dh} = -\rho g$ (See 2.13) $\qquad\qquad\qquad$ (1)

But, from $\qquad p = C\rho^n$ (where C is, a const) $\dfrac{dp}{d\rho} = Cn\,\rho^{n-1}$ $\qquad$ (2)

We have from gas low $\quad p = \rho\dfrac{R}{M}T,\;$ so using (2)

$$C\rho^n = \rho\frac{R}{M}\cdot T, \quad \text{or} \quad T = \frac{M}{R}C\rho^{n-1}$$

Thus, $\qquad\qquad\qquad \dfrac{dT}{d\rho} = \dfrac{M}{R}\cdot C\,(n-1)\,\rho^{n-2}$ $\qquad\qquad$ (3)

But, $\qquad\qquad\qquad \dfrac{dT}{dh} = \dfrac{dT}{d\rho}\cdot\dfrac{d\rho}{dp}\cdot\dfrac{dp}{dh}$

So, $\qquad \dfrac{dT}{dh} = \dfrac{M}{R}C\,(n-1)\,\rho^{n-2}\dfrac{1}{Cn\,\rho^{n-1}}\,(-\rho g) = \dfrac{-Mg\,(n-1)}{nR}$

2.15 We have, $dp = -\rho g\,dh$ and from gas law $\rho = \dfrac{M}{RT}p$ $\qquad\qquad$ (1)

Thus $\qquad\qquad\qquad \dfrac{dp}{p} = -\dfrac{Mg}{RT}dh$

Integrating, we get

or, $\qquad \displaystyle\int_{p_o}^{P}\frac{dp}{p} = -\frac{Mg}{RT}\int_{0}^{h}dh \quad \text{or,} \quad \ln\frac{p}{p_0} = -\frac{Mg}{RT}h,$

(where p_0 is the pressure at the surface of the Earth.)

$$p = p_0\,e^{-Mgh/RT}, \quad .$$

[Under standard condition, $p_0 = 1$ atm, $T = 273$ K

Pressure at a height of 5 atm $= 1\times e^{-28\times 9\cdot 81\times 5000/8314\times 273} = 0\cdot5$ atm.

Pressure in a mine at a depth of 5 km $= 1\times e^{-28\times 9\cdot 81\times (-5000)/8314\times 273} = 2$ atm.]

2.16 We have $dp = -\rho g\,dh$ but from gas law $p = \dfrac{\rho}{M}RT,$

Thus $\qquad\qquad\qquad dp = \dfrac{d\rho}{M}RT$ at const. temperature

So, $\qquad\qquad\qquad \dfrac{d\rho}{\rho} = \dfrac{gM}{RT}dh$

Integrating within limits $\displaystyle\int_{\rho_o}^{\rho}\frac{d\rho}{\rho} = \int_{0}^{h}\frac{gM}{RT}dh$

or,
$$\ln \frac{\rho}{\rho_0} = -\frac{gM}{RT} h$$

So, $\rho = \rho_0 e^{-Mgh/RT}$ and $h = -\frac{RT}{Mg} \ln \frac{\rho}{\rho_0}$

(a) Given $T = 273°K$, $\frac{\rho_0}{\rho} = e$

Thus
$$h = -\frac{RT}{Mg} \ln e^{-1} = 8 \text{ km}.$$

(b) $T = 273° K$ and

$$\frac{\rho_0 - \rho}{\rho_0} = 0.01 \text{ or } \frac{\rho}{\rho_0} = 0.99$$

Thus
$$h = -\frac{RT}{Mg} \ln \frac{\rho}{\rho_0} = 0.09 \text{ km on substitution}$$

2.17 From the Barometric formula, we have
$$p = p_0 e^{-Mgh/RT}$$

and from gas law
$$\rho = \frac{pM}{RT}$$

So, at constant temperature from these two Eqs.

$$\rho = \frac{Mp_0}{RT} e^{-Mgh/RT} = \rho_0 e^{-Mgh/RT} \tag{1}$$

Eq. (1) shows that density varies with height in the same manner as pressure. Let us consider the mass element of the gas contained in the column.

$$dm = \rho \,(Sdh) = \frac{Mp_0}{RT} e^{-Mgh/RT} Sdh$$

Hence the sought mass,

$$m = \frac{Mp_0 S}{RT} \int_0^h e^{-Mgh/RT} dh = \frac{p_0 S}{g} \left(1 - e^{-Mgh/RT}\right)$$

2.18 As the gravitational field is constant the centre of gravity and the centre of mass are same. The location of C.M.

$$h = \frac{\displaystyle\int_0^\infty h \, dm}{\displaystyle\int_0^\infty dm} = \frac{\displaystyle\int_0^\infty h \rho \, dh}{\displaystyle\int_0^\infty \rho \, dh}$$

But from Barometric formula and gas law $\rho = \rho_0 e^{-Mgh/RT}$

So,
$$h = \frac{\int_0^\alpha h\left(e^{-Mg\,h/RT}\right)dh}{\int_0^\alpha \left(e^{-Mg\,h/RT}\right)dh} = \frac{RT}{Mg}$$

2.19 (a) We know that the variation of pressure with height of a fluid is given by :
$$dp = -\rho\,g\,dh$$

But from gas law
$$p = \frac{\rho}{M}RT \quad \text{or,} \quad \rho = \frac{pM}{RT}$$

From these two Eqs.
$$dp = -\frac{p\,Mg}{RT}\,dh \qquad (1)$$

or,
$$\frac{dp}{p} = \frac{-M\,g\,dh}{R\,T_0\,(1-ah)}$$

Integrating,
$$\int_{P_0}^{P} \frac{dp}{p} = \frac{-Mg}{R\,T_0} \int_0^h \frac{dh}{(1-ah)}, \text{ we get}$$

$$\ln\frac{p}{P_0} = \ln(1-ah)^{Mg/aRT_0}$$

Hence,
$$p = p_0(1-ah)^{Mg/aRT_0}. \quad \text{Obviously } h < \frac{1}{a}$$

(b) Proceed up to Eq. (1) of part (a), and then put $T = T_0(1 + a\,h)$ and proceed further in the same fashion to get
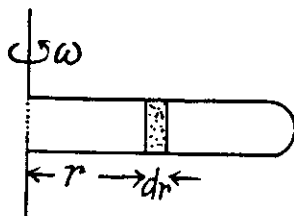$$p = \frac{p_0}{(1+ah)^{Mg/aRT_0}}$$

2.20 Let us consider the mass element of the gas (thin layer) in the cylinder at a distance r from its open end as shown in the figure.

Using Newton's second law for the element
$$F_n = mw_n:$$

$$(p + dp)\,S - pS = (\rho\,S\,dr)\,\omega^2\,r$$

or,
$$dp = \rho\,\omega^2\,r\,dr = \frac{pM}{RT}\,\omega^2\,r\,dr$$

So, $\quad \dfrac{dp}{p} = \dfrac{M\omega^2}{RT} r\, dr$ or, $\displaystyle\int_{p_0}^{p} \dfrac{dp}{p} = \dfrac{M\omega^2}{RT} \int_{0}^{r} r\, dr,$

Thus, $\quad \ln\dfrac{p}{p_0} = \dfrac{M\omega^2}{2RT} r^2$ or, $p = p_0\, e^{M\omega^2 r^2/2RT}$

2.21 For an ideal gas law

$$p = \dfrac{\rho}{M} RT$$

So, $\quad p = 0.082 \times 300 \times \dfrac{500}{44}$ atms $= 279.5$ atmosphere

For Vander Waal gas Eq.

$$\left(p + \dfrac{v^2 a}{V^2}\right)(V - vb) = vRT, \quad \text{where } V = vV_M$$

or, $\quad p = \dfrac{vRT}{V - vb} - \dfrac{av^2}{V^2} = \dfrac{mRT/M}{V - \dfrac{mb}{M}} - \dfrac{am^2}{V^2 M^2}$

$$= \dfrac{\rho RT}{M - \rho b} - \dfrac{a\rho^2}{M^2} = 79.2 \text{ atm}$$

2.22 (a) $p = \left[\dfrac{RT}{V_M - b} - \dfrac{a}{V_M^2}\right](1 + \eta) = \dfrac{RT}{V_M}$

(The pressure is less for a Vander Waal gas than for an ideal gas)

or, $\quad \dfrac{a(1+\eta)}{V_M^2} = RT\left[\dfrac{-1}{V_M} + \dfrac{1+\eta}{V_M - b}\right] = RT\dfrac{\eta V_M + b}{V_M(V_M - b)}$

or, $\quad T = \dfrac{a(1+\eta)(V_M - b)}{R V_M(\eta V_M + b)}$, (here V_M is the molar volume.)

$$= \dfrac{1.35 \times 1.1 \times (1 - 0.039)}{0.082 \times (0.139)} \approx 125 \text{ K}$$

(b) The corresponding pressure is

$$p = \dfrac{RT}{V_M - b} - \dfrac{a}{V_M^2} = \dfrac{a(1+\eta)}{V_M(\eta V_M + b)} - \dfrac{a}{V_M^2}$$

$$= \dfrac{a}{V_M^2} \dfrac{(V_M + \eta V_M - \eta V_M - b)}{(\eta V_M + b)} = \dfrac{a}{V_M^2} \dfrac{(V_M - b)}{(V_M + b)}$$

$$= \dfrac{1.35}{1} \times \dfrac{0.961}{0.139} \approx 9.3 \text{ atm}$$

2.23 $p_1 = RT_1 \dfrac{1}{V-b} - \dfrac{a}{V^2}$, $p_2 = R T_2 \dfrac{1}{V-b} - \dfrac{a}{V^2}$

So, $$p_2 - p_1 = \frac{R\,(T_2 - T_1)}{V - b}$$

or, $$V - b = \frac{R\,(T_2 - T_1)}{p_2 - p_1} \quad \text{or,} \quad b = V - \frac{R\,(T_2 - T_1)}{p_2 - p_1}$$

Also, $$p_1 = T_1 \frac{p_2 - p_1}{T_2 - T_1} - \frac{a}{V^2},$$

$$\frac{a}{V^2} = \frac{T_1\,(p_2 - p_1)}{T_2 - T_1} - p_1 = \frac{T_1 p_2 - p_1 T_2}{T_2 - T_1}$$

or, $$a = V^2 \frac{T_1 p_2 - p_1 T_2}{T_2 - T_1}$$

Using $T_1 = 300$ K, $p_1 = 90$ atms, $T_2 = 350$ K, $p_2 = 110$ atm, $V = 0.250$ litre

$$a = 1.87 \text{ atm. litre}^2/\text{mole}^2, \quad b = 0.045 \text{ litre/mole}$$

2.24 $p = \dfrac{R T}{V - b} - \dfrac{a}{V^2} - V\left(\dfrac{\partial p}{\partial V}\right)_T = \dfrac{R T V}{(V - b)^2} - \dfrac{2a}{V^2}$

or, $$\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$= \left[\frac{R T V^3 - 2a\,(V - b)^2}{V^2\,(V - b)^2}\right]^{-1} = \frac{V^2\,(V - b)}{\left[R T V^3 - 2a\,(V - b)^2\right]}$$

2.25 For an ideal gas $\kappa_0 = \dfrac{V}{RT}$

Now $\kappa = \dfrac{(V - b)^2}{RTV}\left\{1 - \dfrac{2a\,(V - b)^2}{RTV^3}\right\}^{-1} = \kappa_0\left(1 - \dfrac{b}{V}\right)^2\left\{1 - \dfrac{2a}{RTV}\left(1 - \dfrac{b}{V}\right)^2\right\}^{-1}$

$$= \kappa_0\left\{1 - \frac{2b}{V} + \frac{2a}{RTV}\right\}, \text{ to leading order in } a, b$$

Now $\kappa > \kappa_0$ if $\dfrac{2a}{RTV} > \dfrac{2b}{V}$ or $T < \dfrac{a}{bR}$

If a, b do not vary much with temperature, then the effect at high temperature is clearly determined by b and its effect is repulsive so compressibility is less.