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, $$\Delta m = \frac{(p_1 - p_2) VM}{R T_0} = \frac{\Delta p \, VM}{R T_0} \qquad (1)$$

We also know $p = \rho \frac{R}{M} T$ so, $\frac{M}{R T_0} = \frac{\rho}{p_0}$ $\qquad (2)$

(where $p_0 =$ standard atmospheric pressure and $T_0 = 273$ K)
From Eqs. (1) and (2) we get

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

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 v_1 and v_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

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

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

$$m = m_1 + m_2 \quad \text{or} \quad m = v_1 M_1 + v_2 M_2 \tag{1}$$

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

$$v = v_1 + v_2 \tag{2}$$

Solving (1) and (2) for v_1 and v_2, we get,

$$v_1 = \frac{(v M_2 - m)}{M_2 - M_1}, \quad v_2 = \frac{m - v M_1}{M_2 - M_1}$$

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

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

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

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

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 :

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

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)

$$pV = \nu R T, \quad \text{so} \quad p_0 V = \nu RT$$

where, ν is the total number of moles of the gases (mixture) present and V is the volume of the vessel. If ν_1 and ν_2 are number of moles of N_2 and CO_2 respectively present in the mixture, then

$$\nu = \nu_1 + \nu_2$$

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

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

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

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

$$= \frac{p_0}{RT} \cdot \frac{m_1 + m_2}{\nu_1 + \nu_2} = \frac{p_0 \, (m_1 + m_2) \, M_1 M_2}{RT \, (m_1 M_2 + m_2 M_1)}$$

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

2.5 (a) The mixture contains ν_1, ν_2 and ν_3 moles of O_2, N_2 and CO_2 respectively. Then the total number of moles of the mixture

$$\nu = \nu_1 + \nu_2 + \nu_3$$

We know, ideal gas equation for the mixture

$$pV = \nu R T \quad \text{or} \quad p = \frac{\nu R T}{V}$$

or, $$p = \frac{(\nu_1 + \nu_2 + \nu_3) \, RT}{V} = 1 \cdot 968 \text{ atm on substitution}$$

(b) Mass of oxygen (O_2) present in the mixture : $m_1 = \nu_1 M_1$

Mass of nitrogen (N_2) present in the mixture : $m_2 = \nu_2 M_2$

Mass of carbon dioxide (CO_2) present in the mixture : $m_3 = \nu_3 M_3$

So, mass of the mixture

$$m = m_1 + m_2 + m_3 = \nu_1 M_1 + \nu_2 M_2 + \nu_3 M_3$$

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

$$= \frac{\nu_1 M_1 + \nu_2 M_2 + \nu_3 M_3}{\nu_1 + \nu_2 + \nu_3} = 36 \cdot 7 \text{ g/mol. on substitution}$$

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 :

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

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

So, $\qquad \dfrac{RT_o}{\eta V_0} + \dfrac{mg}{S} = \dfrac{RT_0}{V_0} \quad \text{or,} \quad \dfrac{mg}{S} = \dfrac{RT_0}{V_0}\left(1 - \dfrac{1}{\eta}\right)$ $\qquad\qquad$ (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, $\qquad \dfrac{mg}{S} = \dfrac{RT}{V'}\left(1 - \dfrac{1}{\eta'}\right)$ $\qquad\qquad$ (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

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

$$= \frac{T_0(\eta^2 - 1)\eta'}{(\eta'^2 - 1)\eta} = 0{\cdot}42\,\text{k K}$$

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 $\Delta t - 0$, 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 $\displaystyle\int_p^{p_0} \frac{dp}{p} = -\frac{C}{V}\int_t^0 dt \quad \text{or} \quad \ln\frac{p}{p_0} = -\frac{C}{V}t$

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 Cdt.

So, $\qquad\qquad V\rho = (V + Cdt)(\rho + d\rho)$

(because mass remains constant in a short interval dt)

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

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

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

or
$$t = \frac{V}{C}\ln\frac{p_1}{p_2} = \frac{V}{C}\ln\frac{1}{\eta} \quad 1\cdot0 \text{ min}$$

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

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

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

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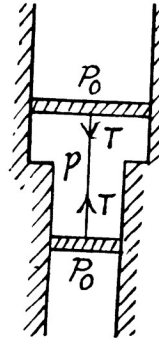
or, $\quad (p - p_0)\Delta S = mg$

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

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

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

Hence, $\quad \Delta T = \dfrac{1}{R}(p_0 \Delta S + mg)\, l = 0\cdot9 \text{ K}$

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

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

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

For T_{max}, $\quad \dfrac{d\left(p_0 p^2 - p^3\right)}{dp}$ 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 $$\frac{\beta RT}{p} = \ln \frac{p_o}{p}, \text{ and } T = \frac{p}{\beta R} \ln \frac{p_0}{p} \qquad (1)$$

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 $$p_{min}, \frac{dp}{dT} = 0, \text{ which gives}$$

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

From (1) and (2), we get,

$$p_{min} = \sqrt{\alpha} R 2T_0 (2T_0 - T_0)^{-1/2} = 2R \sqrt{\alpha T_0}$$

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.

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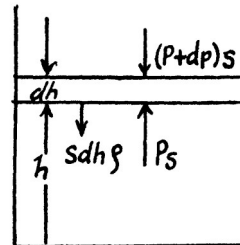
So, $$\frac{dp}{dh} = -\rho g \qquad (1)$$

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, $\frac{dp}{dh} = -\rho g$ (See 2.13)   (1)

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

We have from gas low $p = \rho\frac{R}{M}T$, 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, $\frac{dT}{d\rho} = \frac{M}{R}\cdot C\,(n-1)\,\rho^{n-2}$ (3)

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

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

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

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

Integrating, we get

or, $\int_{P_o}^{P}\frac{dp}{p} = -\frac{Mg}{RT}\int_{0}^{h}dh$ or, $\ln\frac{p}{p_0} = -\frac{Mg}{RT}h,$

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

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

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

Pressure at a height of 5 atm $= 1\times e^{-28\times9\cdot81\times5000/8314\times273} = 0\cdot5$ atm.

Pressure in a mine at a depth of 5 km $= 1\times e^{-28\times9\cdot81\times(-5000)/8314\times273} = 2$ atm.]

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

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

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

Integrating within limits $\int_{P_0}^{P}\frac{d\rho}{\rho} = \int_{0}^{h}\frac{gM}{RT}dh$

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

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

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.

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

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

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

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 $\qquad p = \dfrac{\rho}{M}RT \quad \text{or,} \quad \rho = \dfrac{pM}{RT}$

From these two Eqs.

$$dp = -\frac{pMg}{RT}\,dh \qquad (1)$$

or, $\qquad \dfrac{dp}{p} = \dfrac{-Mg\,dh}{RT_0(1-ah)}$

Integrating, $\qquad \displaystyle\int_{p_0}^{p}\frac{dp}{p} = \frac{-Mg}{RT_0}\int_0^h \frac{dh}{(1-ah)}, \text{ we get}$

$$\ln\frac{p}{p_0} = \ln(1-ah)^{Mg/aRT_0}$$

Hence, $\qquad p = p_0(1-ah)^{Mg/aRT_0}.$ Obvionsly $h < \dfrac{1}{a}$

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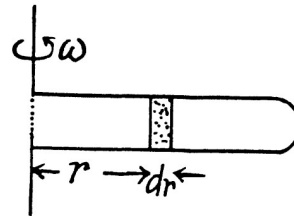
$$p = \frac{p_0}{(1+ah)^{Mg/aRT_0}}$$

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, $\qquad dp = \rho\,\omega^2 r \, dr = \dfrac{pM}{RT}\omega^2 r \, dr$

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

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

2.21 For an ideal gas law

$$p = \frac{\rho}{M} R T$$

So, $p = 0\cdot082 \times 300 \times \dfrac{500}{44}$ atms $= 279\cdot5$ atmosphere

For Vander Waal gas Eq.

$$\left(p + \frac{v^2 a}{\cdot\, V^2}\right)(V - v\, b) = v\, R\, T, \quad \text{where } V = v V_M$$

or, $p = \dfrac{v R T}{V - v b} - \dfrac{av^2}{V^2} = \dfrac{m R T/M}{V - \dfrac{mb}{M}} - \dfrac{am^2}{V^2 M^2}$

$$= \frac{\rho R T}{M - \rho b} - \frac{a\rho^2}{M^2} = 79\cdot2 \text{ atm}$$

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

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

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

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

$$= \frac{1\cdot35 \times 1\cdot1 \times (1 - 0\cdot039)}{0\cdot082 \times (0\cdot139)} \approx 125 \text{ K}$$

(b)   The corresponding pressure is

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

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

$$= \frac{1\cdot35}{1} \times \frac{0\cdot961}{0\cdot139} \approx 9\cdot3 \text{ atm}$$

2.23 $\quad p_1 = RT_1 \dfrac{1}{V-b} - \dfrac{a}{V^2}, \ p_2 = RT_2 \dfrac{1}{V-b} - \dfrac{a}{V^2}$

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

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

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

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

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

Using $\ T_1 = 300\,K, \ p_1 = 90\,atms, \ T_2 = 350\,K, \ p_2 = 110\,atm, \ V = 0{\cdot}250\ $ litre

$\qquad\qquad a = 1{\cdot}87\ atm.\ litre^2/mole^2, \ b = 0{\cdot}045\ litre/mole$

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

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

$\qquad\qquad = \left[\dfrac{RTV^3 - 2a(V-b)^2}{V^2(V-b)^2}\right]^{-1} = \dfrac{V^2(V-b)}{\left[RTV^3 - 2a(V-b)^2\right]}$

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

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

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

Now $\qquad\qquad \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.

2.2 THE FIRST LAW OF THERMODYNAMICS. HEAT CAPACITY

2.26 Internal energy of air, treating as an ideal gas

$$U = \frac{m}{M} C_V T = \frac{m}{M} \frac{R}{\gamma - 1} T = \frac{pV}{\gamma - 1} \tag{1}$$

Using $\quad C_V = \frac{R}{\gamma - 1}, \quad$ since $\quad C_p - C_V = R$ and $\frac{C_p}{C_V} = \gamma$

Thus at constant pressure $U =$ constant, because the volume of the room is a constant.

Puting the value of $p = p_{atm}$ and V in Eq. (1), we get $U = 10$ MJ.

2.27 From energy conservation

$$U_i + \frac{1}{2}(vM) v^2 = U_f$$

or, $$\Delta U = \frac{1}{2} vM v^2 \tag{1}$$

But from $U = v \frac{RT}{\gamma - 1}, \quad \Delta U = \frac{vR}{\gamma - 1} \Delta T$ (from the previous problem) $\tag{2}$

Hence from Eqs. (1) and (2).

$$\Delta T = \frac{Mv^2 (\gamma - 1)}{2R}$$

2.28 On opening the valve, the air will flow from the vessel at heigher pressure to the vessel at lower pressure till both vessels have the same air pressure. If this air pressure is p, the total volume of the air in the two vessels will be $(V_1 + V_2)$. Also if v_1 and v_2 be the number of moles of air initially in the two vessels, we have

$$p_1 V_1 = v_1 RT_1 \text{ and } p_2 V_2 = v_2 RT_2 \tag{1}$$

After the air is mixed up, the total number of moles are $(v_1 + v_2)$ and the mixture is at temperature T.

Hence $$p (V_1 + V_2) = (v_1 + v_2) RT \tag{2}$$

Let us look at the two portions of air as one single system. Since this system is contained in a thermally insulated vessel, no heat exchange is involved in the process. That is, total heat transfer for the combined system $Q = 0$

Moreover, this combined system does not perform mechanical work either. The walls of the containers are rigid and there are no pistons etc to be pushed, looking at the total system, we know $A = 0$.

Hence, internal energy of the combined system does not change in the process. Initially energy of the combined system is equal to the sum of internal energies of the two portions of air :

$$U_i = U_1 + U_2 = \frac{v_1 R T_1}{\gamma - 1} + \frac{v_2 R T_2}{\gamma - 1} \tag{3}$$

Final internal energy of $(n_1 + n_2)$ moles of air at temperature T is given by

$$U_f = \frac{(v_1 + v_2) RT}{\gamma - 1} \qquad (4)$$

Therefore, $U_i = U_f$ implies :

$$T = \frac{v_1 T_1 + v_2 T_2}{v_1 + v_2} = \frac{p_1 V_1 + p_2 V_2}{(p_1 V_1/T_1) + (p_2 V_2/T_2)} = T_1 T_2 \frac{p_1 V_1 + p_2 V_2}{p_1 V_1 T_2 + p_2 V_2 T_2}$$

From (2), therefore, final pressure is given by :

$$p = \frac{v_1 + v_2}{V_1 + V_2} RT = \frac{R}{V_1 + V_2} (v_1 T_1 + v_2 T_2) = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

This process in an example of free adiabatic expansion of ideal gas.

2.29 By the first law of thermodynamics,

$$Q = \Delta U + A$$

Here $A = 0$, as the volume remains constant,

So, $$Q = \Delta U = \frac{vR}{\gamma - 1} \Delta T$$

From gas law, $$p_0 V = v R T_0$$

So, $$\Delta U = \frac{p_0 V \Delta T}{T_0 (\gamma - 1)} = -0.25 \text{ kJ}$$

Hence amount of heat lost $= -\Delta U = 0.25$ kJ

2.30 By the first law of thermodynamics $Q = \Delta U + A$

But $$\Delta U = \frac{p \Delta V}{\gamma - 1} = \frac{A}{\gamma - 1} \text{ (as } p \text{ is constant)}$$

$$Q = \frac{A}{\gamma - 1} + A = \frac{\gamma \cdot A}{\gamma - 1} = \frac{1 \cdot 4}{1 \cdot 4 - 1} \times 2 = 7 \text{ J}$$

2.31 Under isobaric process $A = p\Delta V = R \Delta T$ (as $v = 1$) $= 0.6$ kJ

From the first law of thermodynamics

$$\Delta U = Q - A = Q - R \Delta T = 1 \text{ kJ}$$

Again increment in internal energy $\Delta U = \dfrac{R \Delta T}{\gamma - 1}$, for $v = 1$

Thus $$Q - R \Delta T = \frac{R \Delta T}{\gamma - 1} \text{ or } \gamma = \frac{Q}{Q - R \Delta T} = 1.6$$

2.32 Let $v = 2$ moles of the gas. In the first phase, under isochoric process, $A_1 = 0$, therefore from gas law if pressure is reduced n times so that temperature i.e. new temperature becomes T_0/n.

Now from first law of thermodynamics

$$Q_1 = \Delta U_1 = \frac{v R \Delta T}{\gamma - 1}$$

$$= \frac{\nu R}{\gamma - 1} \left(\frac{T_o}{n} - T_0 \right) = \frac{\nu RT_0 (1 - n)}{n (\gamma - 1)}$$

During the second phase (under isobaric process),

$$A_2 = p\Delta V = \nu R \Delta T$$

Thus from first law of thermodynamics :

$$Q_2 = \Delta U_2 + A_2 = \frac{\nu R \Delta T}{\gamma - 1} + \nu R \Delta T$$

$$= \frac{\nu R \left(T_0 - \frac{T_0}{n} \right) \gamma}{\gamma - 1} = \frac{\nu RT_0 (n - 1) \gamma}{n (\gamma - 1)}$$

Hence the total amount of heat absorbed

$$Q = Q_1 + Q_2 = \frac{\nu RT_0 (1 - n)}{n (\gamma - 1)} + \frac{\nu RT_0 (n - 1) \gamma}{n (\gamma - 1)}$$

$$= \frac{\nu RT_0 (n - 1) \gamma}{n (\gamma - 1)} (-1 + \gamma) = \nu RT_0 \left(1 - \frac{1}{n} \right)$$

2.33 Total no. of moles of the mixture $\nu = \nu_1 + \nu_2$

At a certain temperature, $U = U_1 + U_2$ or $\nu C_V = \nu_1 C_{V_1} + \nu_2 C_{V_2}$

Thus
$$C_V = \frac{\nu_1 C_{V_1} + \nu_2 C_{V_2}}{\nu} = \frac{\left(\nu_1 \frac{R}{\gamma_1 - 1} + \nu_2 \frac{R}{\gamma_2 - 1} \right)}{\nu}$$

Similarly
$$C_p = \frac{\nu_1 C_{P_1} + \nu_2 C_{P_2}}{\nu}$$

$$= \frac{\nu_1 \gamma_1 C_{V_1} + \nu_2 \gamma_2 C_{V_2}}{\nu} = \frac{\left(\nu_1 \frac{\gamma_1 R}{\gamma_1 - 1} + \nu_2 \frac{\gamma_2 R}{\gamma_2 - 1} \right)}{\nu}$$

Thus
$$\gamma = \frac{C_p}{C_V} = \frac{\nu_1 \frac{\gamma_1}{\gamma_1 - 1} R + \nu_2 \frac{\gamma_2}{\gamma_2 - 1} R}{\nu_1 \frac{R}{\gamma_1 - 1} + \nu_2 \frac{R}{\gamma_2 - 1}}$$

$$= \frac{\nu_1 \gamma_1 (\gamma_2 - 1) + \nu_2 \gamma_2 (\gamma_1 - 1)}{\nu_1 (\gamma_2 - 1) + \nu_2 (\gamma_1 - 1)}$$

2.34 From the previous problem

$$C_V = \frac{\nu_1 \frac{R}{\gamma_1 - 1} + \nu_2 \frac{R}{\gamma_2 - 1}}{\nu_1 + \nu_2} = 15 \cdot 2 \text{ J/mole. K}$$
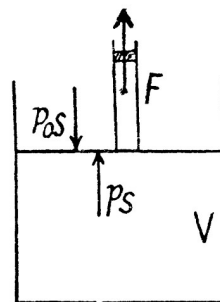
and $$C_p = \frac{v_1 \dfrac{\gamma_1 R}{\gamma_1 - 1} + v_2 \dfrac{\gamma_2 R}{\gamma_2 - 1}}{v_1 + v_2} = 23 \cdot 85 \text{ J/mole. K}$$

Now molar mass of the mixture $(M) = \dfrac{\text{Total mass}}{\text{Total number of moles}} = \dfrac{20 + 7}{\dfrac{1}{2} + \dfrac{1}{4}} = 36$

Hence $c_V = \dfrac{C_V}{M} = 0 \cdot 42 \text{ J/g} \cdot \text{K}$ and $c_p = \dfrac{C_p}{M} = 0 \cdot 66 \text{ J/g} \cdot \text{K}$

2.35 Let S be the area of the piston and F be the force exerted by the external agent. Then, $F + pS = p_0 S$ (Fig.) at an arbitrary instant of time. Here p is the pressure at the instant the volume is V. (Initially the pressure inside is p_0)

A (Work done by the agent)$= \displaystyle\int_{V_0}^{\eta V_0} F \, dx$

$$= \int_{V_0}^{\eta V_0} (p_0 - p) S \cdot dx = \int_{V_0}^{\eta V_0} (p_0 - p) \, dV$$

$$= p_0 (\eta - 1) V_0 - \int_{V_0}^{\eta V_0} p \, dV = p_0 (\eta - 1) V_0 - \int_{V_0}^{\eta V_0} vRT \cdot \frac{dV}{V}$$

$= (\eta - 1) p_0 V_0 - nRT \ln \eta = (\eta - 1) vRT - vRT \ln \eta$

$= vRT (\eta - 1 - \ln \eta) = RT (\eta - 1 - \ln \eta)$ (For $v = 1$ mole)

2.36 Let the agent move the piston to the right by x. In equilibirium position,

$$p_1 S + F_{agent} = p_2 S, \quad \text{or,} \quad F_{agent} = (p_2 - p_1) S$$

Work done by the agent in an infinitesmal change dx is

$$F_{agent} \cdot dx = (p_2 - p_1) S dx = (p_2 - p_1) \, dV$$

By applying $pV = $ constant, for the two parts,

$$p_1 (V_0 + Sx) = p_0 V_0 \quad \text{and} \quad p_2 (V_0 - Sx) = p_0 V_0$$

So, $$p_2 - p_1 = \frac{p_0 V_0 2Sx}{V_0^2 - S^2 x^2} = \frac{2p_0 V_0 V}{V_0^2 - V^2} \quad \text{(where } Sx = V)$$

When the volume of the left end is η times the volume of the right end

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

$$A = \int\limits_0^V (p_2 - p_1)\, dV = \int\limits_0^V \frac{2p_0 V_0 V}{V_0^2 - V^2}\, dV = -p_0 V_0 \left[\ln (V_0^2 - V^2)\right]_0^V$$

$$= -p_0 V_0 \left[\ln (V_0^2 - V^2) - \ln V_0^2\right]$$

$$= -p_0 V_0 \left[\ln \left\{ V_0^2 - \left(\frac{\eta - 1}{\eta + 1}^2\right) V_0^2 \right\} - \ln V_0^2 \right]$$

$$= -p_0 V_0 \left(\ln \frac{4\eta}{(\eta + 1)^2}\right) = p_0 V_0 \ln \frac{(\eta + 1)^2}{4\eta}$$

2.37 In the isothermal process, heat transfer to the gas is given by

$$Q_1 = v R T_0 \ln \frac{V_2}{V_1} = v R T_0 \ln \eta \quad \left(\text{For } \eta = \frac{V_2}{V_1} = \frac{p_1}{p_2}\right)$$

In the isochoric process, $A = 0$

Thus heat transfer to the gas is given by

$$Q_2 = \Delta U = v C_V \Delta T = \frac{vR}{\gamma - 1} \Delta T \quad \left(\text{for } C_V = \frac{R}{\gamma - 1}\right)$$

But $\dfrac{p_2}{p_1} = \dfrac{T_0}{T}$,   or, $T = T_0 \dfrac{p_1}{p_2} = \eta\, T_0 \quad \left(\text{for } \eta = \dfrac{p_1}{p_2}\right)$

or, $\Delta T = \eta\, T_0 - T_0 = (\eta - 1) T_0$,   so, $Q_2 = \dfrac{vR}{\gamma - 1} \cdot (\eta - 1) T_0$

Thus, net heat transfer to the gas

$$Q = v R T_0 \ln \eta + \frac{vR}{\gamma - 1} \cdot (\eta - 1) T_0$$

or, $\dfrac{Q}{vRT_0} = \ln \eta + \dfrac{\eta - 1}{\gamma - 1}$,   or, $\dfrac{Q}{vRT_0} - \ln \eta = \dfrac{\eta - 1}{\gamma - 1}$

or, $\gamma = 1 + \dfrac{\eta - 1}{\dfrac{Q}{vRT_0} - \ln \eta} = 1 + \dfrac{6 - 1}{\left(\dfrac{80 \times 10^3}{3 \times 8\cdot314 \times 273}\right) - \ln 6} = 1\cdot4$

2.38 (a) From ideal gas law $p = \left(\dfrac{vR}{V}\right) T = kT \quad \left(\text{where } k = \dfrac{vR}{V}\right)$

For isochoric process, obviously $k = $ constant, thus $p = kT$, represents a straight line passing through the origin and its slope becomes k.

For isobaric process $p = $ constant, thus on $p - T$ curve, it is a horizontal straight line parallel to T - axis, if T is along horizontal (or x - axis)

For isothermal process, $T = $ constant, thus on $p - T$ curve, it represents a vertical straight line if T is taken along horizontal (or x - axis)

For adiabatic process $T^\gamma p^{1-\gamma} = $ constant

After diffrentiating, we get $(1 - \gamma) p^{-\gamma}\, dp \cdot T^\gamma + \gamma p^{1-\gamma} \cdot T^{\gamma - 1} \cdot dT = 0$

$$\frac{dp}{dT} = \left(\frac{\gamma}{1-\gamma}\right)\left(\frac{p^{1-\gamma}}{p^{-\gamma}}\right)\left(\frac{T^{\gamma-1}}{T^{\gamma}}\right) = \left(\frac{\gamma}{\gamma-1}\right)\frac{p}{T}$$

The approximate plots of isochoric, isobaric, isothermal, and adiabatic processess are drawn in the answersheet.

(b) As p is not considered as variable, we have from ideal gas law

$$V = \frac{vR}{p}T = k'\,T\left(\text{where } k' = \frac{vR}{p}\right)$$

On $V - T$ co-ordinate system let us, take T along x - axis.

For isochoric process $V =$ constant, thus $k' =$ constant and $V = k'T$ obviously represents a straight line pasing through the origin of the co-ordinate system and k' is its slope.

For isothermal process $T =$ constant. Thus on the stated co- ordinate system it represents a straight line parallel to the $V -$ axis.

For adiabatic process $TV^{\gamma-1} =$ constant

After differentiating, we get $(\gamma - 1)\,V^{\gamma-2}\,dV\cdot T + V^{\gamma-1}\,dT = 0$

$$\frac{dV}{dT} = -\left(\frac{1}{\gamma-1}\right)\cdot\frac{V}{T}$$

The approximate plots of isochoric, isobaric, isothermal and adiabatic processess are drawn in the answer sheet.

2.39 According to $T - p$ relation in adiabatic process, $T^{\gamma} = kp^{\gamma-1}$ (where $k =$ constant)

and $\quad \left(\dfrac{T_2}{T_1}\right)^{\gamma} = \left(\dfrac{p_2}{p_1}\right)^{\gamma-1} \quad$ So, $\quad \dfrac{T^{\gamma}}{T_0^{\gamma}} = \eta^{\gamma-1}\left(\text{for } \eta = \dfrac{p_2}{p_1}\right)$

Hence $\quad T = T_0\cdot\eta^{\frac{\gamma-1}{\gamma}} = 290 \times 10^{(1.4-1)/1.4} = 0.56\,\text{kK}$

(b) Using the solution of part (a), sought work done

$$A = \frac{vR\,\Delta T}{\gamma-1} = \frac{vRT_0}{\gamma-1}\left(\eta^{(\gamma-1)/\gamma} - 1\right) = 5.61\,\text{kJ} \quad\text{(on substitution)}$$

2.40 Let (p_0, V_0, T_0) be the initial state of the gas.

We know $A_{adia} = \dfrac{-vR\Delta T}{\gamma-1}$ (work done by the gas)

But from the equation $TV^{\gamma-1} =$ constant, we get $\Delta T = T_0\left(\eta^{\gamma-1} - 1\right)$

Thus $\qquad A_{\text{adia}} = \dfrac{-vRT_0\left(\eta^{\gamma-1} - 1\right)}{\gamma-1}$

On the other hand, we know $A_{iso} = vRT_0\ln\left(\dfrac{1}{\eta}\right) = -vR\,T_0\ln\eta$ (work done by the gas)

Thus $\qquad \dfrac{A_{\text{adia}}}{A_{\text{iso}}} = \dfrac{\eta^{\gamma-1} - 1}{(\gamma-1)\ln\eta} = \dfrac{5^{0.4} - 1}{0.4 \times \ln 5} = 1.4$

2.41 Since here the piston is conducting and it is moved slowly the temperature on the two sides increases and maintained at the same value.

Elementary work done by the agent = Work done in compression - Work done in expansion i.e. $dA = p_2\,dV - p_1\,dV = (p_2 - p_1)\,dV$

where p_1 and p_2 are pressures at any instant of the gas on expansion and compression side respectively.

From the gas law $p_1(V_0 + Sx) = \nu RT$ and $p_2(V_0 - Sx) = \nu RT$, for each section

(x is the displacement of the piston towards section 2)

So, $\qquad p_2 - p_1 = \nu RT\dfrac{2Sx}{V_0^2 - S^2 x^2} = \nu RT \cdot \dfrac{2V}{V_0^2 - V^2}$ (as $Sx = V$)

So $\qquad\qquad\qquad dA = \nu RT\dfrac{2V}{V_0^2 - V^2}\,dV$

Also, from the first law of thermodynamics

$dA = -dU = -2\nu\dfrac{R}{\gamma - 1}\,dT$ (as $dQ = 0$)

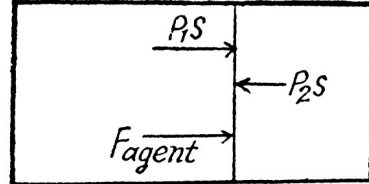So, work done on the gas $= -dA = 2\nu\cdot\dfrac{R}{\gamma - 1}\,dT$

Thus $2\nu\dfrac{R}{\gamma - 1}\,dT = \nu RT\dfrac{2V\cdot dV}{V_0^2 - V^2}$,

or, $\qquad \dfrac{dT}{T} = \gamma - 1\dfrac{V\,dV}{V_0^2 - V^2}$

When the left end is η times the volume of the right end.

$(V_0 + V) = \eta(V_0 - V)$ or $V = \dfrac{\eta - 1}{\eta + 1}V_0$

On integrating $\qquad \displaystyle\int_{T_0}^{T}\dfrac{dT}{T} = (\gamma - 1)\int_{0}^{V}\dfrac{V\,dV}{V_0^2 - V^2}$

or $\qquad \ln\dfrac{T}{T_0} = (\gamma - 1)\left[-\dfrac{1}{2}\ln(V_0^2 - V^2)\right]_0^V$

$\qquad = -\dfrac{\gamma - 1}{2}\left[\ln(V_0^2 - V^2) - \ln V_0^2 - V^2) - \ln V_0^2\right]$

$\qquad = \dfrac{\gamma - 1}{2}\left[\ln V_0^2 - \ln V_0^2\left\{1 - \left(\dfrac{\eta - 1}{\eta + 1}\right)^2\right\}\right] = \dfrac{\gamma - 1}{2}\ln\dfrac{(\eta + 1)^2}{4\eta}$

Hence $\qquad T = T_0\left(\dfrac{(\eta + 1)^2}{4\eta}\right)^{\frac{\gamma - 1}{2}}$

2.42 From energy conservation as in the derivation of Bernoullis theorem it reads

$$\frac{p}{\rho} + \frac{1}{2}v^2 + gz + u + Q_d = \text{constant} \qquad (1)$$

In the Eq. (1) u is the internal energy per unit mass and in this case is the thermal energy per unit mass of the gas. As the gas vessel is thermally insulated $Q_d = 0$, also in our case.

Just inside the vessel $u = \dfrac{C_V T}{M} = \dfrac{RT}{M(\gamma - 1)}$ also $\dfrac{p}{\rho} = \dfrac{RT}{M}$. Inside the vessel $v = 0$ also. Just outside $p = 0$, and $u = 0$. Ingeneral gz is not very significant for gases.

Thus applying Eq. (1) just inside and outside the hole, we get

$$\frac{1}{2}v^2 = \frac{p}{\rho} + u$$

$$= \frac{RT}{M} + \frac{RT}{M(\gamma - 1)} = \frac{\gamma RT}{M(\gamma - 1)}$$

Hence $\quad v^2 = \dfrac{2\gamma RT}{M(\gamma - 1)} \quad$ or, $\quad v = \sqrt{\dfrac{2\gamma RT}{M(\gamma - 1)}} = 3.22 \text{ km/s}.$

Note : The velocity here is the velocity of hydrodynamic flow of the gas into vaccum. This requires that the diameter of the hole is not too small ($D >$ mean free path l). In the opposite case ($D < < l$) the flow is called effusion. Then the above result does not apply and kinetic theory methods are needed.

2.43 The differential work done by the gas

$$dA = pdV = \frac{vRT^2}{a}\left(-\frac{a}{T^2}\right)dT = -vRdT$$

$$\left(\text{as } pV = vRT \text{ and } V = \frac{a}{T}\right)$$

So, $\qquad A = -\displaystyle\int_{T}^{T+\Delta T} vRdT = -vR\Delta T$

From the first law of thermodynamics

$$Q = \Delta U + A = \frac{vR}{\gamma - 1}\Delta T - vR\Delta T$$

$$= vR\Delta T \cdot \frac{2-\gamma}{\gamma - 1} = R\,\Delta T \cdot \frac{2-\gamma}{\gamma - 1} \quad \text{(for } v = 1 \text{ mole)}$$

2.44 According to the problem : $A \propto U$ or $dA = aU$ (where a is proportionality constant)

or, $\qquad pdV = \dfrac{a\,vR\,dT}{\gamma - 1} \qquad (1)$

From ideal gas law, $\quad pV = vRT$, on differentiating

$$pdV + Vdp = vRdT \qquad (2)$$

Thus from (1) and (2)

$$pdV = \frac{a}{\gamma - 1}(pdV + Vdp)$$

or, $pdV\left(\frac{a}{\gamma - 1} - 1\right) + \frac{a}{\gamma - 1}Vdp = 0$

or, $pdV(k - 1) + kVdp = 0$ (where $k = \frac{a}{\gamma - 1} =$ another constant)

or, $pdV\frac{k - 1}{k} + Vdp = 0$

or, $pdVn + Vdp = 0$ (where $\frac{k - 1}{k} = n =$ ratio)

Dividing both the sides by pV

$$n\frac{dV}{V} + \frac{dp}{p} = 0$$

On integrating $n \ln V + \ln p = \ln C$ (where C is constant)

or, $\ln (pV^n) = \ln C$ or, $pV^n = C$ (const.)

2.45 In the polytropic process work done by the gas

$$A = \frac{vR[T_i - T_f]}{n - 1}$$

(where T_i and T_f are initial and final temperature of the gas like in adiabatic process)

and $\Delta U = \frac{vR}{\gamma - 1}(T_f - T_i)$

By the first law of thermodynamics $Q = \Delta U + A$

$$= \frac{vR}{\gamma - 1}(T_f - T_i) + \frac{vR}{n - 1}(T_i - T_f)$$

$$= (T_f - T_i)vR\left[\frac{1}{\gamma - 1} - \frac{1}{n - 1}\right] = \frac{vR[n - \gamma]}{(n - 1)(\gamma - 1)}\Delta T$$

According to definition of molar heat capacity when number of moles $v = 1$ and $\Delta T = 1$ then $Q =$ Molar heat capacity.

Here, $C_n = \frac{R(n - \gamma)}{(n - 1)(\gamma - 1)} < 0$ for $1 < n < \gamma$

2.46 Let the process be polytropic according to the law $pV^n =$ constant

Thus, $p_f V_f^n = p_i V_i^n$ or, $\left(\frac{p_i}{p_f}\right) = \beta$

So, $\alpha^n = \beta$ or $\ln \beta = n \ln \alpha$ or $n = \frac{\ln \beta}{\ln \alpha}$

In the polytropic process molar heat capacity is given by

$$C_n = \frac{R\,(n-\gamma)}{(n-1)\,(\gamma-1)} = \frac{R}{\gamma-1} - \frac{R}{n-1}$$

$$= \frac{R}{\gamma-1} - \frac{R\ln\alpha}{\ln\beta - \ln\alpha}, \quad \text{where } n = \frac{\ln\beta}{\ln\alpha}$$

So, $$C_n = \frac{8\cdot314}{1\cdot66-1} - \frac{8\cdot314\ln 4}{\ln 8 - \ln 4} = -42\,\text{J/mol.K}$$

2.47 (a) Increment of internal energy for ΔT, becomes

$$\Delta U = \frac{\nu R \Delta T}{\gamma-1} = \frac{R\,\Delta T}{\gamma-1} = -324\,\text{J (as } \nu = 1 \text{ mole)}$$

From first law of thermodynamics

$$Q = \Delta U + A = \frac{R\,\Delta T}{\gamma-1} - \frac{R\Delta T}{n-1} = 0\cdot11\,\text{kJ}$$

(b) Sought work done, $A_n = \int p\,dV = \int_{V_i}^{V_f} \frac{k}{V^n}\,dV$

(where $pV^n = k = p_i V_i^n = p_f V_f^n$)

$$= \frac{k}{1-n}\left(V_f^{1-n} - V_i^{1-n}\right) = \frac{\left(p_f V_f^n V_f^{1-n} - p_i V_i^n V_i^{1-n}\right)}{1-n}$$

$$= \frac{p_f V_f - p_i V_i}{1-n} = \frac{\nu R\,(T_f - T_i)}{1-n}$$

$$= \frac{\nu R\Delta T}{n-1} = -\frac{R\Delta T}{n-1} = 0\cdot43\,\text{kJ (as } \nu = 1 \text{ mole)}$$

2.48 Law of the process is $p = \alpha V$ or $pV^{-1} = \alpha$

so the process is polytropic of index $n = -1$

As $p = \alpha V$ so, $p_i = \alpha V_0$ and $p_f = \alpha \eta V_0$

(a) Increment of the internal energy is given by

$$\Delta U = \frac{\nu R}{\gamma-1}[T_f - T_i] = \frac{p_f V_f - p_i V_i}{\gamma-1}$$

(b) Work done by the gas is given by

$$A = \frac{p_i V_i - p_f V_f}{n-1} = \frac{\alpha V_0^2 - \alpha\eta V_0 \cdot \eta V_0}{-1-1}$$

$$= \frac{\alpha V_0^2\,(1-\eta^2)}{-2} = \frac{1}{2}\alpha V_0^2(\eta^2 - 1)$$

(c) Molar heat capacity is given by

$$C_n = \frac{R\,(n-\gamma)}{(n-1)\,(\gamma-1)} = \frac{R\,(-1-\gamma)}{(-1-1)\,(\gamma-1)} = \frac{R}{2}\frac{\gamma+1}{\gamma-1}$$

2.49 (a) $\Delta U = \dfrac{\nu R}{\gamma - 1}\Delta T$ and $Q = \nu C_n \Delta T$

where C_n is the molar heat capacity in the process. It is given that $Q = -\Delta U$

So, $\qquad C_n \Delta T = \dfrac{R}{\gamma - 1}\Delta T$, or $C_n = -\dfrac{R}{\gamma - 1}$

(b) By the first law of thermodynamics, $dQ = dU + dA$,

or, $\qquad\qquad 2\,dQ = dA$ (as $dQ = -dU$)

$$2\nu C_n\,dT = p\,dV, \quad \text{or,} \quad \dfrac{2R\nu}{\gamma - 1}\,dT + p\,dV = 0$$

So, $\qquad \dfrac{2RV}{\gamma - 1}\,dT + \dfrac{\nu RT}{V}\,dV = 0$, or, $\dfrac{2}{(\gamma - 1)}\dfrac{dT}{T} + \dfrac{dV}{V} = 0$

or, $\qquad \dfrac{dT}{T} + \dfrac{\gamma - 1}{2}\dfrac{dV}{V} = 0$, or, $TV^{(\gamma - 1)/2} = $ constant.

(c) We know $C_n = \dfrac{(n - \gamma)R}{(n - 1)(\gamma - 1)}$

But from part (a), we have $C_n = -\dfrac{R}{\gamma - 1}$

Thus $\qquad -\dfrac{R}{\gamma - 1} = \dfrac{(n - \gamma)R}{(n - 1)(\gamma - 1)}$ which yields

$$n = \dfrac{1 + \gamma}{2}$$

From part (b); we know $TV^{(\gamma - 1)/2} = $ constant

So, $\qquad \dfrac{T_o}{T} = \left(\dfrac{V}{V_0}\right)^{(\gamma - 1)/2} = \eta^{(\gamma - 1)/2}$ (where T is the final temperature)

Work done by the gas for one mole is given by

$$A = R\dfrac{(T_0 - T)}{n - 1} = \dfrac{2RT_0[1 - \eta^{(1 - \gamma)/2}]}{\gamma - 1}$$

2.50 Given $p = aT^\alpha$ (for one mole of gas)

So, $\qquad\qquad pT^{-\alpha} = a$ or, $p\left(\dfrac{pV}{R}\right)^{-\alpha} = a$,

or, $\qquad\qquad p^{1 - \alpha}V^{-\alpha} = aR^{-\alpha}$ or, $pV^{\alpha/(\alpha - 1)} = $ constant

Here polytropic exponent $n = \dfrac{\alpha}{\alpha - 1}$

(a) In the polytropic process for one mole of gas :

$$A = \dfrac{R\Delta T}{1 - n} = \dfrac{R\Delta T}{\left(1 - \dfrac{\alpha}{\alpha - 1}\right)} = R\Delta T(1 - \alpha)$$

(b) Molar heat capacity is given by

$$C = \dfrac{R}{\gamma - 1} - \dfrac{R}{n - 1} = \dfrac{R}{\gamma - 1} - \dfrac{R}{\dfrac{\alpha}{\alpha - 1} - 1} = \dfrac{R}{\gamma - 1} + R(1 - \alpha)$$

2.51 Given $U = aV^{\alpha}$

or, $\qquad \nu C_V T = a V^{\alpha}$, or, $\nu C_V \dfrac{pV}{\nu R} = a V^{\alpha}$

or, $\qquad aV^{\alpha} \cdot \dfrac{R}{C_V} \cdot \dfrac{1}{pV} = 1$, or, $V^{\alpha-1} \cdot p^{-1} = \dfrac{C_V}{Ra}$

or $\qquad pV^{1-\alpha} = \dfrac{Ra}{C_V} = $ constant $= a\,(\gamma-1)\left[\text{as } C_V = \dfrac{R}{\gamma-1}\right]$

So polytropric index $n = 1 - \alpha$.

(a) Work done by the gas is given by

$$A = \frac{-\nu R\,\Delta T}{n-1} \text{ and } \Delta U = \frac{\nu R\Delta T}{\gamma-1}$$

Hence $\qquad A = \dfrac{-\Delta U\,(\gamma-1)}{n-1} = \dfrac{\Delta U\,(\gamma-1)}{\alpha}$ (as $n = 1 - \alpha$)

·By the first law of thermodynamics, $Q = \Delta U + A$

$$= \Delta U + \frac{\Delta U\,(\gamma-1)}{\alpha} = \Delta U\left[1 + \frac{\gamma-1}{\alpha}\right]$$

(b) Molar heat capacity is given by

$$C = \frac{R}{\gamma-1} - \frac{R}{n-1} = \frac{R}{\gamma-1} - \frac{R}{1-\alpha-1}$$

$$= \frac{R}{\gamma-1} + \frac{R}{\alpha} \text{ (as } n = 1 - \alpha)$$

2.52 (a) By the first law of thermodynamics

$$dQ = dU + dA = \nu C_V dT + pdV$$

Molar specific heat according to definition

$$C = \frac{dQ}{\nu dT} = \frac{C_V dT + pdV}{\nu dT}$$

$$= \frac{\nu C_V dT + \dfrac{\nu RT}{V} dV}{\nu dT} = C_V + \frac{RT}{V}\frac{dV}{dT},$$

We have $\qquad T = T_0 e^{\alpha V}$

After differentiating, we get $dT = \alpha T_0 e^{\alpha V} \cdot dV$

So, $\qquad \dfrac{dV}{DT} = \dfrac{1}{\alpha T_0 e^{\alpha V}}$,

Hence $\quad C = C_V + \dfrac{RT}{V} \cdot \dfrac{1}{\alpha T_0 e^{\alpha V}} = C_V + \dfrac{RT_0 e^{\alpha V}}{\alpha VT_0 e^{\alpha v}} = C_V + \dfrac{R}{\alpha V}$

(b) Process is $p = p_0 e^{\alpha V}$

$$p = \frac{RT}{V} = p_0 e^{\alpha V}$$

$$\text{or,} \quad T = \frac{p_0}{R} e^{\alpha V} \cdot V$$

$$\text{So,} \quad C = C_V + \frac{RT}{V} \frac{dV}{dT} = C_V + p_0 e^{\alpha V} \cdot \frac{R}{p_0 e^{\alpha V}(1 + \alpha V)} = C_V + \frac{R}{1 + \alpha V}$$

2.53 Using 2.52

(a) $\quad C = C_V + \frac{RT}{V} \frac{dV}{dT} = C_V + \frac{p\,dV}{dT}$ (for one mole of gas)

We have $p = p_0 + \frac{\alpha}{V}$, or, $\frac{RT}{V} = p_0 + \frac{\alpha}{V}$, or, $RT = p_0 V + \alpha$

Therefore $\qquad RdT = p_0\, dV$, So, $\frac{dV}{dT} = \frac{R}{p_0}$

Hence $\qquad C = C_V + \left(p_0 + \frac{\alpha}{V}\right) \cdot \frac{R}{p_0} = \frac{R}{\gamma - 1} + \left(1 + \frac{\alpha}{p_0 V}\right) R$

$$= \left(R + \frac{R}{\gamma - 1}\right) + \frac{\alpha R}{p_0 V} = \frac{\gamma R}{\gamma - 1} + \frac{\alpha R}{p_0 V}$$

(b) Work done is given by

$$A = \int_{V_1}^{V_2} \left(p_0 + \frac{\alpha}{V}\right) dV = p_0 (V_2 - V_1) + \alpha \ln \frac{V_2}{V_1}$$

$$\Delta U = C_V (T_2 - T_1) = C_V \left(\frac{p_2 V_2}{R} - \frac{p_1 V_1}{R}\right) \text{ (for one mole)}$$

$$= \frac{R}{(\gamma - 1) R} (p_2 V_2 - p_1 V_1)$$

$$= \frac{1}{\gamma - 1}\left[\left(p_0 + \alpha V_2\right) V_2 - \left(p_0 + \frac{\alpha}{V_1}\right) V_1\right] = \frac{p_0 (V_2 - V_1)}{\gamma - 1}$$

By the first law of thermodynamics $Q = \Delta U + A$

$$= p_0 (V_2 - V_1) + \alpha \ln \frac{V_2}{V_1} + \frac{p_0 (V_2 - V_1)}{(\gamma - 1)}$$

$$= \frac{\gamma p_0 (V_2 - V_1)}{\gamma - 1} + \alpha \ln \frac{V_2}{V_1}$$

2.54 (a) Heat capacity is given by

$$C = C_V + \frac{RT}{V} \frac{dV}{dT} \text{ (see solution of 2.52)}$$

We have $\qquad T = T_0 + \alpha V$ or, $V = \frac{T}{\alpha} - \frac{T_0}{\alpha}$

After differentiating, we get, $\frac{dV}{dT} = \frac{1}{\alpha}$

Hence $\quad C = C_V + \dfrac{RT}{V} \cdot \dfrac{1}{\alpha} = \dfrac{R}{\gamma - 1} + \dfrac{R\,(T_0 + \alpha\,V)}{V} \cdot \dfrac{1}{\alpha}$

$$= \dfrac{R}{\gamma - 1} + R\left(\dfrac{T_0}{\alpha V} + 1\right) = \dfrac{\gamma R}{\gamma - 1} + \dfrac{RT_0}{\alpha V} = C_V + \dfrac{RT}{\alpha V} = C_p + \dfrac{RT_0}{\alpha V}$$

(b) Given $T = T_0 + \alpha V$

As $T = \dfrac{pV}{R}$ for one mole of gas

$$p = \dfrac{R}{V}\,(T_0 + \alpha V) = \dfrac{RT}{V} = \alpha R$$

Now $\quad A = \displaystyle\int\limits_{V_1}^{V_2} p\,dV = \int\limits_{V_1}^{V_2} \left(\dfrac{RT_0}{V} + \alpha R\right) dV$ (for one mole)

$$= RT_0 \ln \dfrac{V_2}{V_1} + \alpha\,(V_2 - V_1)$$

$$\Delta U = C_V\,(T_2 - T_1)$$

$$= C_V[T_0 + \alpha\,V_2 - T_0\,\alpha\,V_1] = \alpha C_V\,(V_2 - V_1)$$

By the first law of thermodynamics $Q = \Delta U + A$

$$= \dfrac{\alpha R}{\gamma - 1}\,(V_2 - V_1) + RT_0 \ln \dfrac{V_2}{V_1} + \alpha R\,(V_2 - V_1)$$

$$= \alpha R\,(V_2 - V_1)\left[1 + \dfrac{1}{\gamma - 1}\right] + RT_0 \ln \dfrac{V_2}{V_1}$$

$$= \alpha C_p\,(V_2 - V_1 + RT_0 \ln \dfrac{V_2}{V_1}$$

$$= \alpha C_p\,(V_2 - V_1) + RT_0 \ln \dfrac{V_2}{V_1}$$

2.55 Heat capacity is given by $C = C_V + \dfrac{RT}{V}\dfrac{dV}{dT}$

(a) Given $C = C_V + \alpha T$

So, $\quad C_V + \alpha T = C_V + \dfrac{RT}{V}\dfrac{dV}{dT}$ or, $\quad \dfrac{\alpha}{R} dT = \dfrac{dV}{V}$

Integrating both sides, we get $\dfrac{\alpha}{R} T = \ln V + \ln C_0 = \ln VC_0$, C_0 is a constant.

Or, $\qquad V \cdot C_0 = e^{\alpha T/R}$ or $V \cdot e^{\alpha T/R} = \dfrac{1}{C_0} =$ constant

(b) $C = C_V + \beta V$

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and $\qquad C = C_V + \dfrac{RT}{V}\dfrac{dV}{dT}$ so, $C_V\dfrac{RT}{V}\dfrac{dV}{dT} = C_V + \beta V$

or, $\qquad \dfrac{RT}{V}\dfrac{dV}{dT} = \beta V$ or, $\dfrac{dV}{V^2} = \dfrac{\beta}{R}\dfrac{dT}{T}$ or, $V^{-2} = \dfrac{dT}{T}$

Integrating both sides, we get $\dfrac{R}{\beta}\dfrac{V^{-1}}{\beta - 1} = \ln T + \ln C_0 = \ln\, T\cdot C_0$

So, $\ln T\cdot C_0 = -\dfrac{R}{\beta V}$ $T\cdot C_0 = e^{-R/\beta V}$ or, $T e^{-R/\beta V} = \dfrac{1}{C_0} =$ constant

(c) $C = C_V + ap$ and $C = C_V + \dfrac{RT}{V}\dfrac{dV}{dT}$

So, $\qquad C_V + ap = C_V + \dfrac{RT}{V}\dfrac{dV}{dT}$ so, $ap = \dfrac{RT}{V}\dfrac{dV}{dT}$

or, $\qquad a\dfrac{RT}{V} = \dfrac{RT}{V}\dfrac{dV}{dT}$ (as $p = \dfrac{RT}{V}$ for one mole of gas)

or, $\qquad \dfrac{dV}{dT} = a$ or, $dV = adT$ or, $dT = \dfrac{dV}{a}$

So,$T = \dfrac{V}{a} +$ constant or $V - aT =$ constant

2.56 (a) By the first law of thermodynamics $A = Q - \Delta U$

or, $\qquad = CdT - C_V dT = (C - C_V)\, dT$ (for one mole)

Given $\qquad\qquad\qquad\qquad C = \dfrac{\alpha}{T}$

So, $\qquad A = \displaystyle\int_{T_0}^{\eta T_0}\left(\dfrac{\alpha}{T} - C_V\right) dT = \alpha \ln \dfrac{\eta T_0}{T_0} - C_V(\eta\, T_0 - T_0)$

$\qquad\qquad = \alpha \ln \eta - C_V T_0\,(\eta - 1) = \alpha \ln \eta + \dfrac{RT}{\gamma - 1}(\eta - 1)$

(b) $C = +\dfrac{dQ}{dT} = \dfrac{RT}{V}\dfrac{dV}{dT} + C_V$

Given $\qquad\qquad C = \dfrac{\alpha}{T}$, so $C_V + \dfrac{RT}{V}\dfrac{dV}{dT} = \dfrac{\alpha}{T}$

or, $\qquad\qquad \dfrac{R}{\gamma - 1}\dfrac{1}{RT} + \dfrac{dV}{V} = \dfrac{\alpha}{RT^2}dT$

or, $\qquad\qquad \dfrac{dV}{V} = \dfrac{\alpha}{RT^2}dT - \dfrac{1}{\gamma - 1}\cdot\dfrac{dT}{T}$

or, $\qquad\qquad (\gamma - 1)\dfrac{dV}{V} = \dfrac{\alpha\,(\gamma - 1)}{RT^2}dT - \dfrac{dT}{T}$

Integrating both sides, we get

or,

$$(\gamma - 1) \ln V = -\frac{\alpha (\gamma - 1)}{RT} - \ln T + \ln K$$

or,

$$\ln V^{\gamma - 1} \frac{T}{K} = \frac{-\alpha(\gamma - 1)}{RT}$$

$$\ln V^{\gamma - 1} \cdot \frac{pV}{RK} = \frac{-\alpha (\gamma - 1)}{pV}$$

or,

$$\frac{pV^{\gamma}}{RK} = e^{-\alpha (\gamma - 1)/pV}$$

or,

$$pV^{\gamma} e^{\alpha (\gamma - 1)/pV} = RK = \text{constant}$$

2.57 The work done is

$$A = \int_{V_1}^{V_2} p \, dV = \int_{V_1}^{V_2} \left(\frac{RT}{v - b} - \frac{a}{V^2} \right) dV$$

$$= RT \ln \frac{V_2 - b}{V_1 - b} + a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

2.58 (a) The increment in the internal energy is

$$\Delta U = \int_{V_1}^{V_1} \left(\frac{\partial U}{\partial V} \right)_T dV$$

But from second law

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - p = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

On the other hand

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

or,

$$T \left(\frac{\partial p}{\partial T} \right)_V = \frac{RT}{V - b} \text{ and } \left(\frac{\partial U}{\partial V} \right)_t = \frac{a}{V^2}$$

So,

$$\Delta U = a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

(b) From the first law

$$Q = A + \Delta U = RT \ln \frac{V_2 - b}{V_1 - b}$$

2.59 (a) From the first law for an adiabatic

$$dQ = dU + pd V = 0$$

From the previous problem

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT + \frac{a}{V^2} dV$$

So,

$$0 = C_V dT + \frac{RT \, dV}{V - b}$$

This equation can be integrated if we assume that C_V and b are constant then

$$\frac{R}{C_V}\frac{dV}{V-b}+\frac{dT}{T}=0, \quad \text{or,} \quad \ln T+\frac{R}{C_V}\ln(V-b)=\text{constant}$$

or,
$$T(V-b)^{R/C_V}=\text{constant}$$

(b) We use

$$dU=C_V dT+\frac{a}{V^2}dV$$

Now,
$$dQ=C_V dT+\frac{RT}{V-b}dV$$

So along constant p,
$$C_p=C_V+\frac{RT}{V-b}\left(\frac{\partial V}{\partial T}\right)_p$$

Thus
$$C_p-C_V=\frac{RT}{V-b}\left(\frac{\partial V}{\partial T}\right)_p, \quad \text{But } p=\frac{RT}{V-b}-\frac{a}{V^2}$$

On differentiating,
$$0=\left(-\frac{RT}{(V-b)^2}+\frac{2a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p+\frac{R}{V-b}$$

or,
$$T\left(\frac{\partial V}{\partial T}\right)_p=\frac{RT/V-b}{\dfrac{RT}{(V-b)^2}-\dfrac{2a}{V^3}}=\frac{V-b}{1-\dfrac{2a(V-b)^2}{RTV^3}}$$

and
$$C_p-C_V=\frac{R}{1-\dfrac{2a(V-b)^2}{RTV^3}}$$

2.60 From the first law

$Q=U_f-U_i+A=0$, as the vessels are thermally insulated.

As this is free expansion, $A=0$, so, $U_f=U_i$

But
$$U=\nu C_V T-\frac{a\nu^2}{V}$$

So,
$$C_V(T_f-T_i)=\left(\frac{a}{V_1+V_2}-\frac{a}{V_1}\right)\nu=\frac{-aV_2\nu}{V_1(V_1+V_2)}$$

or,
$$\Delta T=\frac{-a(\gamma-1)V_2\nu}{RV_1(V_1+V_2)}$$

Substitution gives $\Delta T=-3\,\text{K}$

2.61 $Q=U_f-U_i+A=U_f-U_i$, (as $A=0$ in free expansion).

So at constant temperature.

$$Q=\frac{-a\nu^2}{V_2}-\left(-\frac{a\nu^2}{V_1}\right)=a\nu^2\frac{V_2-V_1}{V_1\cdot V_2}$$

$=0.33\,\text{kJ}$ from the given data.

2.3 KINETIC THEORY OF GASES. BOLTZMANN'S LAW AND MAXWELL'S DISTRIBUTION

2.62 From the formula $p = nkT$

$$n = \frac{p}{kT} = \frac{4 \times 10^{-15} \times 1 \cdot 01 \times 10^5}{1 \cdot 38 \times 10^{-23} \times 300} \quad \text{per } m^3$$

$$= 1 \times 10^{11} \text{ per } m^3 = 10^5 \text{ per c.c}$$

Mean distance between molecules

$$(10^{-5} \text{ c.c.})^{1/3} = 10^{1/3} \times 10^{-2} \text{ cm} = 0 \cdot 2 \text{ mm.}$$

2.63 After dissociation each N_2 molecule becomes two N-atoms and so contributes, 2×3 degrees of freedom. Thus the number of moles becomes

$$\frac{m}{M}(1 + \eta) \quad \text{and} \quad p = \frac{mRT}{MV}(1 + \eta)$$

Here M is the molecular weight in grams of N_2.

2.64 Let n_1 = number density of He atoms, n_2 = number density of N_2 molecules

Then
$$\rho = n_1 m_1 + n_2 m_2$$

where m_1 = mass of He atom, m_2 = mass of N_2 molecule also $p = (n_1 + n_2) kT$
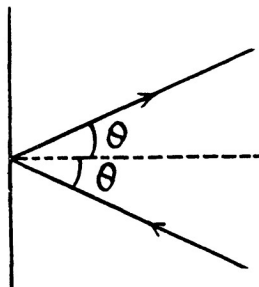
From these two equations we get

$$n_1 = \left(\frac{p}{kT} - \frac{\rho}{m_2}\right) \Big/ \left(1 - \frac{m_1}{m_2}\right)$$

2.65 $$p = \frac{nv \times 2\,mv \cos \theta \times dA \cos \theta}{dA}$$

$$= 2\,m\,n\,v^2 \cos^2 \theta$$

2.66 From the formula

$$v = \sqrt{\frac{\gamma p}{\rho}}, \quad \gamma = \frac{\rho V^2}{p}$$

If i = number of degrees of freedom of the gas then

$$C_p = C_V + RT \quad \text{and} \quad C_V = \frac{i}{2} RT$$

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{i} \quad \text{or} \quad i = \frac{2}{\gamma - 1} = \frac{2}{\dfrac{\rho v^2}{p} - 1}$$

2.67 $$v_{\text{sound}} = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{\gamma RT}{M}}, \quad \text{and} \quad v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

so,
$$\frac{v_{\text{sound}}}{v_{\text{rms}}} = \sqrt{\frac{\gamma}{3}} = \sqrt{\frac{i+2}{3i}}$$

(a) For monoatomic gases $i = 3$

$$\frac{v_{sound}}{v_{rms}} = \sqrt{\frac{5}{9}} = 0.75$$

(b) For rigid diatomic molecules $i = 5$

$$\frac{v_{sound}}{v_{rms}} = \sqrt{\frac{7}{15}} = 0.68$$

2.68 For a general noncollinear, nonplanar molecule

mean energy $= \frac{3}{2}kT$ (translational) $+ \frac{3}{2}kT$ (rotational) $+ (3N - 6)kT$ (vibrational)

$= (3N - 3)kT$ per molecule

For linear molecules, mean energy $= \frac{3}{2}kT$ (translational)

$+ kT$ (rotational) $+ (3N - 5)kT$ (vibrational)

$= \left(3N - \frac{5}{2}\right)kT$ per molecule

Translational energy is a fraction $\dfrac{1}{2(N-1)}$ and $\dfrac{1}{2N - \frac{5}{3}}$ in the two cases.

2.69 (a) A diatomic molecule has 3 translational, 2 rotational and one vibrational degrees of freedom. The corresponding energy per mole is

$$\frac{3}{2}RT, \text{ (for translational)} + 2 \times \frac{1}{2}RT, \text{ (for rotational)}$$

$$+ 1 \times RT, \text{ (for vibrational)} = \frac{7}{2}RT$$

Thus, $\qquad C_V = \frac{7}{2}R, \text{ and } \gamma = \frac{C_p}{C_V} = \frac{9}{7}$

(b) For linear $N-$ atomic molecules energy per mole

$$= \left(3N - \frac{5}{2}\right)RT \text{ as before}$$

So, $\qquad C_V = \left(3N - \frac{5}{2}\right)R \text{ and } \gamma = \frac{6N - 3}{6N - 5}$

(c) For noncollinear $N-$ atomic molecules

$C_V = 3(N - 1)R$ as before (2.68) $\quad \gamma = \frac{3N - 2}{3N - 3} = \frac{N - 2/3}{N - 1}$

2.70 In the isobaric process, work done is

$$A = pdv = RdT \text{ per mole.}$$

On the other hand heat transferred $Q = C_p dT$

Now $C_p = (3N - 2)R$ for non-collinear molecules and $C_p = \left(3N - \frac{3}{2}\right)R$ for linear molecules

Thus $\quad\dfrac{A}{Q} = \begin{cases} \dfrac{1}{3N-2} \text{ non collinear} \\[2mm] \dfrac{1}{3N-\dfrac{3}{2}} \text{ linear} \end{cases}$

For monoatomic gases, $c_p = \dfrac{5}{2}$ and $\dfrac{A}{Q} = \dfrac{2}{5}$

2.71 Given specific heats c_p, c_v (per unit mass)

$$M(c_p - c_v) = R \quad\text{or,}\quad M = \dfrac{R}{c_p - c_v}$$

Also $\quad\gamma = \dfrac{c_p}{c_v} = \dfrac{2}{i}+1, \quad\text{os,}\quad i = \dfrac{2}{\dfrac{c_p}{c_v}1} = \dfrac{2c_v}{c_p - c_v}$

2.72 (a) $\quad C_v = 29\,\dfrac{J}{^\circ\text{K mole}} = \dfrac{29}{8\cdot3}R$

$$C_v = \dfrac{20\cdot7}{8\cdot3}R, \quad \gamma = \dfrac{29}{20\cdot7} = 1\cdot4 = \dfrac{7}{5}$$

$$i = 5$$

(b) In the process $pT =$ const.

$$\dfrac{T^2}{V} = \text{const}, \quad\text{So } 2\dfrac{dT}{T} - \dfrac{dV}{V} = 0$$

Thus $\quad CdT = C_v dT + p\,dV = C_v dT + \dfrac{RT}{V}dV = C_v dT + \dfrac{2RT}{T}dT$

or $\quad C = C_v + 2R = \left(\dfrac{29}{8\cdot3}\right)R \quad\text{So }\quad C_v = \dfrac{12\cdot4}{8\cdot3}R = \dfrac{3}{2}R$

Hence $i = 3$ (monoatomic)

2.73 Obviously

$$\dfrac{1}{R}C_v = \dfrac{3}{2}\gamma_1 + \dfrac{5}{2}\gamma_2$$

(Since a monoatomic gas has $C_v = \dfrac{3}{2}R$ and a diatomic gas has $C_v = \dfrac{5}{2}R$. [The diatomic molecule is rigid so no vibration])

$$\dfrac{1}{R}C_p = \dfrac{3}{2}\gamma_1 + \dfrac{5}{2}\gamma_2 + \gamma_1 + \gamma_2$$

Hence $\quad\gamma = \dfrac{C_p}{C_v} = \dfrac{5\gamma_1 + 7\gamma_2}{3\gamma_1 + 5\gamma_2}$

2.74 The internal energy of the molecules are

$$U = \dfrac{1}{2}mN < (\vec{u}-\vec{v})^2 > = \dfrac{1}{2}mN <u^2 - v^2>$$

where $\vec{v}$ = velocity of the vessel, N = number of molecules, each of mass m. When the vessel is stopped, internal energy becomes $\frac{1}{2}mN <u^2>$

So there is an increase in internal energy of $\Delta U = \frac{1}{2}mNv^2$. This will give rise to a rise in temperature of

$$\Delta T = \frac{\frac{1}{2}mNv^2}{\frac{i}{2}R}$$

$$= \frac{mNv^2}{iR}$$

there being no flow of heat. This change of temperature will lead to an excess pressure

$$\Delta p = \frac{R\Delta T}{V} = \frac{mNv^2}{iV}$$

and finally

$$\frac{\Delta p}{p} = \frac{Mv^2}{iRT} = 2 \cdot 2\%$$

where M = molecular weight of N_2, i = number of degrees of freedom of N_2

2.75 (a) From the equipartition theorem

$$\bar{\epsilon} = \frac{3}{2}kT = 6 \times 10^{-21} \text{ J}; \text{ and } v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = 0 \cdot 47 \text{ km/s}$$

(b) In equilibrium the mean kinetic energy of the droplet will be equal to that of a molecule.

$$\frac{1}{2}\frac{\pi}{6}d^3 \rho v_{rms}^2 = \frac{3}{2}kT \text{ or } v_{rms} = 3\sqrt{\frac{2kT}{\pi d^3 \rho}} = 0 \cdot 15 \text{ m/s}$$

2.76 Here $i = 5, C_V = \frac{5}{2}R, \gamma = \frac{7}{5}$ given

$$v'_{rms} = \sqrt{\frac{3RT'}{M}} = \frac{1}{\eta}v_{rms} = \frac{1}{\eta}\sqrt{\frac{3RT}{M}} \text{ or } T' = \frac{1}{\eta^2}T$$

Now in an adiabatic process

$$TV^{\gamma-1} = TV^{2/i} = \text{constant or } VT^{i/2} = \text{constant}$$

$$V'\left(\frac{1}{\eta^2}T\right)^{i/2} = VT^{i/2} \text{ or } V'\eta^{-i} = V \text{ or } V' = \eta^i V$$

The gas must be expanded η^i times, i.e 7·6 times.

2.77 Here $\qquad C_V = \frac{5}{2}\frac{m}{M}R \ (i = 5 \text{ here})$

m= mass of the gas, M= molecular weight. If v_{rms} increases η times, the temperature will have increased η^2 times. This will require (neglecting expansion of the vessels) a heat flow of amount

$$\frac{5}{2}\frac{m}{M}R(\eta^2 - 1)T = 10 \text{ kJ.}$$

2.78 The root mean square angular velocity is given by

$$\frac{1}{2} I \omega^2 = 2 \times \frac{1}{2} kT \text{ (2 degrees of rotations)}$$

or

$$\omega = \sqrt{\frac{2kT}{I}} = 6.3 \times 10^{12} \text{ rad/s}$$

2.79 Under compression, the temperature will rise

$$TV^{\gamma-1} = \text{constant}, \quad TV^{2/i} = \text{constant}$$

or,

$$T (\eta^{-1} V_0)^{2/i} = T_0 V_0^{2/i} \quad \text{or,} \quad T = \eta^{+2/i} T_0$$

So mean kinetic energy of rotation per molecule in the compressed state

$$= kT = k T_0 \eta^{2/i} = 0.72 \times 10^{-20} \text{ J}$$

2.80 No. of collisions $= \frac{1}{4} n <v> = v$

Now,

$$\frac{v'}{v} = \frac{n'}{n} \frac{<v'>}{<v>} = \frac{1}{\eta} \sqrt{\frac{T}{T}}$$

(When the gas is expanded η times, n decreases by a factor η). Also

$$T (\eta V)^{2/i} = TV^{2/i} \quad \text{or} \quad T = \eta^{2/i} T \quad \text{so,} \quad \frac{v'}{v} = \frac{1}{\eta} \eta^{-1/i} = \eta^{\frac{-i-1}{i}}$$

i.e. collisions decrease by a factor $\eta^{\frac{i+1}{i}}$, $i = 5$ here.

2.81 In a polytropic process $pV^n = $ constant., where n is called the polytropic index. For this process

$$pV^n = \text{constant or } TV^{n-1} = \text{constant}$$

$$\frac{dT}{T} + (n-1) \frac{dV}{V} = 0$$

Then

$$dQ = C dT = dU + p dV = C_V dT + p dV$$

$$= \frac{i}{2} R dT + \frac{RT}{V} dV = \frac{i}{2} R dT - \frac{1}{n-1} R dT = \left(\frac{i}{2} - \frac{1}{n-1} \right) R dT$$

Now

$$C = R \quad \text{so} \quad \frac{i}{2} - \frac{1}{n-1} = 1$$

or,

$$\frac{1}{n-1} = \frac{i}{2} - 1 = \frac{i-2}{2} \quad \text{or} \quad n = \frac{i}{i-2}$$

Now

$$\frac{v'}{v} = \frac{n'}{n} \frac{<v'>}{<v>} = \frac{1}{\eta} \sqrt{\frac{T}{T}} = \frac{1}{\eta} \left(\frac{V}{V'} \right)^{\frac{n-1}{2}}$$

$$= \frac{1}{\eta} \left(\frac{1}{\eta} \right)^{\frac{1}{i-2}} = \left(\frac{1}{\eta} \right)^{\frac{i-1}{i-2}} = \eta^{\frac{-i-1}{i-2}} \text{ times} = \frac{1}{2.52} \text{ times}$$

2.82 If α is the polytropic index then

$$pV^{\alpha} = \text{constant}, \quad TV^{\alpha-1} = \text{constant}.$$

Now

$$\frac{v'}{v} = \frac{n'}{n}\frac{<v'>}{<v>} = \frac{V}{V'}\sqrt{\frac{T'}{T}} = \frac{VT^{-1/2}}{V'T'^{-1/2}} = 1$$

Hence

$$\frac{1}{\alpha-1} = -\frac{1}{2} \quad \text{or} \quad \alpha = -1$$

Then

$$C = \frac{iR}{2} + \frac{R}{2} = 3R$$

2.83 $v_p = \sqrt{\dfrac{2kT}{m}} = \sqrt{\dfrac{2RT}{M}} = \sqrt{\dfrac{2p}{\rho}} = 0\cdot45$ km/s,

$$v_{av} = \sqrt{\frac{8}{\pi}\frac{p}{\rho}} = \cdot51 \text{ km/s} \quad \text{and} \quad v_{rms} = \sqrt{\frac{3p}{\rho}} = 0\cdot55 \text{ km/s}$$

2.84 (a) The formula is

$$df(u) = \frac{4}{\sqrt{\pi}}u^2 e^{-u^2}du, \quad \text{where} \quad u = \frac{v}{v_p}$$

Now Prob $\left(\dfrac{|v-v_p|}{v_p} < \delta\eta\right) = \displaystyle\int_{1-\delta\eta}^{1+\delta\eta} df(u)$

$$= \frac{4}{\sqrt{\pi}}e^{-1}\times 2\,\delta\eta = \frac{8}{\sqrt{\pi}\,e}\,\delta\eta = 0\cdot0166$$

(b) Prob $\left(\left|\dfrac{v-v_{rms}}{v_{rms}}\right| < \delta\eta\right) = $ Prob $\left(\left|\dfrac{v}{v_p} - \dfrac{v_{rms}}{v_p}\right| < \delta\eta\,\dfrac{v_{rms}}{v_p}\right)$

$$= \text{Prob}\left(\left|u - \sqrt{\frac{3}{2}}\right| < \sqrt{\frac{3}{2}}\,\delta\eta\right)$$

$$= \int_{\sqrt{\frac{3}{2}}-\sqrt{\frac{3}{2}}\,\delta\eta}^{\sqrt{\frac{3}{2}}+\sqrt{\frac{3}{2}}\,\delta\eta} \frac{4}{\sqrt{\pi}}u^2 e^{-u^2}du$$

$$= \frac{4}{\sqrt{\pi}}\times\frac{3}{2}e^{-3/2}\times 2\sqrt{\frac{3}{2}}\,\delta\eta = \frac{12\sqrt{3}}{\sqrt{2\pi}}e^{-3/2}\,\delta\eta = 0\cdot0185$$

2.85 (a) $v_{rms} - v_p = (\sqrt{3} - \sqrt{2}) \sqrt{\frac{kT}{m}} = \Delta v,$

$$T = \frac{m}{k} \left(\frac{\Delta v}{(\sqrt{3} - \sqrt{2})} \right)^2 / K = 384 \text{ K}$$

(b) Clearly v is the most probable speed at this temperature. So

$$\sqrt{\frac{2kT}{m}} = v \quad \text{or} \quad T = \frac{mv^2}{2k} = 342 \text{ K}$$

2.86 (a) We have,

$$\frac{v_1^2}{v_p^2} e^{-v_1^2/v_p^2} = \frac{v_2^2}{v_p^2} e^{-v_2^2/v_p^2} \quad \text{or} \quad \left(\frac{v_1}{v_2} \right)^2 = e^{v_1^2 - v_2^2/v_p^2} \quad \text{or} \quad v_p^2 = \frac{2kT}{m} = \frac{v_1^2 - v_2^2}{(\ln v_1^2/v_2^2)}$$

So $$T = \frac{m(v_1^2 - v_2^2)}{2k \ln \frac{v_1^2}{v_2^2}} = 330 \text{ K}$$

(b) $F(v) = \frac{4}{\sqrt{\pi}} \frac{v^2}{v_p^2} e^{-v^2/v_p^2} \times \frac{1}{v_p} \left(\frac{1}{v_p} \right.$ comes from $F(v)\,dv = d f(u), \quad du = \frac{dv}{v_p} \left. \right)$

Thus $\frac{v^2}{v_p^3} e^{-v^2/v_p^2}_{P_1} = v^2/v_{P_2} e^{-v_2/v_2}, \quad v_{P_1}^2 = \frac{2kT_0}{m}, \quad v_{P_2}^2 = \frac{2kT_0}{m} \eta$ now

$$e^{-\frac{mv^2}{2kT_0}\left(1 - \frac{1}{\eta}\right)} = \frac{1}{\eta^{3/2}} \quad \text{or} \quad \frac{mv^2}{2kT_0}\left(1 - \frac{1}{\eta}\right) = \frac{3}{2} \ln \eta$$

Thus $$v = \sqrt{\frac{3kT_0}{m}} \sqrt{\frac{\ln \eta}{1 - 1/\eta}}$$

2.87 $v_{pN} = \sqrt{\frac{2kT}{m_N}} = \sqrt{\frac{2RT}{M_N}}, \quad v_{p_0} = \sqrt{\frac{2RT}{M_0}}$

$$v_{p_N} - v_{p_0} = \Delta v = \sqrt{\frac{2RT}{M_N}} \left(1 - \sqrt{\frac{M_N}{M_0}} \right)$$

$$T = \frac{M_N (\Delta v)^2}{2R \left(1 - \sqrt{\frac{M_N}{M_0}} \right)^2} = \frac{m_N (\Delta v)^2}{2k \left(1 - \sqrt{\frac{m_N}{M_0}} \right)^2} = 363 \text{ K}$$

2.88 $\frac{v^2}{v_{p_H}^3} e^{-v^2/v_{p_H}^2} = \frac{v^2}{v_{p_{He}}^3} e^{-v^2/v_{p_{He}}^2} \quad \text{or} \quad e^{v^2 \left(\frac{m_{He}}{2kT} - \frac{m_H}{2kT} \right)} = \left(\frac{m_{He}}{m_H} \right)^{3/2}$

$v^2 = 3kT \frac{\ln m_{He}/m_H}{m_{H_e} - m_H}$, Putting the values we get $v = 1.60 \text{ km/s}$

2.89 $dN(v) = \dfrac{N\,4}{\sqrt{\pi}}\,\dfrac{v^2\,dv}{v_p^3}\,e^{-v^2/v_p^2}$

For a given range v to $v + dv$ (i.e. given v and dv) this is maximum when

$$\frac{\delta}{\delta v_p}\,\frac{dN(v)}{N\,v^2\,dv} = 0 = \left(-3v_p^{-4} + \frac{2v^2}{v_p^6}\right)e^{-v^2/v_p^2}$$

or, $v^2 = \dfrac{3}{2}v_p^2 = \dfrac{3kT}{m}$.   Thus $T = \dfrac{1}{3}\dfrac{mv^2}{k}$

2.90 $d^3 v = 2\pi v_\perp\,dv_\perp\,dv_x$

Thus $d\,n(v) = N\left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}\left(v_x^2 + v_\perp^2\right)} dv_x\,2\pi v_\perp\,d v_\perp$

2.91 $<v_x> = 0$ by symmetry

$$<|v_x|> = \int_{-\infty}^{\infty} |v_x|\,e^{-\frac{mv_x^2}{2kT}}\,dv_x \Big/ \int_{0}^{\infty} e^{-\frac{mv_x^2}{2kT}}\,dv_x = \int_{0}^{\infty} v_x\,e^{-\frac{mv_x^2}{2kT}}\,dv_x \Big/ \int_{0}^{\infty} e^{-\frac{mv^2}{2kT}}\,dv_x$$

$$= \sqrt{\frac{2kT}{m}} \int_{0}^{\infty} u\,e^{-u^2}\,du \Big/ \int_{0}^{\infty} e^{-u^2}\,du$$

$$= \sqrt{\frac{2kT}{m}} \int_{0}^{\infty} \frac{1}{2}e^{-x}\,dx \Big/ \int_{0}^{\infty} e^{-x}\,\frac{dx}{2\sqrt{x}}$$

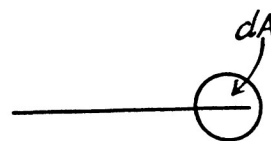$$= \sqrt{\frac{2kT}{m}}\; \Gamma(1) \Big/ \Gamma\left(\frac{1}{2}\right) = \sqrt{\frac{2kT}{m\pi}}$$

2.92 $<v_x^2> = \int_{0}^{\infty} v_x^2\,e^{-\frac{mv_x^2}{2kt}}\,dv_x \Big/ \int_{0}^{\infty} e^{-\frac{mv_x^2}{2kt}}\,dv_x$

$$= \frac{2kT}{m} \int_{0}^{\infty} x\,e^{-x}\,\frac{dx}{2\sqrt{x}} \Big/ \int_{0}^{\infty} e^{-x}\,\frac{dx}{2\sqrt{x}}$$

$$= \frac{2kT}{m}\,\Gamma\left(\frac{3}{2}\right) \Big/ \Gamma\left(\frac{1}{2}\right) = \frac{kT}{m}$$

2.93 Here vdA = No. of molecules hitting an area dA of the wall per second

$$= \int_{0}^{\infty} dN(v_x)\,v_x\,dA$$

or,

$$v = \int_0^\infty n \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}} v_x \, dv_x$$

$$= \int_0^\infty \frac{n}{\sqrt{\pi}} \left(\frac{2kT}{m}\right)^{1/2} e^{-u^2} u \, du$$

$$= \frac{1}{2} n \sqrt{\frac{2kT}{m\pi}} = n \sqrt{\frac{kT}{2m\pi}} = \frac{1}{4} n <v>,$$

$$\left(\text{where } <v> = \sqrt{\frac{8kT}{m\pi}}\right)$$

2.94 Let, $dn(v_x) = n \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x$

be the number of molecules per unit volume with x component of velocity in the range v_x to $v_x + dv_x$

Then

$$p = \int_0^\infty 2 mv_x \cdot v_x \, dn(v_x)$$

$$= \int_0^\infty 2 mv_x^2 \, n \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x$$

$$= 2mn \frac{1}{\sqrt{\pi}} \frac{2kT}{m} \int_0^\infty u^2 e^{-u^2} du$$

$$= \frac{4}{\sqrt{\pi}} nkT \cdot \int_0^\infty x e^{-x} \frac{dx}{2\sqrt{x}} = nkT$$

2.95

$$<\frac{1}{v}> = \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2 \, dv \frac{1}{v}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \frac{1}{2} \frac{2kT}{m} \int_0^\infty e^{-x} dx$$

$$= 2\left(\frac{m}{2\pi kT}\right)^{1/2} = \left(\frac{2m}{\pi kT}\right)^{1/2} = \left(\frac{16}{\pi^2} \frac{m\pi}{8kT}\right)^{1/2} = \frac{4}{\pi <v>}$$

2.96 $\quad dN\,(v) = N\left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\,4\,\pi\,v^2\,dv = dN\,(\varepsilon) = \dfrac{dN\,(\varepsilon)}{d\varepsilon}\,d\varepsilon$

or, $\quad \dfrac{dN\,(\varepsilon)}{d\varepsilon} = N\left(\dfrac{m}{2\,\pi kT}\right)^{3/2} e^{-mv^2/2RT}\,4\,\pi\,v^2\,\dfrac{dv}{d\varepsilon}$

Now, $\quad\quad \varepsilon = \dfrac{1}{2}\,mv^2 \quad$ so $\quad \dfrac{dv}{d\varepsilon} = \dfrac{1}{mv}$

or, $\quad \dfrac{dN\,(\varepsilon)}{d\varepsilon} = N\left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-\varepsilon/kT}\,4\,\pi\,\sqrt{\dfrac{2\varepsilon}{m}}\,\dfrac{1}{m}$

$\quad\quad\quad\quad\quad\quad = N\dfrac{2}{\sqrt{\pi}}\,(kT)^{-3/2}\,e^{-\varepsilon/kT}\,\varepsilon^{1/2}$

i.e. $\quad\quad dN\,(\varepsilon) = N\dfrac{2}{\sqrt{\pi}}\,(kT)^{-3/2}\,e^{-\varepsilon/kT}\,\varepsilon^{1/2}\,d\varepsilon$

The most probable kinetic energy is given from

$\dfrac{d}{d\varepsilon}\,\dfrac{dN\,(\varepsilon)}{d\varepsilon} = 0 \quad$ or, $\quad \dfrac{1}{2}\varepsilon^{-1/2}\,e^{-\varepsilon/kT} - \dfrac{\varepsilon^{1/2}}{kT}\,e^{\varepsilon/kT} = 0 \quad$ or $\quad \varepsilon = \dfrac{1}{2}kT = \varepsilon_{pr}$

The corresponding velocity is $v = \sqrt{\dfrac{kT}{m}} \neq v_{pr}$

2.97 The mean kinetic energy is

$<\varepsilon> = \displaystyle\int_0^\infty \varepsilon^{3/2}\,e^{-\varepsilon/kT}\,d\varepsilon \Big/ \int_0^\infty \varepsilon^{1/2}\,e^{-\varepsilon/kT}\,d\varepsilon = kT\dfrac{\Gamma\,(5/2)}{\Gamma\,(3/2)} = \dfrac{3}{2}kT$

Thus

$$\dfrac{\delta N}{N} = \int_{\frac{3}{2}kT(1-\delta\eta)}^{\frac{3}{2}(1+\delta\eta)kT} \dfrac{2}{\sqrt{\pi}}\,(kT)^{-3/2}\,e^{-\varepsilon/kT}\,\varepsilon^{1/2}\,d\varepsilon$$

$$= \dfrac{2}{\sqrt{\pi}}\,e^{-3/2}\left(\dfrac{3}{2}\right)^{3/2}\,2\,\delta\,\eta = 3\sqrt{\dfrac{6}{\pi}}\,e^{3/2}\,\delta\eta$$

If $\delta\,\eta = 1\%$ this gives 0·9 %

2.98 $\quad \dfrac{\Delta N}{N} = \dfrac{2}{\sqrt{\pi}}\,(kT)^{-3/2}\displaystyle\int_{\varepsilon_0}^{\infty}\sqrt{\varepsilon}\,e^{-\varepsilon/kT}\,d\varepsilon$

$\quad\quad\quad \approx \dfrac{2}{\sqrt{\pi}}\,(kT)^{-3/2}\,\sqrt{\varepsilon_0}\displaystyle\int_{\varepsilon_0}^{\infty}e^{-\varepsilon/kT}\,d\varepsilon\;(\varepsilon_0 \gg kT)$

$$\blacksquare \frac{2}{\sqrt{\pi}} (kT)^{-3/2} \sqrt{\varepsilon_0}\, kT\, e^{-\varepsilon_0/kT} \blacksquare 2\sqrt{\frac{\varepsilon_0}{\pi\, kT}}\; e^{-\varepsilon_0/kT}$$

(In evaluating the integral, we have taken out $\sqrt{\varepsilon}$ as $\sqrt{\varepsilon_0}$ since the integral is dominated by the lower limit.)

2.99 (a) $F(v) = A v^3\, e^{-mv^2/2kT}$

For the most probable value of the velocity

$$\frac{dF(v)}{dv} = 0 \quad \text{or} \quad 3A\, v^2\, e^{-mv^2/2kT} - A\, v^3\, \frac{2\, mv}{2kT}\, e^{-mv^2/2kT} = 0$$

So,
$$v_{pr} = \sqrt{\frac{3kT}{m}}$$

This should be compared with the value $v_{pr} = \sqrt{\dfrac{2kT}{m}}$ for the Maxwellian distribution.

(b) In terms of energy, $\varepsilon = \dfrac{1}{2} m v^2$

$$F(\varepsilon) = A v^3\, e^{-mv^2/2kT}\, \frac{dv}{d\varepsilon}$$

$$\blacksquare A \left(\frac{2\varepsilon}{m}\right)^{3/2} e^{-\varepsilon/kT}\, \frac{1}{\sqrt{2\, m\, \varepsilon}} = A\, \frac{2\varepsilon}{m^2}\, e^{-\varepsilon/kT}$$

From this the probable energy comes out as follows : $F'(\varepsilon) = 0$ implies

$$\frac{2A}{m^2}\left(e^{-\varepsilon/kT} - \frac{\varepsilon}{kT}\, e^{-\varepsilon/kT}\right) = 0, \quad \text{or,} \quad \varepsilon_{pr} = kT$$

2.100 The number of molecules reaching a unit area of wall at angle between θ and $\theta + d\theta$ to its normal per unit time is

$$dv = \int_{v=0}^{v=\infty} dn(v)\, \frac{d\Omega}{4\pi}\, v \cos\theta$$

$$= \int_0^\infty n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, v^3\, dv \sin\theta \cos\theta\, d\theta \times 2\pi$$

$$= n \left(\frac{2kT}{m\,\pi}\right)^{1/2} \int_0^\infty e^{-x} x\, dx\, \sin\theta \cos\theta\, d\theta = n \left(\frac{2kT}{m\pi}\right)^{1/2} \sin\theta \cos\theta\, d\theta$$
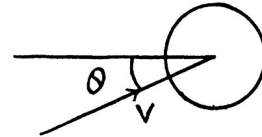
2.101 Similarly the number of molecules reaching the wall (per unit area of the wall with velocities in the interval v to $v + dv$ per unit time is

$$dv = \int_{\theta=0}^{\theta=\pi/2} dn(v)\, \frac{d\Omega}{4\pi}\, v \cos 0$$

$$= \int_{\theta=0}^{\theta=\pi/2} n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} v^3 \, dv \sin\theta \cos\theta \, d\theta \times 2\pi$$

$$= n\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} v^3 \, dv$$

2.102 If the force exerted is F then the law of variation of concentration with height reads

$$n(Z) = n_0 e^{-FZ/kT} \quad \text{So,} \quad \eta = e^{F\Delta h/kT} \quad \text{or} \quad F = \frac{kT \ln \eta}{\Delta h} = 9 \times 10^{-20} \text{ N}$$

2.103 Here $F = \frac{\pi}{6} d^3 \Delta\rho \, g = \frac{RT \ln \eta}{N_a h}$ or $N_a = \frac{6RT \ln \eta}{\pi d^3 g \Delta\rho h}$

In the problem, $\frac{\eta}{\eta_0} = 1.39$ here

$T = 290$K, $\eta = 2$, $h = 4 \times 10^{-5}$ m, $d = 4 \times 10^{-7}$ m, $g = 9.8$ m/s^2, $\Delta\rho = 0.2 \times 10^3$ kg/m^3
and $R = 8.31$ J/k

Hence, $N_a = \frac{6 \times 8.31 \times 290 \times \ln 2}{\pi \times 64 \times 9.8 \, 200 \times 4} \times 10^{26} = 6.36 \times 10^{23}$ mole^{-1}

2.104 $\eta = \frac{\text{concetration of } H_2}{\text{concentration of } N_2} = \eta_0 \frac{e^{-M_{H_2} gh/RT}}{e^{-M_{N_2} gh/RT}} = \eta_0 e^{(M_{N_2} - M_{H_2}) gh/RT}$

So more N_2 at the bottom, $\left(\frac{\eta}{\eta_0} = 1.39 \text{ here}\right)$

2.105 $n_1(h) = n_1 e^{-m_1 gh/kt}$, $n_2(h) = n_2 e^{-m_2 gh/kT}$

They are equal at a height h where $\frac{n_1}{n_2} = e^{gh(m_1 - m_2)/kT}$

$$\text{or} \quad h = \frac{kT}{g} \frac{\ln n_1 - \ln n_2}{m_1 - m_2}$$

2.106 At a temperature T the concentration $n(z)$ varies with height according to

$$n(z) = n_0 e^{-mgz/kT}$$

This means that the cylinder contains $\int_0^\infty n(z) \, dz$

$$= \int_0^\infty n_0 e^{-mgz/kT} \, dz = \frac{n_0 kT}{mg}$$

particles per unit area of the base. Clearly this cannot change. Thus $n_0 kT = p_0 = $ pressure at the bottom of the cylinder must not change with change of temperature.

2.107

$$<U> = \frac{\int\limits_0^\infty mgz\, e^{-mgz/kt}\, dz}{\int\limits_0^\infty e^{-mgz/kT}\, dz} = kT\, \frac{\int\limits_0^\infty x\, e^{-x}\, dx}{\int\limits_0^\infty e^{-x}\, dx} = kT\, \frac{\Gamma(2)}{\Gamma(1)} = kT$$

When there are many kinds of molecules, this formula holds for each kind and the average energy

$$<U> = \frac{\sum f_i\, kT}{\sum f_i} = kT$$

where f_i α fractional concentration of each kind at the ground level.

2.108 The constant acceleration is equivalent to a pseudo force wherein a concentration gradient is set up. Then

$$e^{-M_A w\, l/RT} = 1 - \eta$$

or

$$w = -\frac{RT \ln(1-\eta)}{M_A\, l} = \frac{\eta\, RT}{M_A\, l} = 70\, g$$

2.109 In a centrifuge rotating with angular velocity ω about an axis, there is a centrifugal acceleration $\omega^2 r$ where r is the radial distance from the axis. In a fluid if there are suspended colloidal particles they experience an additional force. If m is the mass of each particle then its volume is $\dfrac{m}{\rho}$ and the excess force on this particle is

$\dfrac{m}{\rho}(\rho - \rho_0)\, \omega^2\, r$ outward corresponding to a potential energy $-\dfrac{m}{2\rho}(\rho - \rho_0)\, \omega^2\, r^2$

This gives rise to a concentration variation

$$n(r) = n_0 \exp\left(+\frac{m}{2\rho\, kT}(\rho - \rho_0)\, \omega^2\, r^2 \right)$$

Thus

$$\frac{n(r_2)}{n(r_1)} = \eta = \exp\left(+\frac{M}{2\rho\, RT}(\rho - \rho_0)\, \omega^2\, (r_2^2 - r_1^2) \right)$$

where

$$\frac{m}{k} = \frac{M}{R}, \quad M = N_A\, m \text{ is the molecular weight}$$

Thus

$$M = \frac{2\rho\, RT \ln \eta}{(\rho - \rho_0)\, \omega^2\, (r_2^2 - r_1^2)}$$

2.110 The potential energy associated with each molecule is : $-\dfrac{1}{2} m\, \omega^2\, r^2$

and there is a concentration variation

$$n(r) = n_0 \exp\left(\frac{m\, \omega^2\, r^2}{2kT} \right) = n_0 \exp\left(\frac{M\, \omega^2\, r^2}{2RT} \right)$$

Thus

$$\eta = \exp\left(\frac{M\, \omega^2\, l^2}{2RT} \right) \quad \text{or} \quad \omega = \sqrt{\frac{2RT}{M\, l^2} \ln \eta}$$

Using $M = 12 + 32 = 44\,\text{gm}$, $l = 100\,\text{cm}$, $R = 8\cdot31 \times 10^7 \frac{\text{erg}}{^\circ\text{K}}$, $T = 300$,

we get $\omega = 280$ radians per second.

2.111 Here $n\,(r) = n_0 \exp\left(-\frac{ar^2}{kT}\right)$

(a) The number of molecules located at the distance between r and $r + dr$ is

$$4\,\pi\,r^2\,dr\,n\,(r) = 4\,\pi\,n_0 \exp\left(-\frac{ar^2}{kT}\right) r^2\,dr$$

(b) r_{pr} is given by $\frac{d}{dr} r^2 n\,(r) = 0$ or, $2r - \frac{2ar^3}{kT} = 0$ or $r_{pr} = \sqrt{\frac{kT}{a}}$

(c) The fraction of molecules lying between r and $r + dr$ is

$$\frac{dN}{N} = \frac{4\,\pi\,r^2\,dr\,n_0 \exp\,(-ar^2/kT)}{\displaystyle\int_0^\infty 4\,\pi\,r^2\,dr\,n_0 \exp\,(-ar^2/kT)}$$

$$\int_0^\infty 4\,\pi\,r^2\,dr \exp\left(-\frac{ar^2}{kT}\right) = \left(\frac{kT}{a}\right)^{3/2} 4\,\pi \int_0^\infty x\,\frac{dx}{2\sqrt{x}} \exp\,(-x)$$

$$= \left(\frac{kT}{a}\right)^{3/2} 2\,\pi\,\Gamma\left(\frac{3}{2}\right) = \left(\frac{\pi\,kT}{a}\right)^{3/2}$$

Thus $\dfrac{dN}{N} = \left(\dfrac{a}{\pi\,kT}\right)^{3/2} 4\,\pi\,r^2\,dr \exp\left(\dfrac{-ar^2}{kT}\right)$

(d) $dN = N\left(\dfrac{a}{\pi\,kT}\right)^{3/2} 4\,\pi\,r^2\,dr \,\exp\left(\dfrac{-ar^2}{kT}\right)$,

So $n\,(r) = N\left(\dfrac{a}{\pi\,kT}\right)^{1/2} \exp\left(\dfrac{-ar^2}{kT}\right)$

When T decreases η times $n(0) = n_0$ will increase $\eta^{3/2}$ times.

2.112

Write $U = ar^2$ or $r = \sqrt{\dfrac{U}{a}}$, so $dr = \sqrt{\dfrac{1}{a}}\,\dfrac{dU}{2\sqrt{U}} = \dfrac{dU}{2\sqrt{a\,U}}$

so $dN = n_0\,4\,\pi\,\dfrac{U}{a}\,\dfrac{dU}{2\sqrt{a\,U}} \exp\left(\dfrac{U}{kT}\right)$

$$= 2\,\pi\,n_0\,a^{-3/2}\,U^{1/2} \exp\left(\dfrac{-U}{kT}\right) dU$$

The most probable value of U is given by

$$\frac{d}{dU}\left(\frac{dN}{dU}\right) = 0 = \left(\frac{1}{2\sqrt{u}} - \frac{U^{1/2}}{kT}\right) \exp\left(\frac{-U}{kT}\right) \quad \text{or,} \quad U_{pr} = \frac{1}{2}kT$$

From 2.111 (b), the potential energy at the most probable distance is kT.

2.4 THE SECOND LAW OF THERMODYNAMICS. ENTROPY

2.113 The efficiency is given by

$$\eta = \frac{T_1 - T_2}{T_1}, \quad T_1 > T_2$$

Now in the two cases the efficiencies are

$$\eta_h = \frac{T_1 + \Delta T - T_2}{T_1 + \Delta T}, \quad T_1 \text{ increased}$$

$$\eta_l = \frac{T_1 - T_2 + \Delta T}{T_1}, \quad T_2 \text{ decreased}$$

Thus $\qquad\qquad \eta_h < \eta_l$

2.114 For H_2, $\gamma = \dfrac{7}{5}$

$$p_1 V_1 = p_2 V_2, \ p_3 V_3 = p_4 V_4$$

$$p_2 V_2^\gamma = p_3 V_3^\gamma, \ p_1 V_1^\gamma = p_4 V_4^\gamma$$

Define n by $V_3 = n V_2$

Then $p_3 = p_2 n^{-\gamma}$ so

$$p_4 V_4 = p_3 V_3 = p_2 V_2 n^{1-\gamma} = p_1 V_1 n^{1-\gamma}$$

$$p_4 V_4^\gamma = p_1 V_1^\gamma \text{ so } V_4^{1-\gamma} = V_1^{1-\gamma} n^{1-\gamma} \text{ or } V_4 = n V_1$$

Also $\qquad Q_1 = p_2 V_2 \ln \dfrac{V_2}{V_1}, \ Q'_2 = p_3 V_3 \ln \dfrac{V_3}{V_4} n^{1-\gamma} = p_2 v_2 \ln \dfrac{V_3}{v_4}$

Finally $\qquad \eta = 1 - \dfrac{Q_2}{Q_1} = 1 - n^{1-\gamma} = 0.242$

(b) Define n by $p_3 = \dfrac{p_2}{n}$

$$p_2 V_2^\gamma = \frac{p_2}{n} V_3^\gamma \text{ or } V_3 = n^{1/\gamma} V_2$$

So we get the formulae here by $n \to n^{1/\gamma}$ in the previous case.

$$\eta = 1 - n^{(1/\gamma)-1} = 1 - n^{-\frac{2}{7}} \approx 0.18$$

2.115 Used as a refrigerator, the refrigerating efficiency of a heat engine is given by

$$\varepsilon = \frac{Q'_2}{A} = \frac{Q'_2}{Q_1 - Q_2} = \frac{Q'_2/Q_1}{1 - \dfrac{Q'_2}{Q_1}} = \frac{1-\eta}{\eta} = 9 \text{ here,}$$
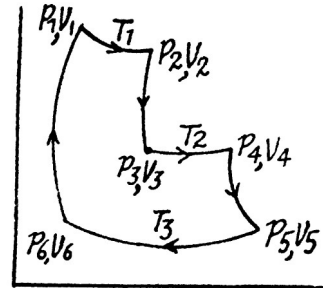
where η is the efficiency of the heat engine.
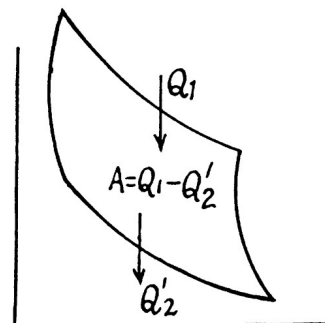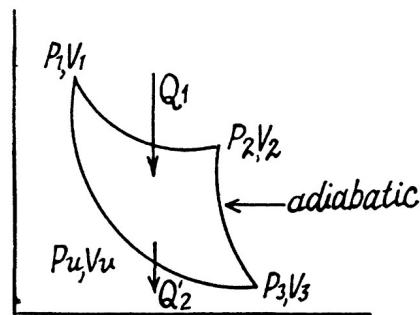
2.116 Given $V_2 = nV_1$, $V_4 = nV_3$

$Q_1 =$ Heat taken at the upper temperature

$$= RT_1 \ln n + R T_2 \ln n = R (T_1 + T_2) \ln n$$

Now $\quad T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad$ or $\quad V_3 = \left(\dfrac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} V_2$

Similarly $\quad V_5 = \left(\dfrac{T_2}{T_3}\right)^{\frac{1}{\gamma-1}} V_4$, $\quad V_6 = \left(\dfrac{T_1}{T_3}\right)^{\frac{1}{\gamma-1}} V_1$

Thus $Q_2 =$ heat ejected at the lower temperature $= -RT_3 \ln \dfrac{V_6}{V_5}$

$$= -R T_3 \ln \left(\dfrac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} \dfrac{V_1}{V_4} = -RT_3 \ln \left(\dfrac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} \dfrac{V_2}{n^2 V_3}$$

$$= -RT_3 \ln \left(\dfrac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} \dfrac{1}{n^2} \left(\dfrac{T_1}{T_2}\right)^{-\frac{1}{\gamma-1}} = 2 R T_3 \ln n$$

Thus $\quad\quad\quad\quad\quad\quad \eta = 1 - \dfrac{2T_3}{T_1 + T_2}$

2.117 $\quad Q'_2 = C_V (T_2 - T_3) = \dfrac{C_V}{R} V_2 (p_2 - p_3)$

$$Q_1 = \dfrac{C_V}{R} V_1 (p_1 - p_4)$$

Thus $\quad \eta = 1 - \dfrac{V_2 (p_2 - p_3)}{V_1 (p_1 - p_4)}$

On the other hand,

$6p_1 V_1^\gamma = p_2 V_2^\gamma$, $\quad p_3 V_2^\gamma = p_4 V_1^\gamma$ also $V_2 = n V_1$

Thus $\quad p_1 = p_2 n^\gamma$, $\quad p_4 = p_3 n^\gamma$

and $\quad \eta = 1 - n^{1-\gamma}$, with $\gamma = \dfrac{7}{5}$ for N_2 this is $\eta = 0.602$
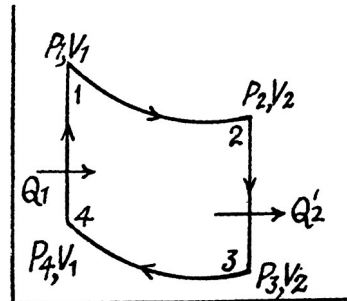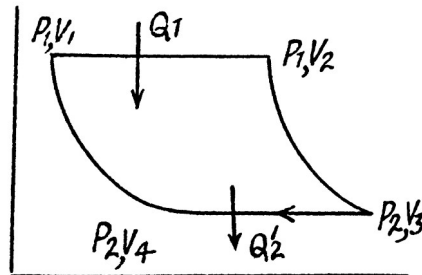
2.118 $\quad Q_1 = \dfrac{C_p}{R} p_1 (V_2 - V_1)$, $\quad Q'_2 = \dfrac{C_p}{R} p_2 (V_3 - V_4)$

So $\quad \eta = 1 - \dfrac{p_2 (V_3 - V_4)}{p_1 (V_2 - V_1)}$

Now $p_1 = n p_2$, $p_1 V_2^\gamma$ or $V_3 = n^{\frac{1}{\gamma}} V_2$

$p_2 V_4^\gamma = p_1 V_1^\gamma$ or $V_4 = n^{\frac{1}{\gamma}} V_1$

so $\quad \eta = 1 - \dfrac{1}{n} \cdot n^{\frac{1}{\gamma}} = 1 - n^{\frac{1}{\gamma}-1}$

2.119 Since the absolute temperature of the gas rises n times both in the isochoric heating and in the isobaric expansion

$$p_1 = np_2 \text{ and } V_2 = nV_1. \text{ Heat taken is}$$
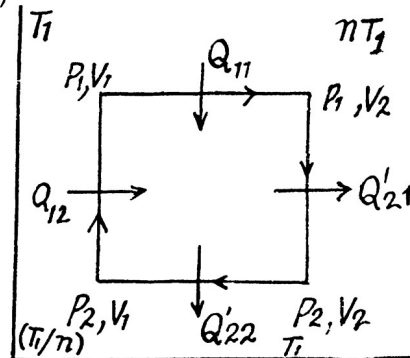
$$Q_1 = Q_{11} + Q_{12}$$

where $Q_{11} = C_p(n-1)T_1$ and $Q_{12} = C_V T_1\left(1 - \frac{1}{n}\right)$

Heat rejected is

$$Q'_2 = Q'_{21} + Q'_{22} \text{ where}$$

$$Q'_{21} = C_V T_1(n-1), \quad Q'_{22} = C_p T_1\left(1 - \frac{1}{n}\right)$$

Thus $\eta = 1 - \dfrac{Q'_2}{Q_1} = 1 - \dfrac{C_V(n-1) + C_p\left(1 - \frac{1}{n}\right)}{C_p(n-1) + C_V\left(1 - \frac{1}{n}\right)}$

$$= 1 - \frac{n - 1 + \gamma\left(1 - \frac{1}{n}\right)}{\gamma(n-1) + \left(1 - \frac{1}{n}\right)} = 1 - \frac{1 + \frac{\gamma}{n}}{\gamma + \frac{1}{n}} = 1 - \frac{n + \gamma}{1 + n\gamma}$$

2.120 (a) Here $p_2 = np_1$, $p_1 V_1 = p_0 V_0$,

$$np_1 V_1^\gamma = p_0 V_0^\gamma$$

$$Q'_2 = RT_0 \ln \frac{V_0}{V_1}, \quad Q_1 = C_V T_0(n-1)$$

But $nV_1^{\gamma-1} = V_0^{\gamma-1}$ or, $V_1 = V_0 n^{\frac{-1}{\gamma-1}}$

$$Q'_2 = RT_0 \ln n^{\frac{1}{\gamma-1}} = \frac{RT_0}{\gamma-1} \ln n$$

Thus $\eta = 1 - \dfrac{\ln n}{n-1}$, on using $C_V = \dfrac{R}{\gamma-1}$

(b) Here $V_2 = nV_1$, $p_1 V_1 = p_0 V_0$

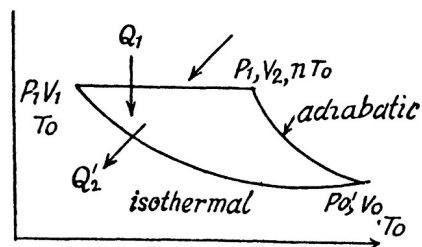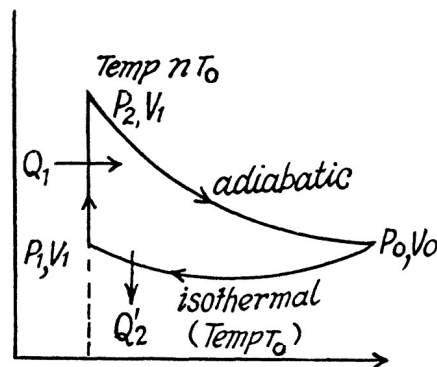and $p_1(nV_1)^\gamma = p_0 V_0^\gamma$

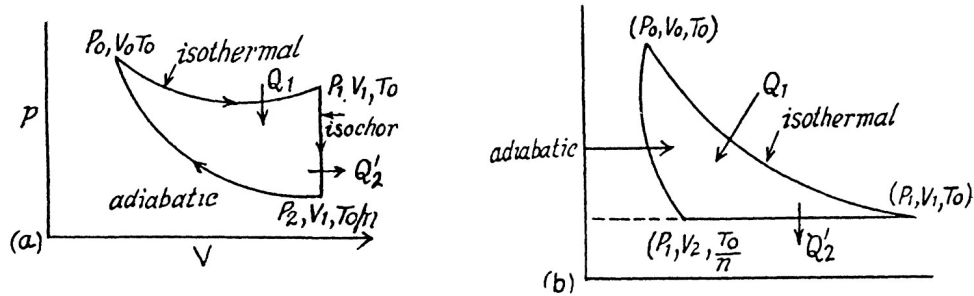i.e. $n^\gamma V_1^{\gamma-1} = V_0^{\gamma-1}$ or $V_1 = n^{-\frac{\gamma}{\gamma-1}} V_0$

Also $Q_1 = C_p T_0(n-1)$, $Q'_2 = RT_0 \ln \dfrac{V_0}{V_1}$

or $Q'_2 = RT_0 \ln n^{\frac{\gamma}{\gamma-1}} = \dfrac{R\gamma}{\gamma-1} T_0 \ln n = C_p T_0 \ln n$

Thus $\eta = 1 - \dfrac{\ln n}{n-1}$

2.121 Here the isothermal process proceeds at the maximum temperature instead of at the minimum temperature of the cycle as in 2.120.

(a) Here $p_1 V_1 = p_0 V_0$, $p_2 = \dfrac{p_1}{n}$

$$p_2 V_1^\gamma = p_0 V_0^\gamma \quad \text{or} \quad p_1 V_1^\gamma = n p_0 V_0^\gamma$$

i.e. $\qquad V_1^{\gamma-1} = n V_0^{\gamma-1} \quad \text{or} \quad V_1 = V_0 \, n^{\frac{1}{\gamma-1}}$

$$Q'_2 = C_V T_0 \left(1 - \frac{1}{n}\right), \quad Q_1 = R T_0 \ln \frac{V_1}{V_0} = \frac{R T_0}{\gamma - 1} \ln n = C_V T_0 \ln n.$$

Thus $\qquad \eta = 1 - \dfrac{Q'_2}{Q_1} = 1 - \dfrac{n-1}{n \ln n}$

(b) Here $V_2 = \dfrac{V_1}{n}$, $p_0 V_0 = p_1 V_1$

$$p_0 V_0^\gamma = p_1 V_2^\gamma = p_1 n^{-\gamma} V_1^\gamma = V_0^{-1} n^{-\gamma} V_1^{\gamma-1} \quad \text{or} \quad V_1 = n^{(\gamma/\gamma - 1)} V_0$$

$$Q'_2 = C_p T_0 \left(1 - \frac{1}{n}\right), \quad Q_1 = R T_0 \ln \frac{V_1}{V_0} = \frac{R\gamma}{\gamma - 1} T_0 \ln n = C_p T_0 \ln n$$

Thus $\qquad \eta = 1 - \dfrac{n-1}{n \ln n}$

2.122 The section from $(\dot p_1, V_1, T_0)$ to $(p_2, V_2, T_0/n)$ is a polytropic process of index α. We shall assume that the corresponding specific heat C is + ve.
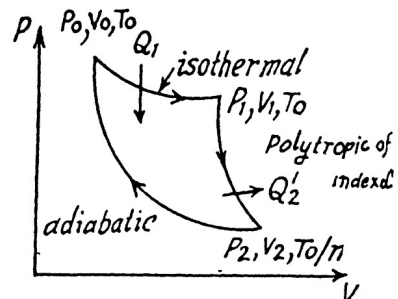
Here, $dQ = C dT = C_V dT + p dV$

Now $pV^\alpha = $ constant or $TV^{\alpha - 1} = $ constant.

so $pdV = \dfrac{RT}{V} dV = -\dfrac{R}{\alpha - 1} dT$

Then $C = C_V - \dfrac{R}{\alpha - 1} = R\left(\dfrac{1}{\gamma - 1} - \dfrac{1}{\alpha - 1}\right)$

We have $p_1 V_1 = R T_0 = p_2 V_2 = \dfrac{R T_0}{n} = \dfrac{p_1 V_1}{n}$

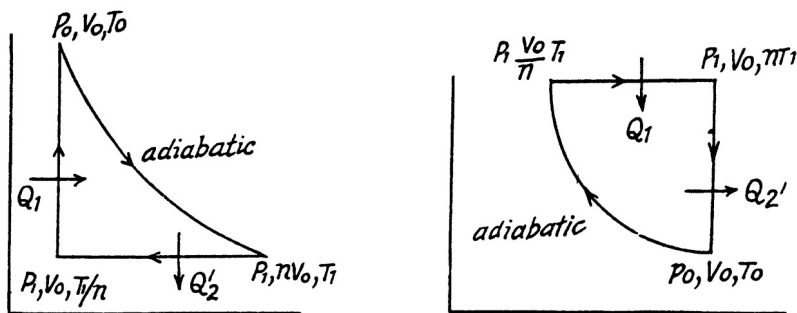$$p_0 V_0 = p_1 V_1 = n p_2 V_2, \, p_0 V_0^\gamma = p_2 V_2^\gamma,$$

$$p_1 V_1^{\alpha} = p_2 V_2^{\alpha} \quad \text{or} \quad V_0^{\gamma - 1} = \frac{1}{n} V_2^{\gamma - 1} \quad \text{or} \quad V_2 = V_0 \, n^{\frac{1}{\gamma - 1}}$$

$$V_1^{\alpha - 1} = \frac{1}{n} V_2^{\alpha - 1} \quad \text{or} \quad V_1 = n^{-\frac{1}{\alpha - 1}} V_2 = n^{\frac{1}{\gamma - 1} - \frac{1}{\alpha - 1}} V_0$$

Now $Q'_2 = CT_0 \left(1 - \frac{1}{n}\right)$, $Q_1 = RT_0 \ln \frac{V_1}{V_0} = RT_0 \left(\frac{1}{\gamma - 1} - \frac{1}{\alpha - 1}\right) \ln n = CT_0 \ln n$

Thus
$$\eta = 1 - \frac{n - 1}{n \ln n}$$

2.123

(a) Here $Q'_2 = C_p \left(T_1 - \frac{T_1}{n}\right) = C_p T_1 \left(1 - \frac{1}{n}\right)$, $Q_1 = C_V \left(T_0 - \frac{T_1}{n}\right)$

Along the adiabatic line
$$T_0 V_0^{\gamma - 1} = T_1 (n V_0)^{\gamma - 1} \quad \text{or,} \quad T_0 = T_1 n^{\gamma - 1}.$$

so $\quad Q_1 = C_V \dfrac{T_1}{n} (n^{\gamma} - 1)$. Thus $\eta = 1 - \dfrac{\gamma (n - 1)}{n^{\gamma - 1}}$

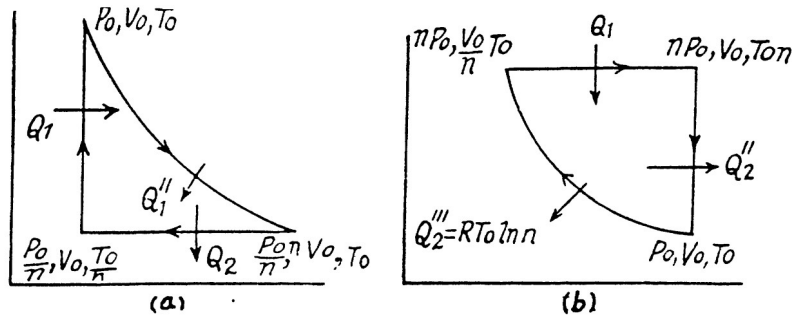(b) Here $Q'_2 = C_V (n T_1 - T_0)$, $Q_1 = C_p \cdot T_1 (n - 1)$

Along the adiabatic line $TV^{\gamma - 1} = $ constant
$$T_0 V_0^{\gamma - 1} = T_1 \left(\frac{V_0}{n}\right)^{\gamma - 1} \quad \text{or} \quad T_1 = n^{\gamma - 1} T_0$$

Thus
$$\eta = 1 - \frac{n^{\gamma} - 1}{\gamma \, n^{\gamma - 1} (n - 1)}$$

2.124

(a) $Q'_2 = C_p T_0 \left(1 - \dfrac{1}{n}\right)$, $Q''_1 = RT_0 \ln n$, $Q'_1 = C_V T_0 \left(1 - \dfrac{1}{n}\right)$, $Q_1 = Q'_1 + Q''_1$

So $\quad \eta = 1 - \dfrac{Q'_2}{Q_1} = 1 - \dfrac{C_p \left(1 - \dfrac{1}{n}\right)}{C_V \left(1 - \dfrac{1}{n}\right) + R \ln n}$

$= 1 - \dfrac{\gamma}{1 + \dfrac{R}{C_V} \dfrac{n \ln n}{n - 1}} = 1 - \dfrac{\gamma (n - 1)}{n - 1 + (\gamma - 1) n \ln n}$

(b) $Q_1 = C_p T_0 (n - 1)$, $Q''_2 = C_V T_0 (n - 1)$ $\quad Q'''_2 = RT_0 \ln n$, $Q'_2 = Q''_2 + Q'''_2$

So $\quad \eta = 1 - \dfrac{Q'_2}{Q_1} = 1 - \dfrac{n - 1 + (\gamma - 1) \ln n}{\gamma (n - 1)}$
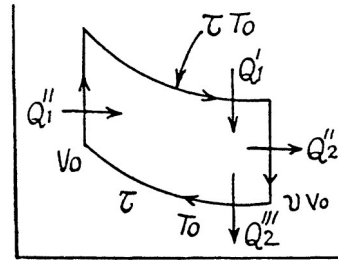
2.125 We have

$Q'_1 = \tau RT_0 \ln v$, $Q''_2 = C_V T_0 (\tau - 1)$ $Q_1 = Q'_1 + Q''_1$ and

$Q'''_2 = RT_0 \ln v$, $Q''_1 = C_V T_0 (\tau - 1)$

as well as $Q_1 = Q_1' + Q_1''$ and

$Q_2' = Q_2'' + Q_2'''$

So $\eta = 1 - \dfrac{Q'_2}{Q_1} + 1 = \dfrac{C_V (\tau - 1) + R \ln v}{C_V (\tau - 1) + \tau R \ln v}$

$= 1 - \dfrac{\dfrac{\tau - 1}{\gamma - 1} + \ln v}{\dfrac{\tau - 1}{\gamma - 1} + \tau \ln v} = \dfrac{(\tau - 1) \ln v}{\tau \ln v + \dfrac{\tau - 1}{\gamma - 1}}$

2.126 Here $Q_1'' = C_p T_0 (\tau - 1)$, $Q'1'' = \tau RT_0 \ln n$ and

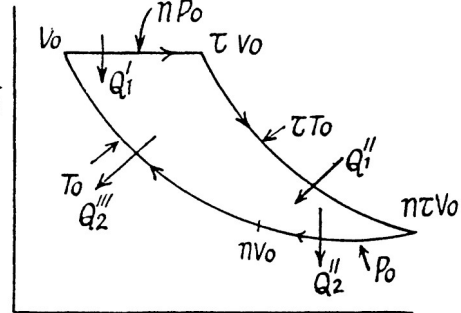$Q_2'' = C^p T_0 (\tau - 1)$, $Q_2''' = RT_0 \ln n$

in addition to we have

$Q_1 = Q_1' + Q_1''$ and

$Q_2' = Q_2'' + Q_2'''$

So $\quad \eta = 1 - \dfrac{Q'_2}{Q_1} = 1 - \dfrac{C_p (\tau - 1) + R \ln n}{C_p (\tau - 1) + \tau R \ln n}$

$= 1 - \dfrac{\tau - 1 + \left(1 - \dfrac{1}{\gamma}\right) \ln n}{\tau - 1 + \left(1 - \dfrac{1}{\gamma}\right) \tau \ln n}$

$= 1 - \dfrac{\tau - 1 + \left(1 - \dfrac{1}{\gamma}\right) \ln n}{\tau - 1 + \left(1 - \dfrac{1}{\gamma}\right) \tau \ln n} = \dfrac{(\tau - 1) \ln n}{\tau \ln n + \dfrac{\gamma (\tau - 1)}{\gamma - 1}}$

2.127 Because of the linearity of the section

BC whose equation is

$$\frac{p}{p_0} = \frac{vV}{V_0} \, (\equiv p = \alpha V)$$

We have $\frac{\tau}{v} = v$ or $v = \sqrt{\tau}$

Here $Q''_2 = C_V T_0 (\sqrt{\tau} - 1),$

$$Q'''_2 = C_p T_0 \left(1 - \frac{1}{\sqrt{\tau}}\right) = C_p \frac{T_0}{\sqrt{\tau}} (\sqrt{\tau} - 1)$$
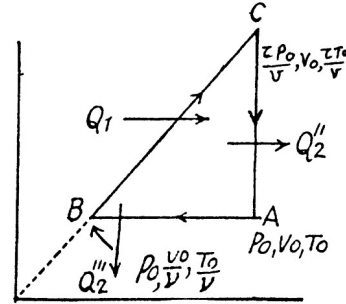
Thus $Q'_2 = Q''_2 + Q'''_2 = \frac{RT_0}{\gamma - 1} (\sqrt{\tau} - 1)\left(1 + \frac{\gamma}{\sqrt{\tau}}\right)$

Along BC, the specific heat C is given by

$$CdT = C_V dT + pdV = C_V dT + d\left(\frac{1}{2}\alpha V^2\right) = \left(C_V + \frac{1}{2}R\right)dT$$

Thus $\qquad Q_1 = \frac{1}{2} R \, T_0 \frac{\gamma + 1}{\gamma - 1} \frac{\tau - 1}{\sqrt{\tau}}$

Finally $\qquad \eta = 1 - \frac{Q'_2}{Q_1} = 1 - 2 \frac{\sqrt{\tau} + \gamma}{\sqrt{\tau} + 1} \frac{1}{\gamma + 1} = \frac{(\gamma - 1)(\sqrt{\tau} - 1)}{(\gamma + 1)(\sqrt{\tau} + 1)}$

2.128 We write Claussius inequality in the form

$$\int \frac{d_1 Q}{T} - \int \frac{d_2 Q}{T} \leq 0$$

where $d'Q$ is the heat transeferred to the system but $d_2 Q$ is heat rejected by the system, both are +ve and this explains the minus sign before $d_2 Q$,

In this inequality $T_{max} > T > T_{min}$ and we can write

$$\int \frac{d_1 Q}{T_{max}} - \int \frac{d_2 Q}{T_{min}} < 0$$

Thus $\qquad \frac{Q_1}{T_{max}} < \frac{Q'_2}{T_{min}}$ or $\frac{T_{min}}{T_{max}} < \frac{Q'_2}{Q_1}$

or $\qquad \eta = 1 - \frac{Q'_2}{Q_1} < 1 - \frac{T_{min}}{T_{max}} = \eta_{carnot}$

2.129 We consider an infinitesimal carnot cycle with isothermal process at temperatures $T + dT$ and T.

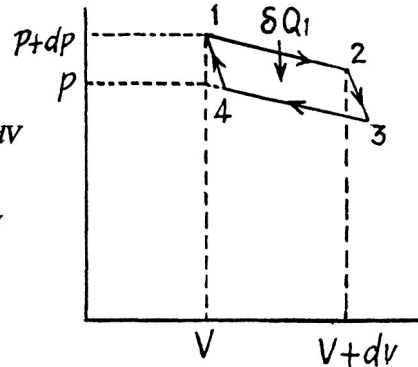Let δA be the work done in the cycle and δQ, be the heat received at the higher temperature. Then by Carnot's theorem

$$\frac{\delta A}{\delta Q_1} = \frac{dT}{T}$$

On the other hand $\delta A = dp\, dV = \left(\frac{\partial p}{\partial T}\right)_v dT\, dV$

while $\delta Q_1 = dU_{12} + pdV = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV$

Hence $\left(\frac{\partial U}{\partial V}\right)_T + p = T\left(\frac{\partial p}{\partial T}\right)_v$

2.130 (a) In an isochoric process the entropy change will be

$$\Delta S = \int\limits_{T_i}^{T_f} \frac{C_V dT}{T} = C_V \ln\frac{T_f}{T_i} = C_V \ln n = \frac{R \ln n}{\gamma - 1}$$

For carbon dioxide $\gamma = 1\cdot30$

so, $\Delta S = 19\cdot2$ Joule/°K – mole
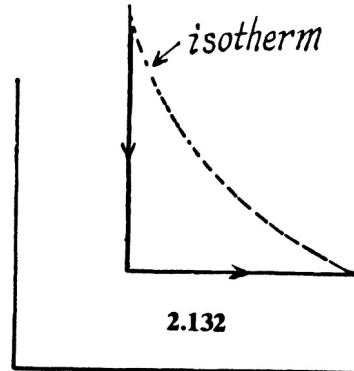
(b) For an isobaric process,

$$\Delta S = C_p \ln\frac{T_f}{T_i} = C_p \ln n = \frac{\gamma R \ln n}{\gamma - 1}$$

$= 25$ Joule/°K – mole

2.131 In an isothermal expansion

$$\Delta S = \nu R \ln\frac{V_f}{V_i}$$

so, $\dfrac{V_f}{V_i} = e^{\Delta S/\nu R} = 2\cdot0$ times

2.132 The entropy change depends on the final & initial states only, so we can calculate it directly along the isotherm, it is $\Delta S = 2R\ln n = 20$ J/°K

(assuming that the final volume is n times the inital volume)

2.133 If the initial temperature is T_0 and volume is V_0 then in adiabatic expansion.

$$TV^{\gamma-1} = T_0 V_0^{\gamma-1}$$

so, $T = T_0 n^{1-\gamma} = T_1$ where $n = \dfrac{V_1}{V_0}$

V_1 being the volume at the end of the adiabatic process. There is no entropy change in this process. Next the gas is compressed isobarically and the net entropy change is

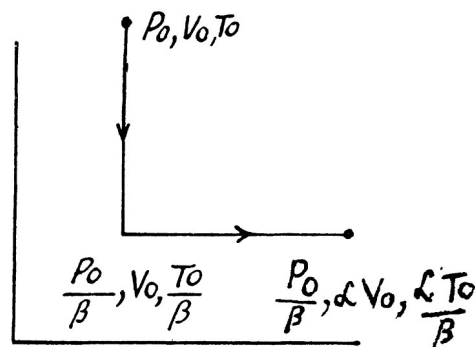$$\Delta S = \left(\frac{m}{M}C_p\right)\ln\frac{T_f}{T_1}$$

But $\qquad \dfrac{V_1}{T_1} = \dfrac{V_0}{T_f}$, or $T_f = T_1\dfrac{V_0}{V_1} = T_0\,n^{-\gamma}$

So $\quad \Delta S = \left(\dfrac{m}{M}C_p\right)\ln\dfrac{1}{n} = -\dfrac{m}{M}C_p\ln n = -\dfrac{m}{M}\dfrac{R\gamma}{\gamma-1}\ln n = -9\cdot7\,\text{J/K}$

2.134 The entropy change depends on the initial and final state only so can be calculated for any process whatsoever.

We choose to evaluate the entropy change along the pair of lines shown above. Then

$$\Delta S = \int\limits_{T_0}^{\frac{T_0}{\beta}} \frac{\nu C_V\,dT}{T} + \int\limits_{\frac{T_0}{\beta}}^{\frac{\alpha T_0}{\beta}} \nu\,C_p\,\frac{dT}{T}$$

$= (-C_V\ln\beta + C_p\ln\alpha)\,\nu = \dfrac{\nu R}{\gamma-1}(\gamma\ln\alpha - \ln\beta) \approx -11\,\dfrac{\text{Joule}}{^\circ\text{K}}$

2.135 To calculate the required entropy difference we only have to calculate the entropy difference for a process in which the state of the gas in vessel 1 is changed to that in vessel 2.

$$\Delta S = \nu\left(\int\limits_{T_1}^{\frac{T_1}{\alpha\beta}} C_V\frac{dT}{T} + \int\limits_{\frac{T_1}{\alpha\beta}}^{\frac{T_1}{\beta}} C_p\frac{dT}{T}\right)$$

$= \nu\,(C_p\ln\alpha - C_V\ln\alpha\beta)$

$= \nu\left(R\ln\alpha - \dfrac{R}{\gamma-1}\ln\beta\right) = \nu R\left(\ln\alpha - \dfrac{\ln\beta}{\gamma-1}\right)$

With $\gamma = \dfrac{5}{3}$, $\alpha = 2$ and $\beta = 1\cdot5$, $\nu = 1\cdot2$,

this gives $\Delta S = 0\cdot85\,\text{Joule}/^\circ\text{K}$
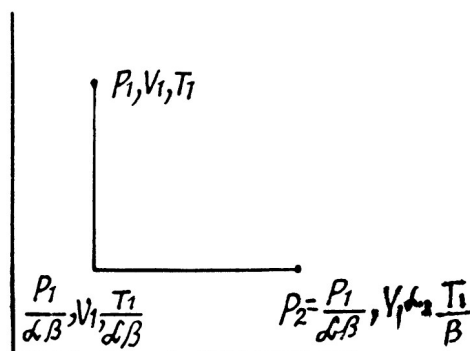
2.136 For the polytropic process with index n

$$p\,V^n = \text{constant}$$

Along this process (See 2.122)

$$C = R\left(\frac{1}{\gamma-1} - \frac{1}{n-1}\right) = \frac{n-\gamma}{(\gamma-1)(n-1)}\cdot R$$

So $\qquad \Delta S = \int\limits_{T_0}^{\tau T_0} C\,\dfrac{dT}{T} = \dfrac{n-\gamma}{(\gamma-1)(n-1)}R\ln\tau$

2.137 The process in question may be written as

$$\frac{p}{p_0} = \alpha \frac{V}{V_0}$$

where α is a constant and p_0, V_0 are some reference values. For this process (see 2.127) the specific heat is

$$C = C_V + \frac{1}{2}R = R\left(\frac{1}{\gamma - 1} + \frac{1}{2}\right) = \frac{1}{2}R\frac{\gamma + 1}{\gamma - 1}$$

Along the line volume increases α times then so does the pressure. The temperature must then increase α^2 times. Thus

$$\Delta S = \int_{T_0}^{\alpha^2 T_0} \nu C \frac{dT}{T} = \frac{\nu R}{2}\frac{\gamma + 1}{\gamma - 1}\ln \alpha^2 = \nu R \frac{\gamma + 1}{\gamma - 1}\ln \alpha$$

if $\quad\quad \nu = 2, \gamma = \frac{5}{3}, \alpha = 2, \Delta S = 46 \cdot 1 \text{ Joule/}^\circ\text{K}$

2.138 Let (p_1, V_1) be a reference point on the line

$$p = p_0 - \alpha V$$

and let (p, V) be any other point.
The entropy difference

$$\Delta S = S(p, V) - S(p_1, V_1)$$

$$= C_V \ln \frac{p}{p_1} + C_p \ln \frac{V}{V_1} = C_V \ln \frac{p_0 - \alpha V}{p_1} + C_p \ln \frac{V}{V_1}$$

For an exetremum of ΔS

$$\frac{\partial \Delta S}{\partial V} = \frac{-\alpha C_V}{p_0 - \alpha V} + \frac{C_p}{V} = 0$$

or $\quad C_p(p_0 - \alpha V) - \alpha V C_V = 0$

or $\quad \gamma(p_0 - \alpha V) - \alpha V = 0 \quad$ or $\quad V = V_m = \dfrac{\gamma p_0}{\alpha(\gamma + 1)}$

This gives a maximum of ΔS because $\dfrac{\partial^2 \Delta S}{\partial V^2} < 0$
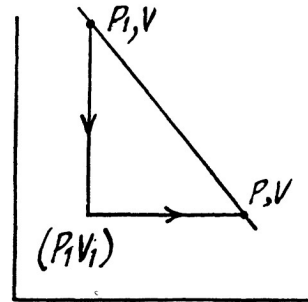
(Note :- a maximum of ΔS is a maximum of $S(p, V)$)

2.139 Along the process line : $S = aT + C_V \ln T$

or the specific heat is : $C = T\dfrac{dS}{dT} = aT + C_V$

On the other hand : $dQ = CdT = C_V dT + pdV$ for an ideal gas.

Thus, $\quad\quad\quad\quad\quad pdV = \dfrac{RT}{V}dV = aT\,dT$

or $\qquad \dfrac{R}{a}\dfrac{dV}{V} = dT$ or, $\dfrac{R}{a}\ln V + \text{constant} = T$

Using $\qquad T = T_0$ when $V = V_0$, we get, $T = T_0 + \dfrac{R}{a}\ln\dfrac{V}{V_0}$

2.140 For a Vander Waal gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

The entropy change along an isotherm can be calculated from

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

It follows from (2.129) that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V - b}$$

assuming a, b to be known constants.

Thus $\qquad \Delta S = R\ln\dfrac{V_2 - b}{V_1 - b}$

2.141

We use, $\Delta S = \displaystyle\int_{V_1, T_1}^{V_2, T_2} dS\,(V, T) = \int_{T_1}^{T_2}\left(\frac{\partial S}{\partial T}\right)_{V_1} dT + \int_{V_1}^{V_2}\left(\frac{\partial S}{\partial V}\right)_{T=T_2} dV$

$$= \int_{T_1}^{T_2} \frac{C_V\,dT}{T} + \int_{V_1}^{V_2} \frac{R}{V - b}\,dV = C_V\ln\frac{T_2}{T_1} + R\ln\frac{V_2 - b}{V_1 - b}$$

assuming C_V, a, b to be known constants.

2.142 We can take $S \to 0$ as $T \to 0$ Then

$$S = \int_0^T C\frac{dT}{T} = \int_0^T aT^2\,dT = \frac{1}{3}aT^3$$

2.143 $\Delta S = \displaystyle\int_{T_1}^{T_2} \frac{C\,dT}{T} = \int_{T_1}^{T_2} \frac{m(a + bT)}{T}\,dT = mb\,(T_2 - T_1) + ma\ln\frac{T_2}{T_1}$

2.144 Here $T = aS^n$ or $S = \left(\dfrac{T}{a}\right)^{\frac{1}{n}}$

Then $\qquad C = T\dfrac{1}{n}\dfrac{T^{\frac{1}{n}-1}}{a^{1/n}} = \dfrac{S}{n}$

Clearly $\qquad C < 0$ if $n < 0$.

2.145 We know,

$$S - S_0 = \int_{T_0}^{T} \frac{CdT}{T} = C \ln \frac{T}{T_0}$$

assuming C to be a known constant.

Then $\qquad T = T_0 \exp\left(\dfrac{S - S_0}{C}\right)$

2.146 (a) $C = T\dfrac{dS}{dT} = -\dfrac{\alpha}{T}$

(b) $Q = \displaystyle\int_{T_1}^{T_2} CdT = \alpha \ln\dfrac{T_1}{T_2}$

(c) $W = \Delta Q - \Delta U \qquad = \alpha \ln\dfrac{T_1}{T_2} + C_V(T_1 - T_2)$

Since for an ideal gas C_V is constant
and $\Delta U = C_V(T_2 - T_1)$

(U does not depend on V)

2.147 (a) We have from the definition

$Q = \displaystyle\int TdS = $ area under the curve

$Q_1 = T_0(S_1 - S_0)$
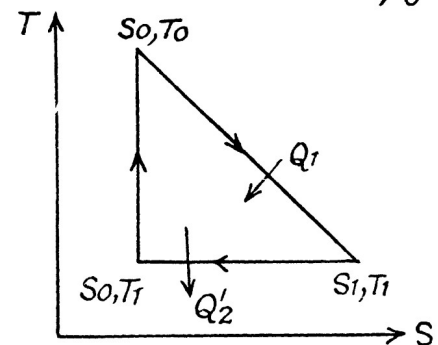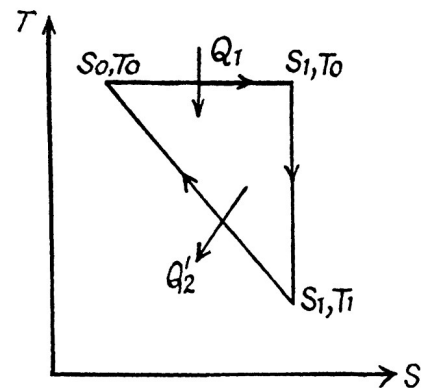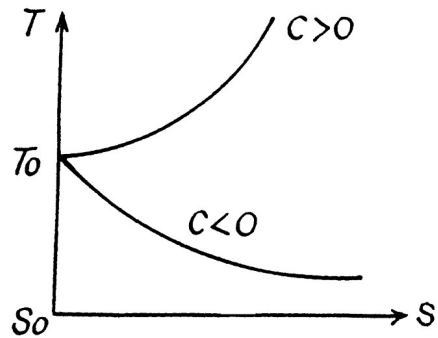
$Q'_2 = \dfrac{1}{2}(T_0 + T_1)(S_1 - S_0)$

Thus, using $T_1 = \dfrac{T_0}{n}$,

$$\eta = 1 - \frac{T_0 + T_1}{2T_0} = 1 - \frac{1 + \dfrac{1}{n}}{2} = \frac{n-1}{2n}$$

(b) Here $Q_1 = \dfrac{1}{2}(S_1 - S_0)(T_1 + T_0)$

$Q'_2 = T_1(S_1 - S_0)$

$$\eta = 1 - \frac{2T_1}{T_1 + T_0} = \frac{T_0 - T_1}{T_0 - T_1} = \frac{n-1}{n+1}$$

2.148 In this case, called free expansion no work is done and no heat is exchanged. So internal energy must remain unchanged $U_f = U_i$. For an ideal gas this implies constant temperature $T_f = T_i$. The process is irreversible but the entropy change can be calculated by considering a reversible isothermal process. Then, as before

$$\Delta S = \int \frac{dQ}{T} = \int_{V_1}^{V_2} \frac{pdV}{T} = \nu R \ln n = 20.1 \text{ J/K}$$

2.149 The process consists of two parts. The first part is free expansion in which $U_f = U_i$. The second part is adiabatic compression in which work done results in change of internal energy. Obviously,

$$0 = U_F - U_f + \int_{V_f}^{V_0} pdV, \quad V_f = 2V_0$$

Now in the first part $p_f = \frac{1}{2}p_0$, $V_f = 2V_0$, because there is no change of temperature.

In the second part, $p\, V^\gamma = \frac{1}{2}p_0\,(2V_0)^\gamma = 2^{\gamma-1}p_0\,V_0^\gamma$

$$\int_{2V_0}^{V_0} pdV = \int_{2V_0}^{V_0} \frac{2^{\gamma-1}p_0 V_0^\gamma}{V^\gamma} dV = \left[\frac{2^{\gamma-1}p_0 V_0^\gamma}{-\gamma+1} V^{1-\gamma} \right]_{2V_0}^{V_0}$$

$$= 2^{\gamma-1}p_0 V_0^\gamma V_0^{-\gamma+1} \frac{2^{-\gamma+1}-1}{\gamma-1} = -\frac{(2^{\gamma-1}-1)}{\gamma-1}RT$$

Thus
$$\Delta U = U_F - U_i = \frac{RT_0}{\gamma-1}(2^{\gamma-1}-1)$$

The entropy change $\Delta S = \Delta S_I + \Delta S_{II}$

$\Delta S_I = R \ln 2$ and $\Delta S_{II} = 0$ as the process is reversible adiabatic. Thus $\Delta S = R \ln 2$.

2.150 In all adiabatic processes
$$Q = U_f - U_i + A = 0$$
by virtue of the first law of thermodynamics. Thus,
$$U_f = U_i - A$$

For a slow process, $A' = \int_{V_0}^{V} pdV$ where for a quasistatic adiabatic process $pV^\gamma = $ constant.

On the other hand for a fast process the external work done is $A'' < A'$. In fact $A'' = 0$ for free expansion. Thus U'_f (slow) $< U''_f$ (fast)

Since U depends on temperature only, $T'_f < T''_f$

Consequently, $p''_f > p'_f$

(From the ideal gas equation $pV = RT$)

2.151 Let $V_1 = V_0$, $V_2 = n V_0$

Since the temperature is the same, the required entropy change can be calculated by considering isothermal expansion of the gas in either parts into the whole vessel.

Thus
$$\Delta S = \Delta S_I + \Delta S_{II} = v_1 R \ln \frac{V_1 + V_2}{V_1} + v_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$= v_1 R \ln (1 + n) + v_2 R \ln \frac{1 + n}{n} = 5 \cdot 1 \text{ J/K}$$

2.152 Let c_1 = specific heat of copper specific heat of water = c_2

Then
$$\Delta S = \int_{7 + 273}^{T_0} \frac{c_2 m_2 \, dT}{T} - \int_{T_0}^{97 + 273} \frac{m_1 c_1 \, dT}{T} = m_2 c_2 \ln \frac{T_0}{280} - m_1 c_1 \ln \frac{370}{T_0}$$

T_0 is found from

$$c_2 m_2 (T_0 - 280) = m_1 c_1 (370 - T_0) \quad \text{or} \quad T_0 = \frac{280 \, m_2 c_2 + 370 \, m_1 c_1}{c_2 m_2 + m_1 c_1}$$

using
$$c_1 = 0 \cdot 39 \text{ J/g } °K, \quad c_2 = 4 \cdot 18 \text{ J/g } °K,$$

$$T_0 = 300°K \text{ and } \Delta S = 28 \cdot 4 - 24 \cdot 5 = 3 \cdot 9 \text{ J / }°K$$

2.153 For an ideal gas the internal energy depends on temperature only. We can consider the process in question to be one of simultaneous free expansion. Then the total energy $U = U_1 + U_2$. Since

$$U_1 = C_V T_1, \quad U_2 = C_V T_2, \quad U = 2C_V \frac{T_1 + T_2}{2} \text{ and } (T_1 + T_2)/2 \text{ is the final temperature. The}$$

entropy change is obtained by considering isochoric processes because in effect, the gas remains confined to its vessel.

$$\Delta S = \int_{T_1}^{(T_1 + T_2)/2} \frac{C_V \, dT}{T} - \int_{(T_1 + T_2)/2}^{T_2} C_V \frac{dT}{T} = C_V \ln \frac{(T_1 + T_2)^2}{4 T_1 T_2}$$

Since
$$(T_1 + T_2)^2 = (T_1 - T_2)^2 + 4 T_1 T_2, \quad \Delta S > 0$$

2.154 (a) Each atom has a probability $\frac{1}{2}$ to be in either compartment. Thus

$$p = 2^{-N}$$

(b) Typical atomic velocity at room temperature is $\sim 10^5$ cm/s so it takes an atom 10^{-5} sec to cross the vessel. This is the relevant time scale for our problem. Let $T = 10^{-5}$ sec, then in time t there will be t/T crossing or arrangements of the atoms. This will be large enough to produce the given arrangement if

$$\frac{t}{\tau} 2^{-N} \sim 1 \quad \text{or} \quad N \sim \frac{\ln t/\tau}{\ln 2} \sim 75$$

2.155 The statistical weight is

$$N_{C_{N/2}} = \frac{N!}{N/2\,!\,\dfrac{N}{2}!} = \frac{10 \times 9 \times 8 \times 7 \times 6}{8 \times 4 \times 3 \times 2} = 252$$

The probability distribution is

$$N_{C_{N/2}}\,2^{-N} = 252 \times 2^{-10} = 24{\cdot}6\,\%$$

2.156 The probabilites that the half A contains n molecules is

$$N_{C_n} \times 2^{-N} = \frac{N!}{n!\,(N-n)!}\,2^{-N}$$

2.157 The probability of one molecule being confined to the marked volume is

$$p = \frac{V}{V_0}$$

We can choose this molecule in many (N_{C_1}) ways. The probability that n molecules get confined to the marked volume is cearly

$$N_{C_n}\,p^{n}\,(1-p)^{N-n} = \frac{N!}{n!\,(N-n)!}\,p^{n}\,(1-p)^{N-n}$$

2.158 In a sphere of diameter d there are

$$N = \frac{\pi d^3}{6}\,n_0 \quad \text{molecules}$$

where $n_0 =$ Loschmidt's number = No. of molecules per unit volume (1 cc) under NTP. The relative fluctuation in this number is

$$\frac{\partial N}{N} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} = \eta$$

or $\quad \dfrac{1}{\eta^2} = \dfrac{\pi}{6}\,d^3\,n_0 \quad$ or $\quad d^3 = \dfrac{6}{\pi n_0 \eta^2} \quad$ or $\quad d = \left(\dfrac{6}{\pi \eta^2 n_0}\right)^{1/3} = 0{\cdot}41\ \mu\text{m}$

The average number of molecules in this sphere is $\dfrac{1}{\eta^2} = 10^6$

2.159 For a monoatomic gas $C_V = \dfrac{3}{2}R$ per mole

The entropy change in the process is

$$\Delta S = S - S_0 = \int_{T_0}^{T_0 + \Delta T} C_V\frac{dT}{T} = \frac{3}{2}R \ln\left(1 + \frac{\Delta T}{T_0}\right)$$

Now from the Boltzmann equation

$$S = k \ln \Omega$$

$$\frac{\Omega}{\Omega_0} = e^{(S - S_0)/k} = \left(1 + \frac{\Delta T}{T_0}\right)^{\frac{3N_A}{2}} = \left(1 + \frac{1}{300}\right)^{\frac{3 \times 6}{2} \times 10^{23}} = 10^{13} \times 10^{21}$$

Thus the statistical weight increases by this factor.

2.5 LIQUIDS. CAPILLARY EFFECTS

2.160

(a) $\Delta p = \alpha \left(\dfrac{1}{d/2} + \dfrac{1}{d/2}\right) = \dfrac{4\alpha}{d}$

$$= \frac{4 \times 490 \times 10^{-3}}{1\cdot5 \times 10^{-6}} \frac{N}{m^2} = 1\cdot307 \times 10^6 \frac{N}{m^2} = 13 \text{ atmosphere}$$

(b) The soap bubble has two surfaces

so $\qquad \Delta p = 2\alpha \left(\dfrac{1}{d/2} + \dfrac{1}{d/2}\right) = \dfrac{8\alpha}{d}$

$$= \frac{8 \times 45}{3 \times 10^{-3}} \times 10^{-3} = 1\cdot2 \times 10^{-3} \text{ atomsphere.}$$

2.161 The pressure just inside the hole will be less than the outside pressure by $4\,\alpha/d$. This can support a height h of Hg where

$$\rho g h = \frac{4\alpha}{d} \quad \text{or} \quad h = \frac{4\alpha}{\rho g d}$$

$$= \frac{4 \times 490 \times 10^{-3}}{13\cdot6 \times 10^3 \times 9\cdot8 \times 70 \times 10^{-6}} = \frac{200}{13\cdot6 \times 70} \approx \cdot21 \text{ m of Hg}$$

2.162 By Boyle's law

$$\left(p_0 + \frac{8\alpha}{d}\right)\frac{4\pi}{3}\left(\frac{d}{2}\right)^3 = \left(\frac{p_0}{n} + \frac{8\alpha}{\eta d}\right)\frac{4\pi}{3}\left(\frac{\eta\,d}{2}\right)^3$$

or $\qquad p_0\left(1 - \dfrac{\eta^3}{n}\right) = \dfrac{8\alpha}{d}(\eta^2 - 1)$

Thus $\qquad \alpha = \dfrac{1}{8}p_0\,d\left(1 - \dfrac{\eta^3}{n}\right)(\eta^2 - 1)$

2.163 The pressure has terms due to hydrostatic pressure and capillarity and they add

$$p = p_0 + \rho g h + \frac{4\alpha}{d}$$

$$= \left(1 + \frac{5 \times 9\cdot8 \times 10^3}{10^5} + \frac{4 \times \cdot73 \times 10^{-3}}{4 \times 10^{-6}} \times 10^{-5}\right) \text{atoms} = 2\cdot22 \text{ atom.}$$

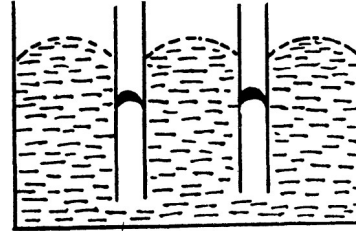**2.164** By Boyle's law

$$\left(p_0 + h\,g\,\rho + \frac{4\alpha}{d}\right)\frac{\pi}{6}d^3 = \left(p_0 + \frac{4\alpha}{nd}\right)\frac{\pi}{6}n^3\,d^3$$

or $\qquad \left[h g\rho - p_0(n^3 - 1)\right] = \dfrac{4\alpha}{d}(n^2 - 1)$

or $\qquad h = \left[p_0(n^3 - 1) + \dfrac{4\alpha}{d}(n^2 - 1)\right]\Big/ g\,\rho = 4\cdot98 \text{ meter of water}$

2.165 Clearly

$$\Delta h \, \rho \, g = 4\,\alpha \,|\cos\theta\,| \left(\frac{1}{d_1} - \frac{1}{d_2}\right)$$

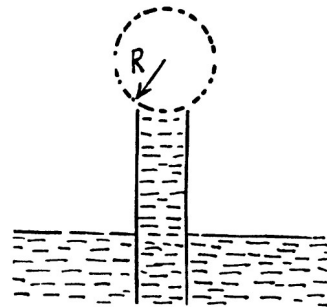$$\Delta h = \frac{4\,\alpha\,|\cos\theta\,|\,(d_2 - d_1)}{d_1 \, d_2 \, \rho g} = 11 \text{ mm}$$

2.166 In a capillary with diameter $d = 0.5$ mm water will rise to a height

$$\frac{2\alpha}{\rho\,g\,r} = \frac{4\alpha}{\rho\,g\,d}$$

$$= \frac{4 \times 73 \times 10^{-3}}{10^3 \times 9.8 \times 0.5 \times 10^{-3}} = 59.6 \text{ mm}$$

Since this is greater than the height (= 25 mm) of the tube, a meniscus of radius R will be formed at the top of the tube, where

$$R = \frac{2\alpha}{\rho\,gh} = \frac{2 \times 73 \times 10^{-3}}{10^3 \times 9.8 \times 25 \times 10^{-3}} \approx 0.6 \text{ mm}$$

2.167 Initially the pressure of air in the cppillary is p_0 and it's length is l. When submerged under water, the pressure of air in the portion above water must be $p_0 + 4\dfrac{\alpha}{d}$, since the level of water inside the capillary is the same as the level outside. Thus by Boyle's law

$$\left(p_0 + \frac{4\alpha}{d}\right)(l - x) = p_0\, l$$

or $\qquad \dfrac{4\alpha}{d}(l - x) = p_0\, x \quad$ or $\quad x = \dfrac{l}{1 + \dfrac{p_0\, d}{4\alpha}}$

2.168 We have by Boyle's law

$$\left(p_0 - \rho g h + \frac{4\,\alpha\cos\theta}{d}\right)(l - h) = p_0\, l$$

or, $\qquad \dfrac{4\,\alpha\cos\theta}{d} = \rho\,gh + \dfrac{p_0\, h}{l - h}$

Hence, $\qquad \alpha = \left(\rho\,gh + \dfrac{p_0\, h}{l - h}\right)\dfrac{d}{4\cos\theta}$

2.169 Suppose the liquid rises to a height h. Then the total energy of the liquid in the capillary is

$$E\,(h) = \frac{\pi}{4}\,(d_2^2 - d_1^2)\, h \times \rho g \times \frac{h}{2} - \pi\,(d_2 - d_1)\,\alpha h$$
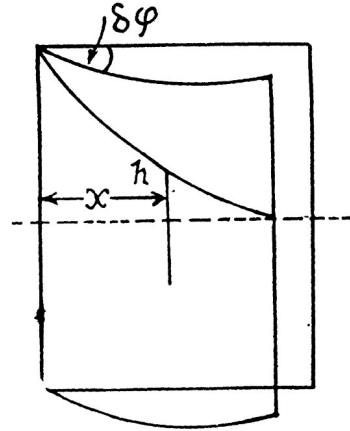
Minimising E we get

$$h = \frac{4\alpha}{\rho g\,(d_2 - d_1)} = 6 \text{ cm.}$$

2.170 Let h be the **height of the water level at a distance** x **from the edge. Then the total energy of water in the wedge above the level outside is.**

$$E = \int x\,\delta\varphi\cdot dx\cdot h\cdot\rho g\frac{h}{2} - 2\int dx\cdot h\cdot\alpha\cos 0$$

$$= \int dx\,\frac{1}{2}x\,\rho\,g\,\delta\varphi\left(h^2 - 2\frac{2\,\alpha\cos\theta}{x\,\rho\,g\,\delta\varphi}h\right)$$

$$= \int dx\,\frac{1}{2}x\,\rho g\,\delta\varphi\left[\left(h - \frac{2\,\alpha\cos\theta}{x\,\rho\,g\,\delta\varphi}\right)^2 - \frac{4\,\alpha^2\cos^2\theta}{x^2\,\rho^2\,g^2\,\delta\,\varphi^2}\right]$$

This is minimum when $h = \dfrac{2\,\alpha\cos\theta}{x\,\rho\,g\,\delta\varphi}$

2.171 From the equation of continuity

$$\frac{\pi}{4}d^2\cdot v = \frac{\pi}{4}\left(\frac{d}{n}\right)^2\cdot V \quad\text{or}\quad V = n^2 v.$$

We then apply Bernoulli's theorem

$$\frac{p}{\rho} + \frac{1}{2}v^2 + \Phi = \text{constant}$$

The pressure p differs from the **atmospheric pressure** by capillary effects. At the **upper** section

$$p = p_0 + \frac{2\alpha}{d}$$

neglecting the curvature in the vertical plane. Thus,

$$\frac{p_0 + \dfrac{2\alpha}{d}}{\rho} + \frac{1}{2}v^2 + gl = \frac{p_0 + \dfrac{2n\alpha}{d}}{\rho} + \frac{1}{2}n^4 v^2$$

or

$$v = \sqrt{\frac{2gl - \dfrac{4\alpha}{\rho d}(n-1)}{n^4 - 1}}$$

Finally, the liquid coming out per second is,

$$V = \frac{1}{4}\pi d^2\sqrt{\frac{2gl - \dfrac{4\alpha}{\rho d}(n-1)}{n^4 - 1}}$$

2.172 The radius of curvature of the drop is R_1 at the upper end of the drop and R_2 at the lower end. Then the pressure inside the drop is $p_0 + \dfrac{2\alpha}{R_1}$ at the top end and $p_0 + \dfrac{2\alpha}{R_2}$ at the bottom end. Hence

$$p_0 + \frac{2\alpha}{R_1} = p_0 + \frac{2\alpha}{R_2} + \rho gh \quad\text{or}\quad \frac{2\,\alpha\,(R_2 - R_1)}{R_1 R_2} = \rho gh$$

To a first approximation $R_1 \approx R_2 \approx \dfrac{h}{2}$ so $R_2 - R_1 \approx \dfrac{1}{8}\rho\,gh^3/\alpha. \approx 0.20$ mm

if $\qquad\qquad h = 2\cdot3$ mm, $\alpha = 73$ mN/m

2.173 We must first calculate the pressure difference inside the film from that outside. This is

$$p = \alpha \left(\frac{1}{r_1} + \frac{1}{r_2} \right).$$

Here $2 r_1 |\cos \theta| = h$ and $r_2 \sim -R$ the radius of the tablet and can be neglected. Thus the total force exerted by mercury drop on the upper glass plate is

$$\frac{2 \pi R^2 \alpha |\cos \theta|}{h} \quad \text{typically}$$

We should put h / n for h because the tablet is compresed n times. Then since Hg is nearly, incompressible, $\pi R^2 h = $ constants so $R \to R\sqrt{n}$. Thus,
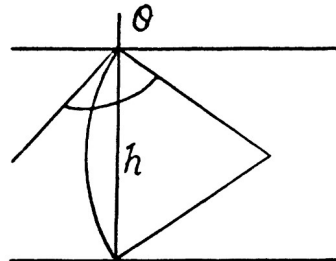
$$\text{total force} = \frac{2 \pi R^2 \alpha |\cos \theta|}{h} n^2$$

Part of the force is needed to keep the Hg in the shape of a table rather than in the shape of infinitely thin sheet. This part can be calculated being putting $n = 1$ above. Thus

$$mg + \frac{2 \pi R^2 \alpha |\cos \theta|}{h} = \frac{2 \pi R^2 \alpha |\cos \theta|}{h} n^2$$

or

$$m = \frac{2 \pi R^2 \alpha |\cos \theta|}{hg} (n^2 - 1) = 0 \cdot 7 \, \text{kg}$$

2.174 The pressure inside the film is less than that outside by an amount $\alpha \left(\dfrac{1}{r_1} + \dfrac{1}{r_2} \right)$ where r_1 and r_2 are the principal radii of curvature of the meniscus. One of these is small being given by $h = 2 r_1 \cos \theta$ while the other is large and will be ignored. Then

$$F \approx \frac{2 A \cos \theta}{h} \alpha \quad \text{where } A = \text{area of the water film between the plates.}$$

Now $A = \dfrac{m}{\rho h}$ so $F = \dfrac{2 m \alpha}{\rho h^2}$ when θ (the angle of contact) $= 0$

2.175 This is analogous to the previous problem except that : $A = \pi R^2$

So

$$F = \frac{2 \pi R^2 \alpha}{h} = 0 \cdot 6 \ \text{kN}$$

2.176 The energy of the liquid between the plates is

$$E = l \, d \, h \, \rho \, g \frac{h}{2} - 2 \alpha l h = \frac{1}{2} \rho \, g \, l \, d \, h^2 - 2 \alpha l h$$

$$= \frac{1}{2} \rho \, g \, l \, d \left(h - \frac{2 \alpha}{\rho \, g \, d} \right)^2 - \frac{2 \alpha^2 l}{\rho \, g \, d}$$

This energy is minimum when, $h = \dfrac{2 \alpha}{\rho \, g \, d}$ and
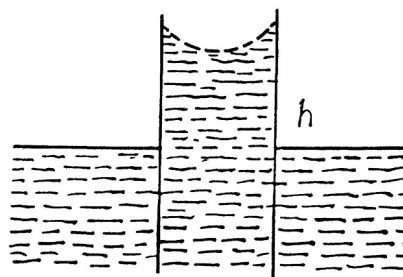
the minimum potential energy is then $E_{\text{min}} = -\dfrac{2 \alpha^2 l}{\rho \, g \, d}$

The force of attraction between the plates can be obtained from this as

$$F = \frac{- \partial E_{\text{min}}}{\partial d} = -\frac{2 \alpha^2 l}{\rho \, g \, d^2} \ (\text{minus sign means the force is attractive.})$$

Thus

$$F = -\frac{\alpha \, l \, h}{d} = 13 \, \text{N}$$

2.177 Suppose the radius of the bubble is x at some instant. Then the pressure inside is $p_0 + \dfrac{4\alpha}{x}$. The flow through the capillary is by Poiseuille's equation,

$$Q = \frac{\pi r^4}{8 \eta l}\frac{4\alpha}{x} = -4\pi^2\frac{dx}{dt}$$

Integrating $\dfrac{\pi r^4 \alpha}{2\eta l}t = \pi(R^4 - x^4)$ where we have used the fact that $t = 0$ where $x = R$.

This gives $t = \dfrac{2\eta l R^4}{\alpha r^4}$ as the life time of the bubble corresponding to $x = 0$

2.178 If the liquid rises to a height h, the energy of the liquid column becomes

$$E = \rho g \pi r^2 h \cdot \frac{h}{2} - 2\pi r h \alpha = \frac{1}{2}\rho g \pi \left(r h - 2\frac{\alpha}{\rho g}\right)^2 - \frac{2\pi \alpha^2}{\rho g}$$

This is minimum when $rh = \dfrac{2\alpha}{\rho g}$ and that is relevant height to which water must rise.

At this point, $\qquad E_{\min} = -\dfrac{2\pi\alpha^2}{\rho g}$

Since $E = 0$ in the absence of surface tension a heat $Q = \dfrac{2\pi\alpha^2}{\rho g}$ must have been liberated.

2.179 (a) The free energy per unit area being α,

$$F = \pi \alpha d^2 = 3\ \mu J$$

(b) $F = 2\pi\alpha d^2$ because the soap bubble has two surfaces. Substitution gives $F = 10\ \mu J$

2.180 When two mercury drops each of diameter d merge, the resulting drop has diameter d_1

where $\qquad \dfrac{\pi}{6}d_1^3 = \dfrac{\pi}{6}d^3 \times 2 \quad$ or, $\quad d_1 = 2^{1/3}d$

The increase in free energy is

$$\Delta F = \pi 2^{2/3} d^2 \alpha - 2\pi d^2 \alpha = 2\pi d^2 \alpha (2^{-1/3} - 1) = -1{\cdot}43\ \mu J$$

2.181 Work must be done to stretch the soap film and compress the air inside. The former is simply $2\alpha \times 4\pi R^2 = 8\pi R^2\alpha$, there being two sides of the film. To get the latter we note that the compression is isothermal and work done is

$$-\int_{V_i = V_0}^{V_f = V} p dV \quad \text{where} \quad V_0 p_0 = \left(p_0 + \frac{4\alpha}{R}\right)\cdot V,\ V = \frac{4\pi}{3}R^3$$

or $\qquad V_0 = \dfrac{pV}{p_0},\ p = p_0 + \dfrac{4\alpha}{R}$

and minus sign is needed becaue we are calculating work done on the system. Thus since pV remains constants, the work done is

$$pV \ln\frac{V_0}{V} = pV\ln\frac{p}{p_0}$$

So $\qquad A' = 8\pi R^2 \alpha + pV\ln\dfrac{p}{p_0}$

2.182 When heat is given to a soap bubble the temperature of the air inside rises and the bubble expands but unless the bubble bursts, the amount of air inside does not change. Further we shall neglect the variation of the surface tension with temperature. Then from the gas equations

$$\left(p_0 + \frac{4\,\alpha}{r}\right)\frac{4\,\pi}{3}r^3 = \nu R\,T, \quad \nu = \text{Constant}$$

Differentiating

$$\left(p_0 + \frac{8\alpha}{3r}\right)4\,\pi\,r^2\,dr = \nu R\,d\,T$$

or

$$dV = 4\,\pi\,r^2\,dr = \frac{\nu R dT}{p_0 + \frac{8\,\alpha}{3r}}$$

Now from the first law

$$\text{d}\,Q = \nu CdT = \nu\,C_V\,dT + \frac{\nu R\,dT}{p_0 + \frac{8\alpha}{3r}}\cdot\left(p_0 + \frac{4\alpha}{r}\right)$$

or

$$C = C_V + R\,\frac{p_0 + \frac{4\alpha}{r}}{p_0\,\frac{8\alpha}{3r}}$$

using

$$C_p = C_V + R,\quad C = C_p + \frac{\frac{1}{2}R}{1 + \frac{3\,p_0\,r}{8\alpha}}$$

2.183 Consider an infinitesimal Carnot cycle with isotherms at $T - dT$ and T. Let A be the work done during the cycle. Then

$$A = [\alpha\,(T - dT) - \alpha\,(T)\,]\,\delta\,\sigma = -\frac{d\alpha}{dT}\,dT\,\delta\sigma$$

Where $\delta\sigma$ is the change in the area of film (we are considering only one surface).

Then $\eta = \dfrac{A}{Q_1} = \dfrac{dT}{T}$ by Carnot theorm.

or $\dfrac{-\dfrac{d\alpha}{dT}\,dT\,\delta\,\sigma}{q\,\delta\,\sigma} = \dfrac{dT}{T}$ or $q = -T\dfrac{d\alpha}{dT}$
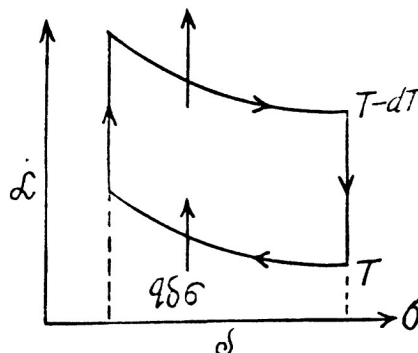
2.184 As before we can calculate the heat required. It, is taking into account two sides of the soap film

$$\delta q = -T\frac{d\alpha}{dT}\,\delta\,\sigma \times 2$$

Thus

$$\Delta S = \frac{\delta q}{T} = -2\frac{d\alpha}{dT}\,\delta\,\sigma$$

Now $\quad \Delta F = 2\,\alpha\,\delta\,\sigma\quad$ so, $\quad\Delta U = \Delta F + T\,\Delta S = 2\left(\alpha - T\frac{d\alpha}{dT}\right)\delta\sigma$

2.6 PHASE TRANSFORMATIONS

2.185 The condensation takes place at constant pressure and temperature and the work done is

$$p \Delta V$$

where ΔV is the volume of the condensed vapour in the vapour phase. It is

$$p \Delta V = \frac{\Delta m}{M} RT = 120 \cdot 6 \text{ J}$$

where $M = 18$ gm is the molecular weight of water.

2.186 The specific volume of water (the liquid) will be written as V'_l. Since $V'_v > > V'_l$, most of the weight is due to water. Thus if m_l is mass of the liquid and m_v that of the vapour then

$$m = m_l + m_v$$

$$V = m_l V'_l + m_v V'_v \quad \text{or} \quad V - mV'_l = m_v (V'_v - V'_l)$$

So $m_v = \dfrac{V - mV'_l}{V'_v - V'_1} = 20$ gm in the present case. Its volume is $m_v V'_v = 1 \cdot 01$

2.187 The volume of the condensed vapour was originally $V_0 - V$ at temperature $T = 373$ K. Its mass will be given by

$$p (V_0 - V) = \frac{m}{M} RT \quad \text{or} \quad m = \frac{Mp (V_0 - V)}{RT} = 2 \text{ gm where } p = \text{ atmospheric pressure}$$

2.188 We let $V'_l =$ specific volume of liquid. $V'_v = N V'_l =$ specific volume of vapour.

Let $V =$ Original volume of the vapour. Then

$$M \frac{pV}{RT} = m_l + m_v = \frac{V}{N V'_l} \quad \text{or} \quad \frac{V}{n} = (m_l + Nm_v) V'_l$$

So $(N - 1) m_l V'_l = V \left(1 - \dfrac{1}{n} \right) = \dfrac{V}{n} (n - 1) \quad \text{or} \quad \eta = \dfrac{m_l V'_l}{V/n} = \dfrac{n - 1}{N - 1}$

In the case when the final volume of the substance corresponds to the midpoint of a horizontal portion of the isothermal line in the p, v diagram, the final volume must be $(1 + N) \dfrac{V'_l}{2}$ per unit mass of the substance. Of this the volume of the liquid is $V'_l/2$ per unit total mass of the substance.

Thus $\qquad\qquad\qquad \eta = \dfrac{1}{1 + N}$

2.189 From the first law of thermodynamics

$$\Delta U + A = Q = m q$$

where q is the specific latent heat of vaporization

Now $\qquad\qquad A = p (V'_v - V'_l) m = m \dfrac{RT}{M}$

Thus $\qquad\qquad \Delta U = m \left(q - \dfrac{RT}{M} \right)$

For water this gives $\approx 2 \cdot 08 \times 10^6$ Joules.

2.190 Some of the heat used in heating water to the boiling temperature

$$T = 100°C = 373 \text{ K. The remaining heat}$$

$$= Q - m c \Delta T$$

(c = specific heat of water, ΔT = 100 K) is used to create vapour. If the piston rises to a height h then the volume of vapour will be ~ sh(neglecting water). Its mass will be $\dfrac{p_0 \, sh}{RT} \times M$ and heat of vapourization will be $\dfrac{p_0 \, sh \, Mq}{RT}$. To this must be added the work done in creating the saturated vapour ~ $p_0 \, sh$. Thus

$$Q - m c \Delta T \approx p_0 S h \left(1 + \frac{qM}{RT}\right) \quad \text{or} \quad h = \frac{Q - m c \Delta T}{p_0 s \left(1 + \dfrac{qM}{RT}\right)} = 20 \text{ cm}$$

2.191 A quantity $\dfrac{mc\,(T - T_0)}{q}$ of saturated vapour must condense to heat the water to boiling point $T = 373°K$

(Here c = specific heat of water, T_0 = 295 K = initial water temperature).

The work done in lowering the piston will then be

$$\frac{mc\,(T - T_0)}{q} \times \frac{RT}{M} = 25 \text{ J,}$$

since work done per unit mass of the condensed vapour is $p\,V = \dfrac{RT}{M}$

2.192 Given $\Delta P = \dfrac{\rho_v}{\rho_l} \dfrac{2\alpha}{r} = \dfrac{\rho_v}{\rho_l} \times \dfrac{4\alpha}{d} = \eta\, p_{vap} = \eta\, \dfrac{\dfrac{m}{M} RT}{V_{vap}} = \dfrac{\eta\, RT}{M}\, \rho_v$

or $$d = \frac{4\alpha M}{\rho_1 RT \eta}$$

For water $\alpha = 73$ dynes/cm, $M = 18$gm, $\rho_l = $ gm/cc, $T = 300$ K, and with $\eta \approx 0.01$, we get

$$d \approx 0.2 \, \mu \, m$$

2.193 In equilibrium the number of "liquid" molecules evaporoting must equals the number of "vapour" molecules condensing. By kinetic theory, this number is

$$\eta \times \frac{1}{4} n <v> = \eta \times \frac{1}{4} n \times \sqrt{\frac{8}{\pi} \frac{kT}{m}}$$

Its mass is

$$\mu = m \times \eta \times n \times \sqrt{\frac{kT}{2\pi m}} = \eta\, n\, kT \sqrt{\frac{m}{2\pi kt}}$$

$$= \eta\, p_0 \sqrt{\frac{M}{2\pi RT}} = 0.35 \text{ g/cm}^2 \cdot \text{s.}$$

where p_0 is atmospheric pressure and $T = 373$ K and M = molecular weight of water.

2.194 Here we must assume that μ is also the rate at which the tungsten filament loses mass when in an atmosphere of its own vapour at this temperature and that η (of the previous problem) $\approx$ 1. Then

$$p = \mu \sqrt{\frac{2\pi RT}{M}} = 0\cdot9 \text{ n Pa}$$

from the previous problem where $p =$ pressure of the saturated vapour.

2.195 From the Vander Waals equation

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

where $V =$ Volume of one gm mole of the substances.

For water $V = $ 18 c.c. per mole $=$ $1\cdot8 \times 10^{-2}$ litre per mole

$$a = 5\cdot47 \text{ atmos} \cdot \frac{\text{litre}^2}{\text{mole}^2}$$

If molecular attraction vanished the equation will be

$$p' = \frac{RT}{V-b}$$

for the same specific volume. Thus

$$\Delta p = \frac{a}{V^2} = \frac{5\cdot47}{1\cdot8 \times 1\cdot8} \times 10^4 \text{ atmos} \approx 1\cdot7 \times 10^4 \text{ atmos}$$

2.196 The internal pressure being $\frac{a}{V^2}$, the work done in condensation is

$$\int_{V_l}^{V_g} \frac{a}{V^2} dV = \frac{a}{V_l} - \frac{a}{V_g} \approx \frac{a}{V_l}$$

This by assumption is Mq, M being the molecular weight and V_l, V_g being the molar volumes of the liquid and gas.

Thus
$$p_i = \frac{a}{V_l^2} = \frac{Mq}{V_l} = \rho q$$

where ρ is the density of the liquid. For water $p_i \approx 3\cdot3 \times 10^{13}$ atm

2.197 The Vandar Waal's equation can be written as (for one mole)

$$p(V) = \frac{RT}{V-b} - \frac{a}{V^2}$$

At the critical point $\left(\frac{\partial p}{\partial V}\right)_T$ and $\left(\frac{\partial^2 p}{\partial V^2}\right)_T$ vanish. Thus

$$0 = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad \text{or} \quad \frac{RT}{(V-b)^2} = \frac{2a}{V^3}$$

$$0 = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \quad \text{or} \quad \frac{RT}{(V-b)^3} = \frac{3a}{V^4}$$

Solving these simultaneously we get on division

$$V - b = \frac{2}{3} V, \quad V = 3 b = V_{MCr}$$

This is the critical molar volume. Putting this back

$$\frac{R T_{Cr}}{4 b^2} = \frac{2a}{27 b^3} \quad \text{or} \quad T_{Cr} = \frac{8a}{27 bR}$$

Finally $\qquad p_{Cr} = \dfrac{RT_{Cr}}{V_{MCr} - b} - \dfrac{a}{V_{MCr}^2} = \dfrac{4a}{27 b^2} - \dfrac{a}{9 b^2} = \dfrac{a}{27 b^2}$

From these we see that $\qquad \dfrac{p_{Cr} V_{MCr}}{RT_{Cr}} = \dfrac{a/9b}{8a/27 b} = \dfrac{3}{8}$

2.198 $\dfrac{P_{Cr}}{RT_{Cr}} = \dfrac{a/27 b^2}{8 a/27 b} = \dfrac{1}{8 b}$

Thus $\qquad b = R \dfrac{T_{Cr}}{8 p_{Cr}} = \dfrac{0.082 \times 304}{73 \times 8} = 0.043 \text{ litre/mol}$

and $\qquad \dfrac{(RT_{Cr})^2}{p_{Cr}} = \dfrac{64a}{27} \quad \text{or} \quad a = \dfrac{27}{64}(RT_{Cr})^2/p_{Cr} = 3.59 \dfrac{\text{atm·litre}^2}{(\text{mol})^2}$

2.199 Specific volume is molar volume divided by molecular weight. Thus

$$V_{Cr} = \frac{V_{MCr}}{M} = \frac{3 RT_{Cr}}{8 M p_{Cr}} = \frac{3 \times .082 \times 562}{8 \times 78 \times 47} \frac{\text{litre}}{g} = 4.71 \frac{\text{cc}}{g}$$

2.200 $\left(p + \dfrac{a}{V_M^2}\right)(V_m - b) = RT$

or $\qquad \dfrac{p + \dfrac{a}{V_m^2}}{P_{Cr}} \times \dfrac{V_m - b}{V_{MCr}} = \dfrac{8}{3} \dfrac{T}{T_{Cr}}$

or $\qquad \left(\pi + \dfrac{a}{p_{Cr} V_m^2}\right) \times \left(v - \dfrac{b}{V_{MCr}}\right) = \dfrac{8}{3} \tau,$

where $\qquad \pi = \dfrac{p}{p_{Cr}}, \ v = \dfrac{V_m}{V_{MCr}}, \ \tau = \dfrac{T}{T_{Cr}}$

or $\qquad \left(\pi + \dfrac{27 b^2}{V_M^2}\right)\left(v - \dfrac{1}{3}\right) = \dfrac{8}{3} \tau, \quad \text{or} \quad \left(\pi + \dfrac{3}{v^2}\right)\left(v - \dfrac{1}{3}\right) = \dfrac{8}{3} \tau$

When $\qquad \pi = 12 \text{ and } v = \dfrac{1}{2}, \ \tau = \dfrac{3}{8} \times 24 \times \dfrac{1}{6} = \dfrac{3}{2}$

2.201 (a) The ciritical Volume V_{MCr} is the maximum volume in the liquid phase and the minimum volume in the gaseous. Thus

$$V_{max} = \frac{1000}{18} \times 3 \times .030 \text{ litre} = 5 \text{ litre}$$

(b) The critical pressure is the maximum possible pressure in the vapour phase in equilibrium with liquid phase. Thus

$$p_{max} = \frac{a}{27\,b^2} = \frac{5\cdot47}{27 \times \cdot03 \times \cdot03} = 225\,\text{atmosphere}$$

2.202 $T_{Cr} = \dfrac{8}{27}\dfrac{a}{bR} = \dfrac{8}{27} \times \dfrac{3\cdot62}{\cdot043 \times \cdot082} \approx 304\ \text{K}$

$$\rho_{Cr} = \frac{M}{3b} = \frac{44}{3 \times 43}\,\text{gm/c.c.} = 0\cdot34\,\text{gm/c.c.}$$

2.203 The vessel is such that either vapour or liquid of mass m occupies it at critical point. Then its volume will be

$$v_{Cr} = \frac{m}{M}\,V_{MCr} = \frac{3}{8}\frac{RT_{Cr}}{p_{Cr}}\frac{m}{M}$$

The corresponding volume in liquid phase at room temperature is

$$V = \frac{m}{\rho}$$

where $\rho =$ density of liquid ether at room tmeperature. Thus

$$\eta = \frac{V}{V_{Cr}} = \frac{8\,Mp_{Cr}}{3\,RT_{Cr}\,\rho} \approx 0\cdot254$$

using the given data (and $\rho = 720\,$gm per litre)

2.204 We apply the relation $(T = \text{constant})$

$$T\oint\ dS = \oint\ dU + \oint\ pdV$$

to the cycle 1234531.

Here $\oint\ dS = \oint\ dU = 0$

So $\oint\ pdV = 0$

This implies that the areas I and II are equal. This reasoning is inapplicable to the cycle 1231, for example. This cycle is irreversible because it involves the irreversible transition from a single phase to a two-phase state at the point 3.
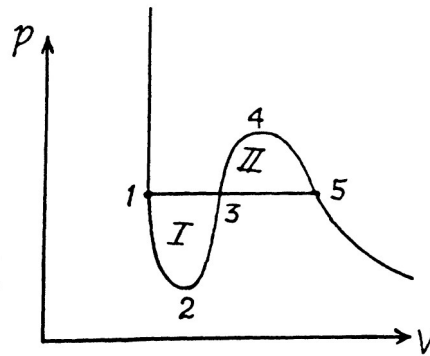
2.205 When a portion of supercool water turns into ice some heat is liberated, which should heat it upto ice point. Neglecting the variation of specific heat of water, ·the fraction of water turning inot ice is clearly

$$f = \frac{c\,|t|}{q} = 0\cdot25$$

where $c =$ specific heat of water and $q =$ latent heat of fusion of ice, Clearly $f = 1$ at $t = -80°C$

2.206 From the Claussius-Clapeyron $(C-C)$ equations

$$\frac{dT}{dp} = \frac{T\left(V'_2 - V'_1\right)}{q_{12}}$$

q_{12} is the specific latent heat absorbed in $1 \rightarrow 2$ $(1 = \text{solid}, 2 = \text{liquid})$

$$\Delta T = \frac{T\left(V'_w - V'_{ice}\right)}{q_{12}} \Delta p = -\frac{273 \times \cdot 091}{333} \times 1 \frac{\text{atm} \times \text{cm}^3 \times \text{K}}{\text{joule}}$$

$$1 \frac{\text{atm} \times \text{cm}^3}{\text{Joule}} \approx \frac{10^5 \frac{\text{N}}{\text{m}^2} \times 10^{-6} \text{m}^3}{\text{Joule}} = 10^{-1}, \ \Delta T = - \cdot 0075 \text{ K}$$

2.207 Here $1 = \text{liquid}$, $2 = \text{Steam}$

$$\Delta T = \frac{T\left(V'_s - V'_{liq}\right)}{q_{12}} \Delta P$$

or

$$V'_s \approx \frac{q_{12}}{T} \frac{\Delta T}{\Delta p} = \frac{2250}{373} \times \frac{0\cdot9}{3\cdot2} \times 10^{-3} \text{ m}^3/\text{g} = 1\cdot7 \text{ m}^3/\text{kg}$$

2.208 From $C\text{-}C$ equations

$$\frac{dp}{dT} = \frac{q_{12}}{T(V'_2 - V'_1)} \approx \frac{q_{12}}{TV'_2}$$

Assuming the saturated vapour to be ideal gas

$$\frac{1}{V'_2} = \frac{mp}{RT}, \ \text{Thus} \ \Delta p = \frac{Mq}{RT^2} p \Delta T$$

and

$$p \approx p_0 \left(1 + \frac{Mq}{RT^2} \Delta T\right) = 1\cdot04 \text{ atmosphere}$$

2.209 From $C\text{-}C$ equation, neglecting the voolume of the liquid

$$\frac{dp}{dT} = \frac{q_{12}}{TV'_2} = \frac{Mq}{RT^2} p, \ (q = q_{12})$$

or

$$\frac{dp}{p} = \frac{Mq}{RT} \frac{dT}{T}$$

Now

$$pV = \frac{m}{M} RT \ \text{or} \ m = \frac{MpV}{RT} \ \text{for a perfect gas}$$

So

$$\frac{dm}{m} = \frac{dp}{p} - \frac{dT}{T} \ (V \text{ is Const} = \text{specific volume})$$

$$= \left(\frac{Mq}{RT} - 1\right) \frac{dT}{T} = \left(\frac{18 \times 2250}{8\cdot3 \times 373} - 1\right) \times \frac{1\cdot5}{373} \approx 4\cdot85 \ \%$$

2.210 From C-C equation

$$\frac{dp}{dT} = \frac{q}{TV_2} = \frac{Mq}{RT^2}p$$

Integrating $\quad \ln p = \text{constant} - \frac{Mq}{RT}$

So $\qquad p = p_0 \exp\left[\frac{Mq}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$

This is reasonable for $|T - T_0| \ll T_0$, and far below critical temperature.

2.211 As before (2.206) the lowering of melting point is given by

$$\Delta T = -\frac{T\,\Delta V'}{q}\,p$$

The superheated ice will then melt in part. The fraction that will melt is

$$\eta = \frac{C\,T\,\Delta V'}{q^2}\,p \approx \cdot 03$$

2.212 (a) The equations of the transition lines are

$$\log p = 9\cdot05 - \frac{1800}{T}: \text{ Solid gas}$$

$$= 6\cdot78 - \frac{1310}{T}: \text{ Liquid gas}$$

At the triple point they intersect. Thus

$$2\cdot27 = \frac{490}{T_{tr}} \quad \text{or} \quad T_{tr} = \frac{490}{2\cdot27} = 216\,\text{K}$$

corresponding p_{tr} is 5.14 atmosphere.

In the formula $\log p = a - \dfrac{b}{T}$, we compare b with the corresponding term in the equation in 2.210. Then

$$\ln p = a \times 2\cdot303 - \frac{2\cdot303\,b}{T} \quad \text{So,} \quad 2\cdot303 = \frac{Mq}{R}$$

or, $\qquad q_{sublimation} = \dfrac{2\cdot303 \times 1800 \times 8\cdot31}{44} = 783\,\text{J/gm}$

$$q_{liquid-gas} = \frac{2\cdot303 \times 1310 \times 8\cdot31}{44} = 570\,\text{J/gm}$$

Finally $q_{solid-liquid} = 213\,\text{J/gm}$ on subtraction

2.213 $\Delta S = \displaystyle\int_{T_1}^{T_2} mc\,\frac{dT}{T} + \frac{mq}{T_2} = m\left(c\ln\frac{T_2}{T_1} + \frac{q}{T_2}\right)$

$$= 10^3\left(4\cdot18\ln\frac{373}{283} + \frac{2250}{373}\right) \approx 7\cdot2\,\text{kJ/K}$$

2.214 $\Delta S = \dfrac{q_m}{T_1} + c \ln \dfrac{T_2}{T} + \dfrac{q_v}{T_2}$

$$= \dfrac{333}{273} + 4\cdot18 \ln \dfrac{373}{283} \approx 8\cdot56 \text{ J/°K}$$

2.215 $c =$ specific heat of copper $= 0\cdot39 \dfrac{\text{J}}{\text{g}\cdot\text{K}}$. Suppose all ice does not melt, then

heat rejected $= 90 \times 0\cdot39 \, (90-0) = 3159$ J

heat gained by ice $= 50 \times 2\cdot09 \times 3 + x \times 333$

Thus $x = 8\cdot5$ gm

The hypothesis is correct and final temperature will be $T = 273$K.

Hence change in entropy of copper piece

$$= mc \ln \dfrac{273}{363} = -10 \text{ J/K}.$$

2.216 (a) Here $t_2 = 60$°C. Suppose the final temperature is t °C. Then

$$\text{heat lost by water} = m_2 \, c \, (t_2 - t)$$

$$\text{heat gained by ice} = m_1 \, q_m + m_1 \, c \, (t - t_1), \text{ if all ice melts}$$

In this case $m_1 \, q_m = m_2 \times 4\cdot18 \, (60 - t)$, for $m_1 = m_2$

So the final temperature will be 0°C and only some ice will melt.

Then $100 \times 4\cdot18 \, (60) = m'_1 \times 333$

$m'_1 = 75\cdot3$ gm $=$ amount of ice that will melt

Finally $\Delta S = 75\cdot3 \times \dfrac{333}{273} + 100 \times 4\cdot18 \ln \dfrac{273}{333}$

$$\Delta S = \dfrac{m'_1 \, q_m}{T_1} + m_2 \, c \ln \dfrac{T_1}{T_2}$$

$$= m_2 \, c \, \dfrac{(T_2 - T_1)}{T_1} - m_2 \ln \dfrac{T_2}{T_1}$$

$$= m_2 \, C \left[\dfrac{T_2}{T_1} - 1 - \ln \dfrac{T_2}{T_1} \right] = 8\cdot8 \text{ J/K}$$

(b) If $m_2 \, c \, t_2 > m_1 \, q_m$ then all ice will melt as one can check and the final temperature can be obtained like this

$$m_2 \, c \, (T_2 - T) = m_1 \, q_m + m_1 \, c \, (T - T_1)$$

$$(m_2 \, T_2 + m_1 \, T_1) \, c - m_1 \, q_m = (m_1 + m_2) \, cT$$

or $T = \dfrac{m_2 \, T_2 + m_1 \, T_1 - \dfrac{m_1 \, q_m}{c}}{m_1 + m_2} = 280$ K

and $\Delta S = \dfrac{m_1 \, q}{T_1} + c \left(m_1 \ln \dfrac{T}{T_1} - m_2 \ln \dfrac{T_2}{T} \right) = 19$ J/K

2.217 $\Delta S = -\dfrac{m\,q_1}{T_2} - mc\ln\dfrac{T_2}{T_1} + \dfrac{M\,q_{ice}}{T_1}$

where $M\,q_{ice} = m\left(q_2 + c\,(T_2 - T_1)\right)$

$$= mq_2\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + mc\left(\frac{T_2}{T_1} - 1 - \frac{T_2}{T_1}\right)$$

$$= 0{\cdot}2245 + 0{\cdot}2564 \approx 0{\cdot}48\,\text{J/K}$$

2.218 When heat dQ is given to the vapour its temperature will change by dT, pressure by dp and volume by dV, it being assumed that the vapour remains saturated.
Then by C-C equation

$$\frac{dp}{dT} = \frac{q}{TV'}\,(V'_{vapour} \gg V'_{Liq}), \quad\text{or}\quad dp = \frac{q}{TV'}\,dT$$

on the other hand, $pV' = \dfrac{RT}{M}$

So $\qquad\qquad pdV' + V'\,dp = \dfrac{RdT}{M}$,

Hence $\qquad\qquad pdV' = \left(\dfrac{R}{M} - \dfrac{q}{T}\right)dT$

finally $\qquad\qquad dQ = CdT = dU + pdV'$

$$= C_V dT + \left(\frac{T}{M} - \frac{q}{T}\right)dT = C_p\,dT - \frac{q}{T}\,dT$$

$(C_p,\ C_V$ refer to unit mass here). Thus

$$C = C_p - \frac{q}{T}$$

For water $C_p = \dfrac{R\gamma}{\gamma - 1}\cdot\dfrac{1}{M}$ with $\gamma = 1{\cdot}32$ and $M = 18$

So $\qquad\qquad C_p = 1{\cdot}90\,\text{J/gm K}$

and $\qquad\qquad C = -4{\cdot}13\,\text{J/gm}^\circ\text{K} = -74\,\text{J/mole K}$

2.219 The required entropy change can be calculated along a process in which the water is heated from T_1 to T_2 and then allowed to evaporate. The entropy change for this is

$$\Delta S = C_p\ln\frac{T_2}{T_1} + \frac{qM}{T_2}$$

where $q =$ specific latent heat of vaporization.

2.7 TRANSPORT PHENOMENA

2.220 (a) The fraction of gas molecules which traverses distances exceeding the mean free path without collision is just the probability to traverse the distance $s = \lambda$ without collision.

Thus $\qquad P = e^{-1} = \dfrac{1}{e} = 0.37$

(b) This probability is
$$P = e^{-1} - e^{-2} = 0.23$$

2.221 From the formula
$$\frac{1}{\eta} = e^{-\Delta l/\lambda} \quad \text{or} \quad \lambda = \frac{\Delta l}{\ln \eta}$$

2.222 (a) Let $P(t)$ = probability of no collision in the interval $(0, t)$. Then
$$P(t + dt) = P(t)(1 - \alpha\, dt)$$

or $\qquad \dfrac{dP}{dt} = -\alpha P(t) \quad \text{or} \quad P(t) = e^{-\alpha t}$

where we have used $P(0) = 1$

(b) The mean interval between collision is also the mean interval of no collision. Then

$$<t> = \frac{\displaystyle\int_0^\infty t e^{-\alpha t}\, dt}{\displaystyle\int_0^\infty e^{-\alpha t}\, dt} = \frac{1}{\alpha}\frac{\Gamma(2)}{\Gamma(1)} = \frac{1}{\alpha}$$

2.223 (a) $\lambda = \dfrac{1}{\sqrt{2}\,\pi d^2 n} = \dfrac{kT}{\sqrt{2}\,\pi d^2 p}$

$$= \frac{1.38 \times 10^{-23} \times 273}{\sqrt{2}\,\pi\,(0.37 \times 10^{-9})^2 \times 10^5} = 6.2 \times 10^{-8}\,\text{m}$$

$$\tau = \frac{\lambda}{<v>} = \frac{6.2 \times 10^{-8}}{454}\,s = 0.136\,\text{n s}$$

$\lambda = 6.2 \times 10^6\,\text{m}$

(b) $\eta = 1.36 \times 10^4\,\text{s} = 3.8\,\text{hours}$

2.224 The mean distance between molecules is of the order

$$\left(\frac{22.4 \times 10^{-3}}{6.0 \times 10^{23}}\right)^{1/3} = \left(\frac{224}{6}\right)^{1/3} \times 10^{-9}\,\text{meters} \approx 3.34 \times 10^{-9}\,\text{meters}$$

This is about 18.5 times smaller than the mean free path calculated in 2.223 (a) above.

2.225 We know that the Vander Waal's constant b is four times the molecular volume. Thus

$$b = 4 N_A \frac{\pi}{6} d^3 \quad \text{or} \quad d = \left(\frac{3b}{2\pi N_A}\right)^{1/3}$$

Hence $\qquad \lambda = \left(\frac{kT_0}{\sqrt{2}\,\pi p_0}\right)\left(\frac{2\pi N_A}{3b}\right)^{2/3}$

2.226 The volocity of sound in N_2 is

$$\sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{\gamma RT}{M}}$$

so,

$$\frac{1}{v} = \sqrt{\frac{\gamma RT_0}{M}} = \frac{RT_0}{\sqrt{2}\,\pi\, d^2 p_0\, N_A}$$

or,

$$v = \pi\, d^2 p_0\, N_A \sqrt{\frac{2\gamma}{MRT_0}}$$

2.227 (a) $\lambda > l$ if $p < \dfrac{kT}{\sqrt{2}\,\pi\, d^2\, l}$

Now $\dfrac{kT}{\sqrt{2}\,\pi\, d^2\, l}$ for O_2 of O is 0.7 Pa.

(b) The corresponding n is obtained by dividing by kT and is 1.84×10^{20} per

$m^3 = 1.84^{14}$per c.c. and the corresponding mean distance is $\dfrac{l}{n^{1/3}}$.

$$= \frac{10^{-2}}{(0.184)^{1/3} \times 10^5} = 1.8 \times 10^- m \approx 0.18\ \mu m.$$

2.228 (a) $v = \dfrac{1}{\tau} = \dfrac{1}{\lambda/<v>} = \dfrac{<v>}{\lambda}$

$$= \sqrt{2}\,\pi\, d^2 n <v> = .74 \times 10^{10}\, s^{-1} \text{ (see 2.223)}$$

(b) Total number of collisions is

$$\frac{1}{2} nv \approx 1.0 \times 10^{29}\, s\, cm^{-3}$$

Note, the factor $\dfrac{1}{2}$. When two molecules collide we must not count it twice.

2.229 (a) $\lambda = \dfrac{1}{\sqrt{2}\,\pi\, d^2\, n}$

d is a constant and n is a constant for an isochoric process so λ is constant for an isochoric process.

$$v = \frac{<v>}{\lambda} = \frac{\sqrt{\dfrac{8RT}{M\pi}}}{\lambda}\, \alpha\, \sqrt{T}$$

(b) $\lambda = \dfrac{1}{\sqrt{2}\,\pi d^2}\dfrac{kT}{p}\,\alpha\, T$ for an isobaric process.

$$v = \frac{<v>}{\lambda}\,\alpha\,\frac{\sqrt{T}}{T} = \frac{1}{\sqrt{T}} \text{ for an isobaric process.}$$

2.230 (a) In an isochoric process λ is constant and

$$v\,\alpha\,\sqrt{T}\,\alpha\,\sqrt{pV}\,\alpha\,\sqrt{p}\,\alpha\,\sqrt{n}$$

(b) $\lambda = \dfrac{kT}{\sqrt{2}\,\pi d^2 p}$ must decrease n times in an isothermal process and v must increase

n times because $<v>$ is constant in an isothermal process.

2.231 (a) $\lambda \alpha \dfrac{1}{n} \Rightarrow \dfrac{1}{N/V} = \dfrac{V}{N}$

Thus $\qquad\qquad\qquad \lambda \alpha V$ and $\nu \alpha \dfrac{T^{1/2}}{V}$

But in an adiabatic process $\left(\gamma = \dfrac{7}{5}\text{ here}\right)$

$$TV^{\gamma-1} = \text{constant so } TV^{2/5} = \text{constant}$$

or $\qquad\qquad\qquad T^{1/2} \alpha V^{-1/5}$ Thus $\nu \alpha V^{-6/5}$

(b) $\lambda \alpha \dfrac{T}{p}$

But $p\left(\dfrac{T}{p}\right)^{\gamma} = \text{constant}$ or $\dfrac{T}{p}\alpha p^{-1/\gamma}$ or $T \alpha p^{1-1/\gamma}$

Thus $\qquad\qquad\qquad \lambda \alpha p^{-1/\gamma} = p^{-5/7}$

$$\nu = \dfrac{<\nu>}{\lambda} \alpha \dfrac{p}{\sqrt{T}} \alpha p^{1/2 + \frac{1}{2\gamma}} = p^{\frac{\gamma+1}{2\gamma}} = p^{6/7}$$

(c) $\lambda \alpha V$

But $\qquad\qquad\qquad TV^{2/5} = \text{constant}$ or $V \alpha T^{-5/2}$

Thus $\qquad\qquad\qquad \lambda \alpha T^{-5/2}$

$$\nu \alpha \dfrac{T^{1/2}}{V} \alpha T^3$$

2.232 In the polytropic process of index n

$$pV^n = \text{constant}, TV^{n-1} = \text{constant and } p^{1-n}T^n = \text{constant}$$

(a) $\lambda \alpha V$

$$\nu \alpha \dfrac{T^{1/2}}{V} = V^{\frac{1-n}{2}}V^{-1} = V^{\frac{-n+1}{2}}$$

(b) $\lambda \alpha \dfrac{T}{p}$, $T^n \alpha p^{n-1}$ or $T \alpha p^{1-\frac{1}{n}}$

so $\qquad\qquad\qquad \lambda \alpha p^{-1/n}$

$$\nu = \dfrac{<\nu>}{\lambda} \alpha \dfrac{p}{\sqrt{T}} \alpha p^{1-\frac{1}{2}+\frac{1}{2n}} = p^{\frac{n+1}{2n}}$$

(c) $\lambda \alpha \dfrac{T}{p}$, $p \alpha T^{\frac{n}{n-1}}$

$$\lambda \alpha T^{1-\frac{n}{n-1}} = T^{-\frac{1}{n-1}} = T^{\frac{1}{1-n}}$$

$$\nu \alpha \dfrac{p}{\sqrt{T}} \alpha T^{\frac{n}{n-1}-\frac{1}{2}} = T^{\frac{n+1}{2(n-1)}}$$

2.233 (a) The number of collisions between the molecules in a unit volume is

$$\frac{1}{2} n \, \nu = \frac{1}{\sqrt{2}} \pi d^2 n^2 <\!v\!> \, \alpha \frac{\sqrt{T}}{V^2}$$

This remains constant in the poly process $pV^{-3} =$ constant
Using (2.122) the molar specific heat for the polytropic process

$$pV^{\alpha} = \text{constant},$$

is

$$C = R\left(\frac{1}{\gamma - 1} - \frac{1}{\alpha - 1}\right)$$

Thus

$$C = R\left(\frac{1}{\gamma - 1} + \frac{1}{4}\right) = R\left(\frac{5}{2} + \frac{1}{4}\right) = \frac{11}{4} R$$

It can also be written as $\frac{1}{4} R \, (1 + 2\,i)$ where $i = 5$

(b) In this case $\frac{\sqrt{T}}{V} =$ constant and so $pV^{-1} =$ constant

so

$$C = R\left(\frac{1}{\gamma - 1} + \frac{1}{2}\right) = R\left(\frac{5}{2} + \frac{1}{2}\right) = 3R$$

It can also be written as $\frac{R}{2} (i + 1)$

2.234 We can assume that all molecules, incident on the hole, leak out. Then,

$$- dN = - d\,(nV) = \frac{1}{4} n <\!v\!> S \, dt$$

or

$$dn = - n \frac{dt}{4v/S <\!v\!>} = - n \frac{dt}{\tau}$$

Integrating $\qquad n = n_0 \, e^{-t/\tau}$. Hence $<\!v\!> = \sqrt{\dfrac{8RT}{\pi M}}$

2.235 If the temperature of the compartment 2 is η times more than that of compartment 1, it must contain $\dfrac{1}{\eta}$ times less number of molecules since pressure must be the same when the big hole is open. If $M =$ mass of the gas in 1 than the mass of the gas in 2 must be $\dfrac{M}{\eta}$. So immediately after the big hole is closed.

$$n_1^0 = \frac{M}{mV}, \quad n_2^0 = \frac{M}{mV\eta}$$

where $m =$ mass of each molecule and n_1^0, n_2^0 are concentrations in 1 and 2. After the big hole is closed the pressures will differ and concentration will become n_1 and n_2 where

$$n_1 + n_2 = \frac{M}{m V\eta} (1 + \eta)$$

On the other hand

$$n_1 <\!v_1\!> = n_2 <\!v_2\!> \quad \text{i.e.} \quad n_1 = \sqrt{\eta} \; n_2$$

Thus $\qquad n_2\dot{}(1+\sqrt{\eta}) = \dfrac{m}{mV\eta}(1+\eta) = n_2^0(1+\eta)$

So $\qquad n_2 = n_2^0\dfrac{1+\eta}{1+\sqrt{\eta}}$

2.236 We know

$$\eta = \frac{1}{3}<v>\lambda\,\rho = \frac{1}{3}<v>\frac{1}{\sqrt{2}\,\pi d^2}\,m\,\alpha\,\sqrt{T}$$

Thus η changing α times implies T changing α^2 times.

On the other hand

$$D = \frac{1}{3}<v>\lambda = \frac{1}{3}\sqrt{\frac{8kT}{\pi m}}\,\frac{kT}{\sqrt{2}\,\pi d^2 p}$$

Thus D changing β times means $\dfrac{T^{3/2}}{p}$ changing β times

So p must change $\dfrac{\alpha^3}{\beta}$ times

2.237 $D\,\alpha\,\dfrac{\sqrt{T}}{n}\,\alpha\,V\sqrt{T}$, $\eta\propto\sqrt{T}$

(a) D will increase n times

η will remain constant if T is constant

(b) $D\,\alpha\,\dfrac{T^{3/2}}{p}\,\alpha\,\dfrac{(pV)^{3/2}}{p} = p^{1/2}\,V^{3/2}$

$$\eta\,\alpha\,\sqrt{pV}$$

Thus D will increase $n^{3/2}$ times, η will increase $n^{1/2}$ times, if p is constant

2.238 $D\,\alpha\,V\sqrt{T}$, $\eta\,\alpha\,\sqrt{T}$

In an adiabatic process

$$TV^{\gamma-1} = \text{constant, or } T\propto V^{1-\gamma}$$

Now V is decreased $\dfrac{1}{n}$ times. Thus

$$D\,\alpha\,V^{\frac{3-\gamma}{2}} = \left(\frac{1}{n}\right)^{\frac{3-\gamma}{2}} = \left(\frac{1}{n}\right)^{4/5}$$

$$\eta\,\alpha\,\text{of}\,V^{\frac{1-\gamma}{2}} = \left(\frac{1}{n}\right)^{-1/5} = n^{1/5}$$

So D decreases $n^{4/5}$ times and η increase $n^{1/5}$ times.

2.239 (a) $D\,\alpha\,V\sqrt{T}\,\alpha\,\sqrt{pV^3}$

Thus D remains constant in the process $pV^3 = $ constant

So polytropic index $n = 3$

(b) $\eta\,\alpha\,\sqrt{T}\,\alpha\,\sqrt{pV}$

So η remains constant in the isothermal process

$$pV = \text{constant}, \quad n = 1, \text{ here}$$

(c) Heat conductivity $\kappa = \eta \, C_V$

and C_V is a constant for the ideal gas

Thus $n = 1$ here also,

2.240 $\eta = \dfrac{1}{3}\sqrt{\dfrac{8\,kT}{\pi\,m}}\,\dfrac{m}{\sqrt{2}\,\pi\,d^2} = \dfrac{2}{3}\sqrt{\dfrac{m\,kT}{\pi^3}}\,\dfrac{1}{d^2}$

or $d = \left(\dfrac{2}{3\,\eta}\right)^{1/2}\left(\dfrac{m\,kT}{\pi^3}\right)^{1/4} = \left(\dfrac{2}{3\times18\cdot9}\times10^6\right)^{1/2}\left(\dfrac{4\times8\cdot31\times273\times10^{-3}}{\pi^3\times36\times10^{46}}\right)^{1/4}$

$= 10^{-10}\left(\dfrac{2}{3\times18\cdot9}\right)^{1/2}\left(\dfrac{4\times83\cdot1\times273}{\pi^3\times\cdot36}\right)^{1/4} \approx 0\cdot178\ \text{nm}$

2.241 $\kappa = \dfrac{1}{3}<v>\lambda\,\rho\,c_V$

$= \dfrac{1}{3}\sqrt{\dfrac{8\,kT}{m\,\pi}}\,\dfrac{1}{\sqrt{2}\,\pi\,d^2\,n}\,mn\,\dfrac{C_V}{M}$

$\left(C_V \text{ is the specific heat capacity which is } \dfrac{C_V}{M}\right)$. Now C_V is the same for all monoatomic gases such as He and A. Thus

$$\kappa\,\alpha\,\dfrac{1}{\sqrt{M}\,d^2}$$

or $\dfrac{\kappa_{He}}{\kappa_A} = 8\cdot7 = \dfrac{\sqrt{M_A}\,d_A^2}{\sqrt{M_{H_e}}\,d_{H_e}^2} = \sqrt{10}\,\dfrac{d_A^2}{d_{H_e}^2}$

$\dfrac{d_A}{d_{H_e}} = \sqrt{\dfrac{8\cdot7}{\sqrt{10}}} = 1\cdot658 \approx 1\cdot7$

2.242 In this case

$$N_1\,\dfrac{r_2^2 - r_1^2}{r_1^2\,r_2^2} = 4\,\pi\,\eta\,\omega$$

or $N_1\,\dfrac{2R\,\Delta R}{R^4} \approx 4\,\pi\,\eta\,\omega$ or $N_1 = \dfrac{2\,\pi\,\eta\,\omega\,R^3}{\Delta R}$

To decrease N_1, n times η must be decreased n times. Now η does not depend on pressure until the pressure is so low that the mean free path equals, say, $\dfrac{1}{2}\Delta R$. Then the mean free path is fixed and η decreases with pressure. The mean free path equals $\dfrac{1}{2}\Delta R$ when

$$\dfrac{1}{\sqrt{2}\,\pi\,d^2\,n_0} = \Delta R \quad (n_0 = \text{concentration})$$

Corresponding pressure is $p_0 = \dfrac{\sqrt{2}\ kT}{\pi\,d^2\,\Delta R}$

The sought pressure is n times less

$$p = \frac{\sqrt{2}\ kT}{\pi\,d^2\,n\,\Delta R} = 70{\cdot}7 \times \frac{10^{-23}}{10^{-18} \times 10^{-3}} \approx 0{\cdot}71\ \text{Pa}$$

The answer is qualitative and depends on the choice $\dfrac{1}{2}\Delta R$ for the mean free path.

2.243 We neglect the moment of inertia of the gas in a shell. Then the moment of friction forces on a unit length of the cylinder must be a constant as a function of r.

So, $\qquad 2\pi r^3\,\eta\,\dfrac{d\omega}{dr} = N_1 \quad$ or $\quad \omega\,(r) = \dfrac{N_1}{4\pi\eta}\left(\dfrac{1}{r_1^2} - \dfrac{1}{r^2}\right)$

and $\qquad \omega = \dfrac{N_1}{4\pi\eta}\left(\dfrac{1}{r_1^2} - \dfrac{1}{r_2^2}\right) \quad$ or $\quad \eta = \dfrac{N_1}{4\pi\omega}\left(\dfrac{1}{r_1^2} - \dfrac{1}{r_2^2}\right)$

2.244 We consider two adjoining layers. The angular velocity gradient is $\dfrac{\omega}{h}$. So the moment of the frictional force is

$$N = \int_0^a r \cdot 2\pi r\,dr \cdot \eta\,r\,\frac{\omega}{h} = \frac{\pi\,\eta\,a^4\,\omega}{2h}$$

2.245 In the ultrararefied gas we must determine η by taking $\lambda = \dfrac{1}{2}h$. Then

$$\eta = \frac{1}{3}\sqrt{\frac{8kT}{m\pi}} \times \frac{1}{2}h \times \frac{mp}{kT} = \frac{1}{3}\sqrt{\frac{2M}{\pi RT}}\,hp$$

so, $\qquad N = \dfrac{1}{3}\,\omega\,a^4\,p\,\sqrt{\dfrac{\pi M}{2RT}}$

2.246 Take an infinitesimal section of length dx and apply Poiseuilles equation to this. Then

$$\frac{dV}{dt} = \frac{-\pi a^4}{8\eta}\frac{\partial p}{\partial x}$$

From the formula $\qquad pV = RT \cdot \dfrac{m}{M}$

$$p\,dV = \frac{RT}{M}\,dm$$

or $\qquad \dfrac{dm}{dt} = \mu = -\dfrac{\pi a^4 M}{8\eta RT}\dfrac{p\,dp}{dx}$

This equation implies that if the flow is isothermal then $p\,\dfrac{dp}{dx}$ must be a constant and so

equals $\dfrac{\left|p_2^2 - p_1^2\right|}{2\,l}$ in magnitude.

Thus, $\qquad \mu = \dfrac{\pi a^4 M}{16\,\eta\,R\,T}\dfrac{\left|p_2^2 - p_1^2\right|}{l}$

2.247 Let T = temperature of the interface.

Then heat flowing from left = heat flowing into right in equilibrium.

Thus, $\kappa_1 \dfrac{T_1 - T}{l_1} = \kappa_2 \dfrac{T - T_2}{l_2}$ or $T = \dfrac{\left(\dfrac{\kappa_1 T_1}{l_1} + \dfrac{\kappa_2 T_2}{l_2}\right)}{\left(\dfrac{\kappa_1}{l_1} + \dfrac{\kappa_2}{l_2}\right)}$

2.248 We have

$$\kappa_1 \frac{T_1 - T}{l_1} = \kappa_2 \frac{T - T_2}{l_2} = \kappa \frac{T_1 - T_2}{l_1 + l_2}$$

or using the previous result

$$\frac{\kappa_1}{l_1}\left(T_1 - \frac{\dfrac{\kappa_1 T_1}{l_1} + \dfrac{\kappa_2 T_2}{l_2}}{\dfrac{\kappa_1}{l_1} + \dfrac{\kappa_1}{l_2}}\right) = \kappa \frac{T_1 - T_2}{l_1 + l_2}$$

or $\quad\dfrac{\kappa_1}{l_1} \dfrac{\dfrac{\kappa_2}{l_2}(T_1 - T_2)}{\dfrac{\kappa_1}{l_1} + \dfrac{\kappa_2}{l_2}} = \kappa \dfrac{T_1 - T_2}{l_1 + l_2}$ or $\kappa = \dfrac{l_1 + l_2}{\dfrac{l_1}{\kappa_1} + \dfrac{l_2}{\kappa_2}}$

2.249 By definition the heat flux (per unit area) is

$$\dot{Q} = -K\frac{dT}{dx} = -\alpha \frac{d}{dx}\ln T = \text{constant} = +\alpha \frac{\ln T_1/T_2}{l}$$

Integrating $\qquad \ln T = \dfrac{x}{l}\ln\dfrac{T_2}{T_1} + \ln T_1$

where T_1 = temperature at the end $x = 0$

So $\qquad T = T_1\left(\dfrac{T_2}{T_1}\right)^{x/l}$ and $\dot{Q} = \dfrac{\alpha \ln T_1/T_2}{l}$

2.250 Suppose the chunks have temperatures T_1, T_2 at time t and $T_1 - dT_1$, $T_2 + dT_2$ at time $dt + t$.

Then $\qquad C_1 dT_1 = C_2 dT_2 = \dfrac{\kappa S}{l}(T_1 - T_2)\,dt$

Thus $\qquad d\Delta T = -\dfrac{\kappa S}{l}\left(\dfrac{1}{C_1} + \dfrac{1}{C_2}\right)\Delta T\,dt$ where $\Delta T = T_1 - T_2$

Hence $\qquad \Delta T = (\Delta T)_0\, e^{-t/\tau}$ where $\dfrac{1}{\tau} = \dfrac{\kappa S}{l}\left(\dfrac{1}{C_1} + \dfrac{1}{C_2}\right)$

2.251 $\dot{Q} = \kappa \dfrac{\partial T}{\partial x} = -A\sqrt{T}\,\dfrac{\partial T}{\partial x}$

$$= -\dfrac{2}{3}A\,\dfrac{\partial T^{3/2}}{\partial x}, \quad (A = \text{constant})$$

$$= \dfrac{2}{3}A\,\dfrac{(T_1^{3/2} - T_2^{3/2})}{l}$$

Thus $\qquad T^{3/2} = \text{constant} - \dfrac{x}{l}\left(T_1^{3/2} - T_2^{3/2}\right)$

or using $\qquad T = T_1$ at $x = 0$

$$T^{3/2} = T_1^{3/2} + \dfrac{x}{l}\left(T_2^{3/2} - T_1^{3/2}\right) \quad \text{or} \quad \left(\dfrac{T}{T_1}\right)^{3/2} = 1 + \dfrac{x}{l}\left(\left(\dfrac{T_2}{T}\right)^{3/2} - 1\right)$$

$$T = T_1\left[1 + \dfrac{x}{l}\left\{\left(\dfrac{T_2}{T_1}\right)^{3/2} - 1\right\}\right]^{2/3}$$

2.252 $\kappa = \dfrac{1}{3}\sqrt{\dfrac{8RT}{\pi M}}\,\dfrac{1}{\sqrt{2}\,\pi d^2 n}\,mn\,\dfrac{R\dfrac{i}{2}}{M} = \dfrac{R^{3/2}\,i\,T^{3/2}}{3\pi^{3/2}d^2\sqrt{M}\,N_A}$

Then from the previous problem

$$q = \dfrac{2i\,R^{3/2}\,(T_2^{3/2} - T_1^{3/2})}{9\pi^{3/2}d^2\sqrt{M}\,N_A\,l}, \quad i = 3 \text{ here.}$$

2.253 At this pressure and average temparature $= 27°C = 300\text{K} = T = \dfrac{(T_1 + T_2)}{2}$

$\lambda = \dfrac{1}{\sqrt{2}\,\pi d^2}\dfrac{\kappa T}{P} = 2330 \times 10^{-5}\text{m} = 23\cdot3\text{mm} >> 5\cdot0\text{mm} = l$

The gas is ultrathin and we write $\lambda = \dfrac{1}{2}l$ here

Then $\qquad q = \kappa\dfrac{dT}{dx} = \kappa\,\dfrac{T_2 - T_1}{l}$

where $\qquad \kappa = \dfrac{1}{3}<v> \times \dfrac{1}{2}l \times \dfrac{MP}{RT} \times \dfrac{R}{\gamma - 1} \times \dfrac{1}{M} = \dfrac{p<v>}{6T(\gamma - 1)}l$

and $\qquad q = \dfrac{p<v>}{6T(\gamma - 1)}(T_2 - T_1)$

where $\quad <v> = \sqrt{\dfrac{8RT}{M\pi}}$. We have used $T_2 - T_1 << \dfrac{T_2 + T_1}{2}$ here.

2.254 In equilibrium $2\pi r \kappa \dfrac{dT}{dr} = -A =$ constant. So $T = B - \dfrac{A}{2\pi\kappa}\ln r$

But $T = T_1$ when $r = R_1$ and $T = T_2$ when $r = R_2$.

From this we find $T = T_1 + \dfrac{T_2 - T_1}{\ln\dfrac{R_2}{R_1}}\ln\dfrac{r}{r_1}$

2.255 In equilibrium $4\pi r^2 \kappa \dfrac{dT}{dr} = -A =$ constant

$$T = B + \frac{A}{4\pi\kappa}\frac{1}{r}$$

Using $T = T_1$ when $r = R_1$ and $T = T_2$ when $r = R_2$,

$$T = T_1 + \frac{T_2 - T_1}{\dfrac{1}{R_2} - \dfrac{1}{R_1}}\left(\frac{1}{r} - \frac{1}{R_1}\right)$$

2.256 The heat flux vector is $-\kappa\,\text{grad}\,T$ and its divergence equals w. Thus

$$\nabla^2 T = -\frac{w}{\kappa}$$

or $\qquad \dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial T}{\partial r}\right) = -\dfrac{w}{\kappa}$ in cylindrical coordinates.

or $\qquad T = B + A\ln r - \dfrac{\omega}{2x}r^2$

Since T is finite at $r = 0, A = 0$. Also $T = T_0$ at $r = R$

so $\qquad B = T_0 + \dfrac{w}{4\kappa}R^2$

Thus $\qquad T = T_0 + \dfrac{w}{4\kappa}(R^2 - r^2)$

r here is the distance from the axis of wire (axial radius).

2.257 Here again

$$\nabla^2 T = -\frac{w}{\kappa}$$

So in spherical polar coordinates,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) = -\frac{w}{\kappa} \text{ or } r^2\frac{\partial T}{\partial r} = -\frac{w}{3\kappa}r^3 + A$$

or $\qquad T = B - \dfrac{A}{r} - \dfrac{w}{6\kappa}r^2$

Again $\qquad A = 0$ and $B = T_0 + \dfrac{w}{6\kappa}R^2$

so finally $\qquad T = T_0 + \dfrac{w}{6\kappa}(R^2 - r^2)$

ELECTRODYNAMICS

3.1 CONSTANT ELECTRIC FIELD IN VACUUM

3.1 F_{el} (for electorns) $= \dfrac{q^2}{4\pi\varepsilon_0 r^2}$ and $F_{gr} = \dfrac{\gamma m^2}{r^2}$

Thus $\dfrac{F_{el}}{F_{gr}}$ (for electrons) $= \dfrac{q^2}{4\pi\varepsilon_0 \gamma m^2}$

$$= \dfrac{(1\cdot602 \times 10^{-19}\, C)^2}{\left(\dfrac{1}{9 \times 10^9}\right) \times 6\cdot67 \times 10^{-11}\, m^3 / (kg\cdot s^2) \times (9\cdot11 \times 10^{-31}\, kg)^2} = 4 \times 10^{42}$$

Similarly $\dfrac{F_{el}}{F_{gr}}$ (for proton) $= \dfrac{q^2}{4\pi\varepsilon_0 \gamma m^2}$

$$= \dfrac{(1\cdot602 \times 10^{-19}\, C)^2}{\left(\dfrac{1}{9 \times 10^9}\right) \times 6\cdot67 \times 10^{-11}\, m^3 /(kg\cdot s^2) \times (1\cdot672 \times 10^{-27}\, kg)^2} = 1 \times 10^{36}$$

For $F_{el} = F_{gr}$

$$\dfrac{q^2}{4\pi\varepsilon_0 r^2} = \dfrac{\gamma m^2}{r^2} \quad \text{or} \quad \dfrac{q}{m} = \sqrt{4\pi\varepsilon_0 \gamma}$$

$$= \sqrt{\dfrac{6\cdot67 \times 10^{-11}\, m^3\, (kg - s^2)}{9 \times 10^9}} = 0\cdot86 \times 10^{-10}\, C/kg$$

3.2 Total number of atoms in the sphere of mass 1 gm $= \dfrac{1}{63\cdot54} \times 6\cdot023 \times 10^{23}$

So the total nuclear charge $\lambda = \dfrac{6\cdot023 \times 10^{23}}{63\cdot54} \times 1\cdot6 \times 10^{-19} \times 29$

Now the charge on the sphere = Total nuclear charge − Total electronic charge