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

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

or,

$$\Delta U = \frac{1}{2} \nu M v^2 \tag{1}$$

But from $U = \nu \frac{RT}{\gamma - 1}$, $\Delta U = \frac{\nu R}{\gamma - 1} \Delta T$ (from the previous problem) (2)

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

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

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 ν_1 and ν_2 be the number of moles of air initially in the two vessels, we have

$$p_1 V_1 = \nu_1 R T_1 \text{ and } p_2 V_2 = \nu_2 R T_2 \tag{1}$$

After the air is mixed up, the total number of moles are $(\nu_1 + \nu_2)$ and the mixture is at temperature T.

Hence

$$p (V_1 + V_2) = (\nu_1 + \nu_2) R T \tag{2}$$

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 :

$$U_i = U_1 + U_2 = \frac{\nu_1 R T_1}{\gamma - 1} + \frac{\nu_2 R T_2}{\gamma - 1} \tag{3}$$

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

$$U_f = \frac{(\nu_1 + \nu_2) RT}{\gamma - 1} \tag{4}$$

Therefore, $U_i = U_f$ implies :

$$T = \frac{\nu_1 T_1 + \nu_2 T_2}{\nu_1 + \nu_2} = \frac{p_1 V_1 + p_2 V_2}{(p_1 V_1/T_1) + (p_2 V_2/T_2)} = T_1 T_2 \frac{p_1 V_1 + p_2 V_2}{p_1 V_1 T_2 + p_2 V_2 T_2}$$

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

$$p = \frac{\nu_1 + \nu_2}{V_1 + V_2} RT = \frac{R}{V_1 + V_2} (\nu_1 T_1 + \nu_2 T_2) = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

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, $$Q = \Delta U = \frac{\nu R}{\gamma - 1} \Delta T$$

From gas law, $$p_0 V = \nu R T_0$$

So, $$\Delta U = \frac{p_0 V \Delta T}{T_0 (\gamma - 1)} = -0{\cdot}25 \text{ kJ}$$

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 $\nu = 1$) = 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 $\Delta U = \frac{R\,\Delta T}{\gamma - 1}$, for $\nu = 1$

Thus $$Q - R\,\Delta T = \frac{R\,\Delta T}{\gamma - 1} \quad \text{or} \quad \gamma = \frac{Q}{Q - R\,\Delta T} = 1{\cdot}6$$

2.32 Let $\nu = 2$ 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

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

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

During the second phase (under isobaric process),

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

Thus from first law of thermodynamics :

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

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

Hence the total amount of heat absorbed

$$Q = Q_1 + Q_2 = \frac{\nu R T_0 (1-n)}{n(\gamma-1)} + \frac{\nu R T_0 (n-1)\gamma}{n(\gamma-1)}$$

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

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

$$C_V = \frac{\nu_1 \frac{R}{\gamma_1 - 1} + \nu_2 \frac{R}{\gamma_2 - 1}}{\nu_1 + \nu_2} = 15{\cdot}2\ \text{J/mole. K}$$

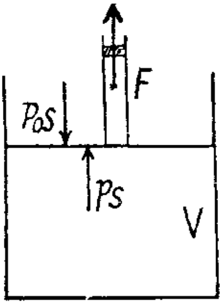
and $$C_p = \frac{\nu_1 \frac{\gamma_1 R}{\gamma_1 - 1} + \nu_2 \frac{\gamma_2 R}{\gamma_2 - 1}}{\nu_1 + \nu_2} = 23{\cdot}85 \text{ J/mole. K}$$

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

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

2.35 Let S be the area of the piston and F be the force exerted by the external agent. Then, $F + p\,S = p_0 S$ (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)

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



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

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

$$= (\eta - 1)\,p_0 V_0 - nRT \ln \eta = (\eta - 1)\,\nu RT - \nu RT \ln \eta$$

$$= \nu RT(\eta - 1 - \ln \eta) = RT(\eta - 1 - \ln \eta) \text{ (For } \nu = 1 \text{ mole)}$$

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,

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

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

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

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

$$A = \int_0^V (p_2 - p_1)\, dV = \int_0^V \frac{2p_0 V_0 V}{V_0^2 - V^2}\, dV = -p_0 V_0 \Big[\ln (V_0^2 - V^2) \Big]_0^V$$

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

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

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

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

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

In the isochoric process, $A = 0$

Thus heat transfer to the gas is given by

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

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

or, $$\Delta T = \eta T_0 - T_0 = (\eta - 1) T_0, \quad \text{so,} \quad Q_2 = \frac{\nu R}{\gamma - 1} \cdot (\eta - 1) T_0$$

Thus, net heat transfer to the gas

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

or, $$\frac{Q}{\nu R T_0} = \ln \eta + \frac{\eta - 1}{\gamma - 1}, \quad \text{or,} \quad \frac{Q}{\nu R T_0} - \ln \eta = \frac{\eta - 1}{\gamma - 1}$$

or, $$\gamma = 1 + \frac{\eta - 1}{\dfrac{Q}{\nu R T_0} - \ln \eta} = 1 + \frac{6 - 1}{\left(\dfrac{80 \times 10^3}{3 \times 8{\cdot}314 \times 273} \right) - \ln 6} = 1{\cdot}4$$

2.38 (a) From ideal gas law $p = \left(\frac{\nu R}{V} \right) T = kT$ $\left(\text{where } k = \frac{\nu R}{V} \right)$

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 $(1 - \gamma) p^{-\gamma} dp \cdot T^{\gamma} + \gamma p^{1 - \gamma} \cdot T^{\gamma - 1} \cdot dT = 0$

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

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

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

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

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

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

Hence $T=T_0\cdot\eta^{\frac{\gamma-1}{\gamma}}=290\times 10^{(1\cdot4-1)/1\cdot4}=0{\cdot}56\text{ kK}$

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

$$A=\frac{\nu R\,\Delta T}{\gamma-1}=\frac{\nu RT_0}{\gamma-1}\left(\eta^{(\gamma-1)/\gamma}-1\right)=5{\cdot}61\text{ kJ}\quad\text{(on substitution)}$$

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

We know $A_{adia}=\frac{-\nu R\Delta T}{\gamma-1}$ (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 $$A_{\text{adia}}=\frac{-\nu RT_0\left(\eta^{\gamma-1}-1\right)}{\gamma-1}$$

On the other hand, we know $A_{iso}=\nu RT_0\ln\left(\frac{1}{\eta}\right)=-\nu R\,T_0\ln\eta$ (work done by the gas)

Thus $$\frac{A_{\text{adia}}}{A_{\text{iso}}}=\frac{\eta^{\gamma-1}-1}{(\gamma-1)\ln\eta}=\frac{5^{0\cdot4}-1}{0{\cdot}4\times\ln 5}=1{\cdot}4$$

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

So $$dA = \nu RT\frac{2V}{V_0^2 - V^2}dV$$

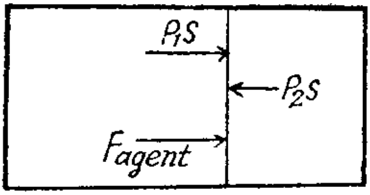
Also, from the first law of thermodynamics

$$dA = -dU = -2\nu\frac{R}{\gamma - 1}dT \quad (\text{as } dQ = 0)$$

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

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

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



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

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

On integrating $$\int_{T_0}^{T}\frac{dT}{T} = (\gamma - 1)\int_0^V\frac{VdV}{V_0^2 - V^2}$$

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

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

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

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

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

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

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 $u=\frac{C_V T}{M}=\frac{RT}{M(\gamma-1)}$ also $\frac{p}{\rho}=\frac{RT}{M}\cdot$ 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 $\quad v^2=\frac{2\gamma RT}{M(\gamma-1)}\quad$ or, $\quad v=\sqrt{\frac{2\gamma RT}{M(\gamma-1)}}=3.22$ 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, $$A=-\int_T^{T+\Delta T} vRdT=-vR\Delta T$$

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, $$pdV=\frac{a\,v\,R\,dT}{\gamma-1} \tag{1}$$

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

$$pdV+Vdp=vRdT \tag{2}$$

Thus from (1) and (2)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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, $$C_n = \frac{8{\cdot}314}{1{\cdot}66-1} - \frac{8{\cdot}314\ln 4}{\ln 8 - \ln 4} = -42\text{ J/mol.K}$$

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

$$Q = \Delta U + A = \frac{R\,\Delta T}{\gamma-1} - \frac{R\Delta T}{n-1} = 0{\cdot}11\text{ kJ}$$

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

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

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

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

$$= \frac{\nu R\Delta T}{n-1} = -\frac{R\Delta T}{n-1} = 0{\cdot}43\text{ kJ (as } \nu = 1\text{ mole)}$$

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) $\Delta U = \frac{\nu R}{\gamma - 1} \Delta T$ 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, $$C_n \Delta T = \frac{R}{\gamma - 1} \Delta T, \quad \text{or} \quad C_n = -\frac{R}{\gamma - 1}$$

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

or, $$2\,dQ = dA \text{ (as } dQ = -dU\text{)}$$

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

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

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

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

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

Thus $$-\frac{R}{\gamma - 1} = \frac{(n - \gamma) R}{(n - 1)(\gamma - 1)} \text{ which yields}$$

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

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

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

Work done by the gas for one mole is given by

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

2.50 Given $p = a\,T^{\alpha}$ (for one mole of gas)

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

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

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

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

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

(b) Molar heat capacity is given by

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

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

or, $$\nu C_V T = a\,V^{\alpha}, \quad \text{or,} \quad \nu C_V \frac{pV}{\nu R} = a\,V^{\alpha}$$

or, $$aV^{\alpha}\cdot\frac{R}{C_V}\cdot\frac{1}{pV} = 1, \quad \text{or,} \quad V^{\alpha-1}\cdot p^{-1} = \frac{C_V}{Ra}$$

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

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 $$A = \frac{-\Delta U(\gamma-1)}{n-1} = \frac{\Delta U(\gamma-1)}{\alpha} \quad (\text{as } n = 1-\alpha)$$

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

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

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

2.52 (a) By the first law of thermodynamics

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

Molar specific heat according to definition

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

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

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

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

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

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

(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) $C = C_V + \frac{RT}{V}\frac{dV}{dT} = C_V + \frac{p dV}{dT}$ (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 $\quad RdT = p_0\, dV$, So, $\frac{dV}{dT} = \frac{R}{p_0}$

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

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

(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 $\quad T = T_0 + \alpha V$ or, $V = \frac{T}{\alpha} - \frac{T_0}{\alpha}$

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

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

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

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

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

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

Now $$A = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2}\left(\frac{RT_0}{v} + \alpha\, R\right) dV \text{ (for one mole)}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

So, $$C_V + ap = C_V + \frac{RT}{V}\frac{dV}{dT} \text{ so, } ap = \frac{RT}{V}\frac{dV}{dT}$$

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

or, $$\frac{dV}{dT} = a \text{ or, } dV = adT \text{ or, } dT = \frac{dV}{a}$$

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

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

or, $$= CdT - C_V dT = (C - C_V)\, dT \text{ (for one mole)}$$

Given $$C = \frac{\alpha}{T}$$

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

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

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

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

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

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

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

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

$$dQ = dU + p\,dV = 0$$

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 themally 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 $\Delta T=-3$ K

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

So at constant temperature.

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

$=0{\cdot}33$ kJ from the given data.