## 2.4 THE SECOND LAW OF THERMODYNAMICS. ENTROPY

**2.113** The efficiency is given by

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

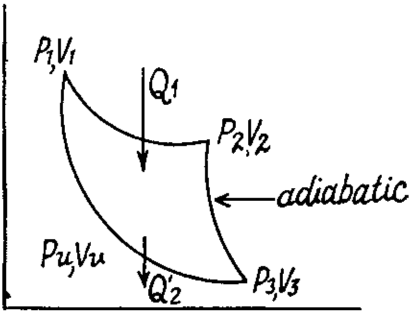
Now in the two cases the efficiencies are

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

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

Thus $$\eta_h < n_l$$

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



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

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

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

Finally $$\eta = 1 - \frac{Q_2}{Q_1} = 1 - n^{1-\gamma} = 0{\cdot}242$$

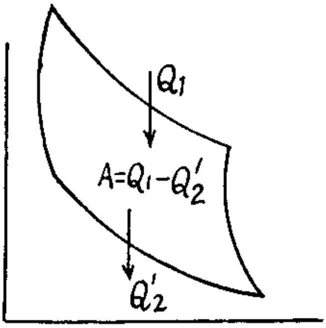
(b) Define $n$ *by* $p_3 = \frac{p_2}{n}$

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

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

$$\eta = 1 - n^{(1/\gamma)-1} = 1 - n^{-\frac{2}{7}} = 0{\cdot}18$$

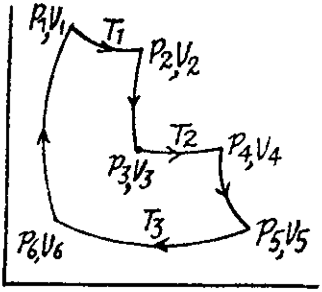
**2.115** Used as a refrigerator, the refrigerating efficiency of a heat engine is given by



$$\varepsilon = \frac{Q_2'}{A} = \frac{Q_2'}{Q_1 - Q_2} = \frac{Q_2'/Q_1}{1 - \frac{Q_2'}{Q_1}} = \frac{1-\eta}{\eta} = 9 \text{ here,}$$

where $\eta$ is the efficiency of the heat engine.

**2.116** Given $V_2 = n\, V_1$ , $V_4 = n\, V_3$



$Q_1 =$ Heat taken at the upper temperature

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

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

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

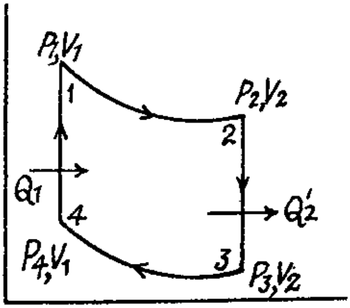
Thus $Q_2 =$ heat ejected at the lower temperature $= -RT_3 \ln \frac{V_6}{V_5}$

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

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

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

**2.117** $Q\,'_2 = C_V (T_2 - T_3) = \frac{C_V}{R} V_2 (p_2 - p_3)$



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

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

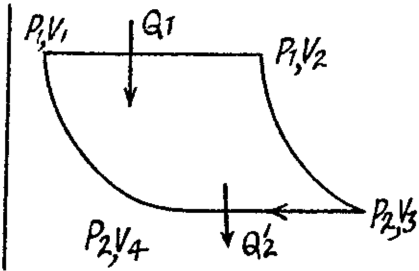
On the other hand,

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

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

and $\eta = 1 - n^{1 - \gamma}$, with $\gamma = \frac{7}{5}$ for $N_2$ this is $\eta = 0{\cdot}602$

**2.118** $Q_1 = \frac{C_p}{R} p_1 (V_2 - V_1)$ , $Q\,'_2 = \frac{C_p}{R}\, p_2 (V_3 - V_4)$



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

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

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

$$p_1 = np_2 \text{ and } V_2 = n\,V_1 \text{. Heat taken is}$$

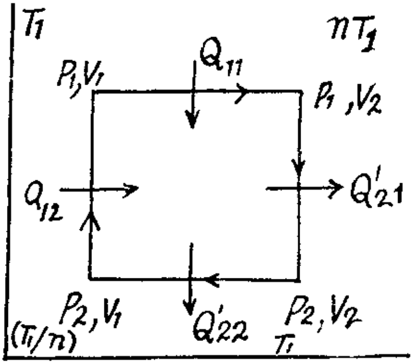
$$Q_1 = Q_{11} + Q_{12}$$

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

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

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



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

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

**2.120** (a) Here $p_2 = n\,p_1$, $p_1\,V_1 = p_0\,V_0$,

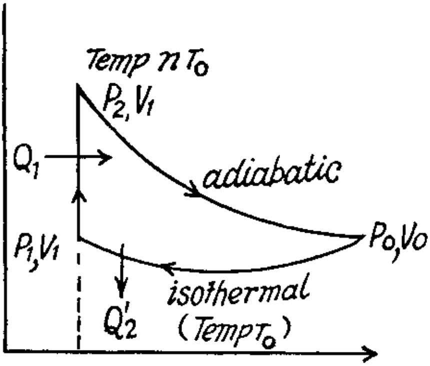
$$n\,p_1\,V_1^{\gamma} = p_0\,V_0^{\gamma}$$

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

But $n\,V_1^{\gamma-1} = V_0^{\gamma-1}$ 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 $\eta = 1-\frac{\ln n}{n-1}$, on using $C_V = \frac{R}{\gamma-1}$



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

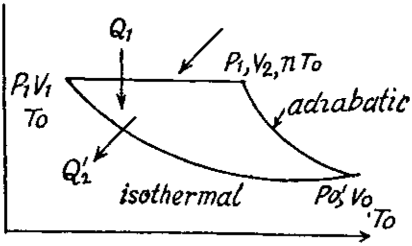
and $\quad p_1\,(n\,V_1)^{\gamma} = p_0\,V_0^{\gamma}$

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

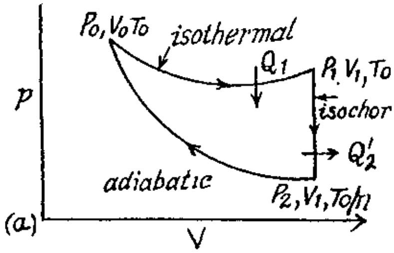
Also $Q_1 = C_p\,T_0\,(n-1)$, $Q'_2 = RT_0\ln\frac{V_0}{V_1}$

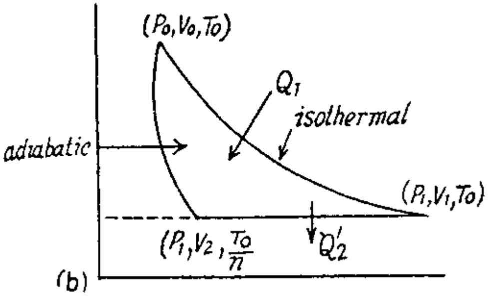
or $Q'_2 = RT_0\ln n^{\frac{\gamma}{\gamma-1}} = \frac{R\gamma}{\gamma-1}\,T_0\ln n = C_p\,T_0\ln n$

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



**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 $p_1 V_1 = p_0 V_0$, $p_2 = \dfrac{p_1}{n}$

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

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

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

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

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

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

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

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

**2.122** The section from $(p_1, V_1, T_0)$ to $(p_2, V_2, T_0/n)$ is a polytropic process of index $\alpha$. We shall assume that the corresponding specific heat $C$ is + ve.

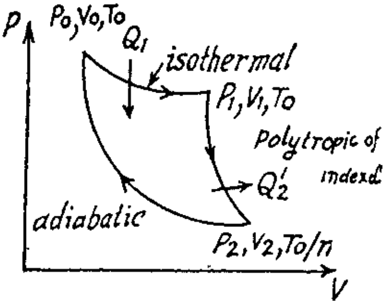
Here, $dQ = C dT = C_V dT + p dV$

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

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

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

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



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

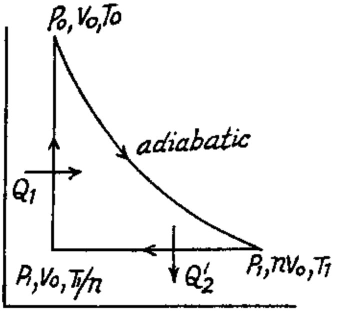
$p_1 V_1^{\alpha} = p_2 V_2^{\alpha}$ or $V_0^{\gamma-1} = \frac{1}{n} V_2^{\gamma-1}$ or $V_2 = V_0\, n^{\frac{1}{\gamma-1}}$

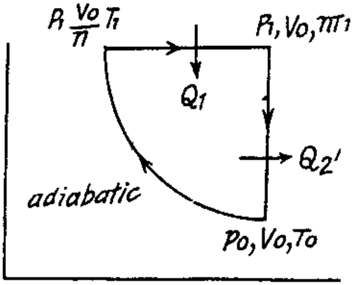
$V_1^{\alpha-1} = \frac{1}{n} V_2^{\alpha-1}$ or $V_1 = n^{-\frac{1}{\alpha-1}} V_2 = n^{\frac{1}{\gamma-1}-\frac{1}{\alpha-1}} V_0$

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

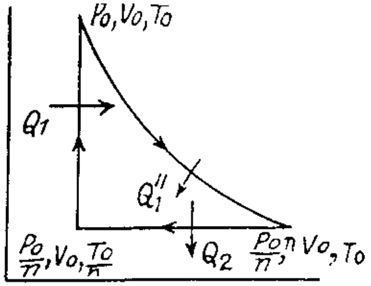
so
$$Q_1 = C_V \frac{T_1}{n}(n^{\gamma}-1). \quad \text{Thus} \quad \eta = 1 - \frac{\gamma(n-1)}{n^{\gamma}-1}$$

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

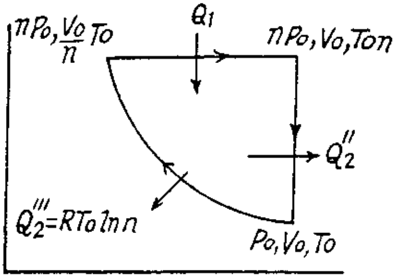
Along the adiabatic line $TV^{\gamma-1} =$ constant
$$T_0 V_0^{\gamma-1} = T_1 \left(\frac{V_0}{n}\right)^{\gamma-1} \quad \text{or} \quad T_1 = n^{\gamma-1} T_0$$

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

**2.124**



(a)



(b)

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

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

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

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

So
$$\eta = 1 - \frac{Q'_2}{Q_1} = 1 - \frac{n - 1 + (\gamma - 1) \ln n}{\gamma (n-1)}$$

**2.125** We have

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

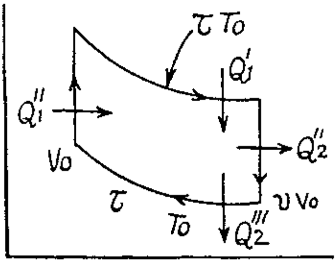
$Q'''_2 = RT_0 \ln \nu$, $Q''_1 = C_V T_0 (\tau - 1)$

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

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

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

$$= 1 - \frac{\frac{\tau - 1}{\gamma - 1} + \ln \nu}{\frac{\tau - 1}{\gamma - 1} + \tau \ln \nu} = \frac{(\tau - 1) \ln \nu}{\tau \ln \nu + \frac{\tau - 1}{\gamma - 1}}$$



**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

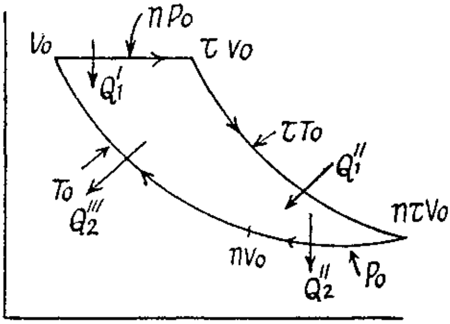
$Q_1 = Q_1' + Q_1''$ and

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

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

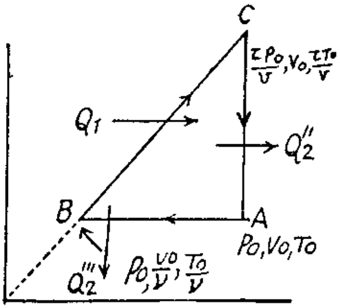
$$= 1 - \frac{\tau - 1 + \left(1 - \frac{1}{\gamma}\right) \ln n}{\tau - 1 + \left(1 - \frac{1}{\gamma}\right) \tau \ln n}$$

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



**2.127** Because of the linearity of the section $BC$ whose equation is

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



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

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

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

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

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

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

**2.128** We write Claussius inequality in the form

$$\int \frac{\text{đ}_1 Q}{T} - \int \frac{\text{đ}_2 Q}{T} \le 0$$

where $\text{đ} Q$ is the heat transeferred to the system but $\text{đ}_2 Q$ is heat rejected by the system, both are $+ve$ and this explains the minus sign before $\text{đ}_2 Q$,

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

$$\int \frac{\text{đ}_1 Q}{T_{\max}} - \int \frac{\text{đ}_2 Q}{T_{\min}} < 0$$

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

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

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

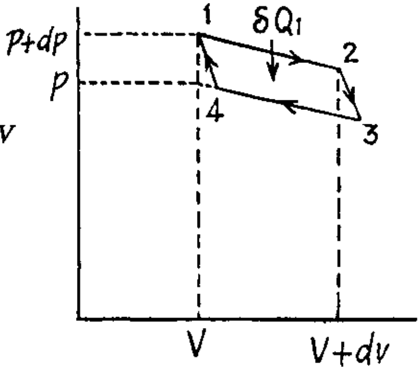
Let $\delta A$ be the work done in the cycle and $\delta Q$, be the heat received at the higher temperature. Then by Carnot's theorem

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

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

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

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

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

For carbon dioxide $\gamma = 1{\cdot}30$

so, $\Delta S = 19{\cdot}2$ Joule/°K – mole

(b) For an isobaric process,

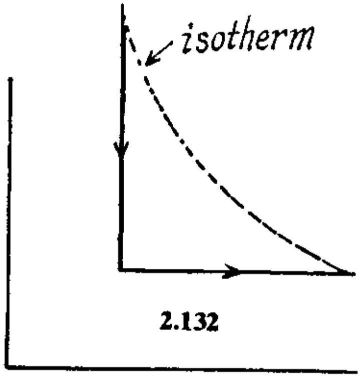
$$\Delta S = C_p \ln\frac{T_f}{T_i} = C_p \ln n = \frac{\gamma R \ln n}{\gamma - 1}$$

$$= 25 \text{ Joule/°K – mole}$$

**2.131** In an isothermal expansion

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

so, $\frac{V_f}{V_i} = e^{\Delta S/VR} = 2{\cdot}0$ times



2.132

**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.

$$T V^{\gamma-1} = T_0 V_0^{\gamma-1}$$

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

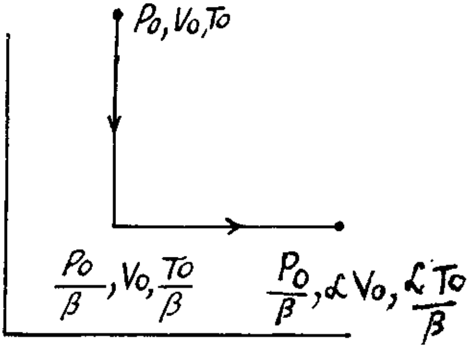
$V_1$ being the volume at the end of the adiabatic process. There is no entropy change in this process. Next the gas is compressed isobarically and the net entropy change is

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

But $$\frac{V_1}{T_1} = \frac{V_0}{T_f}, \quad \text{or} \quad T_f = T_1 \frac{V_0}{V_1} = T_0 n^{-\gamma}$$

So $$\Delta S = \left(\frac{m}{M} C_p\right) \ln \frac{1}{n} = -\frac{m}{M} C_p \ln n = -\frac{m}{M} \frac{R\gamma}{\gamma - 1} \ln n = -9{\cdot}7 \text{ J/K}$$

**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

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

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

**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.

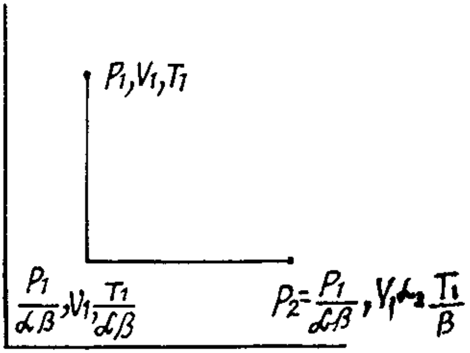
$$\Delta S = \nu \left( \int_{T_1}^{\frac{T_1}{\alpha\beta}} C_V \frac{dT}{T} + \int_{\frac{T_1}{\alpha\beta}}^{\frac{T_1}{\beta}} C_p \frac{dT}{T} \right)$$

$$= \nu (C_p \ln \alpha - C_V \ln \alpha\beta)$$

$$= \nu \left( R \ln \alpha - \frac{R}{\gamma - 1} \ln \beta \right) = \nu R \left( \ln \alpha - \frac{\ln \beta}{\gamma - 1} \right)$$

With $\gamma = \frac{5}{3}$, $\alpha = 2$ and $\beta = 1{\cdot}5$, $\nu = 1{\cdot}2$,

this gives $\Delta S = 0{\cdot}85$ Joule/°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 $$\Delta S = \int_{T_0}^{\tau T_0} C \frac{dT}{T} = \frac{n - \gamma}{(\gamma - 1)(n - 1)} R \ln \tau$$

**2.137** The process in question may be written as

$$\frac{p}{p_0} = \alpha \frac{V}{V_0}$$

where $\alpha$ 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 $\alpha$ times then so does the pressure. The temperature must then increase $\alpha^2$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 $\quad \nu = 2\,,\ \gamma = \frac{5}{3},\ \alpha = 2, \Delta S = 46{\cdot}1$ Joule/°K

**2.138** Let $(p_1,\ V_1)$ be a reference point on the line

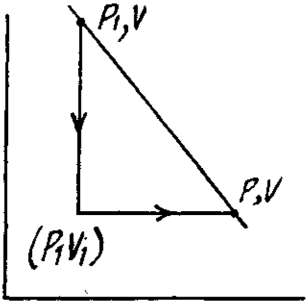
$$p = p_0 - \alpha V$$

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 $\Delta S$

$$\frac{\partial\,\Delta\,S}{\partial V} = \frac{-\,\alpha\,C_V}{p_0 - \alpha\,V} + \frac{C_p}{V} = 0$$

or $\ C_p\,(p_0 - \alpha\,V) - \alpha\,V\,C_V = 0$

or $\ \gamma\,(p_0 - \alpha\,V) - \alpha\,V = 0\ $ or $\ V = V_m = \dfrac{\gamma\,p_0}{\alpha\,(\gamma + 1)}$

This gives a maximum of $\Delta S$ because $\dfrac{\partial^2\,\Delta S}{\partial V^2} < 0$

**(Note :-** a maximum of $\Delta S$ 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, $$pdV = \frac{RT}{V}\,dV = aT\,dT$$

or $$\frac{R}{a}\frac{dV}{V} = dT \quad \text{or,} \quad \frac{R}{a}\ln V + \text{constant} = T$$

Using $T = T_0$ when $V = V_0$, we get, $T = T_0 + \frac{R}{a}\ln\frac{V}{V_0}$

**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 $$\Delta S = R\ln\frac{V_2 - b}{V_1 - b}$$

**2.141** We use, $$\Delta S = \int_{V_1, T_1}^{V_2, T_2} dS(V, T) = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_{V_1} dT + \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_{T = T_2} dV$$

$$= \int_{T_1}^{T_2} \frac{C_V dT}{T} + \int_{V_1}^{V_2} \frac{R}{V - b}\, dV = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2 - b}{V_1 - b}$$

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** $$\Delta S = \int_{T_1}^{T_2} \frac{C dT}{T} = \int_{T_1}^{T_2} \frac{m(a + bT)}{T} dT = mb(T_2 - T_1) + ma\ln\frac{T_2}{T_1}$$

**2.144** Here $T = a\,S^n$ or $S = \left(\frac{T}{a}\right)^{\frac{1}{n}}$

Then $$C = T\frac{1}{n}\frac{T^{\frac{1}{n}-1}}{a^{1/n}} = \frac{S}{n}$$

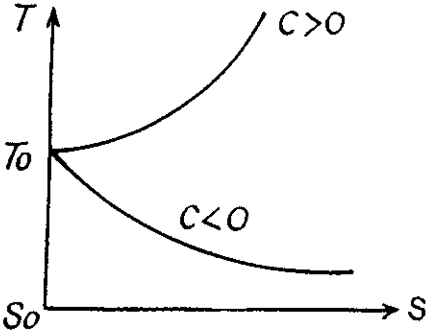
Clearly $$C < 0 \text{ if } n < 0.$$

**2.145** We know,

$$S - S_0 = \int_{T_0}^{T} \frac{C\,dT}{T} = C\ln\frac{T}{T_0}$$

assuming $C$ to be a known constant.

Then $T = T_0 \exp\left(\frac{S - S_0}{C}\right)$



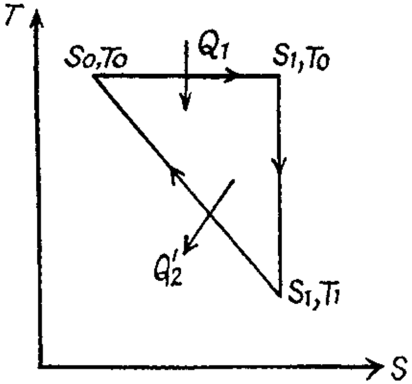
**2.146** (a) $C = T\frac{dS}{dT} = -\frac{\alpha}{T}$

(b) $Q = \int_{T_1}^{T_2} C\,dT = \alpha\ln\frac{T_1}{T_2}$

(c) $W = \Delta Q - \Delta U \qquad = \alpha\ln\frac{T_1}{T_2} + C_V(T_1 - T_2)$

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

$$Q = \int T\,dS = \text{ area under the curve}$$

$$Q_1 = T_0(S_1 - S_0)$$

$$Q'_2 = \frac{1}{2}(T_0 + T_1)(S_1 - S_0)$$

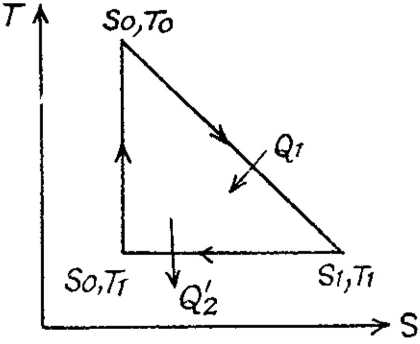
Thus, using $T_1 = \frac{T_0}{n}$,

$$\eta = 1 - \frac{T_0 + T_1}{2\,T_0} = 1 - \frac{1 + \frac{1}{n}}{2} = \frac{n-1}{2n}$$

(b) Here $Q_1 = \frac{1}{2}(S_1 - S_0)(T_1 + T_0)$

$$Q'_2 = T_1(S_1 - S_0)$$

$$\eta = 1 - \frac{2T_1}{T_1 + T_0} = \frac{T_0 - T_1}{T_0 - T_1} = \frac{n-1}{n+1}$$



**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

$$\Delta S = \int \frac{dQ}{T} = \int_{V_1}^{V_2} \frac{pdV}{T} = \nu R \ln n = 20{\cdot}1 \text{ J/K}$$

**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,

$$0 = U_F - U_f + \int_{V_f}^{V_0} pdV, \; V_f = 2\,V_0$$

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 $$\Delta\,U = U_F - U_i = \frac{R\,T_0}{\gamma-1}(2^{\gamma-1}-1)$$

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 $$\Delta S = \Delta S_I + \Delta S_{II} = \nu_1 R \ln \frac{V_1 + V_2}{V_1} + \nu_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$= \nu_1 R \ln (1 + n) + \nu_2 R \ln \frac{1 + n}{n} = 5{\cdot}1 \text{ J/K}$$

**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 $$c_1 = 0{\cdot}39 \text{ J/g °K},\ c_2 = 4{\cdot}18 \text{ J/g °K},$$

$$T_0 = 300\text{°K and } \Delta S = 28{\cdot}4 - 24{\cdot}5 = 3{\cdot}9 \text{ J / °K}$$

**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

$U_1 = C_V T_1$, $U_2 = C_V T_2$, $U = 2C_V \frac{T_1 + T_2}{2}$ and $(T_1 + T_2)/2$ 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 $$(T_1 + T_2)^2 = (T_1 - T_2)^2 + 4 T_1 T_2,\ \Delta S > 0$$

**2.154** (a) Each atom has a probability $\frac{1}{2}$ to be in either campartment. 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

$$N_{C_{N/2}} = \frac{N!}{N/2\,!\,\frac{N}{2}!} = \frac{10 \times 9 \times 8 \times 7 \times 6}{8 \times 4 \times 3 \times 2} = 252$$

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 $\dfrac{1}{\eta^2} = \dfrac{\pi}{6}\,d^3\,n_0$ or $d^3 = \dfrac{6}{\pi\,n_0\,\eta^2}$ or $d = \left(\dfrac{6}{\pi\,\eta^2\,n_0}\right)^{1/3} = 0{\cdot}41\ \mu\text{m}$

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.