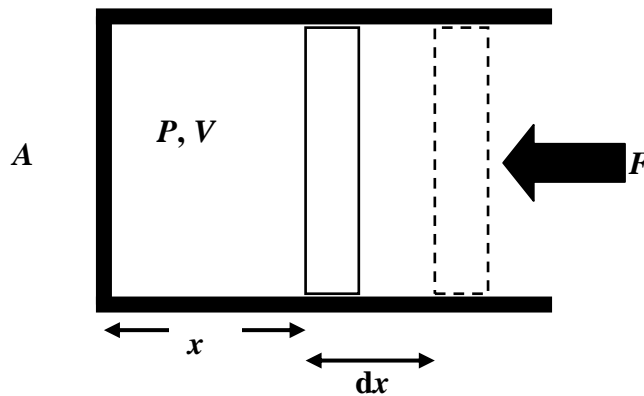


3 THE FIRST LAW OF THERMODYNAMICS.

3.1 Work

One of the most important ideas in thermodynamics is the concept of work, of a system's capability to perform mechanical work in a system transition between equilibrium states. Continuing with our use of the fluid/gas system as the paradigm to stand for general systems we can explore the concept of work with the aid, once again, of the piston now acting as a moving wall with which the contained gas particles may exchange energy, something we have already looked at.

Consider the piston system sketched below.



The force acting on the piston due to the pressure P of the gas is

$$F = PA$$

And this acts to the right and an equal but opposite external force $-F$ acting to the left will maintain the position of the piston. If the position of the piston changes under this force from $x + dx$ to x , thus changing the volume of the gas from

$$V = (x + dx)A \text{ to } V + dV = xA \text{ with } dV = V_f - V_i = -Adx$$

The infinitesimal work done on the gas by an external force is

$$dW = Fdx = PAdx = -PdV \quad (3.1)$$

The infinitesimal work done on a fluid during an infinitesimal change of volume, dV is then;

$$\delta W = -PdV \quad (3.2)$$

Note that because in this case (compression) dV is negative the value of $-PdV$ is itself positive. This is an example of a very important sign convention;

Work done on a system is positive

To compress the gas work was done on it by the surroundings.

It is important to note that in defining the work in this way we must ensure that the pressure remains well defined at all times and this requires that *the process must be performed quasi statically*, that is, it must proceed such that *at any instant the system is in an equilibrium state*. This further, means that at any instant we could reverse the change and return the system to its original state (along with the surroundings in as much as they are affected by the system). This is called a **reversible process**.

To be reversible we cannot have any loss or dissipation in the system and therefore the piston must be frictionless.

In 3.2 where an infinitesimal amount of work, δW has been performed (in this case on the system) the bar through the δ indicates the fact that the amount of work for a given volume change depends on the path chosen ie how we made the change dV . The change from V_A to V_B can be made in an infinity of ways and any one of them can be performed quasistatically and reversibly but requiring different amounts of work to be performed.

NB The basic difference between δW and dV is simply stated as;

dV represents a change of state from one equilibrium state to another and *its value is path independent*.

whereas

δW represents a process and *its value is path dependent*

dV is said to be a perfect differential whereas dW is an imperfect differential.

A perfect differential therefore represents a change in a function of state (U, T, V, P, \dots) while an imperfect differential represents how that change was carried out (a process or flow).

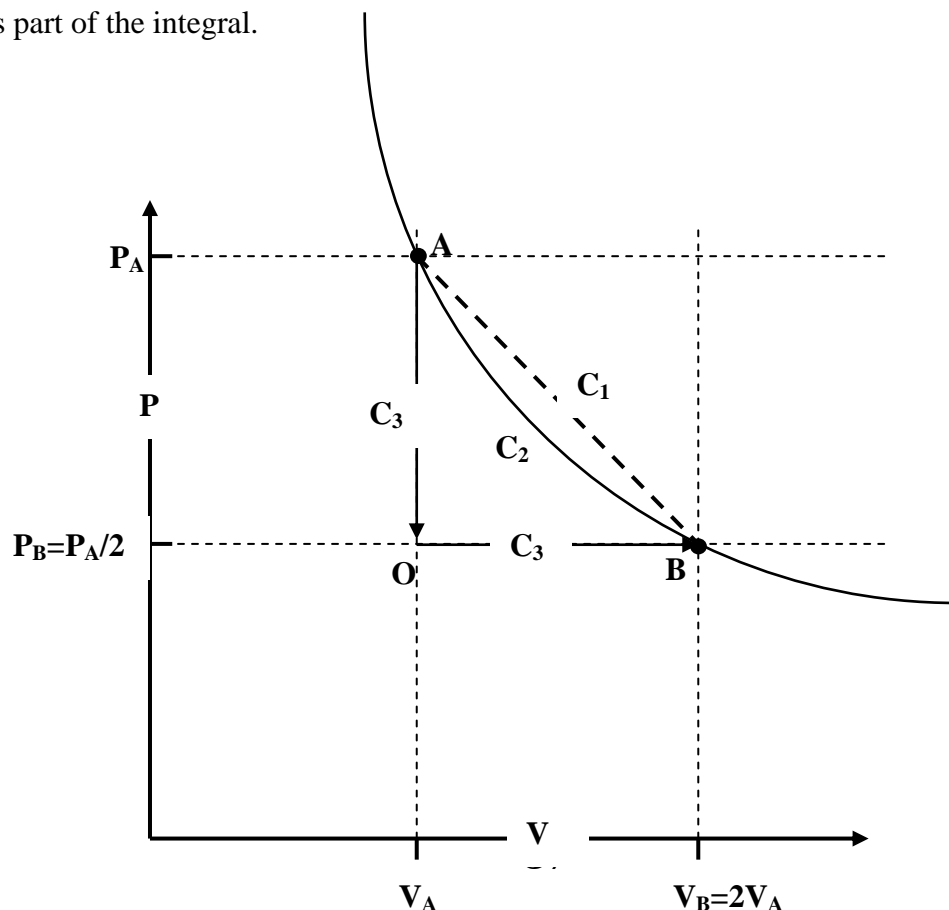
If we make a large change in the volume we need to find the net effect through integration and we have to take care in evaluating any integral in accounting for how the large changes were made, ie. the path followed. The volume change in going from A to B is easily evaluated

$$\Delta V = V_B - V_A = \int_{V_A}^{V_B} dV$$

The work performed has to be more carefully evaluated because in the integral

$$\Delta W = \int_{V_A}^{V_B} -P dV \quad (3.3)$$

There is no “initial work” W_A or “final work” W_B the concept is meaningless as we are talking about a process. There will be an amount of work done represented by the integral but we need caution here as depending on the path chosen to get from A to B the value of P inside the integral will change in different ways and needs to be included as part of the integral.



The PV diagram shown above, includes the start and end point of a process taking an ideal gas from equilibrium point A (P_A , V_A) to the equilibrium point B ($P_A/2$, $2V_A$). There are three processes (pathways) indicated and we examine each in turn to find the work done in going from A to B.

Example 1.

C_1 shows the direct route from A to B (on the diagram anyway). To find the work we need to know how P can be written in terms of V in order to evaluate the integral of PdV . In general the equation of the straight line joining (x_1, y_1) to (x_2, y_2) may be written as

$$y = y_1 + [(y_2 - y_1) / (x_2 - x_1)] \cdot (x - x_1)$$

Using this the equation of the line C_1 is

$$P = P_A + \left[\frac{P_A/2 - P_A}{2V_A - V_A} \right] (V - V_A) = P_A - \frac{P_A}{2V_A} (V - V_A) = \frac{3}{2} P_A - \frac{P_A}{2V_A} V \quad (3.4)$$

Therefore we can write the integral

$$\Delta W = \int_{V_A}^{V_B} P dV = -\frac{3}{2} P_A \int_{V_A}^{V_B} dV + \frac{P_A}{2V_A} \int_{V_A}^{V_B} V dV = -\frac{3}{2} P_A (V_B - V_A) + \frac{P_A}{2V_A} \left(\frac{V_B^2 - V_A^2}{2} \right) \quad (3.5)$$

We know $V_B = 2V_A$ and can tidy up to obtain

$$\Delta W = -\frac{3}{4} P_A V_A = -\frac{3}{4} nRT \quad (3.6)$$

Example 2

C_2 shows the isotherm. We know the equation of state for the ideal gas and as the temperature is constant along C_2 ,

$$P = \frac{nRT}{V}$$

The integral is then

$$\Delta W = \int_{V_A}^{V_B} -PdV = -nRT \int_{V_A}^{V_B} \frac{dV}{V} = -nRT [\ln V]_{V_A}^{V_B} = nRT \ln \left(\frac{V_A}{V_B} \right) \quad (3.7)$$

$$\Delta W = -nRT \ln 2 \quad (3.8)$$

Example 3

The path C_3 is in fact an isochore ($V = V_A = \text{constant}$) followed by an isobar ($P = P_A/2 = \text{constant}$). We break this into two integrals and

$$\Delta W = \int_{V_A}^{V_A} -PdV - \frac{P_A}{2} \int_{V_A}^{V_B} dV \quad (3.9)$$

The first integral is zero as $\Delta V = 0$ and the second is easily evaluated

$$\Delta W = -\frac{P_A}{2} (V_B - V_A) = -\frac{P_A V_A}{2} = -\frac{nRT}{2} \quad (3.10)$$

In summary

$$C_1 \quad \Delta W = -1.5nRT$$

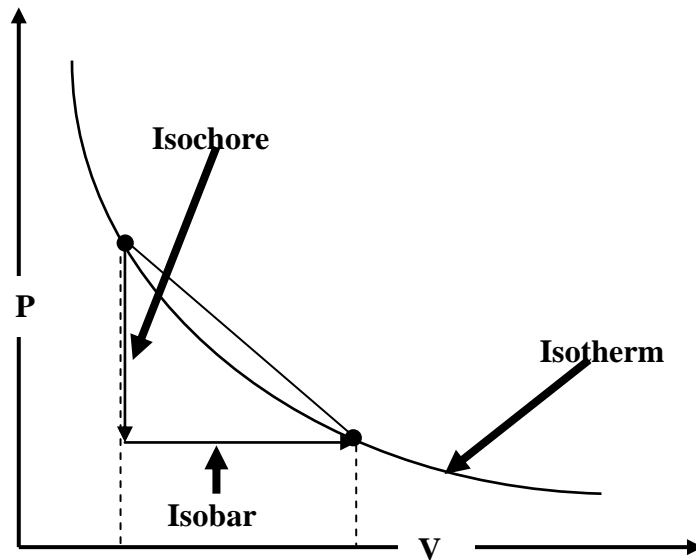
$$C_2 \quad \Delta W = -nRT \ln 2 = -0.69nRT$$

$$C_3 \quad \Delta W = -0.5nRT$$

Going from A to B necessitated the system doing work on the surroundings (all processes have negative values for the work). This was of necessity the case as the gas expanded!

The work expended by the system was different for each path. Being the least for C_3 and the greatest for C_1 .

Another view of the work can be seen from our use of the integral $\int_{V_A}^{V_B} -PdV$ and the PV diagram.



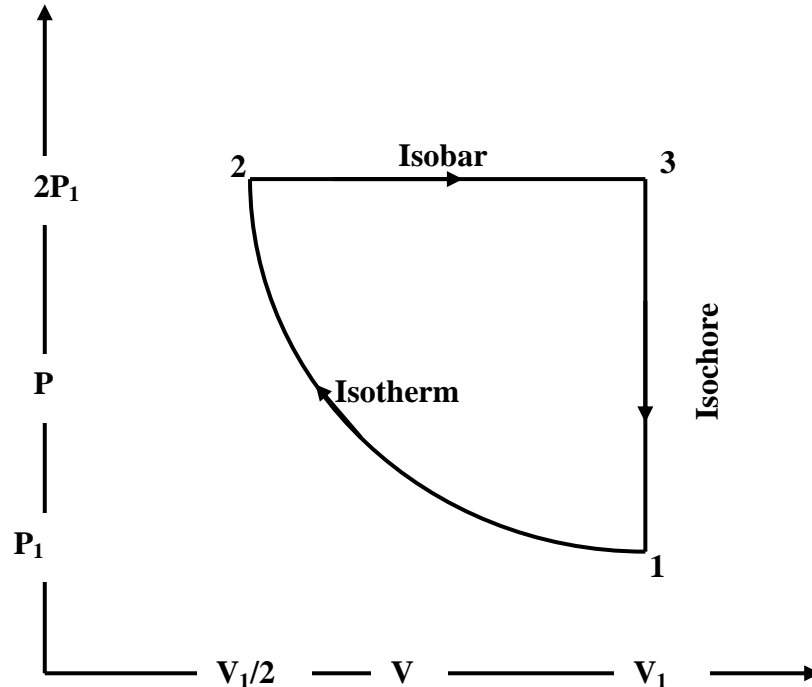
The integral $\int_{V_A}^{V_B} -PdV$ is seen to be the area under the line of the path between the path

and the $P = 0$ volume axis and looking at the above pressure volume indicator graph we can easily see the results obtained earlier for C_1 and C_3 by geometric area evaluation. This is not so easily done for path C_2 the isotherm. To get the sign correct we must take note of the direction in which the path is traversed. If going from left to right the sign convention, positive for work done on a system, the area is taken as negative. Proceeding from right to left or high to low volumes the area is positive as the gas is compressed and work is therefore done on the system.

Many times in this course we will be interested in cyclic processes that may be represented on the PV diagram and the work carried out by or done on the system can

be calculated over a cycle where the system at an equilibrium state A is caused to pass through a series of points (not all equilibrium points) before returning to A.

Example 4.



An ideal gas is compressed isothermally from V_1 to $V_1/2$ on the path $1 \rightarrow 2$. It is then expanded isobarically at $2P_1$ back to its original volume on path $2 \rightarrow 3$ before finally being returned isochorically to its original equilibrium state on the path $3 \rightarrow 1$

What is the work done by/on the gas?.

We need to evaluate and add three integrals, one for each path.

Path $1 \rightarrow 2$ is an integral we evaluated in an earlier example

$$\Delta W_{1 \rightarrow 2} = \int_{V_1}^{V_2} -PdV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT [\ln V]_{V_1}^{V_2} = nRT \ln \left(\frac{V_1}{V_2} \right) = nRT \ln 2 \quad (3.11)$$

Path $2 \rightarrow 3$ is isobaric and P is constant (again this was done earlier)

$$\Delta W_{2 \rightarrow 3} = -P_2(V_1 - V_2) = -P_2 \frac{V_1}{2} = -P_1 V_1 = -nRT \quad (3.12)$$

And path $3 \rightarrow 1$ is isochoric, $\Delta V = 0$ and therefore no work is done

$$\Delta W_{3 \rightarrow 1} = 0 \quad (3.13)$$

The total work done in the closed cycle is therefore

$$\Delta W_{tot} = \Delta W_{1 \rightarrow 2} + \Delta W_{2 \rightarrow 3} + \Delta W_{3 \rightarrow 1} = nRT \ln 2 - nRT + 0 \quad (3.14)$$

$$\Delta W_{tot} = nRT(0.69 - 1) = -0.31nRT \quad (3.14a)$$

Note the signs of ΔW in each of the arms of the cycle recalling that positive means work is done on the gas. The net work is negative meaning that overall in the cycle work is carried out by the gas.

If we now reverse the cycle

$$\Delta W_{1 \rightarrow 3} = 0 \quad (3.15)$$

$$\Delta W_{3 \rightarrow 2} = -P_2(V_2 - V_1) = +P_2 \frac{V_1}{2} = +P_1 V_1 = +nRT \quad (3.16)$$

$$\Delta W_{2 \rightarrow 1} = \int_{V_2}^{V_1} -P dV = -nRT \int_{V_2}^{V_1} \frac{dV}{V} = -nRT [\ln V]_{V_2}^{V_1} = -nRT \ln \left(\frac{V_1}{V_2} \right) = -nRT \ln 2 \quad (3.17)$$

This time the net work is

$$\Delta W_{Tot} = \Delta W_{1 \rightarrow 3} + \Delta W_{3 \rightarrow 2} + \Delta W_{2 \rightarrow 1} = 0 + nRT - 0.69nRT \quad (3.18)$$

$$\Delta W_{Tot} = nRT(1 - 0.69) = 0.31nRT \quad (3.18a)$$

and is positive, ie. the system has work done on it by the surroundings.

In fact, when the work extracted in one direction is equal to the work done in the other direction. **The cycle is said to be reversible.**

3.2 Internal Energy

We now want to ask about the internal energy changes during the cycle having looked at the work.

We had previously found that for an ideal monatomic gas (no rotation or vibration) that

the internal energy was given by the expression $U = \frac{3}{2}PV$

We can ask what are the changes in U as we traverse the cycle, first in the clockwise sense from $1 \rightarrow 2 \rightarrow 3$

$$\Delta U_{1 \rightarrow 2} = U_2 - U_1 = \frac{3}{2}(P_2V_2 - P_1V_1) = \frac{3}{2}(nRT_2 - nRT_1) = 0 \quad (3.19)$$

Because 1 and 2 lie on an isotherm and $T_1 = T_2$

For the next stage

$$\Delta U_{2 \rightarrow 3} = U_3 - U_2 = \frac{3}{2}(P_3V_3 - P_2V_2) = \frac{3}{2}(P_1V_1 - P_2V_2) = \frac{3}{2}(nRT_1 - nRT_2) = \frac{3}{2}nRT_1 \quad (3.20)$$

And for the final stage

$$\Delta U_{3 \rightarrow 1} = U_1 - U_3 = \frac{3}{2}(P_1V_1 - P_3V_3) = \frac{3}{2}(P_1V_1 - 2P_1V_1) = -\frac{3}{2}nRT_1 \quad (3.21)$$

The net change in internal energy around the cycle is then

$$\Delta U_{1 \rightarrow 2} + \Delta U_{2 \rightarrow 3} + \Delta U_{3 \rightarrow 1} = 0 + \frac{3}{2}nRT_1 - \frac{3}{2}nRT_1 = 0 \quad (3.22)$$

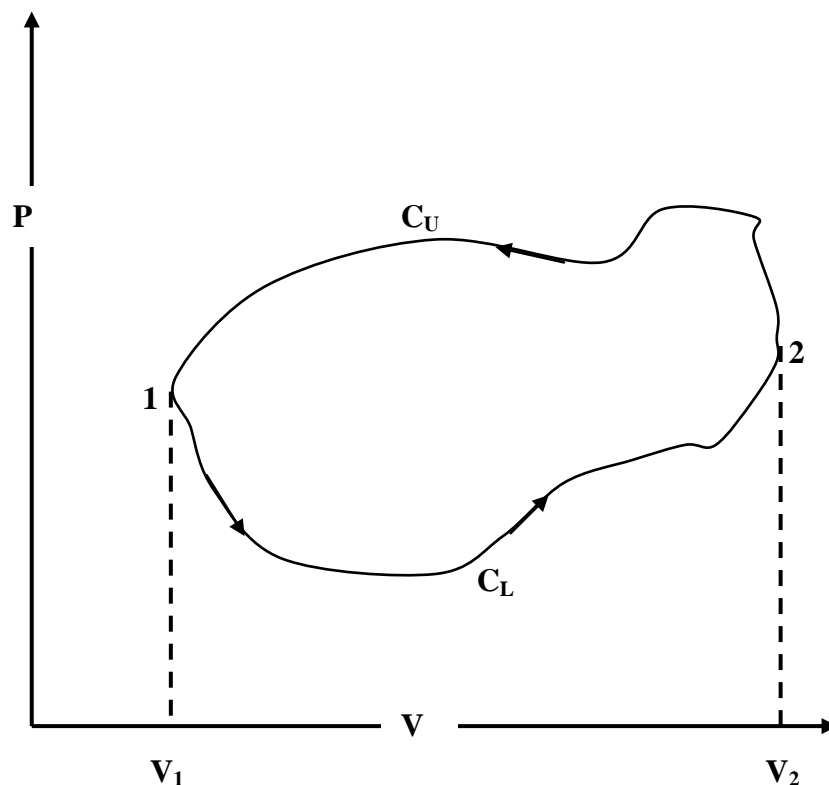
In performing this analysis we have learned two important things about the changes in internal energy after undergoing processes of a certain type;

(i) **Around a closed loop there is no change in internal energy.**

This is because there is no net temperature change and therefore the molecules cannot be going slower or faster otherwise continuous looping would lead to infinite or zero velocities. More succinctly, there is no change in U because it is a **STATE VARIABLE** and its value is representative of the particular equilibrium state. Unlike W which is not a state variable and is not therefore associated with any particular equilibrium state but rather with the process of going from one state to another.

(ii) Also note that **equilibrium states on an isotherm all have the same internal energy and we have $\Delta U_{1 \rightarrow 2} = 0$ along the isotherm.**

It is obviously true that ΔU is zero if we traverse the loop in the opposite sense (try it) for the same reason, U is a state variable. In fact we can be completely general, whatever closed loop from A back to A there will be no change in U because it is a state variable.



The above arbitrary closed cycle shows the general situation

$$\Delta U = \oint_C dU = 0$$

For ΔW we can find the work done after one cycle by finding the area of the upper and lower curve and subtracting the lower curve, work done by the system, (going from left to right with volume increasing) from the upper curve, work done on the system, (going from right to left with volume decreasing) to obtain the net work done on the system. It is the area enclosed by the circuit.

If we traversed the circuit in the other sense then the upper and lower curves would have their signs altered and work done on the system would be minus the area enclosed.

$$\Delta W = +\text{Area Enclosed (counter clockwise)}$$

$$\Delta W = -\text{Area Enclosed (clockwise)}$$

Around a closed cycle

- (i) **The work done depends on direction traversed and on the particular cycle chosen. It is path dependent and dW is an imperfect differential.**
- (ii) **The internal energy is unaltered independent of the closed cycle. U is a state variable and dU a perfect differential.**

Adiabatic Work

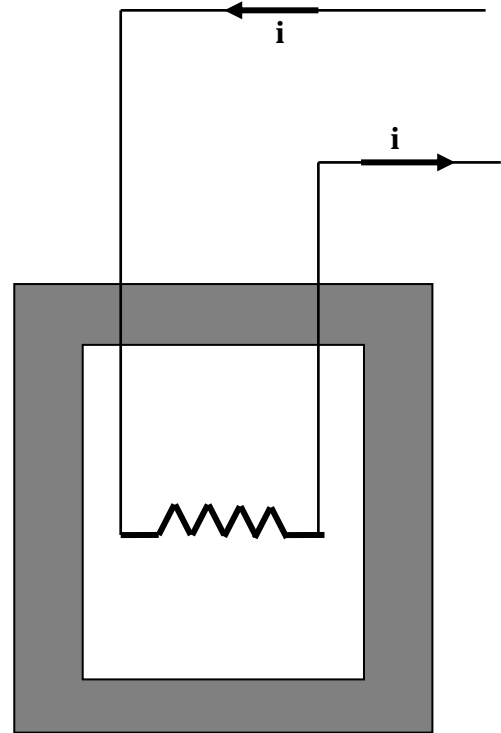
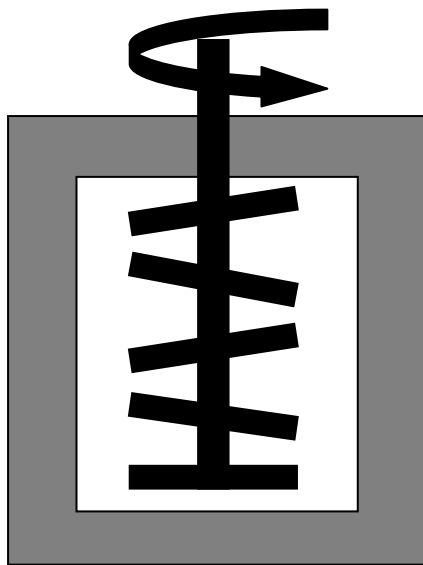
In a classic set of experiments it was demonstrated by Joule that if he enclosed a system within adiabatic walls (insulating walls allowing no heat transfer into or out of the system) then by doing a known amount of work on the system,

Eg.

stirring with paddles

or

heating with a known current and resistance



that starting from a particular equilibrium state the final end state depended only on the work done and not on how we go from the initial to the final state. He showed that the temperature rise $\Delta T \propto \Delta U = \Delta W$ the adiabatic work done on the system. In fact this is the empirical definition of the internal energy

$$\Delta W_{\text{Adiabatic}} = U_{\text{final}} - U_{\text{initial}} \quad (3.23)$$

3.3 Heat and the First Law

The case of a thermally/adiabatically isolated system is a special one and the observations noted previously have important implications when followed through.

When the system is not adiabatically isolated then it is the case that

$$\Delta U \neq \Delta W \quad (3.24)$$

This is of great consequence since at first sight it implies non-conservation of energy! By now the conservation of energy had taken its place in the pantheon of physical principles as an inviolable requirement and this position could only be reversed at great cost to the existing understanding of the universe. It was now an item of faith that the amount of energy in the universe was a constant and unchanging, only the form in which it was present altered, it's actual quantity was God given, from the start of the universe and could not be added to or subtracted from by any mechanism. In this respect it had been a late comer to the group of conserved quantities which included momentum and angular momentum (Newton), again fixed quantities which were present at the creation and continued unaltered, and mass (Lavoisier). To maintain this inviolability of energy conservation in the face of the evidence of careful thermodynamic measurements where heat flows were allowed to occur it was recognised that in thermodynamic systems **the concept of heat flow, ΔQ was essential** and that ΔQ was just another form of energy. Heat flow like work however was a form of energy in transit. No body could be said to hold a quantity of work or heat, the two only existed as transient forms while energy changes from one form to another. Thus

The First Law of Thermodynamics

was born, the change in internal energy after some process is carried through is given by

$$\Delta U = \Delta Q + \Delta W \quad (3.25)$$

ΔW is the work done on the system in that process and ΔQ is the heat transferred to the system by that process.

Note that ΔQ like ΔW is not a state variable and should be formally written with the strikethrough across the Δ or d . dQ and dW are both path dependent and imperfect differentials unlike dV , dP , dT and dU .

The sign convention must be upheld when using the first law.

- (i) *Earlier we had the convention that ΔW was positive when the system has work done on it and negative when it is the system that does work.*
- (ii) *Similarly the convention for heat flow is that ΔQ is positive when it flows into the system and negative when it flows from the system.*

The first law may also be written in infinitesimal form as

$$dU = dQ + dW \quad (3.26)$$

In the infinitesimal form the first law holds for all processes reversible and irreversible.

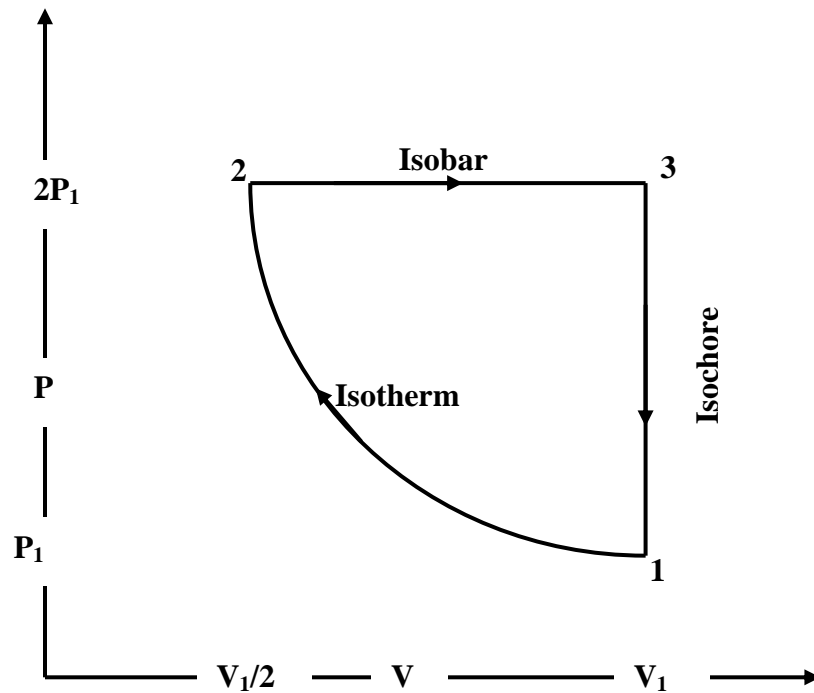
When the process is reversible we may use our expression(s) for dW to cast the first law in the form

$$\text{Fluid} \quad dU = dQ - PdV \quad (\text{Reversible}) \quad (3.27)$$

The heat flow must be path dependent as the work is path dependent and we need the first law to hold for any path.

$$\Delta Q = \int_A^B dQ \quad (3.28)$$

We return to our previous example to look at heat flow around a closed cycle using the first law



$$\Delta Q_{1 \rightarrow 2} = \Delta U_{1 \rightarrow 2} - \Delta W_{1 \rightarrow 2} = 0 - nRT_1 \ln \frac{V_1}{V_2} = -nRT_1 \ln 2 \quad (3.29)$$

This is negative on going from $1 \rightarrow 2$ and means that heat flows out from the system.

$$\Delta Q_{2 \rightarrow 3} = \Delta U_{2 \rightarrow 3} - \Delta W_{2 \rightarrow 3} = \frac{3}{2} P_1 V_1 - (-P_1 V_1) = \frac{5}{2} P_1 V_1 = +\frac{5}{2} nRT_1 \quad (3.30)$$

This is positive and on going from $2 \rightarrow 3$ heat flows into the gas.

$$\Delta Q_{3 \rightarrow 1} = \Delta U_{3 \rightarrow 1} - \Delta W_{3 \rightarrow 1} = -\frac{3}{2} P_1 V_1 - 0 = -\frac{3}{2} nRT_1 \quad (3.31)$$

This is negative and therefore on going from $3 \rightarrow 1$ heat flows out of the gas.

The net heat flow around the cycle is

$$\Delta Q_{net} = \Delta Q_{1 \rightarrow 2} + \Delta Q_{2 \rightarrow 3} + \Delta Q_{3 \rightarrow 1} = -nRT \ln 2 + \frac{5}{2} nRT_1 - \frac{3}{2} nRT_1 = nRT_1 (1 - \ln 2) \quad (3.32)$$

This is positive and therefore there is net heat flow into the gas if this closed cycle is traversed. Previously we found that the net work was

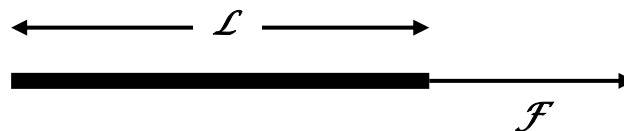
$$\Delta W_{net} = nRT(\ln 2 - 1) < 0$$

The net work was done by the gas and is equal to the net flow of heat into the gas. They balance one another leaving $\Delta U = 0$ as required after traversing a closed cycle and in order to satisfy the first law of thermodynamics.

Before continuing it is worth pausing at this point to note that whilst we have focused on the fluid system with two independent variables P and V **what has preceded is equally applicable to other systems once we have discovered the correct independent or state variables to use and the relevant equation of state.** Briefly some examples of these are;

Example 1. Rubber band (or wire)

We can consider doing work on a rubber band by pulling on it and causing its extension. Two obvious variables are then the tension in, and the length of the rubber band.



When the elastic band is extended from its equilibrium length, L_0 , by an amount dL , there is a tension in the band and a balancing external force \mathcal{F} has to be applied to keep the system in equilibrium. This involves work being **done on** the band (positive work).

$$dW = \mathcal{F}dL \quad (3.33)$$

The first law for the rubber band may be written for reversible process using our definition of work ($-PdV$ is replaced by $\mathcal{F}dL$)

First Law of Thermodynamics

$$dU = dQ + \mathcal{F}dL \quad \text{(Reversible)} \quad (3.34)$$

An **Equation of State** may be discovered of the form

$$\mathcal{F} = aT \left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right] \quad (3.35)$$

Where L_0 is some reference length, the length when the band is not under tension and the square bracket in the state equation goes to zero. We may use this equation of state to find for example the thermal expansion coefficient, α , at constant tension

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{\mathcal{F}} \quad (3.36)$$

Using the reciprocal relation,
$$\left(\frac{\partial L}{\partial T} \right)_{\mathcal{F}} = \frac{1}{\left(\frac{\partial T}{\partial L} \right)_{\mathcal{F}}} \quad (3.37)$$

Phrasing the equation of state in terms of T

$$T = \frac{\mathcal{F}}{a \left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right]} \quad (3.38)$$

$$\left(\frac{\partial T}{\partial L} \right)_{\mathcal{F}} = \frac{-\mathcal{F}}{a \left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right]^2} \left(\frac{1}{L_0} + \frac{2L_0^2}{L^3} \right) = \frac{-T \left(\frac{1}{L_0} + \frac{2L_0^2}{L^3} \right)}{\left[\frac{L}{L_0} - \left(\frac{L_0}{L} \right)^2 \right]} \quad (3.39)$$

Therefore

$$\alpha = \frac{1}{\mathcal{L}} \left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\mathcal{F}} = \frac{1}{\mathcal{L}} \frac{1}{\left(\frac{\partial T}{\partial \mathcal{L}} \right)_{\mathcal{F}}} = - \frac{\left[\frac{\mathcal{L}}{\mathcal{L}_0} - \left(\frac{\mathcal{L}_0}{\mathcal{L}} \right)^2 \right]}{T \left[\frac{\mathcal{L}}{\mathcal{L}_0} + \frac{2\mathcal{L}_0^2}{\mathcal{L}^2} \right]} \quad (3.40)$$

This result can also be arrived at through implicit differentiation by differentiating both sides of the equation of state with respect to T whilst holding \mathcal{F} constant;

$$\left(\frac{\partial \mathcal{F}}{\partial T} \right)_{\mathcal{F}} = 0 = a \left[\frac{\mathcal{L}}{\mathcal{L}_0} - \left(\frac{\mathcal{L}_0}{\mathcal{L}} \right)^2 \right] + aT \left[\frac{1}{\mathcal{L}_0} + \frac{2\mathcal{L}_0^2}{\mathcal{L}^3} \right] \left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\mathcal{F}} \quad (3.41)$$

This, we can solve for $\left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\mathcal{F}}$

$$\left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\mathcal{F}} = - \frac{\left[\frac{\mathcal{L}}{\mathcal{L}_0} - \left(\frac{\mathcal{L}_0}{\mathcal{L}} \right)^2 \right]}{T \left[\frac{\mathcal{L}}{\mathcal{L}_0} + \frac{2\mathcal{L}_0^2}{\mathcal{L}^2} \right]} \quad (3.42)$$

A Test for Perfect Differentials

The differences between perfect and imperfect differentials have been mentioned frequently with respect to state variables such as internal energy which are examples of the former and work and heat, which are associated with particular processes therefore depending on the path taken from initial to final state and are examples of the latter. We now establish a test for the perfect differential as follows;

Suppose $z = z(x, y)$ is a function of state which depends on two independent variables, x and y .

Then

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (3.43)$$

And hence

$$dz = a(x, y)dx + b(x, y)dy \quad (3.44)$$

Also for dz to be a perfect differential requires by definition that

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} \quad (3.45)$$

implying

$$\frac{\partial a(x, y)}{\partial y} = \frac{\partial b(x, y)}{\partial x} \quad (3.46)$$

If we are given a differential in the form

$$dz = a(x, y)dx + b(x, y)dy \quad (3.47)$$

Such that

$$\frac{\partial a}{\partial y} = \frac{\partial b}{\partial x} \quad (3.48)$$

Then the differential is perfect and can be integrated to give z independent of the path, and z is a function of state.

If

$$\frac{\partial a}{\partial y} \neq \frac{\partial b}{\partial x} \quad (3.49)$$

Then the differential is imperfect and the integral of dz depends on the path. z is not a function of state.

Example.

An ideal monatomic gas, $U = \frac{3}{2}PV$

$$(i) \quad dU = \left(\frac{\partial U}{\partial P} \right)_V dP + \left(\frac{\partial U}{\partial V} \right)_P dV = \frac{3}{2}(VdP + PdV) \quad (3.50)$$

$$a = \frac{3}{2}V \quad b = \frac{3}{2}P \quad (3.51)$$

$$\frac{\partial a}{\partial V} = \frac{3}{2} = \frac{\partial b}{\partial P} = \frac{3}{2} \quad (3.52)$$

U is a perfect differential.

$$(ii) \quad dW = -PdV \quad (3.53)$$

First law $dQ = dU - dW = \frac{3}{2}(VdP + PdV) + PdV = \frac{3}{2}VdP + \frac{5}{2}PdV$

$$a = \frac{3}{2}V \quad b = \frac{5}{2}P \quad (3.54)$$

$$\frac{\partial a}{\partial V} = \frac{3}{2} \neq \frac{\partial b}{\partial P} = \frac{5}{2} \quad (3.55)$$

dQ is not a perfect differential

Applications of the First Law may now be examined.

(i) Heat Capacities

There are many simple applications of the first law and we begin by using it to define heat capacity.

If an amount of heat ΔQ is introduced to a finite system there will be an increase in temperature, ΔT and the heat capacity is defined as

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q_{\text{Rev}}}{\Delta T} = \frac{dQ_{\text{Rev}}}{dT} \quad \text{(Reversible change)} \quad (3.56)$$

It is defined when the change in temperature is a reversible one, that is to say at each intermediate temperature the new state is an equilibrium state obeying the state equation. In this case the input or output of heat will raise or lower the temperature by the same amount.

The specific/molar heat capacity is the heat capacity per unit mass/mole,

$$c = \frac{1}{m} \frac{dQ_{\text{Rev}}}{dT} = \frac{C}{m} \quad c = \frac{1}{n} \frac{dQ_{\text{Rev}}}{dT} = \frac{C}{n} \quad (3.57)$$

The value of C depends on the type of process in which the heat was transferred.

a) Constant Volume Heat capacity

$$C_V = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q_{\text{Rev}}}{\Delta T} \bigg|_{V=\text{const}} \quad (3.58)$$

From the first law

$$\Delta U = \Delta Q - \int PdV = \Delta Q \quad (V = \text{const}, dV = 0) \quad (3.59)$$

This allows for a measure of the specific heat capacity for a gas at constant volume that involves only state functions;

$$C_V = \lim_{\Delta T \rightarrow 0} \frac{\Delta U}{\Delta T} \bigg|_{V=const} = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} nR \quad (3.60)$$

b) Constant Pressure Heat Capacity

$$C_P = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} \bigg|_{P=const} \quad (3.61)$$

From the first law

$$\Delta U = \Delta Q - \int P dV = \Delta Q - \Delta(PV) \quad (3.62)$$

so for the heat

$$\Delta Q = \Delta U + \Delta(PV) = \Delta(U + PV) \quad (3.63)$$

A new state function, **Enthalpy**, H is defined

$$H = U + PV \quad (3.64)$$

We can find the infinitesimal change in H

$$dH = dU + PdV + VdP$$

And for isobaric processes where $dP = 0$ we have for the heat change,

$$dQ = dU + PdV = dH \quad (3.65)$$

Therefore a useful definition of the specific heat capacity for a gas at constant pressure that involves only state functions is

$$C_P = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q_{Rev}}{\Delta T} = \lim_{\Delta T \rightarrow 0} \frac{\Delta H}{\Delta T} \bigg|_{P=const} = \left(\frac{\partial H}{\partial T} \right)_P \quad (3.66)$$

$$U = \frac{3}{2} PV = \frac{3}{2} nRT \quad (3.67)$$

$$H = U + PV = \frac{3}{2}PV + PV = \frac{5}{2}PV = \frac{5}{2}nRT \quad (3.68)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}nR \quad (3.69)$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{5}{2}nR \quad (3.70)$$

And the relationship between C_P and C_V is then

$$C_P - C_V = nR \quad (3.71)$$

It should be noted that all of the above only applies to a monatomic gas, (no potential, rotational or vibrational contributions to U) where $U = \frac{3}{2}PV = \frac{3}{2}nRT$.

Taking a closer look at **ENTHALPY** the newly defined state function

$$H = U + PV = \frac{3}{2}PV + PV = \frac{5}{2}PV = \frac{5}{2}nRT \quad (3.72)$$

$$dH = dU + PdV + VdP \quad (3.73)$$

In situations where the pressure is constant, and these situations arise frequently in liquids or solutions which are often at atmospheric pressure

$$dH = dU + PdV = dQ \quad (3.74)$$

And the **natural variables** of the state function, H , *in an isobaric situation* are U (or T) and V where by natural variables we mean those variables which when held constant lead to no further change occurring in that state function ie. for the state function enthalpy if U and V are constant, $dU = dV = 0$ and the enthalpy is constant. A further

example is for the internal energy of an ideal gas where $U = \frac{3}{2}PV$ and

$$dU = \frac{3}{2}(PdV + VdP).$$

Clearly it is V and P that are the natural variables of U as when $dV = dP = 0$ then $dU = 0$.

If there is heat flow during a chemical reaction it is equal to the enthalpy of that reaction and the enthalpy is widely used in physical chemistry and is tabulated for common reactions.

In the definition of heat capacity the need for a reversible heat flow process was stressed. This is similar to reversible work previously encountered as it means the heat flow is induced by infinitesimal temperature differences rather than by finite difference in temperature, ie. it occurs quasi statically.

An example of irreversible heat flow is the dropping of a hot metal (metals conduct heat well and therefore the temperature of the metal will be uniform from inside to out and remain so) into a bowl of water at room temperature. The metal will rapidly transfer heat to the water in an irreversible process passing through non-equilibrium intermediate states. There is no way to take the metal back to its original (hot) state by infinitesimal changes to the environment.

An example of reversible heat flow is to place a finite system eg. the bowl of water in contact with a heat reservoir at a slightly different temperature (higher or lower). This could raise/lower the temperature of the water by dT before iterating with a reservoir at a slightly higher/lower temperature than the previous one. In this way the water could be taken from one equilibrium state to another at a higher/lower temperature in incremental steps, reversibly.

At this point we may define a **HEAT RESERVOIR** which is an important concept. Recalling, that we stated earlier that it is wrong to think of an object as containing heat, where heat like work is the result of a process and is correctly termed heat flow. The heat reservoir is a body of such large heat capacity that a flow of heat ΔQ to or from the system we are interested in, whilst changing the temperature of that system will have no

effect in changing the temperature of the reservoir. Using a series of heat reservoirs at different temperatures we can remove or add heat to our system reversibly.

(ii) Adiabatic Process for an Ideal Gas.

We begin by analysing an ideal gas undergoing a reversible adiabatic change (expansion/compression) and starting with the first law,

$$dU = dQ + dW = dQ - PdV \quad (3.75)$$

In an adiabatic process $dQ = 0$ by definition.
whence

$$dU = -PdV \quad (3.76)$$

For an ideal monatomic gas we have already established that $U = \frac{3}{2}PV$

And therefore

$$dU = \frac{3}{2}(PdV + VdP) = -PdV \quad (3.77)$$

Re-arranging

$$\frac{5}{2}PdV + \frac{3}{2}VdP = 0 \quad (3.78)$$

and

$$\frac{5}{2} \frac{dV}{V} = -\frac{3}{2} \frac{dP}{P} \quad \frac{5}{3} \frac{dV}{V} = -\frac{dP}{P} \quad (3.79)$$

By integration

$$\frac{5}{3} \ln V = -\ln P + \text{const} \quad (3.80)$$

Rewritten using $n \ln x = \ln(x^n)$

$$\ln P + \ln \left(V^{5/3} \right) = \text{const} \quad (3.81)$$

Combining the logs

$$PV^{5/3} = PV^\gamma = (PV)V^{\gamma-1} = nRTV^{\gamma-1} = \text{const} \quad (3.82)$$

We have then demonstrated that at all points on the adiabatic PV curve (where in this case T does vary) are linked through the relationship

$$PV^{5/3} = PV^\gamma = \text{const} \quad (3.83)$$

and

$$TV^{\gamma-1} = \text{const} \quad (3.84)$$

that remain true. **NB the constants in the two equations are not the same!**

This problem could have been approached in a different fashion;

$$U = U(T) \quad (3.85)$$

Meaning that

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT = -PdV \quad (1^{\text{st}} \text{ Law with } dQ = 0) \quad (3.86)$$

$$C_V dT = -\frac{nRT}{V} dV \quad (3.87)$$

$$C_V \frac{dT}{T} = -nR \frac{dV}{V} \quad (3.88)$$

Integrating and using the relationship $C_P - C_V = nR$

$$C_V \ln T = -nR \ln V + \text{const} = (C_V - C_P) \ln V + \text{const} \quad (3.89)$$

$$\ln T + \left(\frac{C_P}{C_V} - 1 \right) \ln V = \text{const} \quad (3.90)$$

$$TV^{C_P/C_V - 1} = TV^{\gamma - 1} = \text{const} \quad (3.91)$$

With the important exponent γ given by

$$\gamma = \frac{C_P}{C_V} \quad (3.92)$$

Diatomic Gases

All of the foregoing was related to monatomic gases where the relations

$$U = \frac{3}{2}PV = \frac{3}{2}nRT$$

were found by considering the translational momentum exchange

of a molecule at a container wall and how this contributed to the pressure. We now wish to turn to the case of diatomic gases in order to be able to compare and contrast their behaviour with that of the monatomic gases.

Previously it was shown that for the monatomic gas where there is only translational energy to be considered

$$U = N \left\langle \frac{1}{2} m \vec{v}^2 \right\rangle = N \left(\left\langle \frac{1}{2} m v_x^2 \right\rangle + \left\langle \frac{1}{2} m v_y^2 \right\rangle + \left\langle \frac{1}{2} m v_z^2 \right\rangle \right) = \frac{3}{2} N k_B T$$

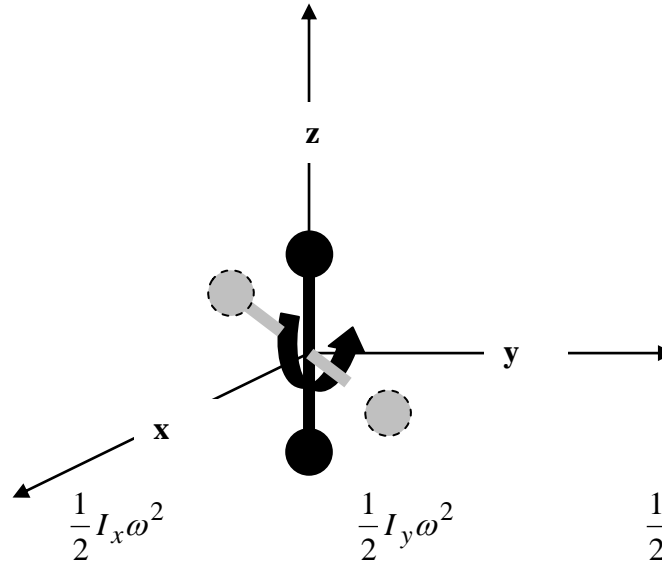
It is the case that for each degree of freedom available to the atom there was

$\frac{1}{2} k_B T$ average thermal energy. With this reminder we may now ask what happens if we

allow more degrees of freedom or in other words more independent or orthogonal ways in which a constituent part of a system may hold energy.

(i) We now suppose that the gas is composed of **rigid diatomic molecules** where by rigid we mean that there is a constant internuclear separation.

The molecule shown as a dumbbell is now able to rotate about the x, y and z axes with kinetic energies



$$\frac{1}{2} I_x \omega^2 \quad \frac{1}{2} I_y \omega^2 \quad \frac{1}{2} I_z \omega^2 \quad (3.93)$$

respectively. With the molecule aligned along the z axis and the atoms treated as point like objects the moment of inertia $I_z \ll I_x = I_y$ and there are effectively two new degrees of freedom added to each molecule.

For each of these

$$\left\langle \frac{1}{2} I_x \omega^2 \right\rangle = \frac{1}{2} k_B T \quad \text{and} \quad \left\langle \frac{1}{2} I_y \omega^2 \right\rangle = \frac{1}{2} k_B T \quad (3.94)$$

The internal energy of a collection of N of these rigid diatomic molecules is

$$U = N(\langle E_{Trans} \rangle + \langle E_{Rot} \rangle) = N \left(\left\langle \frac{1}{2} m v_x^2 \right\rangle + \left\langle \frac{1}{2} m v_y^2 \right\rangle + \left\langle \frac{1}{2} m v_z^2 \right\rangle + \left\langle \frac{1}{2} I_x \omega^2 \right\rangle + \left\langle \frac{1}{2} I_y \omega^2 \right\rangle \right) = \frac{5}{2} N k_B T \quad (3.95)$$

Now we have for C_V

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{5}{2} nR \quad (3.96)$$

And for $H = U + PV$

$$H = U + PV = \frac{5}{2} PV + PV = \frac{7}{2} PV = \frac{7}{2} nRT \quad (3.97)$$

So for C_P

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{7}{2} nR \quad (3.98)$$

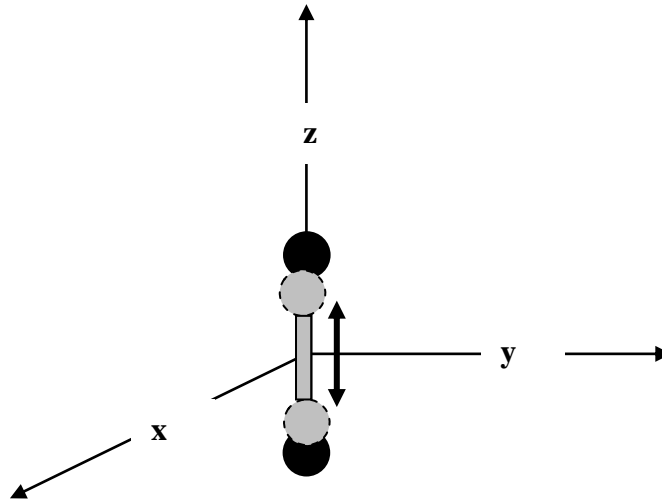
and

$$\gamma = \frac{C_P}{C_V} = \frac{7}{5} \quad (3.99)$$

For an adiabatic process T and V are always related by

$$TV^{C_P/C_V - 1} = TV^{2/5} = TV^{\gamma-1} = \text{const} \quad (3.100)$$

(ii) If the condition of rigidity were to be relaxed and the diatomic molecule was allowed to vibrate



The **vibration** occurs along the axis joining the two atoms and this motion has **potential energy** and **kinetic energy** associated with it, adding a further two degrees of freedom and a further $k_B T$ per molecule to the internal energy of the gas which is now

$$U = \frac{7}{2} N k_B T \quad (3.101)$$

And the changes to C_V , H and C_P that follow this change in internal energy are now;

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{7}{2} nR \quad (3.102)$$

and

$$H = U + PV = \frac{7}{2} PV + PV = \frac{9}{2} PV = \frac{9}{2} nRT \quad (3.103)$$

with

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{9}{2} nR \quad (3.104)$$

and

$$\gamma = \frac{C_P}{C_V} = \frac{9}{7} \quad (3.105)$$

and finally for an adiabatic process on a gas of non rigid diatomic molecules

$$TV^{C_P/C_V - 1} = TV^{2/7} = TV^{\gamma-1} = \text{const} . \quad (3.106)$$

HEAT CAPACITY OF CLASSICAL IDEAL GASES**Equation of state $PV = nRT$**

Monatomic Gas	Rigid Diatomic Gas	Vibrating Diatomic Gas
$U = \frac{3}{2}nRT$	$U = \frac{5}{2}nRT$	$U = \frac{7}{2}nRT$
$C_V = \frac{3}{2}nR$	$C_V = \frac{5}{2}nR$	$C_V = \frac{7}{2}nR$
$H = \frac{5}{2}nRT$	$H = \frac{7}{2}nRT$	$H = \frac{9}{2}nRT$
$C_P = \frac{5}{2}nR$	$C_P = \frac{7}{2}nR$	$C_P = \frac{9}{2}nR$
$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$	$\gamma = \frac{C_P}{C_V} = \frac{7}{5}$	$\gamma = \frac{C_P}{C_V} = \frac{9}{7}$
Internal energy due to 3 translational DoF .	Internal energy due to 3 translational DoF plus 2 rotational DoF.	Internal energy due to 3 translational DoF plus 2 Rotational DoF plus 2 Vibrational DoF.

For more complex gases there may be even more degrees of freedom and the measurement of $\frac{C_P}{C_V}$ may provide valuable insights into the make up of the gas molecules.

It should be remarked upon here that classically all is fine with the foregoing and we have nice relationships between specific heat capacities and the numbers of degrees of freedom. However if we examined the behaviour of the heat capacity of an actual diatomic gas we would find that the heat capacity would depend on temperature, a fact that is not reflected in our classical model. To explain this we turn to quantum mechanics where we know that the energies of rotation and vibration are in fact quantised;

For vibrational states;

$$E_{Vib} = \left(n + \frac{1}{2} \right) \hbar \omega \quad (3.107)$$

Where ω is the frequency of oscillation of the simple harmonic oscillator

$$\omega = \sqrt{\frac{\kappa}{\mu}} \quad (3.108)$$

With κ the spring constant (related to bond strength) and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced

mass and n the vibrational quantum number or occupancy of the vibrational level. The quantised vibration behaves as a boson and therefore it is not restricted by Pauli's exclusion principle and may have multiple occupancy, the quantum equivalent of an increased classical amplitude of oscillation.

For rotational states;

$$E_{Rot} = \frac{J(J+1)\hbar^2}{2I} \quad (3.109)$$

where J is the rotational quantum number and I the moment of inertia.

For both of these quantised energies, if the unit of quantisation is larger than $\frac{1}{2}k_B T$, the process is effectively unavailable to the molecule and the degree of freedom therefore unavailable also. This means that as we lower temperature the extra processes are “frozen” out and the internal energy is dropped in an almost stepwise fashion causing the specific heats to drop “suddenly”. A non rigid diatomic molecule will first lose the two degrees of freedom due to vibration as temperature is lowered before losing the two rotational degrees of freedom. There is always the zero point vibrational energy $\frac{1}{2}\hbar\omega$, but this does not contribute to the heat capacity as it doesn't contribute to a rise in internal energy as heat is introduced into the system. ie. it is always there irrespective.

ADIABATIC PROCESSES

Adiabatic processes, we saw, are described by the equation

$$PV^\gamma = \text{const} \quad P = \frac{\text{const}}{V^\gamma} \quad (3.83)$$

cf Isothermal processes

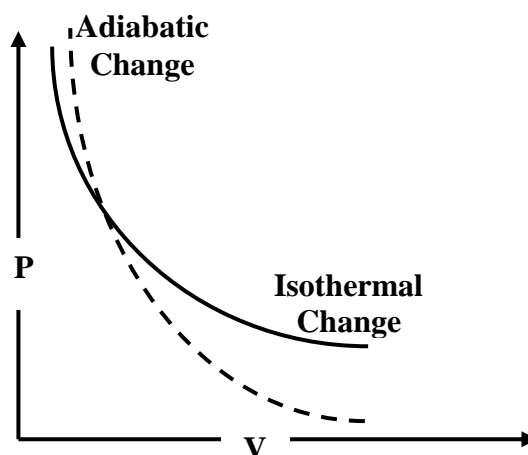
$$PV = nRT = \text{const} \quad P = \frac{\text{const}}{V} \quad (3.110)$$

For adiabatic changes we find the rate of change of pressure with volume or slope of the adiabatic line on a P V diagram

$$\frac{dP}{dV} = \frac{-\gamma \text{const}}{V^{\gamma+1}} = \frac{-\gamma PV^\gamma}{V^{\gamma+1}} = \frac{-\gamma P}{V} \quad (3.111)$$

Cf Isothermal changes

$$\frac{dP}{dV} = \frac{-\text{const}}{V^2} = \frac{-PV}{V^2} = \frac{-nRT}{V^2} = \frac{-P}{V} \quad (3.112)$$



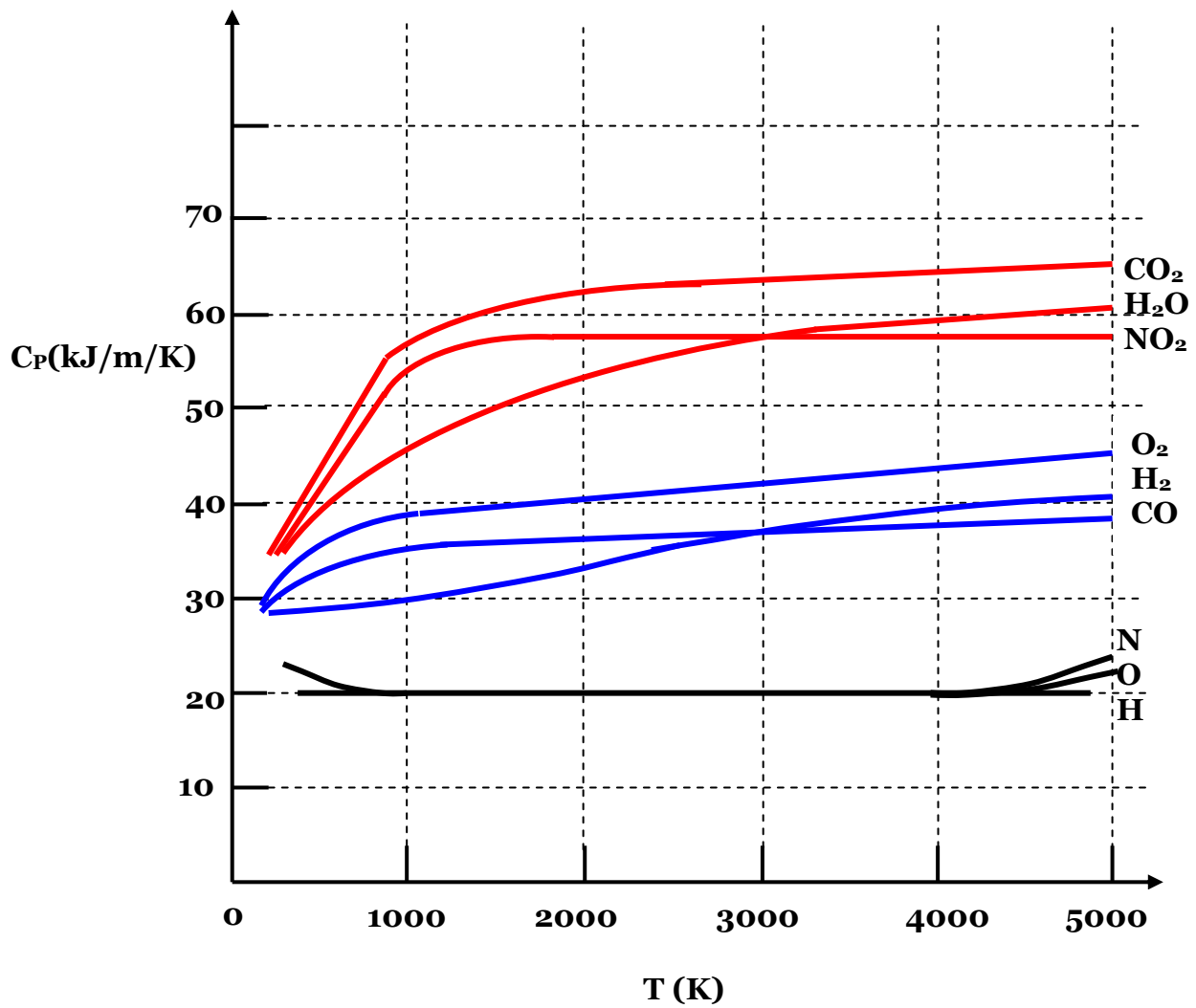
We note that the magnitude of the local slope in a PV diagram is always greater for

$$\text{adiabatic change than for isothermal change, } \left| \frac{-\gamma P}{V} \right|_{\text{Adiabatic}} > \left| \frac{-nRT}{V^2} \right|$$

We now look at actual gases to see how well the foregoing discussion describes them;

Gas	C_V	C_P	γ
Oxygen, O ₂	0.658	0.981	1.49
Nitrogen, N ₂	0.743	1.04	1.40
Hydrogen, H ₂	10.2	14.3	1.402
Carbon Monoxide, CO	0.744	1.04	1.398
Water, H ₂ O	1.4	1.86	1.33
Carbon Dioxide, CO ₂	0.657	0.846	1.287
Sulphur Dioxide SO ₂	0.47	0.60	1.276
Ammonia, NH ₃	1.66	2.15	1.295
Benzene, C ₆ H ₆	0.67	0.775	1.157

Table of specific heat capacities for several monatomic, diatomic, triatomic and more complex gases. The values are taken at high temperature where all the degrees of freedom are allowed to play a role, ie. $k_B T > E_{\text{quantum}}$



Graph showing variation of C_p with temperature for a variety of monatomic, diatomic and triatomic gases.

The Van Der Waals Gas.

Having looked at other types of “ideal” gas (rigid diatomic and non rigid diatomic) and their behaviours we now turn our attention to real gases. The most well known of these is the van der Waals gas, where the modified equation of state is what is being referred to in the name, the ideal gas equation of state, $PV = nRT$, being replaced by

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad (3.113)$$

The constant a and the alteration to the pressure term in the first part of the LHS are found to approximate real gases taking care of the problem of interaction which ideal gases avoid by going to the dilute limit. The term $\left(\frac{n}{V} \right)^2$ reflects the effect of increasing concentration on the contribution to internal energy made by molecule-molecule interactions. In the second term, the volume V is reduced by an amount b per mole in order to account for the finite size of the atoms themselves. This has been the most successful modification made to the ideal gas equation of state and is widely used.

The internal energy of the Van der Waals gas.

When $T = 0$ and kinetic energy is zero. In an ideal gas the pressure would go to zero as well as it is the direct result of the exchange of molecular momenta with the walls in which the gas is contained. However, the VdW equation of state reduces to

$$P = -\frac{n^2 a}{V^2} \quad (T = 0) \quad (3.114)$$

Where we see that the pressure is finite at zero temperature and is proportional to the square of the density of molecules, and this is physically the result of the mutual attraction of molecules. If we begin with an extreme dilution which we take as the reference energy level and compress this gas we can calculate the work required to achieve the compression,

$$\Delta W = - \int_{\infty}^V P dV = n^2 a \int_{\infty}^V \frac{dV'}{V'^2} \quad (3.115)$$

integrating,

$$\Delta W = -n^2 a \frac{1}{V'} \Big|_{\infty}^V = -\frac{n^2 a}{V} \quad (3.116)$$

ie. after doing this work at $T = 0$ the gas has some energy which we take to be the stored molecular potential energy at a volume V , not available to ideal gases! This means that the total internal energy of a VdW gas has both, kinetic and potential energy contributions

$$U_{VdW} = \frac{3}{2} nRT - \frac{n^2 a}{V} \quad (3.117)$$

This is for monatomic VdW (real) gases with three translational degrees of freedom.

NB, from the above expression for U_{VdW} and the equation for the heat capacity at constant volume

$$C_V(VdW) = \left(\frac{\partial U_{VdW}}{\partial T} \right)_V = \frac{3}{2} nR \quad (3.118)$$

Is unchanged from that of a real gas. This is of course as it should be as the increase in heat flow should only affect the kinetic part of the internal energy and not the potential energy part.

We note in passing that the internal energy is now a function of 2 state variables unlike previously;

$$U_{VdW} = U(T, V)$$

$$U_{Ideal} = U(T)$$

We can re-cast the internal energy of the VdW gas using the equation of state to obtain it in terms of pressure and volume;

$$U_{VdW} = \frac{3n}{2} \left(P + \frac{n^2 a}{V^2} \right) \left(\frac{V}{n} - b \right) - \frac{n^2 a}{V} \quad (3.119)$$

NB we have taken the factor n outside of the second bracket on the RHS.

Now expand the brackets

$$U_{VdW} = \frac{3n}{2} \left[\frac{PV}{n} - Pb + \frac{na}{V} - \frac{n^2 ab}{V^2} \right] - \frac{n^2 a}{V} \quad (3.120)$$

Simplify

$$U_{VdW} = \frac{3}{2} P(V - nb) + \frac{1}{2} \frac{n^2 a}{V} - \frac{3}{2} \frac{n^3 b}{V^2} \quad (3.121)$$

and

$$U_{VdW} = U(P, V)$$

The adiabatic law for Van der Waals gases.

We have the equation of state of the Van der Waals gas (3.113);

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

And it is sensible to ask if we can find an equation describing an adiabatic law, equivalent to that which we have already found for an ideal gas,

$PV^{5/3} = PV^\gamma = \text{const}$ (where $5/3$ indicates that it is a monatomic gas that we have in mind).

We have previously obtained the internal energy of the Van der Waals gas,

$U_{VdW} = \frac{3}{2} nRT - \frac{n^2 a}{V}$. To find the adiabatic law we use the first law as follows;

$$dU = dQ + dW = 0 - PdV \quad (3.122)$$

Finding dU from the equation for U_{vdW} , a rearranged equation of state with pressure as the subject

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad (3.123)$$

and using it in the first law

$$dU = \frac{3}{2} nRdT + \frac{n^2 a}{V^2} dV = -PdV = \frac{-nRT}{V - nb} dV + \frac{n^2 a}{V^2} dV \quad (3.124)$$

$$\frac{3}{2} \frac{dT}{T} = - \frac{dV}{V - nb} \quad (3.125)$$

By integrating the above

$$\frac{3}{2} [\ln T]_i^f = - [\ln(V - nb)]_i^f \quad (3.126)$$

Re-arranging

$$\ln \left(\frac{T_f}{T_i} \right)^{3/2} = - \ln \left[\frac{V_f - nb}{V_i - nb} \right] \quad (3.127)$$

Therefore re arranging

$$\ln \frac{T_f^{3/2} (V_f - nb)}{T_i^{3/2} (V_i - nb)} = \text{const} \quad (3.128)$$

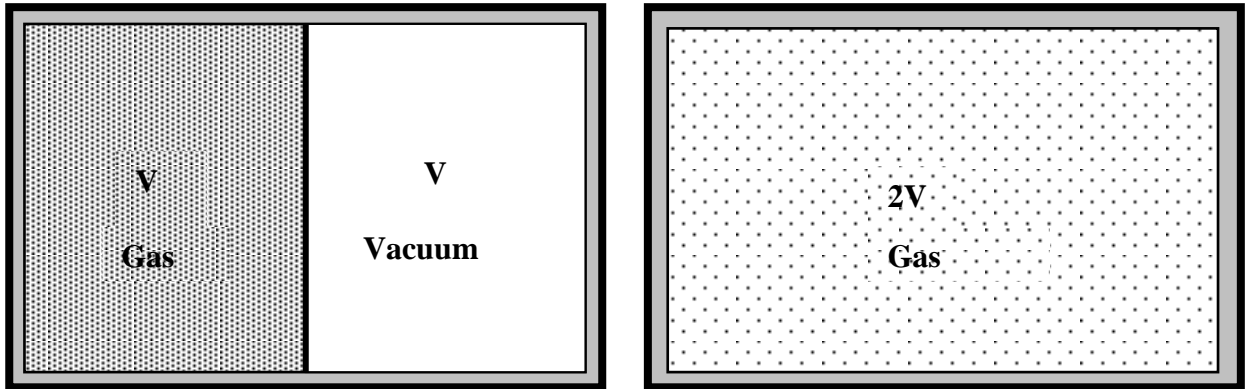
And finally

$$T^{3/2} (V - nb) = \text{const} \quad (3.129)$$

Is the adiabatic rule for a Van der Waals gas.

Joule Free Expansion.

We now consider another irreversible process to see its consequences for ideal and real gases. This is the Joule free expansion illustrated below,



Represented diagrammatically, above is the free expansion where we initially have a gas contained in one half of a container by a separating internal wall and with adiabatic and rigid external walls. These constraints mean that $\Delta W = 0$ and that $\Delta Q = 0$.

If we remove/break the internal wall the gas is free to expand into the other half of the container.

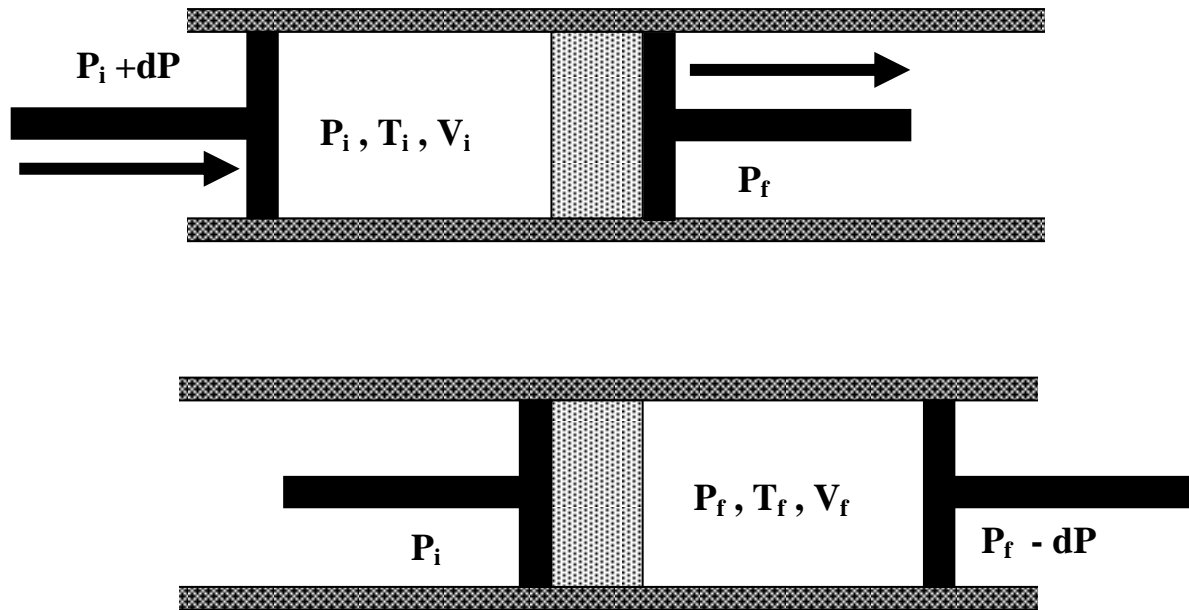
Applying the first law to this process is straight forward and

$$\Delta U = \Delta Q + \Delta W = 0 \quad (3.130)$$

This means there is no change in temperature and for an isothermal process as V doubles the pressure halves. It is an irreversible process clearly as it can't run backwards. This is approximately what was found for air by Joule. In fact there is a very slight cooling. The molecules on the right hand side are on average further apart and therefore their potential attraction drops meaning that their potential energy goes up (recall that the attractive potential is a negative quantity). If the potential increases then the kinetic must decrease in order that the total, $U = 0$. This is the origin of the slight cooling. It is an effect that can be expected for real gases where $U = U(T, V)$ but not for an ideal gas where $U = U(T)$. However that the effect is small shows that the ideal approximation is a good one.

Joule Kelvin Effect.

The Joule Kelvin effect is used in the liquefaction of gases and is also known as the throttling effect.



We begin with the situation depicted in the top figure where a porous plug divides a chamber with adiabatic walls into two. There is a piston either side, on the left hand side it is withdrawn and there is gas in the left hand side at initial pressure and temperature, P_i and T_i . The pressure is slightly greater on the outside of the piston forcing it slowly in and pushing the gas through the porous plug into the right hand chamber where the right hand piston slowly withdraws (the pressure is slightly lower on the outside of this piston to allow this) to accommodate the arriving gas at a final pressure and temperature, P_f and T_f . This is an isobaric process where the pressure doesn't change and the work *done on the gas* in forcing it through the plug is

$$\Delta W_{\text{Before Plug}} = - \int_{V_i}^0 P_i dV = P_i V_i \quad (3.131)$$

The work done by the gas expanding into the right hand side is

$$\Delta W_{AfterPlug} = - \int_0^{V_f} P_f dV = -P_f V_f \quad (3.132)$$

We can apply the first law recalling that the walls are adiabatic and therefore $\Delta Q = 0$

$$\Delta U = U_f - U_i = \Delta Q + \Delta W = P_i V_i - P_f V_f \quad (3.133)$$

Or re-expressed as

$$U_f + P_f V_f = U_i + P_i V_i \quad (3.134)$$

and therefore we find

$$H_i = H_f \quad \Delta H = 0 \quad (3.135)$$

This is an isenthalpic process.

In general there will be a temperature change in the process and either heating or cooling can occur.

$$dT = \left(\frac{\partial T}{\partial P} \right)_H dP = \mu_{JT} dP \quad (3.136)$$

or

$$dT = \left(\frac{\partial T}{\partial V} \right)_U dV = \mu_J dV \quad (3.137)$$

Where μ_{JT} is called the Joule Kelvin or Joule Thomson coefficient (Lord Kelvin and Thomson are of course the same person!) and μ_J is the Joule coefficient.

To proceed further we need to examine the enthalpy of real gases and for this we shall use the Van der Waals equation of state 3.113.

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

And its internal energy 3.117

$$U_{VdW} = \frac{3}{2} nRT - \frac{n^2 a}{V}$$

The enthalpy is defined in the usual way,

$$H_{VdW} = U_{VdW} + PV$$

We can proceed by multiplying out the terms in the equation of state and rewrite the equation as

$$PV = nRT - \frac{n^2 a}{V} + nbP + \left(\frac{n^2 a}{V^2} \right) (nb) \quad (3.138)$$

We can now make approximations to the equation of state because the correction terms are small ie,

$$\frac{n^2 a}{V^2} \ll P \quad (3.139a)$$

and

$$nb \ll V \quad (3.139b)$$

The approximation we use is to neglect all terms of second order in smallness in the equation of state

$$PV \approx nRT - \frac{n^2 a}{V} + nbP \quad (3.140)$$

We can use this and the expression for U_{vdW} to write down the enthalpy

$$H_{vdW} = U_{vdW} + PV = \frac{5}{2}nRT - \frac{2n^2 a}{V} + nbP \quad (3.141)$$

We need $\left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT}$ to get the Joule Thomson coefficient

Since T and P are the state variables of interest we need the enthalpy in terms of these two variables, the above expression is in terms of T , V and P . We need to replace $\frac{a}{V}$ in favour of P and T

$$\frac{a}{V} = \frac{aP}{PV} = \frac{aP}{nRT} \quad (3.142)$$

where we have dropped terms in first order of smallness.

Thus

$$H_{vdW} = \frac{5}{2}nRT - \frac{2naP}{RT} + nbP \quad (3.143)$$

Now we can proceed to obtain the Joule Thomson coefficient

$$\left(\frac{\partial H}{\partial P}\right)_H = 0 = \frac{5}{2}nR\left(\frac{\partial T}{\partial P}\right)_H + nb - \frac{2na}{RT} + \frac{2naP}{RT^2}\left(\frac{\partial T}{\partial P}\right)_H \quad (3.144)$$

Now solving for $\left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT}$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{\frac{2a}{RT} - b}{\frac{5}{2}R + \frac{2aP}{RT^2}} \quad (3.145)$$

All of the terms in the denominator on the RHS have positive values and it is therefore positive, however the numerator may take either sign dependant on the temperature and so then may μ_{JK} .

For $\frac{2a}{RT} > b$ we have a positive coefficient, ie. for low enough T we have $\mu_{JK} > 0$ and a

drop in pressure produces a drop in temperature whereas if $T < \frac{2a}{Rb}$ a drop in pressure will cause an increase in temperature

$T_{Inv} = \frac{2a}{Rb}$ is known as the inversion temperature and divides the two regimes.

This process is used in a continuous flow process (rather than the single shot process schematically described earlier) called the Linde liquefaction process which is described in Finn page 140.