

Internal Energy

The total energy of the system. Contribution from translation + rotation + vibrations.

Equipartition theorem for the translation and rotational degrees of freedom. $1/2 k_B T$

Work

Path function, not a state function

$$\delta w = -p_{ext}dV$$

Notation

When system does work to the surroundings: negative (expansion)

When surroundings does work on the system: positive (compression)

Two paths - compression

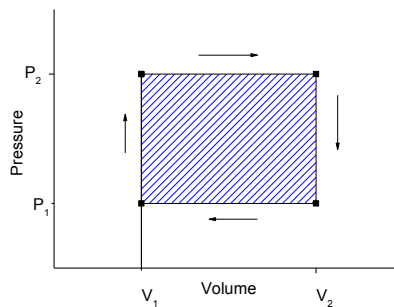
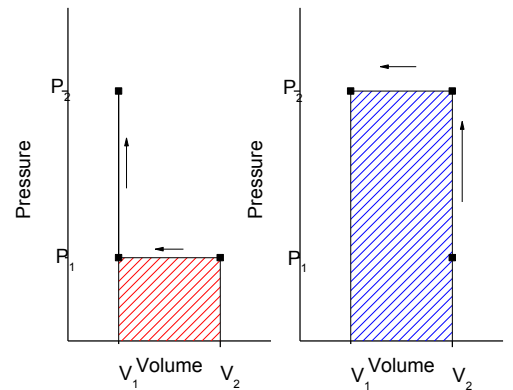
Work done in first path: $w = -\int_{V_2}^{V_1} p_1 dV - \int_{V_1}^{V_2} p_{ext} dV = -p_1(V_1 - V_2)$

Work done in second path $w = -\int_{V_2}^{V_1} p_{ext} dV - \int_{V_1}^{V_2} p_2 dV = -p_2(V_1 - V_2)$

Connect the two paths

$$w = -p_1(V_1 - V_2) + p_2(V_1 - V_2) \neq 0$$

$$\oint dw \neq 0$$



Heat

Another path function

The First Law

$$dU = \oint dq + dw = 0$$

$$\Delta U = q + w$$

The internal energy of an isolated system is constant. U is a state function. U Does not depend on path.

We need two variables (other than the number of moles) to define a state function $U = U(T, V)$

U is an extensive quantity. However, U/n is intensive

Since $U = U(T, V)$, we can write $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

In general $dU = dq + dw_{exp} + dw_{extra}$

The extra work could be electrical, chemical...

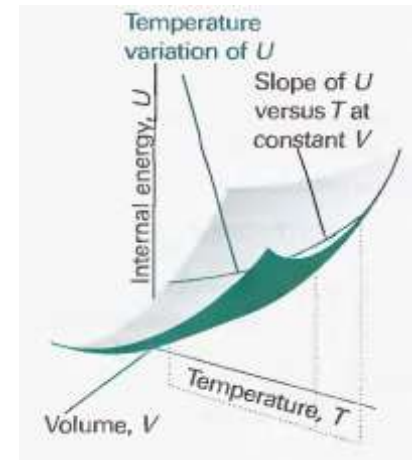
Lets keep the volume constant i.e. $dw_{exp} = 0$ and ensure no additional work i.e. $dw_{extra} = 0$

Then, $dU = dq$ or $dU = dq_V$

We are measuring a change in the internal energy by supplying heat to the system

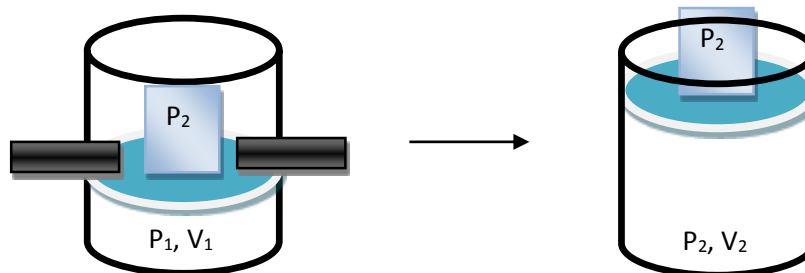
Also, we can write, $dU = \left(\frac{\partial U}{\partial T}\right)_V dT$ at constant V . Define $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

So, $dq_V = C_V dT$

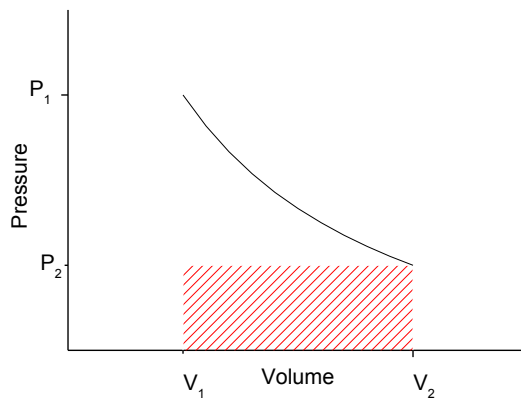


Isothermal Expansions

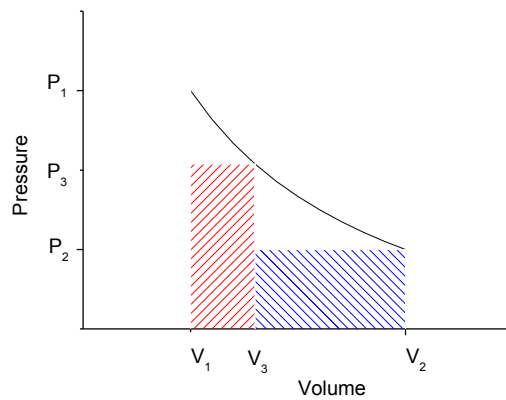
- Free expansion, against vacuum: $p_{ext} = 0 \therefore dw = -p_{ext}dV = 0$
- Irreversible expansion



$$dw = -p_{ext}dV = -p_2dV \text{ and } w = \int_{V_1}^{V_2} -p_2 dV = -p_2 \int_{V_1}^{V_2} dV = -p_2(V_2 - V_1)$$

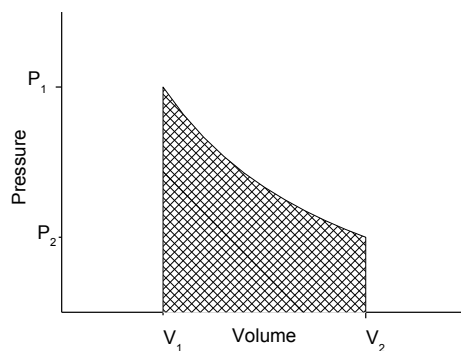


c) Irreversible expansion – 2 steps



$$w = -p_3(V_3 - V_1) - p_2(V_2 - V_3) \quad \text{more work than single step expansion}$$

d) Reversible expansion



$$w = - \int_{V_1}^{V_2} p_{ext} dV = - \int_{V_1}^{V_2} p dV$$

For an Ideal Gas

$$w = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

Joule Expansion

In the expression, $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$,

$\left(\frac{\partial U}{\partial T}\right)_V$ is C_V . Now what is $\left(\frac{\partial U}{\partial V}\right)_T$?

Lets construct an experiment to determine $\left(\frac{\partial U}{\partial V}\right)_T$ also known as Π_T

So here we have an adiabatic wall

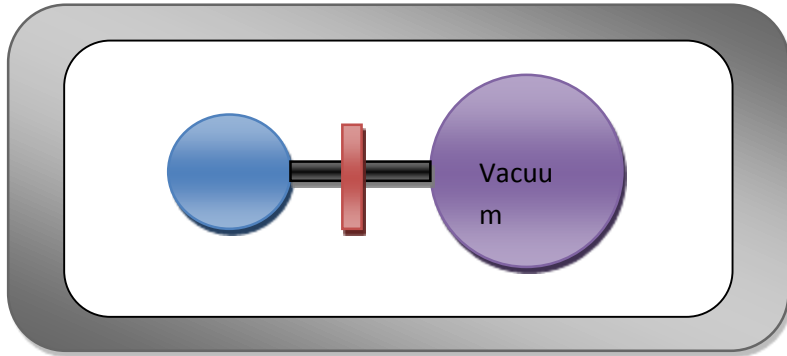
$\therefore q = 0$

and $w = 0$

i.e. $\Delta U = 0$

So, $dU = C_V dT + \Pi_T dV = 0$

i.e. $\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_U = -C_V \eta_J$



Now we can determine Π_T as we can measure the change in T as a function of V.

Joule found this η_J to be zero for all the gases.

For an I.G. U is only a function of T $\rightarrow U(T) = U(0) + \frac{3}{2}RT$ (for a monatomic IG) and hence Joule's results are correct for an IG. However, not so for a real gas (we will see later).

Enthalpy, H (a state function)

$$\Delta U = q + w = q - p\Delta V - V\Delta p = q_p - p\Delta V \text{ (constant pressure)}$$

$$\Delta(U + pV) = \Delta H = q_p$$

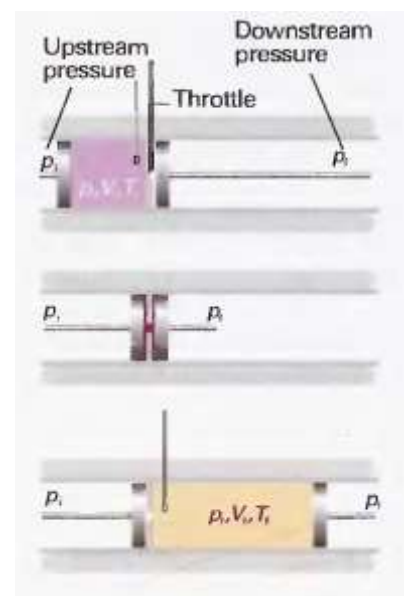
Since, $H = H(p, T)$ we can write $dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p dT + \mu_T dp$

The heat capacity at constant pressure, $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

The isothermal Joule-Thomson coefficient, $\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$ is determined by the Joule-Thomson experiment.

Conditions of the J-T experiment

- a) Adiabatic
- b) $w = p_1V_1 - p_2V_2$
 And $\Delta U = q + w = 0 + p_1V_1 - p_2V_2 = -\Delta(pV)$
 Therefore, $\Delta(U + pV) = 0 = \Delta H$
 i.e. Constant enthalpy experiment



$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = 0$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = -C_p \left(\frac{\partial T}{\partial p}\right)_H = -C_p \mu_{JT}$$

Change in temperature with change in pressure \rightarrow can be measured.

For IG: $\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = 0$

For van der Waals gas:

$$\left(\frac{\partial H}{\partial p}\right)_T \approx b - \frac{2a}{RT}$$

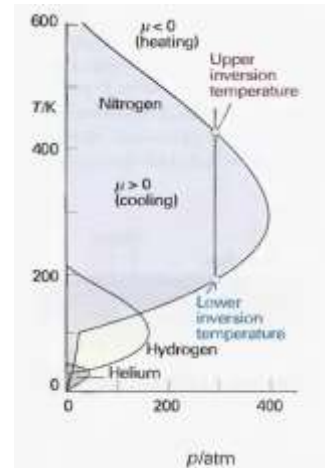
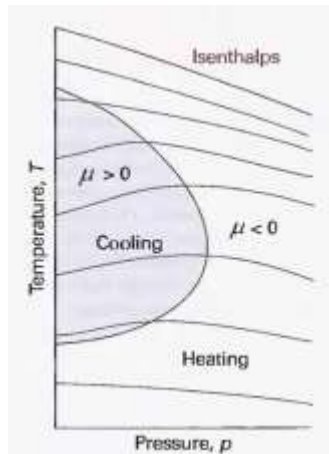
Which gives, $\mu_{JT} = b - \frac{2a}{RT_{inv}} = 0$

i.e. the inversion

temperature, $T_{inv} = \frac{2a}{Rb}$

If $\frac{2a}{RT} < b$ i.e. $T > \frac{2a}{Rb}$ \therefore

$\left(\frac{\Delta T}{\Delta p}\right)_H < 0$ i.e. gas heats on



expanding.

A positive μ implies a cooling on expansion. Principle: Gas expands \rightarrow molecules move apart but are attracted to each other \rightarrow hence lose some KE \rightarrow slow down \rightarrow cool down. This is true when attractive interactions are dominant.

Adiabatic expansions

a) Ideal gas, reversible

Given

$$dq = 0 \text{ (adiabatic)}$$

$$dw = -pdV \text{ (reversible)}$$

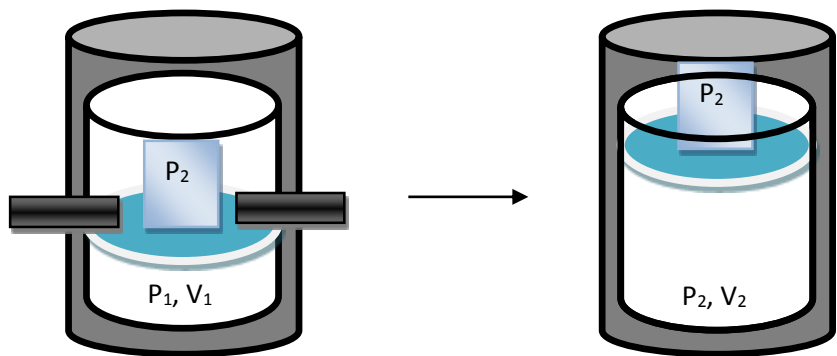
$$dU = \overline{C_V} dT \text{ (I. G. one mole)}$$

$$dU = -pdV \text{ (First Law)}$$

This gives, $\overline{C_V} dT = -pdV = -\frac{RT}{V} dV$

On integrating, $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{\overline{C_V}}}$

$\overline{C_p} - \overline{C_V} = R$ and therefore $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{\overline{C_p} - \overline{C_V}}{\overline{C_V}}} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$ where $\gamma = \overline{C_p} / \overline{C_V}$



Which gives, $TV^{\gamma-1} = \text{constant}$ (for 1 mole gas)

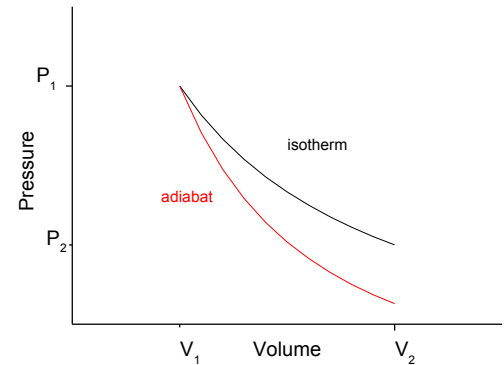
Since $\gamma - 1$ is always positive, adiabatic expansion \rightarrow gas cools. Should be expected because gas does work and no heat is exchanged. So internal energy must decrease implying a decrease in T.

Since $T = PV/R$ we can rearrange $PV^{\gamma} = \text{constant}$

Isotherm: $PV = \text{constant}$

Adiabat: $PV^{\gamma} = \text{constant}$

Since $\gamma > 1$ at the same pressure, adiabatic expansion gives a lower volume



Irreversible Adiabatic Expansion

$$dq = 0$$

$$dw = -p_2 dV$$

$$dU = C_V dT = -p_2 dV$$

Which gives, $T_1(C_V + R) = T_2 \left(C_V + \frac{p_2}{p_1} R \right)$ the gas still cools on expansion as $T_1 > T_2$

Now, since $-(w_{rev}) > -(w_{irr})$, which one gets us to a lower T, irr or rev adiabatic expansion?

What would happen if we carried out irr adiabatic expansion against vacuum?

State functions and exact differentials

State functions: depend on the state and not how the state has been formed. e.g. internal energy, enthalpy. Does not matter how I reach the state. Whether I change T first and hold the V constant and then change V at constant T or I change V at constant T and then change T holding the V constant, I end up at the same value of U . i.e. $\frac{\partial^2 U}{\partial T \partial V} = \frac{\partial^2 U}{\partial V \partial T}$

Path functions: are not for the state but for the way the state has been achieved. e.g. work, heat