First Law:

$\Delta U = Q + W$ ← work, (-) if system did work for us. (+) if we did work to the system.

↑ internal energy (average velocity, rotation of molecules, etc).

↑ net heat

for an ideal gas: $\Delta U = C_v \Delta T$, or $dU = C_v dT$

we deal with intensive, or per kg mass, so $C_v = \frac{C_v}{m_{tot.}}$

in differential form:

$dU = dQ + dW$ (internal energy of 1st law)

↑ ↑

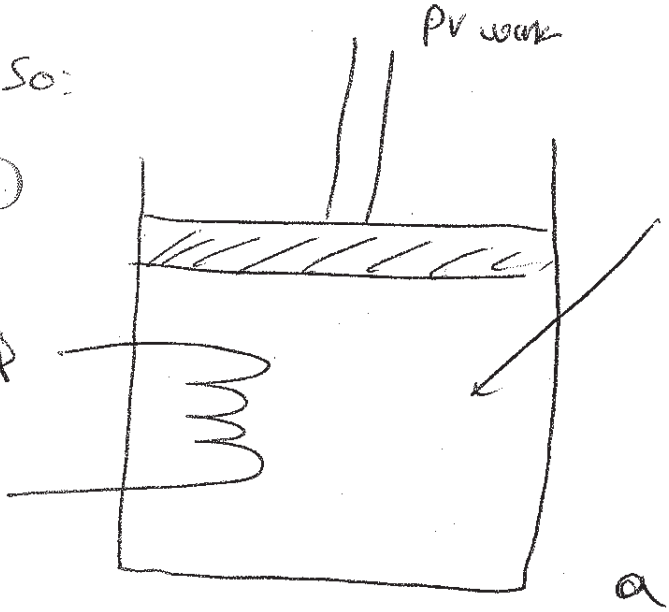
each of these terms are not perfect differential, (because $\oint dQ \neq 0$, $\oint dW \neq 0$), but the sum of both are (i.e, $\oint (dQ + dW) = 0$) because the function U does not depend on how you reach the state, only on the state itself, i.e. $\oint dU = 0$.

In general, $U(v, T)$ ← function of v and T.

Since dU is a perfect differential, it can be written as:

$$dU = \left(\frac{\partial U}{\partial v}\right)_T dv + \left(\frac{\partial U}{\partial T}\right)_v dT$$

So:



$U_{initial} \longrightarrow U_{final}$

Let's take the general case where a gas is put in a cylinder and you do/get p-V work and supply some heat Q.

In general conservation of energy would say

$$\Delta U = Q + W$$

ΔU: change in (internal) energy of system

Q: net heat

W: net work

This is known as the "first law" of thermo

heat convention: + when Q is added to system,

− when Q is removed from system

U: measure of "internal energy" associated with molecules

N $\frac{\text{molecules}}{\text{volume}}$ of temperature T

Kinetic Theory says: for an ideal gas:

$$\underbrace{\frac{1}{2}mv^2}_{\text{k. en. of each molecule}} = \underbrace{\frac{3}{2}kT}_{\text{monatomic molecule (3 d.of freedom)}}$$

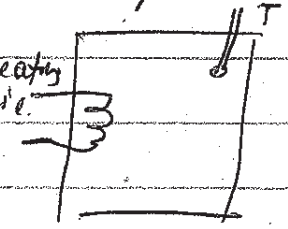
So: for whole gas:

$$\underbrace{\frac{1}{2}Nmv^2}_{\text{internal energy}} = \frac{3}{2}NkT$$

$$U = \underbrace{\frac{3}{2}NkT}_{\text{constant if } V=\text{const (b/c } N \text{ depends on volume)}}$$

So $dU = \left(\frac{3}{2}Nk\right)dT$ ← call that "heat capacity" C_v

Now, if we apply the first law assuming that we only heat the system, but also keep the volume constant:



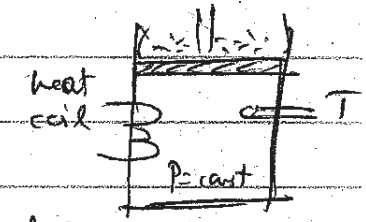
$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T \cancel{dv} = dq + \cancel{dw}$$

$\left(\frac{\partial u}{\partial v}\right)_T = 0$; $dw = 0$

So: $du = dq = \left(\frac{\partial u}{\partial T}\right)_v dT$

↑ by definition $\underline{\underline{c_v}}$

Similarly, for $p = \text{const}$ process; if we define a function $h = u + pv$, then



$$dh = du + d(pv) = du + p\,dv + v\,dp \Rightarrow$$

$$\Rightarrow du = dh - p\,dv - \cancel{v\,dp} = dh - p\,dv$$

and the first law becomes:

$$du = dq \Rightarrow dh = dq + p\,dv$$

but, $dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \cancel{\left(\frac{\partial h}{\partial p}\right)_T dp}$ (assume $h = h(p,T)$)

$\left(\frac{\partial h}{\partial p}\right)_T = 0$

So: $dh = dq + p\,dv = \left(\frac{\partial h}{\partial T}\right)_p dT$

↑ by definition c_p

enthalpy form of first law

Q: Is C_v larger or smaller than C_p?

A: $C_v < C_p$ (for monoatomic ideal gases $C_p = C_v + R$)

Q: Why?

A:

Take a given amount of heat, δQ. No work (i.e. systems from previous page). Let's see what the increase in T can be for $V = \text{const}$ (process 1)

$$\delta Q = \Delta U = C_v \Delta T_1$$

$P = \text{const}$ (process 2)

$$\delta Q = \Delta H = C_p \Delta T_2$$

(but $H = U + pV$)

$\delta Q = \text{same}$

$$\Rightarrow C_v \Delta T_1 = C_p \Delta T_2 \quad (1)$$

but $C_p \Delta T_2 = \Delta (U + pV)_2 = \Delta U_2 + p \Delta V \Rightarrow$

$\Delta U_2 \rightarrow C_v \Delta T_2$; $p \rightarrow \text{const}$

$$\Rightarrow C_v \Delta T_1 = C_v \Delta T_2 + p \Delta V \Rightarrow C_v (\Delta T_1 - \Delta T_2) = p \Delta V$$

since $C_v, p\Delta V > 0$ then $\Delta T_1 - \Delta T_2 > 0 \Rightarrow$

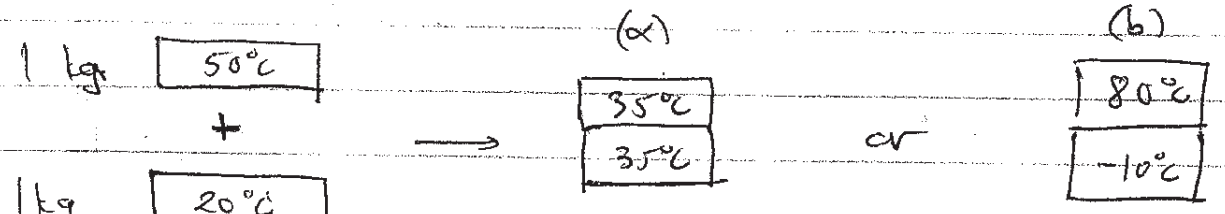
$\Delta T_1 > \Delta T_2$, but from equation ①,

$\frac{C_v}{C_p} = \frac{\Delta T_2}{\Delta T_1}$, so that means $\boxed{\frac{C_v}{C_p} < 1}$

i.e. the amount of heat you need to supply to raise the T of a closed system is smaller than for the cast 9 system, because the heat goes towards work done by the system to raise the cylinder.

Second Law - Introduction.

Conservation of energy (1st law) is a necessary but insufficient condition for a process to be feasible. There is a second law that tells us whether this is possible. Ex:



Both satisfy 1st law!
($\Delta U = \Delta Q$)
But only (a) makes sense.

We don't need a explicit law to figure out (b) can't happen, but for more complicated processes, we do. This is the 2nd law.