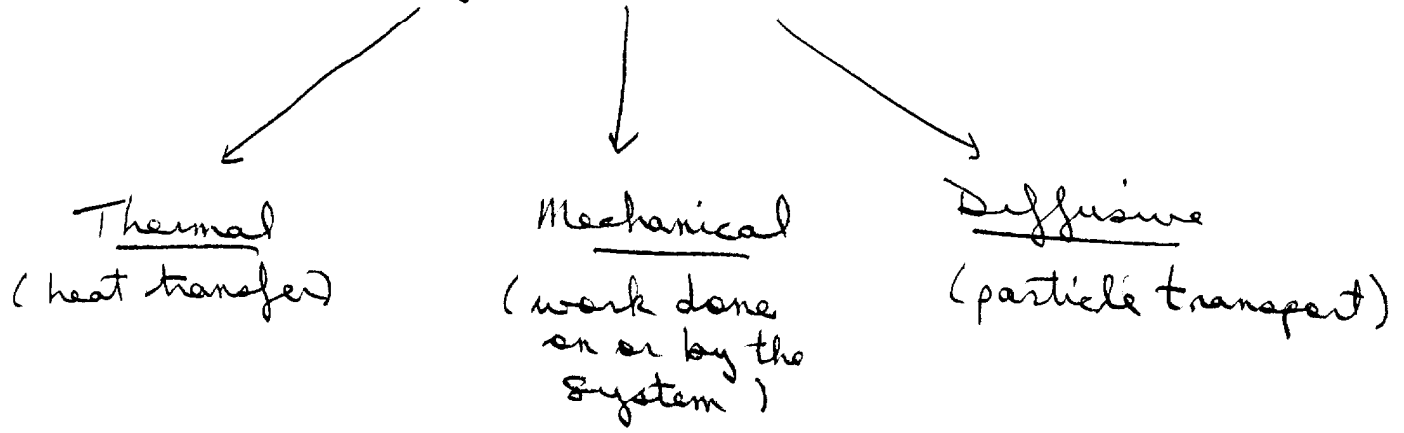
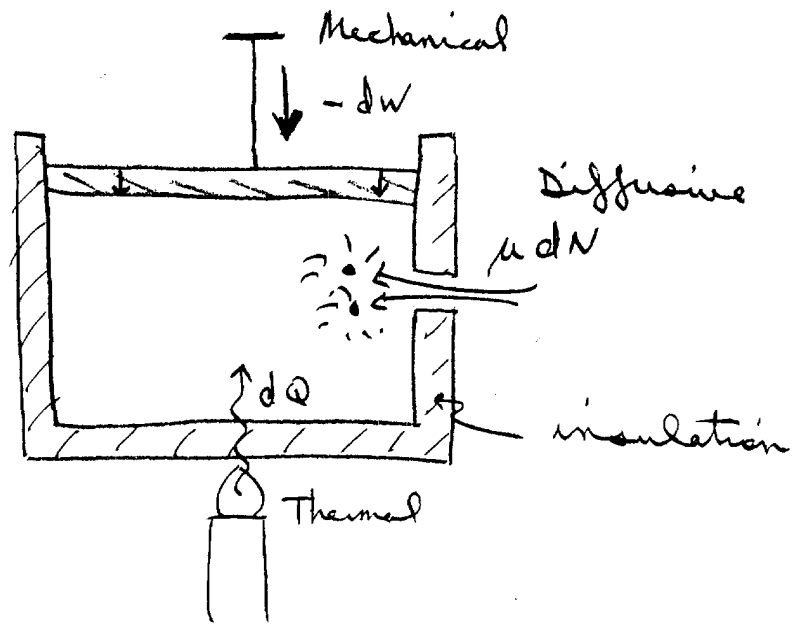


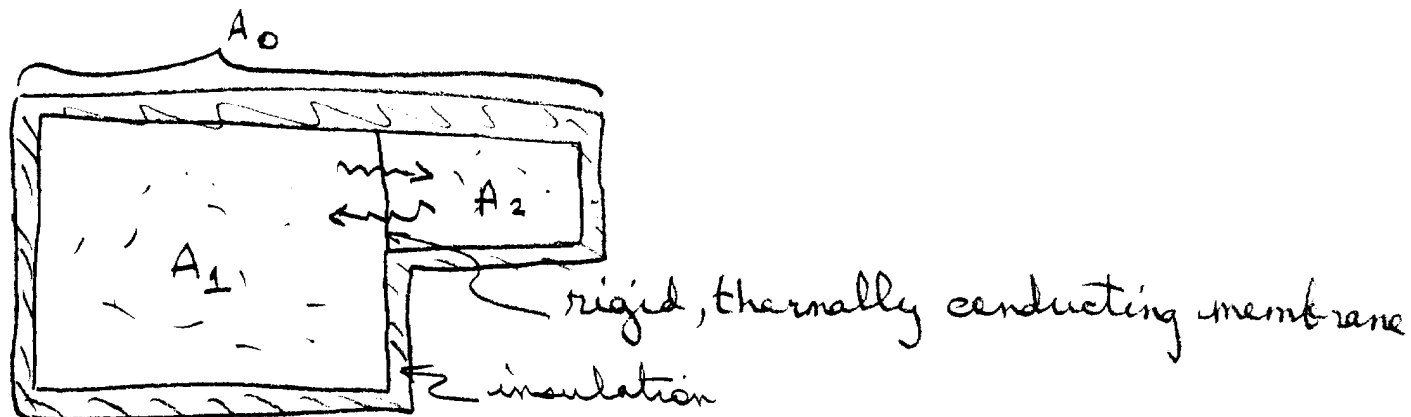
# Chapter 6 Internal Energy and the First Law

Changes in I.E.



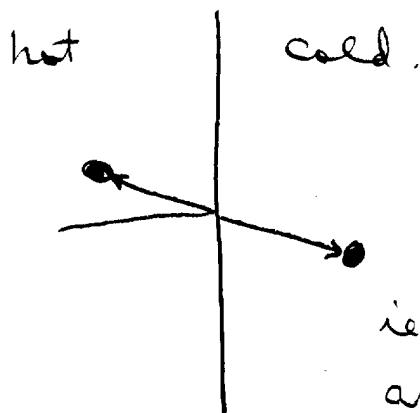
$dE = dQ - dW + \mu dN$  ← This is the 1st Law which is the topic of this chapter.



A. Heat Transfer

Consider system  $A_0$  which is composed of subsystems  $A_1$  and  $A_2$ .

$A_1$  &  $A_2$  interact via the membrane.



Heat is transferred from hot to cold via collisions and radiation.

ie energy is shared equally amongst all degrees of freedom.

$$dE = dQ$$

B. Work

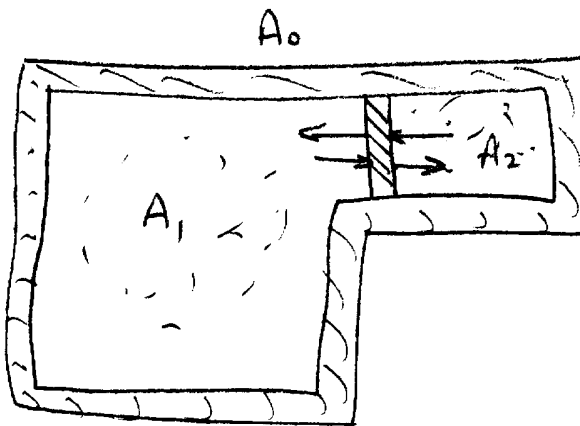
$$W = \int \vec{F} \cdot d\vec{S}$$

No force  $\rightarrow$  No work

No displacement  $\rightarrow$  No work

microscopic  
electrostatic  
magnetic, etc.  
direct impact  
on particles

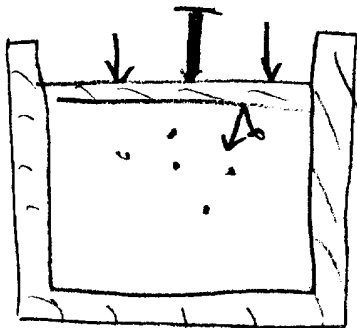
macroscopic  
mechanical  
indirect via boundary



$dW$  +ve when work is done by a system.

When work is done on a system, its I.E.  $\uparrow$

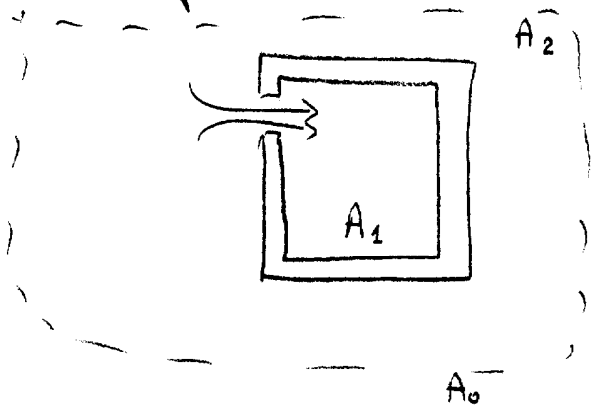
$$dE = -dW$$



When a gas is compressed, its molecules collide with the incoming piston & they gain kinetic energy.

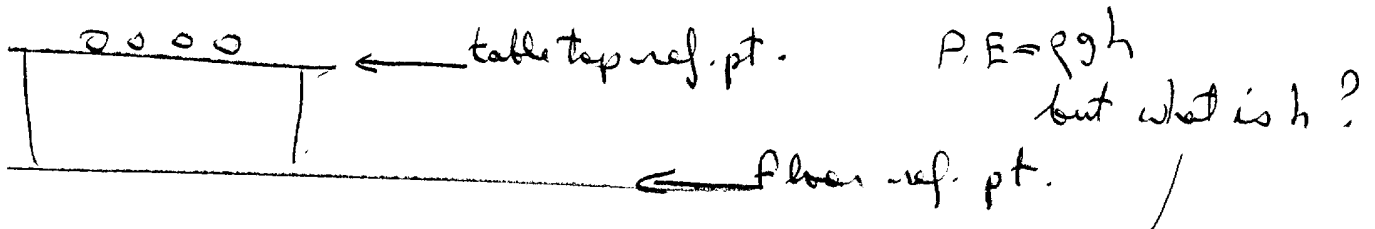
## C. Particle Transfer

Adding particles to a system involves two systems: the one receiving the particles + the one giving the particles



$A_1$  &  $A_2$  can have their own reference points for potential energy considerations.

We have to make sure the reference points are the same for both systems.



w.r.t. what?

Universal zero-energy reference level:

isolated particle at  $\infty$  with no interaction with any neighbours.

A complete hermit, far, far away.

Consider a system of particles formed by hermits getting together

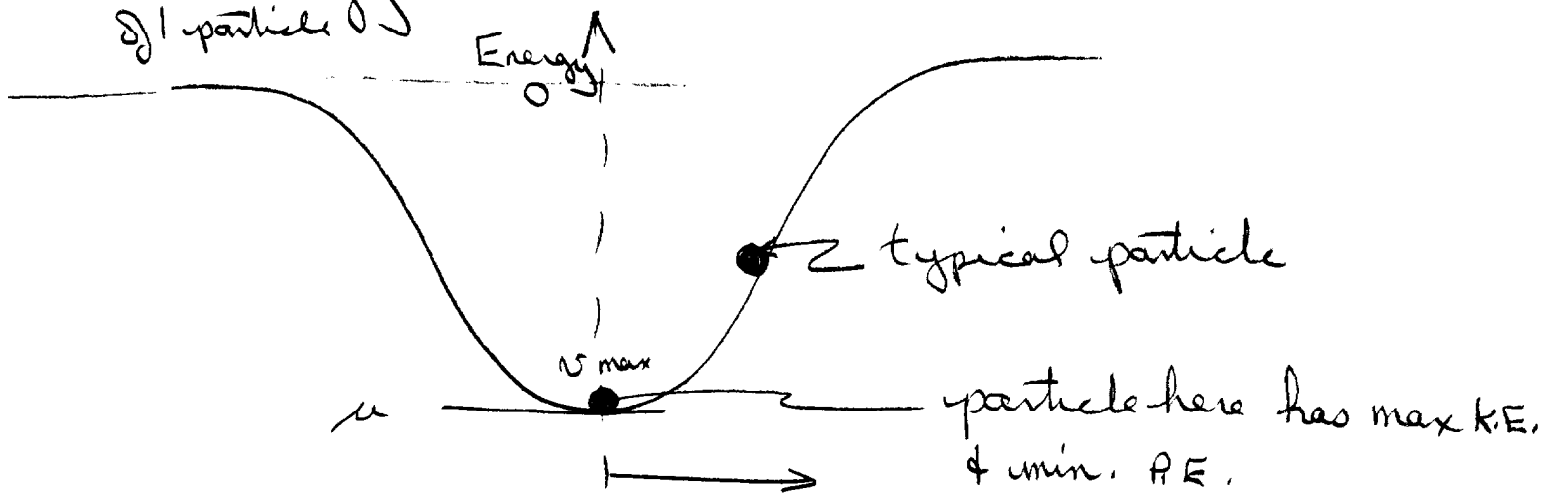
• - - - - -  $\rightarrow$  weak gravitational attraction  $\leftarrow$  - - - - - •



For one of the particles:

$$E = \underbrace{\mu + \frac{1}{2}kr^2}_{\text{P.E., } \mu} + \underbrace{\frac{1}{2}mv^2}_{\text{K.E.}}$$

↑  
internal energy of 1 particle



typical particle doesn't have enough  $\mu$  to escape the attractive forces of the system (eg molecules in a liquid) and become hermits again.

Hence  $\mu$  of bound particle  $<$   $\mu$  of hermit ( $=0$ )

$\therefore$  since  $\frac{1}{2}kr^2 > 0$  &  $\frac{1}{2}mv^2 > 0$ ,  $\mu$  must be  $<< 0$ .

Thus we talk of potential wells.

### Nomenclature

$$U = \mu + \frac{1}{2} k r^2 = \text{potential energy}$$

$$E_k = \frac{1}{2} m v^2 = \text{kinetic energy}$$

$$E_{\text{thermal}} = \frac{1}{2} k r^2 + \frac{1}{2} m v^2 = \text{thermal energy}$$

$$E = \underbrace{\mu + \frac{1}{2} k r^2}_U + \underbrace{\frac{1}{2} m v^2}_{E_k}$$

$E_{\text{thermal}}$

For  $N$  particles:

$$E = E_{\text{thermal}} + \mu N$$

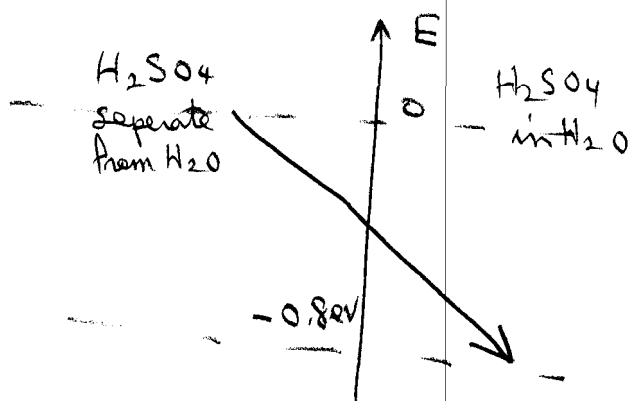
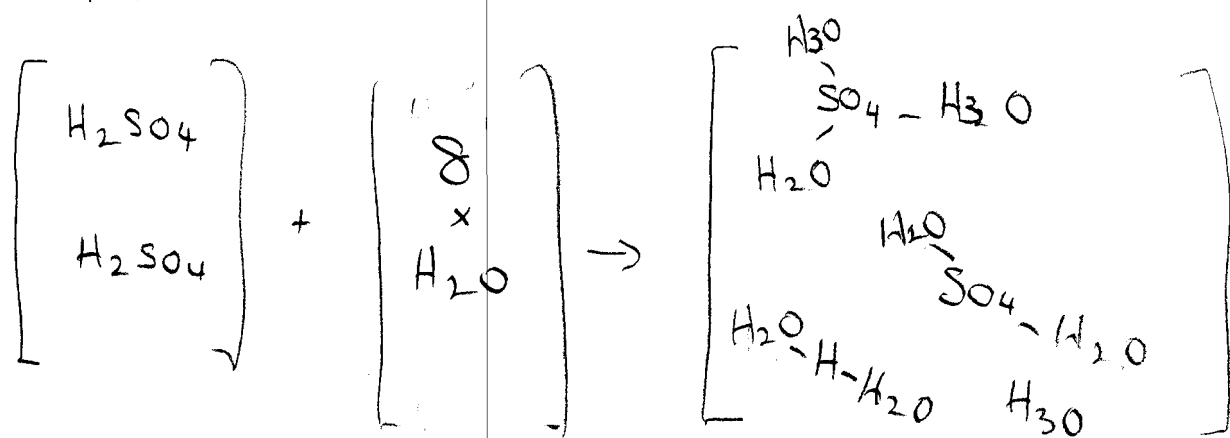
Potential energies are measured relative to the bottom of the potential well,  $\mu$ .

If systems are not exchanging particles, then can ignore the common reference energy level + just talk about  $E_{\text{thermal}}$

- If we were to remove all energy from a particle in a potential well, it would have energy,  $\mu$ , w.r.t. the zero-energy reference point.
- Note  $\mu$  is a negative number. This is the particle's "chemical potential". It is a measure of how much energy would be required to move the particle out of the well.
- $\mu = \mu(T, V, N)$ , i.e. the well depth is a function of the system, just as gravity is a function of earth size.
- If we add a particle of zero energy to a system, then  $\Delta E = 0 = \Delta E_{\text{thermal}} + \mu \Delta N$   
 $\therefore$  as the particle drops into the well, potential energy is converted to thermal energy:  

$$\Delta E_{\text{thermal}} = -\mu \Delta N.$$
This is released to the system as a whole.
- Fluctuations in the system particles cause fluctuations in  $\mu$ .  $\mu$  defined as an average.

Example:



$\text{H}_2\text{SO}_4$  molecules are attracted to the  $\text{H}_2\text{O}$  molecules & fall down a well of depth  $0.8\text{eV}$

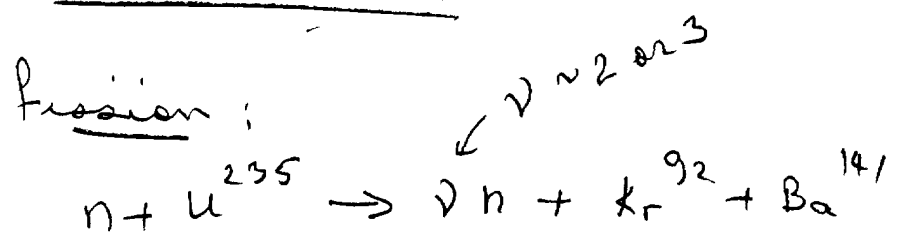
$1\text{eV}$  = energy req'd to move an electron through a potential difference of  $1\text{volt}$ .

Typically, a particle at room temperature ( $\sim 300\text{K}$ ) has an energy  $\sim kT = 0.025\text{eV}$  ( $\frac{1}{40}\text{eV}$ )

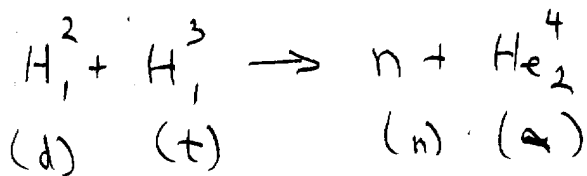
Note:  $k = 0.846 \times 10^{-4}\text{eV/K}$   
 $= 1.381 \times 10^{-23}\text{J/K}$

$\therefore k \times 300 = 2.5 \times 10^{-2}\text{eV}$   
 $= 0.25\text{eV}$

$1\text{eV} = 1.6 \times 10^{-19}\text{J}$

Nuclear interactions:Fission:

Energy released:  $Q = [m_n + m_{235} - (\nu m_n + m_{Kr} + m_{Ba})] c^2$   
 $= 190 \text{ MeV} = 3 \times 10^{-11} \text{ J}.$

Fusion:

deuteron   triton

$$\Delta m = \text{after} - \text{before}$$

$$Q = -\Delta m c^2$$

$$= [(m_d + m_t) - (m_n + m_\alpha)] c^2$$

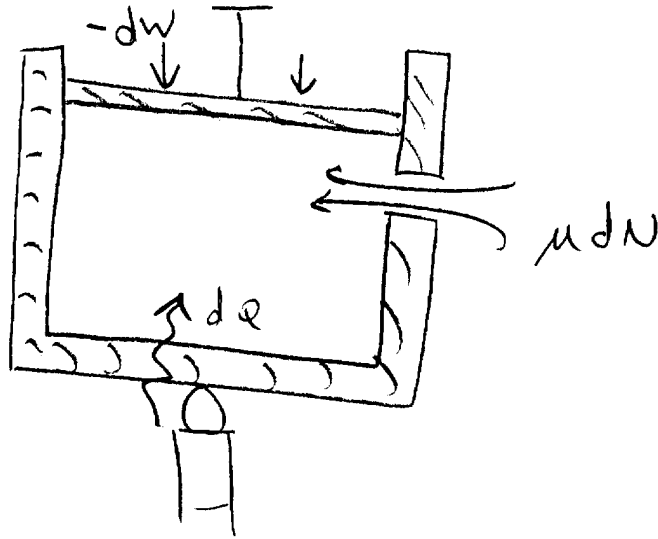
$$= 17.6 \text{ MeV}$$

Note range of energies  $\ll eV \rightarrow > MeV$

## D. The First Law

So we finally have the first law:

$$dE = dQ - dW + \mu dN$$



- This governs the overall changes in energy of a system. It does not govern how energy is partitioned (kinetic vs potential, etc).
- If there are several forms, then:

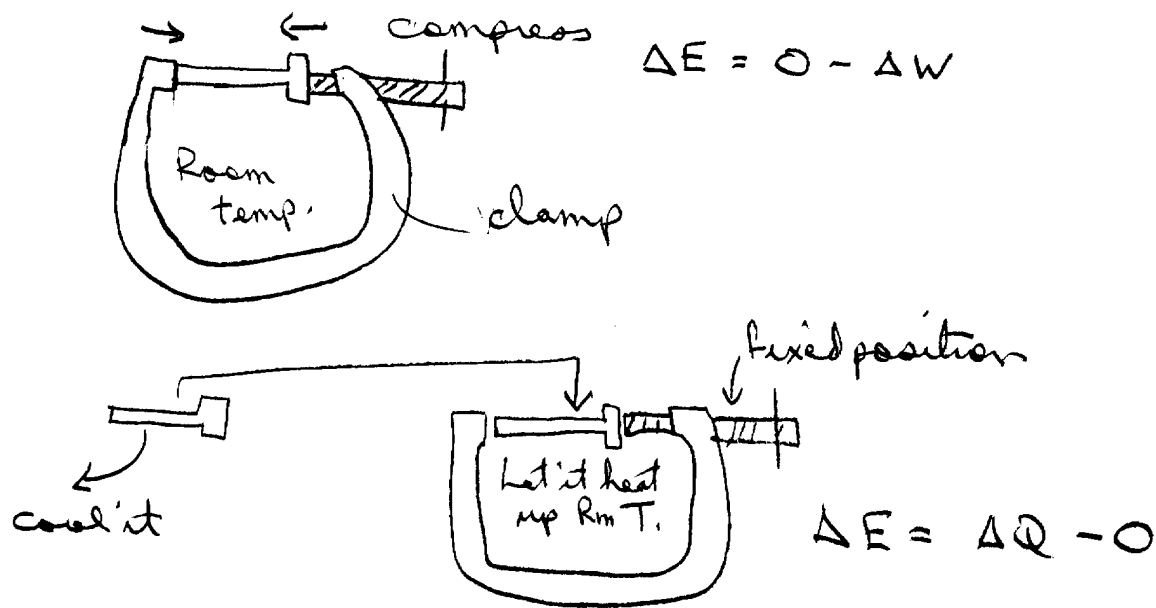
$$dE = \sum_i dQ_i = \sum_j dW_j + \sum_k \mu_k \Delta N_k$$

## E. Exact + Inexact Differentials

Consider a system undergoing change but  $\Delta N = 0$ .

$$\therefore dE = dQ - dW$$

Can get same  $dE$  via different combinations of  $dQ$  &  $dW$



Same end point!

$dE$  is an exact differential (a property of the state of a system)  
- independent of path

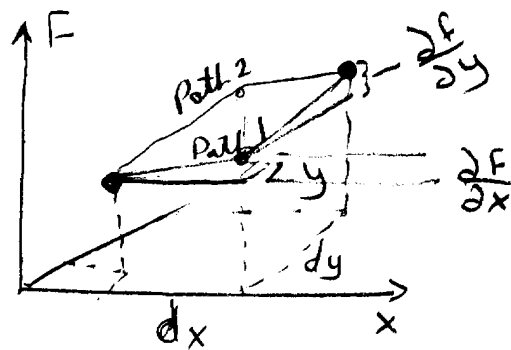
$dQ$  } are inexact differentials (not a prop. of the state)  
 $dW$  } - path dependent.

Sometimes written  $\delta Q$ ,  $\delta W$

$dN$  is an exact differential.

Consider  $F = F(x, y)$

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy$$



In general, if we had

$$dF = g(x, y) dx + h(x, y) dy$$

we could directly integrate it to find

$$F = \int dF \quad \text{if} \quad g(x, y) = \frac{\partial F}{\partial x}$$

$$+ h(x, y) = \frac{\partial F}{\partial y}$$

$$\text{Now } \frac{\partial}{\partial y} \left( \frac{\partial F}{\partial x} \right) = \frac{\partial}{\partial x} \left( \frac{\partial F}{\partial y} \right) = \frac{\partial^2 F}{\partial x \partial y}$$

$\therefore$  if  $\frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}$  then the differential

$dF = g dx + h dy$  is exact if we can directly integrate it.

ie we get a unique answer ( $F = \int dF$ ), ie the value of  $F$  is path independent.

$\therefore$  test for exactness of a function :

$$\frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}$$

Example:

Is  $F = 2xy dx + x^2 dy$  an exact differential?

$$g = \frac{\partial F}{\partial x} \quad h = \frac{\partial F}{\partial y}$$

$$\frac{\partial g}{\partial y} = 2x \quad , \quad \frac{\partial h}{\partial x} = 2x$$

$\therefore$  Yes it is!

$$F = x^2 y + \text{constant}$$

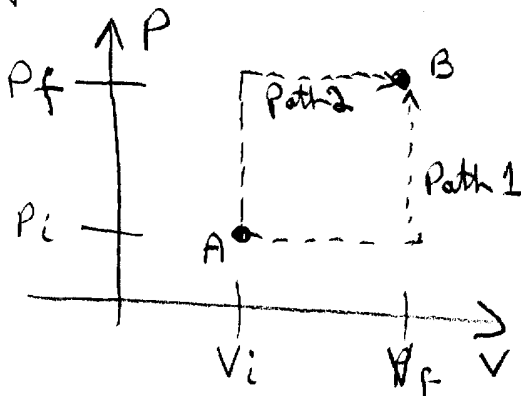
check:  $g = \frac{\partial F}{\partial x} = 2xy$

$$h = \frac{\partial F}{\partial y} = x^2$$

check OK.

This may seem like esoteric math but the concept is important to thermodynamics.

Consider the work done for a system moving from  $P_i, V_i \rightarrow P_f, V_f$



We will see later that

$$W = \int_{A'}^B p dV$$

Path 1:

$$W = P_i (V_f - V_i) + 0$$

Path 2:

$$W = 0 + P_f (V_f - V_i)$$

ie  $W$  is path dependent