Chapter 2

THE FIRST LAW OF THERMODYNAMICS

2.1 Introduction

Definition of T : The property that indicates the direction of the flow of energy through a thermally conducting, rigid wall

Thermal equilibrium - no change of state occurs when two objects are in contact through a diathermic boundary

Zeroth Law of Thermodynamics - If A is in thermal equilibrium with B and B is in thermal equilibrium with C then A is in thermal equilibrium with C

2.3 Internal Energy and the 1st law of Thermodynamics

- Similarly the application of a force f to a body of mass m causes the body to accelerate according to Newton's Law

The work done on the body is thus obtained by integrating

where l is distance.

- integration!

W= ½(mv_2^2 - mv_1^2) = kinetic energy at v_2 - kinetic energy at v_1 (2)

"the work done on the body is independent of the path, only dependent of initial and final state."

2.1 Introduction

Two bodies collide and exchange the energy **in frictionless system**: the work done by the one = the work done on the other, maintaining the total kinetic energy the same.

If friction occurs, with continuing collision and interaction among the bodies, the total dynamic energy decreases with heat generated.

Reasonable to expect: **a relationship** exists **between the dynamic energy dissipated and heat produced** as a result of the effects of friction

The development of thermodynamics: achieved as the result of the invention of convenient thermodynamic functions of state: in this chapter U (internal energy) & H (enthalpy)

2.2 The relationship between heat and work

Joule's experiment:

Work was performed in a certain quantity
of adiabatically contained water and the
resultant increase in the temperature was
measured.
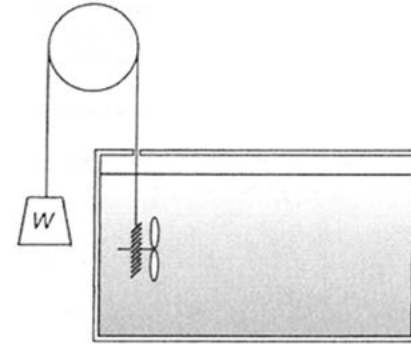
Joule observed **a direct proportionality** between **the work done**
and **the resultant increase in the temperature.**

The proportionality exists regardless of the means to produce work.
(rotating paddle, electric motor, compressing a cylinder of gas
immersed in the water..)

The value of the mechanical equivalent of heat =0.241 calories/joule

2.3 Internal Energy and the 1st law of Thermodynamics

- Joule's Experiment **" the change of a body inside an adiabatic enclosure from an initial state to a final state involves the same amount of work"** by what ever means the process is carried out. → preliminary formulation of the 1st law

- Need to define some function (U) which depends only on the internal state of a system: **internal energy**

- When a body of mass m is lifted in a gravitational field from height h_1 to height h_2, the work w done on the body is given by

- h_2

- h_1

w = force × distance
  = mg × ($h_2 - h_1$)
  = $mgh_2 - mgh_1$
  = potential energy at position h_2 minus potential energy at position h_1 (1)
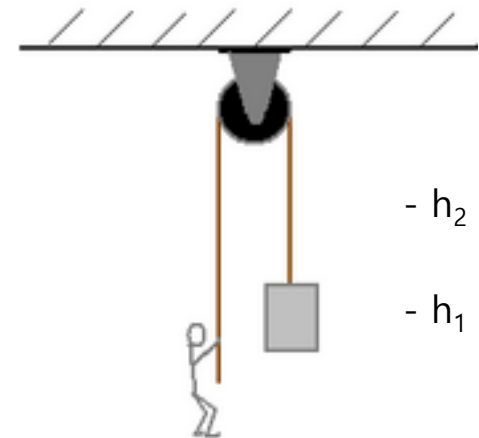
2.3 Internal Energy and the 1st law of Thermodynamics

Work done on or by a body = ΔU

Convention (promise)

As a result of which its state moves from *A* to B

If work w is done on the body, then $U_B > U_A$ and if the body itself performs work, then $U_B < U_A$.

The Relationship between Heat and Work

Heat q changes like

Convention (promise)

When heat flows into the body and $U_B > U_A$, then , q>0,
if heat flows out of the body, $U_B < U_A$, then q<0

A body which performs work (w) and absorbs heat (q) at the same time

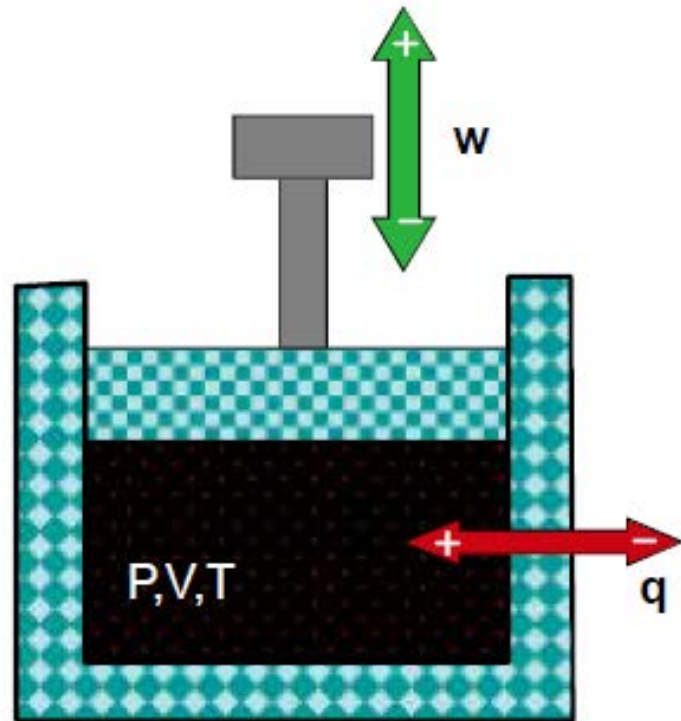A body which performs work (w) and absorbs heat (q) at the same time,

(q increases U while w decreases U)

$$\Delta U = U_B - U_A = q - w \qquad \text{(eq.2.1)}$$

For infinitesimal change of state

(eq.2.2)

The change in internal energy is equal to the heat flowing **into the system minus the work** done **by the system.**

$$dU = \delta q - \delta w$$

dU state function
δ not state function, path dependent!
Need to know the path taken!

If $(U_2-U_1) = -w$ had happened to a system (i.e., q=0),
Then the path of the progress was specified as in Joules experiment.
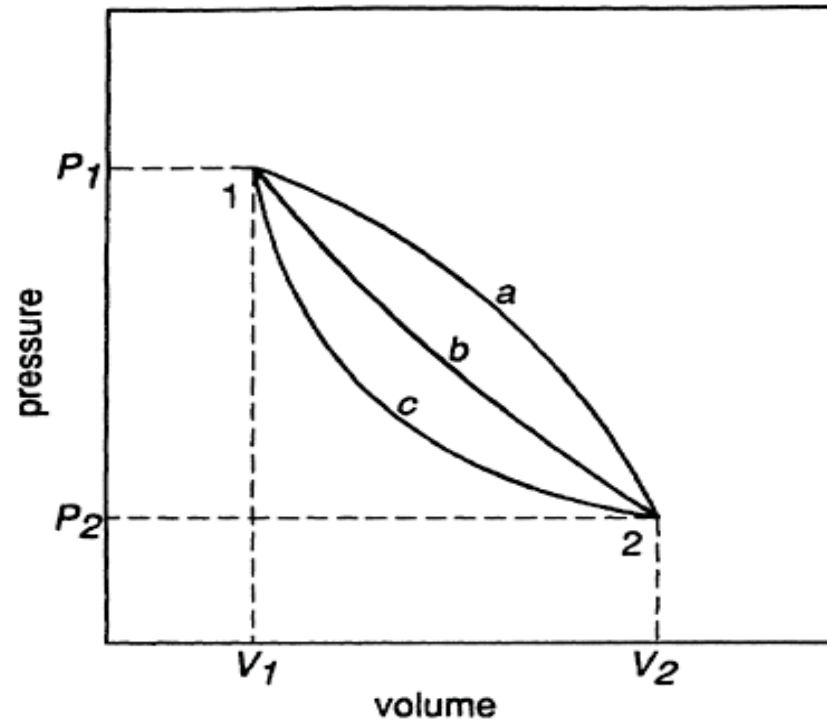
$$\int_1^2 \delta w = \int_1^2 P\,dV$$

Figure 2.1 Three process paths taken by a fixed quality of gas in moving from the state 1 to the state 2.

Property of a state function

If the value of U, a state function, is fixed once any two properties for a simple system (indep. variables are fixed), U will be fixed.

$$U = U(V,T)$$

V, T are fixed?   Then, U will be fixed.
V, P are fixed?   Then,

2.4 Constant-Volume Processes

If the volume of a system is maintained constant,
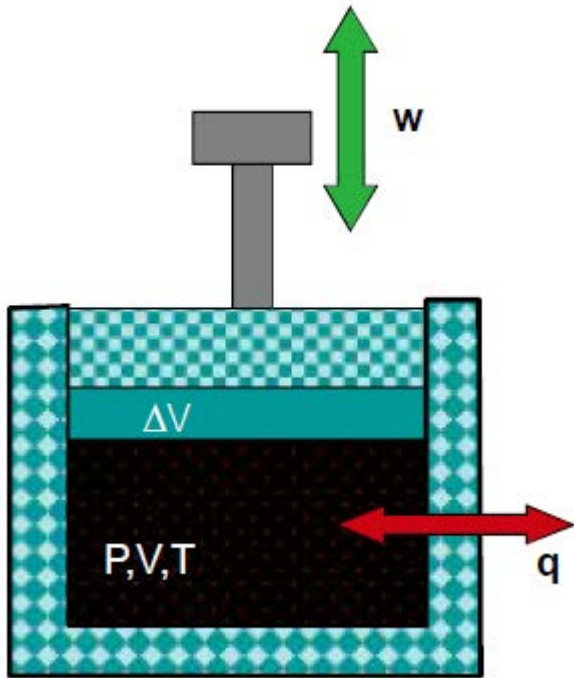then the system does no work ($\int PdV=0$), and from the First Law,

where the subscript v indicates constant volume.

And integration of Eq. above gives,

$$(eq.2.3)$$

This means that
the increase or decrease in the U
= the heat absorbed or rejected by the system during the process

2.5 Constant-Pressure Processes and Enthalpy H

w

ΔV

P,V,T

q

U, P, V are state functions!
Thus, H also is a state function.

If P = const ≠ f(V),

By the 1st law

$$U_2 - U_1 = q_p - P(V_2 - V_1)$$

rearrange,

$$H = U + PV \qquad \text{(eq.2.4)}$$

Hence,

(eq.2.5)

2.6 Heat Capacity

Ratio of the heat added (withdrawn from) to the system to ΔT

$$C = \frac{q}{\Delta T}$$ Or if temperature change is small

not used when a phase change involved, i.e., melting of ice ($\Delta T = 0$)

2.6 Heat Capacity

To specify the final state after T changes, it needs one more variable to define the system like P or V.

The second variable could be varied in a specific manner or could be maintained const. (P= const. more practical!)

Constant Volume

$$C_V = \left(\frac{\delta q}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V$$

(eq.2.6)

Constant Pressure

$$C_P = \left(\frac{\delta q}{dT} \right)_P = \left(\frac{dH}{dT} \right)_P$$

(eq.2.7)

Heat capacity, being dependent on the size of the system,
→ extensive property

Conv. To use heat capacity/unit quantity of the system
→ intensive property

For a system containing *n moles*
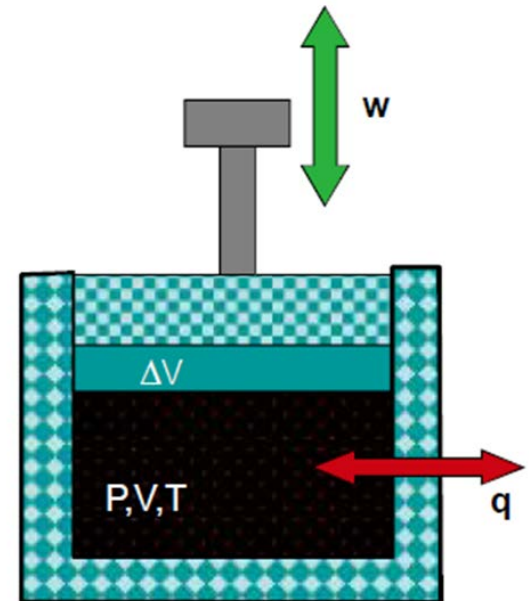
$$nc_p = C_p$$

and

$$nc_v = C_v$$

C_p and C_v : Expected that $C_p > C_v$ for the same ΔT. Why?

work of expansion against the constant pressure per degree of temperature increase

$$\frac{P\,dV}{dT} \text{ or } P\left(\frac{\partial V}{\partial T}\right)_P$$
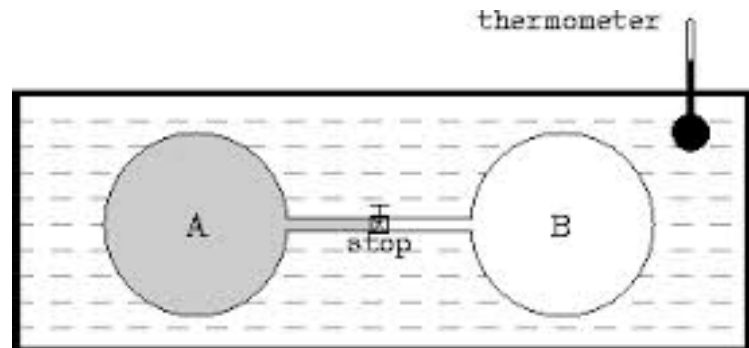
(1) Physical interpretation?

(2) Real calculation

$$c_p - c_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

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

$$c_p - c_v = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \text{(eq.2.8)}$$

Then, $\left(\frac{\partial U}{\partial V}\right)_T = 0$?

Joule's Experiment

For ideal gas, $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$

$$c_p - c_v = P\left(\dfrac{\partial V}{\partial T}\right)_P$$

for one mole of ideal gas, PV=RT, then

(eq.2.11)

Error in Joule's experiment stemmed from the fact that
- Heat capacities of the copper vessel and water- too great.
- Thus, the small ΔT reduction could not be detected by the then-available means of temp. measurement.

$$P\left(\frac{\partial V}{\partial T}\right)_P$$; work done by the system in expanding against P
acting on the system

$$\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$: work done by the system in expanding
against internal cohesive force acting between the
constituent particles of the substance.
(particle expanding= get work, w<0, dU= -w>0.)

For ideal gas consists of non-interacting particles,
Thus, no work is done against internal cohesive force
and
$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

For ideal gas, $p \gg \left(\dfrac{\partial U}{\partial V}\right)_T$

For real liquid, solid (interaction force is large)

$$P \ll \left(\frac{\partial U}{\partial V}\right)_T$$

2.7 Reversible Adiabatic Processes

$q=0$, and thus, from the First Law, $dU=-\delta w$.

For a system (1 mole of ideal gas)

$$c_v \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_1}{V_2}\right)$$

$$\left(\frac{T_2}{T_1}\right)^{c_v} = \left(\frac{V_1}{V_2}\right)^{R}$$

2.7 Reversible Adiabatic Processes

Since $C_p - C_v = R$, if $C_p/C_v = \gamma$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma} = PV^{\gamma} = \text{constant} \qquad \text{(eq.2.9)}$$

The relationship between P and V of an ideal gas undergoing a reversible adiabatic process.

2.8 Reversible Isothermal Pressure or Volume Changes of an Ideal Gas

$$dU = \delta q - \delta w$$

and as dT=0 (isothermal process) and gas is not interacting then dU=0.

Thus,

(2.10)

Thus, for an ideal gas, an isothermal process is one of constant internal energy during which the work done by the system equals the heat absorbed by the system, both of which are given by Eq. (2.10).

2.8 Reversible Isothermal Pressure or Volume Changes of an Ideal Gas

Physical meaning:

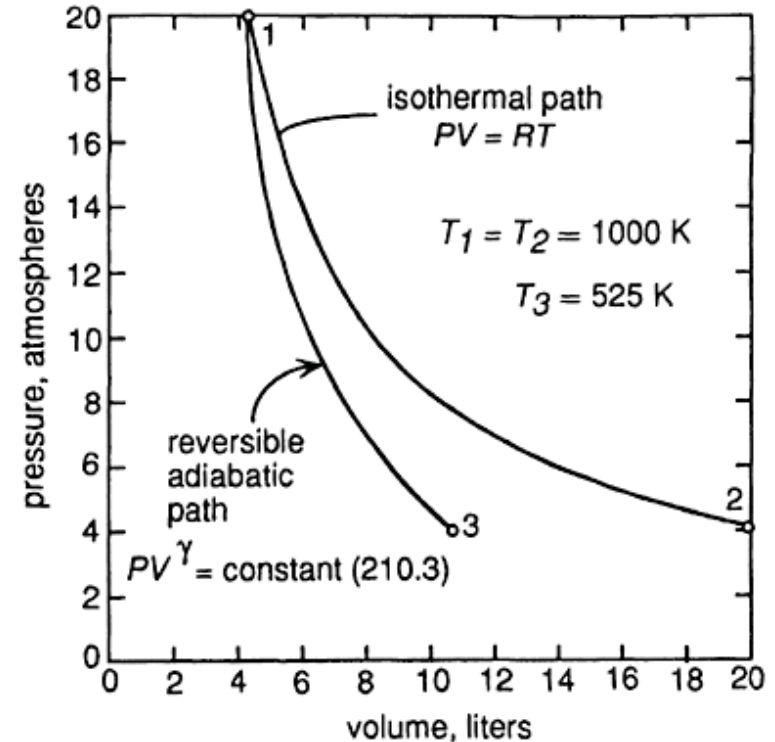For a given pressure decrease, the difference in the work done by two systems is due to the fact that

Figure 2.2 Comparison of the process path taken by a reversible isothermal expansion of an ideal gas with the process path taken by a reversible adiabatic expansion of an ideal gas between an initial pressure of 20 atm and a final pressure of 4 atm.