Work, Heat, and the First Law

- Work:

Epansion work: $w = -(p_{ext}A)\ell = -p_{ext}\Delta V$

If p_{ext} is not constant, then we have to look at infinitesimal changes

$đw = -p_{ext}dV$ đ means this is not an exact differential

Integral $w = -\int_1^2 p_{ext}dV$ depends on the path!!!

Other kinds of work

Surface work: $đw = \gamma_{ext}dA$ ... where γ_{ext} is the surface tension (J/m^2) and dA is the differential change in area. This is the work to change surface area.

Elongation work: $đw = fd\ell$ where f is the force per unit length and dℓ is the length differential. This is important for discussing changing the length of polymers or DNA.

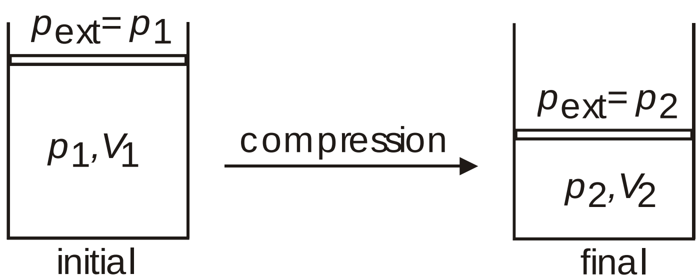
Electrostatic work: $đw = Vde$ where V is a fixed potential and de is the change in charge.

- Path dependence of w

Example: assume a reversible process so that $p_{ext} = p$

$$\text{Ar}(g, p_1, V_1) = \text{Ar}(g, p_2, V_2)$$

Compression $V_1 > V_2$ and $p_1 < p_2$



Two paths:

(1) First $V_1 \rightarrow V_2$ at $p = p_1$
then $p_1 \rightarrow p_2$ at $V = V_2$

(2) First $p_1 \rightarrow p_2$ at $V = V_1$
then $V_1 \rightarrow V_2$ at $p = p_2$

$Ar(g, p_1, V_1) = Ar(g, p_1, V_2) = Ar(g, p_2, V_2)$

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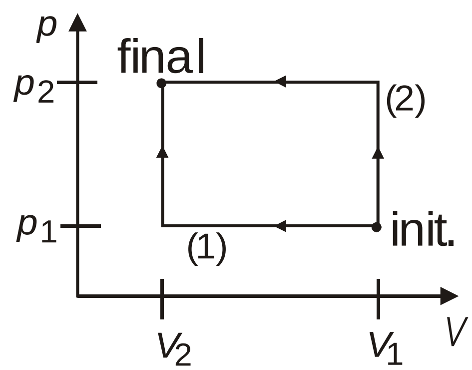


$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext}dV - \int_{V_2}^{V_2} p_{ext}dV$$
$$= -\int_{V_1}^{V_2} p_1 dV = -p_1(V_2 - V_1)$$

$$\boxed{w_{(1)} = p_1(V_1 - V_2)}$$

$$w_{(2)} = -\int_{V_1}^{V_1} p_{ext}dV - \int_{V_1}^{V_2} p_{ext}dV$$
$$= -\int_{V_1}^{V_2} p_2 dV = -p_2(V_2 - V_1)$$

$$\boxed{w_{(2)} = p_2(V_1 - V_2)}$$

(Note $w > 0$, work done <u>to</u> system to compress it)

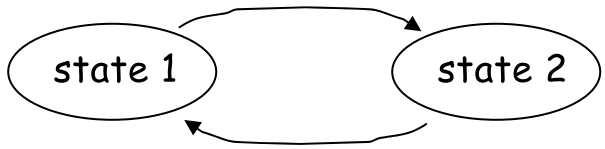
$$\boxed{w_{(1)} \neq w_{(2)} \text{ !!!}}$$

Note for the closed cycle [path (1)] - [path (2)], $\oint đw \neq 0$ ← closed cycle

w is not a state function   cannot write $w = f(p,V)$

WORK

Work (w) is not a function of state.
For a cyclic process, it is possible for $\oint \text{đ}w \neq 0$



HEAT

Heat (q), like w, is a function of path. Not a state function

It is possible to have a change of state

$$(p_1,\ V_1,\ T_1) \quad = \quad (p_2,\ V_2,\ T_2)$$

adiabatically (without heat transferred)
or nonadiabatically.

Historically measured in calories
[1 cal = heat needed to raise 1 g H_2O 1°C,
from 14.5°C to 15.5°C]

The modern unit of heat (and work) is the Joule.

1 cal = 4.184 J

Heat Capacity

$\underline{\underline{C}}$ - connects heat with temperature

$$\text{đ}q = C_{path}\,dT \qquad \text{or} \qquad C_{path} = \left(\frac{\text{đ}q}{dT}\right)_{path}$$

↑ heat capacity is path dependent

Constant volume: C_V

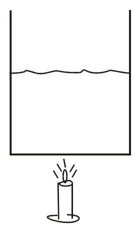
Constant pressure: C_p

$$\therefore \quad q = \int_{path} C_{path} dT$$

Equivalence of work and heat [Joule (1840's)]

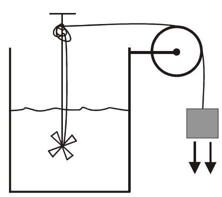
Joule showed that it's possible to raise the temperature of H_2O

(a) with only heat



$T_1 \rightarrow T_2$

(b) with only work
(weight falls &
churns propeller)



$T_1 \rightarrow T_2$

Experimentally it was found that

$$\oint(\text{đ}w + \text{đ}q) = 0$$

⇒ The sum (w + q) is independent of path

⇒ This implies that there is a state function whose differential is $\text{đ}w + \text{đ}q$

We define it as U, the "internal energy" or just "energy"

$$\therefore \quad dU = \text{đ}w + \text{đ}q$$

For a cyclic process $\oint dU = 0$

For a change from state 1 to state 2,

$$\Delta U = \int_1^2 dU = U_2 - U_1 = q + w$$ does not depend on path

each depends on path individually, but not the sum

For fixed n, we just need to know 2 properties, e.g. (T, V), to fully describe the system.

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

U is an extensive function (scales with system size).

$\bar{U} = \dfrac{U}{n}$ is molar energy (intensive function)

THE FIRST LAW

Mathematical statement:

$$dU = đq + đw$$

or

$$\Delta U = q + w$$

or

$$-\oint đq = \oint đw$$

Corollary: Conservation of energy

$$\Delta U_{system} = q + w \qquad \Delta U_{surroundings} = -q - w$$

$$\Rightarrow \quad \Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

Clausius statement of 1st Law:

The energy of the universe is conserved.