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5.60 Thermodynamics & Kinetics
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Work, Heat, and the First Law

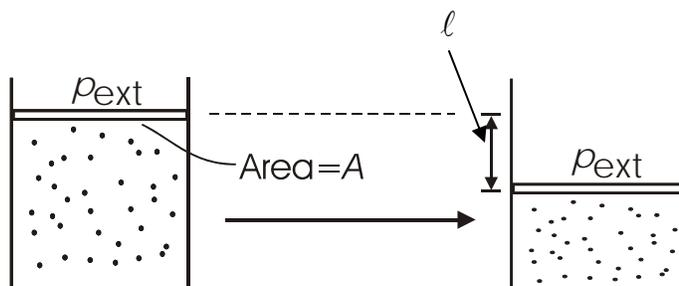
- Work:

$$w = F \cdot \ell$$

↑ applied force ↑ distance

Expansion work

$$F = p_{\text{ext}} A$$



$$w = -(p_{\text{ext}} A) \ell = -p_{\text{ext}} \Delta V$$

convention:

Having a "-" sign here implies $w > 0$ if $\Delta V < 0$, that is, positive work means that the surroundings do work to the system. If the system does work on the surroundings ($\Delta V > 0$) then $w < 0$.

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

$$dw = -p_{\text{ext}} dV \quad d \text{ means this is not an exact differential}$$

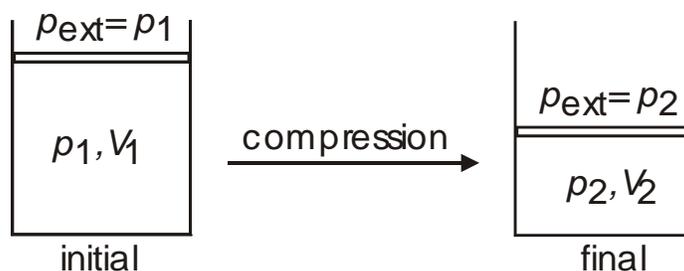
$$\text{Integral } w = -\int_1^2 p_{\text{ext}} dV \quad \text{depends on the path!!!}$$

- Path dependence of w

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

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

$$\text{Compression} \quad V_1 > V_2 \text{ and } p_1 < p_2$$

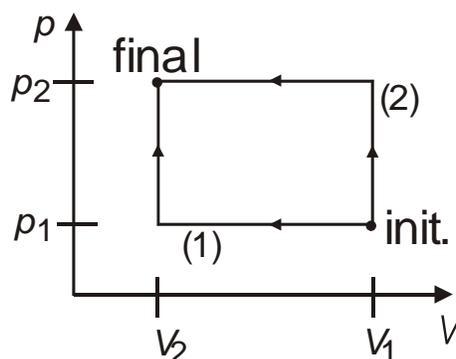


Two paths:

- (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 $p = p_2$

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

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



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

$$= -\int_{V_1}^{V_2} p_1 dV = -p_1(V_2 - V_1)$$

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

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

$$= -\int_{V_1}^{V_2} p_2 dV = -p_2(V_2 - V_1)$$

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

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

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

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

closed cycle

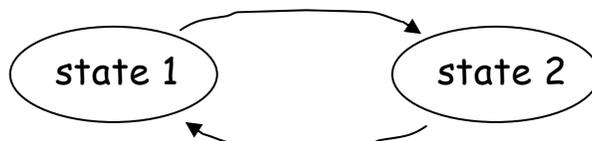
w is not a state function

cannot write $w = f(p, V)$

WORK

Work (w) is not a function of state.

For a cyclic process, it is possible for $\oint dw \neq 0$



HEAT

That quantity flowing between the system and the surroundings that can be used to change the temperature of the system and/or the surroundings.

Sign convention: If heat enters the system, then it is positive.

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

It is possible to have a change of state

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

adiabatically (without heat transferred)
or nonadiabatically.

Historically measured in calories

[1 cal = heat needed to raise 1 g H₂O 1°C,
from 14.5°C to 15.5°C]

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

$$1 \text{ cal} = 4.184 \text{ J}$$

Heat Capacity

C - connects heat with temperature

$$\delta q = C_{\text{path}} dT \quad \text{or} \quad C_{\text{path}} = \left(\frac{\delta q}{dT} \right)_{\text{path}}$$

↑
heat capacity is path dependent

Constant volume: C_V Constant pressure: C_P

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

Equivalence of work and heat

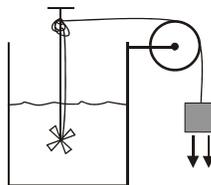
[Joule (1840's)]

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

$$\oint (\delta w + \delta q) = 0$$

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

⇒ This implies that there is a state function whose differential is $\delta w + \delta q$

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

$$\therefore dU = \delta w + \delta q$$

For a cyclic process $\oint dU = 0$

For a change from state 1 to state 2,

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



 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.

$$\text{So } U = U(T, V)$$

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

$$\bar{U} = \frac{U}{n} \quad \text{is molar energy (intensive function)}$$



THE FIRST LAW

Mathematical statement:

$$dU = \delta q + \delta w$$

or

$$\Delta U = q + w$$

or

$$-\oint \delta q = \oint \delta w$$

Corollary: Conservation of energy

$$\Delta U_{system} = q + w$$

$$\Delta U_{surroundings} = -q - w$$

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

Clausius statement of 1st Law:

The energy of the universe is conserved.