Chapter 19 → First Law

We will study the 3 laws of thermodynamics now.

0th Law : statement about equilibrium

Ch.19 1st Law : statement about conservation of energy (energy flows)

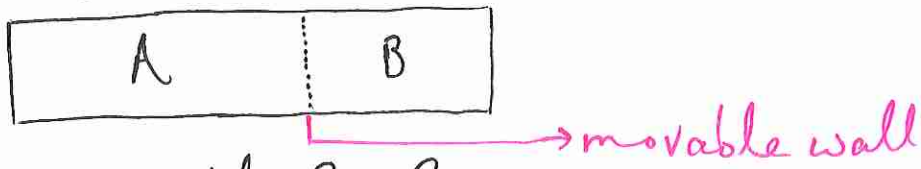
Ch.20 2nd Law : statement about irreversibility (arrow of time)

Ch.21 3rd Law : statement about absolute zero (temperature)

0th Law: if systems A, B are in equilibrium and systems B, C are in equilibrium then systems A, C are in equilibrium.

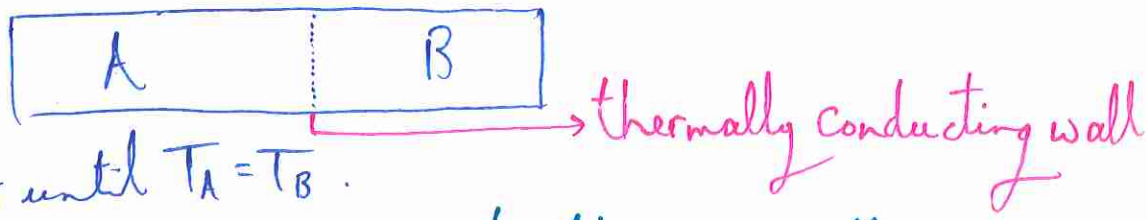
There are different kinds of equilibrium :

mechanical equilibrium : P is the variable



wall will move until $P_A = P_B$.

thermal equilibrium : T is the variable



heat will flow until $T_A = T_B$.

thermally conducting wall → diathermic wall

thermally insulating wall → adiabatic wall

1st Law :

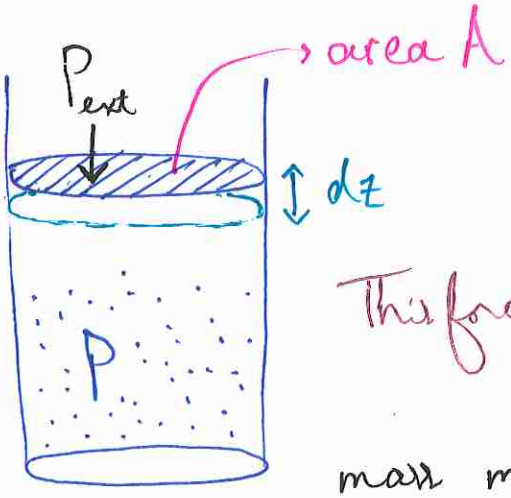
Define heat, q, to be the energy transfer that results from a temperature difference between the system and its surroundings.

System → what we are focusing on
Surroundings → everything else.

Define work, w, to be the transfer of energy between the system and its surroundings as a result of unbalanced forces between them.

work can always be related to the raising or lowering of a mass in the surroundings.

$\underline{F} = m\underline{a}$; $w = \underline{F} \cdot \underline{l}$ $\underline{l}$ = vector length of path.



External pressure P_{ext}.
Force on outer face of plate is $P_{ext} A$.
This force is equivalent to a weight pressing down on the system.

mass m, acceleration g, so
$m = \dfrac{P_{ext} A}{g}$ would be the mass

Plate moves up a distance dz.

Work done is $\delta w = -P_{ext} A\, dz = -P_{ext}\, dV$

negative because work done <u>by</u> system

other way around: $\delta w = P_{ext} |dV|$ for compression

$= -P_{ext}\, dV$ positive because work done <u>on</u> system.

If P_{ext} not constant,

generalizes to $w = -\int_{V_i}^{V_f} P_{ext}\, dV$

Work and heat depend on the path so we need to know the precise path followed to compute them.

What does this mean?

The state of a system is defined by specifying enough properties that the equation of state fills in the rest.

e.g. for ideal gas $PV = nRT$ so given n, P, V : T is determined

q, w are not state functions: if you are given the initial and final states of the system,

this is not enough info. to compute q, w.

e.g. $w = -\int_{V_i}^{V_f} P_{ext}\, dV$: P_{ext} can have any value provided it is large enough to compress the gas (assuming $V_f < V_i$) so w depends on what pressure is used.

Important Concept: reversible process. Show Figs 19.2, 19.3, 19.4

The minimum work required to compress the gas is when P_{ext} is barely greater than the pressure of the gas throughout the compression.

For this case we can replace P_{ext} with P, the gas pressure.

Called reversible because an infinitesimal change in P_{ext} at any stage would reverse the compression to an expansion.

ex: isothermal ~~set~~ reversible compression of an ideal gas:

$$w_{rev} = -\int_{V_1}^{V_2} P\, dV = -\int_{V_1}^{V_2} \frac{nRT}{V}\, dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Work and heat are defined only for processes in which energy is transferred between a system and its surroundings.

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

First Law : U (energy) is a state function.

For a state function we don't need to know the path

$$\int_1^2 dU = U_2 - U_1 = \Delta U.$$

We can write $\Delta U = q + w$.

Even for reversible processes, heat and work depend on the path. We will prove this using an ideal gas, but first we need one fact:

Equipartition Theorem:

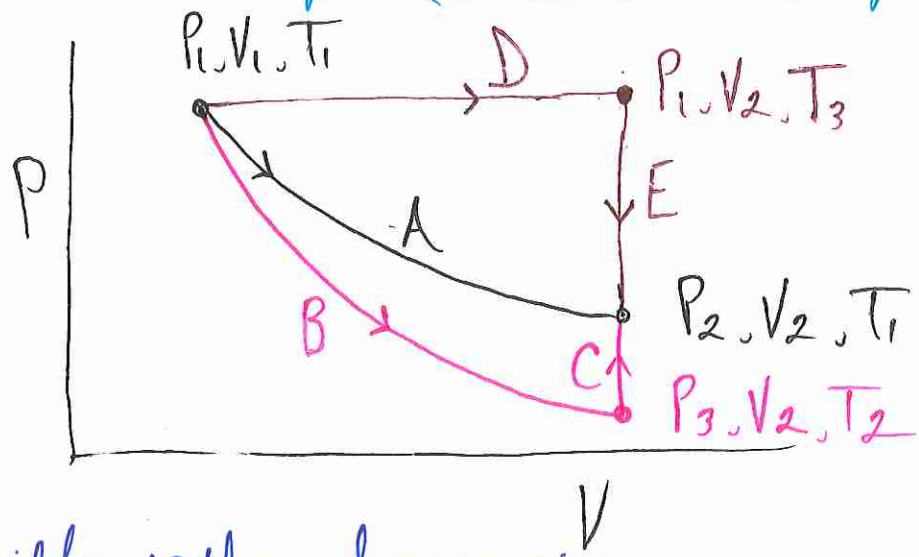
Molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion, and that energy is:

$\frac{1}{2}k_BT$ per molecule $\qquad k_B$ = Boltzmann's constant

$\frac{1}{2}RT$ per mole $\qquad R$ = gas constant

Therefore $U = \frac{3}{2}k_BT$ per molecule or $\frac{3}{2}RT$ per mole for an ideal monoatomic gas (3 translational degrees of freedom)

Fig 19.5:



Path A: reversible isothermal expansion

U depends on T only so $\Delta U = 0 \Rightarrow -q = w$

$$\delta w = -P\,dV = -\frac{RT_1}{V}\,dV$$

So $$w = -q = -RT_1\int_{V_1}^{V_2}\frac{dV}{V} = -RT_1\ln\left(V_2/V_1\right)$$

Note: work is done by the gas.
$q > 0$ because heat enters the system to maintain the temperature constant because the system used energy to do work

Path B + C : adiabatic expansion ($q = 0$) then heat at constant volume

For the adiabatic expansion we will use a state function to compute w because this often makes things easier

$$w = \Delta U = U_2 - U_1 = \int_1^2 dU = \int_{T_1}^{T_2}\frac{dU}{dT}\,dT$$

where we changed limits from U_1 and U_2 to T_1 and T_2. Since $U = U(T)$ only

Also, $$\frac{dU}{dT} = \left.\frac{\partial U}{\partial T}\right)_V \equiv C_V(T)$$ definition of constant volume heat capacity.

So $$w = \int_{T_1}^{T_2} C_V(T)\,dT \quad \text{and} \quad q = \int_{T_2}^{T_1} C_V(T)\,dT$$
↳ heating step C.

For $U = \frac{3}{2}RT$, $\frac{dU}{dT} = \frac{3}{2}R$ and $w = \frac{3}{2}R(T_2 - T_1)$

For the constant volume path $w = 0$ since $dV = 0$.
Therefore w is different for path A vs path B + C.

At constant V, $\delta w = 0$ so $\delta q_V = dU$

Define a new state function $H = U + PV$ = enthalpy

Chemistry is commonly done at constant P, not constant V, so the work $-\int P\,dV$ is not zero.

$$dH = dU + P\,dV \quad (+\,V\,dP \text{ but constant } P)$$

$$= \delta q - P_{ext}\,dV + P\,dV = \delta q_P$$

$\hookrightarrow \delta w = -P_{ext}\,dV$ and $P_{ext} = P =$ constant

This is useful because heat transfer can be measured accurately in experiments.

constant volume

$\Delta U = q_V$

$$C_V \approx \frac{q_V}{\Delta T} \equiv \left.\frac{\partial U}{\partial T}\right)_V$$

constant pressure

$\Delta H = q_P$

$$C_P \approx \frac{q_P}{\Delta T} \equiv \left.\frac{\partial H}{\partial T}\right)_P$$

Heat capacity

For an ideal gas $H = U + PV = U + nRT$

and $U = U(T)$ only, so same for H

$$\Rightarrow \frac{dH}{dT} = \frac{dU}{dT} + nR \Longrightarrow \left.\frac{\partial H}{\partial T}\right)_P = \left.\frac{\partial U}{\partial T}\right)_V + nR$$

$$\Longrightarrow C_P - C_V = nR$$

C_P larger because we do work against atmospheric pressure as the gas expands as it is heated.

At constant P, $dH = \delta q_p = C_p(T)\,dT$

$$\Rightarrow \Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p(T)\,dT$$

$$\Rightarrow H(T) = H(0) + \int_0^T C_p(T)\,dT$$

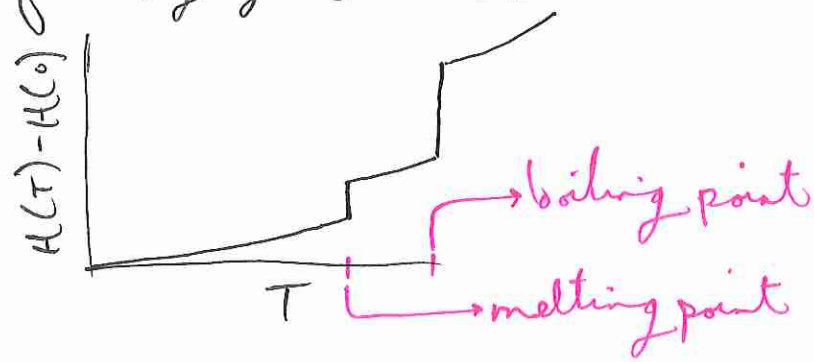
but this ignores phase transitions where a substance absorbs heat without changing temperature.

We have to include the heat of fusion (melting) and the heat of vaporization etc.

$$\Rightarrow H(T) = H(0) + \int_0^{T_{fus}} C_p^s\,dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{vap}} C_p^l\,dT + \Delta H_{vap} + \int_{T_{vap}}^{T} C_p^g\,dT \ \cdots$$

where s = solid, l = liquid, g = gas; $\Delta H_{fus} = H^l(T_{fus}) - H^s(T_{fus})$

See Figs 19.6, 19.7



Exothermic / Endothermic Reactions

$\Delta H_{rxn} = H_{products} - H_{reactants}$ negative = exothermic

Then, since H is a state function, ΔH_{rxn} is additive which is very useful: called Hess's Law

e.g. $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\Delta H = -110.5$ kJ

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -283.0$ kJ

(for quantities as written in moles)

Add: $C(s) + O_2(g) \longrightarrow CO_2(g)$

$\Delta H = -393.5$ kJ

So we don't need to determine ΔH values experimentally for every reaction: can use a library of measured reactions to build the reaction of interest.

$\Delta H(\text{reverse}) = -\Delta H(\text{forward})$ for a reaction since the sum of the forward and backwards reactions would be zero.

§19.11 → ΔH_{rxn} can be computed from heats of formation. This is a systematic way of doing ΔH_{rxn} calculations.

How does this work?

Standard reaction enthalpy ΔH°_{rxn} is ΔH for one mole of the specified reagent when all reactants and products are in their standard states.

What does standard state mean?

gas → 1 bar pressure, any T

solid → 1 bar pressure, any T, pure crystalline form

liquid → 1 bar pressure, any T

Standard molar enthalpy of formation ΔH_f°

ΔH_f° : formation of one mole from constituent elements

ex: ΔH_f° of $H_2O(l) = -285.8$ kJ/mol at $T = 298$ K

This is : $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

So the liquid lies "downhill" in enthalpy relative to its constituent elements

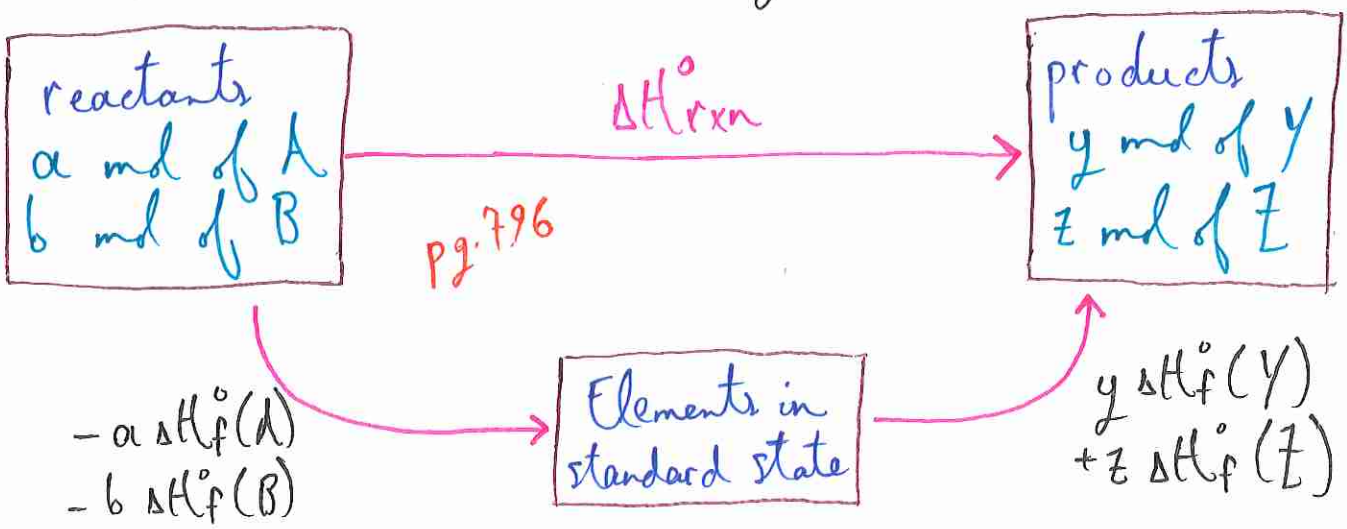
Convention: puts $\Delta H_f^\circ = 0$ for all the elements in their most stable physical state at 1 bar pressure.

So C (diamond) $\neq 0$ because graphite is more stable.
Also $I_2(g) \neq 0$ since solid I is more stable at 1 bar pressure, room temperature.

How do we use ΔH_f° to calculate ΔH_{rxn} ?

(first limit ourselves to 298 K, then remove this limitation)

Consider $aA + bB \longrightarrow yY + zZ$



Now add the final piece: use heat capacities and heats of fusion etc. for phase changes to handle other temp.

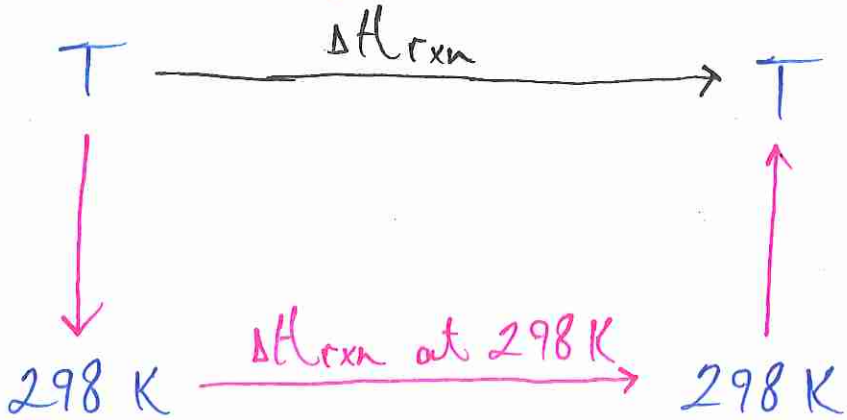


Fig 19.10

Need to know heat capacities of the reactants and products and info. about ΔH for any phase transitions.

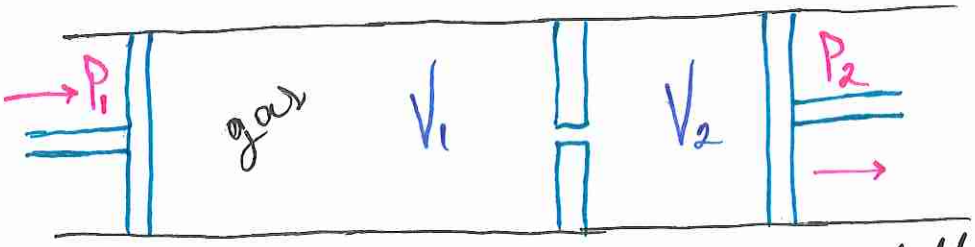
With this ΔH_{rxn} can be calculated for many reactions.

Joule-Thompson Expansion "throttling"

problem 19.52

basis for gas liquefaction, industrially important

adiabatic expansion of a gas from P_1 to P_2 through a nozzle



See Fig 19.11

initial : $V_2 = 0$, all gas on left side

final : $V_1 = 0$, all gas on right side

gas : $V_1, P_1 \longrightarrow V_2, P_2$ (temperature ? might change)

work done on left : P_1V_1

on right : $-P_2V_2$ Total: $\Delta U = w = P_1V_1 - P_2V_2 = U_2 - U_1$

$\Rightarrow U_2 + P_2V_2 = U_1 + P_1V_1$

$\Rightarrow H_2 = H_1 \Rightarrow \Delta H = 0$ isenthalpic process

Writing $H = H(P,T) \Longrightarrow dH = \left.\frac{\partial H}{\partial P}\right)_T dP + \left.\frac{\partial H}{\partial T}\right)_P dT$

At constant H ($dH = 0$) divide through by dT :

$$0 = \left.\frac{\partial H}{\partial P}\right)_T \left.\frac{\partial P}{\partial T}\right)_H + \underbrace{\left.\frac{\partial H}{\partial T}\right)_P}_{C_P} \underbrace{\left.\frac{\partial T}{\partial T}\right)_H}_{1}$$

$$\mu_{JT} = \left.\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\underbrace{\left.\frac{\partial H}{\partial P}\right)_T}_{<0 \text{ for real gases at low } P \text{ due to intermolecular attraction}}$$

zero if ideal because $H = U + PV = \frac{3}{2}RT + RT = 5/2\,RT$

$\mu_{JT} > 0$: if we lower P at const H, T should go down