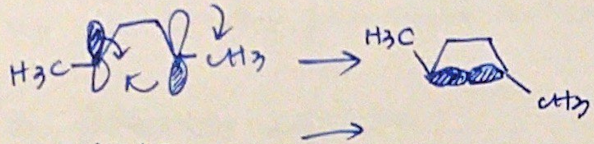
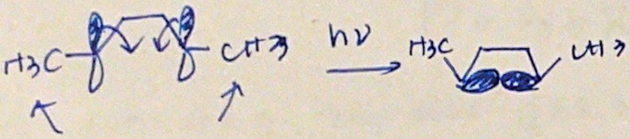
Last time: quantum & reactions



HOMO $\xrightarrow{\text{react}}$



LUMO

Quantum superposition:

$\psi_0 \to$ bit set $= 0$

$\psi_1 \to$ bit set $= 1$.

$\frac{1}{\sqrt{2}}(\psi_0 + \psi_1) \to$ bit set to both!

Today = Statistical mechanics & thermo.

Goal: 2 postulate: laws of thermo → equil. constants for chemical rxns.

Mechanics → Stat mech.

one. few → large number.

ex: concentration → equilibrium constant Keq.

how fast in rx → rate constant K.

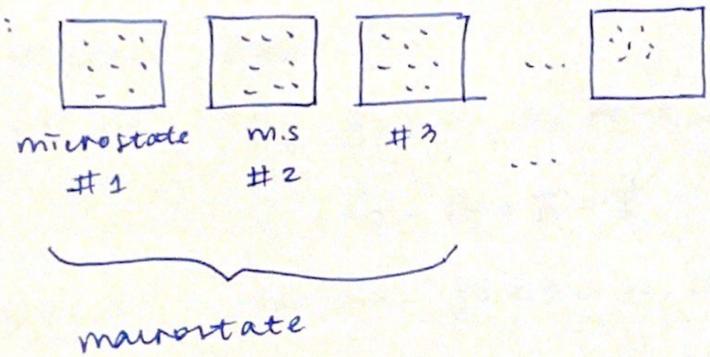
energetics → heat

principle maximize or minimize.

Def:

- Isolated system: idealized case, no mass or energy flow.
- Microstate vs. macrostate:

ex:

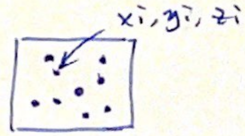


volume V = same.

number of Ar atoms = N is same; color...

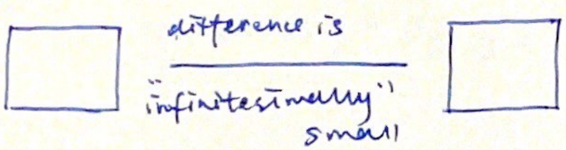
State function: variables needed to specify macrostate: V, P, E, color, ...

ex of not a state function:



Reversibility =

macrostate #1. macrostate #2



Probability density =

↳ probability of a simple event (discrete system) P_{dice}

↳ pobability per unit distance (continuous system) $|\psi(x)|^2$.

a. Discrete system:

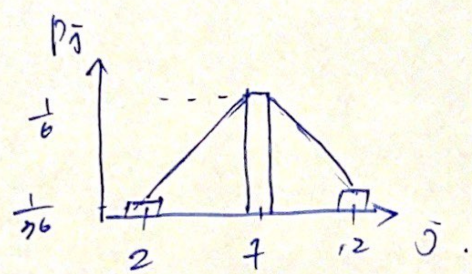
ex: die roll: $j = 1, 2, \ldots 6$; $W = 6$ states.

$$P_j = P_j = \frac{1}{W} = \frac{1}{6}.$$

ex: S1.2 two dice $j = 2, 3 \ldots 12$, $W = 36$.

$P_7 \Rightarrow$
1+6
2+5
3+4
4+3
5+2
6+1

$$P_7 = \frac{6}{36} = \frac{1}{6}.$$



b. continuous system:

(b1) QM $p(x) = |\psi(x)|^2$ Prob of being between $x = -1$ & 1.

no units ↗ $P_{[-1,1]} = \int_{-1}^{1} dx\, |\psi(x)|^2$

↑ m ↖ m^{-1}

(b2) CM $P(x_i, p_i, t) = \rho(x_i, p_i, t)$

$\bar{P} \sim \int dx \int dp \int dt\, \rho(x_i, p_i, t)$

$A_j \overset{?}{\Rightarrow} \bar{A}$ (averages)

$$= \sum_{j=1}^{6} A_j \cdot P_j$$

$$\quad\quad\quad\quad \parallel$$

$$= \sum_{j=1}^{6} A_j \, \underline{\rho_j}$$ (probability density)