Ideal gas kinetic theory

Boltzmann's law $\quad P(\varepsilon) \propto e^{-\varepsilon/k_B T}$

$$\propto e^{-\varepsilon/RT}$$

$$k_B = R/N_A$$

All energy is kinetic energy for an ideal gas

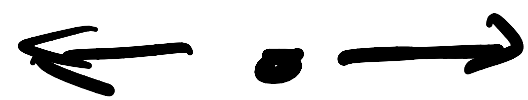
$$\varepsilon_{kinetic} = \sum_{i=1}^{N} \frac{1}{2} m_i |v_i|^2$$

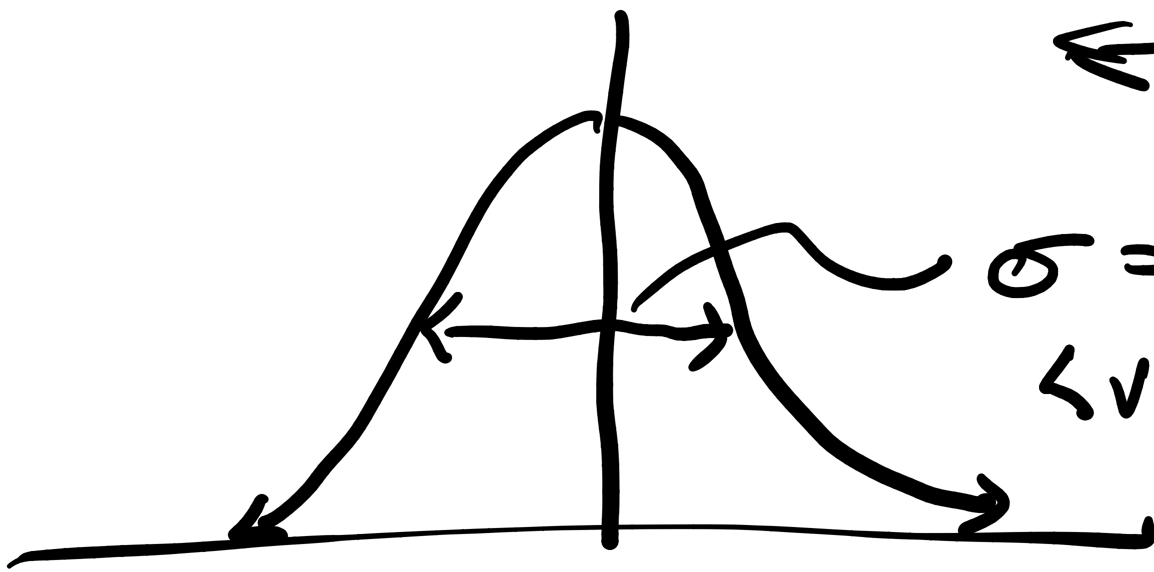
in each dimension

$\sigma^2 = \frac{k_B T}{m}$

$$P(v_i) = \frac{1}{\sqrt{2\pi \frac{k_B T}{m}}} e^{-\frac{1}{2} m v_i^2 / k_B T}$$

v_i





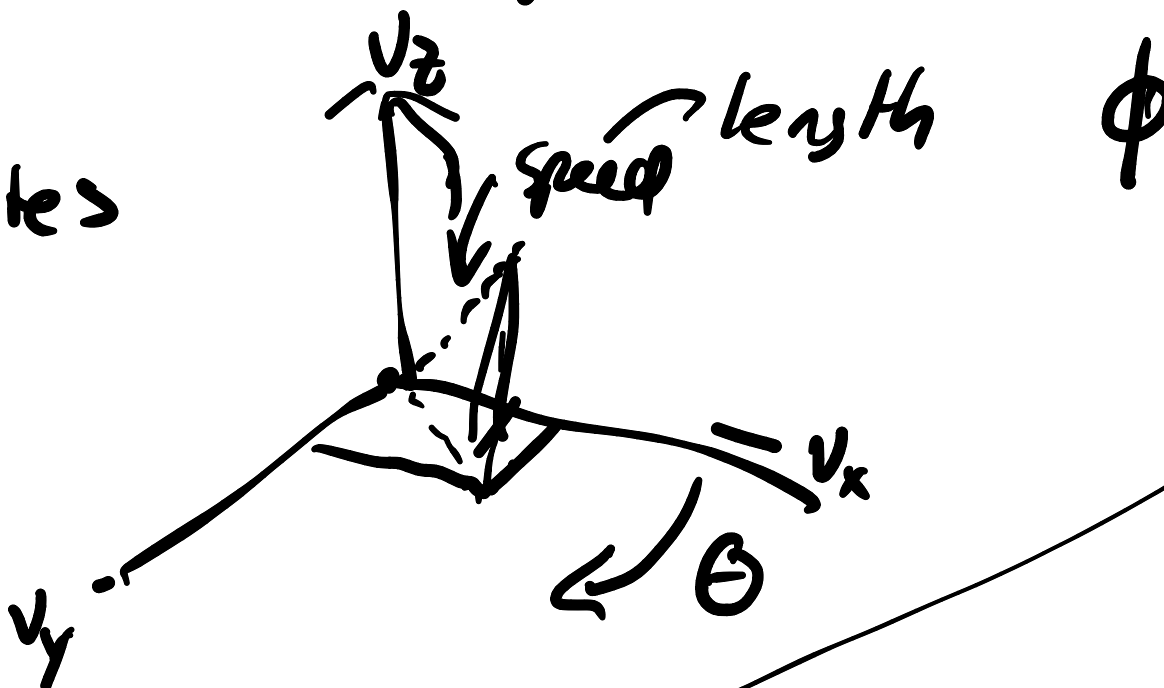
$\sigma = \sqrt{k_B T / m}$

$\langle v_i \rangle = 0$

$$P(v_x, v_y, v_z) = \frac{1}{\left(2\pi \frac{k_B T}{m}\right)^{3/2}} e^{-v_x^2/2mk_BT} e^{-v_y^2/2mk_BT} \times e^{-v_z^2/2mk_BT}$$

$$\text{speed} = |v| = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

spherical coordinates

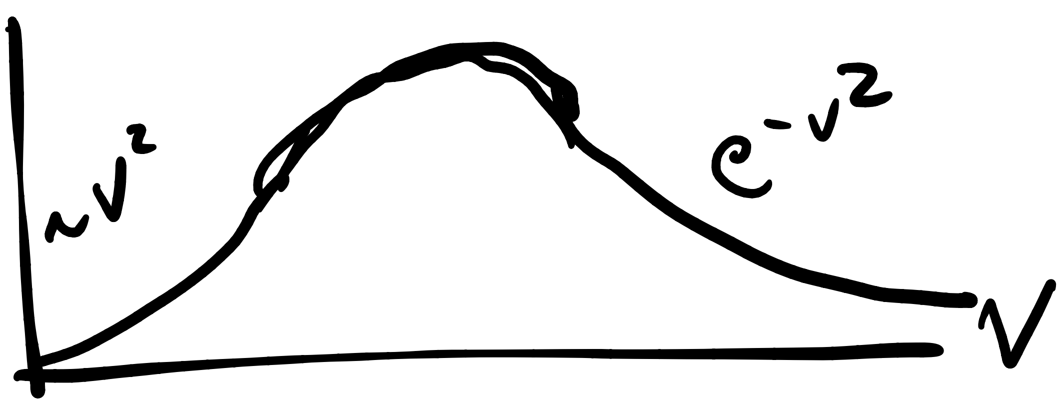


$$P(|v|, \theta, \phi) = \qquad r^2 \sin\phi \; dr\, d\phi\, d\phi$$

$$\underbrace{P(|v|,\theta,\phi)}_{dv\,d\theta\,d\phi} = \frac{1}{\left(2\pi \frac{k_B T}{m}\right)^{3/2}} e^{-mv^2/2mk_BT}\, v^2 \sin\phi \, dv\, d\theta\, d\phi$$

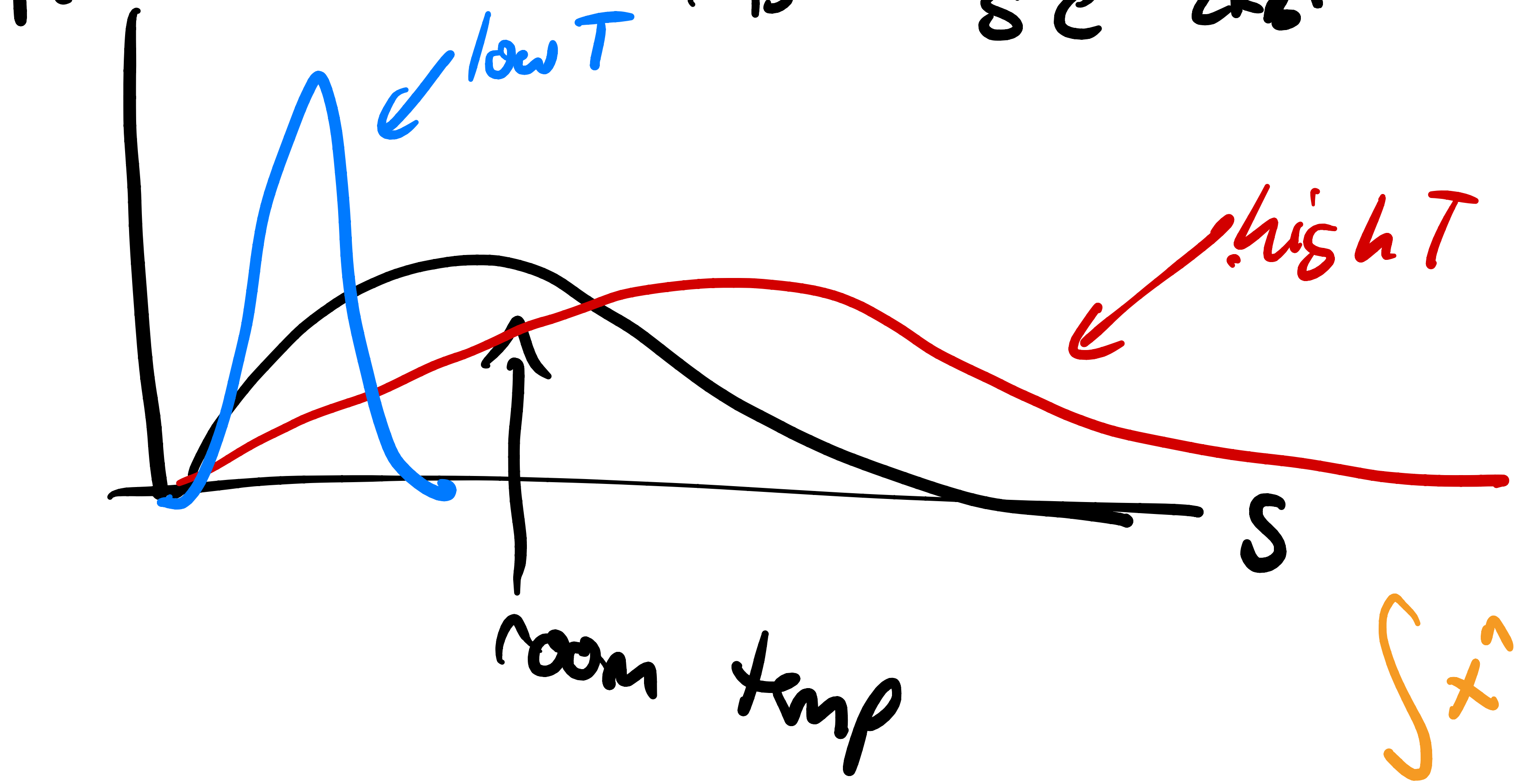
$$P(|v|) = \underbrace{\int d\theta \int d\phi \sin\phi}_{4\pi} \Big[\qquad \Big]$$

$$P(|v|)\,dv = C \quad v^2 e^{-mv^2/2mk_BT} \quad dv$$



(v from 0 to ∞)

Maxwell-Boltzmann $s^2 e^{-\frac{ms^2}{2k_BT}}$



$\int x^n f(x)$

Avg: $\langle s \rangle = \int_0^\infty s\, P(s)\, ds$

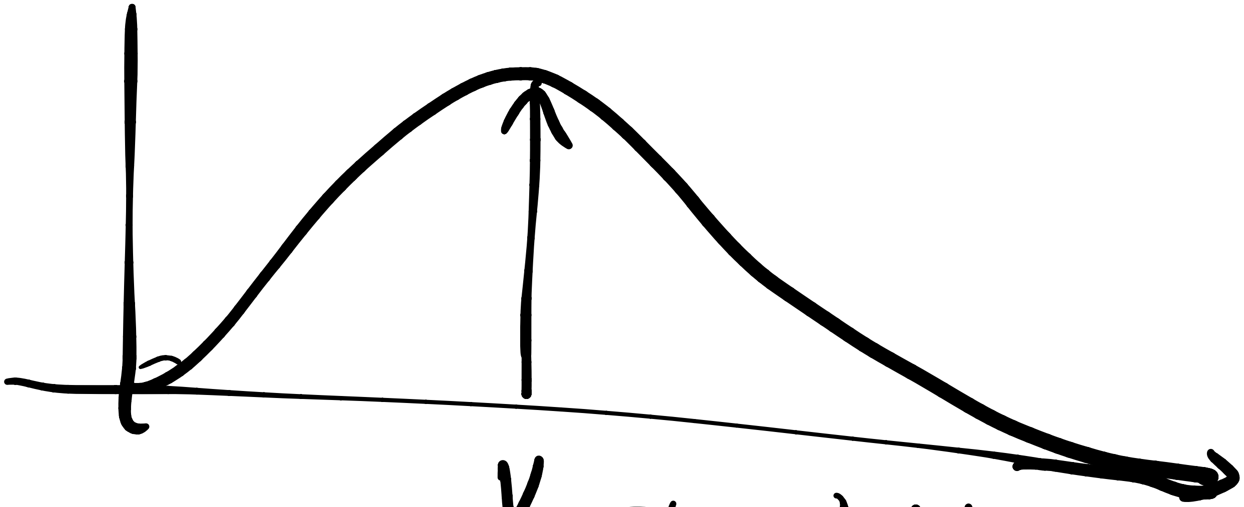
$$= \int_0^\infty s \cdot 4\pi \left(\frac{1}{2\pi \frac{k_B T}{m}} \right)^{3/2} s^2 e^{-s^2 m / k_B T}\, ds$$

$\underset{\text{by parts}}{=} \left(\frac{8 k_B T}{\pi m}\right)^{1/2}$ [pg 111$\overset{?}{\text{i}}$4]
M&S

$$v_{RMS} = \sqrt{\langle s^2 \rangle} = \sqrt{\int_0^\infty s^2 P(s)\, ds}$$

$$= \sqrt{3 k_B T / m}$$

$$\langle s \rangle / v_{rms} = \sqrt{\frac{8}{3\pi}} < 1$$



$V_{\text{most probable}}$

$$C s^2 e^{-s^2 k}$$

$$\frac{m}{2k_B T}$$

$$\frac{dP(s)}{ds} = 0 = C\left[s^2 \cdot -2ks\, e^{-s^2 k} + 2s\, e^{-s^2 k}\right]$$

$$S_{\text{most prob}} = \sqrt{\frac{2k_B T}{M}} < V_{avg}$$

$$S_{mp} < S_{avg} < S_{rms}$$

$86\% < 1 < 109\%$

$$C_{sound} = \sqrt{\gamma/3}\ S_{rms} \qquad \gamma = c_p/c_v$$

Reaction rates: (pg 1116-1127)

@ molecular level →

speed of molecules colliding &

amnt of energy available for reactions

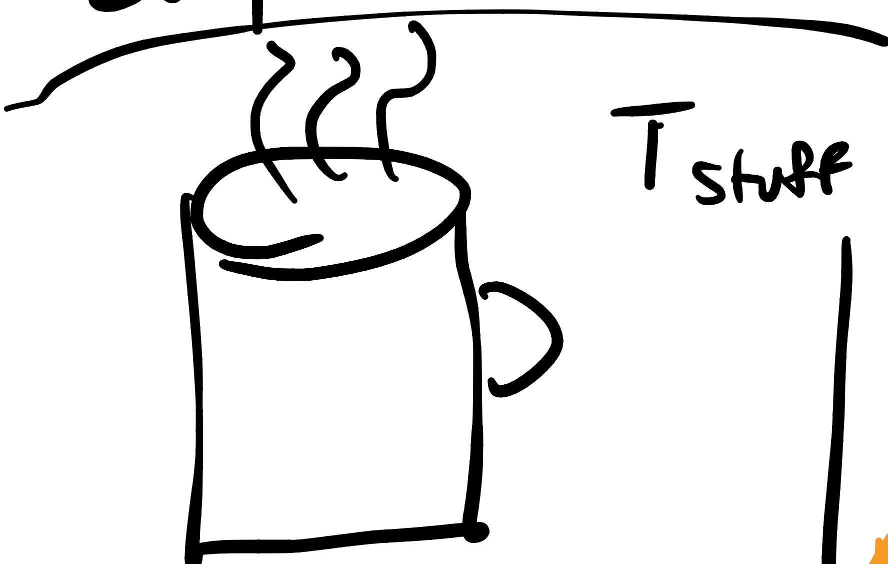
$$Cl-Cl + Br-Br \ ?$$

amnt & frequency of collisions

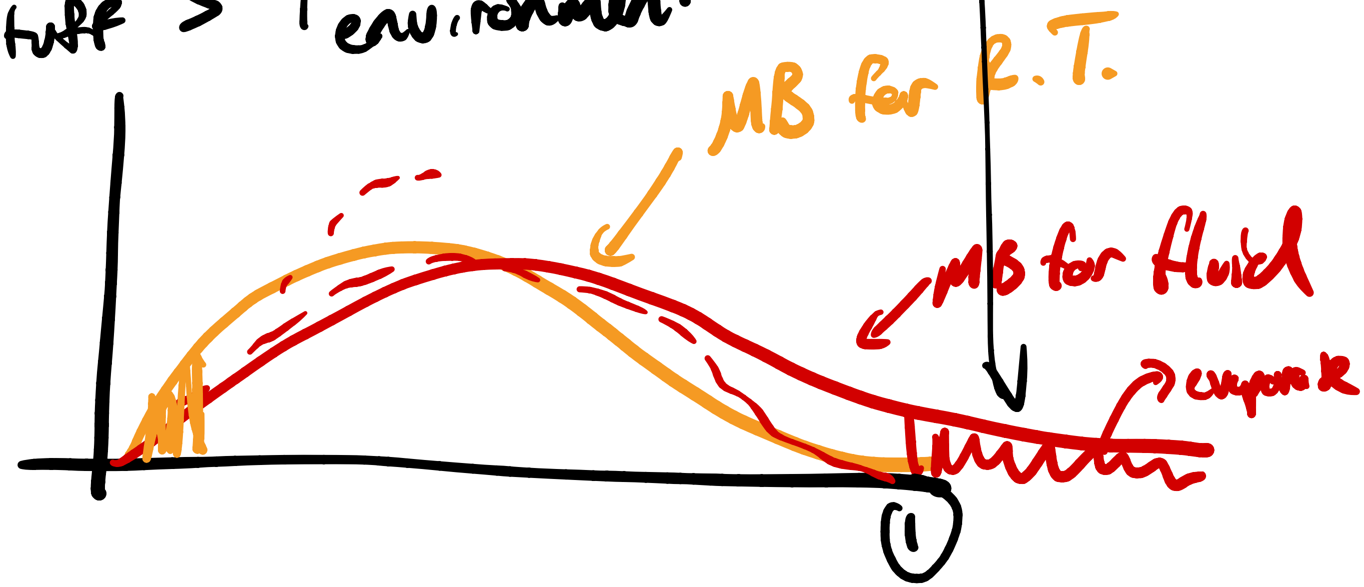
rate arrhenius law $k = A e^{\epsilon^{\ddagger}/k_B T}$

$$\int_{v_1}^{\infty} s^2 e^{-s^2} \cdots$$

Evaporative cooling



$T_{stuff} > T_{environment}$



b/c ideal gas $P(E) = P(KE) = e^{-\sum \frac{1}{2} m v^2 / k_B T}$

interacting $P(E) = P(E_{pot} + E_{KE}) = e^{-E_{pot}/k_B T} \, e^{-E_{kin}/k_B T}$

Rate Laws (M&S Ch 28)

$$\underline{a}A + bB \rightleftharpoons cC + dD$$

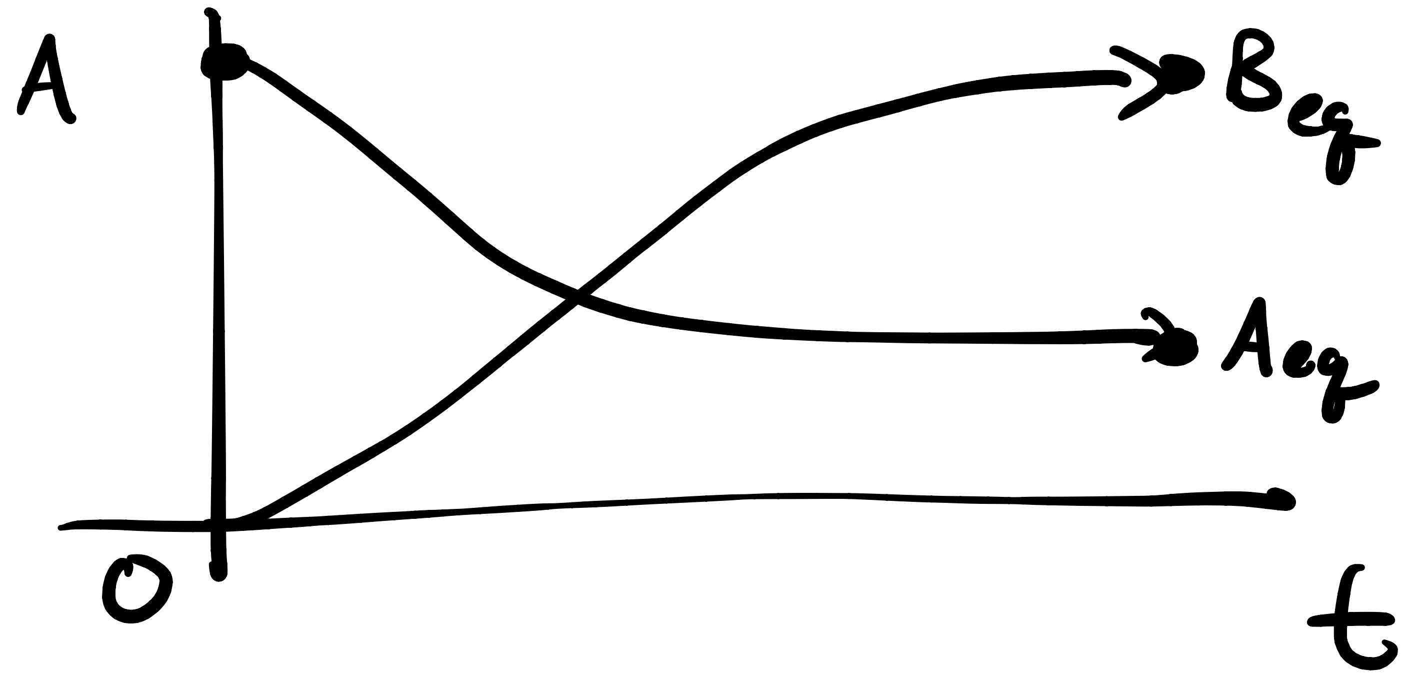
$$dn_i = \nu_i \, d\xi$$

ξ as a time changing quantity

$$n_A(t) = n_A(0) + \nu_A \xi(t)$$
$$= n_A(0) - a\xi(t)$$

⋮

$$A \rightleftarrows B$$



$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$$

$$\int_0^{\tau} \frac{dn}{dt}\,dt = \int_0^{\tau} \nu_i \frac{d\xi}{dt} \rightsquigarrow \Delta n = \nu_i \Delta\xi$$

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$$

$$\frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt}$$ divide by volume

$$\frac{1}{V} \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{d[i]}{dt}$$ $\leftarrow$ reaction rate at time t

Eg $2NO + O_2 \rightarrow 2NO_2$

$$2NO + O_2 \rightarrow 2NO_2$$

$$r(t) = -\frac{1}{2}\frac{d[NO]}{dt}$$

$$= -\frac{d[O_2]}{dt}$$

$$= \frac{1}{2}\frac{d[NO_2]}{dt}$$

next "rate laws"

$$r(t) = k\,[A]^{m_A}[B]^{m_B}[\ldots]$$