

PHYS 320/420: Lecture 15

master eqn for $p_{\vec{n}}(t)$

$$\vec{n} = (n_S, n_E, n_{ES}, n_{S^*})$$

\Rightarrow equations for how avg's change in time:

$$\frac{d\langle n_S \rangle_t}{dt} = -\tilde{K}_b \langle n_S n_E \rangle_t + k_u \langle n_{ES} \rangle_t$$

$$\frac{d\langle n_E \rangle_t}{dt} = -\tilde{K}_b \langle n_S n_E \rangle_t + (k_u + k_{cat}) \langle n_{ES} \rangle_t$$

$$\frac{d\langle n_{ES} \rangle_t}{dt} = \tilde{K}_b \langle n_S n_E \rangle_t - (k_u + k_{cat}) \langle n_{ES} \rangle_t$$

$$\frac{d\langle n_{S^*} \rangle_t}{dt} = k_{cat} \langle n_{ES} \rangle_t$$

recall: binding term in $\Omega_{\vec{n}, \vec{m}}$:

$$\alpha_S K_S \frac{m_S}{V} m_E \equiv \tilde{K}_b m_S m_E$$

$$0 \leq \alpha_S \leq 1$$

$$\tilde{K}_b \equiv \frac{\alpha_S K_S}{V}$$

Unknown funcs:

$$\langle n_S \rangle_t, \langle n_E \rangle_t, \langle n_{ES} \rangle_t, \langle n_{S^*} \rangle_t$$

$$\underline{\text{and}} \quad \langle n_S n_E \rangle_t$$

\Rightarrow 5 unknowns but only 4
eqn's

dirty secret of traditional chem:

$$\text{approx: } \langle n_S n_E \rangle_t \approx \langle n_S \rangle_t \langle n_E \rangle_t$$

Digression: imagine we have
two variables X and Y (i.e.
height + weight).

prob. dist of these variables
in a pop. is $P(X, Y)$

then we can define avgs:

$$\langle X \rangle = \sum_{x,y} x P(x, y)$$

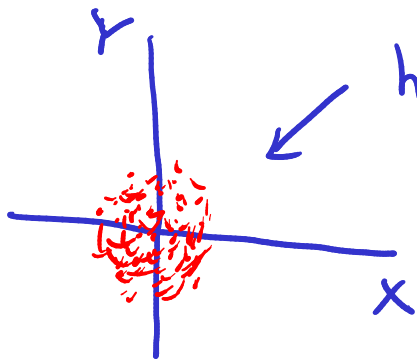
$$\langle Y \rangle = \sum_{x,y} y P(x, y)$$

$$\langle XY \rangle = \sum_{x,y} xy P(x, y)$$

Question: when is

$\langle XY \rangle \approx \langle X \rangle \langle Y \rangle$ a valid approx?

Diff kinds of distrib.



here $X + Y$ are not strongly correlated

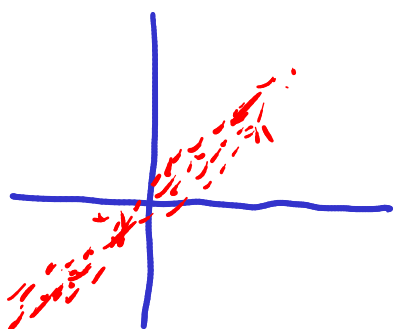
$$\Rightarrow \mathcal{P}(X, Y) \approx \mathcal{P}(X) \mathcal{P}(Y)$$

$$\langle XY \rangle = \sum_{X, Y} X Y \mathcal{P}(X, Y)$$

$$= \sum_{X, Y} X Y \mathcal{P}(X) \mathcal{P}(Y)$$

$$= \left[\sum_X X \mathcal{P}(X) \right] \left[\sum_Y Y \mathcal{P}(Y) \right]$$

$$= \langle X \rangle \langle Y \rangle$$

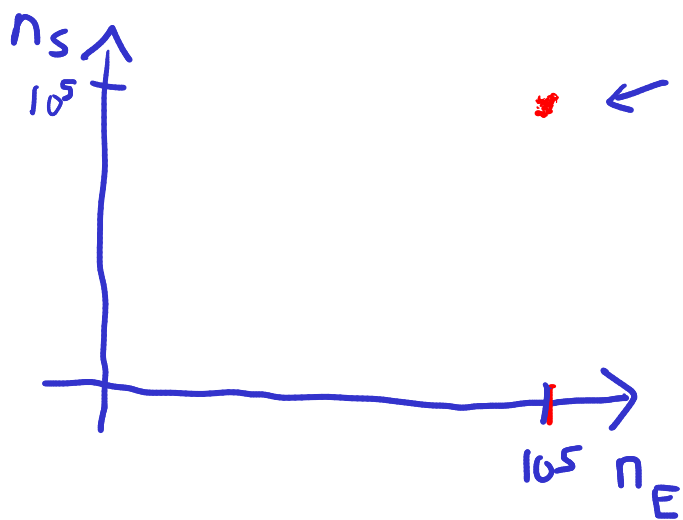


$X + Y$ strongly correlated

$$\Rightarrow \langle XY \rangle \neq \langle X \rangle \langle Y \rangle$$

Note $\langle n_S n_E \rangle_t \approx \langle n_S \rangle_t \langle n_E \rangle_t$

can be a dangerous assumption when species #'s are small, but in many chemistry contexts populations are large ($10^5 \rightarrow 10^5$ mol/cell)



← fluctuations are small relative to populations, so the precise shape of cloud becomes less important

so errors introduced by our assumption \ll population sizes

4 unknowns + 4 equations;

express avg's as concentrations

$$C_S(t) = \frac{\langle n_S \rangle_t}{V}$$

$$C_E(t) = \frac{\langle n_E \rangle_t}{V}, \text{ etc.}$$

Final four eqns: $E + S \xrightleftharpoons[k_{-1}]{k_1} ES \xrightarrow{k_{cat}} E + S^*$

$$\frac{dc_S}{dt} = -\tilde{k}_b V C_S C_E + k_{-1} C_{ES}$$

$$\frac{dC_E}{dt} = -\tilde{k}_b V C_S C_E + (k_{-1} + k_{cat}) C_{ES}$$

$$\frac{dC_{ES}}{dt} = \tilde{k}_b V C_S C_E - (k_{-1} + k_{cat}) C_{ES}$$

$$\frac{dc_{S^*}}{dt} = k_{cat} C_{ES}$$

[chemical kinetics]
(law of mass action)

One example for a specific, but this easily generalizes to others.

Payoff: solve for conc's

$C_\alpha(t)$ for all α

given some initial cond:

$C_\alpha(0)$

$t \rightarrow \infty: C_\alpha(t) \rightarrow C_\alpha^s$ (stationary state)

equilibrium



conc's at long time stop changing

Solve for these stationary conc's by setting left-hand side to zero:

$$0 = k_{cat} C_{ES}^s \Rightarrow C_{ES}^s = 0$$

$$0 = -\tilde{k}_b V C_S^s C_E^s + k_u C_{ES}^s \rightarrow 0$$

$$\Rightarrow C_S^s C_E^s = 0$$

from conserv. laws we know E is

not degraded by our reactions:

$$\Rightarrow C_s^s = 0$$

$C_E^s + C_{S^*}^s$ are constants

What questions remain?

We have eqn's in terms of rate parameters (k_{cat} , k_u , \tilde{k}_b) but no clear connection of these parameters to other physical considerations, like energy.

Next step: connect transition rates (Ω_{nm}) to energy + temperature.