Lecture 3: Equilibrium Conditions

1. Energy
    - A. Entropy
    - B. Transforming energy into other potentials
2. Reaction quotients and equilibrium

What is energy?

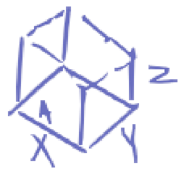
- capacity to produce change

What forms does it take? work, thermal, chemical, etc

equilibrium: no more change, So energy minimized

1st Law of Thermodynamics: $\Delta U = Q + W$

Δ energy = heat + work



$A = xy$

$V = xyz$

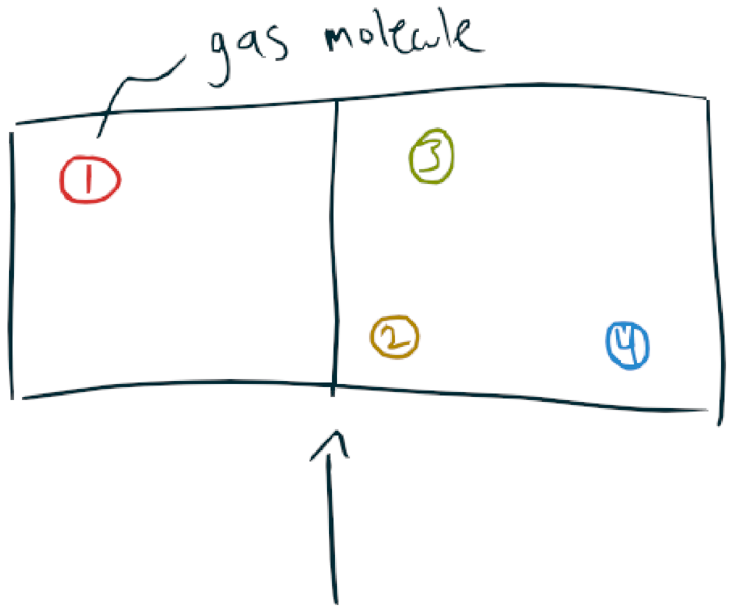
Work $W = \int_{x_0}^{x} F\,dx$ $F = m \cdot \frac{dv}{dt}$ $P = \frac{F}{A}$

P-V work

$$W = \int_{z_0}^{z} \frac{F}{A} A\,dz = -\int_{V_0}^{V} P\,dV$$

← convention defines work the system does as negative

Q or heat: related to T but must also capture that there is a natural direction which reactions proceed



remove partition

What happens?

What are the possible distributions?

$2^4 = 16$ options

$\frac{6}{16}$ options with 2:2

↑

most probable state

entropy is minimized when a system is at the most probable state

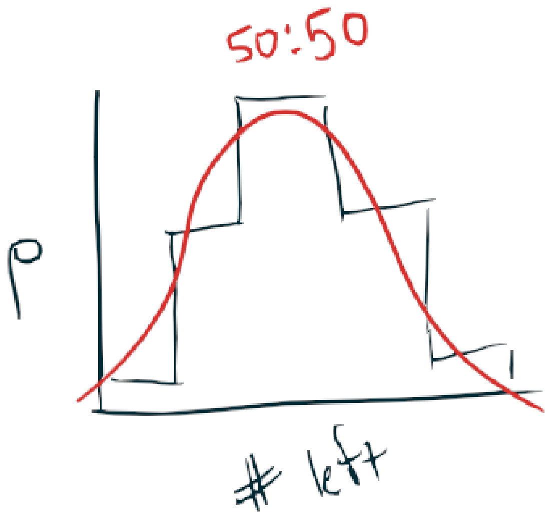
↳ causes change towards max p

2nd law says

$$dS = \frac{dQ}{T}$$

So

$$\Delta U = TdS - PdV$$



$$dU = TdS - PdV$$

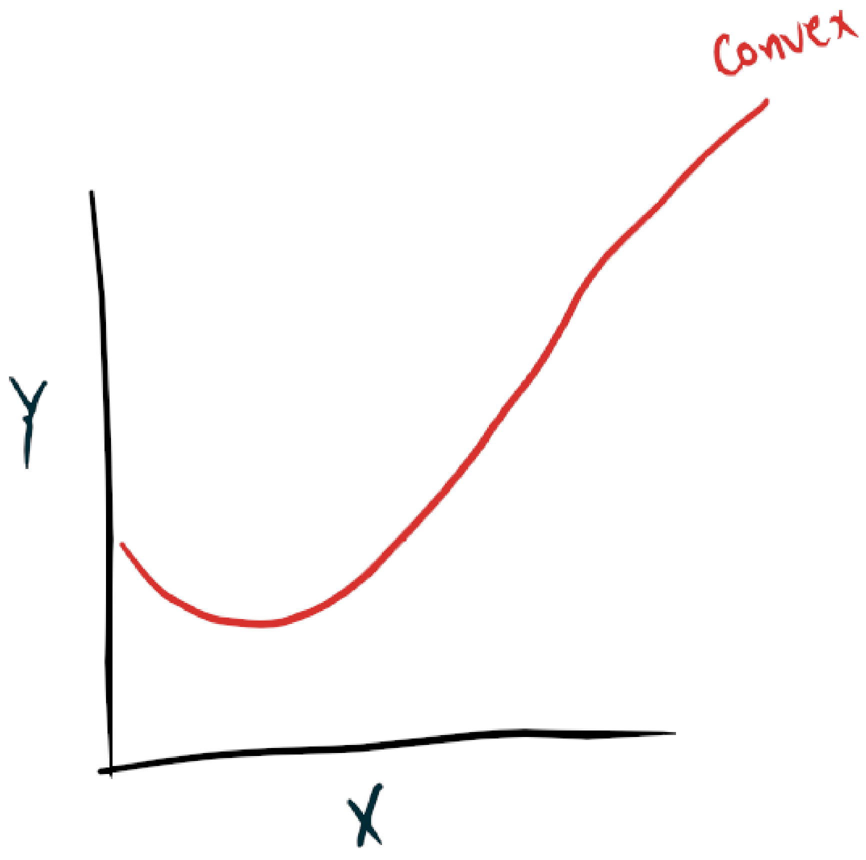
What if our system includes a chemical reaction that changes the amounts of chemical components?

μ_i = chemical potential of species i

$$dU = TdS - PdV + \sum \mu_i dN_i \qquad U(S, V, N_i)$$

T, S and P, V and μ_i, N_i are three conjugate pairs

and we can transform $U(S, V, N_i) \rightarrow G(T, P, N_i)$



$\frac{dy}{dx}$ is montonic which means there is one $\frac{dy}{dx}$ For each x

$\frac{dy}{dx}$ and x are conjugate pairs

$F(x)$ or $G(\frac{dy}{dx})$

are the two transforms of the same relationship

W, Y conjugate pair

$$\begin{tikzcd} f(x,y) \arrow[d] \\ g(x,w) \end{tikzcd}$$

$$df = u\,dx + w\,dy$$

$$dg = df - \underline{d(wy)}$$

$W\,dy + Y\,dw$

$$g = f - wy$$

$$dg = u\,dx + \cancel{w\,dy} - \cancel{w\,dy} - Y\,dw$$

$$dg = u\,dx - Y\,dw$$

$$dU = TdS - PdV + \sum \mu_i dN_i$$

$$\begin{tikzcd} U(\arrow[d] & S, \arrow[d] & V, \arrow[d] & N_i) \\ G(& T, & P, & N_i) \end{tikzcd}$$

product rule

$$dG = dU - d(TS)^{*} - d(-PV)^{*}$$

$$dG = dU - TdS - SdT + VdP + PdV$$

$$dG = \cancel{TdS} - \cancel{PdV} + \sum \mu_i dN_i - \cancel{TdS} - SdT + VdP + \cancel{PdV}$$

$$dG = VdP - SdT + \sum \mu_i dN_i$$

what does this line mean in words?

$$G = \underline{U} - TS + \underline{PV}$$

$$H = U + PV$$

$$\frac{\partial G}{\partial N_i} = \mu_i$$

$$dG = VdP - SdT + \sum \mu_i dN_i$$

$$\frac{\partial G}{\partial N_i} = \mu_i$$

ideal gas $PV = nRT$

$$\left(\frac{\partial G}{\partial P}\right) = V$$

$$P\left(\frac{\partial G}{\partial P}\right) = nRT$$

$$\left(\frac{\partial G}{\partial P}\right)\frac{1}{n} = \frac{RT}{P}$$

$$\int_{P}\left(\frac{\partial \mu_i}{\partial P}\right) = {}_{P}\,\frac{RT}{P}$$

$$\int_{P^\circ}\partial \mu_i = \int_{P^\circ}\frac{RT\,\partial P}{P}$$

reference state

$$\mu_i^P - \mu_i^{P^\circ} = RT(\ln P - \ln P^\circ) = RT\ln\frac{P}{P^\circ}$$

if P° is pure i, then $\frac{P}{P^\circ}$ is mole fraction

$$\mu_i^P = \mu_i^{P^\circ} + RT\ln X_i$$

Lets consider $aA + bB \longleftrightarrow cC + dD$

$$\Delta G = c\mu_C + d\mu_D - b\mu_B - a\mu_A$$

$$\Delta G = \sum \nu_i \mu_i = 0 \text{ at equilibrium}$$

$$\Delta G = \sum \nu_i\left(\mu_i^\circ + RT\ln X_i\right)$$

$$\Delta G = \sum\Big(\underset{\substack{\uparrow \\ \text{standard states}}}{\nu_i\mu_i^\circ} + \nu_i RT\ln \underset{\substack{\uparrow \\ \text{mole fractions}}}{X_i}\Big)$$

$$\Delta G = c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ + \sum \nu_i RT\ln X_i$$

$$\Delta G = \Delta G^\circ + RT\left(c\ln X_C + d\ln X_D - a\ln X_A - b\ln X_B\right)$$

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{X_C^c\cdot X_D^d}{X_A^a\cdot X_B^b}\right)$$

$$0 = \Delta G^\circ + RT\ln Q$$

$$\Delta G^\circ = -RT\ln K$$

Q product quotient

Reference States: only valid for the T measured at

$$\Delta G^\circ = \underline{H^\circ} - T\underline{S^\circ}$$

these can be experimentally determined, but they change w/ Temperature