



Lecture 3: Equilibrium Conditions

1. Energy

A. Entropy

B. Transforming energy into other potentials

2. Law of mass action

3. Condensation of Al_2O_3



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: $\Delta U = Q + W$

$\Delta \text{energy} = \text{heat} + \text{work}$

Work
 $W = \int_{x_0}^x F dx$

$$F = m \cdot \frac{dv}{dt}$$

$$P = \frac{F}{A}$$

P-V work

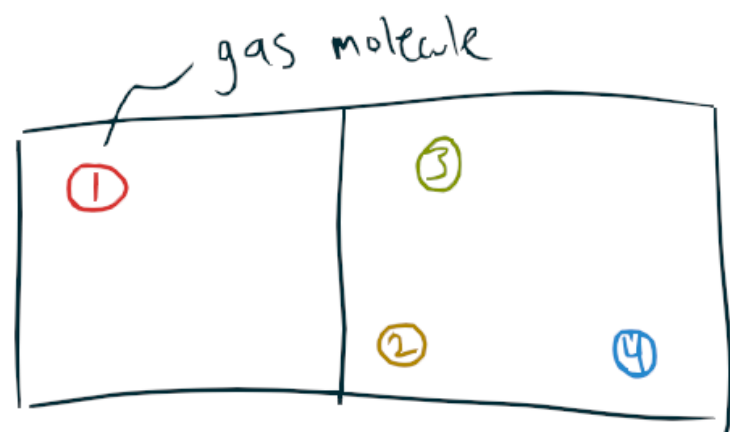
$$W = \int_{z_0}^z \frac{F}{A} A dz = - \int_{V_0}^V P dV$$



$$A = xy$$
$$V = xyz$$

← 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

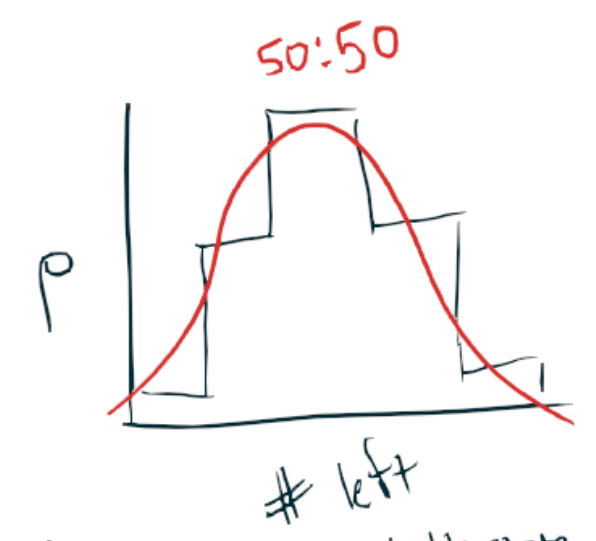
Entropy is minimized when a system is at the most probable state
 ↳ causes change towards max p

2nd law says

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

So

$$\Delta U = TdS - PdV$$



$$dU = TdS - PdV$$

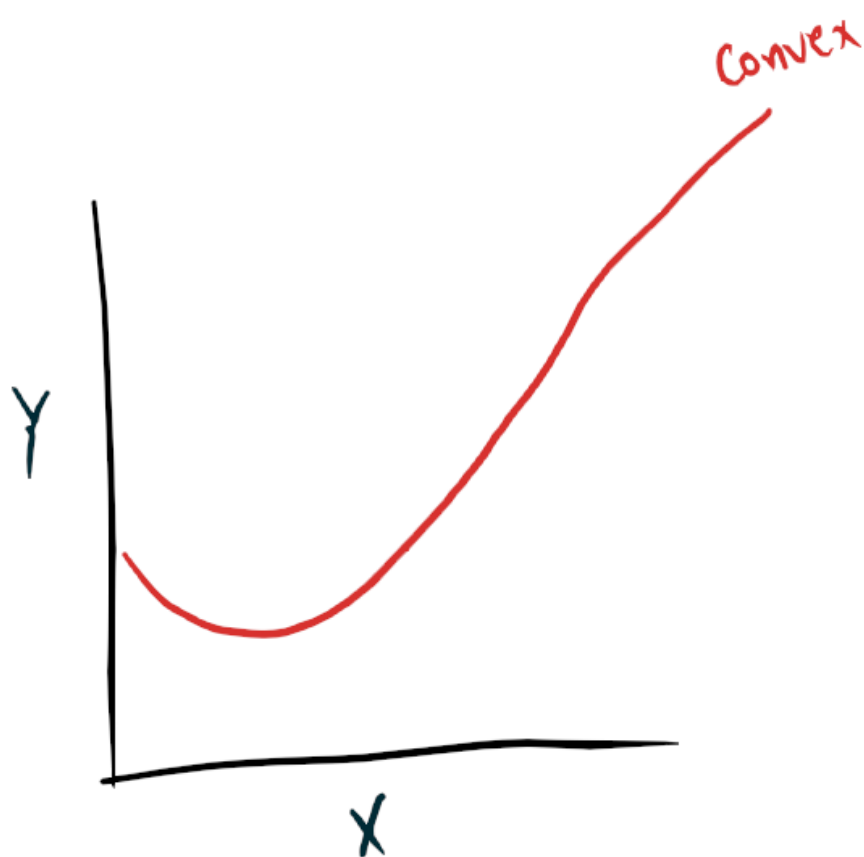
What if our system includes a chemical reaction that changes the amounts of chemical components?

μ_i = chemical potential of species i

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

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 monotonic 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

$$f(x, y)$$

$$g(x, w)$$

$$df = u dx + w dy$$

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

$$g = f - wy$$

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

$$dg = u dx - Y dw$$

w, Y conjugate pair

$$w dy + Y dw$$



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

$$U(S, V, N_i)$$

$$\downarrow \quad \downarrow \quad \downarrow$$

$$G(T, P, N_i)$$

product rule

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

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

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

$$dG = VdP - SdT + \sum \mu_i dN_i \quad \text{what does this line mean in words?}$$

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

$$H = U + PV$$

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



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

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

ideal gas $PV = nRT$

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

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

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

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

$$\int_{P'}^{P} d\mu_i = \int_{P'}^{P} \frac{RT}{P} dP$$

reference state

$$\mu_i^P - \mu_i^{P^0} = RT(\ln P - \ln P^0) = RT \ln \frac{P}{P^0}$$

if P^0 is pure i , then $\frac{P}{P^0}$ is mole fraction

$$\mu_i^P = \mu_i^{P^0} + RT \ln X_i$$

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

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

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

$$\Delta G = \sum v_i (\mu_i^\circ + RT \ln X_i)$$

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

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

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

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

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

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

\nearrow
 Q product quotient

