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?

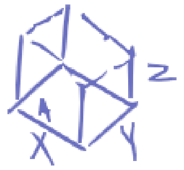
- capacity to produce $\boxed{\text{change}}$

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



$A = xy$

$V = xyz$

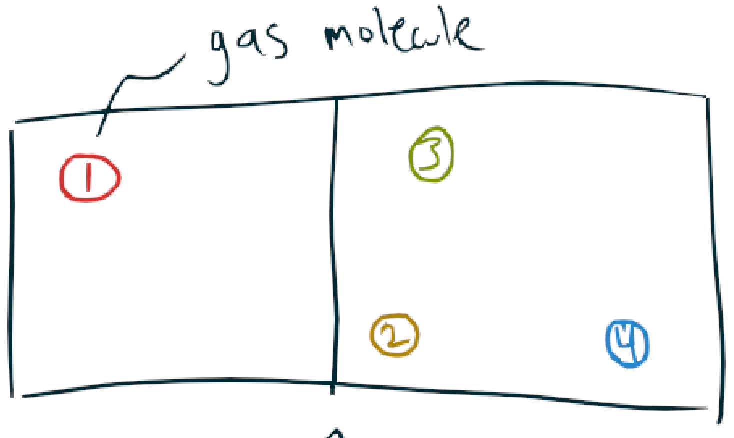
Work $W = \int_{x_0}^{x} F\,dx$ $F = m \cdot \frac{dv}{dt}$ $P = \frac{F}{A}$

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

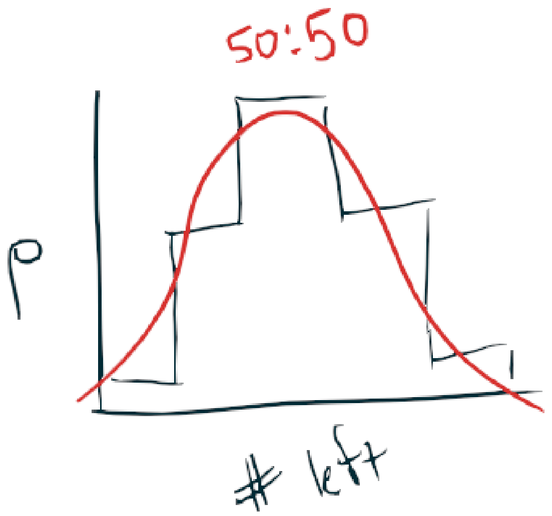
causes change towards max p

2nd law says

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

So

$$\Delta U = TdS - PdV$$



$$dU = TdS - PdV$$

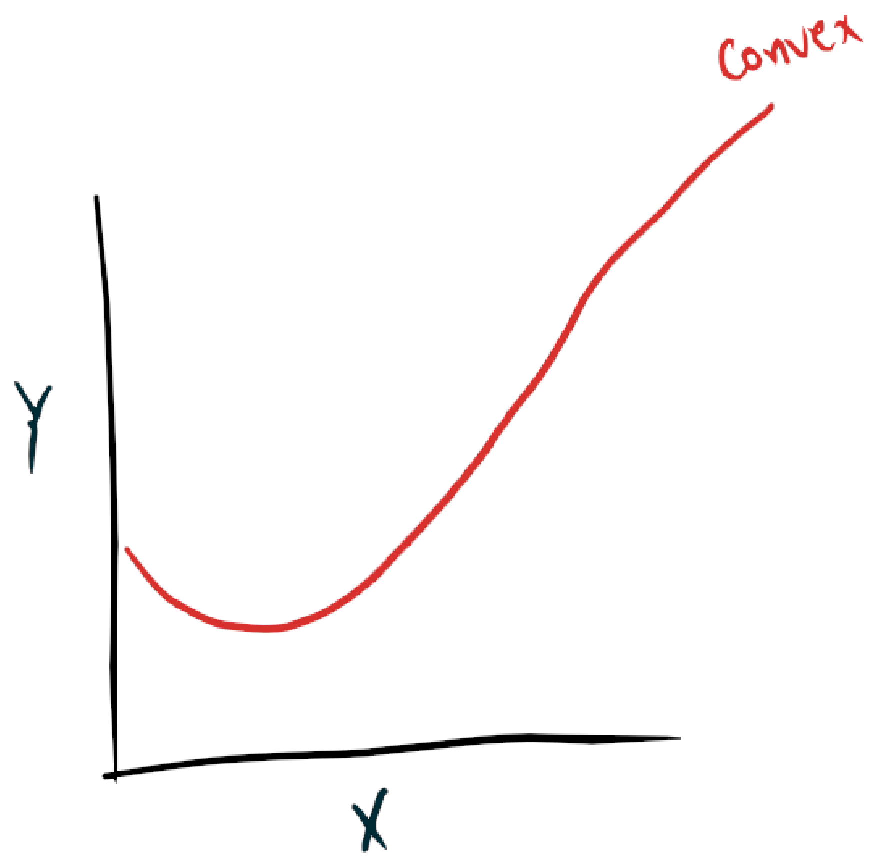
What if our system includes a chemical reaction that changes the amounts of chemical components?

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

$f(x,y)$

$g(x,w)$

W,Y conjugate pair

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

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

$Wdy + Ydw$

$$g = f - wy$$

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

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

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

$$\begin{array}{c} U(S, V, N_i) \\ \downarrow \; \downarrow \; \downarrow \\ G(T, P, N_i) \end{array}$$

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?

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

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

$$dG = V\,dP - S\,dT + \sum \mu_i\, dN_i \qquad \frac{\partial G}{\partial N_i} = \mu_i$$

ideal gas $\quad PV = nRT$

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

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

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

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

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

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 $aA + bB \longleftrightarrow cC + dD$

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

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

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

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

standard states

mole fractions

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

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

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

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

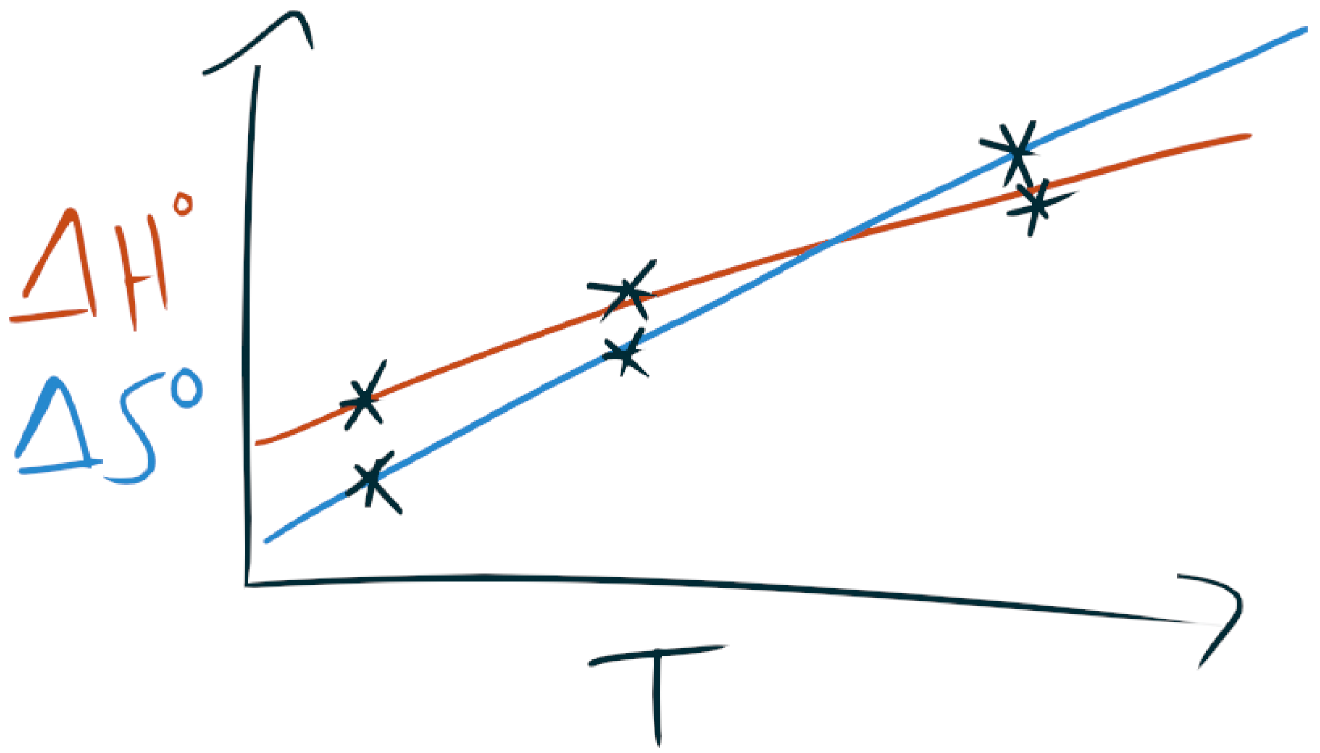
$$\Delta G^\circ = -RT \ln K$$

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



Practice Problem: Condensation of Corundum from the Solar Nebula

Q1: Calculate the temperature that Corundum (Al_2O_3) begins condensing from the solar nebula using the following values (assume no other reactions):

$$2\mathrm{Al} + 3\mathrm{O} \leftrightarrow \mathrm{Al_2O_3}$$

- Solar abundance (atoms) of Al: 8.51 x 10^4
- Solar abundance (atoms) of O: 2.36 x 10^7
- Solar abundance (atoms) of H: 2.6 x 10^{10}
- Pressure in the nebula: 10^{-3} atm
- Gas constant (R): 8.314 J/mol K
- ΔG° (standard free energy of reaction) for condensation of Al_2O_3: -1.23 x 10^6 J/mol

Q2: At what temperature will this reaction finish condensing all of the Aluminum in the nebula?

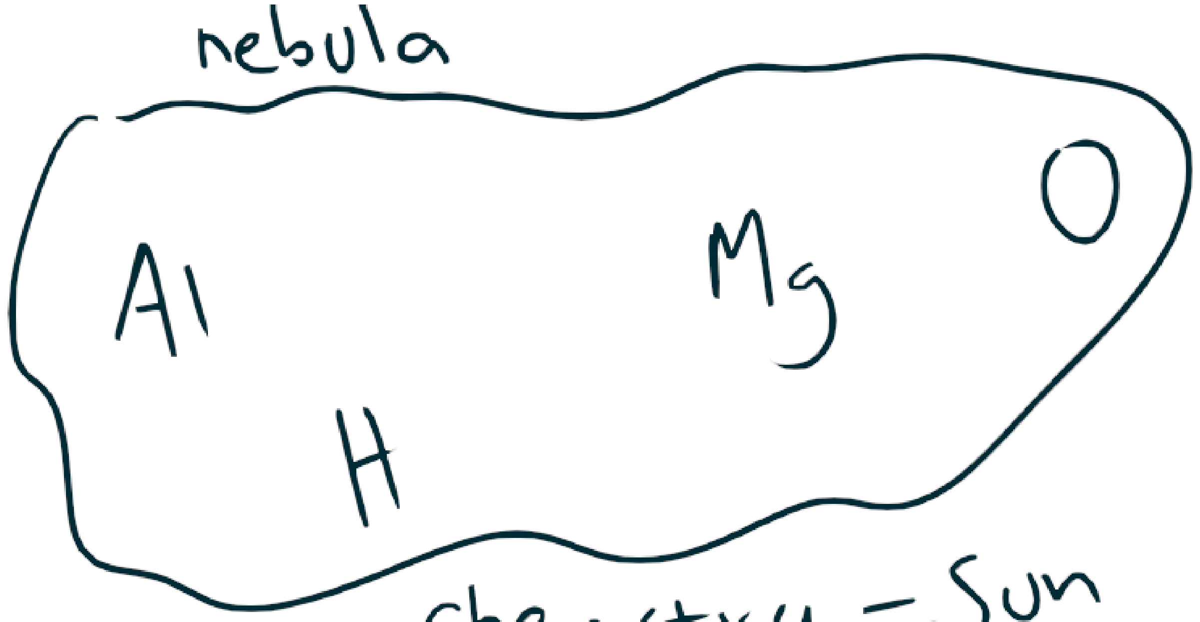
Condensation of corundum (ruby/sapphire)

$$2\,Al_{(g)} + 3\,O_{(g)} \longleftrightarrow Al_2O_{3\,(c)}$$

$$Q = \frac{\{Al_2O_3\}}{\{Al\}^2\{O\}^3} = \frac{1}{P_{Al}^2 \cdot P_O^3}$$

at high T, low P safe to assume ideal gas

$$\{x\} = P_x$$



chemistry = Sun

$P_T = 10^{-3}$ atm

assumption: $P_T = P_{H_2}$

$$\frac{P_x}{P_{H_2}} = \frac{N_x}{N_{H_2}} \qquad N_{H_2} = \frac{1}{2} N_H$$

$$P_{Al} = \frac{N_{Al}}{\frac{1}{2}N_H} \cdot P_{H_2} = \frac{2\,N_{Al}}{N_H} \cdot P_T$$