



# Lecture 3: Equilibrium Conditions

1. Energy
  - A. Entropy
  - B. Transforming energy into other potentials
2. Law of mass action
3. Condensation of  $\text{Al}_2\text{O}_3$



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:  $\Delta U = Q + W$

$\Delta$  energy = heat + work

Work

$$W = \int_{x_0}^x F dx \quad F = m \cdot \frac{dv}{dt}$$

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

P-V work

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

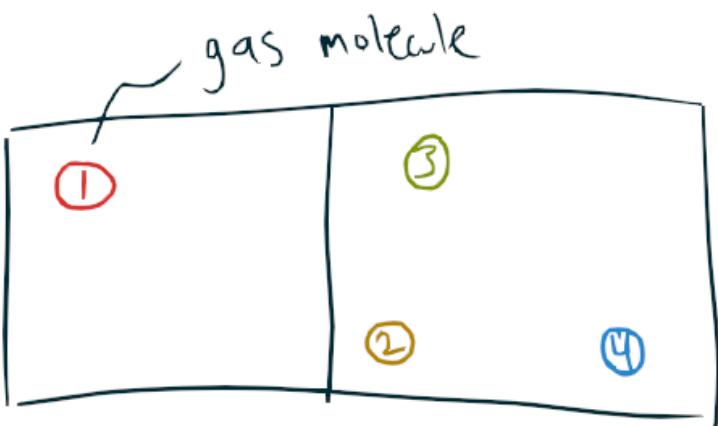


$$A = xy \\ V = xyz$$

← 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

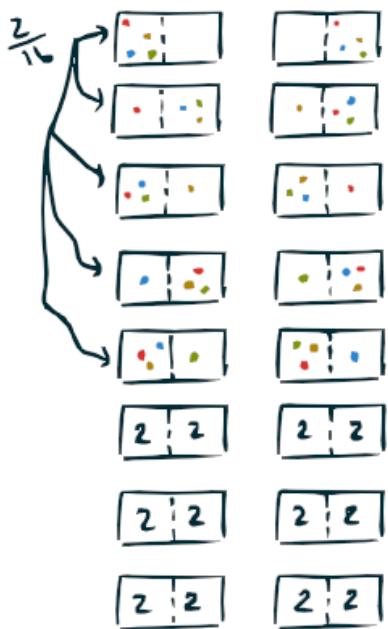




↑  
remove partition

What happens?

What are the possible distributions?



$$2^4 = 16 \text{ options}$$

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

most probable state

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

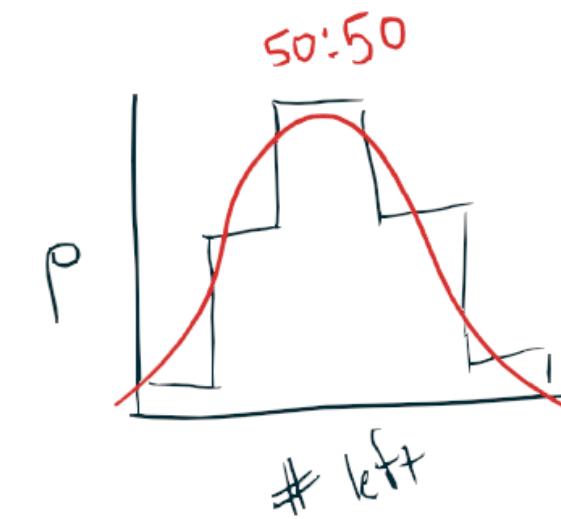
→ causes change towards max p

2nd law says

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

so

$$\Delta U = TdS - PdV$$



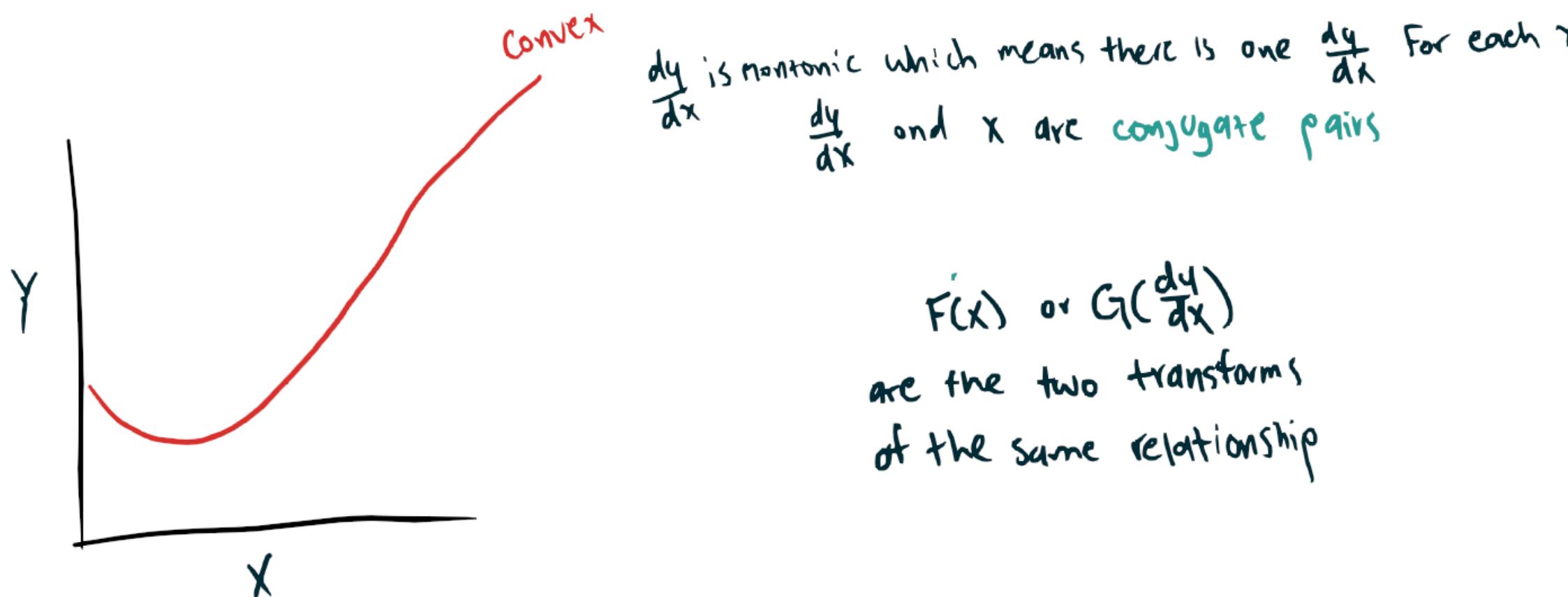
$$dU = TdS - PdV$$

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

$\mu_i$  = 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  $\mu_i, N_i$  are three conjugate pairs  
and we can transform  $U(S, V, N_i) \rightarrow G(T, P, N_i)$



$$\begin{array}{l} f(x,y) \\ \downarrow \\ g(x,w) \end{array}$$

$$df = u dx + w dy$$

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

$$g = f - wy$$

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

$$dg = u dx - Y dw$$

w, y conjugate pair

$$w dy + Y dw$$



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

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

product rule

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

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

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

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

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

what does this line mean in words?

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

$$H = U + PV$$

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



$$dG = VdP - SdT + \sum \mu_i dN_i \quad \frac{\partial G}{\partial N_i} = \mu_i$$

ideal gas  $PV = nRT$

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

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

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

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

$$\int_{P^*}^P \partial \mu_i = \int_{P^*}^P \frac{RT dP}{P}$$

reference state

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

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

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



Let's consider  $aA + bB \rightleftharpoons cC + dD$

$$\Delta G = c\mu_c + d\mu_d - b\mu_B - a\mu_A$$

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

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

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

$\uparrow$  standard states       $\uparrow$  mole fractions

$$\Delta G = c\mu_c^\circ + d\mu_d^\circ - a\mu_A^\circ - b\mu_B^\circ + \sum v_i RT \ln x_i$$

$$\Delta G = \Delta G^\circ + RT (c \ln x_c + d \ln x_d - a \ln x_A - b \ln x_B)$$

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{x_c^c \cdot x_d^d}{x_A^a \cdot x_B^b} \right) \quad O = \Delta G^\circ + RT \ln Q$$

$\overbrace{\hspace{10em}}$   
Q product quotient

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

