

Chemistry 163B
Free Energy
E&R (\approx ch 6)

$$\Delta S \geq \int \frac{\bar{d}q}{T}$$
$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

goal: Define function which allows evaluation of spontaneity in terms of state functions of **SYSTEM** (only)

goals of lecture

- **define Gibbs (G) and Helmholtz (A) free energies**
- **show $\Delta G_{T,P} < 0$ and $\Delta A_{T,V} < 0$ for spontaneity**
- **differentials dG and dA**
- **temperature and pressure dependence of G, A**
- **what's 'free' about free energy**

spontaneity

$$\Delta S_{\text{sys}} \geq \frac{q_{\text{sys}}}{T}$$

$$\Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} \geq 0$$

$$q_{\text{surr}} = -q_{\text{sys}}$$

$$\Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \geq 0$$

motivation for G (spontaneity at const T,P in terms of system)

$$\Delta S_{\text{sys}} + \frac{-q_{\text{sys}}}{T} \geq 0$$

spontaneity at const T,P

$$(q_{\text{sys}})_P = \Delta H_P \quad (\bar{d}w_{\text{other}} = 0)$$

$$\Delta S_{\text{sys}} + \frac{-\Delta H_P}{T} \geq 0$$

$$T\Delta S_{\text{sys}} - \Delta H_P \geq 0$$

$$\Delta H_P - T\Delta S_{\text{sys}} \leq 0$$

define : $G \equiv H - TS$ (general, even if T, P not constant)

but

$$\Delta G_{T,P} = (\Delta H_{T,P})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

spontaneity for constant T, P ($\bar{d}w_{\text{other}} = 0$)

motivation for, A

$$\Delta S_{\text{sys}} + \frac{-q_{\text{sys}}}{T} \geq 0$$

spontaneity at const T,V

$$(q_{\text{sys}})_V = \Delta U_V \quad (d\bar{w}_{\text{other}} = 0)$$

$$\Delta S_{\text{sys}} + \frac{-\Delta U_V}{T} \geq 0$$

$$T\Delta S_{\text{sys}} - \Delta U_V \geq 0$$

$$\Delta U_V - T\Delta S_{\text{sys}} \leq 0$$

define : $A \equiv U - TS$ (general, even if T, V not constant)

but

$$\Delta A_{T,V} = (\Delta U_{T,V})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

spontaneity for constant T,V ($d\bar{w}_{\text{other}} = 0$)

**Definitions: $A \equiv U-TS$
 $G \equiv H-TS$**

Spontaneity (in terms of properties of system):

$$\Delta A_{T,V} \leq 0 \quad (\text{no } w_{\text{other}})$$

$$\Delta G_{T,P} \leq 0 \quad (\text{no } w_{\text{other}})$$

what's 'good for spontaneity'

$$\Delta G_{T,P} = \Delta H - T\Delta S \leq 0$$

spontaneous: $\Delta H < 0$ and $\Delta S > 0 \Rightarrow \Delta G < 0$

$$\Delta H_{\text{sys}} < 0$$

exothermic:

disorders surroundings

$$\Delta S_{\text{sys}} > 0$$

disorders system

what's 'good for spontaneity'; similarly for ΔA at const T, V

$$\Delta A_{T,V} = \Delta U - T \Delta S \leq 0$$

spontaneous: $\Delta U < 0$; $\Delta S > 0 \Rightarrow \Delta A < 0$

$$\Delta U_{\text{sys}} < 0$$

exothermic:

disorders surroundings

$$\Delta S_{\text{sys}} > 0$$

disorders system

$$\Delta G_{T,P} = \Delta H - T\Delta S$$

ΔH	ΔS	Spontaneous ??
— (<i>exothermic</i> : disorders surr)	+ (disorders sys)	yes !!
+ (<i>endothermic</i> : orders surr)	— (orders sys)	no !! <i>(reverse spontaneous)</i>
— (<i>exothermic</i> : disorders surr)	— (orders sys)	maybe !!
+ (<i>endothermic</i> : orders surr)	+ (disorders sys)	maybe !!

$$\Delta G_{T,P}=0$$

$$\Delta G_{T,P} = \Delta H - T \Delta S = 0$$

for reversible, equilibrium process

example: equilibrium phase transition

$$\Delta G_{T,P} = \Delta H_{\phi} - T_{\phi} \Delta S_{\phi} \quad \text{with } \Delta S_{\phi} = \frac{\Delta H_{\phi}}{T_{\phi}}$$
$$= \Delta H_{\phi} - T_{\phi} \left(\frac{\Delta S_{\phi}}{T_{\phi}} \right) = 0$$

[HW6 problem #35, sign of ΔG for T 'around' T_{ϕ}]

differential relationships and Maxwell-Euler

$U \equiv$ internal energy

$H \equiv U + PV$

$A \equiv U - TS$

$G \equiv H - TS$

$$dU = \bar{d}q + \bar{d}w = \bar{d}q - PdV$$

$$dS = \frac{\bar{d}q_{rev}}{T} \quad dq = TdS$$

$$dU = TdS - PdV$$

$$U(S, V)$$

$TdS - PdV$

$$dH = dU + PdV + VdP$$

$$dH = TdS + VdP$$

$$H(S, P)$$

$TdS - PdV$

$$dA = dU - TdS - SdT$$

$$dA = -SdT - PdV$$

$$A(T, V)$$

$TdS + VdP$

$$dG = dH - TdS - SdT$$

$$dG = -SdT + VdP$$

$$G(T, P)$$

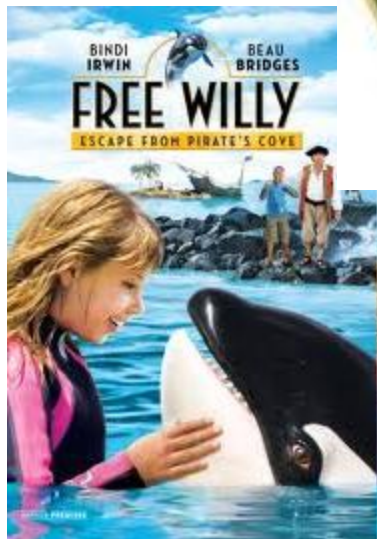
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

G, A what's "FREE" about free energy ?



why “free” energy (E&R eqn 6.9)

$$\Delta S_{\text{sys}} + \frac{-q_{\text{sys}}}{T} \geq 0$$

spontaneity at const T,P

$$(q_{\text{sys}})_P = \Delta H_P \quad (\bar{d}w_{\text{other}} = 0)$$

$$(q_{\text{sys}})_P + \bar{d}w_{\text{other}} = \Delta H_P \quad (\bar{d}w_{\text{other}} \neq 0)$$

$$\Delta S_{\text{sys}} + \frac{-(\Delta H_P - \bar{d}w_{\text{other}})}{T} \geq 0$$

$$T \Delta S_{\text{sys}} - \Delta H_P + \bar{d}w_{\text{other}} \geq 0$$

$$\Delta H_P - T \Delta S_{\text{sys}} - \bar{d}w_{\text{other}} \leq 0$$

$$\Delta G_{T,P} - \bar{d}w_{\text{other}} \leq 0 \quad (\text{eqn 6.9 E\&R})$$

why “free” energy (E&R eqn 6.9)

$$\Delta G_{T,P} - \bar{d}w_{other} \leq 0 \quad (\text{eqn 6.9 E\&R})$$

$$\Delta G_{T,P} \leq \bar{d}w_{other}$$

Thus if $\Delta G_{\text{reaction}} < 0$ (spontaneous), the maximum w_{other} done ON surroundings is $-\Delta G_{\text{reaction}}$

$$-\Delta G_{T,P} \geq -(\bar{d}w_{other})_{\text{system}} = (\bar{d}w_{other})_{\text{surroundings}}$$

For example w_{other} might be the free energy of a reaction converted to electrical work in an electrochemical cell or a neuron.

ΔG : energy **FREE** to do work, other than expansion work

motivation for G, A

$$G \equiv H - TS$$

$$A \equiv U - TS$$

$$\Delta G_{T,P} = \left(\Delta H_{T,P} \right)_{\text{sys}} - T \Delta S_{\text{sys}} \leq 0$$

spontaneity for constant T, P ($\vec{d}_{\text{wother}} = 0$)

$$\Delta A_{T,V} = \left(\Delta U_{T,V} \right)_{\text{sys}} - T \Delta S_{\text{sys}} \leq 0$$

spontaneity for constant T, V ($\vec{d}_{\text{wother}} = 0$)

$$\Delta G_{T,P} \leq w_{\text{other}}$$

$$\Delta A_{T,V} \leq w_{\text{other}}$$

temperature and pressure dependence of G, A (no w_{other})

G: T dependence at constant P

$$\left(\frac{\partial G}{\partial T}\right)_P \quad dG = -SdT + VdP \quad \Rightarrow \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

G: P dependence at constant T

$$\left(\frac{\partial G}{\partial P}\right)_T \quad dG = -SdT + VdP \quad \Rightarrow \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

$$dA = -SdT - PdV \quad \Rightarrow \quad \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

and $\Delta G_{\text{reaction}}$ for chemical reaction (HW 7)

$$\Delta G_{\text{reaction}} = \sum_i \nu_i \bar{G}_i \quad [\text{molar free energy of formation, in a moment and Appendix A}]$$

$$\left(\frac{\partial \bar{G}}{\partial T} \right)_P = -\bar{S}$$

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

$$\left(\frac{\partial \Delta G_{\text{reaction}}}{\partial T} \right)_P = -\Delta S_{\text{reaction}}$$

$$\left(\frac{\partial \Delta G_{\text{reaction}}}{\partial P} \right)_T = \Delta V_{\text{reaction}}$$

$$\Delta S_{\text{reaction}} = \sum_i \nu_i \bar{S}_i$$

$$\Delta V_{\text{reaction}} = \sum_i \nu_i \bar{V}_i$$

$$\left(\frac{\partial \Delta G_{\text{reaction}}}{\partial T} \right)_P = \sum_i \nu_i \left(\frac{\partial \bar{G}_i}{\partial T} \right)_P = \sum_i \nu_i (-\bar{S}_i) = -\Delta \bar{S}_{\text{reaction}} \quad \text{'proof'}$$

$\Delta G_{\text{reaction}}$ and equilibrium (first pass)

here $\Delta G \equiv \Delta G_{\text{reaction}}$

1. $\Delta G < 0$ spontaneous (*'natural', irreversible*)
 $\Delta G = 0$ equilibrium (*reversible*)
 $\Delta G > 0$ spontaneous in reverse direction
2. $\Delta G_T = \Delta H - T\Delta S$
3. ΔG^0 all reactants and products in standard states
4. $\Delta \bar{G}_f^0 \equiv \bar{G}_f^0$ Appendix A at 298.15K (*reaction where reactants are elements in their most stable form and in their standard states, P=1 atm, [conc]=1M, etc*)
 $\Delta \bar{G}_f^0(O_2(g)) \equiv 0$ $\Delta \bar{G}_f^0(C(gr)) = 0$

5.

$$\Delta G_{\text{reaction}}^0 = \sum_i \nu_i \Delta \bar{H}_f^0 - T \sum_i \nu_i \bar{S}_i^0$$
$$\Delta G_{\text{reaction}}^0 = \Delta H_{\text{reaction}}^0 - T \Delta S_{\text{reaction}}^0$$

NOTE : in Appendix A: $\Delta \bar{G}_f^0$ and $\Delta \bar{H}_f^0$ in **kJ mol⁻¹** BUT \bar{S}^0 in **J K⁻¹ mol⁻¹**

End of Lecture

spontaneity (argument II)

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

$$q_{sys} = -q_{surr}$$

statement: the surroundings are so 'massive' that any transfer of heat from system appears reversible to surroundings

thus: $(q_{surr})_{rev} = -q_{sys}$ $\Delta S_{surr} = \frac{(q_{surr})_{rev}}{T} = -\frac{q_{sys}}{T}$

and thus: $\Delta S_{sys} + \frac{-q_{sys}}{T} \geq 0$