

Reminder:

Get final forms from students going to the field trip

Final instructions: be there by 2:05 pm. Meet me at the lobby. Be prepared to answer questions after.

Last time:

- 1) Intro to thermodynamics
- 2) Reactant & product favored reactions
- 3) Chemical reactions and processes  
and dispersal of energy
- 4) Entropy

Today:

- 1) entropy calculations
- 2) Gibb's Free energy
- 3)  $\Delta G$  and  $work_{max}$

Lecture:

(1) Calculation of  $\Delta S$ :

For  $\Delta S_{env}$  it is convenient to use:

$$\Delta S = S_f - S_i = Q_{rev}/T$$

$Q_{rev}$  = heat transferred to environment

if  $\Delta S = 0$  for a rxn, it is "reversible"

if  $\Delta S_{universe} > 0$  it is irreversible (spontaneous)

(2) Another view of entropy (system's point of view):

Every substance has an absolute entropy that can be measured or calculated. These are shown in tables as  $S_f^\circ$  (not  $\Delta S^\circ$ )

$S_f^\circ$  = absolute entropy of formation of standard state of the substance.

$$\Delta S_{system}^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

eg.  $3A + 5B \rightarrow 2C + D$

What is  $\Delta S_{sys}$  for this reaction?

$$\Delta S^\circ = 2S^\circ(C) + S^\circ(D) - \{3S^\circ(A) + 5S^\circ(B)\}$$

(3) Second Law of Thermo:

process lead to increase in  $\Delta S$  universe

reversible process:  $\Delta S_{univ} = 0$

irreversible process:  $\Delta S_{\text{univ}} < 0$

3) Consider the following derivation for a product-favored reaction:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{env}} > 0 \\ &= \Delta S_{\text{sys}} + \Delta Q_{\text{env}}/T > 0\end{aligned}$$

also:  $\Delta Q_{\text{env}}/T = -\Delta Q_{\text{sys}}/T$  (by cons.of E.)

@ constant P:  $\Delta Q_{\text{sys}}/T = \Delta H_{\text{sys}}/T$

so:  $\Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T > 0$

or, multiplying by T:

$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

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

(everything is related to "system"!)

therefore, it becomes convenient to define a new function, related only to the system:

Gibb's Free energy, G. A state function like enthalpy, entropy and energy.

Any system has a value of G.

Define:  $G = H - TS$ :

$$\Delta G = \Delta H - T\Delta S - S\Delta T$$

at const T,  $\Delta T = 0$  and  $\Delta G = \Delta H - T\Delta S$

For a spontaneous process:

$$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = \Delta G_{\text{sys}} \leq 0$$

For a reaction to be product-favored,  
 $\Delta G < 0$

i.e. if we can find the  $\Delta G$  of process, we can determine if it is spont or not!

Criterion for spontaneity or equil is  $\Delta G \leq 0$

If  $\Delta G = G_{\text{final}} - G_{\text{initial}}$

If  $\Delta G < 0$ : spontaneous, product-favored

If  $\Delta G = 0$ : at equil,

if  $\Delta G > 0$ : nonspontaneous, reactant-favored

compare  $\Delta G$ ,  $\Delta H$  and  $\Delta S$

$$\Delta G = \Delta H - T\Delta S$$

scenario	$\Delta H$	$\Delta S$	$\Delta G$	Spont?
1	+	+	+/-	@hi T
2	+	-	+	never
3	-	+	-	always
4	-	-	-/+	@low T

Concept of G:

free energy graph:

G vs course rxn

Significance of G:

G = max work that can be done by the system.

Actual work will be less than that.

$$\Delta G^\circ = \sum nG^\circ(\text{prods}) - \sum mG^\circ(\text{rxts})$$

Relationship of  $\Delta G$  and  $\Delta G^\circ$ :

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