Outline notes for Lecture 6a (maybe 6b)

Summary:
The goals of this week/lecture 6a:
-understand relationship between $\Delta S_{universe}$, spontaneity, and ΔG
-understand relationship between ΔG and ΔH, T and ΔS for the system
-know how to do calculations in all its gory details!
- understand *graphically* how ΔG, ΔH and ΔS are related to temperature.
- be able to predict at what temperatures a reaction will be spontaneous, reversible, non spontaneous.

0) Last time: talked about entropy, S. Comparison of the entropy of different systems.

for a reaction: $\Delta S = S_{final} - S_{initial} = \dfrac{q_{reversible}}{T}$

ΔS° for a reaction can be calculated from thermodynamic tables:

$$\Delta S° = \sum n(\Delta S°(prod)) - \sum m(\Delta S°(rxt))$$

(note that this is the same as $\Delta S°_{sys}$ below)

1) 2nd Law of Thermodynamics: For a reaction or process to be spontaneous:

$\Delta S_{universe} > 0$.

$\Delta S_{universe} = \Delta S_{system=} + \Delta S_{surroundings}$

2) Basic calculations:

$$\Delta S_{system} = S_{products} - S_{reactants} = \sum n(\Delta S°(prod)) - \sum m(\Delta S°(rxt))$$

(expressing it in terms of the system is more convenient)

$$\Delta S_{surroundings} = \frac{q_{reversible}}{T} = +\frac{\Delta H_{surroundings}}{T} = -\frac{\Delta H_{system}}{T}$$

so that:

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

For a spontaneous reaction:

$\Delta S_{sys} - \dfrac{\Delta H_{system}}{T} > 0$ or, $\dfrac{\Delta H_{system}}{T} - \Delta S_{sys} < 0$ or, $\Delta H_{sys} - T\Delta S_{sys} < 0$

I.e. the quantity: ($\Delta H_{sys} - T\Delta S_{sys}$) must be negative for spontaneous reaction.

If it is = 0 , then it's "reversible" , i.e. it is at "equilibrium".

OK? So we don't have to keep calculating ΔH and ΔS, we lump them together as "ΔG"

G= Gibb's function, or Gibb's Free energy (free to do what? To do useful work – but not including pV work).

Definition of G: $G = H - TS$ where all these are "state functions".

So $\Delta G = \Delta H - T\Delta S - S\,\Delta T$ but at constant T (isothermal, or $\Delta T=0$) , it becomes:

$\Delta G = \Delta H - T\Delta S$ (recognize the similarity to what we just derived?: $\Delta H_{sys} - T\Delta S_{sys} < 0$)

It's a very very important and useful thermodynamic function!
Let's summarize so far:

If $\Delta G < 0$ for a reaction (i.e. negative) then reaction is spontaneous.

It's the same as saying $\Delta S_{universe} > 0$ except that ΔG is much easier to think about than $\Delta S_{universe}$ since ΔG is just ΔG of the system.

Sample problem:

Consider the reduction of rust into pure iron using coke (carbon). Assume standard conditions of temperature (298.15 K) and pressure (1 bar). A table for formation of these substances is given below:

$3\,C(s) + 2\,Fe_2O_3(s) <==> 4\,Fe(s) + 3\,CO_2(g)$

Substance	$\Delta H°_f$ kJ/mol	S° J/mol K	$\Delta G°_f$ kJ/mol
C(s, graphite)	0	5.74	0
$Fe_2O_3(s)$	-824	87.4	-742
Fe(s)	0	27.8	0
$CO_2(g)$	-393.5	214	-394.4

a) What is the change of entropy for the universe for this reaction at standard conditions?

$$\Delta S_{univ} = \Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

$$\Delta S_{system} = S_{products} - S_{reactants} = \sum n(\Delta S°(prod)) - \sum m(\Delta S°(rxt)) \quad \text{(where n, m =mol coeffs)}$$

$$\Delta S°_{sys} = 4(27.8) + 3(214) - 3(5.74) - 2(87.4) = 753.2 - 192 = 561 \text{ kJ/mol}$$

$$\Delta S^\circ_{surroundings} = -\frac{\Delta H_{system}}{T} = -\frac{467.5 \times 10^{3}\ \text{J mol}^{-1}}{298.15\text{K}} = -1568\ \text{Jmol}^{-1}\text{K}^{-1}$$

where: ΔH°_{sys} 4(0)+3(-393.5) -3(0)-2(-824) = 467.5 kJ/mol and T = 298.15K

b) Is the reaction spontaneous at standard conditions? Prove it in different ways.
NO it is NOT spontaneous because $\Delta S_{univ} = -1568\ \text{Jmol}^{-1}\text{K}^{-1} < 0$

Or, we can solve for ΔG° to see if it is negative:
You can solve ΔG° from the tables in the same way that you can solve ΔH° and ΔS° from the tables: (note that $\Delta G^\circ_f = 0$ for elements in their usual elemental form)

$$\Delta G^\circ = = \sum n(\Delta G_f^\circ(\text{prod})) - \sum m(\Delta G_f^\circ(\text{rxt})) = 3(-394.4) - 2(-742.2) = +301\ \text{kJ/mol}$$

Or, if you don't have direct ΔG°_f from a table, you can still solve for it using: ΔH°_f and S° from the table:

ΔH°_{rxn} = 4(0)+3(-393.5) -3(0)-2(-824) = 467.5 kJ/mol
ΔS°_{rxn} = 4(27.8) +3(214) – 3(5.74) -2(87.4) = 753.2-192=561 kJ/mol

ΔG° = 4(0) + 3(-394.4) – 3(0) -2(-742.2) = +301 kJ/mol

OK?
NOW LOOK AT THE GRAPHICAL REPRESENTATIONS of $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$
Last time we said:

Scenario	ΔH°	ΔS°	ΔG <0	Spontaneous?
1	-	+	Yes	Yes
2	+	+	Only @ high T	Only @ high T
3	-	-	Only @ low T	Only @ low T
4	+	-	No	No

Look again at the equation:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

Assuming that ΔH° and ΔS° are "constants of temperature". i.e not affected very much by temperature, we predict the sign of ΔG° at various T values (here ΔG° is not limited to 298 K).

We can use a straight line approximation of this relationship.

$$y = b + mx$$

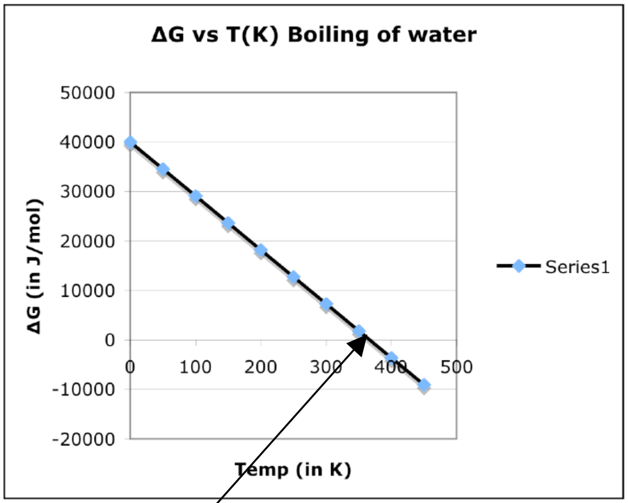
(note: y = ΔG°, x = T; m = -ΔS°, and b (y-intercept) is ΔH°.)

Consider the boiling of *water*:
$\Delta H° = ?$
get enthalpy of vaporization: $\Delta H_{vap} = 2260$ J/g H_2O
we want *molar* enthalpy of vaporization:
$\Delta H_{vap} = 4.07\text{x}10^4$ J/mol

what is the enthalpy of vaporization at the boiling point of water?

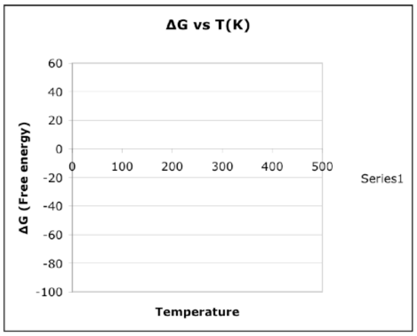
$$\Delta S° = \frac{q_{reversible}}{T} = \frac{4.07\text{x}10^4 \text{ J/mol}}{373 \text{ K}} = 109 \text{ Jmol}^{-1}\text{K}^{-1}$$

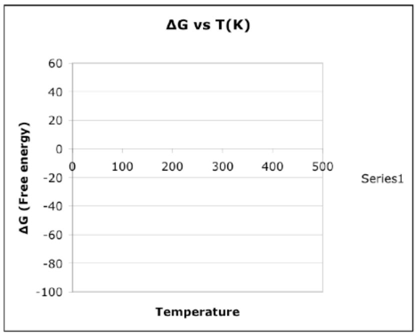
what is the $\Delta G°$ vs T graph for the boiling of water?



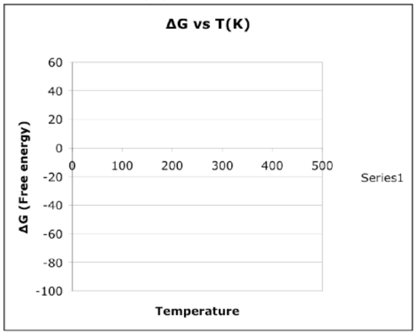
What is this value of temperature and what does it represent?

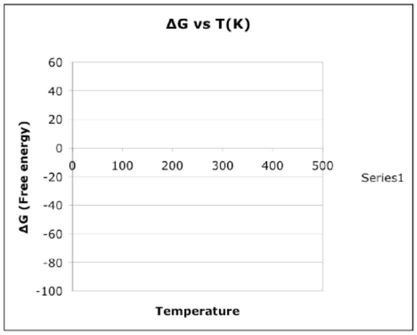
Four graphical representations: here, Y-intercept is $\Delta H°$, X-axis is T . X-intercept is the T at which the reaction is reversible. The straight line represents $\Delta G°$…





scenario (1) scenario (2)





scenario (3) scenario (4)

Which graph would you use to describe:

a) the example in the previous page? Compare it to the scenarios to help you decide.
b) the melting of ice at 2°C
c) the freezing of water at -4°C
d) the burning (oxidation) of glucose molecules (such as in paper) to form CO_2 and H_2O
e) the synthesis of glucose ($C_6H_{12}O_6$) from CO_2 and H_2O.

Other questions to provoke your young inquisitive and brilliant minds:

a) why is photosynthesis spontaneous?
b) why do we *spontaneously* grow to be more complex than the original egg cell we came from?
c) why do oil and water spontaneously separate into two when we mix them to form a water-oil suspension?