

Last time:

- 1) entropy calculations
- 2) Gibb's Free energy

Today: Field Trip – READ CHAPT 15.11

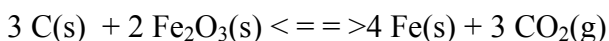
before coming to field trip. Be prepared to ask questions and take notes. No questions, no notes, (almost) no extra credit.

- 1) meaning of G (graphical)
- 2) ΔG° and K_{eq}
- 3) ΔG and $work_{max}$

Lecture:

(1) 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:



Substance	ΔH°_f kJ/mol	S° J/mol K	ΔG°_f kJ/mol
C(s, graphite)	0	5.74	0
Fe ₂ O 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?

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

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

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

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

$$\text{where: } \Delta H^\circ_{sys} = 4(0) + 3(-393.5) - 3(0) - 2(-824) = 467.5 \text{ kJ/mol} \quad \text{and } T = 298.15 \text{ K}$$

b) Is the reaction spontaneous at standard conditions? Prove it in different ways.

NO it is NOT spontaneous because $\Delta S_{\text{univ}} = -1568 \text{ Jmol}^{-1}\text{K}^{-1} < 0$

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:

$$\Delta H^\circ_{\text{rxn}} = 4(0) + 3(-393.5) - 3(0) - 2(-824) = 467.5 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = 4(27.8) + 3(214) - 3(5.74) - 2(87.4) = 753.2 - 192 = 561 \text{ J/mol}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (467.5 \text{ kJ/mol}) - (298\text{K})(561\text{J/mol}) = 301 \text{ kJ/mol}$$

(2)

NOW LOOK AT THE GRAPHICAL REPRESENTATIONS of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Last time we said:

Scenario	ΔH°	ΔS°	$\Delta G < 0$	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).

ΔG°



We can use a straight line approximation of this relationship.

$$y = b + mx$$

(note: $y = \Delta G^\circ$, $x = T$; $m = -\Delta S^\circ$, and b (y-intercept) is ΔH° .)

Consider the boiling of *water*:

$$\Delta H^\circ = ?$$

get enthalpy of vaporization: $\Delta H_{\text{vap}} = 2260 \text{ J/g H}_2\text{O}$

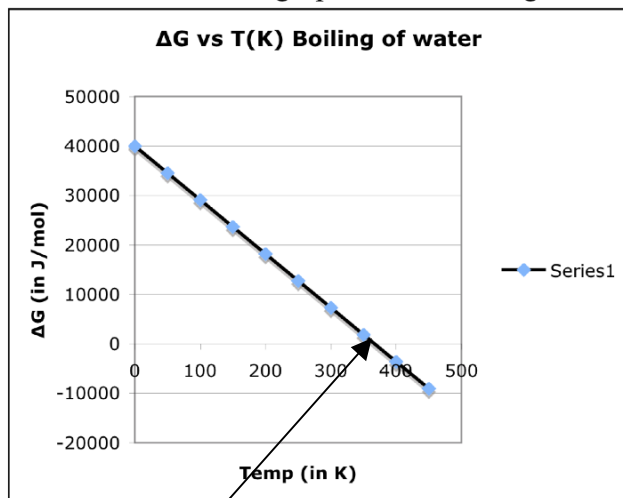
we want *molar* enthalpy of vaporization:

$$\Delta H_{\text{vap}} = 4.07 \times 10^4 \text{ J/mol}$$

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

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

what is the ΔG° 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 ΔH° , X-axis is T. X-intercept is the T at which the reaction is reversible. The straight line represents ΔG° ...

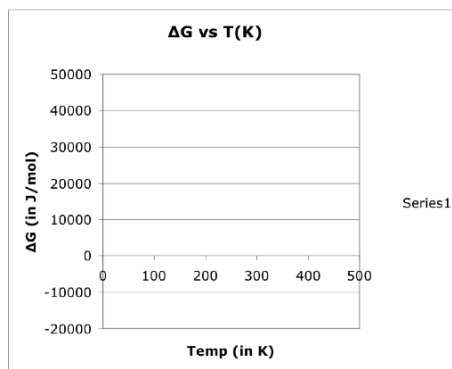
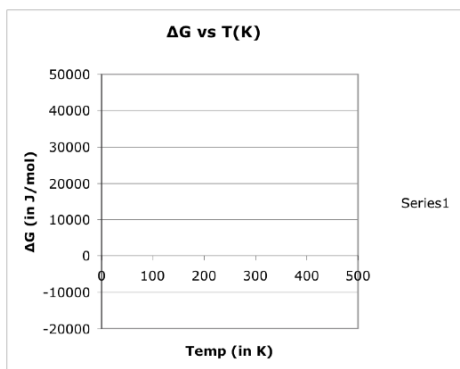
What graphs would represent the following scenarios?

- the example in the previous page? Compare it to the scenarios to help you decide.
- the melting of ice at 2°C
- the freezing of water at -4°C
- the burning (oxidation) of glucose molecules (such as in paper) to form CO_2 and H_2O
- the synthesis of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) from CO_2 and H_2O .

1) graphing ΔG° vs T: (remember: $\Delta G = \Delta H^\circ - T\Delta S$)

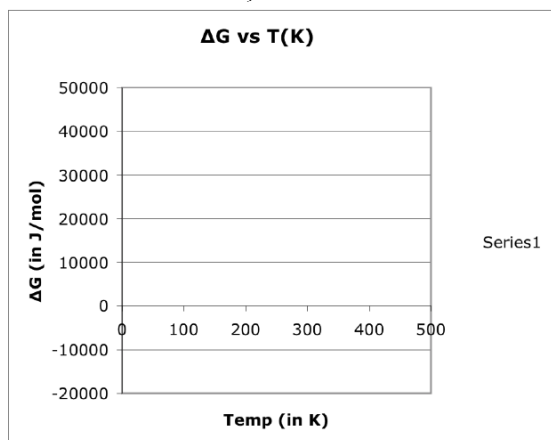
scenario #1 $\Delta H^\circ +$, $\Delta S^\circ -$

scenario #2 $\Delta H^\circ +$, $\Delta S^\circ +$

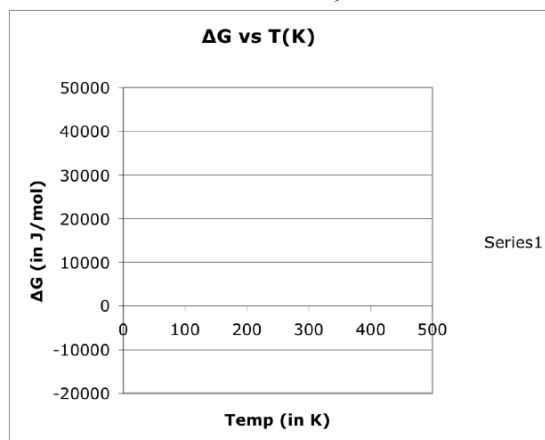


Remember: $\Delta G = \Delta H^\circ - T\Delta S$

scenario #3 $\Delta H^\circ -$, $\Delta S^\circ -$



scenario #4 $\Delta H^\circ -$, $\Delta S^\circ +$



(2) Note that ΔG° is related to the equilibrium constant, K_{eq} by:

$$\Delta G^\circ = -RT \ln K_{eq} \quad \text{where } R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}, T \text{ in Kelvins.}$$

This can be written as: $K_{eq} = e^{\frac{-\Delta G^\circ}{RT}}$. Thus if we know ΔG° for a reaction, we can solve for its K_{eq} and vice-versa.

(3) ΔG° refers to a reaction occurring under standard conditions. This means that all reactants and products are at 1 standard unit of activity. for example: solids = 1, liquids = 1, solutions = molarity, gases = molarity (or partial pressure if so indicated).

The temperature is 298.15 K (or 298 K for short).

For nonstandard conditions, the activities of reactants and products are not usually =1. The corresponding free energy change is ΔG (not ΔG°).

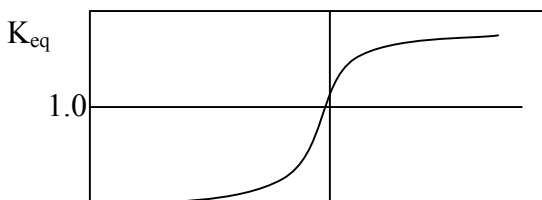
The relationship between ΔG and ΔG° is: $\Delta G = \Delta G^\circ + RT \ln Q$ where $R = 8.314 \text{ J/mol K}$

T = in kelvins, Q = reaction quotient.

Question: a) what is ΔG if $Q = 1$? Does that make sense?

b) What is Q when $\Delta G = 0$? Does that make sense?

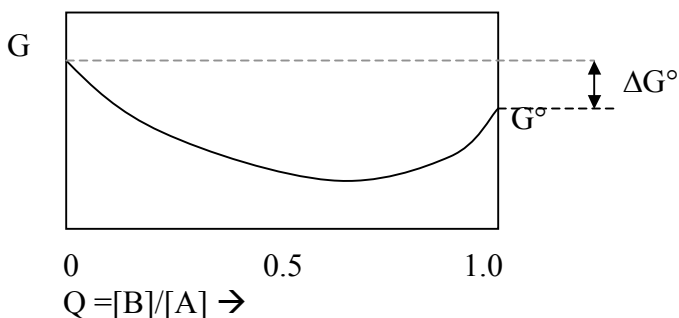
c) Below is a hypothetical graph of $K = [B]/[A]$ for a reaction $A \rightleftharpoons B$. Choose point in the graph and describe whether it is product favored, etc and what ΔG , ΔG° are.



Temperature, K \rightarrow

(4) What is the graphical representation of G vs reaction progress?

(understand figure 18.9) . Say it's for $A \rightleftharpoons B$



(5) Consider: $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$; given that:

	ΔH_f° (kJ/mol)	S° (J/K mol)
$\text{NO}_2(\text{g})$	33.2	240.
$\text{N}_2\text{O}_4(\text{g})$	9.2	304

Questions (answers):

a) What is ΔG° for the reaction? Is it spontaneous? ($\Delta G^\circ = -4750 \text{ J/mol}$, yes spont.)

b) At what temperature does it change its spontaneity? $T = 325 \text{ K} = 52^\circ\text{C}$

(spontaneous at $T \leq 52^\circ\text{C}$; draw a graph of ΔG vs T to show this).

c) What's its K_{eq} ? (answer: $K_{\text{eq}} = 6.8$)

(6) In biology, we often see reactions which are nonspontaneous take place: for example synthesis of complex protein molecules. How can it happen???

One very important consideration is the presence of coupled reactions.

Consider: (i) $A \rightarrow B$

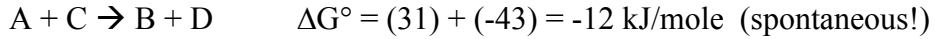
$\Delta G^\circ = +31. \text{ kJ/mole}$

This reaction would not take place by itself. But suppose there is another reaction which is spontaneous:



In biology, the presence of enzymes (highly efficient, highly specific biological catalysts) can *couple* these 2 reactions and force them to take place together:

The net reaction : (i) + (ii) :

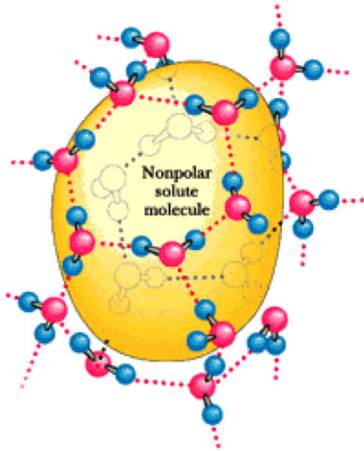


Thus we can say that the reaction (ii) *drives* the reaction (i).

In Biology, ATP is like the molecule "C" in our example.

Other questions to provoke your young inquisitive and brilliant minds:

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



Monday: ΔG° vs ΔG ; ΔG° and work; ΔG° and coupled reactions; and stability.

Also: Redox reactions; oxidation numbers; balancing redox reactions.

Goal is to understand:

(0) relationship of ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (\text{this is used for variations of } Q \text{ usually})$$

The G vs reaction progress is analogous to a crater.

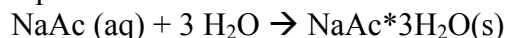


ΔG represents the slope of any position in the crater. If it's product favored at a certain Q value, then $\Delta G < 0$. If it's reactant-favored, then it's $\Delta G > 0$. At the very bottom of the crater, it's : $\Delta G = 0$, here $Q = K_{\text{equilibrium}}$. It's the most stable position. On the other hand, ΔG° represents a position in which $Q = 1$ (when does that happen? Think about it). Usually that would be somewhere on the side of the crater. Usually $\Delta G^\circ \neq 0$ for a reaction. It's some fixed point in the crater.

Example : to test your understanding!

Question: (This is like the classroom demonstration)

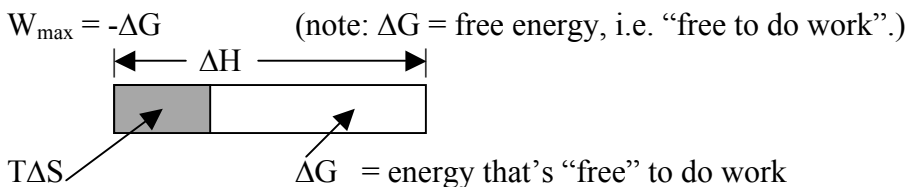
Consider the crystallization of sodium acetate trihydrate crystals ($\text{NaAc} \cdot 3\text{H}_2\text{O}$) from a supersaturated solution of sodium acetate. It's "melting point" is at 54°C .



What are the signs of ΔG and ΔG° for the cases below:

- (a) A supersaturated solution of NaAc at 25°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$
 (b) An unsaturated solution of NaAc at 70°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$
 (c) A saturated solution of NaAc at 54°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$
 (d) Solid crystals of $\text{NaAc} \cdot 3\text{H}_2\text{O}$ at 25°C $\Delta G = \underline{\hspace{2cm}}$, $\Delta G^\circ = \underline{\hspace{2cm}}$,

(1) relationship of ΔG to maximum work, W_{max} , a reaction can do:



Example: How much energy would be available to do work for a reaction at standard conditions? Given: $\Delta H^\circ = -33 \text{ kJ/mol}$ and $\Delta S^\circ = -46 \text{ J/molK}$

(2) A reaction which is not product favored can be made so when coupled with product-favored reactions which have enough ΔG available to drive the former reaction.

The basic idea is that if a reaction $A \rightarrow B$ is not product favored ($\Delta G > 0$, *endergonic*) then it can be coupled to $C \rightarrow D$ which is product favored (i.e. $\Delta G < 0$, *exergonic*), so that the overall reaction is product favored. We can say that the exergonic reaction *drives* the endergonic reaction.

It's like a water wheel utilizing the exergonic process of water flowing downhill to drive endergonic process of grinding grain in a mill.



Example, suppose that $\Delta G^\circ = +23 \text{ kJ/mol}$ for (i) $A \rightarrow B$ and that $\Delta G^\circ = -33 \text{ kJ/mol}$ for (ii) $C \rightarrow D$. By what factor has the coupling of the two (i.e. (i) + (ii)) increased the

equilibrium ratio, $\frac{[B]}{[A]}$, when compared to just the one (i))?(assume that the concentration of $[C] = [D]$).

Solution: (i) $A \rightarrow B$ $\Delta G^\circ = 23\text{kJ/mol}$

$$\Rightarrow K_{(i)} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{-23,000\text{J/mol}}{(8.314\text{J/molK})(298\text{K})}\right) = e^{-9.28} = 9.33 \times 10^{-5} = \frac{[B]}{[A]}$$

Whereas for the coupled case:

(i) + (ii): $A + C \rightleftharpoons B + D$ $\Delta G^\circ = +23 - 33 = -10. \text{kJ/mol}$

$$K_{(i)+(ii)} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{10,000\text{J/mol}}{(8.314\text{J/molK})(298\text{K})}\right) = e^{+4.04} = 56.8 = \frac{[B][D]}{[A][C]} = \frac{[B]}{[A]}$$

The ratio of $\frac{[B]}{[A]}$ has increased by a factor of: $\frac{56.8}{9.33 \times 10^{-5}} = 6.1 \times 10^5$!

This is a huge increase due to the help of the second reaction. Now we see that it is very product favored! (Biological systems, i.e. living cells, use this all the time to manufacture large complex molecules like proteins, carbohydrates, fats and nucleic acids...)

Here's a biochemical example:

(i) $\text{Glucose} + \text{HPO}_4^{2-} \rightleftharpoons \text{Glucose-6-PO}_4^{2-} + \text{H}_2\text{O}$ $\Delta G^\circ = +13.8 \text{kJ/mole}$

This reaction is an *endergonic* first step in the breakdown of glucose (via *glycolysis* – a central metabolic pathway in all cells)

(ii) $\text{ATP} + \text{H}_2\text{O} \rightleftharpoons \text{ADP} + \text{phosphate}$ $\Delta G^\circ = -30.5 \text{kJ/mole}$

This is an *exergonic* reaction that can help drive reaction (i) because it releases enough free energy. The cell just needs to have enough ATP to be able to do this step.

The net reaction is (i) + (ii)

$\text{Glucose} + \text{ATP} \rightleftharpoons \text{Glucose-6-phosphate} + \text{ADP}$ $\Delta G^\circ = (+13.8 + (-30.5)) = -16.7\text{kJ/mole}$

(3) Understand the meaning of *stability*. Distinguish between *kinetic stability* and *thermodynamic stability*.