#6: Thermodynamics

Thermodynamics is one of the big ideas in chemistry. If you're wondering *whether* a chemical reaction will occur spontaneously, or *why* a reaction occurs, the answer comes down to the energetics of the system. (Other ideas that answer big questions are ***equilibrium***, which answers the question "to what extent" a reaction will occur, and ***kinetics***, which answers the question of "how fast" a reaction will occur.)

Part I of this week's recitation will give you more practice applying concepts and calculation skills related to entropy and free energy. Part II applies these concepts to biological systems.

Part I: Concept and calculation review

1. For each process below, predict the sign of ΔH, ΔS, and ΔG. Indicate whether the spontaneity of the process depends on temperature. Describe your reasoning in each case. ***In some cases, you may need to state what additional information is needed in order to make a prediction.***

a. 2O *(g)* → O_2 *(g)* *Short explanation:*

Prediction: ΔH: – 0 +

ΔS: – 0 +

ΔG: – 0 + temp dependent?

b. dissolving $CaCl_2$ *(s)* in water *(solution feels warm)* *Short explanation:*

Prediction: ΔH: – 0 +

ΔS: – 0 +

ΔG: – 0 + temp dependent?

c. 2HF*(g)* → H_2*(g)* + F_2*(g)* *Short explanation:*

Prediction: ΔH: – 0 +

ΔS: – 0 +

ΔG: – 0 + temp dependent?

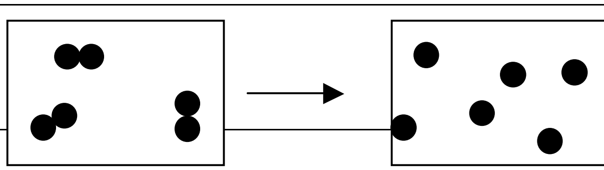
d. Making ice cubes *Short explanation:*

Prediction: ΔH: – 0 +

ΔS: – 0 +

ΔG: – 0 + temp dependent?

e.



Short explanation:

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Prediction: ΔH: - 0 +

ΔS: - 0 +

ΔG: - 0 + temp dependent?

****What is the relationship between parts "a" and "e"?****

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2. You give a pair of small diamond earrings to someone special for her birthday. Thermodynamically speaking, are those diamonds spontaneously turning into graphite? Use the thermodynamic data below to help answer this question. (Assume 298 K)

C(diamond) + O_2 (g) → CO_2 (g) ΔH° = -395.4 kJ	
2 CO (g) → C(graphite) + CO_2 (g) ΔH° = -172.5 kJ	S° for C(graphite) = 5.7 J/mol K
2 CO_2 (g) → 2 CO (g) + O_2 (g) ΔH° = 566.0 kJ	S° for C(diamond) = 2.4 J/mol K
C(graphite) + O_2(g) → CO_2 (g) ΔH° = -393.5 kJ	

3. You titrate a strong acid with a strong base.

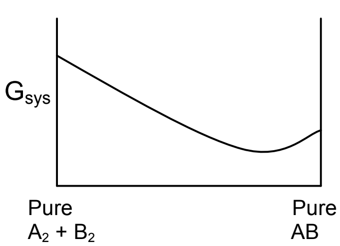
a. Write the net ionic equation for this reaction.
Make a prediction about whether ΔG° will be positive or negative. Explain your prediction.

b. Calculate $\Delta G°_{rxn}$ given that $\Delta G_f°$ of H_2O (l) = -237.10 kJ/mol $\Delta G_f°$ of H_3O^+ (aq) = -237.10 kJ/mol

$\Delta G_f°$ of OH^-(aq) = -157.23 kJ/mol $\Delta G_f°$ of H^+ (aq) = 0 kJ/mol

c. Use your answer in (b) to calculate the equilibrium constant at 298 K for this reaction. (The answer should make sense to you—think of how this relates to "K_w".)

4. Given the representation below, what can you conclude about the spontaneity and equilibrium constant for this reaction? $\rightleftharpoons$ $A_2 + B_2$ 2 AB



<u>Conclusions about spontaneity (choose one):</u>	<u>Conclusions about Kc (choose one):</u>
_____ The forward reaction is spontaneous	_____ Kc >> 1
_____ The reverse reaction is spontaneous	_____ Kc << 1
_____ Neither reaction is spontaneous	_____ Kc = 1

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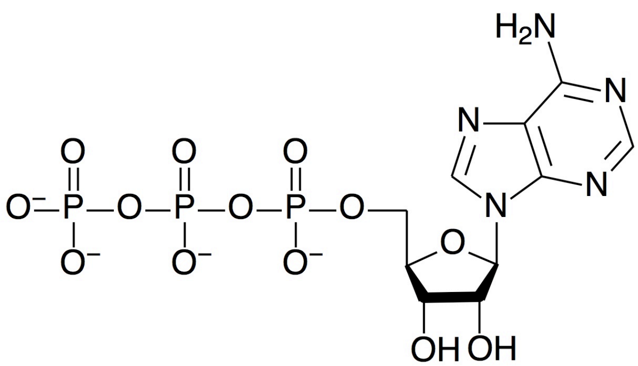
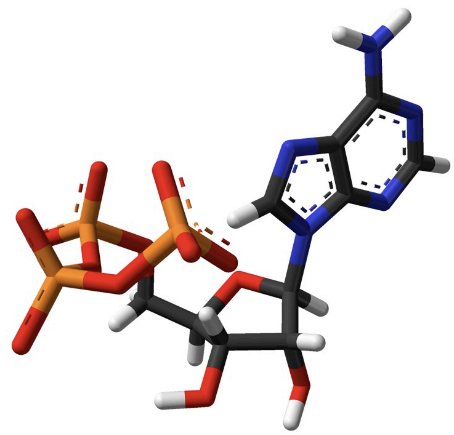
Part II: Coupled Reactions—Bioenergetics

How is it that you have energy to walk, run, or study with friends? What is the source of that energy? How does your body store and use energy on a molecular level? Even if you're not a biology major, chances are you know something about the role of ATP (adenosine triphosphate) as an energy transport molecule within your cells. When ATP is hydrolyzed to ADP (adenosine diphosphate), the overall reaction releases energy, which can be used to power nonspontaneous cellular processes such as making proteins from amino acids, or pumping ions across membranes.

The energy to make ATP from ADP comes from the metabolism of carbohydrates and fats. The questions below relate to a few of these processes, illustrating how thermodynamics applies to reactions occurring within your body right now.





Above: Two representations of ATP (adenosine triphosphate)

1. You will find that different textbooks write the chemical equation for the energy-releasing ATP → ADP reaction in slightly different ways. Here are three examples, from three different biology / chemistry texts:

ATP → ADP + P_i + energy (P_i = "inorganic phosphate")

ATP + H_2O → ADP + H_3PO_4 $\Delta G° = -30.6$ kJ

ATP^{4-} + 2 H_2O → ADP^{3-} + $HOPO_3^{2-}$ + H_3O^+ $\Delta G° = -30.6$ kJ

a. One of the equations above often leads students to think (incorrectly) that *bond-breaking releases energy*. Identify the equation and explain why it is misleading.

b. You know about bond energy, enthalpy, entropy, and free energy. Use what you know (along with chemical equations and structural representations provided on this page) to explain as thoroughly as you can why ATP → ADP releases free energy.

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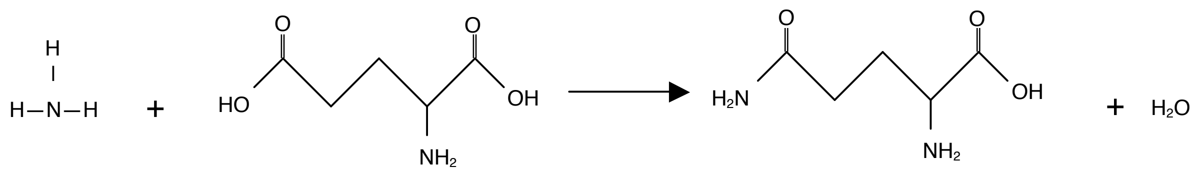
Think about what bonds are breaking, what bonds are being made, and the overall changes in free energy in this system.

2. As mentioned in the introduction, the energy released from the hydrolysis of ATP → ADP is ***coupled*** with reactions that—on their own—are nonspontaneous. One example is the cellular synthesis of the amino acid glutamine:



   a. For the reaction above, $\Delta G° = + 14$ kJ. Write the net reaction and calculate the overall $\Delta G°$ for the coupled reactions below:

$$\text{Glutamic acid} + NH_3 \rightarrow \text{Glutamine} + H_2O$$
$$ATP + H_2O \rightarrow ADP + H_3PO_4$$

Net:

3. Great, so the hydrolysis of ATP can be used to provide energy needed for nonspontaneous reactions and processes inside our cells. How is ATP itself synthesized in our bodies? Where does that energy come from? Ultimately, all of that energy comes from the sun. Plants use solar energy to make carbohydrates. Oxidation of carbohydrates releases energy, as illustrated here:

   Oxidation of glucose: $C_6H_{12}O_6 + 6O_2 \rightarrow 6\,CO_2 + 6H_2O$ $\Delta G° = -2870$ kJ

   As you can see, the oxidation of one mole of glucose releases a lot of energy—too much for cells to handle in one large burst. Thus, our cells harness this energy by producing ATP molecules, which can store the energy until needed in other cellular processes. One mole of glucose is oxidized to produce 36 moles of ATP from ADP.

   a. How much energy is required to synthesize 36 moles of ATP from 36 moles of ADP?

   b. How much energy is "left over" when the energy from oxidizing one mole of glucose is used to synthesize 36 moles of ATP? What percentage of the total energy is used to convert ADP into ATP? Would you consider this a very "efficient" process? What happens to the "left over" energy?

4. In running a mile, an average person consumes about 500 kJ of free energy.

a. How many moles of ATP does this represent?

b. Taking into account the conversion efficiency determined in Question 3b, how many grams of glucose must be "burned"?

Cover page for TA/LA Guide

TA/LA notes for Recitation #6 (Thermodynamics)

[Noyce fellows: Erin Park and John Rowley]

<u>General Comments:</u>

- Students learned about enthalpy (ΔH) in first semester Gen Chem.
    - They learned about endothermic and exothermic reactions, heat of reaction, heat of formation, calorimetry, and bond energy (especially "bond-breaking takes energy and bond-making releases energy"). It may be helpful to remind students of this.
    - This review should alleviate some of the anxiety students feel when first attempting to differentiate between all the seemingly similar relationships.
- The focus of the recitation should be on Part I.
- Part II may be confusing for students who have not had much of a biology background. Try to focus students on the chemistry going on in the problem rather than the biology if they are confused about ATP.
- Analogies can be helpful for students to understand entropy. An example used in the past: Clean rooms are more ordered than messy rooms. Clean rooms spontaneously seem to become messy, while it takes energy to turn a messy room into an ordered room. This is an easy way to remember that the change from ordered to less ordered is spontaneous and positive.

<u>Main Goals:</u>

- To understand the relationship between enthalpy, entropy and Gibb's Free Energy.
- To understand the relationship between Gibb's Free Energy and the Equilibrium Constant.
- To successfully use these relationships to predict the spontaneity of a reaction.
- To calculate ΔG of reactions.
- To relate ΔG to K_w, the water autoionization equilibrium constant.
- To look at a practical application of thermodynamics and to understand some general ideas concerning energy as it relates to biological processes.

<u>Suggestions for the Structure of Recitation:</u>

- A short review of thermodynamic principles (enthalpy, entropy and Gibb's Free Energy) will be useful to start the recitation. Keep this brief so students have ample opportunity to work through Part I in groups. Having to use these terms and defend their reasoning to other students will help them to develop their understanding of the terms and concepts.
- Either discuss the first page as a class once students finish it, or at least make sure everyone has an understanding of the answers.

- Don't simply accept correct answers on Part I (Question 1) as evidence of understanding. Ask students why they answered that way; what was their reasoning? This could be a good place to encourage use of white boards. Designate one member of the group to clearly record group responses to Question 1 so you can see them as you circulate around the room.
- Students who finish Part I should move on to Part II, but it is not necessary to push everyone on to Part II if there is still confusion over Part I.

Excerpt of TA/LA guide for Thermodynamics materials:

[Noyce fellows: Erin Park and John Rowley]

Part I: Concept and calculation review

1. For each process below, predict the sign of ΔH, ΔS, and ΔG. Indicate whether the spontaneity of the process depends on temperature. Describe your reasoning in each case. ***In some cases, you may need to state what <u>additional information is needed</u> in order to make a prediction.***

a. $2O\ (g) \rightarrow O_2\ (g)$

Prediction: ΔH: (−) 0 + | ΔS: (−) 0 + | ΔG: − 0 + (temp dependent?)

Short explanation:
Bonds are being formed, thus ΔH is negative. The number of moles in the gas phase decreases and so ΔS is also negative. Therefore ΔG is negative at low temperatures.

b. dissolving $CaCl_2\ (s)$ in water *(solution feels warm)*

Prediction: ΔH: (−) 0 + | ΔS: − 0 (+) | ΔG: (−) 0 + temp dependent?

Short explanation:
Heat is being released from the system, thus ΔH is negative. As the solid dissolves, the system becomes more disordered and so ΔS is positive. Therefore ΔG is negative.

c. $2HF(g) \rightarrow H_2(g) + F_2(g)$

Prediction: ΔH: − 0 (+) | ΔS: − (0) + | ΔG: − 0 (+) temp dependent?

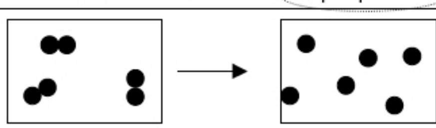
Short explanation:
*Since bonds are both broken and formed, enthalpy cannot be determined without more information. Since two moles of gas is producing two moles of gas, entropy change will be **close** to zero.*

d. Making ice cubes

Prediction: ΔH: (−) 0 + | ΔS: (−) 0 + | ΔG: − 0 + (temp dependent?)

Short explanation:
As ice cubes form heat is released, thus ΔH is negative. As the solid forms the system becomes more ordered and so ΔS is also negative. Therefore ΔG is negative at low temperatures.

e.



Prediction: ΔH: − 0 (+) | ΔS: − 0 (+) | ΔG: − 0 + (temp dependent?)

Short explanation:
Bonds are being broken, thus ΔH is positive. The number of moles in the gas phase increases and so ΔS is also positive. Therefore ΔG is negative at high temperatures.

This should make sense compared to the process in 1a—these are the reverse of each other!!

****What is the relationship between parts "a" and "e"?****

Comment: Before attempting this section, it wou be a good idea to go over enthalpy, entropy and fre energy on a conceptual level. It has been awhile since students have thought about enthalpy, so that especially will need a short discussion. Allowing 5 minutes before recitation to discuss exothermic vs. endothermic reactions will make recitation proceed much smoother.

Comment: It may be useful to write the equation $\Delta G = \Delta H - T\Delta S$ on the board.

Comment: Many students rationalize a + change in enthalpy value by saying that bonds are broken. Make sure to point out that the solution feels warm and ask them what that says about the change in enthalpy of the system.

Comment: Students need more information to determine this. Make students realize this and ask you for this information. Bond energies:
H—F: 565
H—H 432
F—F: 159
Overall: +539, endothermic

Comment: This question may create some disagreement between the LA and TA. Remember that students won't know any numerical values of enthalpy and entropy and these are needed to answ this question! Usually an attempt to answer this question on a conceptual level will only confuse students. Keep it simple. Students need only determine what extra information they need!

Comment: Have students connect knowledge fro life here. Obviously from experience they know ice cubes only form under certain low temperature conditions—it is temperature dependent! (What is the melting point of water?) Point out how delta G further evidence of what they already know.

Sometimes it's useful to get students to think of the reverse process—you would need to put heat into melting ice cubes.

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Agenda for TA/LA meeting related to Thermodynamics:

[Noyce fellows: Erin Park and Melanie Yee]

CHEM 1131: Recitation #6 TA/LA Meeting

1. Board Talk/debrief/teaching goals

Did you try anything new this week? If so, what? Did it work? How can it be improved?

2. Recitation meeting—TA/LA groups

Thursday:

Group 1: Tina, Cal, Jeff
Group 2: Stefanie, Rachael, Emily
Group 3: John, Michael, Kate, Carla

Friday:

Group 1: Julia, Austin, Kyle, Molly
Group 2: Cam, Mike, Jasen, Elizabeth
Group 3: Faria, Carla, Nick, Galen

Like it says on the cover page, the focus of recitation this week should be Part I.

Part I: (#1) The relationships between ΔG, ΔH, ΔS, and temperature are often difficult for students to grasp. It's fine and dandy for us to give them a chart with patterns to memorize (which are easier as teachers to just give them the information), but without understanding the patterns and really thinking about the relationships, students will never remember, nor will they **learn** anything (which is the point, after all). **(#2)** Students will want to use every equation that they're given. They know better. Ask "What do we know? What do we need? How do we get there?"

Part II: It's not essential that students complete Part II, but it does provide good context for thermodynamics (especially since many of our students are biology majors). Be prepared for students' minds to be blown upon finding out that removing inorganic phosphate from ATP does not in fact release energy in and of itself. ATP hydrolysis is non-spontaneous, but in vitro, it is coupled with energetically favorable reactions, yielding a net energy excess. Refer TAs and LAs back to the TA/LA guide for tips. This can be really tough for biology students, especially if they don't connect the dots between their biology world and their chemistry world.

3. Teaching Goals

Make a new one! It may seem stupid and mundane, but just thinking about something you want to improve will put it in the forefront of your brain. Thinking about these things not only makes you a better teacher, it provides a better learning experience for your students!