ChemActivity 6

Part A: Energy Diagrams
(What is the sign of $\Delta H_{\text{reaction}}$ for an exothermic reaction?)

Model 1A: The Slot Machine
Imagine a gambler sitting at a slot machine. Over the course of an hour the gambler puts $100 into the machine and the machine pays out $90. We know a net change ($\Delta$) of ten dollars occurred, but what is the sign of this change in money ($\Delta S$)? To determine if $\Delta S = +10$ or $-10$ we need to decide if we calculate $\Delta S$ from the perspective of the gambler or from the perspective of the slot machine.

Money into slot machine
$100$

Money out of slot machine
$90$

$\Delta S = +10$ or $-10$

To translate this analogy into chemistry remember that:
- Money = energy.
- The slot machine = the reaction.
- The gambler = the experimenter (you).
- All changes ($\Delta$) will be calculated from the perspective of the reaction (a.k.a. the slot machine).

Critical Thinking Questions
1. Using the convention listed above for calculating changes ($\Delta$), what is the sign of $\Delta S$ in the example in Model 1A?

2. Based on this same convention, what sign must be attached to the $100 that the gambler put into the slot machine in Model 1A? The sign of the $90 that comes out is the opposite. Add the appropriate sign to each value in Model 1A.

3. On a different day the gambler puts in a total of $20 and the slot machine pays out a total of $100. What is the sign and value of $\Delta S$ for this day?
Model 1B: Burning of Natural Gas (Methane)
- Breaking bonds requires you to put energy into the molecule (think “slot machine”).
- Making bonds releases energy from the molecule, which is felt by the experimenter (think “gambler”) as heat.

We don’t really know what a transition state looks like because it is too unstable and short-lived to study. This picture is unreasonably simple for this reaction, but for other reactions in this course we will be able to make a much better guess.

Critical Thinking Questions
4. According to the diagram, which has more stored energy (higher in potential energy): methane and oxygen or water and carbon dioxide [circle one]? Is your answer consistent with the fact that one of these pairs is commonly used as a fuel?

5. According to our convention, what is the sign of $E_{\text{activation}}$ (the energy put into the reaction to break bonds).

6. What is the sign of $\Delta E$, the total net change in energy, for this reaction?

Information
The net energy change ($\Delta E$) in an organic reaction is often called the heat of reaction ($\Delta H$)

7. Draw an arrow on the diagram above indicating the heat of reaction for the burning of methane. Be sure to assign a direction to your arrow indicating the sign of this change in heat/energy.

Recall that energy in = up arrow = + energy; and energy out = down arrow = -energy.
8. On a gas stove, what supplies the activation energy ($E_{activation}$) to start the reaction?

9. You do not have to hold a match under your pot to keep a gas flame burning. A spark or match supplies $E_{act}$ for the first molecules of methane. What is the energy source that supplies $E_{act}$ for subsequent molecules of methane coming up through the pipe? (Hint: not all of the energy released by burning methane goes to heating your food.)

10. The reaction in Model IB is called exothermic because it releases heat. Some reactions, such as the one below, are endothermic. Would you expect an endothermic reaction to be self-sustaining like the burning of methane? Explain why or why not.

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--- Energy Diagram ---
Reactants → Transition State → Products
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a) Add an arrow to the energy diagram above indicating the size and direction of the activation energy and label this arrow "$E_{act}$".

b) Add an arrow to the energy diagram above indicating the size and direction of the heat of reaction and label this arrow "$\Delta H_{reaction}$". (Note: $\Delta$ means "the change in" or "net" and $H$ stands for heat.)
Model 2: Ring Strain

In previous ChemActivities you observed that your molecular model set can help predict the best conformation for a molecule. This is because the holes in the atom pieces are consistent with experimentally determined bond angles for carbon (109.5°).

If you tried, you would find it very difficult to build a model of cyclopropane. This is because the 60° bond angles of cyclopropane are very far from carbon's preferred 109.5° bond angles. As you might expect, cyclopropane is unstable and high in potential energy. Organic chemists call the extra energy associated with cyclopropane's strained bonds "ring strain."

Critical Thinking Questions

11. Circle the cycloalkane in Model 2 which you expect is most commonly found in nature, and explain your reasoning.

12. Cyclopropane has a molecular formula of C₃H₆ and a molecular weight of 42 g/mole, making it exactly half the size of cyclohexane, whose molecular formula is C₆H₁₂ and molecular weight is 84g/mole.
   
   • Burning 1 mole (84g) of cyclohexane releases 3900 kJ of heat energy.
   • Burning 2 moles (84g) of cyclopropane releases 4100 kJ of heat energy.

Both reactions produce 6 moles of H₂O and 6 moles of CO₂. On the same set of axes, draw an energy diagram for each of these two reactions and explain why the cyclopropane reaction releases more heat.
Part B: Cyclohexane Conformations
(How do I represent cyclohexane in its lowest potential energy conformation?)

Model 3: The Chair Conformation of Cyclohexane
With zero ring strain, the six member ring is the most stable alkane ring. Not surprisingly, six member rings are very common in Nature and the laboratory. Previously, we have drawn cyclohexane as though the carbons all lie in the same plane, but a flat hexagon has internal angles of 120°, not 109.5°.

The carbons of cyclohexane do NOT form a flat hexagon!

As we will see in the following section, cyclohexane adopts a low potential energy conformation called the chair conformation. In this conformation a cyclohexane molecule has perfect 109.5° bond angles and zero ring strain.

The chair conformation is characterized by three sets of parallel C—C bonds and a "tripod" of C—H bonds on each face (see below).

![Diagram of chair conformation]

Looks like a reclining chair!

Critical Thinking Questions
13. Build a model of cyclohexane in the chair conformation. Check with your instructor or another group to confirm that your model is correct.

14. Six of the H’s of cyclohexane are called "axial," the other six are called "equatorial." Based on these names, find the axial (think axis of the globe) and equatorial (think equator) H’s. Label each H of chair cyclohexane in the diagram above: "A" or "E."

15. With an input of 45 kJ/mole cyclohexane can undergo a change in conformation such that each equatorial H becomes axial and vice versa.

a) Without breaking any bonds, perform this conformation change on your model of cyclohexane. This is often called a "cyclohexane chair flip."
b) Complete the following energy diagram for the chair flip process.

16. Cyclohexanes are often drawn as partial skeletal structures, showing the H's but not the C's. On the left, below, is a drawing of methylcyclohexane in a chair conformation with the methyl group in an axial position. Complete the drawing on the right, showing this same structure after a chair "flip" has occurred. Carbon 1 is marked in each drawing.

17. Make a model of methylcyclohexane with the methyl group in an equatorial position. Construct an explanation for why this is a more favorable conformation than the conformation with CH₃ in an axial position.

18. It is important to know that, in general, it is favorable to have the largest group on a cyclohexane ring in an equatorial position. Draw a chair representation of...
   (Represent the methyl group as CH₃ and the t-butyl group as C(CH₃)₃.)
   a) cis-1-torr-butyl-4-methylocyclohexane in its most favorable conformation.
   b) trans-1-torr-butyl-4-methylocyclohexane in its most favorable conformation.
   c) Which is lower in potential energy: cis or trans [circle one] and explain your reasoning.

1-methyl-4-torr-butylcyclohexane
19. Label each of the following dimethylocyclohexanes as cis, trans or neither.

a) Below each structure that is cis draw the trans stereoisomer and vice versa. The first one is done for you.

b) True or False: When you perform a “chair flip” on a cis stereoisomer, the resulting structure is the trans stereoisomer, and vice versa.

c) Draw chair representations of the lowest potential energy (most favorable) conformation of the two 1,4-dimethylocyclohexane structures shown on the left in the figure above.

Exercises For Part A
1. In the reactants box in Model 1B, why must there be twice as much oxygen as methane?

2. According to Model 1B, in going from the Reactants to the Transition State, were any electrons or atoms gained or lost?

3. By convention, on an energy diagram up arrows are positive (heat is added to the reaction) and down arrows are negative (heat is coming out of the reaction).
   a) According to the above statement, the sign of all activation energies ($E_{act}$) must be positive or negative [circle one].
   b) The sign of $\Delta H_{reaction}$ for an exothermic reaction is positive or negative [circle one].
   c) The sign of $\Delta H_{reaction}$ for an endothermic reaction is positive or negative [circle one].

4. Butane ($\text{C}_4\text{H}_{10}$) is the fuel used in cigarette lighters. To start the combustion reaction, a small amount of energy must be put into the system to get over the initial hump. What is the source of this activation energy in a standard cigarette lighter?