## ChemQuest 53

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## Information: Internal Energy

Thermodynamics involves the study of the energy and disorder of a system. Every system has "internal energy". Internal energy is the total amount of all the potential and kinetic energy that a system has. For an example of a "system" let's take a car. A car has kinetic energy (the energy of motion) if it is moving and it has potential energy (chemical energy of the gasoline) if it has gas in the tank. A car always has a certain amount of energy associated with it. A car has more total energy (chemical potential energy) with a full tank of gas than with a half full tank. Therefore, after driving a car for a while the total amount of energy (called the internal energy) that the car has decreases.

## Critical Thinking Questions

1. If we use KE to symbolize kinetic energy and PE to symbolize potential energy, and $U$ to symbolize internal energy, then write an equation for internal energy.

$$
\mathrm{U}=\mathrm{KE}+\mathrm{PE}
$$

2. Consider a car as described in the table below. Fill in the blanks in the table with the hypothetical values for kinetic energy, potential energy, and internal energy. (Assume that the overall mass of the car stays the same even though the amount of gasoline in the tank decreases.)

|  | A car is setting in <br> the driveway <br> before a long road <br> trip. The gas tank <br> is full. | The car has set out on <br> the trip and has been <br> driving for a while. <br> Cruise control is set <br> for a constant speed. | The car is still <br> driving at the <br> same speed. | The car ran out <br> of gas and is <br> parked along <br> the highway. |
| :---: | :---: | :---: | :---: | :---: |
| Kinetic <br> Energy | 0 | 20 | 20 | 0 |
| Potential <br> Energy | 100 | 70 | 30 | 0 |
| Internal <br> Energy | 100 | 90 | 50 | 0 |

3. The Law of the Conservation of Energy states that energy isn't created or destroyed. The car in question 2 , lost energy. If the energy was not destroyed, hypothesize what happened to it.

The energy changed forms into sound energy, friction, heat, etc. and was lost to the surroundings.
4. What would be the internal energy of the car in question 2 if someone brought enough gas to fill the tank back up completely while the car was stranded at the side of the highway?

100

## Information: First Law of Thermodynamics

As you saw in question 2 above, the internal energy of a system can change. What happens to the energy? The energy merely changes form. In the car example, the internal energy was changed into heat energy as the gasoline burned. Also, some of the internal energy was used to do work by moving the car. The First Law of Thermodynamics states that the change in internal energy of a system equals the sum of the heat and the work. Internal energy of a system can increase or decrease. If a system is heated, it gains internal energy, but if the system loses heat then it decreases in internal energy. If a system does work it loses internal energy, but if work is done on the system then it gains internal energy.

## Critical Thinking Questions

5. For each of the following, state what the "system" is and also state whether the internal energy of the system would increase or decrease in each situation.
a) Lifting a ball from the ground and holding it six feet off the ground.

System: ball; internal energy increases
b) Heating up a piece of pizza in the microwave.

System: pizza; internal energy increases
c) The logs in the fireplace are burning.

System: logs; internal energy decreases
d) An ice cube is melting while it sets on the kitchen counter.

System: ice cube; internal energy increases
e) Two molecules bond together and heat energy is released (exothermic).

System: molecules; internal energy decreases

## Information: Enthalpy

Heat energy is a large factor in how much the internal energy of a system changes. We will now turn our attention to chemical reactions. In your answer to question 5e above you should have identified the two molecules as the "system" and you should have noted that their overall internal energy decreased since they lost heat. Verify that this is correct. The heat energy involved in a chemical reaction is given the name "enthalpy". The change in heat energy for a reaction is called the change in enthalpy and it is given the symbol $\Delta \mathrm{H}$ and it has units of kilojoules ( kJ ). An example of 5 e taking place is when one mole of hydrogen molecules reacts with $1 / 2$ mole of oxygen molecules:

Example Reaction 1: $\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) ; \Delta \mathrm{H}_{\mathrm{f}}=-241.8 \mathrm{~kJ}$ In the following reaction, energy is absorbed by the system (endothermic) instead of being released.

Example Reaction 2: $\mathrm{C}(\mathrm{s})+2 \mathrm{~S}(\mathrm{~s}) \rightarrow \mathrm{CS}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}_{\mathrm{f}}=117 \mathrm{~kJ}$

## Critical Thinking Questions

6. Give the definition for the following terms.
a) endothermic: when energy is absorbed by a system
b) exothermic: when energy is released by a system
7. In the above examples, Example Reaction $1 \Delta \mathrm{H}$ is negative and in Example Reaction $2 \Delta \mathrm{H}$ is positive. What does the sign on $\Delta \mathrm{H}$ tell you?

If $\Delta \mathrm{H}$ is negative, the reaction is exothermic because heat is subtracted from the system. If $\Delta \mathrm{H}$ is positive, the reaction is endothermic because heat is added to the system.
8. In Example Reaction 1, compare the amount of energy that the product has compared to the reactants.

The products have less energy because energy was "lost" during the reaction in the form of heat.
9. In Example Reaction 2, compare the amount of energy that the product has compared to the reactants.

The products have more energy because energy was "gained" during the reaction in the form of heat.

## Information: Enthalpy of Formation

In Example Reaction 1 and 2, one substance was formed out of two. Whenever one substance is made from elements in their standard states, the accompanying enthalpy change is called the enthalpy of formation, given the symbol $\Delta \mathrm{H}_{\mathrm{f}}$. Note the following two example reactions:

Example Reaction 3: $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{S}(\mathrm{s}) \rightarrow \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g}) ; \Delta \mathrm{H}_{\mathrm{f}}=-20 \mathrm{~kJ}$
Example Reaction 4: $\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}_{\mathrm{f}}=-393.5 \mathrm{~kJ}$
Notice that in the previous 4 example reactions, each substance formed is involved in the following reaction:

Example Reaction 5: $2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})+\mathrm{CS}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=$ ?
The $\Delta \mathrm{H}$ for Example Reaction 5 can be calculated from the data for Example Reactions 1-4 as follows:

$$
\Delta \mathrm{H}=[2(-20 \mathrm{~kJ})+(-393.5 \mathrm{~kJ})]-[2(-241.8 \mathrm{~kJ})+(117 \mathrm{~kJ})]=-66.9 \mathrm{~kJ}
$$

## Critical Thinking Questions

10. In Example Reactions 1-4, the enthalpy value was given the symbol $\Delta \mathrm{H}_{\mathrm{f}}$, but in Example

Reaction 5, the enthalpy value was given the symbol $\Delta \mathrm{H}$. Why the difference?
In reactions 1-4 one substance is made from several substances, which is called a formation reaction.
11. In calculating the $\Delta \mathrm{H}$ for Example Reaction 5, why was -20 kJ multiplied by 2? Why was the 241.8 kJ multiplied by 2 ?

Forming $\mathrm{H}_{2} \mathrm{O}$ releases 20kJ (see Example Reaction 3) and since there are two $\mathrm{H}_{2} \mathrm{O}$ molecules present in Example Reaction 5, the -20kJ is multiplied by two.
12. Using a table for standard enthalpies of formation $\left(\Delta \mathrm{H}_{\mathrm{f}}\right)$, verify that $\Delta \mathrm{H}$ for the following reaction is approximately -91.4 kJ .

$$
\begin{gathered}
2 \mathrm{NaF}+\underset{-795 \mathrm{~kJ}}{\mathrm{CaCl}_{2}} \rightarrow \underset{-1215 \mathrm{~kJ}}{\mathrm{CaF}_{2}}+\underset{-411.1 \mathrm{~kJ}}{2 \mathrm{NaCl}} \\
\Delta \mathrm{H}=[2(-411.1)+(-1215)]-[2(-575.4)+(-795)]= \\
-91.4 \mathrm{~kJ}
\end{gathered}
$$

13. Again using a table of standard enthalpy values calculate $\Delta \mathrm{H}$ for each of the following reactions.
$\underset{-408 \mathrm{~kJ}}{\mathrm{LiCl}}+\underset{-361 \mathrm{~kJ}}{\mathrm{NaBr}} \rightarrow \underset{-411.1 \mathrm{~kJ}}{\mathrm{NaCl}} \underset{-351 \mathrm{~kJ}}{\mathrm{LiBr}}$
$\Delta \mathrm{H}=[-411.1+(-351)]-[-361+(-408)]=\mathbf{6 . 9} \mathbf{k J}$
b) $\mathrm{MgCO}_{3}+2 \mathrm{NaCl} \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}+\mathrm{MgCl}_{2}$
$-1112 \mathrm{~kJ} \quad-411.1 \mathrm{~kJ} \quad-1130.8 \mathrm{~kJ} \quad-641.6 \mathrm{~kJ}$
$\Delta \mathrm{H}=[-641.6+(-1130.8)]-[2(-411.1)+(-1112)]=\mathbf{1 6 1 . 8} \mathbf{~ k J}$
c) $\mathrm{CH}_{4}+\mathrm{Cl}_{2} \rightarrow \mathrm{HCl}(\mathrm{g})+\mathrm{CH}_{3} \mathrm{Cl}$
$-74.87 \mathrm{~kJ} \quad 0 \mathrm{~kJ} \quad 92.31 \mathrm{~kJ} \quad-83.7 \mathrm{~kJ}$
$\Delta \mathrm{H}=[-83.7+92.31]-[-74.87+0]=\mathbf{- 8 3 . 4 8}$
14. In 13 c , you should have noted that $\Delta \mathrm{H}_{\mathrm{f}}$ for $\mathrm{Cl}_{2}$ is zero. $\Delta \mathrm{H}_{\mathrm{f}}$ is also zero for $\mathrm{O}_{2}, \mathrm{Na}(\mathrm{s}), \mathrm{Mg}(\mathrm{s})$, and other substances. Why do you think $\Delta \mathrm{H}_{\mathrm{f}}$ is zero for these substances?
$\mathrm{Cl}_{2}, \mathrm{O}_{2}, \mathrm{Na}$, and Mg are in their natural state. We do not speak of forming a sodium atom, for example, because the sodium atom is already formed.
15. Compare the $\Delta \mathrm{H}_{\mathrm{f}}$ for $\mathrm{O}_{2}(\mathrm{~g})$ and for $\mathrm{O}(\mathrm{g})$. Why is $\Delta \mathrm{H}_{\mathrm{f}}$ equal to zero for $\mathrm{O}_{2}$, but not for O ? $\mathrm{O}_{2}$ is its natural state because oxygen exists as diatomic molecule. Monatomic oxygen, however, must be formed.
16. Calculate $\Delta \mathrm{H}$ for the following reaction using a table for standard enthalpy values: $2 \mathrm{CO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})$.
$\Delta \mathrm{H}_{\mathrm{f}}$ for $\mathrm{CO}=-110.5 \mathrm{~kJ} ; \Delta \mathrm{H}_{\mathrm{f}}$ for $\mathrm{O}_{2}=0 \mathrm{~kJ} ; \Delta \mathrm{H}_{\mathrm{f}}$ for $\mathrm{CO}_{2}=-393.5 \mathrm{~kJ}$ $\Delta \mathrm{H}_{\mathrm{rxn}}=2(-393.5)-[2(-110.5)]=\mathbf{- 5 6 6} \mathbf{~ k J}$
17. Consider the following reactions and $\Delta \mathrm{H}$ values

$$
\begin{aligned}
& \mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2} ; \Delta \mathrm{H}_{\mathrm{f}}=-393.5 \mathrm{~kJ} \\
& 2 \mathrm{CO} \rightarrow \mathrm{CO}_{2}+\mathrm{C} ; \Delta \mathrm{H}=-172.5
\end{aligned}
$$

a) Using only the above two $\Delta \mathrm{H}$ values, how can you calculate $\Delta \mathrm{H}$ for the reaction in question 16 ?

Add the two $\Delta \mathrm{H}$ together.
b) What is the relationship between the two reactions above and the reaction in question 16 ?

If you add the two reactions together you get the reaction from question 16.
18. In question 17a, you used Hess's Law to find the $\Delta \mathrm{H}$ for a reaction even though you didn't know what Hess's Law is. In your own words, state what you believe is Hess's Law.

When a reaction is formed by adding several reactions together, then the enthalpy change can be found by adding the enthalpy changes for the individual reactions.
19. Consider the following reaction: $\mathrm{N}_{2}+2 \mathrm{O}_{2}+2 \mathrm{NO} \rightarrow 2 \mathrm{NO}+2 \mathrm{NO}_{2}$. Use Hess's Law along with the following information to find the $\Delta \mathrm{H}$ for this reaction.

$$
\begin{array}{ll}
\text { reaction \#1 } & \mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO} ; \Delta \mathrm{H}=181 \mathrm{~kJ} \\
\text { reaction \#2 } & 2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2} ; \Delta \mathrm{H}=-113 \mathrm{~kJ}
\end{array}
$$

Since the reaction is formed by adding reaction \#1 and reaction \#2, the enthalpy change for the reaction can be found by adding the enthalpy change for reactions \#1 and \#2.

$$
\Delta \mathrm{H}_{\mathrm{rxn}}=181+(-113)=\mathbf{6 8} \mathbf{k} \mathbf{J}
$$

20. Consider the following reaction: $2 \mathrm{NO} \rightarrow \mathrm{N}_{2}+\mathrm{O}_{2} ; \Delta \mathrm{H}=-181 \mathrm{~kJ}$. What relationship exists between this reaction and reaction $\# 1$ in question 19? How could the $\Delta \mathrm{H}$ for this reaction be determined?

The reaction is the reverse of reaction \#1 from question 19. Thus, the $\Delta \mathrm{H}$ value is also reversed in sign.
21. Using only the information presented in question 12 , find the $\Delta \mathrm{H}$ for the following reaction.

$$
\mathrm{CaF}_{2}+2 \mathrm{NaCl} \rightarrow 2 \mathrm{NaF}+\mathrm{CaCl}_{2}
$$

This reaction is the reverse of the reaction in question 12 , so we reverse the sign of the enthalpy change from question 12 to get: $\mathbf{9 1 . 4} \mathbf{~ k J}$

