

## 6.6 Introduction to Enthalpy of Reaction

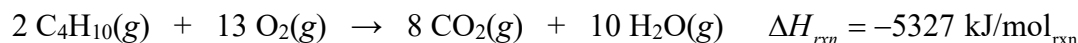
Essential knowledge statement from the AP Chemistry CED:

- The enthalpy change of a reaction gives the amount of heat energy released (for negative values) or absorbed (for positive values) by a chemical reaction at constant pressure.

Enthalpy ( $H$ ) versus Internal Energy ( $U$ )

- In a college chemistry course, students may learn about the difference between enthalpy ( $H$ ) and internal energy ( $U$ ). Distinctions between enthalpy and internal energy will NOT be assessed on the AP Chemistry Exam.
- Most physical and chemical changes studied in chemistry take place at constant pressure. Under these conditions, **the change in enthalpy ( $\Delta H$ )** is equal to the change in heat that occurs with respect to the system.

Classification of a Process	Direction of Heat Flow	Sign of $\Delta H$
endothermic	Heat flows from the surroundings into the system.	positive
exothermic	Heat flows from the system into the surroundings.	negative



Consider the information given in the equation shown above.

- The symbol " $\Delta H_{\text{rxn}}$ " refers to the change in enthalpy ( $H$ ) (i.e., the change in heat) associated with the reaction represented by the equation shown above.
- The units of  $\Delta H_{\text{rxn}}$  are written as " $\text{kJ/mol}_{\text{rxn}}$ ," which is NOT the same as writing " $\text{kJ/mol}$ ."

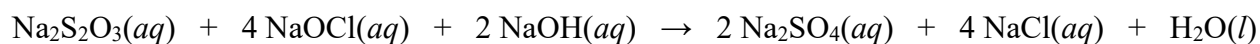
The unit **mole of reaction** is abbreviated as  $\text{mol}_{\text{rxn}}$ . This unit is defined in terms of the specific set of coefficients for a particular chemical equation. The following conversion factors can be written based on the information in the equation shown above.

$\frac{5327 \text{ kJ}}{1 \text{ mol}_{\text{rxn}}}$ or $\frac{1 \text{ mol}_{\text{rxn}}}{5327 \text{ kJ}}$	
$\frac{1 \text{ mol}_{\text{rxn}}}{2 \text{ mol C}_4\text{H}_{10}(\text{g})}$ or $\frac{2 \text{ mol C}_4\text{H}_{10}(\text{g})}{1 \text{ mol}_{\text{rxn}}}$	$\frac{1 \text{ mol}_{\text{rxn}}}{8 \text{ mol CO}_2(\text{g})}$ or $\frac{8 \text{ mol CO}_2(\text{g})}{1 \text{ mol}_{\text{rxn}}}$
$\frac{1 \text{ mol}_{\text{rxn}}}{13 \text{ mol O}_2(\text{g})}$ or $\frac{13 \text{ mol O}_2(\text{g})}{1 \text{ mol}_{\text{rxn}}}$	$\frac{1 \text{ mol}_{\text{rxn}}}{10 \text{ mol H}_2\text{O}(\text{g})}$ or $\frac{10 \text{ mol H}_2\text{O}(\text{g})}{1 \text{ mol}_{\text{rxn}}}$

A student is asked to determine the amount of heat that is released when 1.00 g of  $\text{C}_4\text{H}_{10}(\text{g})$  undergoes complete combustion in the presence of excess  $\text{O}_2(\text{g})$  according to the equation shown on the previous page. The following shows how conversion factors are used to perform this calculation. In the final conversion factor, a negative sign is not used with 5327 kJ because this value represents the *magnitude of heat released*, and not the change in enthalpy for the combustion reaction.

$$1.00 \text{ g C}_4\text{H}_{10}(\text{g}) \times \frac{1 \text{ mol C}_4\text{H}_{10}(\text{g})}{58.12 \text{ g C}_4\text{H}_{10}} \times \frac{1 \text{ mol}_{\text{rxn}}}{2 \text{ mol C}_4\text{H}_{10}(\text{g})} \times \frac{5327 \text{ kJ}}{1 \text{ mol}_{\text{rxn}}} = 45.7 \text{ kJ of heat released}$$

1. Use the information from the combustion reaction on the previous page to answer the following questions.
  - (a) Calculate the mass of  $\text{C}_4\text{H}_{10}(\text{g})$  that is required to produce 125 kJ of heat in this reaction. Assume that  $\text{O}_2(\text{g})$  is present in an excess amount. Include units in your answer.
  - (b) A reaction vessel contains a mixture of 15.0 g  $\text{C}_4\text{H}_{10}(\text{g})$  and 45.0 g  $\text{O}_2(\text{g})$ . The mixture is sparked, initiating a chemical reaction that proceeds until one of the reactants is completely consumed. Calculate the amount of heat released in this experiment. Include units in your answer.



2. A student performs an experiment to determine the value of the enthalpy change,  $\Delta H_{\text{rxn}}$ , for the oxidation-reduction reaction represented by the equation above.
  - (a) Determine the oxidation number of Cl in NaOCl. \_\_\_\_\_
  - (b) Calculate the number of grams of  $\text{Na}_2\text{S}_2\text{O}_3$  needed to prepare 100.00 mL of 0.500 M  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ .

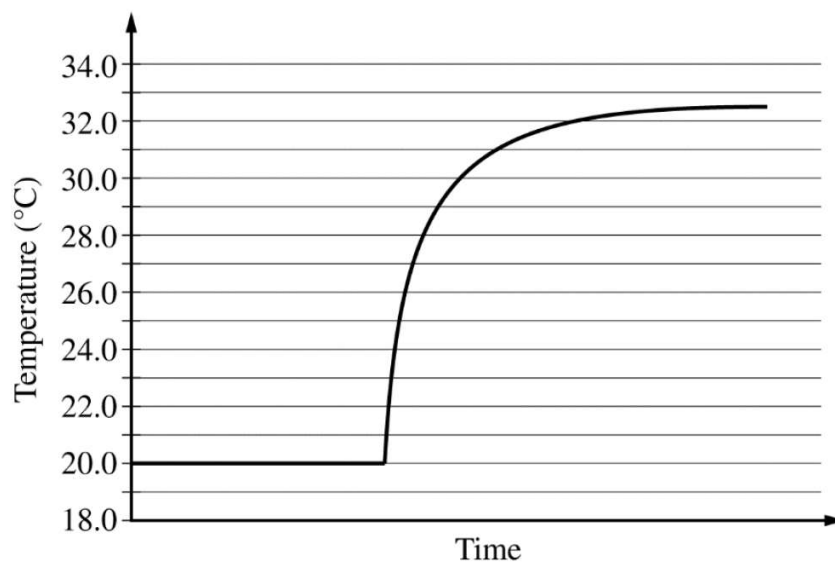
2. (continued)

In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (M)	Volume (mL)
$\text{Na}_2\text{S}_2\text{O}_3(aq)$	0.500	5.00
$\text{NaOCl}(aq)$	0.500	5.00
$\text{NaOH}(aq)$	0.500	5.00

(c) Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

The solutions, all originally at  $20.0^\circ\text{C}$ , are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



(d) According to the graph, what is the temperature change of the reaction mixture? \_\_\_\_\_

2. (continued)

(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is  $3.94 \text{ J}/(\text{g}\cdot^\circ\text{C})$  and that the heat absorbed by the calorimeter is negligible.

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction,  $\Delta H_{rxn}$ , in units of  $\text{kJ}/\text{mol}_{rxn}$ . Include the appropriate algebraic sign with your answer.

The student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

Solution	Concentration ( <i>M</i> )	Volume (mL)
$\text{Na}_2\text{S}_2\text{O}_3(aq)$	0.500	10.0
$\text{NaOCl}(aq)$	0.500	10.0
$\text{NaOH}(aq)$	0.500	10.0

(f) Do you predict that the magnitude of heat (*q*), in joules, released in the second experiment will be less than, equal to, or greater than the value calculated in part (e)(i)? Justify your answer.

(g) Do you predict that the magnitude (i.e., absolute value) of the enthalpy change,  $\Delta H_{rxn}$ , in units of  $\text{kJ}/\text{mol}_{rxn}$ , calculated from the results of the second experiment will be less than, equal to, or greater than the value calculated in part (e)(ii)? Justify your answer.

## 6.7 Bond Enthalpies

Essential knowledge statements from the AP Chemistry CED:

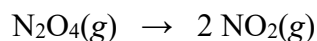
- During a chemical reaction, bonds are broken and/or formed, and these events change the potential energy of the system.
  - The average energy required to break all of the bonds in the reactant molecules can be estimated by adding up the average bond energies of all the bonds in the reactant molecules. Likewise, the average energy released in forming the bonds in the product molecules can be estimated. If the energy released is greater than the energy required, the reaction is exothermic. If the energy required is greater than the energy released, the reaction is endothermic.
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The terms **bond enthalpy** and **bond energy** are used interchangeably. The bond energy values found in reference tables represent average values. This is because the energy required to break a particular bond can vary depending on the structure of the molecule in which the bond exists. Bond energy values are associated with substances that are in the gas phase.

Bond	Bond Enthalpy (kJ/mol)
H–H	436
C–C	348

3. Use the information in the table above to answer the following questions.

- (a) 436 kJ of energy is \_\_\_\_\_ when 1 mole of H–H bonds are broken, and  
436 kJ of energy is \_\_\_\_\_ when 1 mole of H–H bonds are formed.
- (b) Do you predict that the bond energy of the I–I bond should be less than or greater than 436 kJ/mol? Justify your answer.
- (c) Do you predict that the bond energy of the C=C bond should be less than or greater than 348 kJ/mol? Justify your answer.



4. Do you predict that the sign of  $\Delta H_{rxn}$  for the reaction represented by the equation above should be positive or negative? Justify your answer.

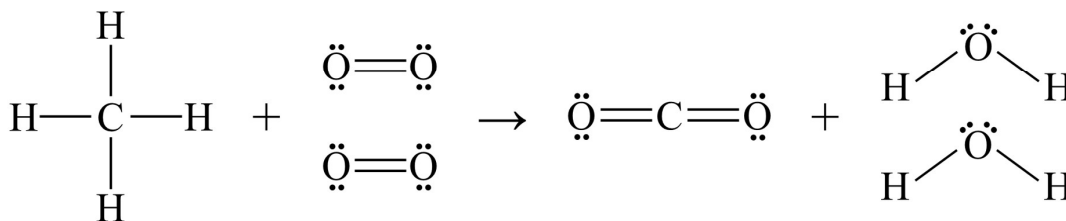
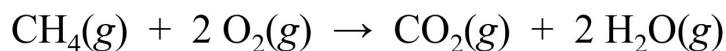
Bond energy data can be used to calculate the value of  $\Delta H_{rxn}$  for a chemical reaction, according to the following equation.

$$\Delta H_{rxn} = \sum (\text{bond enthalpies of bonds broken}) - \sum (\text{bond enthalpies of bonds formed})$$

Bond	Bond Enthalpy (kJ/mol)
C-H	413
O=O	498

Bond	Bond Enthalpy (kJ/mol)
C=O	799
O-H	463

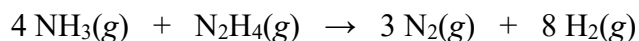
5. Use the bond energy values listed above to calculate the value of  $\Delta H_{rxn}$  for the reaction represented by the equation below.



Bond	Bond Enthalpy (kJ/mol)
H–H	436
N–H	391

Bond	Bond Enthalpy (kJ/mol)
N–N	163
N=N	418
N≡N	945

6. Use the bond energy values listed above to calculate the value of  $\Delta H_{rxn}$  for the reaction represented by the equation below.



## 6.8 Enthalpy of Formation

Essential knowledge statement from the AP Chemistry CED:

- Tables of standard enthalpies of formation can be used to calculate the standard enthalpies of reactions.

$$\Delta H_{rxn}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants})$$

The quantity  $\Delta H_{rxn}^{\circ}$  represents the *standard enthalpy change*, or the enthalpy change for a process occurring at **standard conditions**, which are defined as follows.

Standard Conditions		
gas pressure = 1 atm	solution concentration = 1 mol/L	temperature = 25°C

The **standard enthalpy of formation** ( $\Delta H_f^{\circ}$ ) of a substance is defined as the enthalpy change associated with the formation of one mole of a substance from its constituent elements in their standard states under standard conditions.

7. The standard enthalpy of formation,  $\Delta H_f^{\circ}$ , for nitrogen monoxide,  $\text{NO}(\text{g})$ , is 90.3 kJ/mol. Based on this information, answer the following questions.
- (a) Write a balanced chemical equation for the formation of **1 mole** of  $\text{NO}(\text{g})$  from its constituent elements under standard conditions.

7. (continued)

- (b) Determine the value of  $\Delta H_{rxn}^{\circ}$ , in units of kJ/mol<sub>rxn</sub>, for the equation shown below. Include the appropriate algebraic sign of  $\Delta H^{\circ}$  with your answer.



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Substance	Standard Enthalpy of Formation (kJ/mol)
H <sub>2</sub> O(l)	-285.8
H <sub>2</sub> O(g)	-241.8

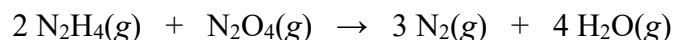
8. Use the information above to answer the following questions.

- (a) How much energy is associated with the process of 36.032 g H<sub>2</sub>O changing from gas to a liquid under standard conditions?
- (b) Does the answer in part (a) represent heat that flows from the surroundings to the sample of H<sub>2</sub>O or heat that flows from the sample of H<sub>2</sub>O to the surroundings?

9. The standard enthalpy of formation ( $\Delta H_f^{\circ}$ ) for an element in its standard state is equal to \_\_\_\_\_.

Substance	Standard Enthalpy of Formation (kJ/mol)
N <sub>2</sub> H <sub>4</sub> (g)	95.4
N <sub>2</sub> O <sub>4</sub> (g)	9.2
H <sub>2</sub> O(g)	-241.8

10. Using the table of standard enthalpies of formation above, calculate the value of  $\Delta H_{rxn}^{\circ}$  for the equation shown below. Include the appropriate algebraic sign of  $\Delta H_{rxn}^{\circ}$  and the correct units with your answer.





Substance	Standard Enthalpy of Formation, $\Delta H_f^\circ$ (kJ/mol)
$\text{C}_8\text{H}_{18}(l)$	?
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(g)$	-241.8



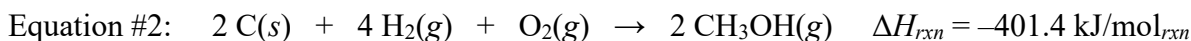
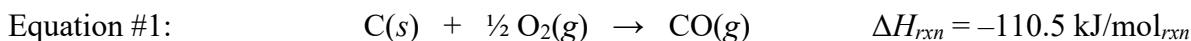
11. Use the information above to calculate standard enthalpy of formation,  $\Delta H_f^\circ$ , for  $\text{C}_8\text{H}_{18}(l)$ . Include the appropriate algebraic sign of  $\Delta H_f^\circ$  and the correct units with your answer.

## 6.9 Hess's Law

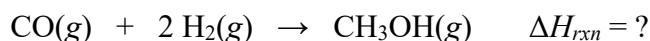
Essential knowledge statement from the AP Chemistry CED:

- Although the concept of "state function" is not required for the course, two principles of Hess's law should be understood. First, when a reaction is reversed, the enthalpy change stays constant in magnitude but becomes reversed in mathematical sign. Second, when two (or more) reactions are added to obtain an overall reaction, the individual enthalpy changes of each reaction are added to obtain the net enthalpy of the overall reaction.

Modification	How $\Delta H_{rxn}$ is Affected
The equation is reversed	The sign of $\Delta H_{rxn}$ is reversed.
The equation is multiplied by a constant N	The $\Delta H_{rxn}$ is multiplied by a constant N.
Two or more equations are added together, producing a new overall equation.	The values of $\Delta H_{rxn}$ from each equation are added together to determine the value of $\Delta H_{rxn}$ for the new overall equation.

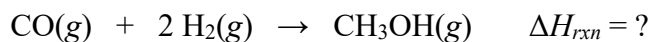


12. Equations #1 and #2 shown above can be modified in a certain way so that, when the modified versions of each equation are added together, the following equation will be formed as a result.



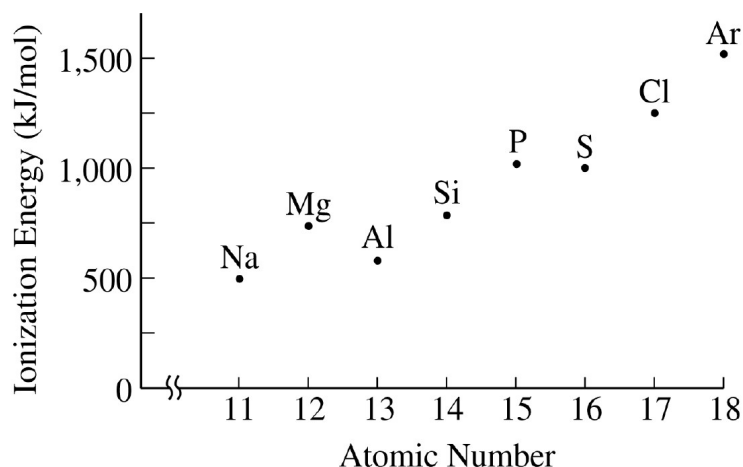
- (a) How should equation #1 be modified? \_\_\_\_\_
- (b) How should equation #2 be modified? \_\_\_\_\_

12. (continued)

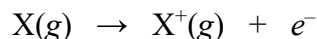


(c) Based on your answers to parts (a) and (b), write the modified versions of Equations #1 and #2 in the space below. Show the modified values of  $\Delta H_{rxn}$  next to each equation, and show how the equations can be added together to produce the equation shown above.

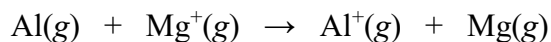
(d) Based on your answer to part (c), determine the value of  $\Delta H_{rxn}$  for the overall reaction.

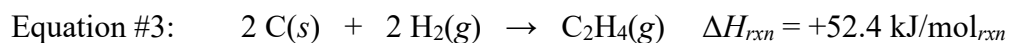
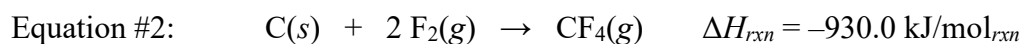
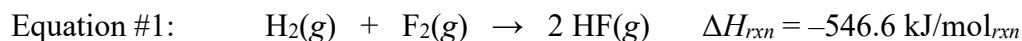


13. The first ionization energy of an element is the energy required to remove an electron from a gaseous atom of the element as shown in the general equation below.

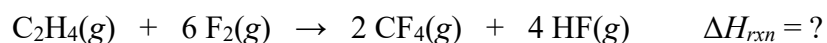


The values of the first ionization energies for the elements located in Period 3 are plotted on the graph shown above. On the basis of this information, do you predict that the equation shown below should be classified as endothermic or exothermic? Justify your answer.

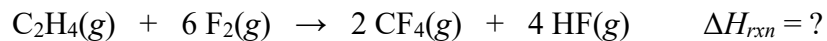




14. Equations #1, #2, and #3 shown above can be modified in a certain way so that, when the modified versions of each equation are added together, the following equation will be formed as a result.



- (a) How should equation #1 be modified? \_\_\_\_\_
- (b) How should equation #2 be modified? \_\_\_\_\_
- (c) How should equation #3 be modified? \_\_\_\_\_



- (d) Based on your answers to parts (a), (b), and (c), write the modified versions of Equations #1 – #3 in the space below. Show the modified values of  $\Delta H_{\text{rxn}}$  next to each equation, and show how the equations can be added together to produce the equation shown above.
- (e) Based on your answer to part (d), determine the value of  $\Delta H_{\text{rxn}}$  for the overall reaction.