# **ACTIVITY 4.3** Enthalpy Changes in Chemical Reactions

## LEARNING OUTCOMES

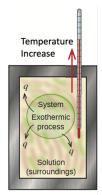
- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions

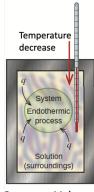
## Start Preparation

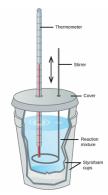
Review Textbook Sections 9.4

#### **VERY IMPORTANT INFORMATION**

Chemical processes involve the release or absorption of energy. Often this change in energy is in the form of heat or thermal energy. The amount of heat absorbed (endothermic) or released (exothermic) during a chemical process depends on the type of bonds present in the reactants and the products, and the intermolecular forces. We can measure this heat using calorimetry techniques, performing the reaction in a container and monitoring changes in temperature. We can do this in two main ways: at constant volume (sealed container) or at constant pressure (open container). Most chemistry experiments happen at constant pressure.







Constant Volume

**Constant Volume** 

**Constant Pressure** 

Because heat is a path function it matters very much how the heat is transferred. Thermodynamics defines two state functions to deal with these two cases. One of them is the Internal Energy, U, the other is called Enthalpy, represented by H. Here are the equations:

$$\Delta U = q + w = q - p\Delta V$$

But, if volume is constant,  $\Delta V = 0$  and  $\Delta U = q$ , meaning that if you measure the heat exchanged by a reaction that was performed in a sealed container, you measure the change in internal energy.

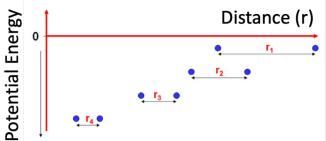
$$\Delta H = \Delta U + \Delta (PV)$$
 =  $q - p\Delta V + p\Delta V + V\Delta p$ 

We see that the second and the third terms cancel, and, if pressure is constant,  $\Delta p = 0$ , so that  $\Delta H = q$ , meaning that if you measure the heat exchanged by a reaction that was performed in a open container, you measure the change in enthalpy. Everything we talked about in the previous activity was at constant pressure, so all the heats we calculated were converted into  $\Delta H$  values instead of  $\Delta U$  values.

### **INFORMATION**

The exchange of energy in the forms of heat or light between a system and its surrounding is a common phenomenon during a chemical change. Energy as heat can be determined using calorimetry to determine if it is absorbed or released during the chemical reaction. Chemical reactions that release heat to the surroundings (**exothermic** processes) cause the temperature to increase, chemical reactions that absorb heat (**endothermic** processes) cause the temperature of the surroundings to decrease. Given that during an exothermic process the system loses energy in the form of heat (q), the energy lost is frequently represented as a negative number (e.g., q = -40 kJ/mol). For endothermic processes, the energy absorbed is indicated using positive quantities (e.g., q = +30 kJ/mol).

**Model 1**: The energy of an interaction between atoms.



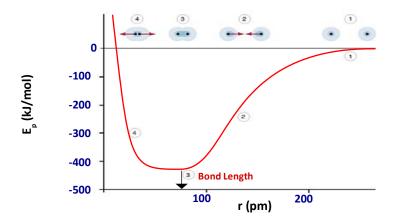
## **Key Questions:**

- 1. What type of energy does the chart depict for two hydrogen atoms?
- 2. What type of energy is the potential energy converted into as it is released when the two atoms *come closer* together as depicted in r<sub>4</sub> through r<sub>1</sub>?
- 3. What types of forces draw the two atoms closer to each other?
- 4. How close can the atoms be? What limits are there on the distance between two atoms? List all the forces and the interactions that form.
- 5. If the atoms are pushed together what type of interaction will increase? What will this do to the potential energy? Draw a line or label this on the plot above.

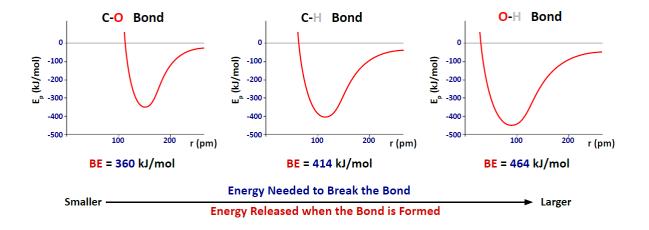
# End Preparation

#### **Model 2:** Bond formation between atoms

The stabilization of a chemical bond between two atoms is a stabilizing process in which the energy of the interacting atoms decreases. The delocalization of valance electrons in the bonding region lead to a more stable state with a lower potential energy. These atoms will move closer together losing potential energy until there is an equilibrium of the attractive forces between the nuclei and the electrons, and the repulsive forces of the two nuclei. As the potential energy is lowered the formation of a bond is an **exothermic** process, releases energy to the surroundings as heat. The energy released is the **bond energy**.



Different combinations of atoms will form bonds of varying potential energy. As a result, distance and potential energy difference will exist for any combination of bonded atoms.



## **Key Questions:**

1. What are the bond lengths for the C-O, C-H and O-H bonds? How much potential energy was lost when each of the bonds formed? What do you notice about the bond length and energy?

- 2. How much energy would be required to separate the C and O atoms in the bond? Which of the three bonds would require the most energy to separate the atoms?
- 3. If the C-O bond is broken and the oxygen forms a bond with hydrogen what will the difference in energy be? Be careful to consider the flow of energy in the system and give appropriate signs to the numerical values.

## Model 3: Thermochemical equations

A compilation of **average bond energies** is listed in the table below. A larger table is given at the end of this document. It is possible to use average bond energies to estimate the energy change of a reaction without having to do a calorimetry experiment with the reaction in the lab!

Bond	BE (KJ/mol)				
Н-Н	436				
C-H	414				
C-C	347				
C=C	611				
C≣C	737				

Bond	BE (KJ/mol)				
C-Cl	339				
C-N	305				
C=N	615				
C-O	360				
C=O	736*				

Bond	BE (KJ/mol)			
C-S	259			
N-H	389			
N-N	163			
N≡N	946			
N-O	201			

Bond	BE (KJ/mol)				
N=O	607				
О-Н	464				
0-0	142				
0=0	498				
S-H	368				

\*799 in CO

**Important!** Reaction energies ( $\Delta H_{reaction}$ , if working at constant pressure) obtained through this method are only an approximation of the true  $\Delta H$  for two reasons: **a**) the values in the table are averages and **b**) intermolecular forces aren't taken into account. Despite this, the method is useful as a rough value and

# **Key Questions:**

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

1. Draw the Lewis structures of each of the molecules in the reaction.

- 2. How many types of bonds involving elements are in the reactants? Does stoichiometry matter? For the combustion reaction of methane with oxygen, what is the energy associated with breaking all the bonds of the reactants? What sign should be assigned to this energy?
- 3. What is the energy for the formation of all the bonds in the products? What sign should be assigned to this energy?
- 4. What is the overall reaction enthalpy? Is it exothermic or endothermic? Why?

This process can be summarized:

 $\Delta H_{rxn} = \Sigma (Energies of Bonds Broken) - \Sigma (Energies of bonds formed)$ 

The amount of energy that can be released or absorbed during a chemical process is derived from the bonds that comprise the reactants and the bonds that are formed by the products. This indicates that the energy will be proportional to the amounts of the substances. The energy that would be transferred can be represented as part of a chemical equation.

## **Exercises:**

When backpacking a pressurized stove may be used to boil water and cook food. These stoves often use a blend of 80% isobutane and 20% propane.

$$2 C_4 H_{10} + 13 O_2 \longrightarrow 8 CO_2 + 10 H_2 O$$
  $\Delta H = -5,228 kJ$ 

- 1. How much energy is released per mole of butane consumed in the presence of excess oxygen?
- 2. Write an expression for how much energy is released per mole of butane combusted with excess oxygen?
- 3. What if 0.25 moles of butane are combusted, how much energy is released?
- 4. How much energy is released if 36 grams of water is formed?
- 5. Using the bond energies, determine the enthalpy that is released when combusting propane? What would the energy content be for the fuel canister per gram of fuel consumed?

$$C_3H_8 + 5 O_2 \longrightarrow 3 CO_2 + 4 H_2O$$

## **PONDER & PROVE**

Complete ALEKS HW 4.3 End-of-Chapter problems in Section 9.4

# Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C-S	260	F–Cl	255
H–C	415	C–CI	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N = N	418	Si–Cl	359
H–P	320	N = N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N-CI	200	P-Cl	330
C–C	345	N–Br	245	P–Br	270
C = C	611	0–0	140	P–I	215
$C \equiv C$	837	O = O	498	S–S	215
C–N	290	O-F	160	S–Cl	250
C = N	615	O–Si	370	S–Br	215
C ≡ N	891	0–P	350	CI-CI	243
C–O	350	O-CI	205	Cl–Br	220
C = 0	741	O–I	200	CI–I	210
C≡O	1080	F–F	160	Br–Br	190