

## Chapter Six: THERMOCHEMISTRY

### The Nature of Energy

- **Thermodynamics** is the study of energy and its transformations.
- **Thermochemistry** is the study of the relationship between chemical reactions and energy changes involving heat.



### Energy and Work

- **Energy** is the capacity to do work or to transfer heat. It has the ability to make things happen.
  - SI unit is the **Joule, J**
  - Traditionally, we use the **calorie**  
 $1 \text{ cal} = 4.184 \text{ J}$       $1 \text{ nut. Cal} = 1,000 \text{ cal}$
- **Work** is energy used to cause an object with mass to move.  
 $\text{work} = \text{Force} \times \text{distance}$

### Kinetic vs. Potential Energy

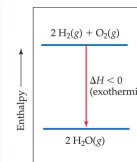
- **Potential Energy** is the energy an object possesses by virtue of its position or composition.
- **Kinetic Energy** is the energy of motion  
 $\text{K.E.} = \frac{1}{2}mv^2$  where  $m$  = mass and  $v$  = velocity



(a)



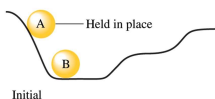
(b)



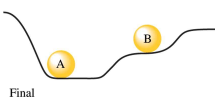
Notes 6.1 2c

### Initial vs. Final Position

In the initial position, ball A has a higher potential energy than ball B.



After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.



### Temperature vs. Heat

- **Temperature** is a property that reflects the *random motions* of the particles in a particular substance.
- **Heat** involves the *transfer of energy* between two objects due to a temperature difference.
  - Heat is not a substance contained by an object, although we often talk of heat as if it were true.
  - Heat is transferred from hotter objects to colder ones.



## Chemical Energy

- The **system** is the part of the universe on which we wish to focus attention.
- The **surroundings** are everything else.
- Energy gained by the surroundings must be equal to energy lost by the system (and visa versa).

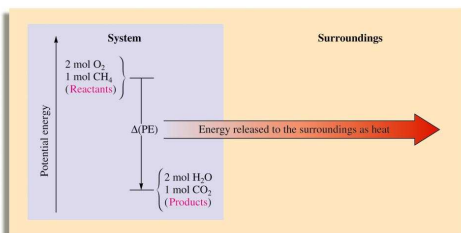
Notes 6.1 2e

## State Function

- **State Function** is a property that is independent of the pathway. It depends only on the initial and final states of the system.
  - Distance between two cities depends on route (depends on pathway – not a state function)
  - Altitude difference between two cities (does not depend on whether you fly or drive – state function)
- Energy is a state function
  - The internal energy of 50 g of liquid water at 25°C does not depend on whether we cool 50 g from 100°C to 25°C or if we heat 50 g of 0°C to 25°C .
  - Work and heat are not state functions

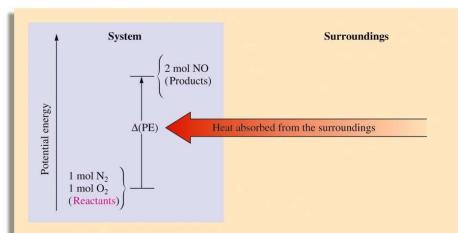
Notes 6.1 2f

## Exothermic Process



In any exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat. Since exothermic processes transfer heat to the surroundings, the reaction feels hot.

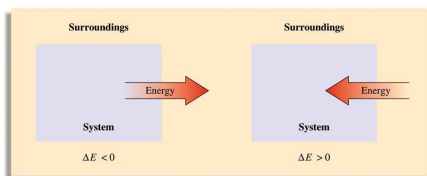
## Endothermic Process



In an endothermic reaction, the situation is reversed. Energy flows into the system as heat and is used to increase the potential energy of the system. Products have a higher potential energy. Since energy is absorbed from surroundings, reaction feels cold.

## Internal Energy

- The total energy of a system is called the **internal energy**. It is the sum of all the kinetic and potential energies of all the components of the system. Absolute energy cannot be measured, only changes in internal energy can.
- Change in internal energy,  $\Delta E = E_{\text{final}} - E_{\text{initial}}$



$\Delta E = -$  means system loses E

$\Delta E = +$  means system gains E

- **The First Law of Thermodynamics** states that energy cannot be created or destroyed.

- The First Law of Thermodynamics is the law of Conservation of Energy. That is, the energy of system + surroundings is constant.
- Thus, any energy transferred from a system must be transferred to the surroundings (and vice versa).

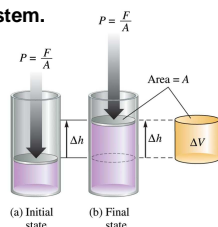
- Change in energy is equals:

$$\Delta E = q + w$$

where  $\Delta E$  represents change in the systems internal energy,  $q$  represents heat, and  $w$  represents work.

## Work by a Gas

- A common type of work associated with chemical processes is work done by a gas through expansion or compression.
- It is always relative to the system.**
- When the system expands, it is doing positive work on the surroundings, therefore it is doing negative work on the system.
- When the system contracts, the surroundings have done work on the system, therefore there is positive work done on the system.



## Pressure-Volume Work

- The expansion/contraction of a gas against constant external pressure can be represented by the equation:

$$w = -P\Delta V$$

- Where  $w$  = work done by/on a system,  $P$  = pressure, and  $\Delta V$  = final minus initial volume.

- conversion factor **101.3 J = 1 L atm**

## Discuss

Which of the following performs more work?

- A gas expanding against a pressure of 2 atm from 1.0 L to 4.0 L
- A gas expanding against a pressure of 3 atm from 1.0 L to 3.0 L

## The importance of Signs

$$\Delta E = q + w \quad w = -P\Delta V \quad \Delta V = V_f - V_i$$

Process	Sign
work done by system on surroundings (gas expands, $\Delta V = +$ )	-
work done on the system by surroundings (gas contracts, $\Delta V = -$ )	+
heat absorbed by the surroundings from the system (exothermic)	-
heat absorbed by the system from surroundings (endothermic)	+

q	+	w	=	$\Delta E$	
+		+		+	energy leaving the system
+		-			depends on size of q and w
-		+			depends on size of q and w
-		-		-	energy entering the system

Practice 6.1 A-G

## Enthalpy

- The term **enthalpy, H**, is used to represent  $E + PV$ , which occurs at constant external pressure.
  - In a way, enthalpy can be considered to be energy with work taken out.
- Change in enthalpy,  $\Delta H$ , will represent the exchange of heat between a system and its surroundings at constant external pressure.
- Enthalpy is often referred to as "heat content"
  - Heat transferred from surroundings to system has a  $+\Delta H$
  - Heat transferred from the system to surroundings has a  $-\Delta H$
- Enthalpy is a state function.

## Change in Enthalpy

Since  $P$  is normally constant

$$\Delta H = \Delta E + P\Delta V$$

if  $P\Delta V$  is sufficiently small, then

$$\Delta H = \Delta E$$

The unit for  $\Delta H$  is usually J/mol or kJ/mol.

## Standard State

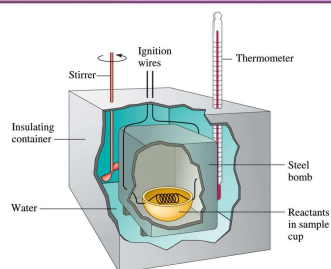
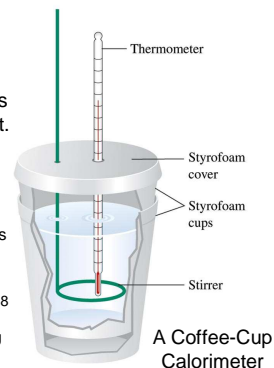
- To compare heats of reaction for different reactions, it is necessary to know the temperatures at which heats of reaction are measured and the physical states of the reactants and products.
- Measurements have been made and tables constructed of heats of reaction with reactants in their "standard states." See Appendix Four
- Standard state** is the most stable physical state of reactants at 1 atmosphere of pressure and a specified temperature—usually 25°C.
  - Standard enthalpy change,  $\Delta H^\circ$

**Calorimetry**, the science of measuring heat, is based on observing the temperature change when a body absorbs or discharges energy as heat.

**Calorimeter** is an apparatus that measure heat flow.

The amount of heat an object gains or loses is directly proportional to temperature change.

**Calorie** = a unit of energy equal to 4.18 joules; formerly defined as the energy needed to raise the temperature of 1 g of water by 1 degree C.



A bomb calorimeter is a sealed insulated container, used for measuring energy released during combustions of substances. A known amount of substance is ignited inside the calorimeter in an atmosphere of pure oxygen, and undergoes complete combustion at constant volume. The resultant rise in temperature is related to the energy released by the reaction ( $\text{J kg}^{-1}$ )

## Heat Capacity

- Heat capacity, C**, with units of  $\text{J/K}$  or  $\text{J/}^\circ\text{C}$  is the amount of energy required to raise the temperature of an object 1 K or  $1^\circ\text{C}$ .
  - Heat capacity is an extensive property because its value is proportional to the amount of material in the object;
  - For example, a bathtub of water has a greater heat capacity than a cup of water.

## Specific Heat Capacity

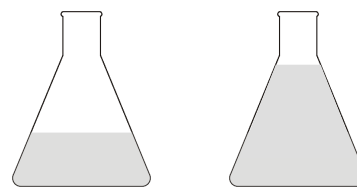
- Specific Heat Capacity, c or s** = heat capacity given per gram of substance
  - units are  $\text{J/}^\circ\text{C} \cdot \text{g}$  or  $\text{J/K} \cdot \text{g}$
- Molar Heat Capacity** = heat capacity given per mole of substance
  - Units are  $\text{J/}^\circ\text{C} \cdot \text{mol}$  or  $\text{J/K} \cdot \text{mol}$
- Heat, q** =  $c \times m \times \Delta T$

**TABLE 6.1 The Specific Heat Capacities of Some Common Substances**

Substance	Specific Heat Capacity ( $\text{J/}^\circ\text{C} \cdot \text{g}$ )
$\text{H}_2\text{O}(l)$	4.18
$\text{H}_2\text{O}(s)$	2.03
$\text{Al}(s)$	0.89
$\text{Fe}(s)$	0.45
$\text{Hg}(l)$	0.14
$\text{C}(s)$	0.71

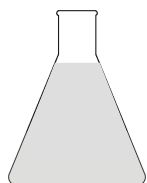
Notes + Practice 6.2 C-E

You have two flasks of liquid: one has 50.0 ml of  $\text{H}_2\text{O}$  and the other has 100.0 ml of  $\text{H}_2\text{O}$ . Assuming both are at  $20^\circ\text{C}$ , if 2,000.0 J of energy are applied to each flask, will each have the same change in temperature?

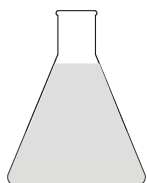


Do some calculations to support your answer.

Similar scenario: you have two flasks of liquid: one has 100.0 ml of H<sub>2</sub>O and the other has 100.0 ml of ethanol. Assuming both are at 20°C, if 2,000.0 J of energy are applied to each flask, will each have the same change in temperature?



100.0 ml of H<sub>2</sub>O  
specific heat = 4.18 J/g·°C

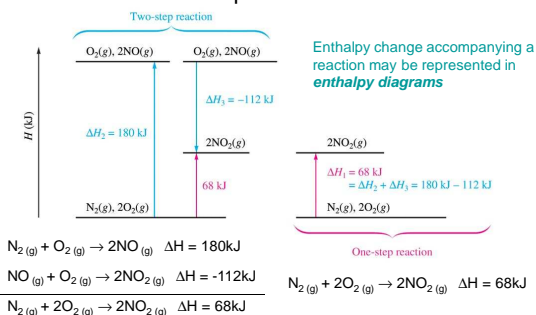


100.0 ml of ethanol  
specific heat = 2.46 J/g·°C

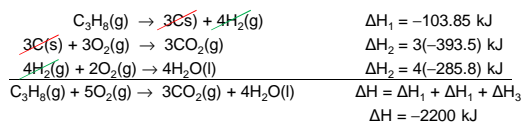
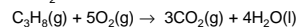
## Hess's Law

- **Hess's Law** states that if a reaction is carried out in a series of steps,  $\Delta H$  for the reaction is the sum of  $\Delta H$  for each of the steps.
  - The total change in enthalpy is independent of the number of steps (state function).
  - This means that in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.
  - The heat for a given reaction is the algebraic sum of the heats of any sequence reactions which yield the reaction in question.

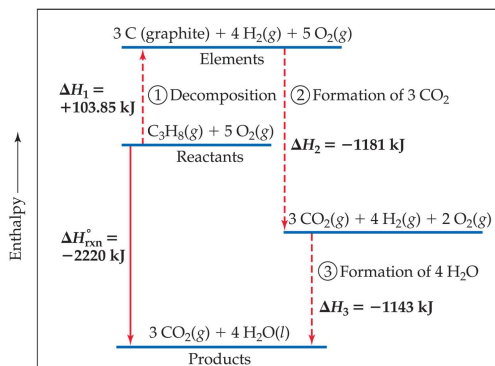
## The Principle of Hess's Law



- For example, consider the combustion of propane gas, C<sub>3</sub>H<sub>8</sub>, with oxygen to form CO<sub>2</sub> and water.



**Let's Look at the Enthalpy Diagram for this reaction**



## Enthalpies of Reactions

- 1) Enthalpy is an extensive property
  - The magnitude of  $\Delta H$  is proportional to the amount of reactant consumed in the process
- 2) The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to  $\Delta H$  for the reverse reaction
  - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \quad \Delta H = -483.6 \text{ kJ}$
  - $2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = +483.6 \text{ kJ}$
- 3) The enthalpy change for a reaction depends on the state of the reactants and products
  - $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \quad \Delta H = 88 \text{ kJ}$

## Hints for Using Hess's Law

- Work backward from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at your disposal.
- Reverse any reactions as needed to give the required reactants and products
- Multiply reactions to give the correct number of reactants and products.

Practice 6.3 A-C

## Enthalpies of Formation

- Many experimental data are tabulated according to type of process:
  - **Enthalpies of vaporization** ( $\Delta H$  for converting liquids to gases)
  - **Enthalpies of combustion** ( $\Delta H$  for combusting substance in oxygen)
  - A particularly important process used for tabulating thermochemical data is the formation of a compound from its constituent elements.
    - This is called the **Enthalpy of Formation** (or heat of formation) and is labeled  $\Delta H_f$

## Enthalpies of Formation

- The magnitude of any enthalpy change depends on the conditions of temperature, pressure and state of the reactants and products.
- In order to compare the enthalpies of different reactions, we must define a set of conditions, called the **standard state**, at which most enthalpies are tabulated.
  - The standard state of a substance is its pure form at 1 atm and 25°C (298 K)

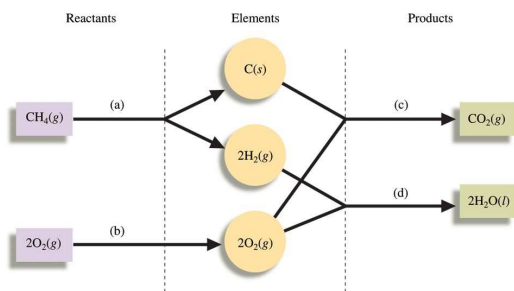
## Enthalpies of Formation

- The **standard enthalpy change** of a reaction is when all reactants and products are in their standard states and is defined as  $\Delta H^\circ$  **Notes 6.4-1**
- The **standard enthalpy of formation** of a compound ( $\Delta H_f^\circ$ ) is the change in enthalpy for the reactions that forms **one mole of the compound from its elements, with all substances in their standard state.**

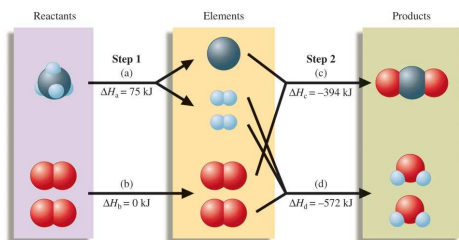
## Standard States

- **Compound**
  - For a gas, pressure is exactly 1 atmosphere.
  - For a solution, concentration is exactly 1 molar.
  - Pure substance (liquid or solid)
- **Element**
  - The form  $[N_2(g), K(s)]$  in which it exists at 1 atm and 25°C.
  - **The standard enthalpy of formation of the most stable form of an element is zero.**

## Pathway for the Combustion of Methane



A Schematic Diagram of the Energy Changes for the Reaction  
 $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$



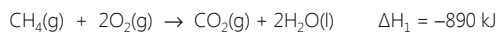
## Change in Enthalpy

- Can be calculated from enthalpies of formation of reactants and products.

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

NOTE – the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. Also if a reaction is reversed, the sign of  $\Delta H$  is reversed

## Pathway for the Combustion of Methane



$$\Delta H^{\circ}_{\text{rxn}} = \sum n_p \Delta H^{\circ}_{\text{products}} - \sum n_r \Delta H^{\circ}_{\text{reactants}}$$

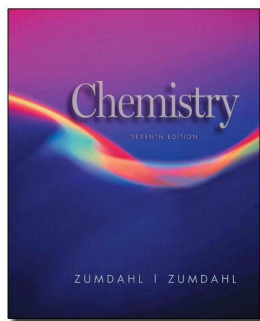
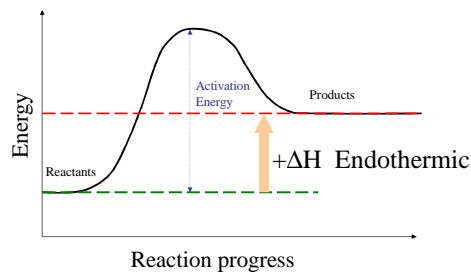
$$\begin{aligned} \Delta H^{\circ}_{\text{products}} &= [(n_{\text{CO}_2})(\Delta H_f^{\circ} \text{CO}_2) + (n_{\text{H}_2\text{O}})(\Delta H_f^{\circ} \text{H}_2\text{O})] \\ &= [(1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-286 \text{ kJ/mol})] \\ &= [(-393.5 \text{ kJ}) + (-572 \text{ kJ})] = [-965.5 \text{ kJ}] \end{aligned}$$

$$\begin{aligned} \Delta H^{\circ}_{\text{reactants}} &= [(n_{\text{CH}_4})(\Delta H_f^{\circ} \text{CH}_4) + (n_{\text{O}_2})(\Delta H_f^{\circ} \text{O}_2)] \\ &= [(1 \text{ mol})(-75 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})] \\ &= [(-75 \text{ kJ}) + (0 \text{ kJ})] = [-75 \text{ kJ}] \end{aligned}$$

**Practice 6.4 A-C**

$$\Delta H^{\circ}_{\text{rxn}} = [-965.5 \text{ kJ}] - [-75 \text{ kJ}] = -890.5 \text{ kJ} \quad (\text{similar to before})$$

## Endothermic Reaction



Sources  
of  
Energy

Answer Questions 6.5 & 6.6