



# General Chemistry

CHEM 101  
(3+1+0)

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*Chapter 4*

## Thermochemistry

## The Nature of Energy and Types of Energy

**Energy** is the capacity to do work.

- **Radiant energy** comes from the sun and is earth's primary energy source. (*Solar energy*)
- **Thermal energy** is the energy associated with the random motion of atoms and molecules.
- **Chemical energy** is the energy stored within the bonds of chemical substances.
- **Nuclear energy** is the energy stored within the collection of neutrons and protons in the atom.
- **Potential energy** is the energy available by virtue of an object's position

## Energy Changes in Chemical Reactions

**Heat** is the transfer of **thermal energy** between two bodies that are at different temperatures.

**Temperature** is a measure of the **thermal energy**.

Temperature ~~≠~~ Thermal Energy

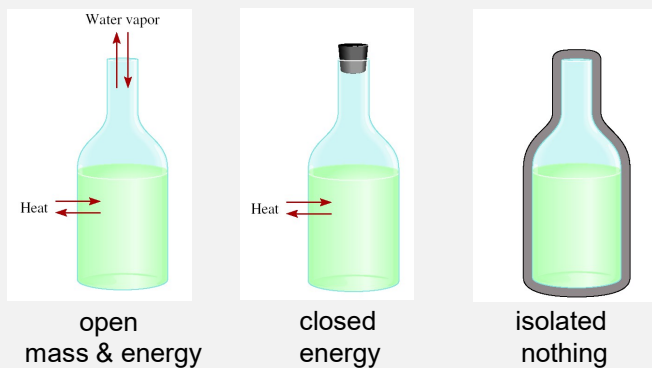


## Energy Changes in Chemical Reactions

**Thermochemistry** is the study of heat change in chemical reactions.

The **system** is the specific part of the universe that is of interest in the study.

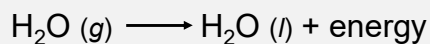
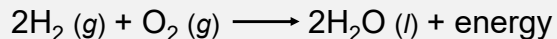
The **surroundings** are the rest of the universe outside the system.



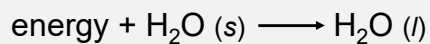
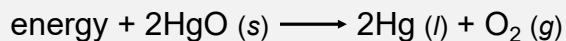
**Exchange:**

## Energy Changes in Chemical Reactions

**Exothermic process** is any process that gives off heat – transfers thermal energy from the system to the surroundings.

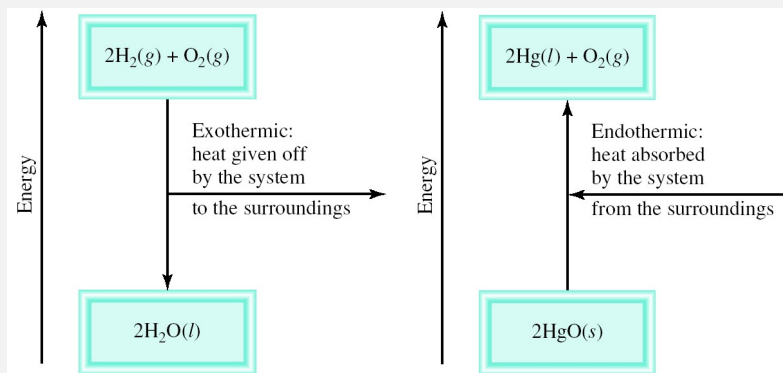


**Endothermic process** is any process in which heat has to be supplied to the system from the surroundings.



## Energy Changes in Chemical Reactions

### Schematic of Exothermic and Endothermic Processes



## Introduction to Thermodynamics

**Thermodynamics** is the scientific study of the interconversion of heat and other kinds of energy.

**State functions** are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$\Delta P = P_{\text{final}} - P_{\text{initial}}$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

## Introduction to Thermodynamics

**First law of thermodynamics** - energy can be converted from one form to another, but cannot be created or destroyed.

The transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero:

$$\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

or

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$$

If one system undergoes an energy change  $\Delta E_{\text{sys}}$ , the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign ( $-\Delta E_{\text{surr}}$ );

Chemical energy **lost** by combustion = Energy **gained** by the surroundings  
                                           system                                                 surroundings



Exothermic chemical reaction!

## Introduction to Thermodynamics

Another form of the *first law* for  $\Delta E_{\text{system}}$

$$\Delta E = q + w$$

$\Delta E$  is the change in internal energy of a system

$q$  is the heat exchange between the system and the surroundings

$w$  is the work done on (or by) the system

$w = -P\Delta V$  when a gas expands against a constant external pressure

**TABLE 6.1** Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	-
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	-

If a system loses heat to the surroundings or does work on the surroundings, its internal energy to decrease because those are energy-depleting processes; both  $q$  and  $w$  are negative.

If heat is added to the system or if work is done on the system, the internal energy of the system would increase; both  $q$  and  $w$  are positive.

## Introduction to Thermodynamics

### Work and Heat

$$w = F \times d$$

$$w = -P \Delta V$$

$$P \times V = \frac{F}{d^2} \times d^3 = F \times d = w$$

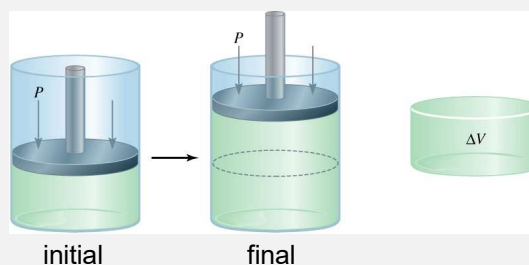
$$\Delta V > 0$$

$$-P \Delta V < 0$$

$$w_{\text{sys}} < 0$$

Work is not a state function.

$$\Delta w \neq w_{\text{final}} - w_{\text{initial}}$$



The units for work done by or on a gas are liters atmospheres.

$$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$$

## Introduction to Thermodynamics

A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

$$w = -P \Delta V$$

$$(a) \quad \Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L} \quad P = 0 \text{ atm}$$

$$W = -0 \text{ atm} \times 3.8 \text{ L} = 0 \text{ L} \cdot \text{atm} = 0 \text{ joules}$$

$$(b) \quad \Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L} \quad P = 3.7 \text{ atm}$$

$$w = -3.7 \text{ atm} \times 3.8 \text{ L} = -14.1 \text{ L} \cdot \text{atm}$$

$$w = -14.1 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -1430 \text{ J}$$

## Enthalpy of Chemical Reactions

### Enthalpy and First law of thermodynamics;

If a chemical reaction is run at constant volume, then  $\Delta V = 0$

$$\Delta E = q + w$$

$$\Delta E = q - P\Delta V$$

$$\Delta E = q_v$$

### Enthalpy

A new thermodynamic function of a system called *enthalpy (H)*

$$H = E + PV$$

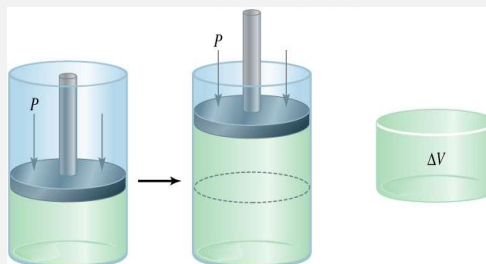
**At constant pressure:**

$$\Delta E = q_p - P\Delta V$$

$$q = \Delta H \quad \text{and} \quad w = -P\Delta V$$

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

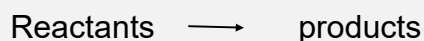
$$\Delta H = \Delta E + P\Delta V$$



## Enthalpy of Chemical Reactions

### Enthalpy of Chemical Reactions

For any reaction of the type



*Enthalpy (H)* is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

*Enthalpy of reaction, ΔH*, as the difference between the enthalpies of the products and the enthalpies of the reactants:

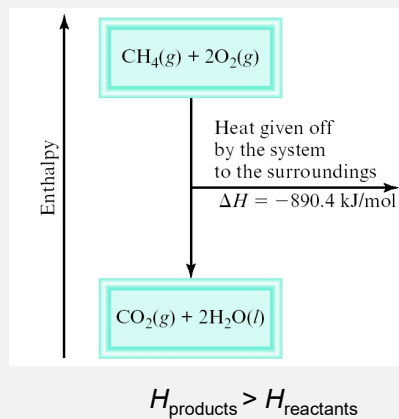
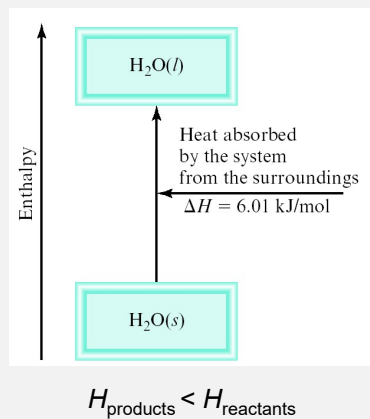
$$\Delta H = H(\text{products}) - H(\text{reactants})$$

$\Delta H$  = heat given off or absorbed during a reaction **at constant pressure**

## Enthalpy of Chemical Reactions

### Enthalpy of Chemical Reactions

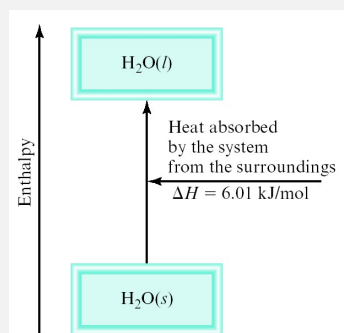
- For an **endothermic process**  $\Delta H$  is positive (that is,  $\Delta H > 0$ ).
- For an **exothermic process**  $\Delta H$  is negative (that is,  $\Delta H < 0$ ).



## Enthalpy of Chemical Reactions

### Thermochemical Equations

**Thermochemical equations**, which show the enthalpy changes as well as the mass relationships.



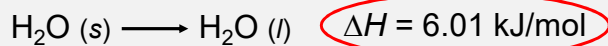
Is  $\Delta H$  negative or positive?

System absorbs heat

Endothermic

$\Delta H > 0$

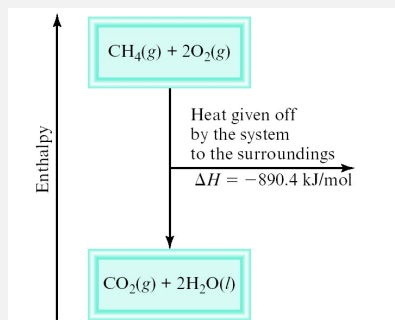
6.01 kJ are absorbed for every 1 mole of ice that melts at 0°C and 1 atm.





## Enthalpy of Chemical Reactions

### Thermochemical Equations



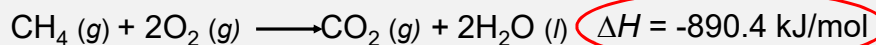
Is  $\Delta H$  negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

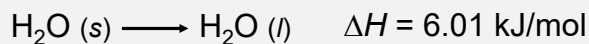
890.4 kJ are released for every 1 mole of methane that is combusted at 25°C and 1 atm.



## Enthalpy of Chemical Reactions

### Thermochemical Equations

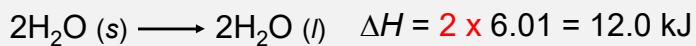
- The stoichiometric coefficients always refer to the number of moles of a substance



- If you reverse a reaction, the sign of  $\Delta H$  changes



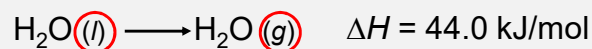
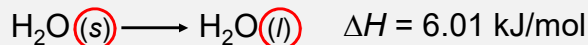
- If you multiply both sides of the equation by a factor  $n$ , then  $\Delta H$  must change by the same factor  $n$ .



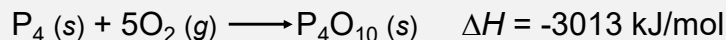
## Enthalpy of Chemical Reactions

### Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.



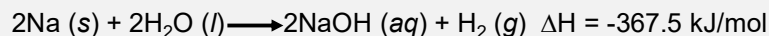
How much heat is evolved when 266 g of white phosphorus ( $\text{P}_4$ ) burn in air?



$$266 \text{ g } \cancel{\text{P}_4} \times \frac{1 \text{ mol } \cancel{\text{P}_4}}{123.9 \text{ g } \cancel{\text{P}_4}} \times \frac{3013 \text{ kJ}}{1 \text{ mol } \cancel{\text{P}_4}} = 6470 \text{ kJ}$$

## Enthalpy of Chemical Reactions

### A Comparison of $\Delta H$ and $\Delta E$

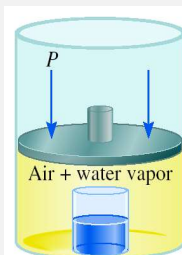


$$\Delta E = \Delta H - P\Delta V \quad \text{At } 25^\circ\text{C}, 1 \text{ mole } \text{H}_2 = 24.5 \text{ L at } 1 \text{ atm}$$

$$P\Delta V = 1 \text{ atm} \times 24.5 \text{ L} = 2.5 \text{ kJ}$$

$$\Delta E = -367.5 \text{ kJ/mol} - 2.5 \text{ kJ/mol} = -370.0 \text{ kJ/mol}$$

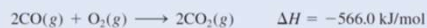
*The reason  $\Delta H$  is smaller than  $\Delta E$  in magnitude is that some of the internal energy released is used to do gas expansion work, so less heat is evolved.*



## Enthalpy of Chemical Reactions

### EXAMPLE 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO<sub>2</sub> at 1 atm and 25°C:



**Strategy** We are given the enthalpy change,  $\Delta H$ , for the reaction and are asked to calculate the change in internal energy,  $\Delta E$ . Therefore, we need Equation (6.10). What is the change in the number of moles of gases?  $\Delta H$  is given in kilojoules, so what units should we use for  $R$ ?

**Solution** From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

$$\begin{aligned} \Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 \\ &= -1 \end{aligned}$$

Using 8.314 J/K · mol for  $R$  and  $T = 298 \text{ K}$  in Equation (6.10), we write

$$\begin{aligned} \Delta E &= \Delta H - RT\Delta n \\ &= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298 \text{ K})(-1) \\ &= -563.5 \text{ kJ/mol} \end{aligned}$$

**Check** Knowing that the reacting gaseous system undergoes a compression (3 moles to 2 moles), is it reasonable to have  $\Delta H > \Delta E$  in magnitude?

**Practice Exercise** What is  $\Delta E$  for the formation of 1 mole of CO at 1 atm and 25°C?



## Enthalpy of Chemical Reactions

### A Comparison of $\Delta H$ and $\Delta E$

To calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature

$$\begin{aligned} \Delta E &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ &= \Delta H - RT\Delta n \end{aligned}$$

## Calorimetry: specific heat and heat capacity

The **specific heat ( $s$ )** of a substance is the amount of heat ( $q$ ) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

The **heat capacity ( $C$ )** of a substance is the amount of heat ( $q$ ) required to raise the temperature of **a given quantity ( $m$ )** of the substance by **one degree** Celsius.

**TABLE 6.2**  
The Specific Heats of Some Common Substances

Substance	Specific Heat ( $\text{J/g} \cdot ^\circ\text{C}$ )
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H <sub>2</sub> O	4.184
C <sub>2</sub> H <sub>5</sub> OH (ethanol)	2.46

$$C = m \times s$$

Heat ( $q$ ) absorbed or released:

$$q = m \times s \times \Delta t$$

$$q = C \times \Delta t$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

## Calorimetry: specific heat and heat capacity

How much heat is given off when an 869 g iron bar cools from 94°C to 5°C?

$$s \text{ of Fe} = 0.444 \text{ J/g} \cdot ^\circ\text{C}$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^\circ\text{C} - 94^\circ\text{C} = -89^\circ\text{C}$$

$$q = ms\Delta t = 869 \cancel{\text{g}} \times 0.444 \text{ J/g} \cdot ^\circ\text{C} \times -89 \cancel{^\circ\text{C}} = -34,000 \text{ J}$$



## Calorimetry: specific heat and heat capacity

### EXAMPLE 6.5

A 466-g sample of water is heated from 8.50°C to 74.60°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

**Strategy** We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed ( $q$ ).

**Solution** Using Equation (6.12), we write

$$\begin{aligned} q &= ms\Delta t \\ &= (466 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(74.60^\circ\text{C} - 8.50^\circ\text{C}) \\ &= 1.29 \times 10^5 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 129 \text{ kJ} \end{aligned}$$

**Check** The units g and °C cancel, and we are left with the desired unit kJ. Because heat is absorbed by the water from the surroundings, it has a positive sign.

**Practice Exercise** An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

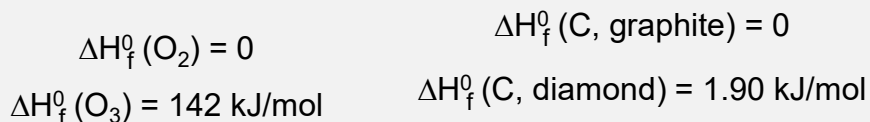
## Standard Enthalpy of Formation and Reaction

*Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?*

Establish an arbitrary scale with the **standard enthalpy of formation** ( $\Delta H_f^\circ$ ) as a reference point for all enthalpy expressions.

**Standard enthalpy of formation** ( $\Delta H_f^\circ$ ) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

The standard enthalpy of formation of any element in its most stable form is zero.



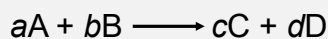
## Standard Enthalpy of Formation and Reaction

**TABLE 6.4** Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	$\Delta H_f^\circ$ (kJ/mol)	Substance	$\Delta H_f^\circ$ (kJ/mol)
Ag(s)	0	H <sub>2</sub> O <sub>2</sub> (l)	-187.6
AgCl(s)	-127.0	Hg(l)	0
Al(s)	0	I <sub>2</sub> (s)	0
Al <sub>2</sub> O <sub>3</sub> (s)	-1669.8	HI(g)	25.9
Br <sub>2</sub> (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO <sub>3</sub> (s)	-1112.9
C(diamond)	1.90	N <sub>2</sub> (g)	0
CO(g)	-110.5	NH <sub>3</sub> (g)	-46.3
CO <sub>2</sub> (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO <sub>2</sub> (g)	33.85
CaO(s)	-635.6	N <sub>2</sub> O(g)	81.56
CaCO <sub>3</sub> (s)	-1206.9	N <sub>2</sub> O <sub>4</sub> (g)	9.66
Cl <sub>2</sub> (g)	0	O(g)	249.4
HCl(g)	-92.3	O <sub>2</sub> (g)	0
Cu(s)	0	O <sub>3</sub> (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F <sub>2</sub> (g)	0	S(monoclinic)	0.30
HF(g)	-271.6	SO <sub>2</sub> (g)	-296.1
H(g)	218.2	SO <sub>3</sub> (g)	-395.2
H <sub>2</sub> (g)	0	H <sub>2</sub> S(g)	-20.15
H <sub>2</sub> O(g)	-241.8	Zn(s)	0
H <sub>2</sub> O(l)	-285.8	ZnO(s)	-348.0

## Standard Enthalpy of Formation and Reaction

The *standard enthalpy of reaction* ( $\Delta H_{\text{rxn}}^0$ ) is the enthalpy of a reaction carried out at 1 atm.



$$\Delta H_{\text{rxn}}^0 = [c\Delta H_f^0(\text{C}) + d\Delta H_f^0(\text{D})] - [a\Delta H_f^0(\text{A}) + b\Delta H_f^0(\text{B})]$$

$$\Delta H_{\text{rxn}}^0 = \sum n\Delta H_f^0(\text{products}) - \sum m\Delta H_f^0(\text{reactants})$$

## Standard Enthalpy of Formation and Reaction

### The direct Method

- Suppose we want to know the enthalpy of formation of carbon dioxide.
- We must measure the enthalpy of the reaction when carbon (graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:



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

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \Delta H_{\text{f}}^{\circ}(\text{CO}_2, \text{g}) - [\Delta H_{\text{f}}^{\circ}(\text{C, graphite}) + \Delta H_{\text{f}}^{\circ}(\text{O}_2, \text{g})] \\ &= -393.5 \text{ kJ/mol} \end{aligned}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

or

$$\Delta H_{\text{f}}^{\circ}(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

## Standard Enthalpy of Formation and Reaction

### The Indirect Method (Hess's Law)

- Many compounds cannot be directly synthesized from their elements.
- The reaction proceeds too slowly, or side reactions produce substances other than the desired compound.

**Hess's Law:** When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

## Standard Enthalpy of Formation and Reaction

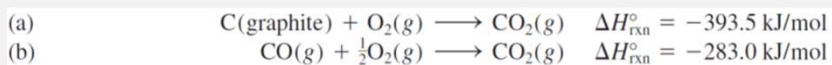
Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO).



However, burning graphite also produces some carbon dioxide ( $\text{CO}_2$ ), so we cannot measure the enthalpy change for CO directly.

We must employ an indirect route, based on Hess's law.

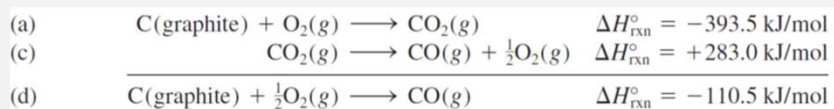
It is possible to carry out the following two separate reactions:



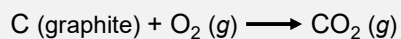
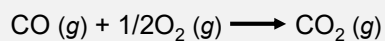
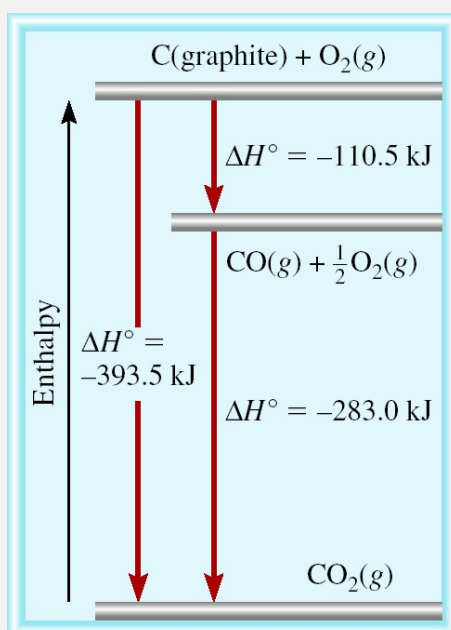
First, we reverse Equation (b) to get



we carry out the operation (a) + (c) and obtain



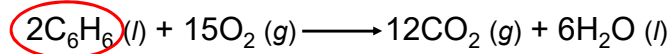
## Standard Enthalpy of Formation and Reaction



32



Benzene (C<sub>6</sub>H<sub>6</sub>) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.



$$\Delta H_{\text{rxn}}^0 = \sum n\Delta H_f^0(\text{products}) - \sum m\Delta H_f^0(\text{reactants})$$

$$\Delta H_{\text{rxn}}^0 = [12\Delta H_f^0(\text{CO}_2) + 6\Delta H_f^0(\text{H}_2\text{O})] - [2\Delta H_f^0(\text{C}_6\text{H}_6)]$$

$$\Delta H_{\text{rxn}}^0 = [12 \times -393.5 + 6 \times -187.6] - [2 \times 49.04] = -5946 \text{ kJ}$$

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol C}_6\text{H}_6$$