



## Chapter 6: Thermochemistry

### Section 6.1: Introduction to Thermochemistry

Thermochemistry refers to the study of heat flow or heat energy in a chemical reaction. In a study of Thermochemistry the chemical energy is transformed into Heat Energy during a chemical reaction.

#### Units of Energy

The System International unit (SI unit) of energy is  $\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$

This was given the name **joule (J)**.

Thus, the SI unit of energy is joule (J).

$$1 \text{ joule (J)} = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$$

$$1000 \text{ J} = 1 \text{ kJ}$$

In order to understand how this unit comes about, remember that the potential energy of an object of mass  $m$  at altitude  $h$  is  $mgh$ .

$m \equiv \text{kg}$       Mass

$g \equiv \text{m}\cdot\text{s}^{-2}$       Acceleration

$h \equiv \text{m}$       Height

The most common unit of energy in chemistry is the **calorie** ( $1 \text{ cal} = 4.184 \text{ J}$ ). Remember the “food” calorie is denoted Calorie (Cal), with a capital C ( $1 \text{ Cal} = 1000 \text{ cal}$ )

Heat energy is the energy that flows into or out of a system because of a difference in temperature between the **system** and its **surroundings**. The system is a part of the universe on which we focus our attention. The **surrounding** is the rest of the universe with which the exchange of heat energy occurs.

**For example:** Consider a beaker of water in contact with a hot plate. The water in the beaker is the System. Here, the hot plate and the beaker holding the water is the surrounding.

For practical purposes only those materials in close contact with the system are called surroundings.

The direction of heat flow must be studied from the “system’s” view point. Heat is expressed by the symbol “ $q$ ”. “ $q$ ”, in common terms, is the quantity of heat. “ $q$ ” is expressed in J or kJ.

When the heat flows from the surroundings into the system, the process is called endothermic. Look at the video of an endothermic process on the DVD. For an endothermic process,  $q > 0$  or  $q$  is positive.

When heat flows from the system into the surroundings, the process is called exothermic. Look at the video of an exothermic process on the DVD. For an exothermic process,  $q < 0$  or  $q$  is negative.

**Remember:** Exothermic reaction = Heat is given off during the reaction ( $q < 0$ ).  
Heat leaves reactants and products and spreads into surroundings.  
Endothermic reaction = Heat is taken up or absorbed during the reaction ( $q > 0$ ). Heat flows from the surroundings into the system.

### Sections 6.2 - 6.3: Magnitude of Heat ( $q$ )

The magnitude of  $q$  is directly proportional to the temperature change.  
Temperature change =  $t_{\text{final}} - t_{\text{initial}} = \Delta t$

$$q \propto \Delta t \quad \text{remember } \Delta t = t_{\text{final}} - t_{\text{initial}}$$

or  $q = C \Delta t$      $C$  is called the **Heat Capacity** of the system  
 $C$  is expressed in J/deg.C.

Heat capacity,  $C$  is defined as the amount of heat required to raise the temperature of the system by one deg.C.

Also, the magnitude of  $q$  is proportional to the mass ( $m$ ) of the system.

$$q \propto m \Delta t \quad \text{or} \quad q = c m \Delta t$$

$c$  (little  $c$ ) is the **Specific Heat Capacity** of the substance (or **Specific Heat**).

$$\text{The specific heat has unit of } \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$$

Specific heat,  $c$ , is defined as the amount of heat required to raise the temperature of one gram of a substance by one deg.C.

The above equation is often written as  $q = m c \Delta t$

Looking at units allows you to differentiate  $C$  from  $c$ .

**Example 1:** The specific heat of iron is  $c = 0.466 \text{ J.g}^{-1}.\text{(}^\circ\text{C)}^{-1}$ . How much heat is given off by a 50.0 g sample of Fe when it cools from 80.0 °C to 50.0 °C?

$$q = mc\Delta t$$

$$m = 50.0 \text{ g}$$

$$c = 0.466 \text{ J.g}^{-1}.\text{(}^\circ\text{C)}^{-1}$$

$$\Delta t = 50.0^\circ\text{C} - 80.0^\circ\text{C} = - 30.0^\circ\text{C}$$

$$q = 50.0 \text{ g} \times 0.466 \text{ J}^{-1}.\text{deg.C}^{-1} \times (- 30.0 \text{ deg.C})$$

$$q = - 699 \text{ J (heat is given off because temperature decreases)}$$

**Example 2:** Cr has a specific heat of iron is  $c = 0.449 \text{ J.g}^{-1}.\text{(}^\circ\text{C)}^{-1}$ . 5.00 g of Cr at 23°C absorbs 60.5 J of heat. Calculate the final temperature.

$$q = mc\Delta t$$

$$\Delta t = \frac{q}{mc}$$

$$m = 5.00 \text{ g}$$

$$c = 0.449 \text{ J.g}^{-1}.\text{(}^\circ\text{C)}^{-1}$$

$$t_i = 23.0^\circ\text{C}$$

$$t_f = ?$$

$$\Delta t = \frac{60.5\text{J}}{5.00\text{g} \times 0.449^\circ\text{C}}$$

$$\Delta t = 26.9^\circ\text{C} = t_f - t_i$$

$$t_f = 49.9 \text{ }^\circ\text{C}$$

In Section 6.3, practice the Interactive Problems.

## Sections 6.4 - 6.5: Measuring Quantities of Heat: Calorimetry

A calorimeter is used for the measurement of heat. A calorimeter is thermally isolated from the surroundings  $\Rightarrow q = 0$  for the whole calorimeter (no heat escapes or enters the calorimeter).

If an exothermic reaction takes place in the calorimeter, the heat released by the reaction will warm up all the internal parts of the calorimeter. Conversely, if an endothermic reaction takes place in the calorimeter, heat will be extracted from the internal parts of the calorimeter (their temperature will decrease) and allow the reaction to proceed.

So overall there is no heat flow between the calorimeter and the surroundings; however, there is heat flow between the reaction chamber and the inner part of the calorimeter.

$$q_{\text{overall}} = 0 = q_{\text{reaction}} + q_{\text{calorimeter}}$$

If one can measure  $q_{\text{calorimeter}}$  then one can obtain the heat associated with the reaction.

$$q_{\text{reaction}} = -q_{\text{calorimeter}} \quad \text{Note the opposite signs}$$

Heat lost by reaction is gained by calorimeter and vice-versa.

To obtain the heat of reaction, we therefore need to estimate the heat received/lost by the internal part of the calorimeter.

Calorimeters often contain a water "bucket" in which a thermometer can be immersed. This allows easy measurement of the temperature change resulting from the heat transferred during the reaction.

So, the most general case, one should write:

$$q_{\text{reaction}} + \begin{array}{c} q_{\text{cal}} \\ \downarrow \\ \text{Internal part} \\ \text{of calorimeter} \\ \text{(metal parts)} \end{array} + \begin{array}{c} q_{\text{water}} \\ \downarrow \\ \text{Water in calorimeter} \end{array} = 0$$

Note that  $q_{\text{cal}}$  and  $q_{\text{water}}$  must be the same sign.

$$q_{\text{cal}} = C_{\text{cal}}\Delta t \quad C_{\text{cal}} \text{ is the heat capacity of the calorimeter (excluding water)}$$

$$q_{\text{water}} = c_{\text{water}} \times m_{\text{water}} \times \Delta t$$

↓  
Specific heat of water

Note that  $t_i$ ,  $t_f$  and  $\Delta t = t_f - t_i$  are the same for the calorimeter and for the water; If they were not, then heat would be flowing between the water and the calorimeter.

In some cases, the calorimeter is designed such that  $q_{\text{cal}} \ll q_{\text{water}}$  (i.e.  $C_{\text{cal}} \ll m_{\text{water}} \times c_{\text{water}}$ ).

In that case, we neglect the heat lost/gained by the calorimeter and we write

$$q_{\text{reaction}} + q_{\text{water}} = 0$$

Note that this is what you would do when your calorimeter is a Styrofoam coffee cup filled with water.

In other cases, if you do not use water in the calorimeter or if the calorimeter heat capacity includes the contribution of the water, you do not include the term  $q_{\text{water}}$  and you should write:

$$q_{\text{reaction}} + q_{\text{calorimeter}} = 0$$

**Example 1:** When 2.00 g of  $\text{MgCl}_2$  is added to 65.0 g of water in a calorimeter, it dissolves according to:  $\text{MgCl}_{2(\text{s})} \rightarrow \text{Mg}^{+2}_{(\text{aq})} + 2 \text{Cl}^{-}_{(\text{aq})}$  The temperature rises from 25.00 °C to 29.87 °C. Calculate the heat of dissolution of  $\text{MgCl}_2$ .

$$q_{\text{reaction}} + q_{\text{water}} = 0$$

Note reaction = dissolution

$$q_{\text{water}} = m_{\text{water}} c_{\text{water}} \Delta t$$

$$m_{\text{water}} = 65.0 \text{ g}$$

$$c_{\text{water}} = 4.18 \text{ J/g} \cdot ^\circ\text{C}$$

$$\Delta t = 29.87^\circ\text{C} - 25.00^\circ\text{C} = 4.87^\circ\text{C}$$

$$q_{\text{water}} = 65 \text{ g} \times 4.18 \text{ J/g} \cdot ^\circ\text{C} \times 4.87^\circ\text{C}$$

$$q_{\text{water}} = + 1320 \text{ J} \quad (\text{note } + \text{ because } t_f > t_i)$$

$$q_{\text{reaction}} = -1320 \text{ J}$$

$$q_{\text{reaction}} = -1.32 \times 10^3 \text{ J in the correct number of significant figures.}$$

**Example 2:** 7.00 mL of  $\text{C}_4\text{H}_{10}\text{O}$  (density = 0.714 g/mL) is burnt in a calorimeter (calorimeter heat capacity = 10.34 kJ/°C). The temperature in the calorimeter rises from 25.0 °C to 39.7 °C.

**a. Calculate the heat of combustion of C<sub>4</sub>H<sub>10</sub>O.**

Here, no mention is made of the water, so, most likely the water heat capacity is already included in that of the calorimeter. So we write:

$$q_{\text{reaction}} + q_{\text{calorimeter}} = 0$$
$$q_{\text{calorimeter}} = C_{\text{cal}}\Delta t = 10.34 \text{ kJ/}^\circ\text{C} \times (39.7 \text{ }^\circ\text{C} - 25.0 \text{ }^\circ\text{C})$$
$$q_{\text{calorimeter}} = + 152 \text{ kJ} \quad (\text{note } + \text{ because } t_f > t_i)$$

**b. Calculate q when 7.00 mL is burned**

$$q_{\text{reaction}} = -152 \text{ kJ}$$

**c. Calculate q when one mole of C<sub>4</sub>H<sub>10</sub>O is burned**

$$\text{Molar mass of C}_4\text{H}_{10}\text{O} = 74.0 \text{ g/mol}$$

$$\text{density} = \frac{\text{mass (g)}}{\text{Volume (mL)}}$$

$$\begin{aligned} \text{mass (g)} &= \text{density} \times \text{Volume (mL)} \\ &= 0.714 \text{ g/mL} \times 7.00 \text{ mL} \\ &= 5.00 \text{ g} \end{aligned}$$

When 5.00 g of C<sub>4</sub>H<sub>10</sub>O is burnt,  $q_{\text{reaction}} = -152 \text{ kJ}$ .

Thus, when 74.0 g/mol C<sub>4</sub>H<sub>10</sub>O is burnt

$$q_{\text{reaction}} = \frac{74.0 \text{ g/mol}}{5.00 \text{ g}} \times (-152 \text{ kJ}) = -2.25 \times 10^3 \text{ kJ/mol}$$

In Section 6.5, practice the Interactive Problems.

## Sections 6.6 - 6.7: Heat Flow: Calorimetry

The specific heat,  $c_{\text{sub}}$ , of a substance can be determined accurately by measuring temperature changes that occur when heat is transferred from the substance to a known quantity of water at constant pressure, P.

$$c_{\text{water}} = 4.18 \text{ J.g}^{-1}.\text{deg.C}^{-1}$$

The sum of heat changes within a given system is zero.

$$\text{Thus, } q_{\text{sub}} + q_{\text{water}} = 0$$

$$q_{\text{sub}} = m_{\text{sub}} \times C_{\text{sub}} \times \Delta t_{\text{sub}}$$

$$\Delta t_{\text{sub}} = (t_{\text{final sub}} - t_{\text{initial sub}})$$

$$q_{\text{sub}} = m_{\text{sub}} \times C_{\text{sub}} \times (t_{\text{final sub}} - t_{\text{initial sub}})$$

$$\text{Similarly, } q_{\text{water}} = m_{\text{water}} \times 4.18 \text{ J.g}^{-1}.\text{deg.C}^{-1} \times (t_{\text{final water}} - t_{\text{initial water}})$$

Hence,

$$[m_{\text{sub}} \times C_{\text{sub}} \times (t_{\text{final sub}} - t_{\text{initial sub}})] + [m_{\text{water}} \times C_{\text{water}} \times (t_{\text{final water}} - t_{\text{initial water}})] = 0$$

$$C_{\text{sub}} = \frac{-m_{\text{water}} \times C_{\text{water}} \times (t_{\text{final}} - t_{\text{initial water}})}{m_{\text{sub}} \times (t_{\text{final}} - t_{\text{initial sub}})}$$

In such an experiment, the substances, initially at different temperatures ( $t_{\text{initial sub}} \neq t_{\text{initial water}}$ ) are placed in contact with each other until they reach the same final temperature ( $t_{\text{final sub}} = t_{\text{final water}} = t_{\text{final}}$ ). Measurements of the initial temperatures for water and for the substance, of the final temperature, knowledge of the specific heat of water, the mass of water and the mass of substance and use of the above equation allow the determination of the substance's specific heat.

**Example: A calorimeter contains 125 g of water and its initial temperature is 21.0 deg.C. A 35.0 g metal sample is heated to 99.8 deg.C and dropped into the calorimeter. The final temperature of the water and the metal is 23.1 deg.C. Calculate the specific heat of the metal.**

$$m_{\text{metal}} = 35.0 \text{ g}$$

$$\text{For the metal: } \Delta t = 23.1 \text{ deg.C} - 99.8 \text{ deg.C} = -76.7 \text{ deg.C}$$

$$m_{\text{water}} = 125 \text{ g}$$

$$\text{For water: } \Delta t = 23.1 \text{ deg.C} - 21.0 \text{ deg.C} = 2.1 \text{ deg.C}$$

$$[35.0 \text{ g} \times C_{\text{metal}} \times (-76.7 \text{ deg.C})] + [125 \text{ g} \times 4.18 \text{ J.g}^{-1}.\text{deg.C}^{-1} \times 2.1 \text{ deg.C}] = 0$$

$$[-2684.5 \times C_{\text{metal}}] + [1097.25] = 0$$

$$[2684.5 \times c_{\text{metal}}] = [1097.25]$$

$$c_{\text{metal}} = \frac{1097.25}{2684.5} = 0.41 \text{ J.g}^{-1}.\text{deg.C}^{-1}$$

In Section 6.7, practice the Interactive Problems.

## Section 6.8: Enthalpy

Enthalpy is a chemical energy represented by the symbol H. Enthalpy (H) is expressed in joules (J) or kilojoules (kJ). The enthalpy change,  $\Delta H$ , for a chemical reaction is expressed as:

$$\Delta H = H_{\text{Products}} - H_{\text{Reactants}}$$

The enthalpy of reaction,  $\Delta H$ , is the heat of reaction  $q_{\text{reaction}}$  at constant pressure.

Consider the chemical reaction:  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H = -483.6 \text{ kJ}$

The chemical equation is balanced and it shows the enthalpy change associated with it. This type of chemical equation is called a **Thermochemical Equation**. The negative value of  $\Delta H$  indicates that the reaction is exothermic.

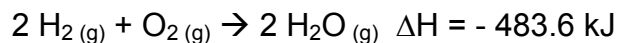
Consider the reaction:  $2 \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CH}_2(\text{g}) + 2 \text{O}_2(\text{g}) \quad \Delta H = 890 \text{ kJ}$

The positive value of  $\Delta H$  indicates that the thermochemical reaction is an endothermic reaction.

## Sections 6.9 - 6.10: Thermochemistry Rules: Rule #1

“The magnitude of  $\Delta H$  is proportional to the amount of products and reactants.”

Consider the chemical reaction:



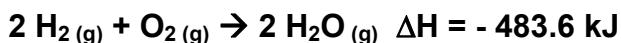
According to this reaction: 2 moles of  $\text{H}_2$  reacts with 1 mole of  $\text{O}_2$  to produce 2 moles of  $\text{H}_2\text{O}$  and the amount of energy released by this reaction is 483.6 kJ.

Therefore, for 1 mole of  $\text{H}_2\text{O}$  produced.



$$\text{According to Rule \#1: } \Delta H = \frac{-483.6 \text{ kJ}}{2} = -241.8 \text{ kJ}\cdot\text{mol}^{-1}$$

**Example: Consider the following thermochemical equation**



**Calculate  $\Delta H$  when (a) 1.00 g  $\text{H}_2$  reacts and (b) 2.50 L of  $\text{H}_2\text{O}$  gas at 100.1 deg.C and 760.0 mm Hg is produced.**

$$\text{(a) mol (n) of H}_2 = \frac{1.00 \text{ g}}{2.00 \text{ g/mol}} = 0.500 \text{ mol H}_2$$

$$\Delta H = 0.500 \text{ mol H}_2 \times \frac{-483.6 \text{ kJ}}{2 \text{ mol H}_2} = -120.9 \text{ kJ}$$

(b) 2.50 L of  $\text{H}_2\text{O}$  gas at 100.1 deg.C and 760.0 mm Hg is produced.  
Calculate the number of moles (n) of  $\text{H}_2\text{O}$  using the ideal gas law:  
 $PV = nRT$

$$P = 1.000 \text{ atm}$$

$$n = \text{to be calculated}$$

$$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$V = 2.50 \text{ L}$$

$$T = 373.25 \text{ K}$$

$$n = \frac{1.000 \text{ atm} \times 2.50 \text{ L}}{0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \times 373.25 \text{ K}} = 0.0816 \text{ mol H}_2\text{O}$$

$$\Delta H = 0.0816 \text{ mol H}_2\text{O} \times \frac{-483.6 \text{ kJ}}{2 \text{ mol H}_2\text{O}} = -19.7 \text{ kJ}$$

$$n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 2.50 \text{ L}}{0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 373.25 \text{ K}} = 0.0816 \text{ mol H}_2\text{O}$$

$$\Delta H = \frac{-483.6 \text{ kJ}}{2 \text{ mol H}_2\text{O}} \times 0.816 \text{ mol H}_2\text{O}$$

$$\Delta H = -19.7 \text{ kJ}$$

In Section 6.10, practice the Interactive Problems.

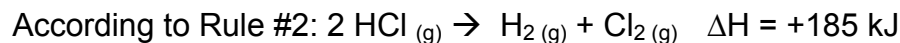
### Sections 6.11 - 6.12: Thermochemistry Rules: Rule #2

“ $\Delta H$  for a reaction is equal in magnitude, but opposite in sign, for the reverse reaction.”

Consider the chemical reaction:

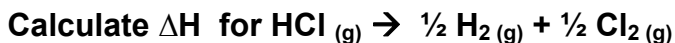


According to this reaction: 1 mole of  $\text{H}_2$  reacts with 1 mole of  $\text{Cl}_2$  to produce 2 moles of  $\text{HCl}$  and the amount of energy released is 185 kJ.



According to this reaction: 2 moles of  $\text{HCl}$  break down to form 1 mole of  $\text{H}_2$  and 1 mole of  $\text{Cl}_2$ . The amount of energy absorbed is 185 kJ.

**Example: Consider the following thermochemical equation:**



Reverse this reaction and apply Rule # 2.



The problem asks to calculate  $\Delta H$  for one mole of  $\text{HCl}$ , hence apply Rule #1.

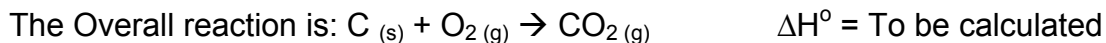
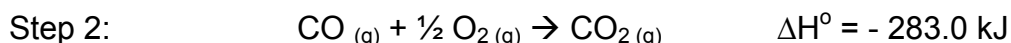
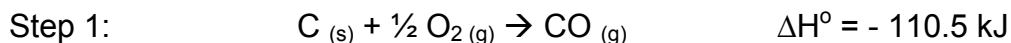
$$\Delta H = \frac{185 \text{ kJ}}{2} = 92.5 \text{ kJ}\cdot\text{mol}^{-1}$$

In Section 6.12, practice the Interactive Problems.

### Sections 6.13 - 6.14: Thermochemistry Rules: Rule #3 (Hess's Law)

A chemical reaction can be represented as a combination of several steps. The  $\Delta H^\circ$  for the overall reaction is the same whether the chemical reaction occurs in one step or several steps.

Consider a chemical reaction that occurs in two steps.



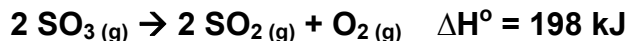
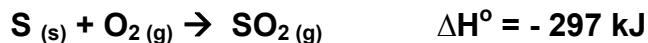
Since Overall reaction = Step 1 reaction + Step 2 reaction, then,

$$\Delta H^\circ_{\text{Overall}} = \Delta H^\circ_{\text{Step 1}} + \Delta H^\circ_{\text{Step 2}}$$

This relationship is called Hess's law.

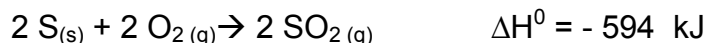
The assumption is that all steps including the overall step occur at the same pressure and temperature.

**Example: Consider the chemical reactions**



Look at the first reactant in the Overall reaction. In Step 1,  $\text{S}_{(s)}$  is a reactant as it is in the Overall reaction. In the Overall reaction, there are 2 moles of  $\text{S}_{(s)}$  whereas in Step 1 there is 1 mole of  $\text{S}_{(s)}$ .

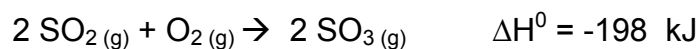
Apply Rule # 1. Multiply Step 1 by 2.



Since  $\text{O}_{2(g)}$  appears in both steps, ignore  $\text{O}_{2(g)}$  at this point.

Now look at  $\text{SO}_{3(g)}$ . It appears as a product in the Overall equation whereas in Step 2,  $\text{SO}_{3(g)}$  appears as a reactant. There are 2 moles of  $\text{SO}_{3(g)}$  in the Overall reaction as well as in Step 2.

Apply Rule # 2 to Step 2 and reverse the reaction.



Add reactants and products of both steps, this would result in the Overall reaction.  $2 \text{S}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$

Now apply Hess's law to calculate  $\Delta H^\circ_{\text{Overall}}$

$$\begin{aligned} \Delta H^\circ_{\text{Overall}} &= (-594 \text{ kJ}) + (-198 \text{ kJ}) \\ &= -792 \text{ kJ} \end{aligned}$$

In Section 6.14, practice the Interactive Problems.

### Section 6.15: Standard Enthalpies of Formation

The **standard enthalpy of formation** is expressed by the symbol  $\Delta H_f^\circ$ . Superscript zero represents **standard condition**. As always, standard condition means that pressure,  $P = 1 \text{ atm}$ .

$\Delta H_f^\circ$  is the enthalpy change when one mole of a compound is formed under standard conditions from its elements in their stable standard state.

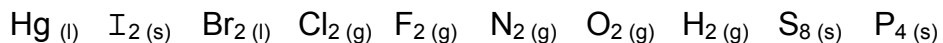
$$\Delta H_f^\circ = H_{\text{Final}} - H_{\text{Initial}}$$

For an element in its stable state, the formation involves no change at all. Thus,  $\Delta H_f^\circ$  of an element in its stable state is zero.

### Section 6.16: Standard Enthalpies of Formation of Elements

In this section an interactive periodic table is given. Click on any element. The name along with its state under standard conditions and the enthalpy of formation is revealed.

Pay special attention to the following elements, Hg, I, Br, Cl, F, N, O, H, S and P as their standard state are:



### Sections 6.17 - 6.18: Calculations of Standard Enthalpies of Reaction (Table of $\Delta H_f^\circ$ for Compounds)

The standard enthalpy change,  $\Delta H^\circ$  for a chemical reaction is the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants. Mathematically, this is expressed as

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

The "Thermo Table" lists the standard enthalpies of formation for a variety of compounds. To access this table click on tables in the main menu of the DVD.

**Example 1: Consider the following reaction:**



**Calculate  $\Delta H^\circ$  for this reaction. Based on your calculations predict whether the reaction is exo- or endothermic.**

For the products, the  $\Delta H_f^\circ$  values are:

$$\Delta H_f^\circ(\text{NO}(\text{g})) = 90.3 \text{ kJ/mol and } \Delta H_f^\circ(\text{H}_2\text{O}(\text{g})) = -241.8 \text{ kJ/mol.}$$

$$\begin{aligned} \sum \Delta H_f^\circ(\text{products}) &= 4 \text{ mol} \times (90.3 \text{ kJ/mol}) + 6 \text{ mol} \times (-241.8 \text{ kJ/mol}) \\ &= 361.2 \text{ kJ} - 1450.8 \text{ kJ} \\ &= -1089.6 \text{ kJ} \end{aligned}$$

For the reactants, the  $\Delta H_f^\circ$  values are:

$$\Delta H_f^\circ(\text{NH}_3(\text{g})) = -45.9 \text{ kJ/mol and } \Delta H_f^\circ(\text{O}_2(\text{g})) = 0 \text{ (by definition)}$$

$$\sum \Delta H_f^\circ(\text{reactants}) = 4 \times (-45.9) = -183.6 \text{ kJ}$$

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

$$\Delta H^\circ = (-1089.6) - (-183.6) = -906 \text{ kJ}$$

The negative value indicates the reaction is exothermic.

**Example 2: Consider the reaction  $2 \text{SO}_3(\text{g}) \rightarrow 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$   $\Delta H^\circ = 198.4 \text{ kJ}$**

$$\Delta H_f^\circ(\text{SO}_2(\text{g})) = -296.8 \text{ kJ/mol}$$

**Calculate  $\Delta H_f^\circ(\text{SO}_3(\text{g}))$  in kJ/mol**

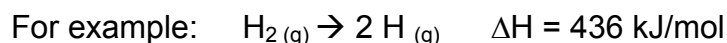
$$\sum \Delta H_f^\circ(\text{products}) = 2 \text{ mol} \times (-296.8 \text{ kJ/mol}) + 0 = -593.6 \text{ kJ}$$

$$\begin{aligned} \Delta H^\circ &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ \downarrow & \quad \downarrow \quad \quad \quad \downarrow \\ 198.4 &= 2 \times (-296.8) - 2 \Delta H_f^\circ(\text{SO}_3(\text{g})) \\ \Rightarrow 2 \Delta H_f^\circ(\text{SO}_3(\text{g})) &= -198.4 - 2 \times 296.8 \\ \Delta H_f^\circ(\text{SO}_3(\text{g})) &= -396.0 \text{ kJ/mol} \end{aligned}$$

In Section 6.18, practice the Interactive Problems.

### Sections 6.19 - 6.20: Bond Enthalpies

The **bond enthalpy** is expressed by the symbol  $\Delta H$  or  $\Delta H_B$ . Bond enthalpy is defined as the change in enthalpy associated with the dissociation of a chemical bond in a gaseous molecule.



This means the H - H bond enthalpy is 436 kJ/mol.

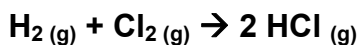
From the values given in the Bond Enthalpy Table (see DVD), one can conclude that:

- (a) Bond enthalpy is a positive quantity. **This is because heat is absorbed when chemical bonds are broken.**
- (b) The higher the bond enthalpy, the stronger the bond. **This is because more heat is required to break stronger bonds.**
- (c) The bond enthalpy for a double bond is less than two times the bond enthalpy for a single bond.

**Note** that for Bond Enthalpy calculations, the enthalpy change for a reaction is equal to the sum of the bond enthalpies for the reactants minus the sum of the bond enthalpies for the products. Mathematically, this is expressed as:

$$\Delta H_{\text{Reaction}} = \sum \Delta H_{\text{Reactants}} - \sum \Delta H_{\text{Products}}$$

**Example: Using the bond enthalpies table, calculate  $\Delta H$  for the following reaction:**



Using the Bond Enthalpy Table on the DVD, we obtain:

$$\Delta H_{\text{Reactants}} = 436 \text{ kJ} + 243 \text{ kJ} = 679 \text{ kJ}$$

$$\Delta H_{\text{Products}} = 2 \text{ mol} \times 431 \text{ kJ/mol} = 862 \text{ kJ}$$

$$\Delta H_{\text{Reaction}} = 679 \text{ kJ} - 862 \text{ kJ} = -183 \text{ kJ}$$

In Section 6.20, practice the Interactive Problem.

## Sections 6.21- 6.22: First Law of Thermodynamics

The first law of thermodynamics can be stated in many different, but equivalent ways.

- “The energy of the universe is constant.”

In this form, the first law implies that energy can neither be created nor destroyed. It can only be changed from one form to another.

- “The change in the energy of a system is equal in magnitude, and opposite in sign, to the change in the energy of the surroundings of that system.”

This statement is equivalent to the first because

$$\text{System} + \text{Surroundings} = \text{Universe}$$

and

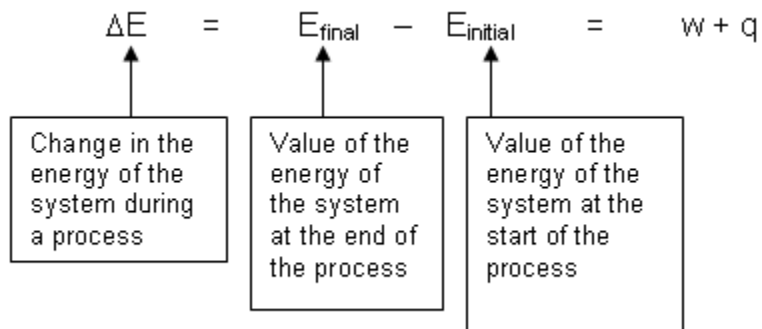
$$\Delta E_{\text{universe}} = 0 \Leftrightarrow E_{\text{universe}} = \text{constant.}$$

- “The change in the energy of a system during a certain process is equal to the sum of the heat and work exchanged by the system and the surroundings.”

This form of the first law specifies that changes in energy can only arise as a result of a transfer of heat or as a result of work being done on or by the system.

In mathematical form, this last statement is written as the very important formula

$$\Delta E = w + q$$



$w \equiv$  work done **on (+)** or **by (-)** the system during the process.

This sign convention is chosen to ensure that work done by the system (negative work) leads to a decrease in the energy of the system (if no heat is involved) and work done on the system (positive work) leads to an increase in the energy of the system.

Note that these sign conventions are similar to those adopted earlier for the heat,  $q$ .

$q > 0 \Rightarrow$  heat flows **into** the system (i.e. from the surroundings):  
Endothermic process.

$q < 0 \Rightarrow$  heat flows **out of** the system (i.e. into the surroundings):  
Exothermic process.

In the absence of work,  $q > 0$  implies an increase in the energy of the system ( $\Delta E > 0$ ), and  $q < 0$  implies a decrease in the energy of the system ( $\Delta E < 0$ ).

The type of work considered in this chapter is the work of expansion or contraction that is encountered in chemical reactions. Before we actually learn how to calculate this work, let us consider the following example of the application of the first law.

**Example 1: Calculate  $\Delta E$  for the gaseous reaction in which 30 J of heat is absorbed by the system and 24 J of expansion work is done by the system.**



$q = + 30 \text{ J}$  (+ because heat is absorbed by the system)

$w = - 24 \text{ J}$  (- because work is done by the system)

$$\Delta E = w + q = - 24 \text{ J} + 30 \text{ J} = + 6 \text{ J}$$

Thus, the system's energy rises by 6 J during this process.

**Example 2: Calculate  $\Delta E$  for a gaseous reaction system in which 30 J of heat evolves and 24 J of work is done as the system contracts.**

$q = - 30 \text{ J}$  heat flows out of the system

$w = + 24 \text{ J}$  work is done on the system

$$\Delta E_{\text{system}} = - 30 \text{ J} + 24 \text{ J} = - 6 \text{ J}$$

In Section 6.22, practice the Interactive Problems.

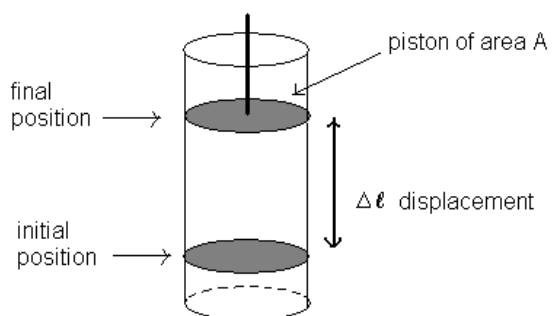
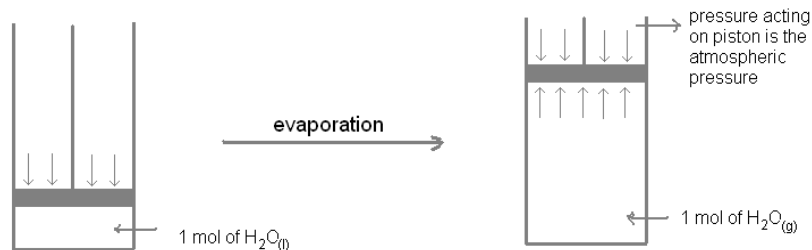
### Sections 6.23 - 6.24: Work

Typically, gases involved in a chemical reaction are either reactants or products or both. Many points covered here are not discussed in the DVD.

Consider the simple process of evaporation of water at a temperature of 373 K.



This process can be described using the following schematic of a cylinder and a piston:



$$\text{Force } (F_{\text{app}}) = P_{\text{atm}} \times A$$

$P_{\text{atm}}$ : atmospheric pressure  
 $A$ : cross-sectional area

The total work done by the gas molecules during the evaporation process is equal to:

$$F_{\text{app}} \times \text{displacement } (\Delta \ell)$$

$$\Rightarrow \text{work} = - P_{\text{atm}} \times A \times \Delta \ell$$

The negative sign is added to ensure that work is negative when done by the system. ( $P_{\text{atm}}$ ,  $A$ ,  $\Delta \ell$  are  $> 0 \Rightarrow$  negative sign in front of  $P_{\text{atm}} \times A \times \Delta \ell$  is necessary.)

The quantity  $A \times \Delta \ell = \Delta V = V_{\text{final}} - V_{\text{initial}}$ , the change in volume of the system during the process.

$\Rightarrow$  The work of expansion of a system under constant external pressure  $P_{\text{ext}}$  is given by:

$$w = - P_{\text{ext}} \times \Delta V$$

In this problem,  $V_{\text{final}} = V_{\text{m}}(\text{g})$ , the molar volume of  $\text{H}_2\text{O}$  gas, and  $V_{\text{initial}} = V_{\text{m}}(\text{l})$ , the molar volume of  $\text{H}_2\text{O}$  liquid.

**Note:** Unless the gas is subjected to an extremely high pressure at a very low temperature, its molar volume will always be much larger than the molar volume of a liquid or solid (review the postulates of gases in [Chapter 5](#)).

Hence  $\Delta V = V_m(g) - V_m(l)$  can be safely approximated as:

$$\Delta V = V_m(g) = R T / P,$$

↑  
using the ideal gas law

and the work in this problem is expressed as:

$$w = - RT \quad \text{for } H_2O_{(l)} \rightarrow H_2O_{(g)}$$

$$\Rightarrow w = - 3100 \text{ J at } 100^\circ\text{C}$$

**Note:** To obtain the work in joules, you need to use  $R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ . In the DVD, we use the approximation  $R = 8.31 \text{ J.K}^{-1}.\text{mol}^{-1}$ .

**Note:** To convince yourself that the molar volume of  $H_2O_{(l)}$  is very much smaller than that of  $H_2O_{(g)}$ , consider 1 mole of  $H_2O_{(l)}$  and 1 mole of  $H_2O_{(g)}$  at 300 K and 1 atm.

$$V_m(g) \approx R T / P \text{ (using the ideal gas law)} \Rightarrow V_m(g) = 24.6 \text{ L / mol.}$$

$$V_m(l) = \frac{18 \text{ g / mol (molar mass of water)}}{1000 \text{ g / L (density of water)}} \Rightarrow V_m(l) = 0.018 \text{ L / mol.}$$

The same amount of gas occupies a volume over 1000 times larger than the liquid!!!

For the case  $H_2O_{(l)} \rightarrow H_2O_{(g)}$  we found that the work was given by  $w = - R T$ .

In general, for a chemical reaction, the work is given by the equation:

$$w = - R T \Delta n_g$$

In this equation,  $\Delta n_g$  is the change in the number of moles of **gas molecules** in the balanced chemical reaction

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

**Example: Consider the following reaction:  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$**

$$w = - P_{\text{ext}} \Delta V = - P_{\text{ext}} (V_{\text{products}} - V_{\text{reactants}}).$$

Now,  $V_{\text{products}} = 2 R T / P$ , since there are 2 mol of  $\text{NH}_3$

and  $V_{\text{reactants}} = 4 R T / P$ , since there are 4 mol of gas (1 mol  $\text{N}_2$  + 3 mol  $\text{H}_2$ )

$$\Rightarrow w = - (2 - 4) R T = + 2 R T.$$

$\uparrow$   

$\Delta n_g = 2 - 4 = -2$
---------------------------

If a reaction creates fewer gas molecules than it consumes, it is accompanied by positive work. It contracts under the action of the external atmospheric pressure.

Contraction:  $\Delta V < 0 \quad \Rightarrow \quad \text{work} > 0.$

Expansion:  $\Delta V > 0 \quad \Rightarrow \quad \text{work} < 0.$

**Example: Consider the reaction  $\text{C}_{(\text{s})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ . Calculate the work  $w$  at 300 K.**

$$w = - R T \Delta n_g$$

In the above reaction,  $\Delta n_g = 1 - 1 = 0$ . (Note that we do not count  $\text{C}_{(\text{s})}$ , as it is not a gas and its volume is negligible compared to that of  $\text{O}_2(\text{g})$  or  $\text{CO}_2(\text{g})$ .)

Hence,  $w = 0$ .

### **Relationship between the work, the enthalpy of reaction in the context of the first law of thermodynamics.**

Consider a chemical reaction taking place at constant pressure.

$\Delta_R H = q_P$ , the heat of reaction is equal to the enthalpy change.

The first law of thermodynamics states that  $\Delta E = w + q$ .

The process is a chemical reaction  $\Rightarrow w = - R T \Delta n_g$ .

Hence, we conclude that the change in energy for a reaction is expressed as:

$$\Delta E = \Delta_R H - R T \Delta n_g$$

**Note:** Now, you can understand why we stated earlier that the enthalpy was a kind of chemical energy.

### **Let us now consider reactions occurring at constant Volume**

Some reactions can be carried out while the volume is kept constant. For example, reaction between gases in a cylinder where the piston cannot slide.

When the volume is constant, there is no work.

$$w = - P_{\text{ext}} \times \Delta V \text{ and } \Delta V = 0, \text{ since } V_{\text{final}} = V_{\text{initial}}$$

$$\text{Thus, } \Delta E = q_V$$

The subscript “V” is used to indicate that the volume is constant. Hence, we conclude that the heat absorbed or released during a reaction occurring at constant volume is simply the change in energy.

### **Relating $q_P$ , $q_V$ and $w$ :**

If we consider a reaction taking place in an open vessel in the laboratory, the reaction occurs at constant pressure. The change in enthalpy associated with the reaction is equal to the heat (see above).

$$\text{Hence, } \Delta H = q_P$$

We just showed above that the change in energy for a reaction is equal to the quantity  $q_V$  and that the relationship between  $\Delta E$ ,  $\Delta H$  and the work is given by:

$$\Delta E = \Delta_R H - R T \Delta n_g$$

Hence, we conclude that:

$$q_V = q_P - R T \Delta n_g$$

where  $q_V$  and  $q_P$  are the heat released or absorbed by the same reaction under conditions of constant volume or of constant pressure, respectively.

### Example of an Expansion/Compression Work Calculation

**Example:** Consider the compression of a gas from volume 60 L to volume 10 L under an external pressure of 2 atm. Calculate the work for this process, expressed in the SI unit of joules.

First, note that the work must be positive since the process is a compression under the influence of the external pressure.

$$w = - P_{\text{ext}} \times \Delta V = w = - P_{\text{ext}} (V_f - V_i)$$

Note that to obtain an expression for w in joules, one must express P in pascals and V in m<sup>3</sup>.

$$P_{\text{ext}} = 2 \text{ atm} = 2 \text{ atm} \times \frac{101325 \text{ Pa}}{1 \text{ atm}} = 202650 \text{ Pa}$$

$$\Delta V = (10 \text{ L} - 60 \text{ L}) = -50 \text{ L} = -50 \text{ L} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = -0.05 \text{ m}^3$$

$$\Rightarrow w = - (202650) \times (-0.05) \text{ J} \quad (1 \text{ J} = 1 \text{ Pa} \cdot \text{m}^3)$$

$$w = 10 \text{ kJ} \quad (1 \text{ significant figure})$$

When calculating work, always remember to use the appropriate conversion factor (see above) or gas constant ( $R = 8.31 \text{ J.K}^{-1}.\text{mol}^{-1}$ ) in the relevant equation.

$$w = - P \Delta V \quad P \text{ in Pa, } V \text{ in m}^3$$

$$w = - R T \Delta n_g \quad R = 8.31 \text{ J.K}^{-1}.\text{mol}^{-1}.$$

In Section 6.24, practice the Interactive Problems.

[Previous Chapter](#)   [Table of Contents](#)   [Next Chapter](#)