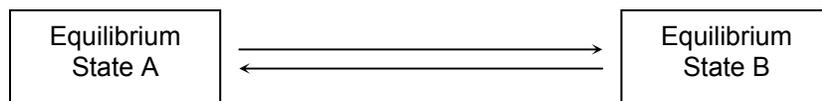


## 4.1 Thermodynamic definitions

In thermodynamics, we focus our attention on a *system* which undergoes some transformation between two *equilibrium states*:



The transformation from state A to B may be *physical* or *chemical*. It may occur in one step or may involve many steps. In thermochemistry, we are interested in answering the following question.

*How much energy is exchanged between a chemical system and its surroundings during the transformation from A to B?*

Thermochemistry is a branch of thermodynamics; it's what we get when we apply the First Law of Thermodynamics to a chemical system that has undergone some physical or chemical transformation. The most general statement of the First Law is:

Energy is conserved. OR Energy in the universe is constant, it is: never created nor destroyed, only transformed between forms.

Before we can apply this principle to problems in chemistry, we must identify not only the various different forms of energy, but also the different ways that a system can exchange energy with its surroundings. After doing this, we will be able to restate the First Law in a way that is more useful for chemical applications.

Thermodynamics is concerned with the interconnection of energy among its many different forms, as well as predicting /understanding the preferred direction of energy transfer. Thermochemistry - which is what we are going to go into, is concerned with part 1 of the definition and not the direction of energy transfer etc..

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Physical <-> no changes in chemical composition or properties.

Chemical <-> The chemical composition of the system is changed, by a rxn etc.

But first, let's define a few important terms.

### A. Types of systems

The *system* is that part of the universe we are interested in, separated from its *surroundings* by real or imaginary boundaries. The system may be classified as *open*, *closed*, or *isolated* depending upon whether energy or matter is allowed to cross the boundaries:

*open system*: Energy & matter flow across boundaries freely

This is what we'll be working with in this course

*closed system*: Only energy flows across boundary.

*isolated system*: neither energy NOR matter flows in/out of the system.

We are interested exclusively in closed systems.

### B. Types of energy

*kinetic energy*: energy a system or object possesses by virtue of its motion (i.e. speed).

*potential energy*: Energy an object or system poses by virtue of its position in space

*internal energy*: Energy a system possesses by virtue of its molecular structure; it is the sum of the K.E's and P.E's of all the individual particles in the system

The internal energy of a system is what we are most interested in. Next, we consider how the internal energy of a system can be changed. 

There are ways of changing the internal energy:  
1) Heat flows into or out of the system  
2) The system does work or has work done on it.

## 4.2 Heat

*Heat* is energy in transition; it is energy that flows from a region of high temperature to a region of low temperature. Heat flows between a system and its surroundings when the system is not in thermal equilibrium with its surroundings.

Let  $Q$  represent the total amount of heat transferred between a system and its surroundings.

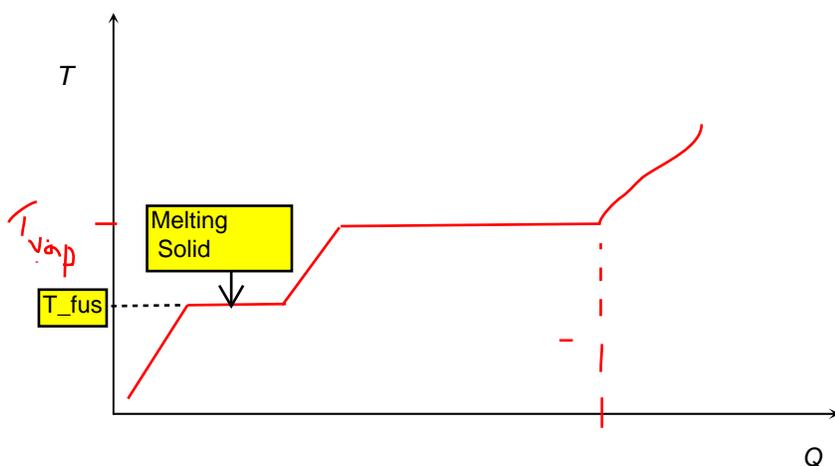
Sign conventions:  $Q$  is |

|                                   |
|-----------------------------------|
| { +ve : heat flows INTO system.   |
| { -ve : heat flows OUT of system. |

When a pure substance is heated, one of two things can happen:

- the temperature increases Energy is used to increase the Temp. i.e. it is absorbed by the particles and the increase in K.E. is shown as increase in temperature.
- a phase change occurs  $\rightarrow$  Energy is being used to increase the P.E. of the molecules (as opposed to K.E., which is when temp. increases.). The energy aggregates the molecules and is used to overcome the attractive molecular forces.

Imagine that we have a solid that we heat continuously at constant pressure. The temperature of the substance will change as shown in the diagram below.



## Heat Capacity

The heat capacity of a substance is the amount of heat required to raise the temperature of an object or a substance by 1°C or 1 K. The heat capacity,  $C$ , is defined via:

$$C = \frac{Q}{\Delta T} \quad \text{where } \Delta T = T_f - T_i$$

$\Delta T = \text{°C} / \text{K}$

To measure the heat capacity of an object, or a substance, we deliver a known quantity of heat and measure the temperature change produced.

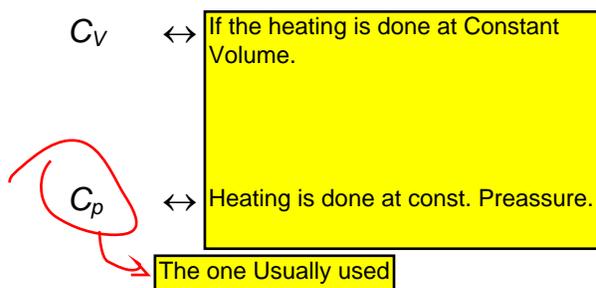
The heat capacity of an object (e.g. a reaction vessel) is given in  $\text{J K}^{-1}$ . The heat capacity of a pure substance is typically given in  $\text{J K}^{-1} \text{g}^{-1}$  or  $\text{J K}^{-1} \text{mol}^{-1}$ .

Once we know 'C' for a substance we can use it to convert a temp. change to heat needed/released to make the change.

Specific Heat Capacity.

Molar Heat Capacity

There are two types of heat capacities that concern us:



The molar heat capacities, at constant pressure, are given in the table for a few different substances

| Substance                      | $\bar{C}_p$ (in $\text{J K}^{-1} \text{mol}^{-1}$ ) |
|--------------------------------|---|
| $\text{N}_2(\text{g})$         | 29.12   |
| $\text{O}_2(\text{g})$         | 29.36   |
| $\text{H}_2\text{O}(\text{l})$ | 75.29   |
| $\text{CCl}_4(\text{l})$       | 131.75  |
| $\text{I}_2(\text{s})$         | 40.12   |
| $\text{C}(\text{graphite})$    | 16.86   |
| $\text{Cu}(\text{s})$          | 24.44   |

**Example:** What mass of water, initially at 20°C, is required to cool 0.250 g Cu(s) from 100°C to 25°C?

### 4.3 Work

Like heat, *work* is also energy in transition. There are many different types of work, examples of which include:

- *expansion work*, which is the work done when the volume of a system changes in the presence of an external pressure. The external pressure opposes (or causes) the volume change.
- *electrical work*, which is the work done to move a charged particle, such as an electron, from a region of high electrical potential to one of low electrical potential.
- *surface tension work*, which is the work done when the surface area of a liquid changes.

We interested exclusively in expansion work. We know that our atmosphere exerts a continuous downward pressure on

any system. If the pressure exerted by the surroundings causes a decrease in the volume of the system, then the surroundings have done work on the system. When the volume of a system changes in the presence of a constant external pressure,  $P_{\text{ex}}$ , then the work done by the surroundings on the system is defined to be:

Remarks:

- Convince yourself that the product of pressure and volume gives you units of energy.
- The minus sign in the definition for  $W$  arises from the fact that the pressure exerted by the surroundings opposes an increase in volume (i.e. the force vector opposes the displacement vector). Consequently, the surroundings do positive work when the system is compressed and negative work when the system expands.

The equation given above for  $W$  only applies if the external pressure does not change throughout the volume change. In the event that the external pressure changes, we need to use a more general expression which is based on dividing the total volume change into an infinite number of infinitely small volume changes,  $dV$ .

From our own experience, we know that the amount of work done in accomplishing some task depends critically upon

how the task is carried out. In the same way, the amount of pressure-volume work depends upon the external pressure at the time the volume change occurs.

**Example:** Calculate  $W$  if 1.0 mol  $\text{H}_2\text{O}(l)$ , initially at  $25^\circ\text{C}$ , is converted into steam at  $115^\circ\text{C}$  under a constant pressure of 1.00 atm. Assume that the vapour behaves ideally. The density of water is 1.0 g/mL at  $25^\circ\text{C}$ .

## 2.3 The First Law

***For a closed system that undergoes a change in state, the change in internal energy is governed by:***

$$dU = Q + W$$

Internal Energy

### Remarks:

1. The First Law provides no definition or interpretation of  $U$ . It provides only a recipe for calculating changes in  $U$ . Our interpretation of the internal energy comes from our understanding of the molecular nature of matter.
2. Sign conventions for  $Q$  and  $W$

$$Q = \begin{cases} + : \text{If energy flows from the surrounding into system [dU is going up.]} \\ - : \text{If energy flow from system into surroundings [dU is going down]} \end{cases}$$

$$W = \begin{cases} +, \text{If work is done ON the system by surrounding [e.g: compression]} \\ -, \text{If system does work ON the surroundings.} \end{cases}$$

3. A given internal energy change ( $\Delta U$ ) can be achieved via heat transfer, doing work or through some combination of the two. However, heat and work affect the molecular motions in different ways.

Heat - affects molecules in a random way.  
Work Affects molecules in an organized manner.

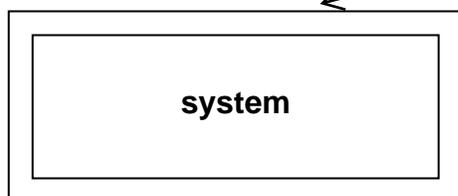
## 2.4 Application of the First Law – Heats of Reaction

Reactions are most commonly carried out at

- constant volume (e.g. in a rigid, sealed reaction vessel)
- constant atmospheric pressure (e.g. “open” to the atmosphere)

What does the heat absorbed or released by a reaction represent? It depends upon whether the reaction is carried out at constant volume or constant pressure.

### Constant volume reaction



"rigid": heat can flow across boundaries BUT volume cannot change.

First Law  $\Rightarrow$

$$dU = Q + W = Q - P_{\text{ex}} dV = P_{\text{ex}} [ \text{since } dV=0 ].$$

$$\text{thus, } dU = Q \text{ and } Q_v = dU [v \text{ is constant}].$$

Conclusion?

When a reaction occurs at constant volume, the heat transferred is equal to the internal energy change ( $\Delta U$ ) for the system.

## Constant pressure Reaction

First Law

⇒

$$\begin{aligned} P_i &= P_f = P_{ex} = \text{const. pressure.} \\ dU &= Q + W = Q - P_{ex}dV. \\ U_f - U_i &= Q - P_fV_f + P_iV_i \\ Q &= [U_f + P_fV_f] - [U_i + P_iV_i] = d[U + PV] \end{aligned}$$

$U + PV = \text{Enthalpy [denoted } H\text{]}. \text{ Thus } Q = \text{Change in Enthalpy} = dH, \text{ for const. pressure process.}$

Conclusion?

When a reaction occurs at constant pressure, the heat absorbed/released is equal to the enthalpy change for the system.

Note carefully:  $H$  is introduced for convenience only.  $H$  does not have any physical significance. However,  $\Delta H$  does have a simple physical interpretation, provided we are talking about a reaction that occurs at constant pressure.

## 2.5 Experimental determination of the heat of reaction

The heat absorbed or released by a reaction is measured using a calorimeter.

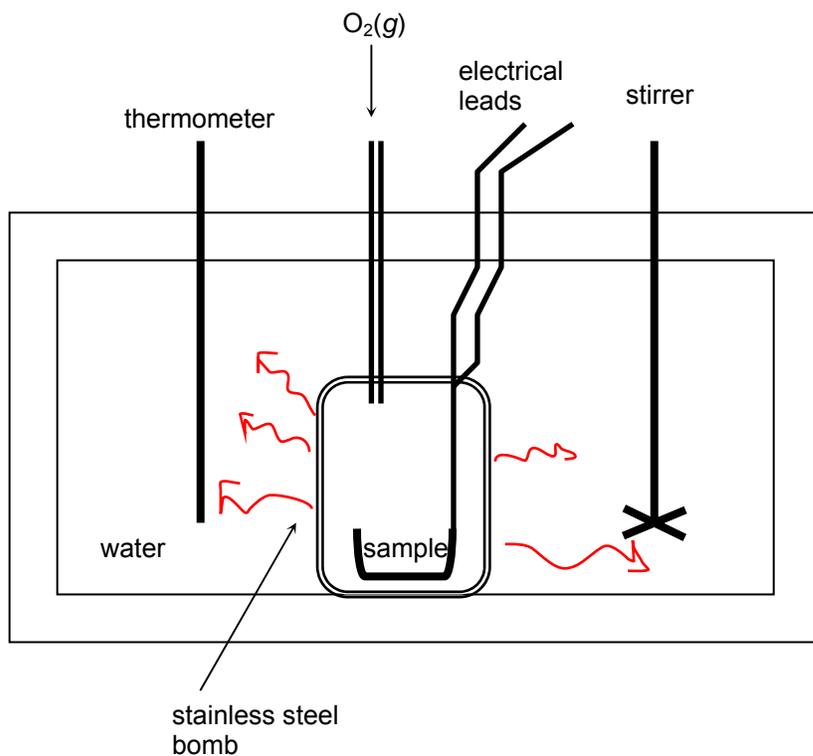
calorimeter = A device or reaction vessel that is thermally insulated from its surroundings.

The temperature change produced in the calorimeter is used to determine how much heat is absorbed (or released) by the reaction. Obviously, we need to know the heat capacity of the calorimeter.

There are many different types of calorimeters.

- bomb calorimeter Good for studying combustion rxn. It is a constant volume calorimeter.
- coffee cup calorimeter "quick and easy". Very cheap to make. Is given in text book. Made of 2 nested coffee cups. All the reactions happen inside the inner coffee cup. The outer cup provides extra insulation.
- ice calorimeter Constant temp (0degree C). Calorimeter. Contains ice and water to absorb all the heat rather than letting it dissipate. Harder to use. The change in amt. or mass of ICE is used to calculate the change in temp. Since the ice will melt/form if more/less heat is given/absorbed.

Most reactions are carried out at constant pressure, so more often than not, we are interested in  $\Delta H$  values. However, the heat absorbed (or released) by a reaction is sometimes measured at constant volume, so we must convert constant volume heats of reaction ( $Q_v$ ) into constant pressure heats of reaction ( $Q_p$ ). In general,  $Q_v \neq Q_p$ .

**Schematic diagram of a bomb calorimeter**

No heat is transferred into the surroundings, and so we must have:

$$Q_{\text{cal}} + Q_{\text{rxn}} = 0.$$

When a combustion reaction is carried out in a bomb calorimeter, the reaction occurs at constant volume.

Therefore:

$$Q_{\text{rxn}} = Q_v = \Delta U$$

**Example:** A bomb calorimeter is heated electrically using a 15.00 watt heater. It takes 568 s to raise the temperature of the calorimeter by 2.00°C. When a 0.6410-g sample of  $C_{10}H_8(s)$  is burned in oxygen in the calorimeter, the temperature rises from 25.00°C to 31.05°C

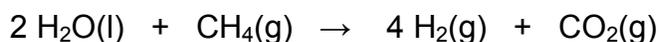
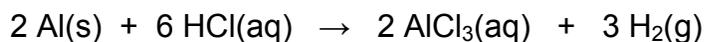
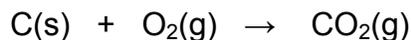
Note: 1 watt = 1 J s<sup>-1</sup>

- (a) What is the constant volume heat of reaction for the reaction below, in kJ mol<sup>-1</sup>?
- (b) What are  $\Delta U$  and  $\Delta$  for the reaction above at 25°C? Give your answers in kJ mol<sup>-1</sup>.

The difference between the constant volume heat of reaction and the constant pressure heat of reaction is equal to the amount of work done during the process.

In the previous example, the system contracts when the reaction occurs at constant pressure, and the surroundings do work on the system (i.e. extra energy flows into the system as a result of work being done on the system). If this energy was not allowed to escape from the system, the system would heat up. The work associated with the contraction process flows back into the surroundings as heat. Thus, we get more heat released into the surroundings when the reaction occurs at constant pressure.

**Example:** For which of the following reactions is  $\Delta H$  not equal to  $\Delta U$ ?

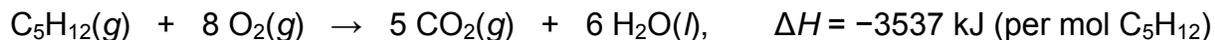


**Example:** The density of liquid benzene,  $C_6H_6(l)$ , is approximately  $0.88 \text{ g mL}^{-1}$  at all temperatures. The standard enthalpy of vaporization of  $C_6H_6(l)$  is  $30.8 \text{ kJ mol}^{-1}$  at  $353 \text{ K}$ , its normal boiling point. Calculate the pressure-volume work ( $w$ ) and the internal energy change ( $\Delta U$ ) when one mole of liquid benzene is vaporized at  $353 \text{ K}$  under a constant pressure of  $101 \text{ kPa}$ .

$$\begin{aligned} & C_6H_6(l) \rightarrow C_6H_6(g) \text{ @ } 353\text{K and } 101\text{kPa} \\ W &= -P_{\text{ex}} dV = -P [V_{\text{gas}} - V_{\text{liq}}] \\ &= -P * [V_{\text{gas}}] \text{ (} V_{\text{liq}} \text{ is too small to notice)} \\ V_{\text{gas}} &= nRT/P_{\text{ext}} \Rightarrow W = -nRT = (1\text{mol}) * \\ & (8.3145\text{J/mol}) * (353.15) = -2.83 \text{ kJ.} \\ Q &= dH \text{ [since it is const. pressure process]} \\ &= 30.8 \text{ [given: enthalpy of vaporisation].} \\ \text{thus, } dU &= Q+W = (30.8 - 2.83)\text{kJ} = 27.9\text{kJ} \end{aligned}$$

## 2.6 Thermochemical Equations

A thermochemical equation is a chemical equation that includes the  $\Delta H$  value for the reaction. For example:



This thermochemical equation tells us that when we burn one mole of  $\text{C}_5\text{H}_{12}$  at constant temperature and pressure, 3537 kJ of heat is released into the surroundings. The amount of heat absorbed (or released) by a reaction depends critically upon the temperature and pressure at which the reaction is carried out. Therefore, we must always specify the temperature and pressure when giving  $\Delta H$  values for a reaction.

The enthalpy change for a formation reaction could be denoted by  $\Delta H(T,P)$  to emphasize that the enthalpy change depends upon the temperature and pressure at which the reaction is carried out. In order to avoid confusion and ambiguity, and to facilitate the tabulation and use of  $\Delta H$  values, it is customary to adhere to conventions set by the International Union of Pure and Applied Chemists (IUPAC).

**IUPAC defines the  $P^\circ = 1 \text{ bar}$  to be the standard pressure.**

Accordingly, we use the superscript “<sup>0</sup>” to denote quantities associated with the standard pressure  $P^\circ = 1 \text{ bar}$ . For example,

$$\Delta H^\circ(T) =$$

$\Delta H^\circ(T)$  is called the standard enthalpy of reaction. Unless specified otherwise, the temperature is usually assumed to be 298 K and we write  $\Delta H^\circ$  instead of  $\Delta H^\circ(T)$ .

In most cases,  $\Delta H^\circ$  is given for 298 K. An important exception arises when we are dealing with phase changes. For a phase change, the  $\Delta H^\circ$  value is given for the temperature at which the phase transition occurs.

## 2.7 Formation reactions and standard enthalpies of formation

A formation reaction is a reaction in which one mole of a substance is formed from its elements in their reference states. For example, the formation reactions for  $\text{H}_2\text{O}(l)$ ,  $\text{NH}_3(g)$  and  $\text{Fe}_2\text{O}_3(s)$  are:

With relatively few exceptions, the reference state of an element is the most stable form of that element at the temperature and pressure of interest.

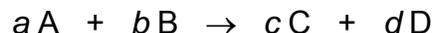
The standard enthalpy change for a formation reaction is denoted  $\Delta H_f^\circ$ .

$\Delta H_f^\circ$  is called the standard enthalpy of formation and in most tabulations,  $\Delta H_f^\circ$  values are given for  $T = 298$  K. (See the table below.) Notice that the standard enthalpy of formation of an element is zero if the element is in its most stable form.

### Standard thermodynamic properties at 298 K

| Substance                          | Mass<br>/ g mol <sup>-1</sup> | $\Delta H_f^\circ$ <sub>298</sub><br>/ kJ mol <sup>-1</sup> | $\bar{S}_{298}^\circ$<br>/ J K <sup>-1</sup> mol <sup>-1</sup> | $\bar{C}_p^\circ$<br>/ J K <sup>-1</sup> mol <sup>-1</sup> |
|------------------------------------|-------------------------------|---|--|--|
| Ar(g)                              | 39.95                         | 0   | 154.84   | 20.79  |
| C(gr.)                             | 12.01                         | 0   | 5.74   | 8.53   |
| C(dia.)                            | 12.01                         | +1.897  | 2.38   | 6.12   |
| CH <sub>4</sub> (g)                | 16.04                         | -74.81  | 186.26   | 35.31  |
| C <sub>6</sub> H <sub>6</sub> (l)  | 78.12                         | +49.00  | 173.30   | 136.1  |
| C <sub>6</sub> H <sub>6</sub> (g)  | 78.12                         | +82.93  | 269.31   | 81.67  |
| CO(g)                              | 28.01                         | -110.53   | 197.67   | 29.14  |
| CO <sub>2</sub> (g)                | 44.01                         | -393.51   | 213.74   | 37.11  |
| Cu(s)                              | 63.55                         | 0   | 33.15  | 24.43  |
| Fe(s)                              | 55.85                         | 0   | 27.3   | 25.1   |
| Fe <sub>2</sub> O <sub>3</sub> (s) | 159.7                         | -824.2  | 87.4   | 103.8  |
| H <sub>2</sub> (g)                 | 2.106                         | 0   | 130.57   | 28.82  |
| H <sub>2</sub> O(l)                | 18.02                         | -285.83   | 69.91  | 75.29  |
| H <sub>2</sub> O(g)                | 18.02                         | -241.82   | 188.83   | 33.58  |
| I <sub>2</sub> (s)                 | 253.81                        | 0   | 116.39   | 54.44  |
| I <sub>2</sub> (g)                 | 253.81                        | +62.44  | 260.69   | 36.90  |
| I(g)                               | 126.90                        | +106.84   | 180.79   | 20.79  |
| N <sub>2</sub> (g)                 | 28.02                         | 0   | 191.50   | 29.12  |
| NH <sub>3</sub> (g)                | 17.04                         | -45.94  | 192.67   | 35.1   |
| NO(g)                              | 30.01                         | +90.25  | 210.76   | 29.84  |
| NO <sub>2</sub> (g)                | 46.01                         | +33.13  | 240.06   | 37.20  |
| O <sub>2</sub> (g)                 | 32.00                         | 0   | 205.04   | 29.35  |
| SO <sub>2</sub> (g)                | 64.06                         | -296.83   | 248.22   | 39.87  |
| SO <sub>3</sub> (g)                | 80.06                         | -395.72   | 256.76   | 50.67  |

$\Delta H_{f,298}^{\circ}$  values are tremendously useful because they can be used to calculate  $\Delta H_{298}^{\circ}$  for any reaction. For the general reaction



$$\Delta H_{298}^{\circ} \equiv$$

$\Delta H_{298}^{\circ}$  is the enthalpy change for the following process:

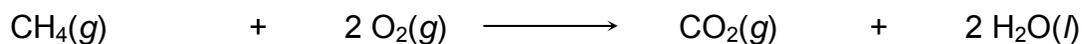


**Example:** Use standard enthalpies of formation (at 298 K) to calculate  $\Delta H_{298}^{\circ}$  for the reaction  $\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$ .

Why is it that we can use  $\Delta H_f^\circ$  values to calculate the standard enthalpy change for any reaction? Since the enthalpy change between two defined states is independent of the path followed, we can imagine that the conversion of reactants into products occurs via the following steps.

- (1) Convert each reactant into its elements.
- (2) Re-combine the elements to give the desired products.

Let's apply this approach to the reaction in the previous example.



## 2.8 Rules for Thermochemical Equations

reverse the reaction  $\Rightarrow$

multiply reaction by “n”  $\Rightarrow$

add reactions together  $\Rightarrow$

## 2.9 Hess' Law

In principle, we could determine the enthalpy change for all reactions experimentally (i.e. via calorimetry). Fortunately, it is not necessary to do so.

Hess' Law states:

*The enthalpy change for a given reaction is the same regardless of whether the reaction is carried out in a single step or occurs via a sequence of steps.*

As a result, we can use the enthalpy changes for a given set to calculate the enthalpy change for a new or different reaction.

**Example:** Use the thermochemical equations below to calculate  $\Delta H^\circ$  for the reaction  $2 \text{C}(s) + 3 \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$ .

