#### Chapter 6: Thermochemistry (Chemical Energy) (Ch6 in Chang, Ch6 in Jespersen)

Energy is defined as the capacity to do work, or transfer heat.

Work (w) - *force* (F) applied through a *distance*.

Force - any kind of *push* or *pull* on an object.

$$\mathbf{F} = \mathbf{ma} \qquad \left( kg \cdot \frac{m}{s^2} \right)$$
$$\mathbf{w} = \mathbf{F} \mathbf{x} \mathbf{d} \qquad \left( kg \cdot \frac{m}{s^2} \times m \right)$$

Chemists define work as *directed* energy change resulting from a process.

The SI unit of work is the Joule  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ 

(Also the calorie 1 cal = 4.184 J (exactly); and the Nutritional calorie 1 Cal = 1000 cal = 1 kcal.

A calorie is the energy needed *to increase the temperature of 1 g of water by 1*  $^{\circ}C$  at standard atmospheric pressure. But since this depends on the atmospheric pressure and the starting temperature, there are several different *definitions* of the "calorie").

There are many *different* types of Energy:

Radiant Energy is energy that comes from the sun (heating the Earth's surface and the atmosphere).

Thermal Energy is the energy associated with the random *motion* of atoms and molecules.

Chemical Energy is *stored* within the *structural units* of *chemical substances*. It is determined by the *type* and *arrangement* of the atoms of the substance.

Nuclear Energy is the energy stored within the collection of *protons* and *neutrons* of an atom.

Kinetic Energy is the energy of *motion*. Chemists usually relate this to molecular and electronic *motion* and *movement*. It depends on the mass (m), and speed (v) of an object.

$$ke = \frac{1}{2} mv^2$$

Potential Energy is due to the *position relative* to other *objects*.

It is "stored energy" that results from attraction or repulsion (e.g. gravity or electrostatic attraction/repulsion).

**PE = mgh** (due to gravity)

The force of electrostatic attraction (or repulsion) between *charged* particles (Coulombs Law):

$$F = k \frac{Q_1 Q_2}{d^2}$$

When one form of energy *disappears*, some other form of energy (of equal magnitude) <u>must</u> appear.  $\Rightarrow$  Law of Conservation of energy: the *total* quantity of energy in the universe is assumed *constant*.

# Transferring Energy: Work and Heat

Heat is the *transfer* of thermal energy between two bodies that are at *different* temperatures. (Remember that temperature is related to the *average kinetic energy* of an object's particles).

Thermochemistry is the study of heat change in chemical reactions.

# Systems and Surroundings

To discuss the energy changes associated with chemical reactions we must first define the specific part of the universe that is of interest to us, which we call the "*system*".

System - what we *study* (e.g. a beaker or flask).

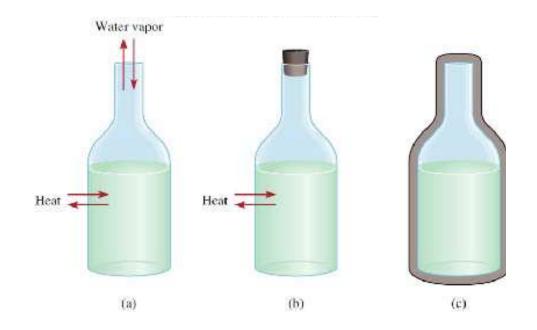
Surroundings - the *rest* of the universe *outside* of our system (e.g. the room where the experiment is performed).

We will study/use three types of systems (open, closed and isolated)...

Open system - can exchange mass (matter) and energy with surroundings (most common).

Closed system - can exchange energy but **not** matter with surroundings.

Isolated system - does **not** allow the transfer of either mass or energy. (E.g. sealed, vacuum coated thermos flask)



Adiabatic Process is defined as a process that occurs in an isolated system, meaning where neither energy nor matter crosses the system/surroundings boundary.

(When permitted) Energy can be exchanged with the surroundings as heat and/or work.

## **Energy Changes and Energy Conservation**

Thermochemistry is a subset of Thermodynamics, which is the scientific study of the interconversion of heat and other kinds of energy.

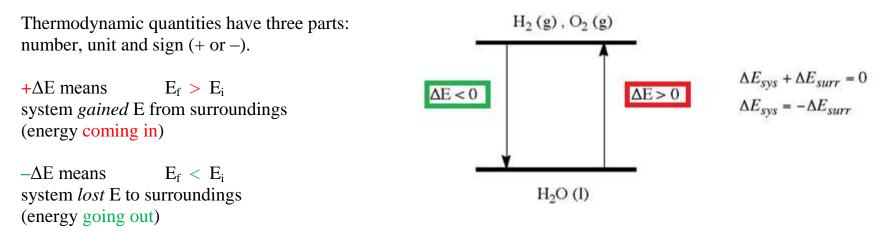
The First Law of Thermodynamics: Energy is neither *created* nor *destroyed*.

Energy is *conserved*. Any energy *lost* by the system is *gained* by the surroundings.

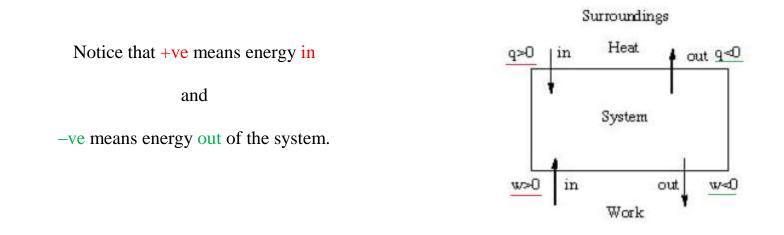
Internal Energy (E) – is the *sum* of all *kinetic* and *potential energy* of *all* components of the *system* (translational, rotational, vibrational, electronic, nuclear, etc).

It is very **difficult** to determine or measure the *absolute total energy* of entities, but it is more *convenient* to measure the *change* in Internal Energy ( $\Delta E$ ) for a given process:

$$\Delta \mathbf{E} = \mathbf{E}_{\text{final}} - \mathbf{E}_{\text{initial}}$$



Heat (q) added to the system, and/or (w) work done on the system, increases the internal energy.



## **Endothermic and Exothermic Processes**

Endothermic – the system absorbs heat. Heat flows into system from surroundings.  $(+\Delta E)$ 

Exothermic – the system evolves heat. Heat flows out of system and into surroundings.  $(-\Delta E)$ 

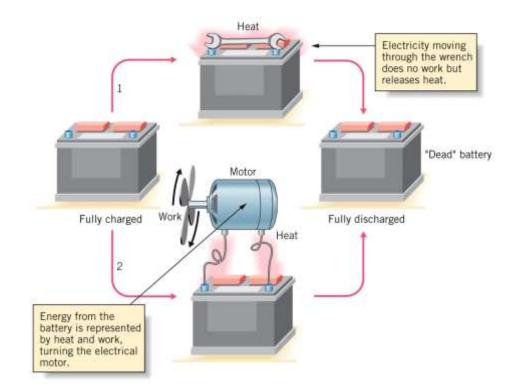
## Relating $\Delta E$ to Heat (q) and Work (w)

Energy is defined as the capacity to *do work*, or *transfer heat*.

Energy can be *exchanged* with the surroundings as heat (q) and/ or work (w).

So we can write this as:

 $\Delta \mathbf{E} = \mathbf{q} + \mathbf{w}$ 



The battery can be *drained* either by heating the wrench, or by work and heat by powering the fan.

# **Internal Energy is a State Function**

The **state** of a system is defined by the *values* of *all relevant macroscopic properties* that *specify* an *object's current condition*. E.g. composition, energy, temperature, pressure and volume, etc.

A state *function* is a property of a system that is determined by specifying its *condition* (in terms of temperature, pressure, internal energy, etc.).

The value of a state function does not depend on the particular history of the sample, only its *present* condition.

The *change* in the state function depends only on the *initial* and *final states* of the *system*, **not** *how* the change occurs.



State functions do **not** depend on the path by which the system arrived at its present state. A state function describes the equilibrium state of a system.

The climbers gain the same gravitational potential energy whether they take the red or blue path.

(Note that work is **not** a state function, since the red path is longer and would take more energy. Work is a *process* function).

#### Work by Expansion

Previously we have seen that (one form of) work can be defined as **force** times **distance** (*mechanical* work). Mechanical work can also be expressed by *expansion* or *compression* of a *gas*.

Pressure-volume work (or PV work) occurs when the volume (V) of a system *changes*:

$$P \times V = \frac{F}{d^2} \times d^3 = Fd = w$$
 1 L·atm = 101.3 J  
volume  
pressure

So at *constant* pressure (such as *atmospheric*):

#### Work, $w = -P\Delta V$

Where P = opposing pressure against which the system (e.g. a *piston*) *pushes*.

 $\Delta V$  = change in volume of gas during expansion =  $V_{\text{final}} - V_{\text{initial.}}$ 



**Problem:** If a gas expands in volume from 1.0 to 4.0 L at constant temperature against a constant pressure of 2.4 atm, how much work is done by the gas?

Work =  $-P\Delta V$ =  $-2.4 \text{ atm} \times (4.0 - 1.0) \text{ L}$ = -7.2 L atm

#### Enthalpy

The *change* in Internal Energy ( $\Delta E$ ) has two components, work (w) and heat (q).

If we operate under a *constant volume*, then  $\Delta V=0$  (and so *no PV work is done*):

$$\Delta E = q + w$$
  
= q - P \Delta V  
$$\Delta E = q_v \qquad \text{at constant V (as indicated by the subscript).}$$

Practically it is **inconvenient** to operate under constant volume, it is much easier to operate under constant pressure (e.g. at atmospheric pressure)...

Heat (q) transferred under *constant-pressure* conditions is called enthalpy, **H**.

Enthalpy is a state function.

E = q + w so q = E - W but W = -PVH = E + PV

E = internal energy; P = pressure; V = volume of the system

The *change* in enthalpy,  $\Delta H$ , equals the heat,  $\mathbf{q}_p$  gained or lost by the system when the process occurs under *constant pressure* (indicated by the subscript p).

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$
$$= q_{\text{p}}$$

We know	ΔΕ	$= \mathbf{q} + \mathbf{w} =$	$\mathbf{q} - \mathbf{P} \Delta \mathbf{V}$
At constant P	ΔΕ	$= q_p - P\Delta V$	
Rearrange to give	$q_p$	$= \Delta E + P \Delta V$	
But also	$q_p$	$= \Delta H$	
SO	$\Delta H$	$= \Delta E + P \Delta V$	

• If  $\Delta H$  is positive the system has gained heat from the surroundings, and is an endothermic process.

• If  $\Delta H$  is negative, the system has released heat to the surroundings, and is an exothermic process.

To recap - for a reaction:

At *constant* volume, the heat change,  $q_v = \Delta E$ .

At constant pressure, the heat change,  $q_p = \Delta H$  (this is the more common scenario).

## The Thermodynamic Standard State

We generally deal with changes in (not absolute values of) energy, so we need some type of reference point.

The standard state of a material (*pure substance*, *mixture* or *solution*) is the reference point used to *calculate* its properties under *different* conditions.

It is that of a pure substance in a *specified* state (its **most stable** *form* and *physical state*), at *1 atm pressure* and at 25 °C; and 1 M concentration for all substances in solution.

It is indicated by the superscript °:

E.g.  $\Delta H^{\circ}$  (means the standard change in Enthalpy)  $\Delta S^{\circ} \qquad \Delta G^{\circ} \qquad E^{\circ}$ 

Now we are ready to talk about *reactions*...

#### **Enthalpies of Physical and Chemical Change - Thermochemical Equations**

For a chemical reaction, the Enthalpy of Reaction is the change in enthalpy going from reactants to products.

 $\Delta \mathbf{H} = \mathbf{H}_{\text{products}} - \mathbf{H}_{\text{reactants}}$ 

The heat of reaction is  $\Delta H_{rxn}$ .

 $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l) \Delta H_{rxn} = -483.6 \text{ kJ/mol}$ 

Enthalpy can be viewed as a measure of *how much heat is stored as potential energy in the system*, or as "*heat content*".

## Three helpful guidelines

1. Enthalpy is an extensive property. The magnitude of  $\Delta H$  is directly proportional to *amount* of reactant consumed in the process.

 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \Delta H = -890 \text{ kJ/mol}$ 

The combustion of two moles of CH<sub>4</sub> would release double the energy, meaning –1780 kJ/mol.

2. The enthalpy change for a reaction is **equal** in magnitude but opposite in sign to  $\Delta H$  for the reverse reaction.

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l) \quad \Delta H = -890 \text{ kJ/mol}$$

$$CO_2(g) + 2 H_2O(l) \rightarrow CH_4(g) + 2 O_2(g) \quad \Delta H = +890 \text{ kJ/mol}$$

3. The enthalpy change for a reaction depends on the physical state of the *reactants* and *products*.

$$\mathbf{H_2O(l)} \rightarrow \mathbf{H_2O(g)} \qquad \Delta \mathbf{H} = +44 \text{ kJ/mol}$$

$$\begin{array}{rcl} \mathbf{CH}_4(\mathbf{g}) & + & \mathbf{2} \ \mathbf{O}_2(\mathbf{g}) & \rightarrow & \mathbf{CO}_2(\mathbf{g}) & + & \mathbf{2} \ \mathbf{H}_2\mathbf{O}(\mathbf{l}) & \Delta \mathbf{H} = -890 \ \mathrm{kJ/mol} \\ \\ & & \mathbf{2} \ \mathbf{H}_2\mathbf{O}(\mathbf{l}) & \rightarrow & \mathbf{2} \ \mathbf{H}_2\mathbf{O}(\mathbf{g}) & \Delta \mathbf{H} = +88 \ \mathrm{kJ/mol} \end{array}$$

Sum and cancel to give...

 $\mathbf{CH}_4(\mathbf{g}) \quad + \quad \mathbf{2} \mathbf{O}_2(\mathbf{g}) \quad \rightarrow \quad \mathbf{CO}_2(\mathbf{g}) \quad + \quad \mathbf{2} \mathbf{H}_2 \mathbf{O}(\mathbf{g}) \quad \Delta \mathbf{H} = -802 \text{ kJ/mol}$ 

**Problem:** The combustion of butane produces heat according to the equation:

 $2 C_4 H_{10}(g) + 13 O_2(g) \rightarrow 8 CO_2(g) + 10 H_2O(l) \Delta H^{\circ}_{rxn} = -5314 \text{ kJ/mol}$ 

What is the heat of combustion per gram of butane?

2 moles of  $C_4H_{10}$  generate -5314 kJ/mol

Molar mass  $C_4H_{10} = 4(12.01) + 10(1.008) = 58.12 \text{ g/mol}$ 

So 2 x 58.12 g/mol generates -5314 kJ/mol

Therefore heat of combustion per g =  $\frac{-5314 \text{ kJ/mol}}{116.24 \text{ g/mol}}$ 

= -45.72 kJ/g

### **Calorimetry and Heat Capacity**

Calorimetry is the measurement of *heat changes*. (Apparatus used is a *calorimeter*).

Understanding calorimetry depends on the concepts of specific heat, and heat capacity.

# Heat Capacity and Specific Heat

Heat capacity (C) is the amount of *heat* required to raise the *temperature* of a given *quantity* of substance by 1 K (or 1 °C).

Specific heat (s) or specific heat capacity is the *heat capacity* of one gram of substance.

Molar heat capacity is the heat capacity of 1 mol of substance.

There is a *practical* issue - we **cannot** measure heat *directly*, but heat *gained* or *lost* (q) is directly proportional to the temperature change ( $\Delta t$ ).

 $\mathbf{q} = \mathbf{C} \Delta t$  where **C** is the *heat capacity*, with units of J/°C, or J/K.

C = s m where m = mass in grams, s has units of J/g °C.

So combining these:  $q = s m \Delta t$  (*Heat exchanged = Specific Heat* × mass × temperature change)

Substance	Specific Heat (J $g^{-1} \circ C^{-1}$ )
Carbon (graphite)	0.711
Copper	0.387
Ethyl alcohol	2.45
Gold	0.129
Granite	0.803
Iron	0.4498
Lead	0.128
Olive oil	2.0
Silver	0.235
Water (liquid)	4.184

# Table of Specific Heats for some Substances

*Larger specific heats* mean it takes *more energy to heat them up*; and conversely, they release a *larger amount* of *heat* as they *cool*.

Notice the large value for water – great for a cooling system like your body; or a heating system like radiators; also explains maritime climates.

**Problem:** The specific heat of ethylene glycol is 2.42 J/gK. How many Joules of heat are necessary to raise the temperature of 62.0 g of ethylene glycol from 15.2 °C to 40.8 °C?

**REMEMBER**  $\Delta t$  in  $^{\circ}C = \Delta t$  in K.  $\Delta t = t_{\text{final}} - t_{\text{initial}}$ 

$$q = m s \Delta t = (62.0 \text{ g}) (2.42 \frac{\text{J}}{\text{g K}}) (40.8 - 15.2 \text{ }^{\circ}\text{C} \left(\frac{1 \text{ K}}{1 \text{ }^{\circ}\text{C}}\right))$$
  
= 3841 J  
= 3.84 kJ

**Problem:** A piece of a newly synthesized material of mass 12.0 g at 88.0 °C is placed in a calorimeter containing 100.0 g of water at 20.0 °C. If the final temperature of the system is 24.0 °C, what is the specific heat capacity of this material?

$$q_{H2O} = -q_{material}$$
  $s_{H2O} = 4.184 \frac{J}{g^{o}C}$   $\Delta t = t_{final} - t_{initial}$ 

 $m_{H2O} S_{H2O} \Delta t_{H2O} = - (m_{mat} S_{mat} \Delta t_{mat})$ 

$$S_{mat} = \frac{m_{H2O} S_{H2O} \Delta t_{H2O}}{-m_{mat} \Delta t_{mat}}$$

$$= \frac{(100.0 \text{ g}) (4.184 \frac{\text{J}}{\text{g}^{\circ}\text{C}}) (24.0 - 20.0 \text{ }^{\circ}\text{C})}{- (12.0 \text{ g}) (24.0 - 88.0 \text{ }^{\circ}\text{C})}$$

$$= 2.18 \frac{J}{g^{o}C}$$

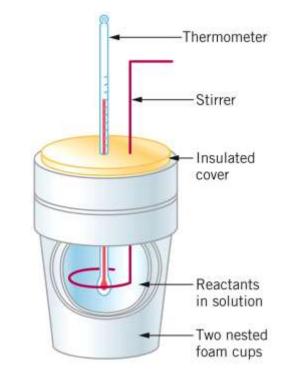
There are two common forms of Calorimeter: constant pressure and constant volume.

Constant Pressure Calorimetry is the simplest.

E.g. a Styrofoam cup calorimeter.

Since it is open to the atmosphere, it is *constant* Pressure. But we **approximate** this as an isolated system. Heat is exchanged between the *reaction* and the *solution* (water). The thermometer measures the change in temperature. The heat of the reaction,  $-q_p = q_{solution}$  $= C \Delta t$ 

= s m  $\Delta t$ 



**Problem:** When a 9.55 g sample of solid sodium hydroxide dissolves in 100.0 g of water in a Styrofoam cup calorimeter, the temperature rises from 23.6  $^{\circ}$ C to 47.4  $^{\circ}$ C.

Calculate  $\Delta$ H (in kJ/mol NaOH) for the solution process:

 $NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$ 

(Assume the specific heat of the solution is the same as that of pure water).

$$q_{soln} = m s \Delta t = -q_{rxn}$$
  $s_{H2O} = 4.184 \frac{J}{g^{o}C}$   $\Delta t = t_{final} - t_{initial}$ 

$$m_{soln} = 9.55 + 100.0 \text{ g} = 109.55 \text{ g}$$

$$q_{soln} = (109.55\text{ g}) (4.184 \frac{\text{J}}{\text{g}^{\text{o}}\text{C}}) (47.4 - 23.6 \text{ }^{\text{o}}\text{C}) = 10908.9 \text{ J}$$

$$9.55 \text{ g} \text{ NaOH x } \frac{1 \text{ mol NaOH}}{40.00 \text{ g} \text{ NaOH}} = 0.23875 \text{ mol}$$

$$\Delta H = \frac{-10908.9 \text{ J}}{1000 \text{ J}} = -45.7 \frac{\text{kJ}}{\text{mol}}$$

0.23875 mol

#### Constant Volume Calorimetry

A bomb calorimeter is used for constant volume reactions.

A known amount of compound is placed the bomb.

The sturdy bomb does not change its volume.

Gas is added to achieve the desired pressure.

The bomb is immersed in a known amount of water.

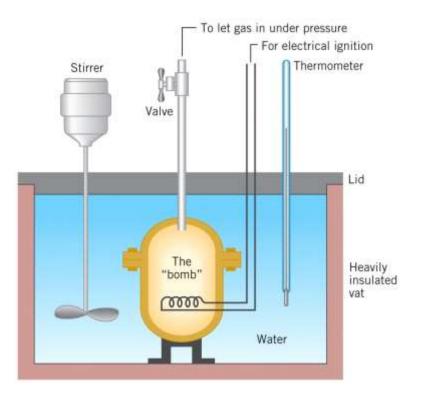
Ignition causes the reaction, and the *heat released raises* the *temperature* of the *water*.

The bomb and the water create an isolated system.

 $\Delta \mathbf{E} = \mathbf{q} - \mathbf{P} \Delta \mathbf{V} = \mathbf{q}_{\mathbf{v}}$  for constant volume.

 $-\mathbf{q}_{rxn} = \mathbf{q}_{calorimter} = \mathbf{C}_{cal} \Delta t$ 

where  $C_{cal}$  = heat capacity of the calorimeter (*determined* by known samples, calibration).



#### **Standard Heats of Formation**

There are some standard enthalpy changes associated with certain processes:

- Enthalpies of vaporization,  $\Delta H_{vap}$  (*liquid* to gas)
- Enthalpies of fusion,  $\Delta H_{fus}$  (*solid* to *liquid*)
- Enthalpies of combustion
- Enthalpy of formation,  $\Delta H_f$ , (or *heat* of *formation*), the formation of a compound from its *constituent elements*.

One of the most useful pieces of information for chemists is...

The standard enthalpy of formation of a compound,  $\Delta H_{f}^{0}$  is the change in enthalpy for the reaction that forms 1 mol of the compound from its elements, with all *substances* in their *standard states*.

(Recall that standard state means the most stable form and physical state of the element at 1 atm and 25 °C).

E.g. the formation of  $CO_2$  uses solid C, gaseous  $O_2$ , and makes gaseous  $CO_2$ ; and for oxygen, we use  $O_2$  not  $O_3$ .

 $C(s) + O_2(g) \rightarrow CO_2(g)$ 

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

Substance	$\Delta H_{\rm f}^{\circ}({\rm kJ/mol})$	Substance	ΔH <sup>°</sup> <sub>f</sub> (kJ/mol)
Ag(s)	0	$H_2O_2(l)$	-187.6
AgCl(s)	-127.0	Hg(l)	0
Al(s)	0	$I_2(s)$	0
$Al_2O_3(s)$	-1669.8	HI(g)	25.9
$Br_2(l)$	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	$N_2(g)$	0
CO(g)	-110.5	$NH_3(g)$	-46.3
$CO_2(g)$	-393.5	NO(g)	90.4
Ca(s)	0	$NO_2(g)$	33.85
CaO(s)	-635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	-1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	O(g)	249.4
HCl(g)	-92.3	$O_2(g)$	0
Cu(s)	0	$O_3(g)$	142.2
CuO(s)	-155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
HF(g)	-271.6	$SO_2(g)$	-296.1
H(g)	218.2	$SO_3(g)$	-395.2
$H_2(g)$	0	$H_2S(g)$	-20.15
$H_2O(g)$	-241.8	Zn(s)	0
$H_2O(l)$	-285.8	ZnO(s)	-348.0

# Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

#### Using Enthalpies of Formation to Calculate Enthalpies of Reaction (Direct Method)

We can calculate the standard enthalpy change for *any* reaction for which we *know* the  $\Delta H^{\circ}_{f}$  values for *all reactants* and *products*.

 $\Delta H^{\circ}_{rxn} = \Sigma n \Delta H^{\circ}_{f}(products) - \Sigma m \Delta H^{\circ}_{f}(reactants)$ (m and n are the equation *coefficients*)

E.g.  $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ 

Substance	$\Delta H^{\circ}_{f}$ (kJ/mol)	
$C_{3}H_{8}(g)$	-103.85	
O <sub>2</sub> (g)	0	
$CO_2(g)$	-393.50	
H <sub>2</sub> O(1)	-285.83	

 $\Delta H^{\circ}_{rxn} = [3 \Delta H^{\circ}_{f}(CO_{2}) + 4 \Delta H^{\circ}_{f}(H_{2}O)] - [\Delta H^{\circ}_{f}(C_{3}H_{8}) + 5 \Delta H^{\circ}_{f}(O_{2})]$ 

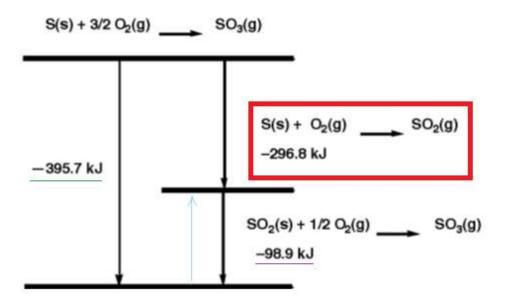
- = [3(-393.50 + 4(-285.83)] [-103.85 5(0)]
- = -2220.05 kJ/mol (addition, so answer to 2 dec. pl.)

## Hess's Law (Indirect Method)

Hess's law states that if a reaction is carried out in a *series* of *steps*,  $\Delta H$  for the **reaction** will be *equal* to the *sum* of the enthalpy changes for the *individual steps*.

Hess pointed out that the heat *absorbed* (or *evolved*) in a given chemical reaction is the same whether the process takes *one* step or *several* steps.

This is *useful* when a reaction **cannot** be measured directly.



Trying to *calculate*:  $S(s) + O_2(g) \rightarrow SO_2(g)$ 

(a) $S + \frac{3}{2}O_2 \longrightarrow SO_3$	$\Delta H = -395.7 \text{ kJ/mol}$
(b) $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$	$\Delta H = -98.9 \text{ kJ/mol}$
$(c) SO_3 \longrightarrow SO_2 + \frac{1}{2}O_2$	$\Delta H = +98.9 \ kJ/mol$

Adding (a) and (c) gives:  $\mathbf{S} + \mathbf{O}_2 \rightarrow \mathbf{SO}_2$ So  $\Delta H = -395.7 + 98.9 = -296.8 \text{ kJ/mol}$  **Problem:** Calculate the enthalpy change for the reaction:

$$3 H_2(g) + O_3(g) \rightarrow 3 H_2O(g)$$

Given the following enthalpies of reaction:

(a)  $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$   $\Delta H = -483.6 \text{ kJ/mol}$ (b)  $3 O_2(g) \rightarrow 2 O_3(g)$   $\Delta H = +284.6 \text{ kJ/mol}$ (c)  $2 O_3(g) \rightarrow 3 O_2(g)$   $\Delta H = -284.6 \text{ kJ/mol}$ 

To generate our desired equation, we must multiply (a) by  $\frac{3}{2}$ , and (c) by  $\frac{1}{2}$ .

$$3 H_2 + \frac{3}{2}O_2 \rightarrow 3 H_2O$$
  $\Delta H = -725.4 \text{ kJ/mol}$   
 $O_3 \rightarrow \frac{3}{2}O_2$   $\Delta H = -142.3 \text{ kJ/mol}$ 

Adding these gives:

 $\Rightarrow$ 

$$3 H_2 + \frac{3}{2} O_2 \rightarrow 3 H_2 O \qquad \Delta H = -725.4 \text{ kJ/mol}$$

$$O_3 \rightarrow \frac{3}{2} O_2 \qquad \Delta H = -142.3 \text{ kJ/mol}$$

$$3 H_2(g) + O_3(g) \rightarrow 3 H_2 O(g) \qquad \Delta H = -867.7 \text{ kJ/mol}$$

**Problem:** Given the following standard reaction enthalpies:

(a)  $O_2(g) \rightarrow 2 O(g) \qquad \Delta H^\circ = +498.4 \text{ kJ} \cdot \text{mol}^{-1}$ (b)  $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \qquad \Delta H^\circ = -200.0 \text{ kJ} \cdot \text{mol}^{-1}$ 

If the standard enthalpy of formation of ozone =  $+142.7 \text{ kJ} \cdot \text{mol}^{-1}$ , calculate the standard reaction enthalpy for the reaction:

$$NO(g) + O(g) \rightarrow NO_2(g)$$

So, (c) The standard enthalpy of formation of ozone:  $\frac{3}{2}O_2 \rightarrow O_3$   $\Delta H = 142.7 \text{ kJ} \cdot \text{mol}^{-1}$ 

So to get our desired equation, we can combine: (c)  $-\frac{1}{2}(a) + (b)$ .

 $\frac{3}{2}O_2 \rightarrow O_3 \qquad \Delta H = +142.7 \text{ kJ} \cdot \text{mol}^{-1}$ 

$$O \rightarrow \frac{1}{2}O_2 \qquad \Delta H^\circ = -249.2 \text{ kJ} \cdot \text{mol}^{-1}$$

 $NO + O_3 \longrightarrow NO_2 + O_2 \qquad \Delta H^\circ = -200.0 \text{ kJ} \cdot \text{mol}^{-1}$ 

 $\Rightarrow \text{ NO } + \text{O } \rightarrow \text{NO}_2 \qquad \qquad \Delta \text{H}^\circ = 142.7 - 249.2 - 200.0 = -306.5 \text{ kJ} \cdot \text{mol}^{-1}$ 

Many physical processes also involve the *absorption* or *release* of heat.

The heat of solution,  $\Delta H_{soln}$ , is the heat *generated* or *absorbed* when a *certain amount* of solute dissolves in a *certain amount* of solvent.

The heat of hydration is the enthalpy change associated with the hydration process.

The heat of dilution is the heat change associated with the dilution process.

The heat of solution represents the difference between the enthalpy of the **final solution** and the enthalpies of its **original components** (i.e. the *solute* and the *solvent*).

The heat of solution can be regarded as the *sum* of the enthalpy changes of three *intermediate steps*:

- 1. The *breaking* of *bonds* within the solute, such as the *electrostatic attraction* between two ions (endothermic)
- 2. The *breaking* of *intermolecular* attractive forces within the solvent, such as hydrogen bonds (endothermic)
- 3. The formation of **new** *attractive* solute-solvent bonds in solution (exothermic).

The value of the *overall* heat of solution is the sum of these steps.

 $\Delta H_{soln} = U + \Delta H_{hydr}$ 

Where U = Lattice energy (the energy required to completely separate one mole of a solid ionic compound into gaseous ions).

The gaseous ions then must become hydrated, which is the heat of hydration.

F	Compound	(kJ/mol)	<u>c Compoun</u>
	LiCl	-37.1	
	CaCl <sub>2</sub>	-82.8	
	NaCl	4.0	
	KCl	17.2	
	NH <sub>4</sub> Cl	15.2	
	NH <sub>4</sub> NO <sub>3</sub>	26.2	

Heats of Solution of Some Ionic Compounds

Notice this can be overall endo- or exothermic depending on the species.

(If you disolve NaCl in water, it actually takes energy, and cools down the solution).