Thermochemistry

❖ The study of the energy transferred as heat during the course of chemical reactions is called **thermochemistry**.

❖ **Thermochemistry** is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the **exchange of energy** between the system and the surroundings.

Thus we can use

Calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy if the reaction occurs at constant volume or with a change in enthalpy if the reaction occurs at constant pressure.

Conversely, if we know ΔU or ΔH for a reaction, we can predict the heat the reaction can produce.

❖ Because the **release** of heat signifies a decrease in the enthalpy of a system, we can now see that **an exothermic process** is one for which **$\Delta H < 0$.**

❖ Conversely, because the **absorption** of heat results in an increase in enthalpy, an endothermic process has **$\Delta H > 0$**:

Exothermic process: **-ΔH**   Endothermic process: **+ΔH**

*Most reactions are conducted **at constant pressure** e.g. **in open vessels** in the laboratory. Energies changes at constant pressure are called the **enthalpy**, given the symbol H.*

In an exothermic change energy is transferred from the system (**chemicals**) to the **surroundings**. The products have less energy than the reactants

University of Al Muthana, college of science, chemistry department

EXOTHERMIC REACTION
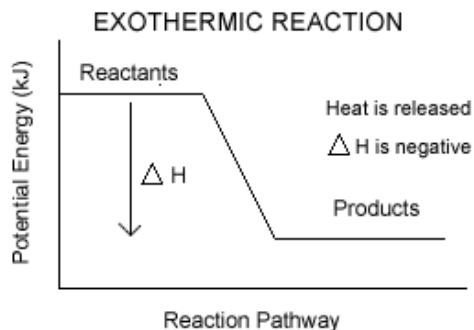
Common oxidation exothermic processes are **the combustion of fuels** and the **oxidation** of carbohydrates such as glucose in respiration.

ENDOTHERMIC REACTION
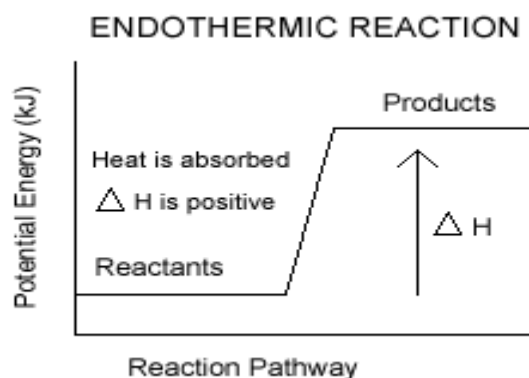
In an endothermic change, energy is transferred from the **surroundings** to the system (**chemicals**). They require an input of heat energy

e.g. thermal decomposition of calcium carbonate. The products have more energy than the reactants.

*The relation between energy change at constant pressure (enthalpy) and internal energy **for gas at the same amount (no. of mole is constant)**:*

$$\Delta H = \Delta U + \Delta(PV)$$
$$\Delta H = \Delta U + nR\,\Delta T$$

In liquid state, the change in the volume V is too small, so

$$\Delta H \approx \Delta U$$

In chemical reaction *no. of mole can be changed, then*

$$\Delta H = \Delta U + RT\,\Delta n$$

Δn= n (products) – n (reactants)

2

University of Al Muthana, college of science, chemistry department

Thermochemical equations

When we write chemical equations to represent chemical reactions, we simply write the **balanced chemical equations**. However, within the realm of the thermodynamics, we must write the chemical equations with change in heat (**enthalpy change**). There are certain properties of thermochemical equations that you should know:

(1)   When heat is lost, the ΔH value is **negative**. The heat value may also be given in the equation itself as a product.

CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (l) ΔH^e = **-890.4 kJ/mol**
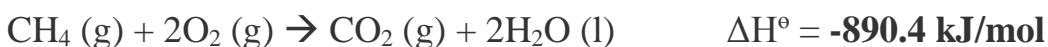
 (2)   When heat is gained, the ΔH value is **positive**. The heat value may also be given in the equation itself as a reactant.

H_2O (s) → H_2O (l) ΔH^e = **+6.01 kJ/mol**

(3) Since heat is a state function, the ΔH value for the same equation may be different if it occurs in **different physical states**. Be sure to specify the phase of the reactants and products using (s), (l), or (g) and be sure to look up the correct ΔH from the heat. The symbol (aq) is used for species in water (aqueous) solution.

H_2O **(s)** → H_2O **(l)** ΔH^e = +6.01 kJ/mol

H_2O **(l)** → H_2O **(g)** ΔH^e = +44 kJ/mol

 The same reactant and product of water but in **different physical states** yields **different enthalpy or ΔH values**!

(4) If a reaction is reversed then the enthalpy (ΔH) value will also **be reversed**. Hence a + becomes a – and vise versa.

H_2O (s) → H_2O (l) ΔH^e = **+6.01 kJ**

H_2O (l) → H_2O (s) ΔH^e = **– 6.01 kJ**

3

(5) If we change the **stoichiometric coefficients** in the chemical reaction, then we also change the enthalpy (ΔH) value ***proportionally!*** Therefore, if **you double** the reactants, you will **double** the products and also **double** the enthalpy (ΔH) and so on…

H_2O (s) → H_2O (l) $ΔH^e$ = **+6.01** kJ/mol
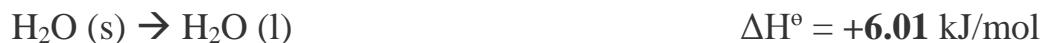
a.) If we **double** the coefficients, we must also **double** the ΔH. Think of it as multiplying the entire equation by 2.

2H_2O (s) → **2**H_2O (l)   ΔH= **+12.02** kJ/mol
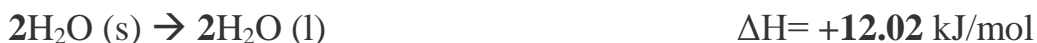
b.) If we **triple** the coefficients, we must also **triple** the ΔH. Think of it as multiplying the entire equation by 3.

3H_2O (s) → **3**H_2O (l)   ΔH= **+18.03** kJ/mol

c.) If we **half** the coefficients, we must also **half** the ΔH. Think of it as multiplying the entire equation by ½.

½ H_2O (s) → ½ H_2O (l)   ΔH = **+3.005** kJ/mol

d.) If we **double** the coefficients AND **reverse**, we must also **double** the ΔH AND **REVERSE** the **sign** of ΔH.

2H_2O (l) → 2H_2O (s)   ΔH = − **12.02** kJ/mol

e) Enthalpy changes are normally quoted at **standard** conditions.

Standard conditions are:

100 kPa (1bar) pressure 298 K (room temperature or 25 °C), Solutions at **1mol dm^{-3}**, All substances should have their **reference state** at 298K

at standard condition, the superscript Plimsoll symbol **(ɵ)** was adopted to indicate the non-zero nature of the standard state.

H_2O (s) → H_2O (l) $ΔH^e$= **+6.01** kJ/mol

4

EX) given the following thermochemical equation

$$CH_4 \text{ (g)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2H_2O \text{ (l)} \qquad \Delta H^\circ = -890.4 \text{ kJ/mol}$$
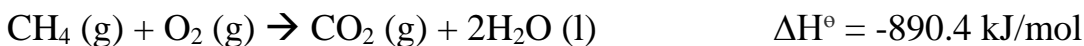
Calculate the heat evolved when 20 g of CH_4 is converted to CO_2 and H_2O.

Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the standard enthalpy of transition and is denoted, $\Delta_{tra}H^\circ$

As an example of a standard enthalpy change, the *standard enthalpy of vaporization, $\Delta_{vap}H^\circ$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in*

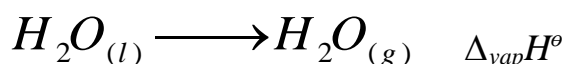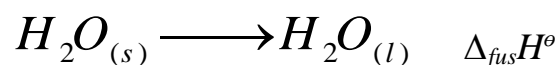$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta_{vap}H^\circ = +44 \text{ kJ mol}^{-1}$$
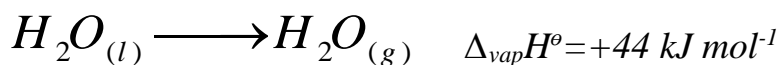
*Another is the **standard enthalpy of fusion, $\Delta_{fus}H^\circ$**, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in*

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \qquad \Delta_{fus}H^\circ = +6.06 \text{ kJ mol}^{-1}$$
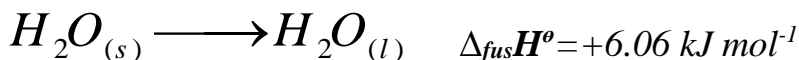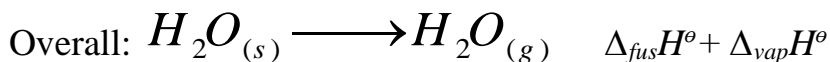
*Because enthalpy is a **state function**, a change in enthalpy is independent of the path between the two states. This feature is of great importance in thermochemistry, For example, we can picture the conversion of a solid to a vapour either as occurring by **sublimation** (the direct conversion from solid to vapour).*

$$H_2O_{(s)} \longrightarrow H_2O_{(g)} \qquad \Delta_{sub}H^\circ$$
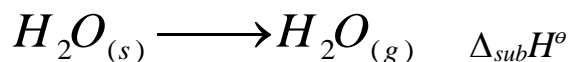
Or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \qquad \Delta_{fus}H^\circ$$

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta_{vap}H^\circ$$

5

Overall: $H_2O_{(s)} \longrightarrow H_2O_{(g)}$ $\Delta_{fus}H^{\theta} + \Delta_{vap}H^{\theta}$

So,

   $\Delta_{sub}H^{\theta} = \Delta_{fus}H^{\theta} + \Delta_{vap}H^{\theta}$

H.W) *Calculate the enthalpy used to convert 5 moles from ice at 273 K to Vapor at 373 K according to following equation:*

$$H_2O_{(g)} \longrightarrow H_2O_{(l)}$$ $\Delta_{con}H^{\theta} = \text{-44 kJ mol}^{-1}$

$$H_2O_{(s)} \longrightarrow H_2O_{(l)}$$ $\Delta_{vap}H^{\theta} = \text{6.06 kJ mol}^{-1}$
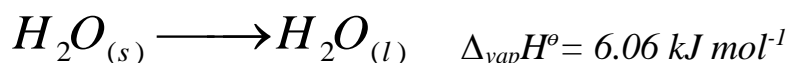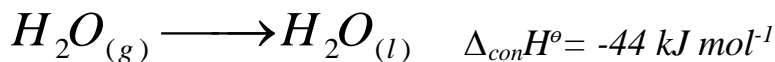
b) Enthalpies of chemical change

Since most of the chemical reactions in laboratory are nothing but the constant-pressure processes, we can write the change in enthalpy (also known as enthalpy of reaction) for a reaction. Consider the following general type of reaction.

 Reactants → products

The ΔH is defined as the difference between the **enthalpies** of **products** and the **reactants**. Thus

 ΔH = H products - H reactants

Alternatively, we write the chemical equation and then report the **standard reaction enthalpy**, Δ_rH (or '**standard enthalpy of reaction**'). Thus, for the combustion of methane, we write

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ $\Delta_rH^{\circ} = \text{-890 kJ/mol}$

For a reaction of the form

$$2A + B \longrightarrow 3C + B$$

$$\Delta_rH^{\ominus} = \{3H_m^{\ominus}(C) + H_m^{\ominus}(D)\} - \{2H_m^{\ominus}(A) + H_m^{\ominus}(B)\}$$

Standard enthalpy change of formation

The **standard enthalpy of formation**, $\Delta_f H^\circ$, of a substance is the standard reaction enthalpy for the formation of **one mole** of the compound from its elements in their **reference states**.

The **reference state** of an element is its most stable state at the specified temperature and 1 bar. For example, at 298 K the reference state of nitrogen is a gas of N_2 molecules that of mercury is liquid mercury, that of carbon is **graphite** not **diamond**, and that of tin is the **white** (metallic) form.

For example, the standard enthalpy of formation of liquid benzene at 298 K refers to the reaction

$$6C_{(s,graphite)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} \quad \Delta_f H^\circ = +49kJ\ mol^{-1}$$
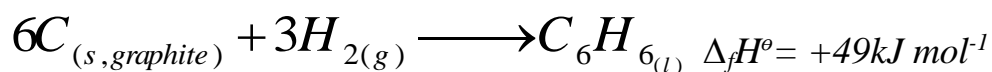
The standard enthalpies of formation of **elements** in their reference states are **zero** at **all** temperatures because they are the enthalpies of such "**null**" reaction.

The standard enthalpy of combustion

The standard enthalpy of combustion of a substance is defined as the **enthalpy change** that occurs when **one mole of** a substance is **combusted completely in oxygen** under **standard conditions. (298K and 100kPa), all reactants and products being in their standard states.** $\Delta_c H^\circ$

An example is the combustion of glucose:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g) \quad \Delta_c H^\circ = -2808kJ\ mol^{-1}$$
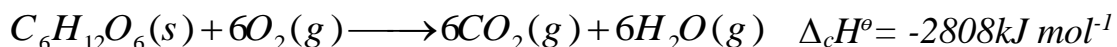
H.W) write **Thermochemical equation of** combustion for the following substance:

1) H_2 (g)   2) C (s)   3) C_5H_{12} (l)   4) C_7H_{14} (l)   5) C_4H_9OH (l)

6) CH_3COOH (l)

University of Al Muthana, college of science, chemistry department