Energetics and Thermodynamics

Energy and Temperature

- Energy is the ability to do work. Some forms of energy include light, sound, and heat.
- Temperature measures the average kinetic energy of molecules

Heat

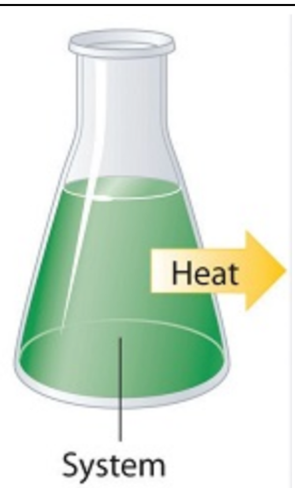
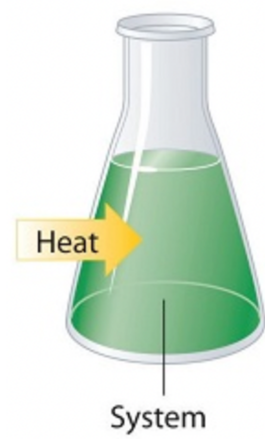
- Heat is a form of energy which is transferred as a result of a difference in temperature.
- They cannot be measured but can only calculated based on experimental data
- Heat based on three factors of nature of substances, mass of substances, and change in temperature of three substances

$$Q = cm\Delta T$$

(c = Heat capacity, with unit of JK, m =mass in kilogram, kg, ΔT = Change in temperature in Kelvin or degree Celsius)

Enthalpy

- Heat content of a substance (at constant pressure)
- Enthalpy is also the internal energy stored in the reactants.
- System – area of interest (Example: beaker and its contents)
- Surroundings – everything else in the universe

Exothermic Reaction	Endothermic Reaction
• The enthalpy change, ΔH, is negative. • The temperature of the surroundings increases (reaction mixture temp increases) • Products are more stable than reactants.	• The enthalpy change, ΔH, is positive. • The temperature of the surroundings decreases. • Reactants are more stable than products.
 Exothermic reaction loses heat to the surrounding	 Endothermic reaction gains heat from the surrounding

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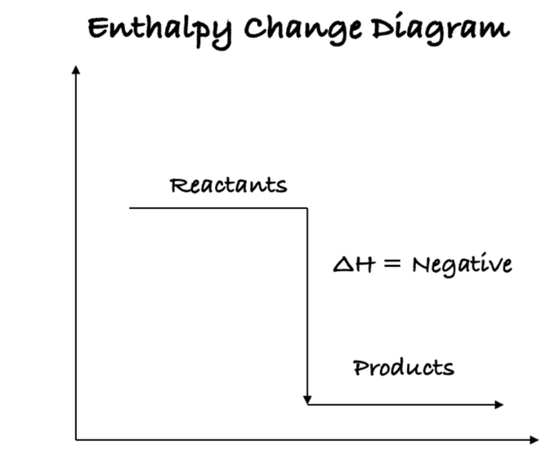

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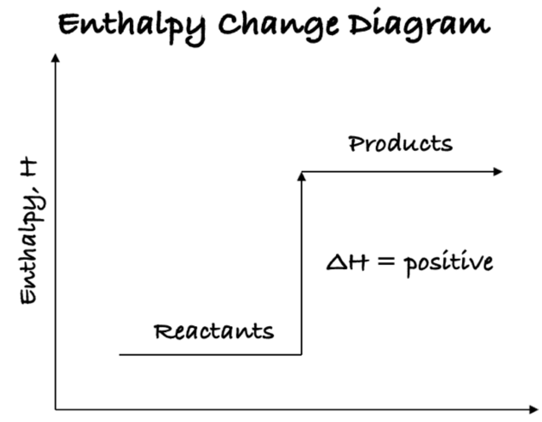

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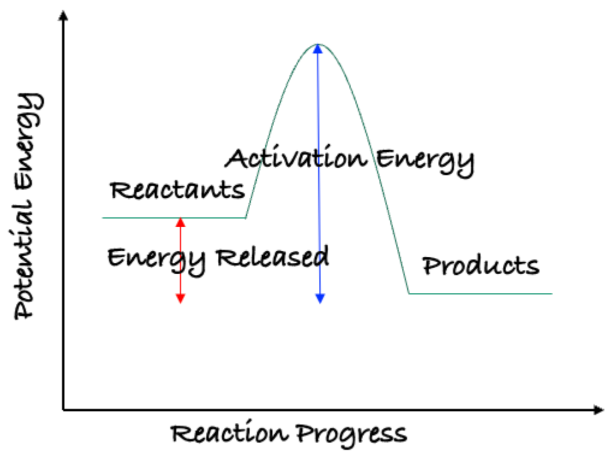

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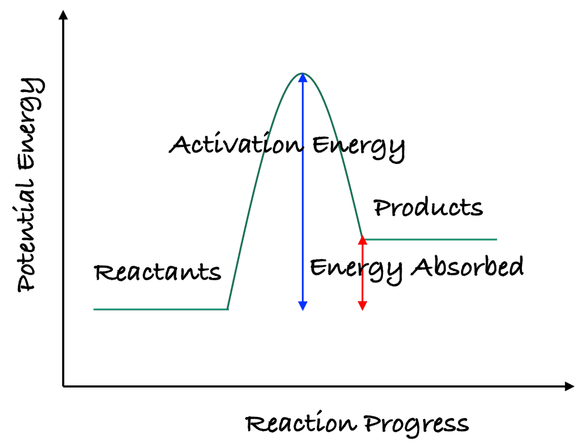

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- Frequent exothermic reactions are combustion, neutralization
- Forming bond releases energy

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- Frequent endothermic reactions are melting, boiling, and evaporation
- Breaking bond requires energy

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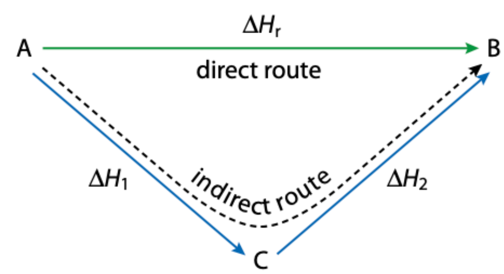
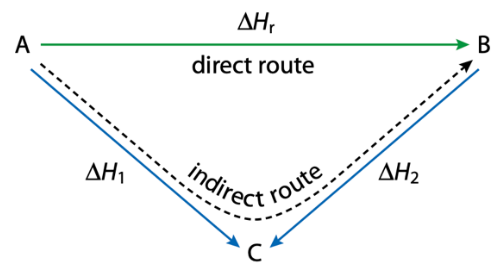
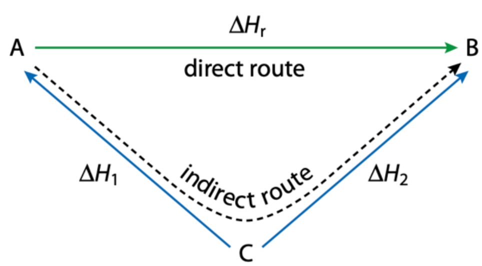
Hess's Law

- The enthalpy change accompanying a chemical reaction is independent of the pathway between the initial and final states.

	$\Delta H = \Delta H_1 + \Delta H_2$
	$\Delta H = \Delta H_1 - \Delta H_2$ This is because you reverse the direction of vector CB, so it changes from ΔH_2 to $-\Delta H_2$
	$\Delta H = -\Delta H_1 + \Delta H_2$ This is because you reverse the direction of vector CA, so it changes from ΔH_1 to $-\Delta H_1$

Two methods of problems solving by using Hess's Law are: energy cycles and manipulating equation

One Example Problem

Use the information given below to calculate the enthalpy change for the reaction:

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$$

$H_2O(l) \rightarrow H_2O(g)\ \ \Delta H = +44kJmol^{-1}$	ΔH_1	Reaction 1
$\Delta H_C^{\ominus}[C_2H_5OH(l)] = -137kJmol^{-1}$	ΔH_2	Reaction 2

$\Delta H_C^{\ominus}[C_2H_4(g)] = -1409 kJmol^{-1}$	ΔH_3	Reaction 3

The Enthalpy changes of formation

- The standard enthalpy of formation is the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions (100 kPa of pressure and 298.15 K).

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

- The enthalpy change of formation of pure elements is zero

One example Problem

Given the enthalpy changes ($kJmol^{-1}$):

$$\Delta H_f^{\ominus}[\mathrm{Fe_2O_3(s)}] = -822; \Delta H_f^{\ominus}[\mathrm{CO(g)}] = -111; \Delta H_f^{\ominus}[\mathrm{CO_2}(g)] = -394$$

Calculate the standard enthalpy change for the reaction

$$\mathrm{Fe_2O_3(s)} + 3\mathrm{CO}(g) \rightarrow 2\mathrm{Fe}(s) + 3\mathrm{CO_2}(g)$$

Solution

1. Enthalpy change of formation is equal to

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

2. Enthalpy change of products is:

$$\sum n\Delta H^{\ominus}_{\text{(products)}} = 2(0) + 3(-394) = -1182 kJmol^{-1}$$

Notice that enthalpy change of formation of an element, is zero

3. Enthalpy change of reactants is:

$$\sum n\Delta H^{\ominus}_{\text{(reactants)}} = -822 + 3(-111) = -1155 kJmol^{-1}$$

4. Subtracting enthalpy change of reactants from products

$$\sum n\Delta H^{\ominus}_{\text{(reactants)}} = -822 + 3(-111) = -1155 kJmol^{-1}$$

$$\Delta H_f^{\ominus} = -27kJmol^{-1}$$

Bond Enthalpy

- Bond enthalpy is the enthalpy change when one mole of covalent bonds, in a gaseous molecule, is broken under standard conditions.

$$\Delta H = \sum H_{(\text{broken})} - \sum H_{(\text{formed})}$$

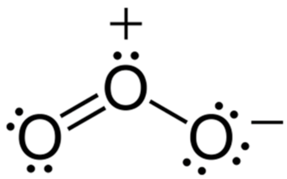
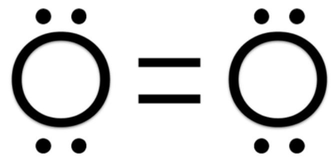
- Average bond enthalpy is the energy required to break one mole of a bond in a gaseous molecule averaged over similar compounds.
    - A positive change in bond enthalpy is to break bonds, and a negative change in bond enthalpy is to form a bond
    - Bond formation is exothermic because it requires energy to over electrostatic forces between atoms, so heat is released.
    - Bond breaking is endothermic, meaning that heat is absorbed. This is because when atoms are hold closely to each other, their potential energy decreases, and kinetic energy increases that is converted into heat.

- Limitations of using bond enthalpy
    - Average bond enthalpy can be used only if both products and reactants are in gaseous state
    - Average bond enthalpies are obtained by considering similar compounds, which vary in different compounds (it will be affected by neighboring atoms). Thus, ΔH values obtained using average bond enthalpies are not necessarily very accurate.

- Values for enthalpy changes of reaction obtained using bond enthalpies are less reliable than those calculated using experimental data such as the enthalpy change of combustion or formation.

Absorption in UV Light

Ozone (O_3) and oxygen (O_2) in the atmosphere protects the Earth surface from damaging effects of ultraviolet radiation as they are absorbed and undergo dissociation – breaking the bond between oxygen atoms.

	
Ozone has a bond order of 1.5	Oxygen molecule has a bond order of 2

$$E = hf = h\frac{C}{\lambda}$$

(E=energy, h=plank's constant, f = frequency, C= speed of high, λ= wavelength)

Since oxygen molecule O_2 has a higher bond order than ozone O_3, it requires more energy to break the bond, and therefore absorbs UV lights with lower wavelength.

Ultraviolet (UV) light from the Sun reaching the Earth can be divided into three components:

- UV-C λ < 280 nm (highest energy)
- UV-B λ = 280–320 nm
- UV-A λ = 320–400 nm

UV rays with a wavelength shorter than 240nm is absorbed by oxygen molecule O_2, causing the molecule to spilite into two individual oxygen atoms that form ozone with other oxygen molecules.

Ozone molecules absorb UW rays up to the wavelength of 330nm. All UV-C λ and UV-B λ are absorbed before reaching earth's surface, and only the less harmful UV- A reaches the earth.

Revision Questions, Paper 1

1. Which combination is correct for the exothermic reaction that occurs between zinc and copper sulfate solution.

	Temperature of solution	Heat released to surroundings	Enthalpy of products greater than enthalpy of reactants
A.	increases	yes	yes
B.	decreases	no	no
C.	increases	yes	no
D.	decreases	no	yes

2. The enthalpy change for the reaction between zinc metal and copper(II) sulfate solution is −217 kJmol−1. Which statement about this reaction is correct?

   A. The reaction is endothermic and the temperature of the reaction mixture initially rises.

B. The reaction is endothermic and the temperature of the reaction mixture initially drops.
C. The reaction is exothermic and the temperature of the reaction mixture initially rises.
D. The reaction is exothermic and the temperature of the reaction mixture initially drops.

3. Which of the following reactions are exothermic?
   I. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_2$
   II. II. NaOH+HCl→NaCl+H_2O
   III. III. Br2→2Br
   A. I and II only
   B. I and III only
   C. II and III only
   D. I, II and III
4. When 100 cm3 of 1.0 moldm−3 HCl is mixed with 100 cm3 of 1.0 moldm−3 NaOH, the temperature of the resulting solution increases by 5.0 °C. What will be the temperature change, in °C, when 50 cm3 of these two solutions are mixed?
   A. 2.5
   B. 5.0
   C. 10
   D. 20

5. Consider the following two equations.

$$2Ca(s) + O_2 \rightarrow 2CaO(s), \Delta H^{\theta} = x \text{ kJ}$$

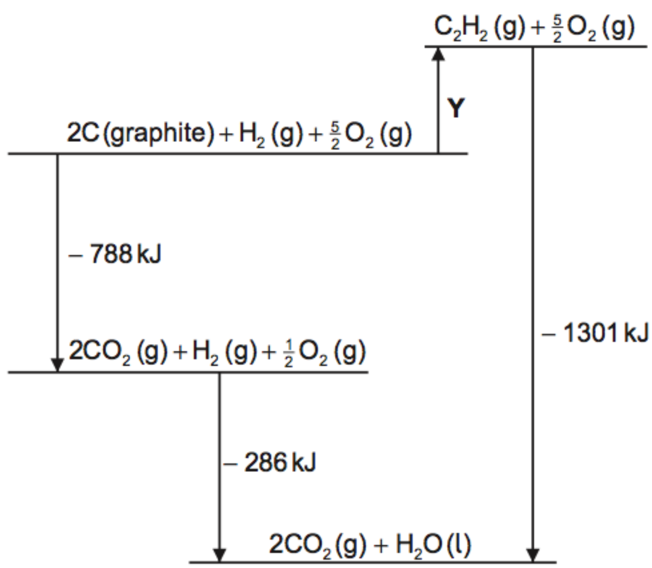
$$2Ca(s) + 0.4O_2 + CO_2 \rightarrow 2CaO_3(s), \Delta H^{\theta} = y \text{ kJ}$$

What is ΔH^{θ}, in kJ, for the following reaction?

$$CaO(s) + CO_2 \rightarrow 2CaO_3(s)$$

   A. y−0.5x
   B. y−x
   C. 0.5−y
   D. x-y
6. 1.0 g of sodium hydroxide, NaOH, was added to 99.0 g of water. The temperature of the solution increased from 18.0 °C to 20.5 °C. The specific heat capacity of the solution is 4.18 $Jg^{-1}K^{-1}$. Which expression gives the heat evolved in $kJmol^{-1}$?
   A. $\frac{25 \times 100.0 \times 4.18 \times 1000}{40.0}$
   B. $\frac{25 \times 100.0 \times 4.18}{40.0 \times 1000}$
   C. $\frac{25 \times 100.0 \times 4.18 \times 40.0}{100}$
   D. $\frac{25 \times 1.0 \times 4.18 \times 40.0}{1000}$

7. What is the enthalpy of formation of ethyne, in kJmol^{-1}, represented by the arrow **Y** on the diagram?



A. −788−286+1301
B. −788−286−1301
C. +788+286−1301
D. +788+286+1301

8. Which equation represents the standard enthalpy change of formation, ΔH_f^Θ, of tetrachloromethane?

A. $C(g) + 4Cl(g) \rightarrow CCl_4(g)$
B. $C(s) + 4Cl(g) \rightarrow CCl_4(l)$
C. $C(g) + 2Cl_2(g) \rightarrow CCl_4(g)$
D. $C(s) + 2Cl_2(g) \rightarrow CCl_4(l)$

9. Which equation represents the standard enthalpy of formation of liquid methanol?

A. $C(g) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$
B. $C(g) + 4H(g) + O(g) \rightarrow CH_3OH(l)$
C. $C(s) + 4H(g) + O(g) \rightarrow CH_3OH(l)$
D. $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$

Revision Questions, Paper 2

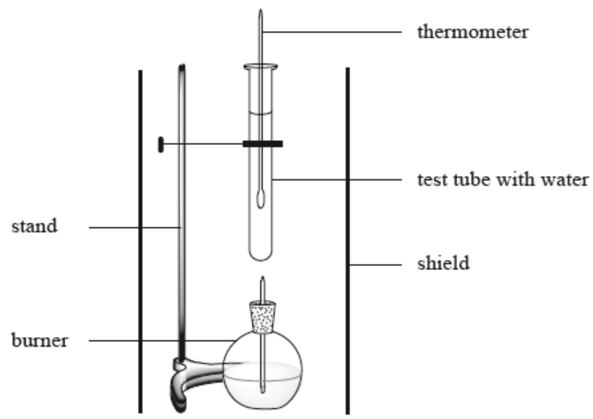
1. Question 1

Methanol is made in large quantities as it is used in the production of polymers and in fuels.

The enthalpy of combustion of methanol can be determined theoretically or experimentally.

$$CH_3OH(l) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

The enthalpy of combustion of methanol can also be determined experimentally in a school laboratory. A burner containing methanol was weighed and used to heat water in a test tube as illustrated below.



The following data were collected.

Initial mass of burner and methanol / g	80.557
Final mass of burner and methanol / g	80.034
Mass of water in test tube / g	20.000
Initial temperature of water / °C	21.5
Final temperature of water / °C	26.4

The Data Booklet value for the enthalpy of combustion of methanol is −726 $\mathrm{kJmol^{-1}}$. Suggest why this value differs from the values calculated in parts (a) and (b).

Using the information from Table 10 of the Data Booklet, determine the theoretical enthalpy of combustion of methanol.

[3]

a.

Calculate the amount, in mol, of methanol burned.

[2]

b.i.

Calculate the heat absorbed, in kJ, by the water.

[3]

b.ii.

Determine the enthalpy change, in $\mathrm{kJmol^{-1}}$, for the combustion of 1 mole of methanol.

[2]

b.iii.
Part (a)

[1]

c.i.
Part (b)

[1]

2. The reaction between ethene and steam is used in the industrial production of ethanol.

C2H4(g)+H2O(g)→C2H5OH(g)

The enthalpy change of the reaction can be calculated either by using average bond enthalpies or by using standard enthalpies of formation.

Determine the enthalpy change of the reaction, in kJmol−1, using the average bond enthalpies in Table 10 of the Data Booklet.

3. [3]

a.

(i) Define the term *standard enthalpy change of formation*.

(ii) Determine the enthalpy change of the reaction, in kJmol−1, between ethene and steam using the enthalpy change of formation values given below.

4.

Compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
C_2H_5OH (g)	−235
C_2H_4 (g)	+52
H_2O (g)	−242

5. [4]

b.

Comment on which of the values obtained in (a) and (b)(ii) is more accurate, giving a reason.

6. [1]

c.

Predict the sign of the entropy change of the reaction, ΔS, giving a reason.

3. Explain, in terms of their bonding, how the presence of oxygen and ozone in the ozone layer helps to prevent both higher and lower energy UV light from reaching the surface of the Earth.