ENERGY
&
THERMOCHEMISTRY

Gasal 2013/2014

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- Energy is essential for life.
- For example:
  - Photosynthesis, which produces energy-rich chemicals such as glucose $C_6H_{12}O_6$.
  - Living organisms extract energy from glucose through a complex web of chemical reactions → the combustion of glucose with oxygen.

$$C_6H_{12}O_{6\,(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{\,(l)} + \text{Energy}$$

  - Decomposition of water molecule

$$2H_2O_{\,(l)} + \text{Energy} \rightarrow 2H_{2(g)} + O_{2(g)}$$

INTRODUCTION

- Energy:
  - Kinetic energy
    - Every moving object has kinetic energy
    - $E_{kinetic} = \frac{1}{2} mv^2$
  - Potential energy: energy due to position or composition
    - Gravitational energy
    - Electrical energy
    - Chemical energy
  - Thermal energy
  - Radiant energy

Law of conservation of energy

"*energy can be converted from one form to another but can be neither created or destroyed*"

THERMODYNAMICS

- **Thermochemistry** is the study of heat changes in chemical reactions.
- Almost all chemical reactions absorb or release energy (ex: combustion, decomposition, dilution, etc.).
- **Thermal energy** is the energy associated with the random motion of atoms and molecules.
- **Heat** is the transfer of the thermal energy between two bodies that are at different temperatures.

- Basically, there are two types of thermal energy transfers in chemical reactions, i.e.:
  - **Exothermic process**

    Any process that gives off heat (transfer thermal energy from the system to its surroundings)

    Example:

    The combustion of hydrogen gas in oxygen that release considerable quantities of energy.

    $$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} + \text{energy}$$

- **Endothermic process**

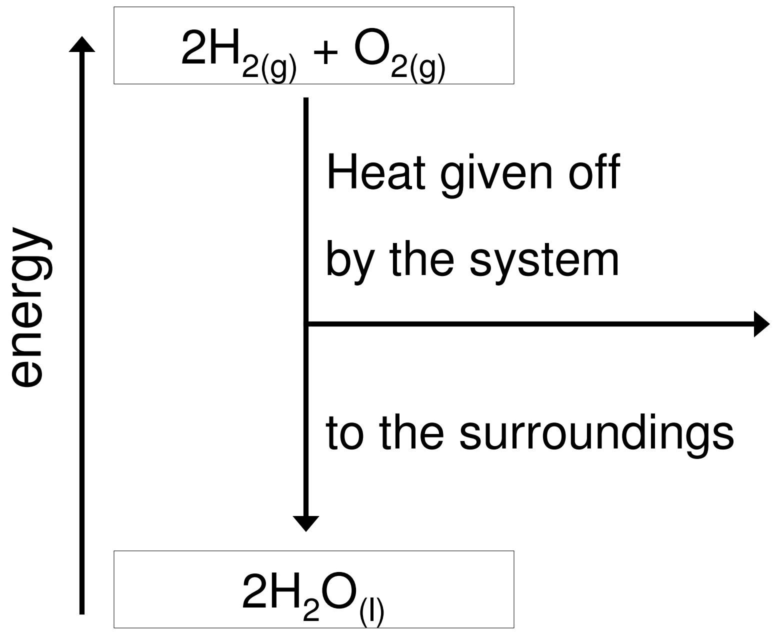
  Heat has to be supplied to the system by the surroundings

  Example:

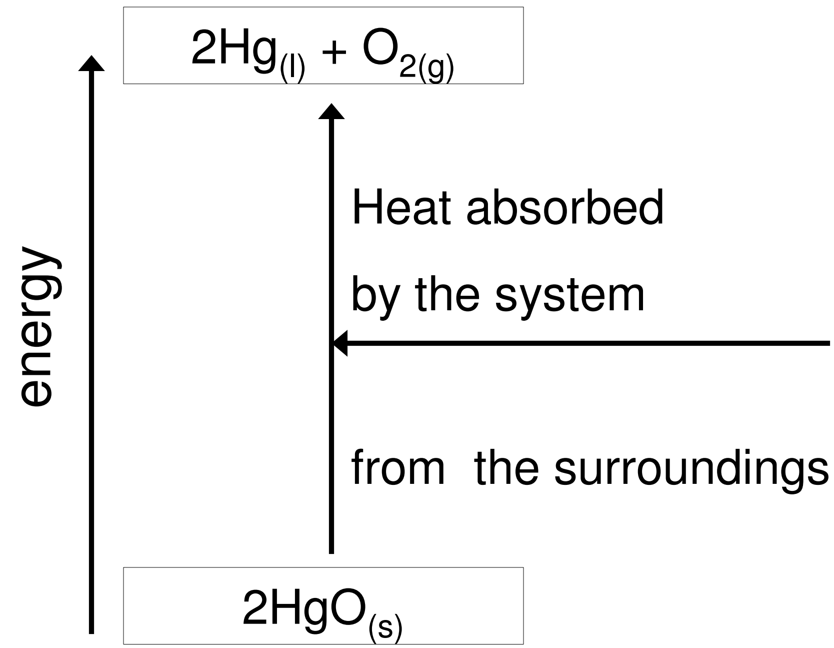
  The decomposition of mercury (II) oxide (HgO) at high temperature

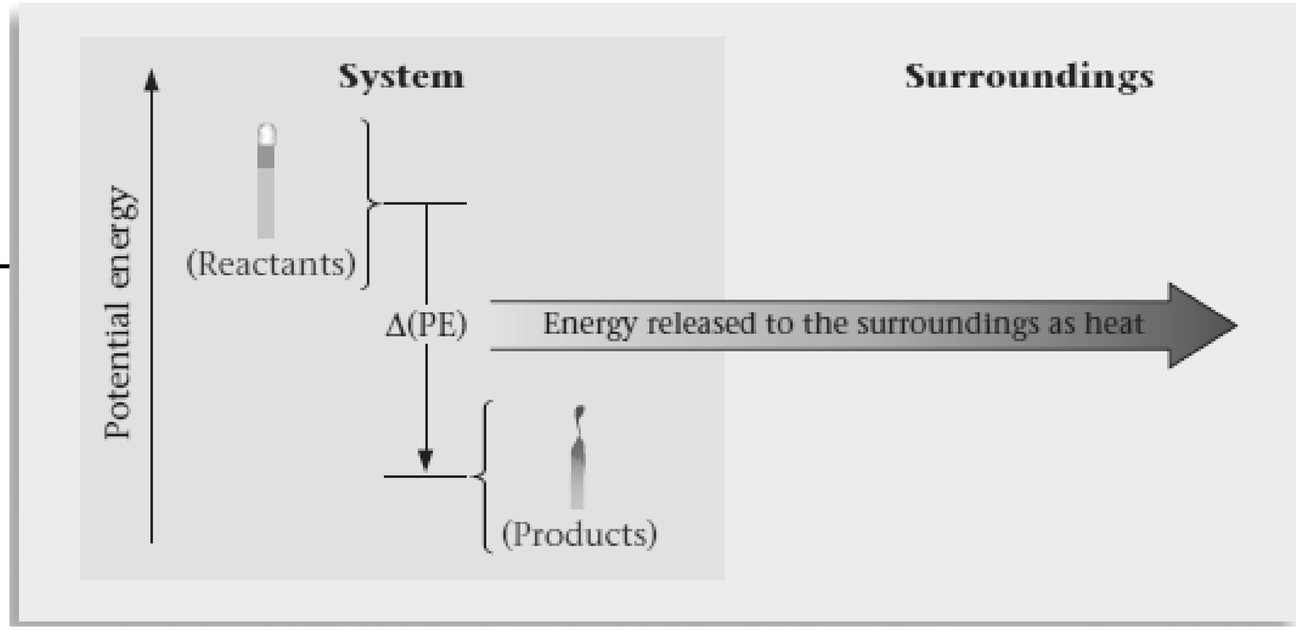
$$\text{energy} + 2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)}$$

Exothermic process



Endothermic process





The heat flow into the surroundings results from a lowering of the potential energy of the reaction system.

In any exothermic reaction, some of the potential energy stored in the chemical bonds is converted to thermal energy (random kinetic energy) via heat.

The first law of thermodynamics

The energy of the universe is constant.

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

ΔE = the change of the internal energy of a system

q = heat

w = work

ENTHALPY AND THERMOCHEMICAL EQUATIONS

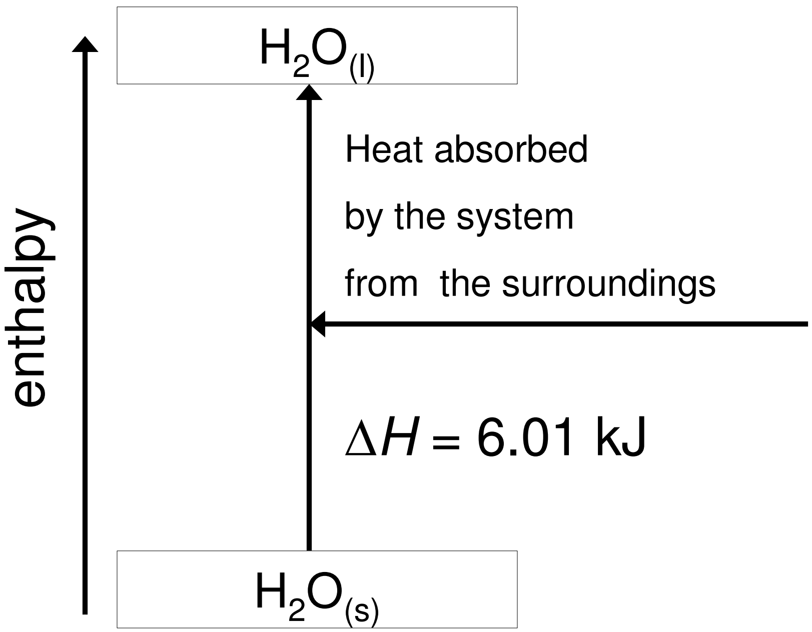
- To express the quantity of the heat released or absorbed in a constant pressure process (H).
- The change in enthalpy = ΔH

  The enthalpy reaction is the difference between the enthalpies of the products and the enthalpies of the reactants.

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

- For endothermic process ΔH is positive, while for exothermic process ΔH is negative.
- Equations showing both mass and enthalpy reactions are called **thermochemical equations**.

Ice can melt to form liquid water at 0°C and a constant pressure of 1 atm. For every mole of ice converted to liquid water, 6.01 kJ of energy are absorbed by the ice.



$H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H = 6.01$ kJ

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

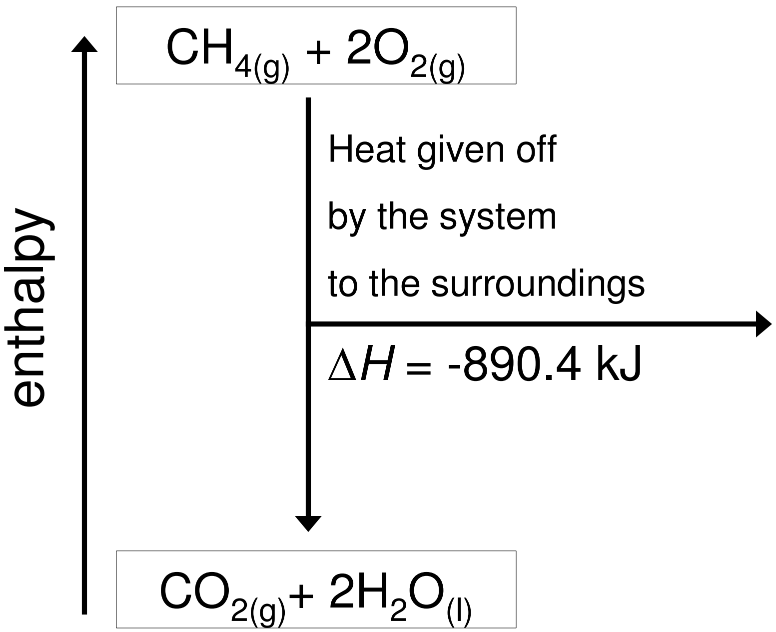
$= H(\text{liquid water}) – H(\text{ice})$

$= 6.01\text{kJ}$

When 1 mole of liquid water is formed from 1 mole of ice at 0°C, the enthalpy change is 6.01kJ

This reaction is an endothermic process.

The combustion of methane



$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$\Delta H = -890.4 \text{ kJ}$$

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

$$= [H(CO_2, g) + 2H(H_2O, l)] - [H(CH_4, g) + 2H(O_2, g)]$$

$$= -890.4 \text{kJ}$$

When 1 mole of gaseous methane reacts with 2 moles of gaseous oxygen to form 1 mole gaseous carbon dioxide and 2 moles of liquid water, the enthalpy change is -890.4 kJ.

This reaction is an exothermic process.

- When the equations are reversed, the roles of reactants and products are changed. The magnitude of for the equation remains the same but its sign changes.
  - $H_2O_{(l)} \rightarrow H_2O_{(s)}$ $\Delta H = -6.01$ kJ
  - $CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_{4(g)} + 2O_{2(g)}$ $\Delta H = 890.4$ kJ
- Multiplying both sides of thermochemical equation by n factor will also change by the same factor.

CALORIMETRY

- The measurement of heat changes, which is influenced by specific heat and heat capacity.
  - Specific heat (s) (J/g.^{o}*C)*

    is the amount of heat required to raise temperature of 1 gram of a substance by 1^{o}C.
  - Heat capacity (C)(J/^{o}*C)*

    is the amount of heat required to raise the temperature of a given quantity of a substance by 1^{o}C.

$$C = m.s$$

m is the mass of a substance in grams

- If the specific heat and the amount of a substance are known, then the change in the sample's temperature (Δt) can determine the amount of heat (q) that has been absorbed or released in a particular process.

$$q = ms\,\Delta t$$

$$q = C\,\Delta t$$

$$\Delta t = t_{final} - t_{initial}$$

Specific Heats of Some Common Substances

Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

Sample question 1

- A 466 g sample of water is heated from 8.5^oC to 74.6^oC. If the specific heat of water is 4.184 J/g. ^oC, calculate the amount of heat absorbed by the water!
- $q = ms\,\Delta t$

  $= (466\ g)\ (4.184\ J/g.\ ^oC)\ (74.6^oC - 8.5^oC)$

  $= 1.29 \times 10^5\ J$

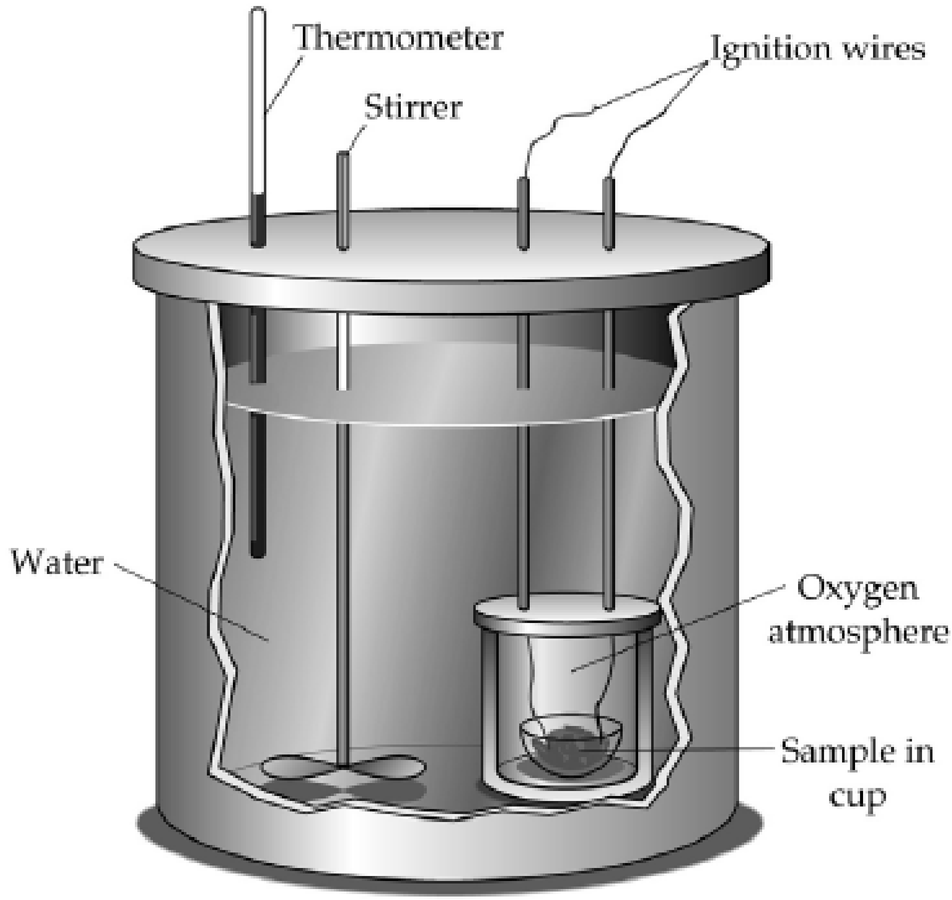
  $= 129\ kJ$

Heat changes can be measured using:

- Constant-Volume Calorimeter
  - It is usually used to measure heats of combustion, by placing a known mass of a compound in a constant-volume bomb calorimeter, which filled with oxygen at about 30 atm of pressure.
  - The closed calorimeter is immersed in a known amount of water. The sample is ignited electrically and heat produced by the combustion can be calculated accurately by recording the rise in temperature of the water. The heat given off by the sample is absorbed by the water and the calorimeter. No heat loss to the surroundings.

$$q_{system} = q_{water} + q_{bomb} + q_{rxn}$$
$$= 0$$
$$q_{rxn} = -(q_{water} + q_{bomb})$$
$$q_{water} = ms\,\Delta t$$
$$q_{bomb} = C_{bomb}\,\Delta t$$

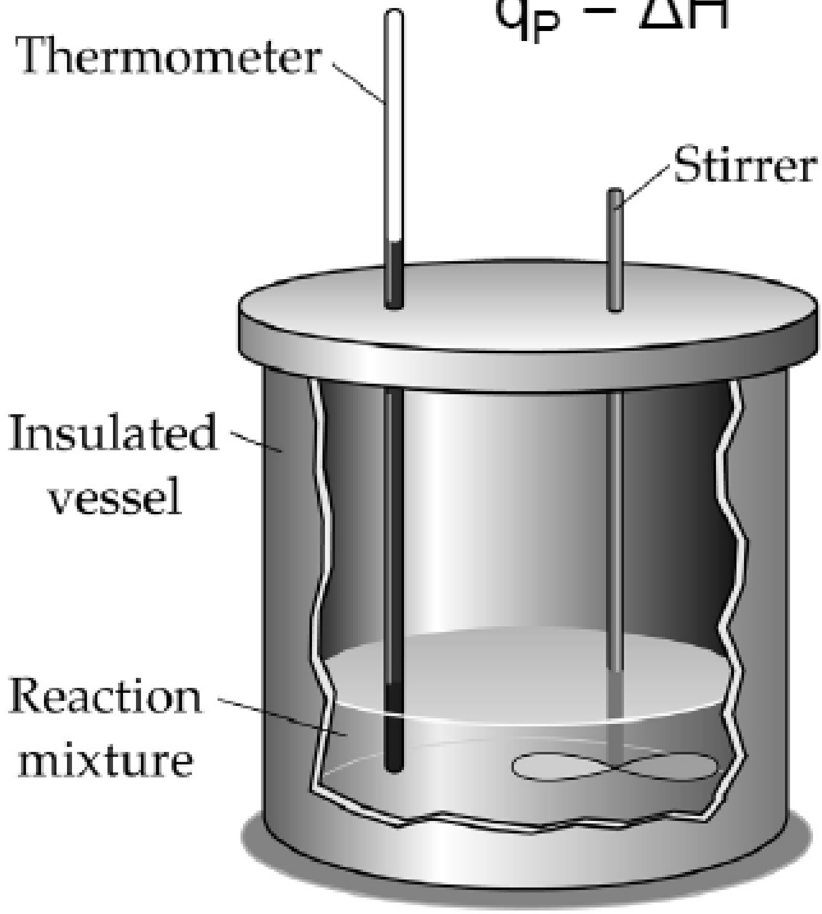
$q_v = \Delta E$



Constant Volume

- Constant-Pressure Calorimeter
  - For determining heats of reactions for other than combustion reactions, including acid-base neutralization reactions, heats of solution and heats of dilution.
  - Because the measurement carried out under constant atmospheric conditions, the heat change for the process (q_{rxn}) is equal to the enthalpy change (ΔH).

$q_P = \Delta H$



Constant Pressure

Heat of some typical reaction measured at constant pressure:

- Heat of neutralization

  $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$, $\Delta H = -56.2$ kj

- Heat of ionization

  $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$ $\Delta H = 56.2$ kj

- Heat of fusion

  $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H = 6.01$kj

- Heat of vaporization

  $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H = 44.0$ kj

- Heat of reaction

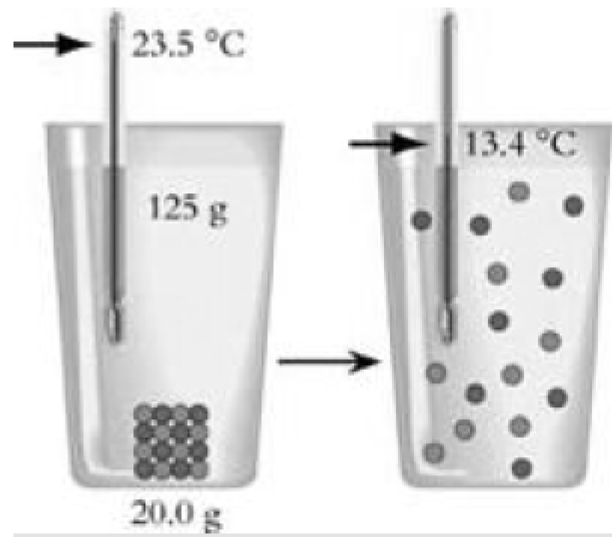
  $MgCl_{2(s)} + 2Na_{(l)} \rightarrow 2NaCl_{(s)} + Mg_{(s)}$ $\Delta H = -180.2$ kj

Sample question 2

- A quantity of 1.435 g of naphthalene ($C_{10}H_8$) was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.17^oC to 25.84^oC. The specific heat of water is 4.184 J/g. ^oC. If the quantity of water surrounding the calorimeter was exactly 2000 g and the heat capacity of the bomb was 1.80 kJ/^oC, calculate the heat of combustion of naphthalene on a molar basis (the molar heat of combustion)!
- $q = ms\,\Delta t$

Sample question 3

- Ammonium nitrate (NH_4NO_3, MM= 80.05 g/mol) is used in cold packs to "ice" injuries. When 20.0 g of this compound dissolves in 125 g of water in a coffee-cup calorimeter, the temperature falls from 23.5 ℃ to 13.4 ℃. Determine q for the dissolving of the compound. Is the process exothermic or endothermic?



STANDARD ENTHALPY OF FORMATION AND REACTION

- The enthalpy value of a substance is relative values, not absolute values → must be compared with arbitrary reference point / "enthalpy of formation".
- Standard enthalpy of formation ($\Delta H°_f$) is the heat change (kJ) when 1 mole of the compound is synthesized from its elements under standard state conditions (constants pressure conditions at 1atm).
- Once we know $\Delta H°_f$, we can calculate the enthalpy reaction.
- Standard enthalpy of reaction:

$$(\Delta H°_{rxn}) = \Sigma n\ \Delta H°_f(\text{products}) - \Sigma m\ \Delta H°_f(\text{reactants})$$

m, n denote the stoichiometric coefficients for reactants and products.

- The standard enthalpy of formation of any element in its most stable form is zero.

Standard States of Elements

ΔH_f^0 for each of these is **zero**

Element	Standard State at 298.15 *K* and 1 *bar*
hydrogen	H_2 (*g*)
carbon	graphite*
nitrogen	N_2 (*g*)
oxygen	O_2 (*g*)
fluorine	F_2 (g)
phosphorous	white (*s*) *
sulfur	S_8 (rhombic) *
chlorine	Cl_2 (*g*)
bromine	Br_2 (*l*)†
xenon	Xe (*g*)

- The standard enthalpy of formation of any element in its most stable form is zero.
  - $\Delta H^0 f$ (O_2) = 0
  - $\Delta H^0 f$ (O_3) = 143 kJ/mol

  - $\Delta H^0 f$ (C, graphite) = 0
  - $\Delta H^0 f$ (C, diamond) = 1.90 kJ/mol

There are two ways to measure *m* $\Delta H°_f$ of compounds:

- Direct method

  Applied to compounds which can be readily synthesized from their elements.

  - Example:

    C(graphite) + $O_{2(g)}$ → $CO_{2(g)}$ $\Delta H°_f$ = -393.5kJ

    $\Delta H°_{rxn}$ = (1mol) $\Delta H°_f$ (CO_2, g) – [(1 mol) $\Delta H°_f$ (C, graphite) + (1mol) $\Delta H°_f$ (O_2, g)]

    = -393.5 kJ

  - Since both graphite and oxygen are stable allotrophic forms, $\Delta H°_f$ (C, graphite) and $\Delta H°_f$ (O_2, g) are zero.

    $\Delta H°_{rxn}$ = (1mol) $\Delta H°_f$ (CO_2, g) = -393.5 kJ

    $\Delta H°_f$ (CO_2, g) = -393.5 kJ/mol

- Indirect Method
  - For many compounds that can’t be directly synthesized from their elements due to:
    - the reactions of interest may proceed too slowly or
    - undesired side reactions may produce substances other than compounds of interest.

Hess's Law

- For determining $\Delta H°_f$ through indirect approach.
- "When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps".
- Example:

  C (diamond) → C (graphite)

  $\Delta H°_{rxn}$ = (1mol) $\Delta H°_f$ (C, graphite) – (1 mol) $\Delta H°_f$ (C, diamond)

  Since $\Delta H°_f$ (C, graphite) = 0,

  $\Delta H°_{rxn}$ = -(1 mol) $\Delta H°_f$ (C, diamond)

The enthalpy changes of the reaction:

a) C (diamond) + $O_{2(g)}$ → $CO_{2(g)}$ $\Delta H°_{rxn}$ = -395.4 kJ

b) C (graphite) + $O_{2(g)}$ → $CO_{2(g)}$ $\Delta H°_{rxn}$ = -393.5 kJ

Reversing equation (b)

c) $CO_{2(g)}$ → C (graphite) + $O_{2(g)}$ $\Delta H°_{rxn}$ = 393.5 kJ

Then:

a) C (diamond) + ~~$O_{2(g)}$~~ → ~~$CO_{2(g)}$~~ $\Delta H°_{rxn}$ = -395.4 kJ

c) ~~$CO_{2(g)}$~~ → C (graphite) + ~~$O_{2(g)}$~~ $\Delta H°_{rxn}$ = 393.5 kJ

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d) C (diamond) → C (graphite) $\Delta H°_{rxn}$ = -1.9 kJ

$\Delta H°_f$ (C, diamond) = - $\Delta H°_{rxn}$ / mol

= + 1.9 kJ

Sample Question 4

- Pentaborane-9, B_5H_9, is a highly reactive substance which will burst into flame or even explode when it exposed to oxygen:

  $$2B_5H_{9(l)} + 12O_{2(g)} \rightarrow 5\ B_2O_{3(s)} + 9H_2O_{(l)}$$

  Pentaborane-9 was once used as rocket fuel since it produces a large amount of heat per gram. Calculate the kJ of heat released per gram of the compound reacted with oxygen. The standard enthalpy of formation of B_5H_9 ,B_2O_3 and water are 73.2 kJ/mol, -1263.6 kJ/mol and -285.8 kJ/mol, respectively.

Question 5

- From the following equations and the enthalpy changes:

a) C (graphite) + $O_{2(g)}$ → $CO_{2(g)}$ $\Delta H°_{rxn}$ = -393.5 kJ

b) $H_{2(g)}$ + $^{1/2}O_{2(g)}$ → $H_2O_{(l)}$ $\Delta H°_{rxn}$ = -285.8 kJ

c) $2C_2H_{2(g)}$ + $5O_{2(g)}$ → 4 $CO_{2(g)}$ + 2 $H_2O_{(l)}$ $\Delta H°_{rxn}$ = -2598.8 kJ

Calculate the standard enthalpy of formation of acetylene from its elements:

2C (graphite) + $H_{2(g)}$ → $C_2H_{2(g)}$

Heats of Formation

Formula	ΔH_f^o (kJ/mol)
Calcium	
$Ca(s)$	0
$CaO(s)$	−635.1
$CaCO_3(s)$	−1206.9
Carbon	
C(graphite)	0
C(diamond)	1.9
$CO(g)$	−110.5
$CO_2(g)$	−393.5
$CH_4(g)$	−74.9
$CH_3OH(l)$	−238.6
$HCN(g)$	135
$CS_2(l)$	87.9
Chlorine	
$Cl(g)$	121.0
$Cl_2(g)$	0
$HCl(g)$	−92.3
Hydrogen	
$H(g)$	218.0
$H_2(g)$	0

Formula	ΔH_f^o (kJ/mol)
Nitrogen	
$N_2(g)$	0
$NH_3(g)$	−45.9
$NO(g)$	90.3
Oxygen	
$O_2(g)$	0
$O_3(g)$	143
$H_2O(g)$	−241.8
$H_2O(l)$	−285.8
Silver	
$Ag(s)$	0
$AgCl(s)$	−127.0
Sodium	
$Na(s)$	0
$Na(g)$	107.8
$NaCl(s)$	−411.1
Sulfur	
S_8(rhombic)	0
S_8(monoclinic)	2
$SO_2(g)$	−296.8
$SO_3(g)$	−396.0

THANK YOU…