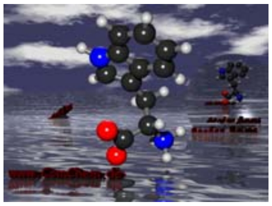
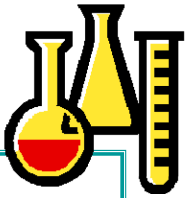
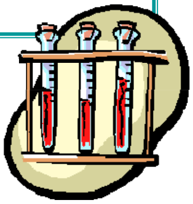




Chapter 5

Thermochemistry

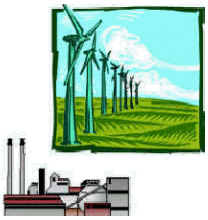


Preview

- Introduction to thermochemistry:
  - Potential energy and kinetic energy.
  - Chemical energy.
  - Internal energy, work and heat.
  - Exothermic vs. endothermic reactions.
  - *PV* work.
  - Enthalpy.
- Calorimetry.
- Hess’s law.
- Standard enthalpies of formation.

Chapter 5 Section 1

The Nature of Energy



- Energy, including all of its different classes, is very essential for our lives.
  - Macroscopic scale: fossil fuels, water and winds, solar, heat (thermal), electricity, etc.
  - Microscopic scale: chemical reactions in living cells, nuclear energy, etc.
- Energy can be converted form one form to another.
- Energy: is the capacity to do work or to transfer heat.

Chapter 5 Section 1

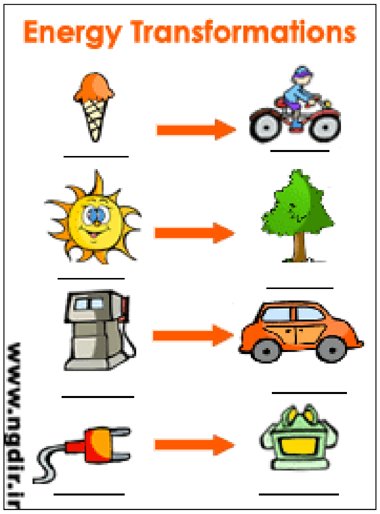
The Transformation of Energy

- *The law of conservation of energy*.

  Energy can be converted from one form to another but can neither be created nor destroyed.

  $$\boxed{E_{\text{Universe}} = \text{constant}}$$

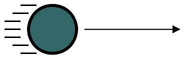
  First law of thermodynamics; the law of conservation of energy
- All forms of energy are either ***potential*** or ***kinetic***.



Chapter 5 Section 1

Kinetic Energy

- **Kinetic Energy (KE):** due to the ***motion*** of an object.
  - KE = ½ (mu^2)



m is mass and u is velocity

  - ***Thermal Energy*** - one form of kinetic energy associated with the random motion of atoms/ molecules.

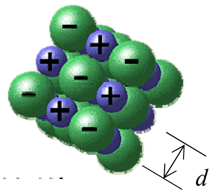
Thermal energy α Temperature.

Chapter 5 Section 1

Potential Energy

- **Potential Energy (PE):** due to ***position*** or ***composition***.
  - ***Chemical energy*** - is stored within structural units of chemical substances.
  - ***Electrostatic energy*** is energy resulting from the interaction of charged particles.

$$\boxed{E_{\mathrm{el}} \propto \frac{Q_1 Q_2}{d}}$$



- Q = charge ; d = distance
- + E_{el}: repulsive
- − E_{el}: attractive

Interconversion between KE and PE

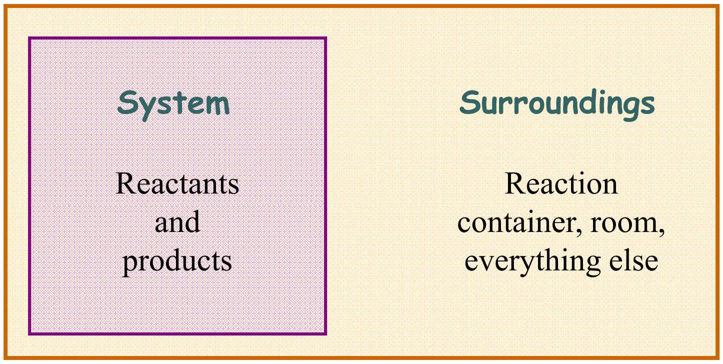
- KE and PE are *interconvertible*.

	PE	**KE**
Macro-scale	Water behind a dam	Water when it falls down from the dam
Micro-scale	Gasoline before it burns (***chemical energy***)	when gasoline burns up and gives power to the engine (***thermal energy***)

Remember that interconversion between PE and KE is always governed by the law of conservation of energy.

Energy Changes in Chemical Reactions

- System vs. surroundings



System

Reactants
and
products

Surroundings

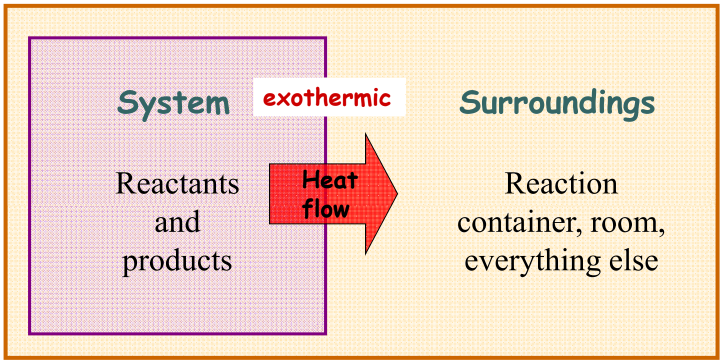
Reaction
container, room,
everything else

Chapter 5 Section 1

Energy Changes in Chemical Reactions

- Combustion of fossil fule:

  $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$ + thermal energy



Energy lost from the system = Energy gained by the surroundings

---

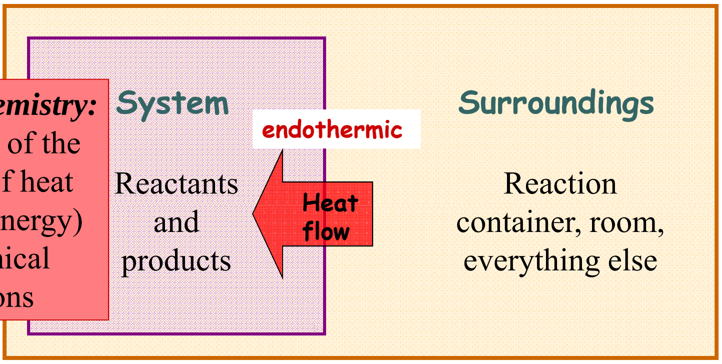
Chapter 5 Section 1

Energy Changes in Chemical Reactions

- Formation of nitric oxide:

  $N_2(g) + O_2(g)$ + thermal energy (*heat*) $\longrightarrow 2NO(g)$

Thermochemistry: The study of the transfer of heat (thermal energy) in chemical reactions



Energy gained by the system = Energy lost from the surroundings

Chapter 5 Section 1

Exothermic and Endothermic Reactions

- In methane combustion the energy (*heat*) flows out of the system.

  It is an exothermic reaction.

Another example: $H_2O(l) \longrightarrow H_2O(s)$ + energy (*heat*)

- Nitric oxide formation is an endothermic reaction.

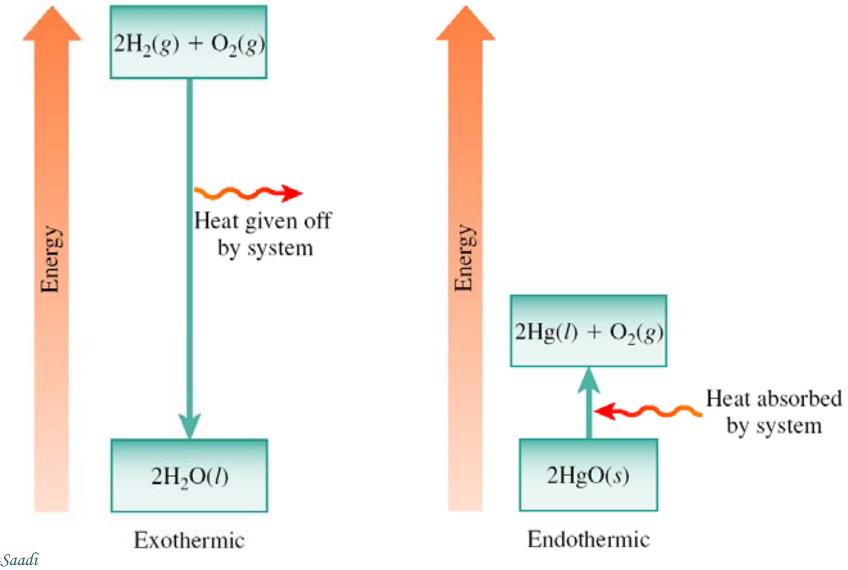
  $N_2(g) + O_2(g)$ + energy (*heat*) $\longrightarrow 2NO(g)$

  Here the heat flows from the surroundings into the system.

Another example: $H_2O(s)$ + energy (*heat*) $\longrightarrow H_2O(l)$

Chapter 5 Section 1

Exothermic and Endothermic Reactions



Units of Energy

- ***Joule* (J)** is the SI unit for energy.
  - The amount of energy possessed by a 2 kg mass moving at a speed of 1 m/s.

$$\begin{aligned} E_{\mathrm{k}} &= \tfrac{1}{2}mu^2 \\ &= \tfrac{1}{2}(2\ \mathrm{kg})(1\ \mathrm{m/s})^2 \\ &= 1\mathrm{kg}\cdot\mathrm{m}^2/\mathrm{s}^2 \quad = 1\ \mathrm{J} \end{aligned}$$

  - The amount of energy exerted when a force of 1 Newton (N) is exerted over 1 m distance.

$$1\ \mathrm{J} = 1\ \mathrm{N}\cdot\mathrm{m}$$
$$1\ \mathrm{N} = 1\ \mathrm{kg}\cdot\mathrm{m/s}^2$$

Units of Energy

- ***Calorie* (cal)** - commonly used on food labels.
  - 1 cal = 4.184 J
  - 1000 cal = 1 Cal = 1 kcal
  - Food calories (Cal) are really 1000 calories (cal).

Nutrition Facts

Serving Size About 24 biscuits (59g/2.1 oz.)

Servings Per Container About 12

Amount Per Serving	Cereal	Cereal with ½ Cup Vitamins A&D Fat Free Milk
Calories	200	240
Calories from Fat	10	10
	% Daily Value**	
Total Fat 1g*	**2**%	**2**%
Saturated Fat 0g	**0**%	**0**%
Monounsaturated Fat 0g		
Polyunsaturated Fat 0.5g		
Trans Fat 0g		
Cholesterol 0mg	**0**%	**0**%
Sodium 5mg	**0**%	**3**%
Potassium 200mg	**6**%	**12**%
Total Carbohydrate 48g	**16**%	**18**%

Chapter 5 Section 1

Exercise

Calculate the kinetic energy of a neon atom moving at a speed of 98 m/s.

$$E_k = \tfrac{1}{2}mu^2$$

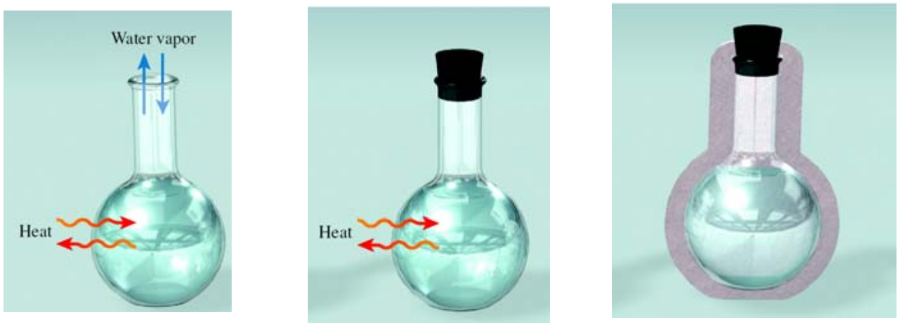
$$E_k = \frac{1}{2}(3.352\times10^{-26}\,\mathrm{kg})(98\,\mathrm{m/s})^2$$

$$E_k = 1.6\times10^{-22}\,\mathrm{J}$$

Chapter 5 Section 2

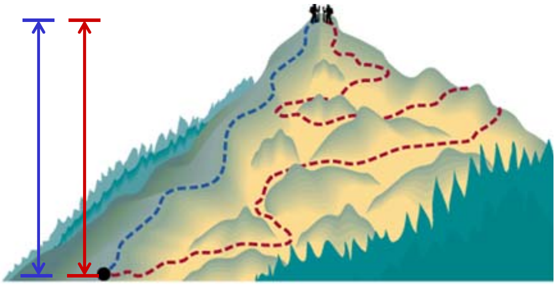
Types of Systems

- Types of systems:
  - **open** (exchange of mass and energy)
  - **closed** (exchange of energy)
  - **isolated** (no exchange)



States and State Functions

- The change in the state function (property) depends only on the ***initial*** and ***final*** states of the system and ***not*** on how the change was carried out.
- Energy, pressure, volume, temperature are examples of state functions.



Elevation is always the same (*state function*).

Distances traveled by the two hikers differ. **Efforts** exercised by them are also not the same (*not state functions*)

Internal Energy (*U*)

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

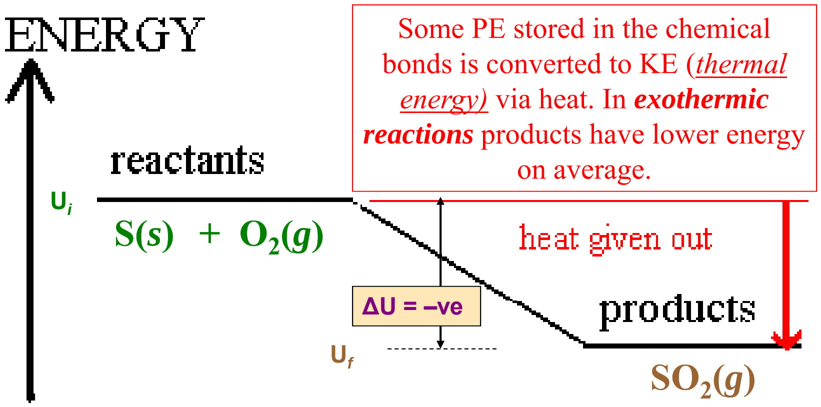
- We can not calculate the total internal energy with any certainty for a individual reactants/products.
- But we can calculate the ***change*** in energy of the system experimentally.

$$\Delta U = U_{\text{products}} \text{ or } U_{\text{final}} - U_{\text{(reactants)}} \text{ or } U_{\text{initial}}$$

$$= \boxed{\text{energy content of 1 mol } SO_2(g)} - \boxed{\text{energy content of 1 mol } S(s) \text{ and 1 mol } O_2(g)}$$

Chapter 5 Section 2

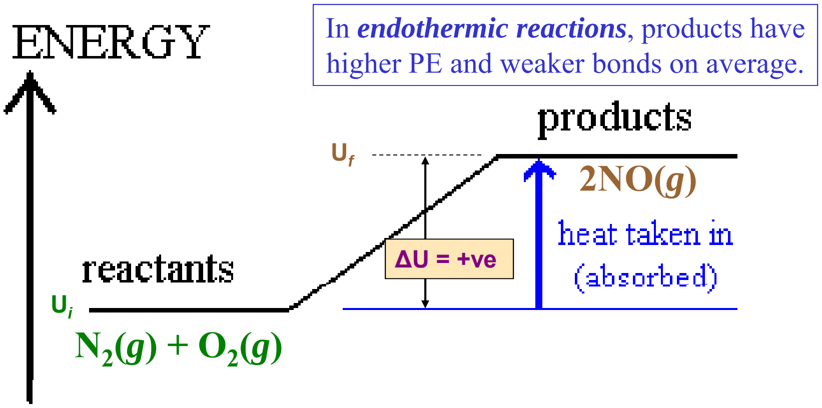
Internal Energy (*U*) in Exothermic Reactions



Some PE stored in the chemical bonds is converted to KE (*thermal energy)* via heat. In ***exothermic reactions*** products have lower energy on average.

Chapter 5 Section 2

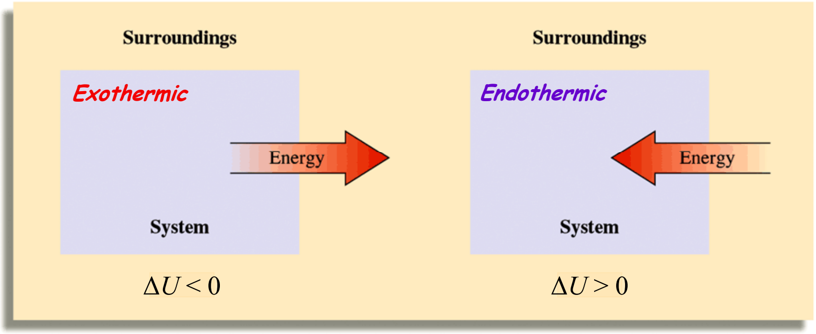
Internal Energy (*U*) in Endothermic Reactions



In ***endothermic reactions***, products have higher PE and weaker bonds on average.

Change in U for System and Surroundings

$$\Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0$$
$$\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$$



Heat and Work

- Energy is defined as the capacity to do work (w) or transfer heat (q).

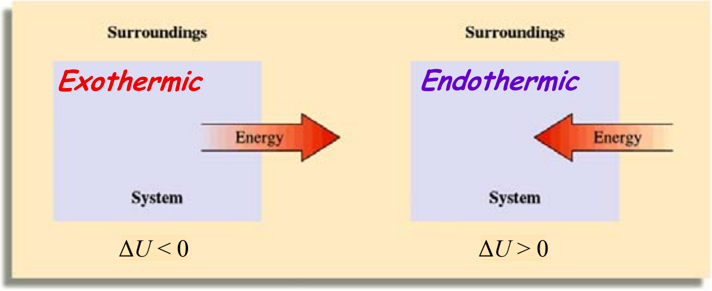
$$\boxed{\Delta U = q + w}$$

  - When a system absorbs or releases heat, its internal energy changes.
  - When a system does work on the surrounding, or when the surrounding does work on the system, the internal energy of the system changes.

Internal Energy (*U*), Heat (*q*) and Work (*w*)

- *U* can be changed by a flow of work, heat, or both:

$$\boxed{\Delta U = q + w}$$



Heat is flowing out of the system	**Heat is going into the system**
(*q* is -)	**(*q* is +)**
Work is done by the system	**Work is done on the system**
(*w* is -)	**(*w* is +)**
***U* is decreasing ($\Delta U < 0$)**	***U* is increasing ($\Delta U > 0$)**

Internal Energy (*U*), Heat (*q*) and Work (*w*)

- **Exercise:**

  What is the ΔU for a system undergoing a process in which 15.6 kJ of heat flows into it and 1.4 kJ of work is done on it?

  In order to calculate ΔU, we must know the values and signs of *q* and *w*.

  It is an endothermic process where:

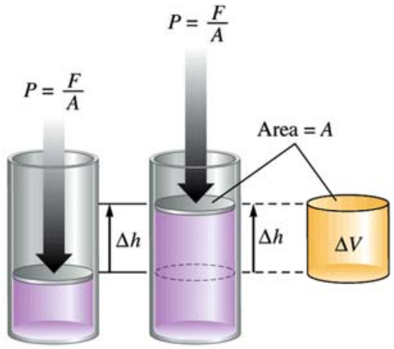
  $q = +15.6$ kJ and $w = +1.4$ kJ.

  $\Delta U = (15.6 + 1.4)\ \text{kJ} = +\ 17.0\ \text{kJ}$

  1 kilojoule (kJ) = 1000 J

The Pressure-Volume, or *PV*, Work

It is work done by or on a gas sample



(a) Initial state (b) Final state

work = force × distance

pressure = force / area

Thus:

work = pressure × area × distance

$w = P \times A \times \Delta h$

$w = P \times \Delta V$

$\boxed{w = -P \times \Delta V}$

This gives how much work is being done by the system to expand a gas ΔV against a constant *external* pressure P.

Decomposition of NaN_3 at Constant Volume

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

At *constant volume* => $\Delta V = 0$

$\Delta U = q - P\Delta V$

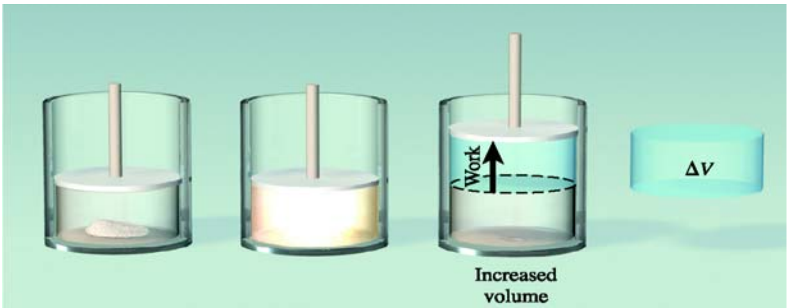
$\boxed{\Delta U = q_V}$

Normally, P is referred to the external pressure.

Chapter 5 Section 3

Decomposition of NaN_3 at Constant Pressure

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$



At *constant pressure* => $\Delta U = q - P\Delta V$

$$\boxed{q_P = \Delta U + P\Delta V}$$

Chapter 5 Section 3

Enthalpy (*H*)

- Enthalpy of a system is defined as:

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta PV$$

- Is *H* a state function? and way?

  Yes it is, because *E*, *P* and *V* are all state functions.

- For a system at constant *P* and its *w* is only *PV* work:

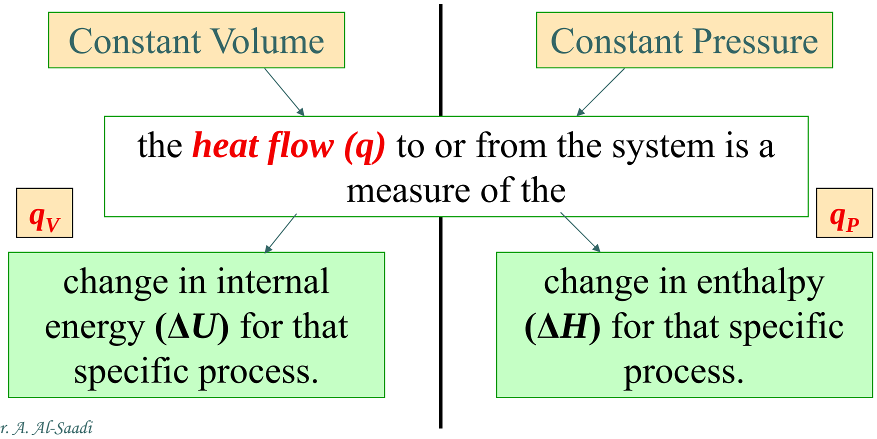
  $\Delta H \;=\; \Delta U + P\Delta V \;\; = q_P$

At constant *P* where only *PV* work is allowed:

$$\Delta H = q_P$$

Internal Energy (*U*) and Enthalpy (*H*)

- For a chemical or physical process taking place under:



Constant Volume

Constant Pressure

the ***heat flow (q)*** to or from the system is a measure of the

q_V

q_P

change in internal energy (**Δ*U***) for that specific process.

change in enthalpy (**Δ*H***) for that specific process.

Enthalpy Change (Δ*H*) for Chemical Reactions

- Most of the chemical reactions performed in the laboratory are constant-pressure processes. Thus, the heat exchanged between the system and the surroundings is equal to the change in enthalpy.

- *Heat of a reaction* and *change in enthalpy* are equivalent terms when chemical reactions are studied at *P* constant.

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

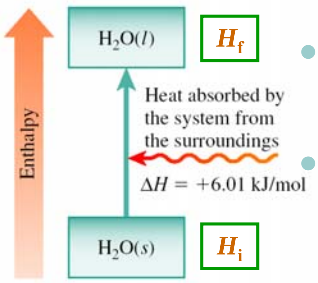
  - For $H_{products} > H_{reactants}$
    $\Delta H_{rxn} = +ve$ => Endothermic reaction.
  - For $H_{products} < H_{reactants}$
    $\Delta H_{rxn} = -ve$ => Exothermic reaction.

Chapter 5 Section 3

Thermochemical Equations

- ***Thermochemical equations*** represent both mass and enthalpy changes.

$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = +\ 6.01\ \text{kJ/mol}$

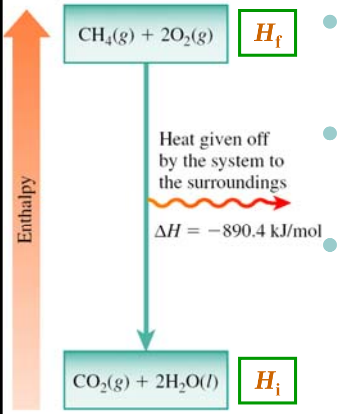


- This is an *endothermic* process. It requires 6.01 kJ to melt one mole of ice, $H_2O(s)$.
- When the process is reversed it becomes *exothermic*. The magnitude of ΔH doesn't change, but the sign becomes –ve.
- The enthalpy value will change if the number of moles varies from the 1:1 reaction stoichiometry. For example, to melt 2 moles of ice, 12.02 kJ energy is required.

Chapter 5 Section 3

Thermochemical Equations

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.4\ \text{kJ/mol}$



- This is an *exothermic* process. It releases 890.4 kJ when one mole of methane, CH_4, reacts.
- When the process is reversed it becomes *endothermic*. The magnitude of ΔH doesn't change, but the sign becomes +ve.
- The enthalpy value will change if the number of moles varies from the 1:2:1:2 reaction stoichiometry. For example, 1790.8 kJ energy is released when 2 moles of methane, CH_4, react.

Exercise

When 1 mole of CH_4 is burned at constant *P*, 890 kJ of energy is released as heat. Calculate ΔH for a process in which a 5.8 g sample of CH_4 is burned at constant *P*.

At constant *P*:

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

Exercise

Given the following equation:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H = -\ 2803\ \text{kJ/mol}$$

Calculate the energy released when 45.00 g of glucose is burned in oxygen.

$$45.00\ \text{g}\ C_6H_{12}O_6 \times \frac{1\ \text{mol}\ C_6H_{12}O_6}{180.2\ \text{g}\ C_6H_{12}O_6} \times \frac{2803\ \text{kJ}}{1\ \text{mol}\ C_6H_{12}O_6} = 700.0\ \text{kJ}$$

Chapter 5 Section 4

Calorimetry

- ***Calorimetry*** is to measure heat by observing the change in *T* when a body absorbs or releases energy as heat.

  Some materials need too much energy to raise their *T* 1˚C.
  Other materials need much less energy to raise their *T* 1˚C.

- ***Heat Capacity***, ***C***, is the amount of heat required to raise *T* of an object by 1˚C.

$$C = \frac{\text{heat absorbed}}{\text{increase in } T}$$

$$= \frac{\text{J}}{{}^\circ\text{C}} = \frac{\text{J}}{\text{K}}$$

C depends on the *amount*
of the substance.
"extensive property"

Chapter 5 Section 4

Specific Heat Capacity

- It would be more useful when *C* is given per unit mass, such as grams.
- ***Specific Heat Capacity*** **(*s*)** of a substance is: the amount of heat required to raise *T* of *1 gram* of that substance by 1˚C.
- ***s*** does NOT depend on the *amount* of the substance. **"intensive property"**
- ***s*** for H_2O = 4.184 J/°C·g

$$s = \frac{q}{mass \times \Delta T}$$

$$q = mass \times s \times \Delta T$$

$$q = C \times \Delta T$$

where q is heat, *m* is mass, *s* is specific heat, *C* is heat capacity, and Δ*T* is change in temp. ($\Delta T = T_{\text{final}} - T_{\text{initial}}$)

Chapter 5 Section 4

Specific Heat Capacity

TABLE 5.2 Specific Heat Values of Some Common Substances

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

It takes much less energy to raise the energy of 1g of a metal than for 1g for water

---

Chapter 5 Section 4

Specific Heat Capacity

Exercise:

Calculate the amount of energy required to heat 95.0 grams of water from 22.5°C to 95.5°C.

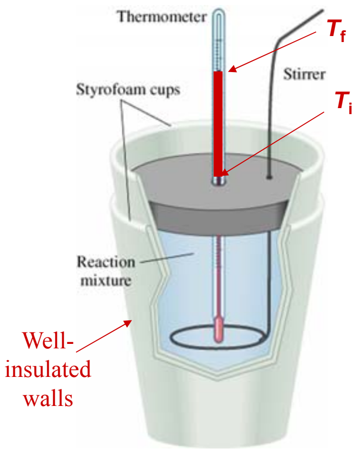
$$q = ms\Delta T$$

q = (95.0 g) (4.184 J/g°C) (95.5°C – 22.5°C)

$q = 2.90 \times 10^4$ J or 29.0 kJ

Chapter 5 Section 4

Constant-Pressure Calorimetry



A simple Styrofoam-cup calorimeter

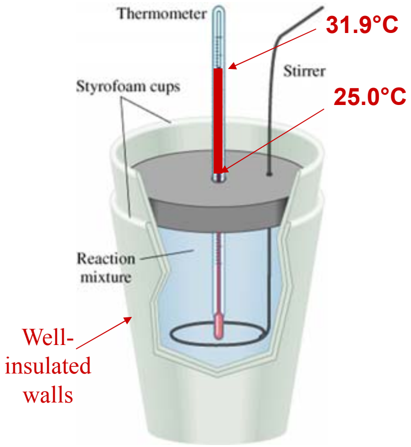
- *P* which is the atmospheric pressure remains constant.
- No heat goes in or out from the calorimeter.
- Surrounding medium is water. So, the heat released by the system is absorbed by water.

$$q_{\text{sys}} = -ms\Delta T$$

$$q_{\text{sys}} = -q_{\text{surr}} = ms\Delta T$$

Chapter 5 Section 4

Constant-Pressure Calorimetry



A simple Styrofoam-cup calorimeter

Consider the following process of mixing a strong acid with a strong base:

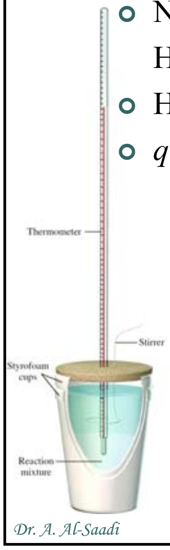
HCl		NaOH
50.0 mL	+	50.0 mL
1.0 M		1.0 M

T goes up from 25.0°C to 31.9°C.

Calculate the heat released by the above acid-base reaction.

Chapter 5 Section 4

Constant-Pressure Calorimetry



HCl + NaOH
50.0 mL + 50.0 mL
1.0 M 1.0 M

- Net ionic equation is:
  $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
- Heat required to raise T of water 1°C is 4.18 J/°C·g.
- q released by rxn = q absorbed by water = q_{sys}

= specific heat capacity for water (s) × mass of solution (m) × increase in T (ΔT)

$$= (4.18\ \frac{J}{^oC \cdot g})\ (100.0\ ml)(1.0\ g/ml)(6.9^oC)$$

$V \times d$

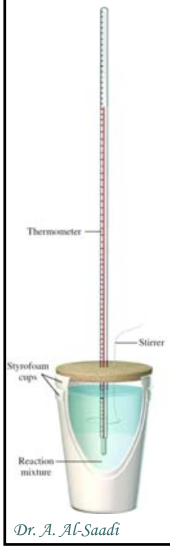
$= 2.9\times10^3$ J

= – 2.9 kJ (which is also the change of enthalpy of this reaction).

Dr. A. Al-Saadi

Chapter 5 Section 4

Constant-Pressure Calorimetry



☞ Can you now find ΔH in kJ/mol for the neutralization reaction.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Dr. A. Al-Saadi

Constant-Pressure Calorimetry

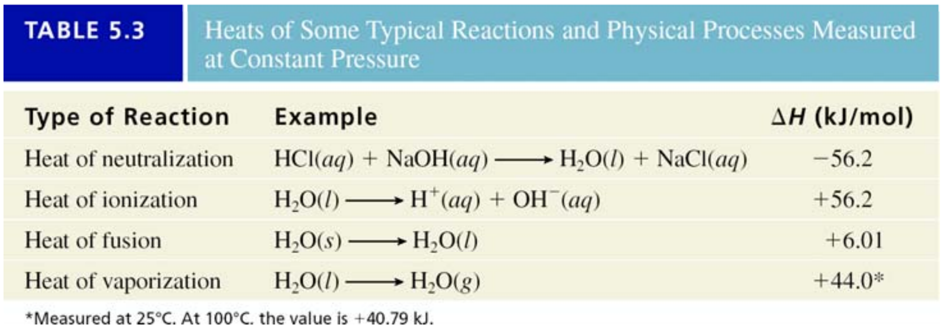
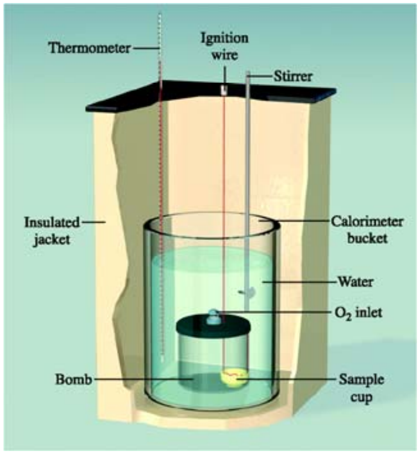


TABLE 5.3 Heats of Some Typical Reactions and Physical Processes Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCl(aq)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	+56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	+6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	+44.0*

*Measured at 25°C. At 100°C. the value is +40.79 kJ.

Constant-Volume Calorimetry



A bomb calorimeter

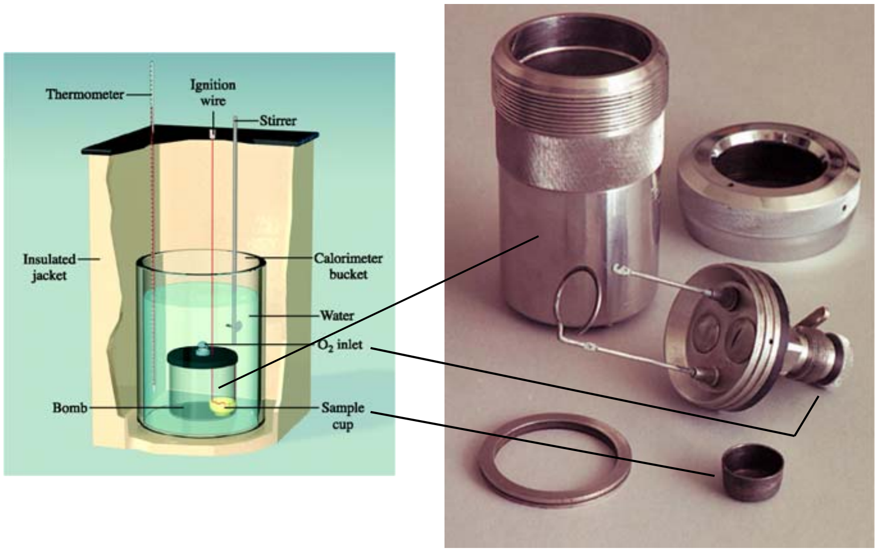
- Because V is constant, $P\Delta V = 0$ and there will be no work done ($w = 0$).

At constant V calorimeter:
$\boldsymbol{\Delta U = q_V}$

- It is also know as "bomb calorimeter", where the sample is ignited.
- Heat of combustion is usually measured using bomb calorimeters.

Chapter 5 Section 4

Bomb Calorimeter



Chapter 5 Section 4

Bomb Calorimeter

- All heat released by the combustion reaction is absorbed by the calorimeter.

$$q_{\text{cal}} = -q_{\text{rxn}}$$

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T$$

- $\boldsymbol{C_{\text{cal}}}$ is the energy required to raise T of water and other parts of the bomb calorimeter by 1˚C.
- C_{cal} for any bomb calorimeter can be determined by burning a substance with a known heat of combustion.

Chapter 5 Section 4

Bomb Calorimeter Calculation

The combustion of 1.00 g of benzoic acid releases 26.38 kJ of heat. In one experiment, we wanted to measure the heat capacity of a bomb calorimeter by burning 1.00 g of benzoic acid. The temperature increased by 4.673°C . What is heat capacity of that bomb calorimeter?

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

Chapter 5 Section 4

Bomb Calorimeter Calculation

- A combustion of 0.5269g of octane (C_8H_{18}) in a bomb calorimeter results in an increase in T by 2.25°C. Calculate ΔU for the reaction if $C_{\text{cal.}}$ = 11.3 kJ/°C.

The reaction is:

$$C_8H_{18}(s) + 25/2\ \overset{\text{excess}}{O_2(g)} \longrightarrow 8CO_2(g) + 9H_2O(g) \quad -5.50\times10^3\ \text{kJ}$$

q released by rxn = $\Delta T \times C_{\text{cal.}}$ = (2.25 °C)(11.3 kJ/°C) = 25.4 kJ

To get ΔU (in kJ/mol) for the reaction:

$$0.5269\ \text{g octane} \times \frac{1\ \text{mol octane}}{114.2\ \text{g octane}} = 4.614\times10^{-3}\ \text{mol octane}$$

For 1 mole of octane: 25.4 kJ / 4.614×10^{-3} mol octane

$= -\,5.50\times10^3$ kJ/mol (Exothermic)

Thus $q_V = \Delta U = -\,5.50\times10^3$ kJ/mol

Chapter 5 Section 5

Hess's Law

- For the reaction:

$$A + B \longrightarrow C + D$$

ΔH is the same whether:

ΔH is a state function

  - The reaction takes place in one step.
  - The reaction takes place in a series of steps (two or more).

$$\begin{array}{lcll}
A + \cancel{E} & \longrightarrow & C + \cancel{F} & \Delta H_1 \\
B + \cancel{F} & \longrightarrow & D + \cancel{E} & \Delta H_2 \\
\hline
A + B & \longrightarrow & C + D & \Delta H = \Delta H_1 + \Delta H_2
\end{array}$$

Chapter 5 Section 5

Hess's Law

- For the reaction:

$$A + B \longrightarrow C + D$$

ΔH is the same whether:

ΔH is a state function

  - The reaction takes place in one step.
  - The reaction takes place in a series of steps (two or more).

- Also notice that:

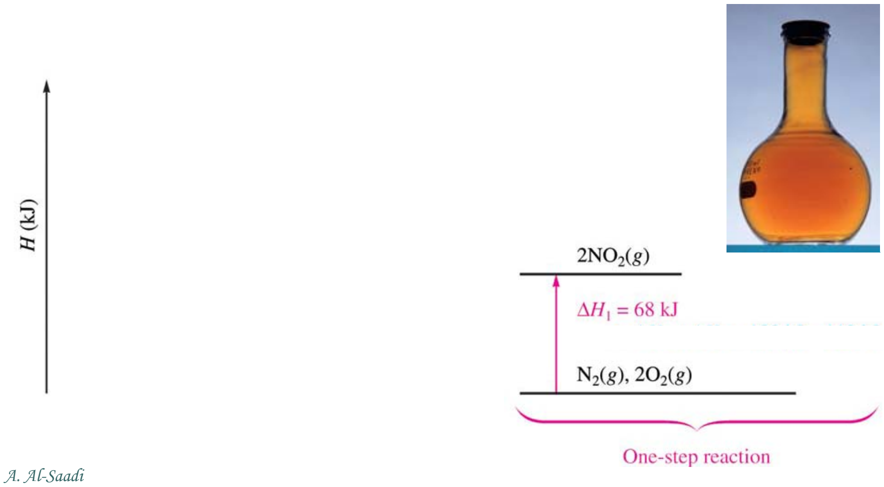
$$\begin{array}{lllll}
\text{When:} & A + B \longrightarrow C + D & \text{has} & \Delta H = +x \ , \\
\text{then} & C + D \longrightarrow A + B & \text{has} & \Delta H = -x \\
\text{and} & 2A + 2B \longrightarrow 2C + 2D & \text{has} & \Delta H = +2x
\end{array}$$

ΔH is an extensive property

Chapter 5 Section 5

Hess's Law for the Oxidation of N_2 to NO_2

$N_2(g) + 2O_2(g)$ + energy (*heat*) $\longrightarrow$ $2NO_2(g)$



Chapter 5 Section 5

Practicing Hess's Law

Given the following data:

× ½ $2ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + F_2O(g)$ $\Delta H_1 = 167.4$ kJ

× (– ½) $2ClF_3(g) + 2O_2(g) \longrightarrow Cl_2O(g) + 3F_2O(g)$ $\Delta H_2 = 341.4$ kJ

× ½ $2F_2(g) + O_2(g) \longrightarrow 2F_2O(g)$ $\Delta H_3 = -43.4$ kJ

Calculate ΔH for the reaction:

$ClF(g) + F_2(g) \longrightarrow ClF_3(g)$

$$ClF(g) + \tfrac{1}{2} O_2(g) \longrightarrow \tfrac{1}{2} Cl_2O(g) + \tfrac{1}{2} F_2O(g) \qquad \tfrac{1}{2}\Delta H_1$$

$$\tfrac{1}{2} Cl_2O(g) + \tfrac{3}{2} F_2O(g) \longrightarrow ClF_3(g) + O_2(g) \qquad -\tfrac{1}{2}\Delta H_2$$

$$F_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow F_2O(g) \qquad \tfrac{1}{2}\Delta H_3$$

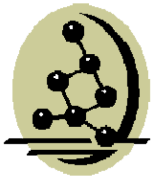
$$ClF(g) + F_2(g) \longrightarrow ClF_3(g) \qquad \Delta H = -108.7 \text{ kJ}$$

Chapter 5 Section 6

Standard Enthalpy of Formation (ΔH_f^o)

- It is defined as the heat change that accompanies the formation of 1 mole of a compound from its elements in their standard states.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = 68\ \text{kJ}$$
$$\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = 34\ \text{kJ}$$



- There is no method to determine the absolute *H* value. We can only calculate the change in *H* (ΔH) from thermodynamics experiments.
- **ΔH_f^o** "Enthalpy of formation" of an element (Na, He) or a compound (O_2, H_2) in its standard state is **zero**

Standard state means 1 atm, 25°C.

Dr. A. Al-Saadi

Chapter 5 Section 6

Standard Enthalpy of Formation (ΔH_f^o)

ΔH_f^o is ΔH that accompanies the formation of 1 mole of a product from its elements with all substances in their standard states.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = 68\ \text{kJ}$$
$$\tfrac{1}{2}\,\underline{N_2(g)} + \underline{O_2(g)} \longrightarrow 1NO_2(g) \qquad \Delta H = 34\ \text{kJ}$$

Elements @ standard states
$\Delta H_f^o = 0$

↑
$\Delta H_f^o = 34$ kJ/mol

$$C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3OH(l) \qquad \Delta H_f^o = -239\ \text{kJ/mol}$$
$$2Fe(s) + \tfrac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s) \qquad \Delta H_f^o = -826\ \text{kJ/mol}$$

Dr. A. Al-Saadi

Standard Enthalpy of Formation (ΔH_f^o)

Can you predict the reactions of formation of the compounds listed in the table from reactants at their standard states?

$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow$

$1/2\ N_2(g) + O_2(g) \rightarrow$

$H_2(g) + 1/2\ O_2(g) \rightarrow$

$2\ Al(s) + 3/2\ O_2(g) \rightarrow$

$2\ Fe(s) + 3/2\ O_2(g) \rightarrow$

$C_{graphite}(s) + O_2(g) \rightarrow$

$C_{graphite}(s) + 1/2\ O_2(g) + 2H_2(g) \rightarrow$

$8\ C_{graphite}(s) + 9H_2(g) \rightarrow$

TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH_f° (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

Calculating ΔH°_{rxn} from Standard Enthalpies of Formation

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$C(s) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta H_f^o\ (a) = –75\ kJ$

$O_2(g)$ "*standard state*" $\Delta H_f^o\ (b) = 0\ kJ$

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_f^o\ (c) = –394\ kJ$

$H_2(g) + ½\ O_2(g) \longrightarrow H_2O(l)$ $\Delta H_f^o\ (d) = –286\ kJ$

TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH_f° (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

$$\Delta H^o_{rxn} = \sum n_{products}\, \Delta H_f^o\ _{(products)} - \sum n_{reactants}\, \Delta H_f^o\ _{(reactants)}$$

$$\begin{aligned}\Delta H^o_{rxn} &= –[\Delta H_f^o\ (a)] – [\Delta H_f^o\ (b)] + [\Delta H_f^o\ (c)] + 2\times[\Delta H_f^o\ (d)]\\ &= –[–75\ kJ] \quad + \quad [0\ kJ] \quad + [–394\ kJ] + \quad 2[–286\ kJ]\\ &= -891\ kJ\end{aligned}$$

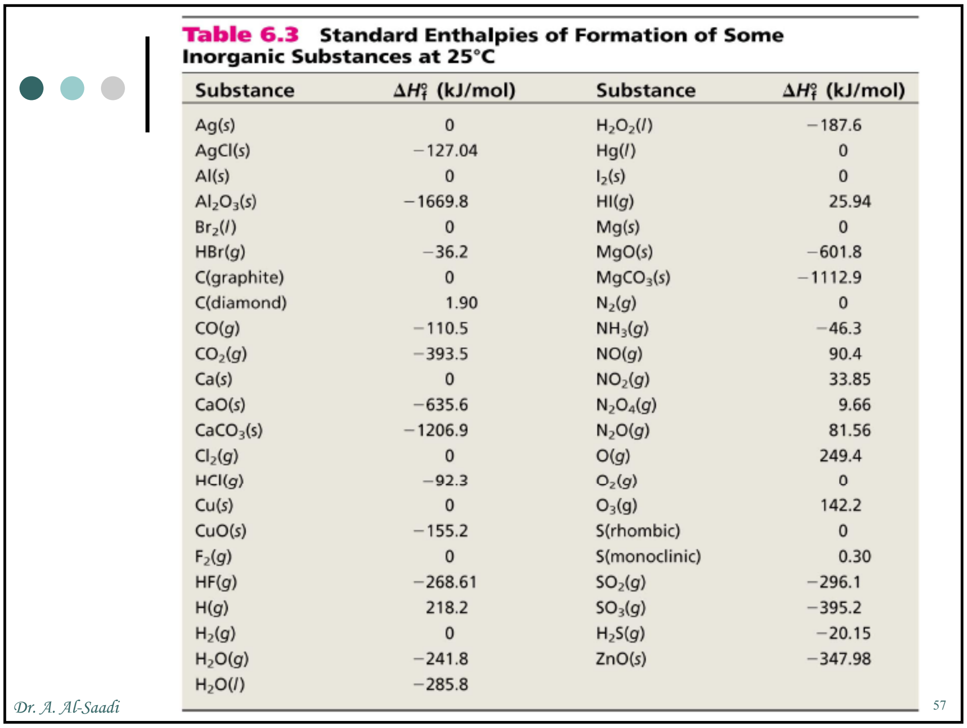


Table 6.3 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(*s*)	0	$H_2O_2(l)$	−187.6
AgCl(*s*)	−127.04	Hg(*l*)	0
Al(*s*)	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	HI(*g*)	25.94
$Br_2(l)$	0	Mg(*s*)	0
HBr(*g*)	−36.2	MgO(*s*)	−601.8
C(graphite)	0	$MgCO_3(s)$	−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	$N_2O_4(g)$	9.66
$CaCO_3(s)$	−1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	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*)	−268.61	$SO_2(g)$	−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	ZnO(*s*)	−347.98
$H_2O(l)$	−285.8		

Dr. A. Al-Saadi

57