

CHEM 2101

Chapter - 6

Lecture Notes

Thermochemistry

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Chapter-6

Thermochemistry

- 6.1 The Nature of Energy
- 6.2 Enthalpy and Calorimetry
- 6.3 Hess's Law
- 6.4 Standard Enthalpies of Formation

IMPORTANT TERMS

Thermodynamics

Thermodynamics is the study of interrelationship between heat and work

Thermochemistry

Thermochemistry is a part of thermodynamics dealing with energy changes associated with physical and chemical changes of reaction.

System

System is defined as the portion of matter under consideration, which is separated from the rest of the universe by real or imaginary boundaries.

Surroundings

Everything in the universe that is not the part of the system and can interact with the system.

Boundary

Anything which separates the system from its surroundings.

(or)

A real or imaginary barrier between the system and its surroundings through which **THERMAL ENERGY** may flow, work may appear or disappear, and matter may or may not be exchanged.

Isolated system

A system which can exchange neither energy nor matter with its surroundings.

Closed system

A system which permits the exchange of energy but not mass, across the boundary with its surroundings.

Open system

A system is said to be open if it can exchange both energy and matter with its surroundings.

Homogeneous system

A system in which all its contents are in the same physical state.

Heterogeneous system

A system in which its contents are in the different physical state.

Extensive properties

Extensive properties are the properties that depend on the mass or size of the system.

Example: Volume, moles, mass and energy.

Intensive properties

Intensive properties are the properties that are independent of the mass or size of the system. Example: Surface tension, density, boiling point, freezing point.

State of a system

State of a system is defined by specific measurable macroscopic properties of the system.

State function

P, V, T that are used to describe the state of the system.

Isothermal process

Isothermal process is defined, as one in which does not exchange heat with its surroundings during the change from initial to final states of the system.

Adiabatic process

Adiabatic process is defined as that one which does not exchange heat with its surroundings during the change from initial to final states of the system.

Isobaric process

Isobaric process is the process in which pressure of the system remains constant.

Isochoric process

Isochoric process is the process in which volume of the system remains constant.

Reversible process

In a reversible process, the series of changes carried out on the system during its transformation from initial to final state may be reversed in the exact manner.

Irreversible process

An irreversible process is one which cannot be retraced to the initial state without making a permanent change in the surroundings.

Endothermic process

A process in which absorption of heat take place.

Exothermic process

A process in which evolution of heat take place.

Path function

Path function is a thermodynamic property of the system whose value depends on the path by which the system goes from its initial to final states.

Zeroth law of thermodynamics

If two systems at different temperatures are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves.

Work

Work is defined as force is acting over a distance.

$$\begin{aligned} \text{Work} &= \text{Force} \times \text{Displacement} \\ W &= F \times d \end{aligned}$$

Energy

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

First law of thermodynamics

Energy may be converted from one form to another, but cannot be created or be destroyed.

Internal or Inherent energy (E)

Energy of atoms and molecules contained as matter of the system.

Enthalpy (H)

Enthalpy (H) is the sum of internal energy U and the product of pressure and volume of the system.

$$H = E + PV$$

Enthalpy of formation

Enthalpy of formation is defined as the enthalpy change for the formation of one mole of the compound from the respective elements existing in their naturally stable state.

Enthalpy of combustion

Enthalpy of combustion is defined as the enthalpy change of the reaction accompanying the complete combustion of one mole of the substance in the presence of excess of oxygen at that temperature.

Enthalpy of neutralization

Enthalpy of neutralization is defined as the enthalpy change accompanied by the complete neutralization of one gram equivalent of an acid by a gram equivalent amount of a base under fully ionized state in dilute solutions.

Spontaneous Change

A change that takes place by itself.

Non-spontaneous Change

The opposite of a spontaneous change.

Entropy

A measure of disorder.

6.1 The Nature of Energy

Thermodynamics

The term thermodynamics is derived from Greek Word, 'Thermos' meaning heat and 'dynamics' meaning flow.

Thermodynamics deals with the inter relationship between heat and work. It is concerned with the inter conversion of one kind of energy into another without actually creating or destroying the energy.

Energy is understood to be the capacity to do work. It can exist in many forms like electrical, chemical, thermal, mechanical, gravitational etc. Transformations from one to another energy form and prediction of the feasibility (possibility) of the processes are the important aspects of thermodynamics.

Thermochemistry

It is the branch of Chemistry which deals with energy changes involved in chemical reactions is called thermochemistry.

The energy change that occurs in a chemical reaction is largely due to change of bond energy, that is change of potential energy that results from the breaking of bonds from the reactants and formation of new bonds in products.

Terminology used in Thermodynamics

It is useful to understand few terms that are used to define and explain the basic concepts and laws of thermodynamics.

- System
- Surroundings
- Boundary

System

Thermodynamically a system is defined as any portion of the universe under study, which is separated from the rest of the universe by real or imaginary boundaries. A system may consist of one or more substances.

Surroundings

Everything in the universe that is not the part of system and can interact with it is called as surroundings. In simple cases, surroundings generally imply air, or a water-bath in which a system under examination is immersed.

Boundary

Anything (fixed or moving) which separates the system from its surroundings is called boundary.

Example

If the reaction between A and B substances are studied, the mixture A and B forms the system. All the rest, that includes beaker, its walls, air, room etc. form the surroundings. The boundaries may be considered as part of the system or surroundings depending upon convenience. The surroundings can affect the system by the exchange of matter or energy across the boundaries.

Types of systems

In thermodynamics different types of systems are considered, which depends on the different kinds of interactions between the system and surroundings.

Isolated System

A system can exchange neither energy nor matter with its surroundings is called an isolated system.

Example

A sample in a sealed thermos flask with walls made of insulating materials represents an isolated system.

Closed System

A system, which permits the exchange of energy but not mass, across the boundary with its surroundings, is called a closed system.

Example

A liquid in equilibrium with its vapours in a sealed tube represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no matter (liquid or vapour) can be added or removed.

Open system

A system is said to be open if it can exchange both energy and matter with its surroundings.

Example

A open beaker containing an aqueous salt solution represents open system. Here, matter and heat can be added or removed simultaneously or separately from the system to its surroundings.

All living things (or systems) are open systems because they continuously exchange matter and energy with the surroundings.

Energy

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

Law of conservation of Energy

Law of conservation of energy states that energy can be converted from one form to another but can be neither created nor destroyed.

The total energy content of the universe is constant.

Classification of Energy

Energy can be classified into:

- Potential energy
- Kinetic Energy

Potential Energy

Energy associated with the position of an object relative to other objects (energy that is stored – can be converted to kinetic energy)

Example

Water behind a dam has potential energy that can be converted to work when the water flows down through turbines, thereby creating electricity.

Kinetic Energy

Energy associated with mass in motion.

The kinetic energy of an object is energy due to the motion of the object and depends on the mass of the object m and its velocity v .

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

Temperature

Temperature is a property that reflects the random motions of the particles in a particular substance.

An indirect measure of the average kinetic energy of the molecules, atoms, or ions in the material; A measure of the “hot- ness” or “coldness” of a material; an INTENSIVE property of matter.

Thermal Energy

The energy that is transferred from hotter objects to colder objects due to the kinetic energy of the molecules, atoms, or ions; an EXTENSIVE property of matter.

Heat

Heat involves the transfer of energy between two objects due to temperature difference.

Heat involves a transfer of energy.

Work

Work is defined as force is acting over a distance.

$$\text{Work} = \text{Force} \times \text{Displacement}$$

$$W = F \times d$$

State Function or State Property

- A state function refers to a property of the system that depends only on its present state.
- A state function (property) does not depend in any way on the system's past (or future).
- In other words, the value of state function does not depend on how the system arrived at the present state; it depends only on the characteristics of the present state.
- Energy is a State Function; work and heat are not.

Energy transfer

Energy (E) can be transferred in two different ways:

1. By doing **work (w)** (applying a force over a distance).

$$W = F \times d$$

Work can be electrical, mechanical, etc.

2. Transferring **heat (q)** (results in a change in temperature).

Note: w, q and E all have the same units (Joule), but:

- w and q depend on path function.
- E is independent of path (state function).

The first law of thermodynamics

The total energy of the universe is constant.

Energy can neither be created nor be destroyed. It can be changed from one form to another.

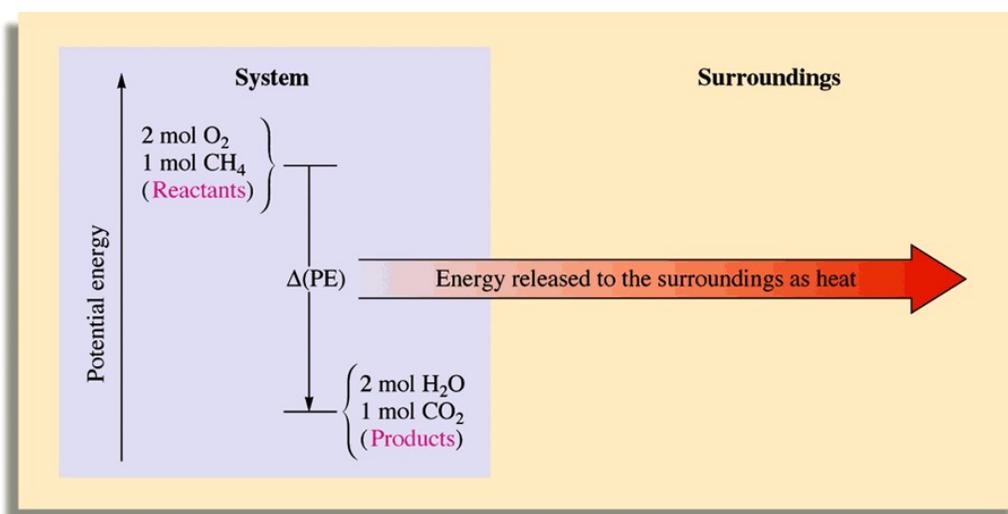
– Conservation of energy.

Exothermic Reaction

Energy given up by the system must be absorbed by the surroundings. This type of change is exothermic.

Example:

The combustion of methane releases the quantity of energy $\Delta(\text{PE})$ to the surroundings via heat flow. This is an exothermic process.

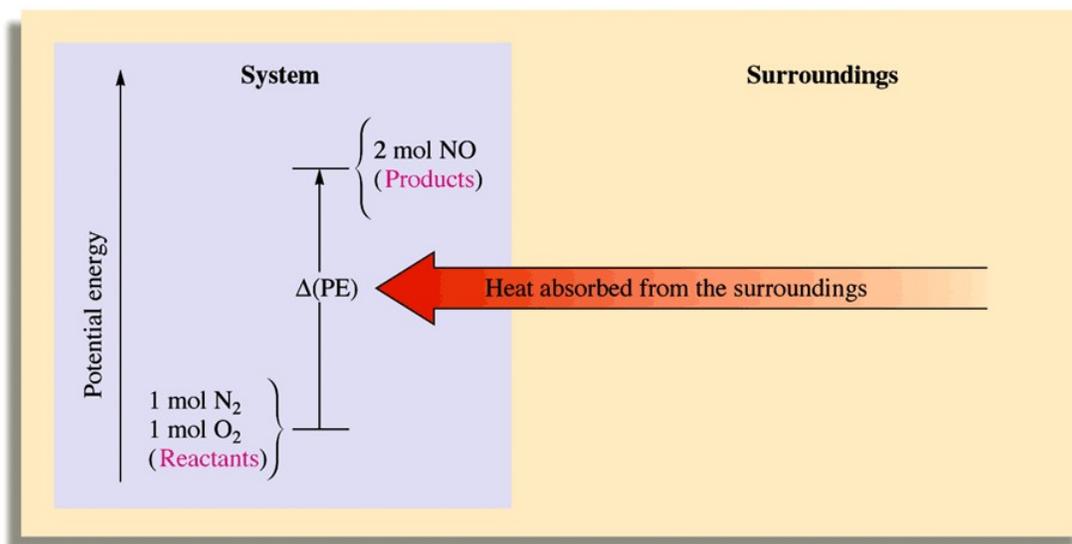


Endothermic Reaction

Energy absorbed by the system must come from the surroundings. This type of Change is Endothermic.

Example:

The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide. This is an endothermic process: Heat flows into the system from the surroundings.



Internal Energy E

The internal Energy E of the system can be defined as the sum of the kinetic and potential energies of all the particles in the system.

The internal energy of a system can be changed by a flow of work, heat or both.

That is

$$\Delta E = q + w$$

Where

ΔE - change in the system's internal energy,
 q - represents heat, and
 w - represent work.

Thermodynamic quantity

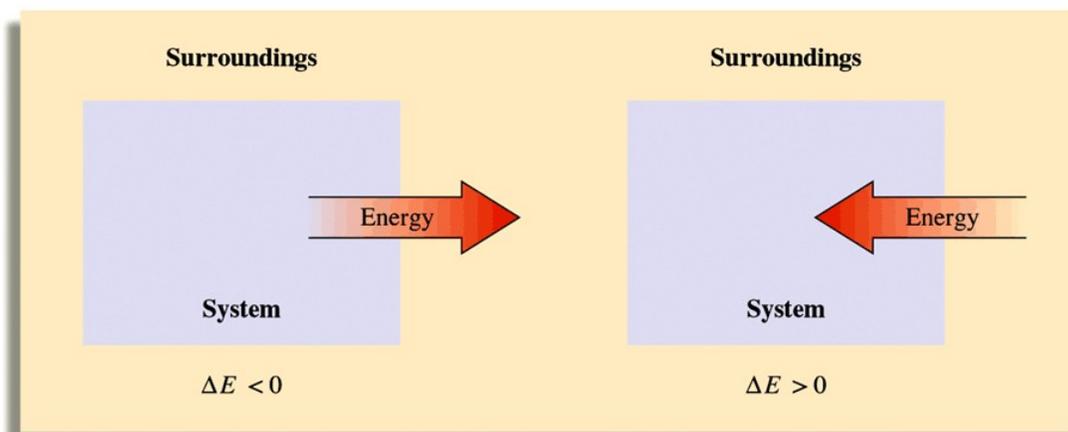
Thermodynamic quantities always consists of two parts:

- A Number – giving the magnitude of the change.
- A sign, indicating the direction of the flow.

The sign reflects the system point of view.

Example

- If a quantity of energy flows into the system via heat (an endothermic Process), **q is equal to +ve**, where the positive sign indicates that the systems energy is increasing.
- If a quantity of energy flows out of the system via heat (an exothermic process), **q is equal to -ve**, where the negative sign indicates that the system's energy is decreasing.



Flow of work

- In this text the same conventions also apply to the flow of work.
- If the system does work on the surroundings (energy flows out of the system), **w is -ve.**
- If the surroundings do work on the system (energy flows into the system), **w is +ve.**

We define work from the system point of view to be consistent for all thermodynamic quantities.

That is the sign of both q and w reflect what happens to the system; thus we use

$$\Delta E = q + w$$

Work that flows out of the systems is treated as positive because the energy of the surroundings has increased.

The first law of thermodynamics is then written $\Delta E = q - w$

Derive the mathematical relationship of heat, internal energy and work

For a system, which absorbs heat and work, is done on the system. Let E_1 be initial internal energy, q is the heat supplied to the system, w is work done on the system, then the final internal energy E_2 is

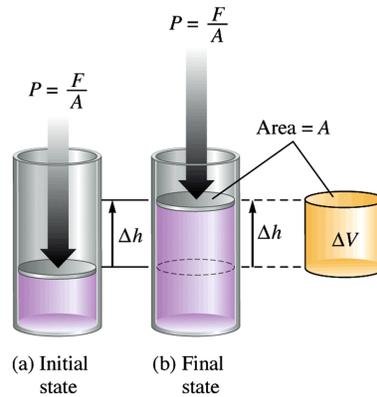
$$E_2 = E_1 + q + w$$

$$E_2 - E_1 = q + w$$

$$\Delta E = q + w$$

ΔE is the change in internal energy.

Pressure Volume work or PV work:



Suppose we have a gas confined to a cylindrical container with a movable piston as shown in the above figure.

Where F is the force acting on a piston of area A . Since pressure is defined as force per unit area, the pressure of the gas is

$$P = \frac{F}{A}$$

Work is defined as force applied over a distance, so if the piston moves a distance Δh , as shown in the above figure, then the work done is

Work = force x distance

$$= F \times \Delta h$$

Since $P = F/A$ or $F = P \times A$

Then,

Work = force x distance

$$= F \times \Delta h$$

Work = $P \times A \times \Delta h$ (1)

Since the volume of a cylinder equals the area of the piston times the height of the cylinder, the change in volume ΔV resulting from the piston moving a distance Δh is

$$\Delta V = \text{final volume} - \text{initial volume}$$

$$= A \times \Delta h$$

Substituting $\Delta V = A \times \Delta h$ into the expression for work (equation 1) gives

$$\text{Work} = P \times A \times \Delta h$$

$$= P \times \Delta V$$

Therefore

$$\text{Work} = P\Delta V$$

This gives the magnitude (size) of the work required to expand a gas ΔV against a pressure P .

The gas (the system) is expanding, moving the piston against the pressure. Thus the system is doing work on the surroundings, so from the system's point of view the sign of the work should be negative.

For an expanding gas, ΔV is a positive quantity because the volume is increasing. Thus ΔV and w must have opposite signs, which leads to the equation

$$w = -P\Delta V$$

[Note that for a gas expanding against an external pressure P , w is a negative quantity as required, since work flows out of the system. When a gas is compressed, ΔV is a negative quantity (the volume decreases), which makes w a positive quantity (work flows into the system)].

[w and $P\Delta V$ have opposite signs because when the gas expands (ΔV is positive), work flows into the surroundings (w is negative)].

6.2 Enthalpy

In chemistry most of the chemical reactions are carried out at constant pressure. To measure heat change of system at constant pressure, it is useful to define a new thermodynamic state function called Enthalpy 'H'.

H is defined as sum of the internal energy 'E' of a system and the products of pressure and Volume of the system.

That is

$$H = E + PV$$

Where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system.

Since internal energy, pressure, and volume are all state functions, enthalpy is also state function. [Since Enthalpy is a state function, a change in enthalpy does not depend on the pathway between two states].

What exactly is enthalpy?

Consider a process carried out at constant pressure and where the only work allowed is pressure – volume work ($w = -P\Delta V$).

Under these conditions, the expression

$$\Delta E = q_p + w$$

[As we may know w and $P\Delta V$ have opposite signs: $w = -P\Delta V$]

$$\Delta E = q_p - P\Delta V$$

$$q_p = \Delta E + P\Delta V \quad \dots(3)$$

where q_p is the heat at constant pressure.

Enthalpy is

$$H = E + PV$$

Therefore

$$\text{Change in } H = (\text{Change in } E) + (\text{Change in } PV)$$

(or)

$$\Delta H = \Delta E + \Delta(PV)$$

Since P is constant, the change in PV is due only to a change in volume. Thus

$$\Delta(PV) = P\Delta V$$

and

$$\Delta H = \Delta E + P\Delta V \quad \dots\dots(4)$$

Equation (4) is identical to the equation (3), then we can write q_p as:

$$q_p = \Delta E + P\Delta V$$

Thus, for a process carried out at constant pressure and where the only work allowed is that from a volume change, we have

$$\Delta H = q_p$$

$[\Delta H = q \text{ only at constant pressure}]$

For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

In a case in which the products of a reaction have a greater enthalpy than the reactants, ΔH will be positive. That is heat will be absorbed by the system, and the reaction is endothermic.

On the otherhand, if the enthalpy of the products is less than that of the reactants, ΔH will be negative.

$[\text{At constant pressure, exothermic means } \Delta H \text{ is negative; endothermic means } \Delta H \text{ is positive}]$.

Calorimetry

Calorimetry - Derived from the Latin and Greek words.

Calor – Heat

Metry – measure

-Calorimetry is the science of measuring the amount of heat.

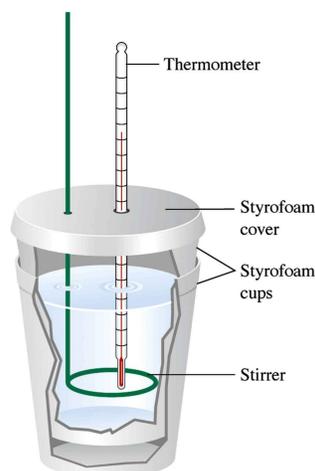
All calorimetric techniques are therefore based on the measurement of heat that may generated (exothermic process) and Consumed (endothermic reaction).

Calorimeter

- **A calorimeter is a device used to measure heat of reaction.**
- **It can be sophisticated and expensive or simple and cheap.**

Constant Pressure Calorimetry

A coffee-cup calorimeter made of two styrofoam cups



- A styrofoam cup is used as a calorimeter, because it is a container with good insulated walls to prevent heat exchange with the environment.
- In order to measure the heats of reactions, we often enclose reactants in a calorimeter, initiate the reaction, and measure the temperature difference before and after the reaction.
- The temperature difference enables us to evaluate the heat released in the reaction.
- A calorimeter may be operated under constant (atmosphere) pressure, or constant volume.
- Whichever kind to use, we first need to know its heat capacity.

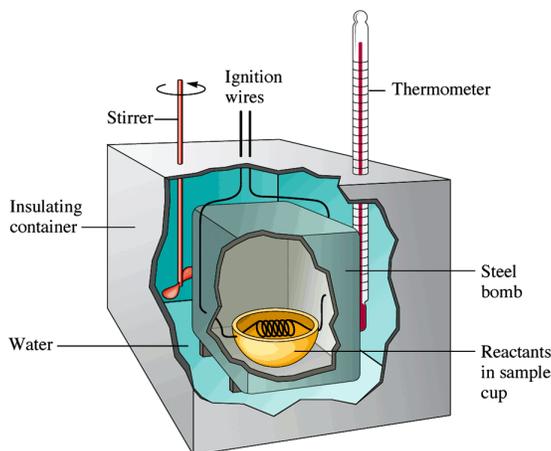
Heat Capacity

- The heat capacity is the amount of heat required to raise the temperature of the entire calorimeter by 1 K, and it is usually determined experimentally before or after the actual measurement of heat of reaction.
- The heat capacity of the calorimeter is determined by transferring a known amount of heat into it and measuring its temperature increase.
- Because the temperature difference are very small, extreme sensitive thermometers are required for these measurements.

Energy released by the reaction

$$\begin{aligned} &= \text{Energy absorbed by the solution} \\ &= \text{Specific heat capacity} \times \text{mass of solution} \times \text{increase in temperature} \\ &= s \quad \times \quad m \quad \times \quad \Delta T \end{aligned}$$

The Bomb Calorimeter (Constant Volume Calorimeter)



- For Combustion reactions, we often enclose all reactants in an explosive proof steel container, called the Bomb whose volume does not change during a reaction.
- The bomb is then submerged in water or other liquid that absorbs the heat of reaction.
- The heat capacity of the bomb and other things is then measured using the same technique as other calorimeters.
- Such an instrument is called a bomb calorimeter, and its application is called the bomb calorimetry.

For a constant –Volume process, the change in Volume ΔV is equal to zero, so work (which is $-P\Delta V$) is also equal to zero.

Therefore,

$$\Delta E = q + w = q = q_v$$

Energy released by the reaction =

$$= \Delta T \times \text{heat capacity of calorimeter}$$

Heat Capacity

The heat capacity C of a substance, which is measure of this property, is defined as

$$C = \frac{\text{Heat absorbed}}{\text{Increase in Temperature}}$$

When an element or a compound is heated, the energy required will depend on the amount of the substance present.

(For example: it takes twice as much energy to raise the temperature of two grams of water by one degree than it takes to raise the temperature of one gram of water by one degree).

Specific Heat Capacity

The energy required to raise to raise the temperature of one gram of a substance by one degree Celsius.

The unit is = $\text{J}/^{\circ}\text{C} \cdot \text{g}$ or $\text{J}/\text{K} \cdot \text{g}$

Specific Heat capacities of some common substance:

TABLE 6.1
The Specific Heat Capacities
of Some Common
Substances

Substance	Specific Heat Capacity ($\text{J}/^{\circ}\text{C} \cdot \text{g}$)
$\text{H}_2\text{O}(l)$	4.18
$\text{H}_2\text{O}(s)$	2.03
$\text{Al}(s)$	0.89
$\text{Fe}(s)$	0.45
$\text{Hg}(l)$	0.14
$\text{C}(s)$	0.71

Molar Heat Capacity

The energy required to raise the temperature of one mole of a substance by one degree Celsius.

If two reactants at the same temperature are mixed and the resulting solution gets warmer, this means the reaction-taking place is exothermic. An endothermic reaction cools the solution.

6.3 Hess's law

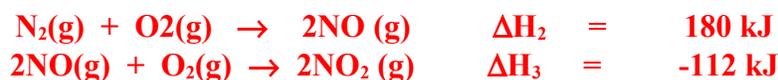
Hess's law states that the enthalpy change of reaction is the same at constant volume or pressure whether it takes place in a single step or several steps provided the initial reactants and final products remain the same.

Example for Hess's law

Oxidation of Nitrogen to produce nitrogen dioxide.



This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH_2 and ΔH_3 :



Net reaction:



The sum of the two steps gives the net, or overall, reaction and that

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68 \text{ kJ}$$

That is the enthalpy of the reaction depends only on the initial reactants and final products and not at all on the intermediate products that may be formed. It is also independent of the path or the manner in which the change is brought about.

Applications or uses of Hess's law

- It is used to calculate enthalpy of the reaction.
- It is used to determine the enthalpy change of slow reaction.
- It is used to calculate the enthalpies of formation.

Characteristics of Enthalpy changes

To use Hess's law to compute enthalpy changes for reaction, it is important to understand two characteristics of ΔH for a reaction:

- If a reaction is reversed, the sign of ΔH is also reversed.

- The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the co-efficient in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

Standard Enthalpy Changes

The standard Enthalpy of a reaction is the enthalpy change for a reaction when all the participating substances (elements and compounds) are present their in standard states.

The standard state of a substance at any specified temperature is its pure form at 1 atm pressure.

Standard conditions are denoted by adding the superscript 0 to the symbol ΔH .

For a reaction, the standard enthalpy change is denoted by $\Delta_r H^0$. Similarly, the standard enthalpy changes for combustion, formation, etc. are denoted by $\Delta_c H^0$ and $\Delta_f H^0$ etc respectively.

Generally the reactants are presented in their standard states during the enthalpy change.

Thermochemical equations

A balanced chemical equation together with standard conventions adopted and including the value of ΔH of the reaction is called a thermochemical equation.

The following conventions are necessarily adopted in a thermochemical equation:

The co-efficients in a balanced thermochemical equation refers to number of moles of reactants and products involved in the reaction.

The enthalpy change of the reaction $\Delta_r H$ has unit KJ mol^{-1} and will remain as it is, even if more than one mole of the reactant or product are involved but with only the magnitude changing.

When a chemical equation is reversed the value of ΔH is reversed in sign with the magnitude remaining the same.

Physical states of all species is important and must be specified in a thermochemical equation since ΔH depends on the phases of reactants and products.

If the thermochemical equation is multiplied through out by a number, the enthalpy change is also be multiplied by the same number value.

The negative sign of $\Delta_r H^0$ indicates the reaction to be an exothermic reaction and positive sign of $\Delta_r H^0$ indicates an endothermic type of reaction.

For Example:

Consider the following reaction,



The above thermochemical equations can be interpreted in several ways.

483.7 KJ given off per 2 moles of $\text{H}_2(\text{g})$ consumed \equiv

483.7 KJ given off per moles of $\text{O}_2(\text{g})$ consumed \equiv

483.7 KJ given off per 2 moles of water vapour formed \equiv

The above equation describes the combustion of H_2 gas to water in a general sense.

The first reaction can be considered as the formation of reaction of water vapour and the second reaction as the formation of liquid water. Both the reaction refers to constant temperature and pressure.

The negative sign of ΔH indicates that it is exothermic reaction.

The reaction which is exothermic in the forward direction is endothermic in the reverse direction and vice – versa. This rule applies to both physical and chemical processes.

Example:



6.4 Standard Enthalpy of Formation

The standard molar enthalpy of formation (ΔH_f°) of a compound is the enthalpy change of the formation reaction of 1 mole of the compound from the respective elements existing in their standard states.

Some reactions with standard molar enthalpies of formation are given below:



Enthalpy of formation of elements in natural state is always zero.

Thus $\Delta_r H^\circ$ value of a formation reaction of a compound is equal to its $\Delta_f H^\circ$ value itself.

Standard Enthalpies of Formation for several Compounds at 25°C:

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

Compound	ΔH_f° (kJ/mol)
$\text{NH}_3(\text{g})$	-46
$\text{NO}_2(\text{g})$	34
$\text{H}_2\text{O}(\text{l})$	-286
$\text{Al}_2\text{O}_3(\text{s})$	-1676
$\text{Fe}_2\text{O}_3(\text{s})$	-826
$\text{CO}_2(\text{g})$	-394
$\text{CH}_3\text{OH}(\text{l})$	-239
$\text{C}_8\text{H}_{18}(\text{l})$	-269

Conventional definitions of standard states

For a Compound

- The standard state of a gaseous substance is a pressure of exactly 1 atmosphere.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For a substance present in a solution, the standard state is a concentration of exactly 1 M.

For an Element

The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25°C.

(The standard state for oxygen is O₂(g) at a pressure of 1 atmosphere; the standard state for sodium is Na(s); the standard state for mercury is Hg(l); and so on.

Important key points for doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.
- When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.
- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H_{\text{reaction}}^0 = \sum n_p \Delta H_f^0 (\text{Products}) - \sum n_r \Delta H_f^0 (\text{Reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is ΔH_f^0 for an element in its standard state is zero.

[standard state is not the same as the standard temperature and pressure (STP) for a gas.]

Most of the Problems of this chapter solved in the Lecture Class.