भारतीय ज्ञान परंपरा

संस्कृति, दर्शन, शैक्षिक विचारधाराएँ और नवाचार

सम्पादक :
डॉ. दिनेश चन्द्र शर्मा

भारतीय ज्ञान परंपरा :

संस्कृति, दर्शन, शिक्षा विचारधाराएँ और नवाचार

सम्पादक :

डॉ. दिनेश चन्द्र शर्मा

Ph.D., D.Lit. (Sub.)

निदेशक, कॉम्पिटिशन प्लस ग्रुप ऑफ इन्स्टीट्यूशन,

अजमेर

छवि पब्लिकेशन्स

अजमेर-305001

प्रकाशक :
छवि पब्लिकेशन्स
अजमेर-305001
मो. 9660111549

संस्करण :
प्रथम 2022-2023

ISBN : 978 - 81 - 89435 - 64 - 6

मूल्य - 300/-

रचना - भारतीय ज्ञान परम्परा में शिक्षा के समाजशास्त्रीय आधार

सम्पादक - डॉ. दिनेश चन्द्र शर्मा

मुद्रक - श्रीनिवास प्रिन्टोग्राफिक्स, अजमेर

32. THERMODYNAMICS OF IDEAL SOLUTION

Kripa Sharma
Assistant Professor (Deptt. of Science and Technology)
Hukumchand Noble Institute of Science and Technology, Ajmer

Introduction:

Thermo (Heat/energy) + Dynamics (flow/motion)

Definition

It is the branch of science which deals with the energy changes taking place in all physical and chemical processes.

Chemical thermodynamics is the branch of thermodynamics which deals with the study of energy changes taking place in chemical processes.

Advantages of Thermodynamics

1. It gives information about various thermodynamics changes.

2. It helps us to predict whether a given chemical reaction will take place or not under the given set of conditions.

3. It gives information about various energy changes.

Limitations of Thermodynamics

1. It deals with the properties like temperature, pressure, volume, etc., in bulk but does not tell us anything about the properties of an individual atom or molecule.

2. It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the rate of reaction.

Some Important Terms

Term	**Definition**

System	A specific part or specified portion of the universe or of the matter which is under experimental investigation.
Surrounding	The rest part of the universe excluding the system is called the surrounding.
Universe	System + Surrounding.
Boundary	Anything which separates the system and surrounding is called the boundary.

Types of Boundary

1. Boundary can be conducting or non-conducting.
2. Boundary can be rigid or non-rigid.
3. Boundary can be real or imaginary.

Types of System

Type	**Exchange with Surrounding**
Open system	Can exchange matter and energy with surrounding.
Closed system	Can exchange energy but not matter with surrounding.
Isolated system	Can neither exchange heat nor matter with the surrounding.

Thermodynamic Quantities

State of the System

State Variables or Thermodynamic Variables or Thermodynamic Quantities are properties which define the state of any system. The state of the system is defined by their measurable properties like temperature, pressure, volume, etc. If any of these properties change, the state of the system is said to be changed.

State Function vs. Path Function

Term	**Definition**	**Examples**
State Function	State variables which depend only upon the	(Internal Energy), (Enthalpy), (Entropy),

	initial and final state of the system but does not depend upon the path or mechanism followed by the system to achieve the final state.	(Gibb's Free Energy), (Temperature), (Pressure), (Volume), etc..
Path Function	Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve the final state.	Work done , heat .

Intensive and Extensive Properties

Property Type	Definition
Intensive Properties	The properties of the system which are independent of the amount of matter present in the system. They are not additive in nature.
Extensive Properties	The properties of the system which are dependent on the amount of matter present in the system. They are additive in nature.

Extensive Properties (Dependent on matter)	**Intensive Properties (Independent of matter)**
Volume	Molar volume
Number of moles	Density
Mass	Gibb's energy per mole

Energy	Pressure
Gibb's Energy	All concentration terms
Entropy	Temperature
Enthalpy	Boiling point
Internal energy	Freezing point
Heat capacity	Cell potential
Force	Specific conductance
Surface Area	Refractive index
-	pH value
-	Vapour pressure

Special Points

* The ratio of two extensive properties is an intensive property. For example, Density.

* An extensive property can be converted into an intensive property when it is defined for a unit amount of the substance.

Types of Thermodynamic Processes

* Isothermal Process :

* Isobaric Process :

* Isochoric Process :

* Adiabatic Process : No heat exchange

Laws of Thermochemistry

1. Lavoisier and Laplace Law

Enthalpy of formation of a compound is numerically equal to the enthalpy of decomposition of that compound but with the opposite sign.

Example:

2. Hess's Law of Constant Heat Summation

The heat change in a complete chemical reaction remains the same whether the reaction completes in one step or more. Example: If a reaction from has in two steps, and in three steps, then .

Laws of Thermodynamics

Law statement

Zeroth Law	If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.
First Law	Energy cannot be created or destroyed, only transferred or changed from one form to another. In an isolated system, the total energy remains constant.
Second Law	In any natural process in an isolated system, the total entropy (a measure of disorder) will always increase over time. A common consequence is that heat does not spontaneously flow from a colder to a warmer body.
Third Law	The entropy of a system approaches a constant value as the temperature approaches absolute zero. For a perfect crystalline solid, this entropy is zero.

Thermodynamics of Ideal Solution

An ideal solution is one which obeys Raoult's Law at all composition and temperature.

* The interaction between , , and molecules are identical.

* There is no enthalpy change and no volume change during mixing.

* Example: Benzene + Toluene, n-Hexane + n-Heptane, Chlorobenzene + Bromobenzene.

Enthalpy, (A State Function)

Enthalpy, is a useful new state function defined as .

The heat absorbed by the system at constant pressure is equal to the change in enthalpy :

At constant pressure, the finite change in enthalpy is given by:

where is negative for exothermic reactions and positive for

endothermic reactions.

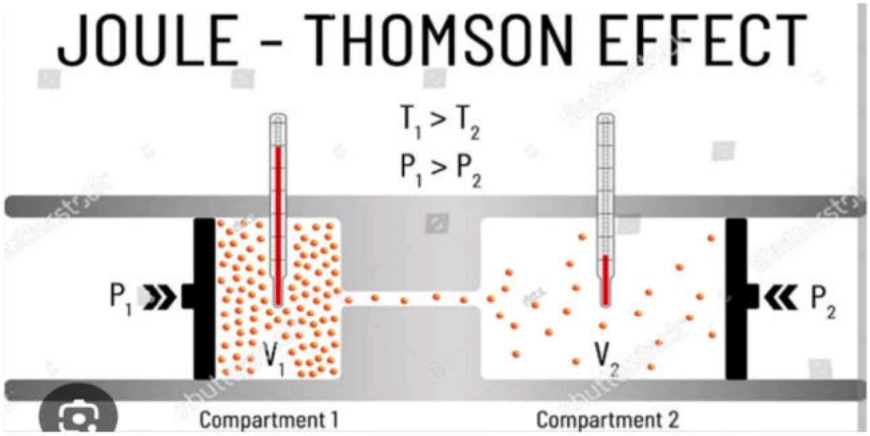
Relationship between and (for gaseous reactions)

Using the ideal gas equation , the relationship between enthalpy change and internal energy change for reactions involving gases is:

where is the difference between the total moles of gaseous product and the total moles of gaseous reactant.

Joule-Thomson Effect

In Joule's experiment, when an ideal gas expands in a vacuum, there is no change in temperature.



In the Joule-Thomson experiment, the expansion is taking place adiabatically. The process of gas expansion through a porous plug is an isenthalpic process; i.e., the enthalpy of the system remains unchanged . A drop in temperature was observed, which was found to be proportional to the pressure difference maintained :

Joule-Thomson Coefficient

The term is known as the Joule-Thomson coefficient and is denoted by the symbol .

Joule-Thomson Coefficient for Ideal Gas

The Joule-Thomson coefficient for ideal gases is zero. This means an ideal gas does not show any cooling effect upon expansion.

Difference between Isothermal and Adiabatic Expansions of an Ideal Gas

* In an isothermal process, .
* In an adiabatic process, where .

Since, when pressure is reduced, the increase in volume in an adiabatic process will be less than in an isothermal process.

In an adiabatic process, the internal energy decreases, so the temperature reduces, which causes a decrease in volume, whereas in an isothermal process, the temperature does not change, so it does not bring any decrease in volume.

The area under the curve is equal to the work done. The work done is more in isothermal expansion than in adiabatic expansion for the same change in pressure or volume.

Enthalpy Changes for Different Types of Reactions

1. Enthalpy of Reaction

The enthalpy change accompanying a reaction is called the heat of reaction or reaction enthalpy.

2. Standard Enthalpy of Reaction

It is the enthalpy change when all participating substances are in their standard states. The standard state of a substance is its pure form at a specified temperature (usually 298 K) and a pressure of 1 bar.

3. Enthalpy Change during Phase Transformation

* Standard Enthalpy of Fusion : The enthalpy change that accompanies the melting of one mole of a solid substance in its standard state.

* Standard Enthalpy of Vapourisation : The amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar).

* Standard Enthalpy of Sublimation : The change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1 bar).

4. Standard Molar Enthalpy of Formation

The enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.

5. Standard Enthalpy of Combustion

The enthalpy change per mole of a substance when it undergoes

combustion and all the reactant and product begin in their standard state at the specified temperature. It is always exothermic.

6. Enthalpy of Atomisation

The enthalpy change in the process of breaking all the bonds in a molecule to form its constituent gaseous atoms.

7. Bond Enthalpy

The amount of energy necessary to break a bond in one mole of a gaseous covalent substance to form product in the gaseous state.

8. Enthalpy of Solution

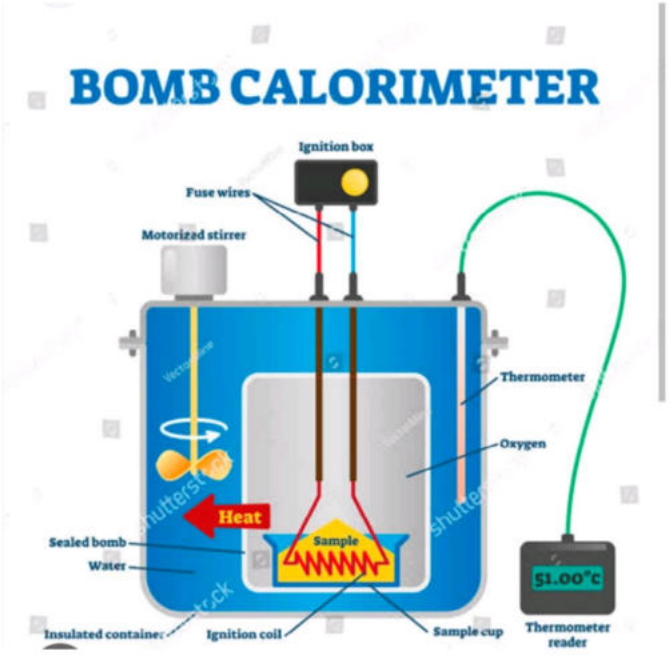
The enthalpy change when one mole of a solute dissolves in a specified amount of solvent.

Calorimetry

Calorimetry is the measurement of the energy change associated with a chemical or physical process by an experimental technique.

* measurement is done using a bomb calorimeter when the process is carried out at constant volume.

* measurement can be done using a calorimeter at constant pressure.



Conclusion of thermodynamics of ideal solution

The thermodynamics of an ideal solution concludes that mixing occurs spontaneously due to the increased entropy, with no change in

enthalpy or volume.

This behavior serves as a crucial theoretical benchmark for understanding the properties of real solutions.

Key thermodynamic properties Based on the assumption that intermolecular forces between components are identical, ideal solutions have the following characteristics:

* **Enthalpy of mixing**

(H mix) is zero: No heat is exchanged upon mixing.

* **Volume of mixing**

(Δ V mix) is zero: The total volume is the sum of the component volumes.

* **Entropy of mixing**

(ΔS mix) is positive: Mixing is spontaneous due to increased randomness.

* **Gibbs free energy of mixing**

(ΔG mix) is negative: Mixing is always spontaneous because

ΔG = ΔH – T ΔS, and since

ΔH is zero, the positive entropy change results in a negative

ΔG

Broader implications

The thermodynamic behavior of ideal solutions has several broader implications:

* Raoult's Law: Ideal solutions obey Raoult's Law, where partial vapor pressure is proportional to the mole fraction.

* Basis for comparison: Ideal solutions serve as a standard for real solutions; deviations indicate differences in intermolecular forces.

* **Foundation of solution theory**: The concept is fundamental for calculating properties like vapor pressure and colligative properties.

* **Theoretical vs. real**: Perfectly ideal solutions are theoretical, but some mixtures with similar components approximate ideal behavior.