**Chemical Thermodynamics-01**

1. Intensive & Extensive Variables
2. State & Path functions
3. Isolated, Closed & Open Systems
4. Zeroth Law of Thermodynamics
5. **Intensive & Extensive Variables-**

[Physical properties](https://en.wikipedia.org/wiki/Physical_properties) of materials and [systems](https://en.wikipedia.org/wiki/System) can often be categorized as being either **intensive** or **extensive**, according to how the property changes when the size (or extent) of the system changes. According to [IUPAC](https://en.wikipedia.org/wiki/International_Union_of_Pure_and_Applied_Chemistry), an **intensive quantity** is one whose magnitude is independent of the size of the system whereas an **extensive quantity** is one whose magnitude is additive for subsystems.

**Intensive Variables:**

An **intensive property** does not depend on the system size or the amount of material in the system. It is not necessarily homogeneously distributed in space; it can vary from place to place in a body of matter and radiation.

Examples of intensive properties include- [temperature](https://en.wikipedia.org/wiki/Temperature), *T*; [refractive index](https://en.wikipedia.org/wiki/Refractive_index), *n*; [density](https://en.wikipedia.org/wiki/Density), *ρ*; and [hardness](https://en.wikipedia.org/wiki/Hardness) of an object, *η*.

**Extensive Variables:**

An **extensive property** is depending on the system size or the amount of material in the system.

Examples of extensive properties include- the [mass](https://en.wikipedia.org/wiki/Mass), [volume](https://en.wikipedia.org/wiki/Volume) and [entropy](https://en.wikipedia.org/wiki/Entropy) of systems these are additive for subsystems.

*(The terms intensive and extensive quantities were introduced into physics by German writer*[*Georg Helm*](https://en.wikipedia.org/wiki/Georg_Helm)*in 1898, and by American physicist and chemist*[*Richard C. Tolman*](https://en.wikipedia.org/wiki/Richard_C._Tolman)*in 1917.)*

1. **State & Path functions-**

**State functions:**

A property whose value doesn’t depend on the path taken to reach that specific value is known to as *state functions*or*point functions*. State functions are the values which depend on the state of the substance like temperature, pressure or the amount or type of the substance. as a matter of fact, state functions do not depend on how the state was reached or established.

For example, density is a state function, because density of a substance is not affected by how the substance is obtained. To decide whether certain property is a state function or not, keep this rule in mind: is this property or value affected by the path or way taken to establish it ? If the answer is yes then it is not a state function and if the answer is no, then the property is a state function.

State functions can be considered as integrals. This is because, integrals depend on only three things: the function, lower limit and its upper limit. Similarly, state functions also depend on three things: the property, initial value and its final value.

Thus, it is evident that state functions depend only on the initial and final value of the property.

For example, the integral of enthalpy H, where *H0* represents the initial state and *Hf* represents the final state is given by,

*ΔH = Hf*– *H0*

As seen in the above example, enthalpy is a state function because its value depends only on initial and final conditions.

**Path Function:**

Those functions which do depend on the path from two points, ie. the path of transformation of a system are known as *path functions.* All functions that depend on the path taken to reach that specific value are known as path functions.

Whereas, state functions are properties whose values do not depend on the path taken to reach that specific function or value.

**Difference Between State Function and Path Function:**

|  |  |
| --- | --- |
| **State function** | **Path function** |
| Independent of the path taken to reach the property or value | Dependent on the path taken to establish the property or value |
| Capable of integrating using initial and final values | Requires multiple integrals and limits of integration in order to integrate |
| Any number of steps results in the same value | Different steps result in different values |
| Based on the established state of the system (temperature, pressure, amount, and identity of a system). | It is based on how the state of the system was established. |

**List of State Functions:**

Pressure:

Pressure is a measure of the average force exerted by the constituent molecules per unit area on the container walls. Pressure does not depend on the path of the molecules and thus it is a state function. It is denoted by symbol P.

Temperature:

Temperature is defined as the measure of the average kinetic energy of the atoms or molecules in the system. Temperature measures a property of a state of a system irrespective of how it got there and thus it is a state function. It is denoted by symbol T.

Volume:

Volume is the amount of physical space occupied by a substance and it will not be dependent on the path followed. Thus, the volume is a state function. It is denoted by symbol V.

Composition:

Along with the other three properties such as pressure, temperature and volume the composition also has fundamental importance. It measures the quantity of constituents present in the system that to involve for transformation. It is denoted by symbol n.

Mass:

The measure of the amount of matter in an object is known as mass and is usually measured in grams (g) or kilograms (kg). Mass measures the quantity of matter regardless of both its location in the universe and the gravitational force applied to it and thus it is a state function. It is denoted by symbol m.

Internal energy:

It can be defined as the sum of all kind of energy associated with molecular motions.

The internal energy of ideal gases is a function of temperature only (Joule’s law) and internal energy of real gases is a function of temperature, pressure and volume (temperature and volume being the dominating quantities and effect of pressure are negligible), So it can be seen that since internal energy depends on quantities like P, T, V which are state functions, the internal energy is also a state function. It is denoted by symbol U.

Enthalpy or Heat Content:

The Pressure (P) and Volume (V) of a system are thermodynamic variables and their products PV is expressed as energy. The sum of two energy terms associated with the system, namely internal energy (U) and the PV energy is universally represented by H and is called the Enthalpy or Heat Content of the system.

H = U + PV

Entropy:

The second law of thermodynamics leads to a definition of a new function. Like internal energy (U) and Enthalpy or Heat Content (H) it is a state function and it helps in the understanding of the condition of the system. This function has been called Entropy by Clausius and is denoted by symbol S.

If the heat change is *dq* and temperature *T,* then the system has a change measured by-

S = dq / T.

Work function:

The internal energy of the system at any point minus the product of the temperature times the entropy of the system is Work function of the system

*A* = *U* – *TS*

The Work function of the system is a state function because it is defined in terms of thermodynamic properties that are state functions.

Gibb’s free energy:

The enthalpy of the system at any point minus the product of the temperature times the entropy of the system is Gibb’s free energy of the system

*G* = *H* – *TS*

The Gibbs free energy of the system is a state function because it is defined in terms of thermodynamic properties that are state functions.

1. **Isolated, Closed & Open Systems-**

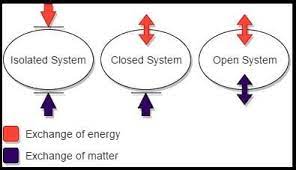
Thermodynamic Systems:-

In thermodynamics a System is defined as an object or a quantity of matter (ie. a part of the universe, chosen for observation, separately from the rest of the universe) The system is enclosed by a boundary which separates it from the rest of universe. All parts of the universe, outside the boundary of the system, are called the Surrounding. Thus,

|  |  |
| --- | --- |
| System = Universe – Surrounding |  |

Different types of systems-

1. Isolated System: A system which is incapable of exchanging either energy or matter (mass) with surrounding is said to be an Isolated System.
2. Closed System: A system which is capable of exchanging energy only with surrounding but no mass is allowed to transfer across the boundary is said to be a Closed System.
3. Open System: A system which is capable of exchanging both energy and matter (mass) with surrounding is said to be an Open System.

1. **Zeroth Law of Thermodynamics:**

The Nernst’s Heat Theorem is the precursor of the more important fundamental principle enunciated by Plank commonly called the Third Law of thermodynamics. One of the consequence of the Nernst’s Heat Theorem is:

LtT→0 ∆CP = 0

Ie. heat capacity of all substances (reactants & products) at absolute zero must be the zero. From quantal principles, it was found that at very low temperatures, the heat capacity, CP of a substance continuously diminishes with lowering of T and ultimately be vanished. Ie.

LtT→0 CP = 0

This is also corroborated by experiments. Hence, at low temperature CP / T is zero or a finite quantity. The entropy changes due to lowering of temperature is given by –

dS = dq / T = (CP / dT) / T

0ʃT dS = 0ʃT (CP / dT) / T

ie. ST - S0 = 0ʃT (CP / T) / dT

Since CP / T is a finite quantity, ie. We can say ST - S0 must be a positive quantity.

ie. ST > S0. In othe words, the entropy of a substance at any temperature must be greater than its entropy at absolute zero.

In 1972, Plank made the striking proposal in this regard and enunciated the third law as –

*“The entropy of a solid or a liquid is zero at absolute zero temperature”*

*THANKS*

*DR. D. CHAKRAVARTY*

\*\*\*\*\*\*\*\*\*\*