CHEMICAL THERMODYNAMICS

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Thermodynamics is a Greek word which means flow of heat (thermo=heat, dynamics =flow) in physical changes and chemical reactions.

Definition

"The branch of science which deals with energy changes in physical and chemical processes is called chemical thermodynamics"**.**

In fact, in chemical reactions bonds in the reactant molecules are to cleave which need certain energy. At the same time, bonds in the products are to be formed. There is release of certain amount of energy. Since, two values of the energies are not normally the same, there is an energy change in chemical reactions responsible for thermodynamics.

Importance of thermodynamics

1. It helps us to predict whether any given chemical reaction can occur under the given set of conditions, or not.
2. It helps in predicting the extent of reaction before the equilibrium is attained.
3. It helps to deduce some important laws like Law of chemical equilibrium, Distribution law etc.

The limitation of thermodynamics

1. It helps to predict the feasibility of a process but does not tell anything about the rate at which it takes place.
2. It deals only with the initial and final states of a system but does not tell anything about the mechanism of the process (i.e., the path followed by the process).
3. It deals with properties like temperature, pressure, etc. of the matter in bulk (macroscopic properties) but does not tell anything about the individual atoms and molecules (microscopic properties).

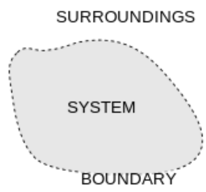
Some basic terms and concepts

System

A specified part of the universe which is under observation is called a system.

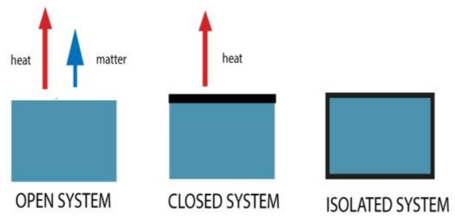
Surroundings

The remaining portion of the universe which is not a part of the system is called surroundings. For example – If we carry a chemical reaction in a glass tube. Glass tube is a system, rest of the universe represent the surrounding. The glass wall of the tube is the boundary between system and surrounding. Thus, system and the surrounding together constitute the universe, i.e.,

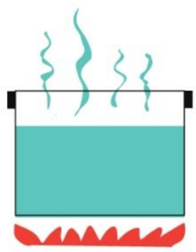


Universe = System + Surrounding.

Types of thermodynamics systems

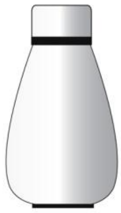


1. **Open system:** A system is said to be an open system if it can exchange both matter and energy with the surroundings. For example- Boiling water without a lid heat escape into the air. At the same steam (which is matter) also escapes into the air. Animal and plants are open systems from the thermodynamics point of view.



2. **Closed system: I**f a system can exchange only energy with the surroundings but not matter, it is called a closed system. For example- Boiling water is placed in a closed metallic vessel. It allows heat to be transferred from the stove to the water. Heat is also transferred to the surrounding. Steam is not allowed to escape.

3. **Isolated system:** If a system can neither exchange matter nor energy with the surroundings, it is called an isolated system. For example- Water is placed in a vessel which is closed as well as insulated. A thermo flask is an isolated system.



State of a system and state variable

The state of a system means the conditions of the system which is described in terms of certain observable or measurable properties such as temperature (T) , pressure (P) and volume (V) etc. of the system. If any of these properties of the system changes, the system is said to be in different state, i.e., the state of the system changes. That is why these properties of a system are called state variables. A process is said to occur when the state of the system changes. The first and the last state of a system are called the initial state and the final state respectively.

State function

A state function is a property of the system whose value depends only upon the state of the system and is independent of the path or manner by which the state is reached. State functions are pressure, temperature, volume, internal energy, entropy and enthalpy etc. For example – A person standing on the roof of a five storied building has a fixed value of potential energy, irrespective of the fact whether he reached there by stairs or by a lift. Thus, the potential energy of the person is a state function. On the other hand, the work done by the legs of the person to reach the same height is not same in two cases, i.e., whether he went by lift or by stairs. Hence, work is not a state function. Instead, it is sometime called a 'path function'.

Macroscopic properties of the system

Thermodynamics does not deal with the properties of the individual atoms and molecules but deals with the matter in bulk. The properties of the system which arise from the bulk behavior of the matter are called macroscopic properties. For example- pressure, volume, temperature, surface tension, viscosity, density, melting point, and boiling point. The macroscopic properties can be classified into two types:

1. Extensive properties
2. Intensive properties

Extensive properties

The properties of the system whose value depends upon the amount of the substance present in the system are called extensive properties. For example- mass, volume, surface area, energy, enthalpy, entropy and free energy.

Intensive properties

These are those properties which depend only upon the nature of the substance and are independent of the amount of the substance present in the system. For example- temperature, pressure, surface tension, viscosity, density, freezing point, boiling point and specific heat. Extensive properties may become intensive properties by specifying unit amount of the substance concerned. Thus, mass and volume are extensive properties but density and specific volume (i.e., mass per unit volume and volume per unit mass respectively) are intensive properties of the substance or the system. Further, extensive properties are additive but intensive properties are not.

Thermodynamic processes

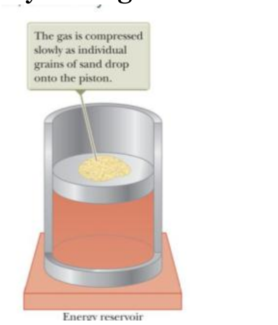
A thermodynamic process is said to occur when the system changes from one state (initial state) to another (final state). The different processes met within the study of chemical thermodynamics are as follows:

1. **Isothermal process:** When a process is carried out in such a manner that the temperature remains constant throughout the process, it is called an isothermal process. Obviously, when such a process occurs, heat can flow from the system to the surrounding and vice versa in order to keep the temperature of the system constant.
2. **Adiabatic process:** When a process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa, i.e., the system is completely insulated from the surrounding, it is called an adiabatic process. In such a process, temperature of the system always changes.
3. **Isochoric process:** It is a process during which the volume of the system remains constant.
4. **Isobaric process:** It is a process during which the pressure of the system is kept constant.

Reversible process

In order to understand a reversible process, imagine a gas confined, within a cylinder provided with a frictionless piston upon which is piled some very fine sand.

Suppose the pressure exerted by the gas on the piston is equal to the combined pressure exerted by the weight of the piston, the pile of sand and the atmospheric pressure. Thus under these conditions, the piston does not move at all and a state of equilibrium is said to exist. Now, if one particle of sand is removed, the gas will expand very slightly but the equilibrium will be restored almost immediately. Such a change is called an infinitesimal change. If the particle of sand is replaced, the gas will return to its original volume. By the continued removal of the particles of sand the gas can be allowed to undergo a finite expansion but each step in this expansion is an infinitesimal one and can be reversed by an infinitesimal change in the external conditions. At all times, the equilibrium is restored immediately. Thus, the necessary condition for reversible compression is $P_{external} = P_{internal} + dp$ and for reversible expansion is $P_{external} = P_{internal} - dp$. Hence, in general, we can write, for reversible process, $P_{external} = P_{internal} \pm dp$. A process carried out in the above manner is called a reversible process and may be define as "a process which is carried out infinitesimally slowly so that all changes occurring in the direct process can be exactly reverse and the system remains almost in a state of equilibrium with the surrounding at every stage of the process."



Irreversible process

An irreversible process is define as that process which is not carried out infinitesimally slowly (instead, it is carried out rapidly) so that the successive steps of the direct process cannot be replaced and any change in the external conditions disturbs the equilibrium.

Cyclic process

A process in which the system undergoes a series of changes and ultimately returns to its original state is called a cyclic process. There is no change in energy in a cyclic process**.**

Internal energy

Every substance possesses a fixed quantity of energy which depends upon its chemical nature and its state of existence, known as internal energy (U). Internal energy is made up of (i) kinetic energy (ii) potential energy of the constituent particles (atoms, ions, molecules). The kinetic energy is due to the motion of all particles, in the form of translational energy, rotational energy, vibrational energy, electronic energy, nuclear energy of constituent atoms. Potential energy of the molecules is due to molecular interaction, chemical bond energy due to existence of bonds between atoms within the molecules etc. The sum of these different forms of energies associated with molecules is called its internal energy. It is usually represented by the symbol 'U' or 'E'. Thus, U or $E = E_e + E_n + E_c + E_p + E_k + E_v$

Change of internal energy

Absolute value of internal energy of a substance cannot be calculated because it is not possible to determine the exact values for the constituent energies. It can be measured, when a system changes from initial state (U_1) to the final state (U_2). The difference between the internal energies of the two states considered as change of internal energy. $\Delta U = U_2 - U_1$

Similarly, in a chemical reaction, if U_R is the internal energy of the reactants and U_P is the internal energy of the products, then change of internal energy would be $\Delta U = U_p - U_R$

The internal energy of a system changes when (i) heat passes in or out of the system (ii) work is done on or by the system (iii) matter enters or leaves the system.

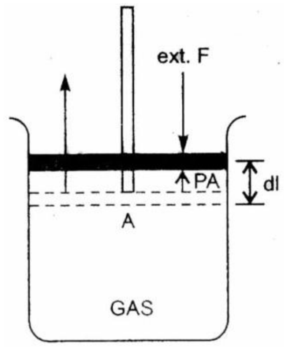
Conclusion

The internal energy depends upon the quantity of the substance contained in the system. Hence, it is an extensive property.

Internal energy is a state function. It depends upon the initial and final state and is independent of the path. For example, one mole of CO_2 at 300K and 1 atmospheric pressure will always have the same internal energy irrespective of the fact that it has been brought to these conditions from 500K and 5 atmospheric pressure or from 1000K and 10 atmospheric pressure. The internal energy of ideal gases is a function of temperature only. Hence, in isothermal processes, as the temperature remains constant, there is no change in internal energy. $\Delta E = 0$

Sign of ΔU - ΔU is negative if energy is evolved, ΔU is positive if energy is absorbed.

The units of energy are ergs (in CGS system) or joules (in SI units). 1joule = 10^7ergs.



Heat – heat is a form of energy exchanged between the system and the surrounding because of the difference of temperature between them. It is expressed as 'q'.

Sign of q – when heat absorbed by the system from the surroundings is taken to be positive. When heat released by the system to the surroundings is taken to be negative.

Units of q –it is measured in terms of calories. "A calorie is defined as the quantity of heat required to raise the temperature of one gram of water through 1°C.

In SI system, it is measured in joules. 1 calorie = 4.184 joules, 1 joules = .2390 calories.

Heat is not a state function, because its values do not depend merely on the initial and final states but depend upon the path followed.

Work- work is said to have been done whenever the point of application of a force is displace in the direction of force. W=F x dl

F =magnitude of the force, dl =the displacement in the direction of the force

Two main type of work used in thermodynamics are (i) Electrical work (ii) Mechanical work

Electrical work

This type of work is involved in case of reactions involving ions. Force is the E.M.F and the displacement is the quantity of electricity flowing through the circuit. Hence, electrical work done = E.M.F x quantity of electricity.

Mechanical work or pressure

Volume work- this type of work is involved in systems consisting of gases. It is the work done when the gas expands or contracts against the external pressure (atmospheric pressure). It is a kind of mechanical work. The expression for such a work may be derived as: Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Suppose, area of cross –section of cylinder = a sq. cm

Pressure on the piston = P (which is slightly less than internal pressure of the gas so that gas can expand) . Distance through which gas expands = dl cm

Then as pressure is force per unit area, force (f) acting on the piston will be f=P x a

∴ work done by the gas (i.e., the system) = force x distance =f x dl = P x a x dl but ax dl = dV, a small increase in the volume of the gas. Hence, the small amount of work (δw) done by the gas can be written as δw= P x dV if the gas expands from initial volume V_1 to the final volume V_2, then the total work done (w) will be

$$w= \int_{V_1}^{V_2} P.dV$$

If the gas expands against constant external pressure (irreversible expansion), the result may be written as

$$w= P\int_{V_1}^{V_2} dV = P (V_2-V_1) = P.\ \Delta V$$

where $\Delta V = (V_2-V_1)$ is the total change in volume of the gas.

w= -P.ΔV (for expansion, work is done by the system).

If the external pressure (P) is slightly more than the pressure of the gas, gas will be contract i.e., the work will be done by the surrounding on the system $V_2<V_1$, w= P. ΔV

Sign of w- according to SI conventions, w is taken as taken as negative if work is done by the system, i.e., for work of expansion. $V_2>V_1$ so that (V_2-V_1) is positive and hence w is negative and it is taken as positive if work is done on the system, i.e., for compression, $V_2<V_1$ so that V_2-V_1 is negative and negative multiplied by negative will be positive.

Units of w – SI units of work are joules or ergs. 1 joules= 10^7 ergs, I joules= 1Nm =1Kgm^{2}s^{-2}

Work done in isothermal reversible expansion of an ideal gas: The small amount of work done,δw, when the gas expands through a small volume, dV, against the external pressure, P_{ext} is given by $\delta w= -P_{ext}\, dV$ .However, for reversible expansion

$P_{ext} = P_{int}-dp$ ∴ $\delta w= -(P_{int}- dp)dV = -P_{int}\, dV$ (dp x dV is negligible) ∴ Total work done when the gas expands from initial volume V_1 to final volume V_2, will be $w= -\int_{V_1}^{V_2} P_{int}.dV$

For an ideal gas, PV = nRT, i.e., $P_{int} = \frac{nRT}{V}$ hence, $w= -\int_{V_1}^{V_2} \frac{nRT}{V}.dV$

For isothermal expansion, T= constant so that, $w= -nRT\int_{V_1}^{V_2} \frac{1}{V}.dV = nRT \ln\frac{V_2}{V_1}$ =w= $2.303nRT \log\frac{V_2}{V_1}$

Assignment

1. Which of the following is not an intensive property?
   (a) entropy (b) pressure
   (c) temperature (d) molar volume
2. If temperature remains constant during the process, it is called an -
   (a) Isothermal process (b) adiabatic process
   (c) isobaric process (d) isochoric process
3. In thermodynamics, a process is called reversible when
   (a) surrounding and system change into each other
   (b) there is no boundary between system and surrounding
   (c) the surrounding are always in equilibrium with the system
   (d) the system changes into surroundings spontaneously.
4. Which of the following statements is false?
   (a) work is a state function
   (b) temperature is a state function
   (c) change in the state is completely defined when the initial and final states are specified
   (d) work appears at the boundary of the system.
5. An isolated system is that system in which
   (a) there is no exchange of energy with the surroundings
   (b) there is exchange of mass and energy with the surroundings
   (c) there is no exchange of mass and energy with the surroundings
   (d) there is exchange of mass with surroundings.
6. If there is no exchange of heat between the system and the surrounding during the process. It is called
   (a) adiabatic process (b) isobaric process
   (c) isothermal process (d) irreversible process.
7. Which of the following is not a state function
   (a) heat (b) internal energy
   (c) enthalpy (d) entropy

Answers to Assignment

1.(a) 2.(a) 3.(c) 4.(a) 5.(c) 6.(a) 7.(a)