**chemical Thermodynamics**

Thermodynamics (TD) deals with the flow of heat and basically establishes the quantitative relationship between the heat and various forms energies. It is firmly based on 3 laws, called laws of TD, and these are more empirical than theoretical. These laws are evolved from observations made on the macroscopic world.

Following are the three broad branches of TD —

1. **Classical TD**: This branch of TD deals with the macroscopic properties of matter and here entire formulation has been developed without the knowledge that the matter is made up of atoms or molecules.
2. **Statistical TD**: This branch of TD based on the statistical mechanics and deals with the calculation of thermodynamic properties of matter from the classical or quantum mechanical behaviour of a large collection of atoms and molecules.
3. **Chemical TD**: Chemical thermodynamics deals with the study of the processes in which only chemical energy is involved. For example, heat is evolves when an acid is neutralised by a base, combustion of coal products, discharge of storage battery, etc.

**Importance of thermodynamics**:

1. Derivation of fundamental laws,
2. Generalization of experimental results by the fundamental laws,
3. Discussion of a chemical reaction and
4. Prediction of relationship between the directly observable properties.

**Definitions of some Important Thermodynamic Terms/ Terminologies**:

1. **System and Surroundings**:

A thermodynamic system is a part of the universe, separated from the rest of the universe by definite boundaries for the purpose of experimental or theoretical studies. The remainder of the universe is called surroundings of the system. Normally, the surroundings are restricted to the region in the **immediate vicinity** of the system under study. Thus,

The boundary, which is essentially a wall, may be —

1. **A rigid wall** — if its position and shape are fixed
2. **An impermeable wall** — if it does not permit the passage of matter
3. **A permeable wall** — if it permits the passage of matter and hence energy
4. **An adiabatic wall** — if through it neither energy nor the matter can passage
5. **A diathermal wall diathermic wall** — if it allows the passage of energy but not matter.

**Different Types of Systems**: Various types of systems are —

1. **Real System** — in experimental work, the system is called real
2. **Ideal System** — in pencil and paper work, the system treated is called ideal. An ideal system is always considered to simplify the thermodynamic problem
3. **Open System** — a TD system that can exchange both matter and energy with its surroundings is termed as an ideal system. For example, a beaker containing water (the system) in a thermostated water bath (the surroundings) is an open system, because the water vapour (matter) will escape into the surroundings whereas the heat (energy) required for vaporisation will be absorbed from the surroundings.
4. **Closed System** — a TD system that can exchange only energy but not matter with its surroundings across the boundary is termed as the closed system. For example, a liquid in equilibrium with its vapour in a sealed tube
5. **Isolated System** — a TD system that can neither exchange energy nor matter with its surroundings is termed as the closed system. For example, a thermally insulated sealed tube containing a liquid and its vapour
6. **Homogenous System** — a TD system is said to be homogenous if it is uniform throughout i.e. containing only one phase. For example, a gas, a mixture of gases, a pure liquid, two miscible liquids, etc.
7. **Heterogeneous system** — a TD system is said to be heterogeneous if it contains two or more phases, separated from each other by interfacial boundaries. For example, a liquid is in contact with its vapour

**Open, closed and isolated systems can be depicted as**:



**State of a system/ State variables/ State properties**:

State variables are the quantities or variables by which we can specify a TD system completely. These are generally —

() Pressure (), () Volume (), () Temperature (), and () Concentration (),

**Two more variables frequently involved are** —

() Work (), and () Heat (),

**State variables may be** —

1. **Dependent**: For example, volume () and
2. **Independent**: For example,

**The equation of state** viz.―

**Properties of the System**: Measurable properties that are used in TD are of two types —

1. **Extensive Properties**: — Mass dependent properties are termed as extensive properties. For example, moles (), mass (), free energy (), entropy (), enthalpy (), heat capacity (), etc.
2. **Intensive Properties**: — Mass independent properties are termed as extensive properties. For example, molar volume (), density (), refractive index (), surface tension (), viscosity (), free energy per mole (), specific heat (), pressure (), temperature (), boiling point (), freezing point (), etc.

**Thermo dynamical Equilibrium**: A system is said to have attain a state of thermodynamic equilibrium when it show no further tendency to change its property with time. It is of three types —

1. **Thermal equilibrium**: A thermodynamic system is said to be in thermal equilibrium if the temperature is same throughout the system. Thus in thermal equilibrium, the temperature of the system and its surroundings is same.
2. **Mechanical equilibrium**: A thermodynamic system is said to be in mechanical equilibrium if it involves no floe of matter within the system or at its boundaries, i.e. with the surroundings.
3. **Chemical equilibrium**: If the chemical composition of a system is not spontaneously changing with time, then it is in a state of chemical equilibrium, which is dynamical in nature as the forward & reverse reactions are continuously occurring in equal rates.

Thus, a **system is said to be in thermodynamic equilibrium** if —

1. Its macroscopic properties do not alter with time,
2. There are no currents of matter and energy within the system or at its boundaries.

**Thermodynamic Process**: A thermodynamic process is the path or operation by which a system changes from one state to another. Following are the various processes connecting an initial state to a final state —

1. **Isothermal Process ()**:

The TD process that occurs at constant temperature is called isothermal process. The constant temperature of the system is maintained either by releasing heat from the system or by absorbing heat from the surroundings. For example, —

When a gas compressed suddenly, some heat is produced, but if the rate of compression is very slow and heat produced is removed at once, so that the temperature remains constant, the change is isothermal. Similarly, when a gas allowed expanding suddenly, work is done by the gas and some heat is absorbed. If the heat is continuously supplied from outside so that the temperature remains constant, the change is isothermal.

For a perfect gas, an isothermal change is represented by Boyle’s law, i.e. , at constant temperature.

1. **Adiabatic Process ()**:

Here, the process is carried out such that there is no net change of heat between the system and surroundings. The constant heat of the system is maintained by the change in temperature of the system through the adiabatic wall, which do not permit the exchange of heat.

For adiabatic process,

If the process is **exothermic**, the heat evolved will remain in the system, and therefore the temperature of the system rises. If, on the other hand, an **adiabatic** process is **endothermic**, the heat required to be absorbed by the system itself and hence the temperature of the system falls.

1. **Isobaric Process ()** **OR** **Isopiestic Process**:

Here, the pressure of the system remains constant during each step of the change in the state of a system. For example, —

() ratio in a cylinder with a weightless, frictionless and airtight piston, on electrically spark, water is formed as —

Here, the volume is decreased, hence the piston will move down for allowing the pressure of the system constant.

() For the reaction of type ―

Here, volume is increased, hence the piston moves up, maintaining the pressure of the system constant.

1. **Isochoric Process ()**:

Here, the volume of the system remains constant during each step of the process. The constancy of the volume is maintained by change in pressure of the system. For example, ―

When is enclosed in a cylinder fitted with a weightless, frictionless piston, it dissociates

Here, the volume of the system tends to increase. In order to keep the volume fixed, pressure is to be applied over the piston.

1. **Cyclic Process**:

When a system undergoes a series of state changes in such a way that the final state becomes identical with the initial state, it is said to have passed through a cyclic process.

If the series of changes are conducted at constant temperature, the cycle is known as the isothermal cycle. On the other hand, if the cycle is carried out reversibly, then it is called reversible cycle. Carnot’s cycle is a well known example of cyclic process.

Since the internal energy of the system depends only upon its state, it means that in a cyclic process, the net change of internal energy is zero, i.e.

1. **Quasistatic (or Reversible) Process**:

A process is said to be quasistatic if it is carried out in such a way that at every moment the system departs only infinitesimally from an equilibrium state. At every instant, the system remains virtually in a state of equilibrium and all the states through which the system passes can be described by means of TD variables referring to the system as a whole. The vanishingly slowness of the process is an essential feature of a quasistatic process.

1. **Reversible & Irreversible Process**:

When a system is allowed to change its state slowly so that at any instant during the transformation, the system does not deviate appreciably from its equilibrium state or not deviate from the state of equilibrium by more than an infinitesimally small amount then it is called reversible process. Thus a truly reversible process has to be carried out in infinitesimal amounts and hence, would require infinite time. So, a strictly reversible process is just a concept only.

On the other hand, if a process that occurs rapidly or spontaneously such that it does not remain in equilibrium during the transformation is called an irreversible process. These processes occurred in **unidirectionally** and certainly not in successive stages of equilibria in minute quantities of transformation. Hence all the natural processes are irreversible.

**Partial Differentiation or Derivatives**:

Let, be a function of two independent variables , i.e.

Here values of , depends on , hence it is dependent variable, and it is single valued function.

If in new coordinate system,

Then the new changed value of is,

Since , hence equation () shows the change of as the sum of two partial rate of change of w.r.t. each variable keeping other constant. Equation () is the general form of the partial changes of variables, as referred to partial derivatives. **For example**, ―

For a system containing a gram- mole of an ideal gas, ―

Since,

Therefore, from equation (2), we have ―

**Cyclic Rule**:

Let,

Since for cyclic system, the system is independent of path hence ―

Equation () expresses the cyclic rule. Similarly, if , then according to cyclic rule:

**Cyclic Rule for 3- independent Variables**:

Considering three independent variables , and suppose, the relation between these variables is —

And any two of these is a function of the other, so that

Substituting equation (2) in equation (1), we have, —

Equation () is applicable for all the general values of .

Assuming and are independent —

**Now Case I**: Let,

From equation (3), —

**Case II**: Let,

From equation (3), —

**Example**: Equation of state can be represented as —

Further, —

For , ideal gas equation is, —

From equation (2), —

From equation (3), —

Thus, the cyclic rule is proved. //

**Perfect/ Exact/ Complete Differentials**:

Let, be a single valued function, and depends on two independent variables i.e.

In the coordinate system, for any particular point , has a particular and definite value. That is, when are given, the quantity is completely determined. Then, the differential is called perfect differential, and is given by —



**Physical significance of Perfect Differentials**:

By the term perfect differential it means that when we go from point , the value of at will be independent of the actual path adopted. From the following figure, one can reach from either by the paths , the value of changes by equal amount, if the change of is independent of path. From this it follows that if we take the quantity through a cycle such that as then, —

From the figure, coordinate of will be

will be and will be

Suppose we choose the path to go from . Then, if the value of the quantity is at, its value at will be . The value of at will be —

Secondly, we choose the path to go from . Then, if the value of at , will be . The value of at will be —

Now, if is perfect differential, the value of must be the same at , whichever path is chosen, i.e.

Which is the mathematical requirement for  to be a perfect differential

**Conditions for Perfect Differentials**:

The term, will be perfect differential if —

1. is single valued function depending entirely on the instantaneous values of , or
2. between any two points or path states is independent of the path of transition, or
3. , i.e. for complete cyclic process is zero, or
4. , i.e. second derivatives/ differentials of w.r.t carried out in either order become equal to one another.

**Examples**:

**Problem (1)**: Show that are perfect differentials.

**Solution:** The pressure of a given quantity of gas (say ) is a function of temperature () and volume () , i.e.

Now, to be perfect differential —

Since, for of an ideal gas,



Similarly, —

Likewise, —

**Different Types for Thermodynamic Functions:**

1. **State Functions**: The thermodynamic functions which depend only on the state of the system, *i.e*. independent of the path chosen are called state functions. These are exact or perfect differential. For example, [internal energy, , enthalpy (), entropy (), etc.
2. **Path Functions**: The thermodynamic functions which solely depend on the path of the change from one state to other are called path functions. These are not exact differential. For example, Heat (), work (), etc.

**Different Types for Thermodynamic Systems**:

Thermodynamics basically deals with some simple systems. Simple systems are those for which the state may be given in terms of mass, pressure, temperature and volume only. For example, —

() **Thermal Expansivity or Coefficient of Thermal Expansion ()**: The rate of change of volume with temperature at constant pressure to a volume ‘’ is the coefficient of thermal expansion. Thus, —

The coefficient of thermal expansion () has the dimension of temperature inverse ().

() **Compressibility coefficient ()**: The rate of change of volume with pressure at constant temperature relative to a volume is the compressibility coefficient. Thus, —

The compressibility coefficient () has the dimension of pressure inverse ().

[The sign introduced in the above equation so that compressibility is a quantity because an increase in pressure in almost all the known substances produces a decrease in volume.]

**Relation between** :

Since, —

Further, for , of an ideal gas

For a condition of constant volume, , hence from the above equation,

**OR**

Since, —

Further, for , of an ideal gas

Differentiating , with respect to , at constant , we get —

Similarly, differentiating , with respect to , at constant , we get —

Since, , therefore, by applying cyclic rule, we have —

**Problem (2)**: Show that, where

**Solution**: Since, —

Similarly, —

Adding equation (1) and (2), we get —

Since is an perfect differential, and , therefore —

Hence equation (3) reduces to —

**Zeroth Law of Thermodynamics:**

The law of TD forms **the basis of temperature** and can be stated as follows: “If two systems are in thermal equilibrium with a system, they must be in thermal equilibrium with each other.”

**Conversely, the law of TD can also be stated as follows**:

“If three or more systems are kept in thermal contact by means of diathermal walls and all are in thermal equilibrium together, than any two systems taken separately will be in thermal equilibrium with one another.”

**Explanation**: Let us consider three fluids . Suppose represents the pressure and volume of ; that for and for .

Let are in thermal equilibrium with one another. Then, one can write —

On solving equation (1) for , we get, —

Suppose are in thermal equilibrium, then —

From equation (2) & (3), we have —

As are in thermal equilibrium with separately, then , in accordance with the law, are also in thermal equilibrium with one another. It means that —

As the equation () has a variable whereas equation () does not have the variable , it means that —

In general, —

From equation (), it follows that all the three functions have the same numerical value but the parameters () of each are different. This numerical value is termed as the temperature () of the body *i.e*. —

Therefore, the **temperature of a system can be defined as** — “*Temperature is the property which determines whether the body is in thermal equilibrium with the neighbouring system or not*.”

From the above definition it is obvious that if two systems are not in thermal equilibrium, they are at different temperature.

**Work ():**

In TD, **work is generally defined** as the product of the force and displacement. When a body is displaced by a distance ‘’ along the direction of the applied force ‘’, then the work done is —

Here, stands for the small amount of work and also the **inexactness** of the function. Following are the ***important points about the definition of work*** —

1. Work is a vector quantity,
2. Work appears only at the boundary of the system,
3. Work appears only during a change in state,
4. Work is manifested by an effect in the surroundings,
5. Work is an algebraic quantity, *i.e*. it can be . Work () is , if work is produced in the surroundings, *i.e*. work is done by the system to the surroundings. Work (w) is if work has been destroyed in the surroundings *i.e*. work is done on the system by the surroundings.
6. In SI system, unit of work is joule () or - () and

**Different types of Works**:

All types of works can be expressed as the product of two factors, *viz*. —

1. An **intensity factor** (force) and
2. A **capacity factor** (displacement)

***Following are the three important types work***:

1. **Gravitational Work**, when a body is raised through a certain height against the gravitational force of attraction
2. **Electrical Work**, due to a movement of charge through a potential difference
3. **Mechanical Work**, work associated with change in volume of a system against an external pressure

**Detailed about the Mechanical work**:

[] **Reversible work of Expansion, or Reversibility and Maximum Work, or Work of Isothermal Reversible Process** —



Considering the isothermal expansion of an ideal gas enclosed in a cylinder fitted with a weightless, frictionless piston of surface area .

Let the pressure applied on the piston be momentarily reduced by an infinitesimally small amount ; the piston will move out very slowly, thereby resulting a small increase in volume . But the pressure of the system is unchanged throughout the process. Therefore, the work obtained from this reversible process will be —

As , hence

Let, the same gas is allowed to expand irreversibly, say by expanding into **vacuum against external pressure of zero**. The work obtained is given by —

Thus, reversible process produces more work than the same process if it is carried out irreversibly for the same increase in volume (). Further the work obtained from such a reversible process always depends upon the magnitude of the difference between the pressure applied on the piston and pressure of the gas. Therefore, the work obtained from such a reversible process would become the maximum if such a difference is infinitesimally small. Under these conditions the work obtained from a system would become maximum i.e.

Hence, the total work for a finite volume change, say from (at constant ) can be obtained by integrating equation (),

For of an ideal gas —

Since, —

Here, denotes the pressure corresponding to volume

[] **Work is a Path Dependent function (not exact differential):**—

() **Physical Proof**: Since, —

As is a function of volume, therefore the integral of equation (1) cannot be evaluated as such. As the dependence of is different for different processes, the numerical values of ‘’ will be different for different processes. For example —

[] **Expansion into Vacuum i.e. work done in the free expansion of gas**: If a gas is expanding into vacuum, it implies that it is expanding into zero external pressure and therefore it will not be able to do any work, *i.e*. . Therefore, equation (1) becomes, —

[] **Expansion against a constant external pressure**: If a gas is expanding against a constant external pressure, it implies that it has no volume dependence and, hence the work done in this case is —

[] **Expansion when :** In this type of expansion is taking place, it would be a reversible process. The work done in this case is given by —

**Mathematical Proof for**:  **is a path function is not a state function is not an exact/ perfect/ complete differential**:

**Proof**: In order to prove that “” is not a state function, *i.e*. is not an exact differential, first of all it is assumed that  is a state and is an exact differential. By this assumption, we will arrive at **wrong conclusions** which will disprove wrong assumption but will prove that is not a state function and is not an exact differential.

The work done is given by —

Since, is a function of , and therefore —

If is constant, and therefore, from equation (1), we have —

Differentiating the above equation with respect to , we have —

Similarly, if is constant, and therefore, from equation (1), we have —

Differentiating the above equation with respect to , we have —

For to be an exact differential, —

But, from equation () and (), we have —

But, to be an exact differential,

As equation () is not true under ordinary conditions, it means that that “” is not an exact differential. In the other word “” is not a state function, or is an exact differential. //

**Irreversible Work of expansion**:

Considering a gas enclosed in a cylinder whose initial and final states are as shown in the figure. Suppose the external pressure is allowed to release suddenly from an initial pressure to a final pressure and then gas will expand against this new final pressure .



Work done is,

Since,

Which is the required expression //

**Comparison of Reversible () & Irreversible () Work**:

The isothermal reversible work of expansion is always greater than that of irreversible expansion of an ideal gas. This can be proved in the following manner —

We have,

And,

Equation (1) can also be written as —

We know that,

Substituting equation (4) in equation (3), we have,

On subtracting equation (2) from equation (5), we have,

Indicating that the, for the isothermal expansion of an ideal gas //

**The net Work in a Reversible Isothermal Cyclic Process is Zero**:

**Proof:** Suppose an ideal gas enclosed in a cylinder has its initial () and is allowed expand at constant temperature , to the final volume by an infinitesimal decrease in pressure . Hence, expansion work done by the system in this reversible expansion is —

Since, is very small, therefore, can be neglected.

Let us now attempt a return of the system to its original state reversibly, and this can be done by an infinitesimal increase in pressure successively until the volume reaches to at the same temperature, i.e. isothermally.

Hence, the total work done in the isothermal expansion and contraction, i.e. in complete cyclic process will be,

**Problem (3)**: For irreversible processes, show that

**Solution**: Consider a cyclic process involving a single stage expansion from against a constant pressure and then bringing back the system to the original stage by compressing against a constant pressure . The works involved are,



Hence,

Now, since and

This means that the surrounding have to do more work in bringing the system back to the original state than the work done by the system during expansion. Hence, for an irreversible cyclic process,

**Problem (4)**: For an ideal gas equation , prove that is an exact differential.

**Solution**: Given that,

The Universal gas constant ()

Differentiating equation () with respect to , at constant , we have,

Again, differentiating the above equation with respect to volume, we have,

Similarly, differentiating equation () with respect to , at constant , we have,

Again, differentiating the above equation with respect to volume, we have,

From equation () and (), we have,

Thus, is an exact differential // Proved

**Problem (5)**: For an ideal gas equation , prove that is an exact differential.

**Solution**: Given that,

The Universal gas constant ()

In order to prove that is an exact differential, we need to prove,

Differentiating equation () with respect to , at constant , we have,

Again, differentiating the above equation with respect to pressure, we have,

Similarly, differentiating equation () with respect to , at constant , we have,

Again, differentiating the above equation with respect to volume, we have,

From equation () and (), we have,

Thus, is an exact differential // Proved

**Problem (6)**: Show that, if , then

**Solution**: () Since,

Similarly,

() Since,

Similarly,

(iii) Since,

Again,

Finally,

Multiplying equations (), () and (), we have,

**Problem (7)**: From the van der Waals equation of state, for

Prove that

is an exact differential,

is a state function, and

**Solution**: (i) For to be an exact differential, we have to prove,

Now,

Differentiating equation () with respect to at constant ,

Again, differentiating the above equation with respect to at constant we get,

However, differentiating equation () with respect to at constant we get,

Differentiating the above equation with respect to at constant we get,

From equation () and (), we get,

Thus, is an exact differential // Proved

() In the equation,

For the first term, first of all a change in volume at constant temperature followed by a change in temperature at constant volume.

Again, for the 2nd term, a change in temperature at constant volume followed by a change in volume at constant temperature. Both the 1st and 2nd terms are same as both of them yield the same 3rd term.

Thereby, it can be inferred that the final change in pressure remains same irrespective of the difference in intermediate changes. Therefore, is a state function as changes in have been found to depend upon the initial and final states of the system.

() Given that,

When the above equation is differentiated, we obtain —

If the volume is constant, and therefore, equation () reduces to —

If the pressure is constant, and therefore, equation () reduces to —

If the temperature is constant, and therefore, equation () reduces to —

Multiplying equations (), () and (), we have,

**Problem (8)**: Calculate for () for an ideal gas obeying gas equation , () for a real gas obeying van der Waal’s equation (in either casemole)

**Solution**: () See page 10 and 11

() **The van der Waal’s equation is**,

Differentiating above equation with respect to at constant , we get,

Since, from van der Waal’s equation,

Again, differentiating equation () with respect to at constant , we get,

Multiplying both sides of equation () by , to get on , and the value is substituted in equation (), we have,

Which is the required value //

**Problem (9)**: For an ideal gas (), show that () is an integrating factor for

**Solution**: Given,

Since,

From equation () and (), we have,

Now,

Hence, is an inexact differential

Suppose, be an integrating factor, then

Thus,

Is an exact differential, while is an integrating factor.

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