

Thermodynamics

Thermodynamics is the branch of science that deals with the relationships between heat and other forms of energy. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter.

The importance of thermodynamics lies in the following facts:

It helps us to predict whether any chemical reaction can occur under the given set of conditions

It helps in predicting the extent of the reaction before the equilibrium is attained

It helps us to deduce some important laws

Energy and work

Work is the quantity of energy transferred from one system to another without an accompanying transfer of entropy.

Pressure Volume Work

PV work is often measured in units of litre-atmospheres where $1\text{L. atm} = 101.325\text{J}$.

Maximum work

For all thermodynamic processes between the same initial and final state, the delivery of work is a maximum for a reversible process.

Work done in chemical reaction

The negative sign associated with PV work done indicates that the system loses energy. If the volume increases at constant pressure ($V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings.

Heat and its sign convention

It is mode of energy exchanged between the system and the surroundings as a result of the difference of temperature between them. It is usually represented by the letter q . When the heat is given by the system to the surroundings, it is given a negative sign. When the heat is absorbed by

the system from the surroundings, it is given a positive sign.

Units of heat are calorie, joule.

1 cal == 4.2 J

Zeroth law of thermodynamics

The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

Applications of first law of thermodynamics

It tells us that energy is neither created nor destroyed. It is used to understand the functioning of heat engines, refrigerators.

Enthalpy change and its mathematical formulation

Enthalpy change of the system is equal to the heat absorbed or evolved by the system at constant pressure. Enthalpy change accompanying a process may also be defined as the sum of the increase in internal energy of the system and the pressure-volume work done. The enthalpy stored within the substance or the system that is available for conversion into heat is called the enthalpy of the substance or the system.

Carnot cycle

The Carnot cycle has the greatest efficiency possible of an engine (although other cycles have the same efficiency) based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures.

The Carnot cycle consists of the following four processes:

A reversible isothermal gas expansion process. In this process, the ideal gas in the system absorbs q_{in} amount of heat from a heat source at a high temperature T_h , expands and does work on surroundings.

A reversible adiabatic gas expansion process: In this process, the system is thermally insulated. The gas continues to expand and do work on the surroundings, which causes the system to cool to a lower temperature, T_l .

A reversible isothermal gas compression process :In this process, surroundings do work to the gas at T_1 , and causes a loss of heat, q_{out} .

A reversible adiabatic gas compression process :In this process, the system is thermally insulated. Surroundings continue to do work to the gas, which causes the temperature to rise back to T_h

Thermodynamic properties

Thermodynamic extensive properties:

amount of substance, mol.

energy, E.

enthalpy, H.

entropy, S.

Gibbs energy, G.

heat capacity, C. p

Helmholtz energy, A or F.

internal energy, U.

Specific heat capacity

It is defined as the amount of heat required to raise the temperature of 1 g of the substance through 1°C

Thompson effect

The Joules Thompson effect the temperature change of a real gas or liquid when it is forced through a valve or porous plug while kept insulated so that no heat is exchanged with the environment. At room temperature, all gases except hydrogen, helium and neon cool upon expansion by the Joule Thomson process; these three gases experience the same effect but only at lower temperatures.

Concept of thomson effect

The Joule-Thomson effect describes the increase or decrease in the temperature of a real gas (as differentiated from an ideal gas) or a liquid when allowed to expand freely through a valve or

other throttling device while kept insulated so that no heat is transferred to or from the fluid, and no external mechanical work is extracted from the fluid.

Thermochemistry

Thermochemistry is the study of the energy and heat associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling.

Thermochemistry

The branch of chemistry concerned with the quantities of heat evolved or absorbed during chemical reactions is known as thermo chemistry

Thermochemical equation and conventions

When a balanced chemical equation not only indicates the quantity of the different reactants and products, but also indicates the amount of heat evolved or absorbed, it is called a thermochemical equations.

Some conventions about Thermochemical equations:

For exothermic reactions, ΔH is negative, for endothermic reactions ΔH is positive.

Unless mentioned, ΔH values are for the standard state of the substances.

The coefficients of different substances represent the number of moles reacted and formed for the heat change represented in the equation

If the reaction is reversed, sign of ΔH changes without the change in magnitude.

s is for solids, l is for liquids, g is for gases.

Factors on which heat of reaction depends

Quantities of the reactants involved

Physical state of the reactants and products

Allotropic modifications

Concentration of solutions

Temperature

Conditions of constant pressure or volume

Enthalpy

A thermodynamic quantity equivalent to the total heat content of a system is known as enthalpy. It is equal to the internal energy of the system plus the product of pressure and volume.

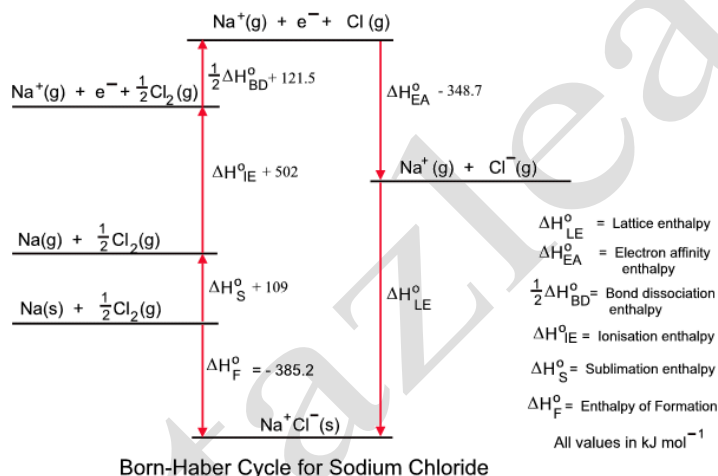
Standard enthalpy of reaction

The standard enthalpy of reaction (denoted H_r) is the enthalpy change that occurs in a system when one mole of matter is transformed by a chemical reaction under standard conditions.

standard molar enthalpy of formation

The enthalpy change of a chemical reaction in which one mole of a pure substance is formed from the free elements in their most stable states under standard state conditions is known as standard molar enthalpy of formation

Calculation of lattice enthalpy by Born Haber cycle



Lattice enthalpy of ionic compound is the enthalpy change that occurs when one mole of the ionic compound dissociates into ions in the gaseous state.

The Born-Haber cycle is shown in the image.

Enthalpy of atomization

The enthalpy of atomization is the enthalpy change that accompanies the total separation of all atoms in a chemical substance (either a chemical element or a chemical compound).

Thermal equilibrium

Two physical systems are in thermal equilibrium if no heat flows between them when they are connected by a path permeable to heat. Thermal equilibrium obeys the zeroth law of thermodynamics. Cooling a hot object. The cooling of a hot object, say in a container of water, is an example of an approach to thermal equilibrium.

Limitations of first law of thermodynamics

1. No restriction on the direction of the flow of heat. The first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work has to be done.
2. Does not specify the feasibility of the reaction. It does not specify that process is feasible or not. For example:
when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.
3. Practically it is not possible to convert the heat energy into an equivalent amount of work.

Spontaneous process

A spontaneous process is the time-evolution of a system in which it releases free energy and moves to a lower, more thermodynamically stable energy state.

Examples are:

A water fall (Niagara Falls or dams) runs spontaneously downhill, but never uphill

When you put a sugar in a cup of coffee, it dissolves spontaneously but it does not reappear in its original form

Non-spontaneous process

An endergonic reaction (also called a non-spontaneous reaction) is a chemical reaction in which the standard change in free energy is positive and energy is absorbed. Endergonic processes can be pushed or pulled by coupling them to highly exergonic reactions.

E.g. Removal of sugar from cup of tea, flow of water up the hill

Driving force

The force which is responsible for the spontaneity of process is called driving force.

The nature of it is:

Tendency for maximum randomness

Tendency for minimum energy

Tendency for minimum energy

It is the criteria for maximum stability. The tendency to attain minimum energy i.e negative value of enthalpy change might be responsible for a process to be spontaneous.

Limitations of the criterion for minimum energy

A number of reactions are known which are endothermic and are spontaneous.

There are a number of reactions for which enthalpy change is zero but still they are spontaneous.

Reversible reactions also occur.

Tendency for maximum randomness

This is the second factor which is responsible for spontaneity of a process, the tendency to acquire maximum randomness. For e.g. evaporation of water takes place because gaseous water molecules are more random than liquid water molecules. Similarly melting of ice is a spontaneous process because liquid state is more random than solid state. It is important to mention here that just as enthalpy factor cannot be the sole criterion for determining the spontaneity. Similarly, randomness factor also cannot be the sole criterion for spontaneity of a process, this is obvious from the fact that if the randomness factor were the only criterion then the process like liquefaction of a gas or solidification of a liquid would not have been feasible since these were accomplished by decrease in randomness.

Limitations of the criterion for maximum randomness

ΔH cannot be the sole factor for determining the spontaneity. The randomness factor also cannot be the sole criterion for the spontaneity of a process. If the randomness factor was the only criterion then the process like liquefaction cannot be possible.

Physical significance of entropy

It is a measure of disorder of the system. It can be used as a measure of probability in such a way that some processes may proceed from less probable state to more probable state.

Entropy change of the universe in reversible and irreversible processes

That is, entropy is a state function. The total entropy of an isolated system that undergoes a change can never decrease. Furthermore, if the process is irreversible, then the total entropy of an isolated system always increases. In a reversible process, the total entropy of an isolated system remains constant

Relationship between entropy and adiabatic change

For an adiabatic free expansion of an ideal gas, the gas is contained in an insulated container and then allowed to expand in a vacuum. Because there is no external pressure for the gas to expand against, the work done by or on the system is zero. Since this process does not involve any heat transfer or work, the First Law of Thermodynamics then implies that the net internal energy change of the system is zero. For an ideal gas, the temperature remains constant because the internal energy only depends on temperature in that case. Since at constant temperature, the entropy is proportional to the volume, the entropy increases in this case, therefore this process is irreversible.

Helmholtz free energy

The Helmholtz free energy is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature. The negative of the difference in the Helmholtz energy is equal to the maximum amount of work that the system can perform in a thermodynamic process in which volume is held constant. If the volume is not held constant, part of this work will be performed as boundary work. The Helmholtz energy is

commonly used for systems held at constant volume.

$$A = U - TS$$

A is the Helmholtz free energy (SI: joules, CGS: ergs),

U is the internal energy of the system (SI: joules, CGS: ergs),

T is the absolute temperature (kelvins) of the surroundings, modelled as a heat bath,

S is the entropy of the system (SI: joules per kelvin, CGS: ergs per kelvin).

Second law of thermodynamics

In any cyclic process, the entropy will either increase or remain the same. Entropy is a state variable whose change is defined for a reversible process at T where Q is the heat absorbed. All spontaneous processes produce an increase in the entropy of the universe. No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work. No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.

Law of thermodynamics

The first law, also known as Law of Conservation of Energy, states that energy cannot be created or destroyed in an isolated system. The second law of thermodynamics states that the entropy of any isolated system always increases.

Mathematical formulation of change in entropy of a given series

If two reactions are given and we have to find the entropy of third reaction, then use the two reactions to form the third reaction. The entropy of third reaction can be found out using the two entropies by using the mathematical tools.

Entropy

Entropy is a measure of disorder or randomness of a system. An ordered system has low entropy. A disordered system has high entropy.

Effect of temperature on spontaneity

An endothermic reaction which may be non-spontaneous at low temperature may become spontaneous at high temperature.

An exothermic reaction which may be non-spontaneous at high temperature may become spontaneous at low temperature.

Standard free energy change

The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of that substance from its component elements, at their standard states (the most stable form of the element at 25°C and 100 kPa).

Third law of thermodynamics

The third law of thermodynamics is stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature: The entropy of a perfect crystal at absolute zero is exactly equal to zero.

The third law essentially tells us that it is impossible, by any procedure, to reach the absolute zero of temperature in a finite number of steps.

Most of the direct use of the third law of thermodynamics occurs in very low temperature applications, to predict the response of various materials to temperature changes. Another useful application of the third law is the computation of absolute entropies of pure substances at temperatures other than 0 K from their heat capacities and heats of transition.

System

The part of the universe chosen for thermodynamic consideration is called a system.

Surroundings

The remaining portion of the universe excluding the system is called surroundings.

Universe = system + surroundings

Open system

A system is said to be an open system if it can exchange both matter and energy with the surroundings. e.g. If water is kept in an open vessel or if some reaction is allowed to take place in an open vessel, exchange of matter and energy takes place.

Closed system

If a system can exchange only energy with the surroundings but not matter, it is called a closed system. e.g if some water is placed in a closed metallic vessel or if some reaction is allowed to take place in a cylinder enclosed by a piston then as the vessel is closed, no exchange of matter between the system and the surrounding can take place.

Isolated system

If a system can neither exchange matter nor energy with the surroundings, it is called an isolated system. e.g If water is placed in a vessel which is closed as well as insulated, no exchange of matter or energy can take place between the system and the surroundings. This constitutes an isolated system.

Homogeneous and heterogeneous system

Any system consisting of a single phase is called Homogeneous and any system has more than one phase of the substance is called Heterogeneous.

State of a system

The state of a system means the condition of the system which is described in terms of certain observable properties as temperature, pressure volume etc. of a system.

Path functions

Path functions are properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are heat and work.

State function

A state function describes the equilibrium state of a system. For example energy, enthalpy, internal and entropy are state quantities because they describe quantitatively an equilibrium state of a thermodynamic system, irrespective of how the system arrived in that state.

State functions

A physical quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained. E.g pressure, volume, temperature.

Extensive properties

These are the properties which depend upon the quantity of matter contained in the system. e.g mass, volume and heat capacity.

Intensive properties

These are the properties which depend only upon the nature of the substance and are independent on the amount of the substance present in the system. E.g temperature, pressure, density.

Thermodynamic equilibrium

A system is said to be thermodynamic equilibrium if its macroscopic properties like temperature, pressure do not change with time.

Isothermal process

When a process is carried out in such a manner that the temperature remains constant throughout the process, it is called isothermal process.

Adiabatic process

When a process is carried out in such a manner that no heat can flow from the system to the surroundings or vice versa i.e the system is completely insulated from the surroundings it is called an adiabatic process.

Isochoric process

It is the process during which the volume of the system is kept constant.

Isobaric process

It is a process during which the pressure of the system is kept constant.

Reversible process

It is a process which is carried out infinitesimally slowly so that all changes occurring in the direct process can be exactly reversed and the system remains almost in a state of equilibrium with the surroundings at every stage of the process.

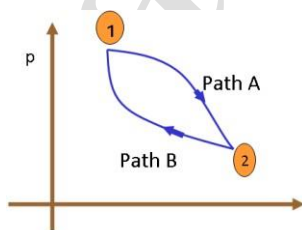
Reversible process

In thermodynamics, a reversible process is a process whose direction can be "reversed" by inducing infinitesimal changes to some property of the system via its surroundings, while not increasing entropy. Throughout the entire reversible process, the system is in thermodynamic equilibrium with its surroundings.

Irreversible process

A process which is not carried out infinitesimally slowly so that the successive steps of the direct process cannot be reversed and any change in the external conditions disturbs the equilibrium.

Cyclic processes

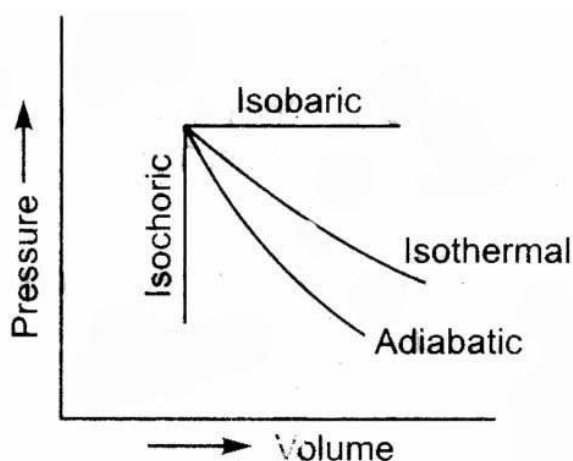


A cyclic process is a sequence of processes that leaves the system in the same state in which it started. When a system is carried through a cyclic process its initial and final internal energies are equal. So the total internal-energy change in any cyclic process is zero.

Free expansion of a gas

The internal energy of a gas depends on both temperature and pressure. So, if U remains constant and pressure changes, the temperature must change. In the ideal gas limit of very low pressures, the pressure dependence of gas weakens and approaches zero.

Graphical representation of basic thermodynamic processes



Reversible and Irreversible processes

Reversible Process	Irreversible Process
<ol style="list-style-type: none"> 1. The process is carried out infinitesimally slowly 2. At any stage, the equilibrium is not disturbed 3. It takes infinite time for completion. 4. Work obtained in this process is maximum. 	<ol style="list-style-type: none"> 1. It is carried out rapidly 2. Equilibrium may exist only after the completion of the process. 3. It takes a finite time for completion. 4. Work obtained in this process is not maximum

Isothermal and adiabatic process

In an adiabatic process is where a system exchanges no heat with its surroundings ($Q = 0$). In other words, in an isothermal process, the value $T = 0$ and therefore $U = 0$ (only for an ideal gas) but $Q \neq 0$, while in an adiabatic process, $T \neq 0$ but $Q = 0$.

Work

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

Types of work:

Electrical work

Pressure-volume work

Pressure Volume Work

PV work is often measured in units of litre-atmospheres where $1 \text{ L} \cdot \text{atm} = 101.325 \text{ J}$.

Condition for maximum work done

The maximum work that the system can do on the surroundings in an isothermal expansion of an ideal gas is obtained if the expansion is carried out reversibly.

Path dependent nature of work

Two important examples of a path function are heat and work. These two functions are dependent on how the thermodynamic system changes from the initial state to final state. These two functions are introduced by the equation U which represents the change in the internal energy of a system.