Thermodynamics

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Thermodynamics is concerned with the energy changes in physical and chemical transformation.

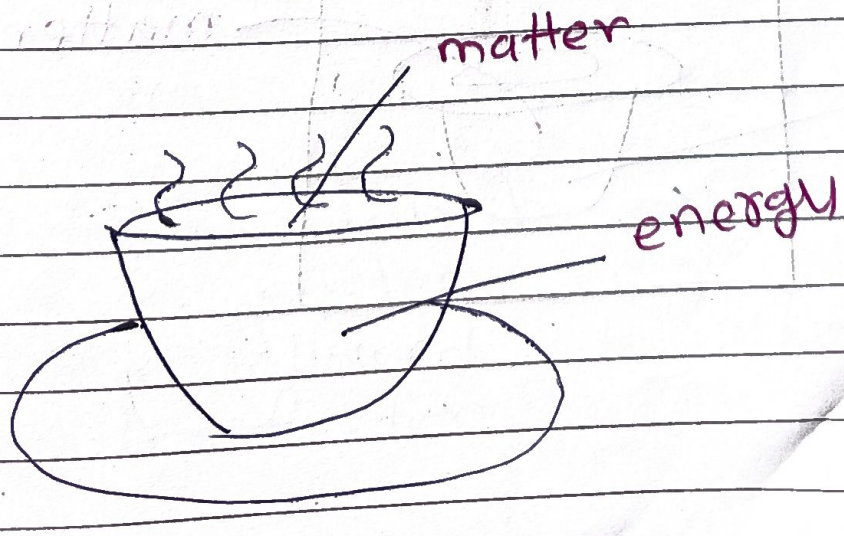
Terms used in thermodynamics

System and Surrounding

A part of the universe under thermodynamic investigation is called the System. All other part of the universe outside the system such as cylinder, room and other, are surrounding

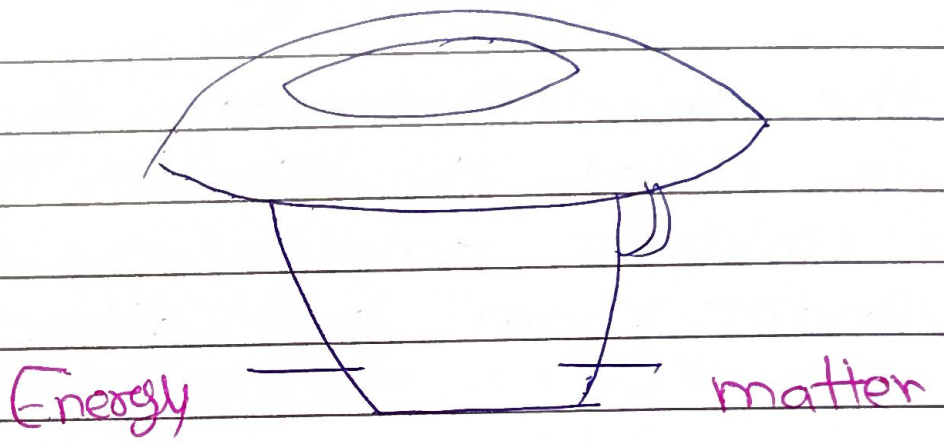
Types of system.

Open system: Fig shows an open cup containing hot coffee placed in a room. You observe coffee cools down releasing heat to the surroundings. The water vapour from coffee simultaneously passes into surroundings. Such a system (coffee) which exchanges both energy and matter with the surrounding is called an open system.



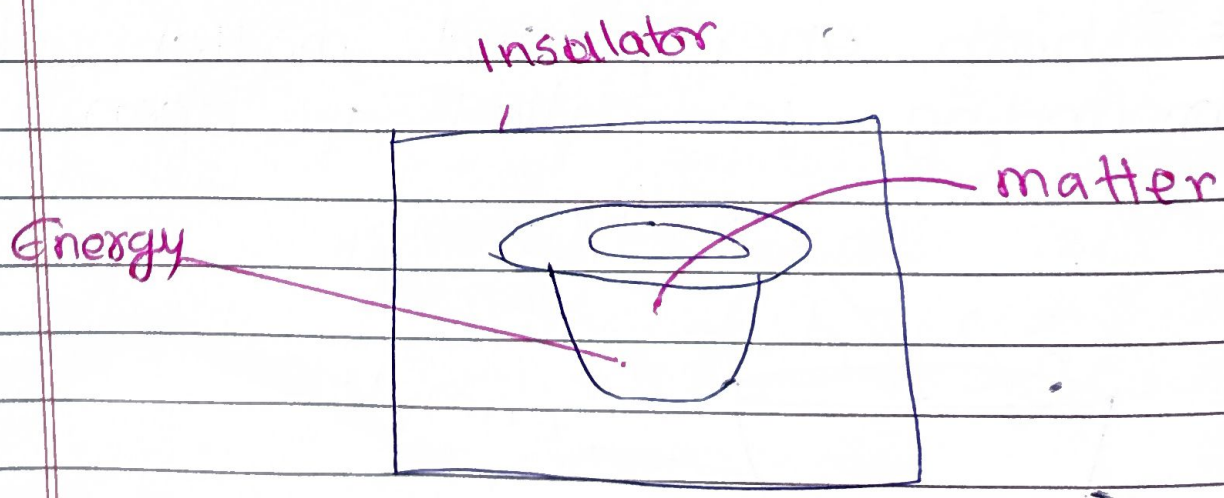
Closed System:

Such a system that exchanges ene and not the matter with the surroundings is called a closed system.



Isolated System.

Such a system that does not allo exchange of either energy or mat with the surroundings is calle Isolated System.



Properties of system

Extensive property

A property which depends on the amount of matter present in a system is called an extensive property.

e.g. mass, Volume, internal energy, heat capacity, number of moles

Intensive Property

A property which is ~~depen~~ independent of the amount of matter in a system is called Intensive Property.

e.g: Pressure, tem., surface tension, viscosity, melting point, specific heat.

Extensive - Intensive
Extensive

State function

The property which depends on the state of a system and independent of a path followed to attain, is called State function.

Path functions

The properties which depend on the path are called path function,

e.g. Heat, work, only

Process and its types:

A transition from one equilibrium state to another is called a process.

Isothermal process:

It is the process in which temperat of the system remains constant throughout the transformation.

$\Delta T = 0$ $\Delta U = 0$ ΔU = Internal energy

Isobaric process:

In isobaric process the pressure remains constant during the transforma

$\Delta P = 0$

Isochoric process:

It is a process during which volume of the system remains constant during the transformation

$\Delta V = 0$

Adiabatic process:

A process in which there is no exchange of heat between system and surrounding is an adiabatic process.

$\Delta q = 0$

Adiabatic Expansion = Temp decr.

Adiabatic Compresion → Temp. incre.

Reversible Process

Very slow and at all step is in equilibrium.

Irreversible Process:

Very fast.

Work

In mechanics the work is defined as the energy by which body is displaced through a distance with an application of force.

$$W = P_{ext} \Delta V$$

→ Expansion : ΔV = +ve, W = -ve

e.g. work is done by the system.

Compression = ΔV = -ve, W = +ve, e.g. work is done on the system.

first law of thermodynamics

$$\Delta U = q + w$$

ΔU = Intenal en

q = heat

w = work

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Enthalpy (H)

Enthalpy of a system is sum of internal energy of a system and the energy equivalent to PV work.

$$H = U + PV$$

change in enthalpy (ΔH) is also state function

$$\Delta H = H_2 - H_1$$

$$H_1 = U_1 + P_1V_1 \qquad H_2 = U_2 + P_2V_2$$

$$\Delta H = (U_2 + P_2V_2) - (V_1 + P_1V_1)$$

$$(U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$\boxed{\Delta H = \Delta U + \Delta(PV)}$$

P for constant pressure, $P_1 = P_2 = P$

$$\boxed{\Delta H = \Delta U + P\Delta V}$$

If the pressure inside and outside is the same or $P_{ext} = P$

$$Q_p = \Delta U + P\Delta V$$

than

$$\Delta H = Q_p$$

Relation between ΔH and ΔU for Chemical reaction

for reactions involving solids and liquids, ΔV usually is very small

for reaction involving gases, ΔV cannot be neglected.

We assume reactant and product behav ideally. Applying ideal gas equation

$PV = nRT$

when n_1 moles of gaseous reactants produce n_2 moles of gaseous product

$P_1V_1 = n_1RT$ $\quad P_2V_2 = n_2RT$

$\Delta H = \Delta U + n_2RT - n_1RT$

$= \Delta U + (n_2 - n_1)RT$

$\boxed{\Delta H = \Delta U + n_gRT}$

Enthalpes of physical transformations

Enthalpy of phase transition ($\Delta_{fus}H$)

Enthalpy change that occurs when one mole of solid is converted into liquid without change in temperature at ~~stan~~ constant pressure is enthalpy of fusion.

ex.

$H_2O_{(s)} \longrightarrow H_2O\ (l)$

$\Delta_{fus}H = +6.01\ kJ\ mol^{-1}$ at $0^\circ C$

A reverse of fusion is freezing of solid.

$H_2O(l) \rightarrow H_2O(s)$, $\Delta_{freez}H = -6.01\ kJ\ mol^{-1}$ at $0^\circ C$

Enthalpy of vaporization ($\Delta_{vap}H$)

It is the enthalpy change acco
the vaporization of one mole of l
without changing its temperature a
constant pressure

ex.

$H_2O(l) \longrightarrow H_2O(g)$, $\Delta_{vap}H = +40$

at 1

$H_2O(l) \longrightarrow H_2O(g)$ $\Delta_{vap}H = +44$

at

on other hand, the condensation to
vapour is accompained with a rele
of heat

$H_2O(g) \longrightarrow H_2O(l)$, $\Delta_{con}H = -40.7$

at

Enthalpy of sublimation ($\Delta_{sub}H$)

It is the enthalpy change for the conversion of one mole of solid directly into vapour at constant temperature and pressure.

Consider

$H_2O(s) \rightarrow H_2O(g)$, $\Delta_{sub}H = 51.08\ kJ\ mol^{-1}$ at 0°C

$H_2O(s) \rightarrow H_2O(l)$ $\Delta_{fus}H = 40.6.01\ kJ\ mol^{-1}$

$H_2O(l) \rightarrow H_2O(g)$ $\Delta_{vap}H = 45.07\ kJ\ mol^{-1}$

$H_2O(s) \rightarrow H_2O(g)$ $\Delta_{sub}H = 51.08\ kJ\ mol^{-1}$

$$\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$$

Enthalpy for the atomic / molecular change

Enthalpy of ionization ($\Delta_{ion}H$)

It is the enthalpy change accompanying the removal of an electron from one mole of gaseous atom

$$Na_{(g)} \longrightarrow Na^{+}_{(g)} + e^{-} \quad \Delta_{ion}H = 494\ KJ\ mol$$

The electron gain enthalpy on the other hand, gives the enthalpy change when one mole of gas-phase atom of an element accept electron to from gaseous anion.

$$Cl_{(g)} + e^{-} \longrightarrow Cl^{-}_{(g)} \quad \Delta_{eg}H = -349\ KJ\ mo$$

Enthalpy of atomization ($\Delta_{atom}H$)

The enthalpy accompanying the dissociatio of one mole of gaseous substance into atom is the enthalpy of atomization.

$$Cl_{2(g)} \longrightarrow Cl_{(g)} + Cl_{(g)}, \quad \Delta_{atom}H = 242\ KJ\ mol$$

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} \quad \Delta_{atom}H = 1660\ KJ\ mol^{-1}$$

Enthalpy of solution ($\Delta_{soln}H$):

Enthalpy of solution is the enthalpy change in a process when one mole of a substance is dissolved in specified amount of solvent.

$NaCl_{(s)} + aq \rightleftharpoons NaCl_{(aq)}$ $\Delta_{soln}H = 4\,kJ\,mol^{-1}$

An ionic compound dissolves in water in two steps

1. The ions are separated from the molecules-

$MX_{(s)} \rightarrow M^{+}_{(g)} + X^{-}_{(g)}$

Eh Enthalpy change for this step is crystal lattice enthalpy, $\Delta_L H$ which is always positive

2. The ions are hydrated with water molecules surrounding them

$M^{+}_{(g)} + x\,H_2O \rightarrow [M(H_2O)x]^{\oplus}$

$MX^{-}_{(g)} + y\,H_2O \rightarrow [X(H_2O)y]^{\ominus}$

The enthalpy change for this step is always negative and called enthalpy of hydration. $\Delta_{hyd}H$

$\Delta_{soln}H$ =

Thermochemistry

Thermochemistry deals with enthalpy changes in chemical reactions

Enthalpy of chemical reaction ($\Delta_r H$)

$$\Delta_r H = \sum H_{products} - \sum H_{reactants}$$

Exothermic and endothermic reactions

The enthalpy of e reactions depends on $\Sigma H_{product}$ and $\Sigma H_{reactant}$

Tus $\Sigma H_{product} > \sum H_{reactant}$

$\Delta_r H$ is positive signifies the reactions is endothermic.

on the other hand, If $\Sigma H_{product} < \Sigma H_{reactant}$ than $\Delta_r H$ is negative and this is the exothermic

Standard enthalpy of reaction ($\Delta_r H^\circ$)

The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states

standard state of a substance at a specified temperature is its pure form at 1 bar

1) The standard state of liquid ethanol at 298K is pure liquid ethanol at 1 bar

2) standard state of solid iron at 500K is pure iron at 1 bar

Standard enthalpy of formation ($\Delta_f H^\circ$)

The standard enthalpy of formation of a compound is the enthalpy change that accompanies a reaction in which one mole of pure compound in its standard state is formed from its elements in their standard states

Standard enthalpy of combustion ($\Delta_c H^\circ$)

The standard enthalpy of combustion of a substance is the standard enthalpy change accompanying a reaction in which one mole of the substance in its standard state is completely oxidised.

Bond enthalpy ($\Delta_{bond} H$)

The enthalpy change required to break particular covalent bond in one mole of gaseous molecule to produce gaseous atoms and/or radicals, is called bond enthalpy.

$$H_{2(g)} \longrightarrow H_{(g)} + H_{(g)} \quad \Delta_r H$$

$$= 436.4 KJ$$

Hess's law of constant heat summation

The laws states that, overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction

Application of Hess's law

The Hess's law has been useful to calculate the enthalpy changes for the reactions with their enthalpies being not known experimentally.

Spontaneous (irreversible) process:

Spontaneous processes have a natural tendency to occur and do not require any external influence for their occurence

Key points of spontaneous process

It occurs of its own and does not require any external agency to occur.

It proceeds in one direction and cannot take place in the opposite direction unless the external stimulant is present

The spontaneous processes can be rapid or slow as spontaneity is not concerned with the rate of the reaction.

The processes continues till equilibrium is reached. The spontaneous (natural) processes tend to occur in a direction that leads to equilibrium.

Entropy

Entropy is a measure of molecular disorder or randomness.
An entropy change of a system is equal to the Amount of heat transferred (Q_{rev}) to it in a reversible manner divided by the temperature in Kelvin
T

$$\Delta S = \frac{Q_{rev}}{T}$$

* ∴ ΔS is a state function

the ΔS is thus expressed in JK^{-1}

Entropy and spontaneity

(

The entropy increases when ice melts above 0°c and water vaporizes at 100 °c. Both are spontaneous.

ii) Consider the spontaneous reaction at room temperature

$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ $\Delta S = +126\ JK^{-1}$

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Entropy increases due to the formation of O_2 gas.

entropy of the system increases in the spontaneous processes.

In this reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$$

$$\Delta S = -327\ J\,K^{-1}$$

The entropy of the system decreases. Note the reaction is spontaneous

Second law of thermodynamics

The SP Second law of thermodynamics states that total entropy of a system and its surrounding increases in a spontaneous process.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

$\Delta S_{total} > 0$, the process is spontaneous

$\Delta S_{total} < 0$, the process is nonspontaneous

$\Delta S_{total} = 0$, the process is at equilibrium

Gibbs energy.

$$G = H - TS$$

Gibbs energy denoted by G

It is a state function

The change in Gibbs energy at constant temperature and constant pressure is given by

$$\Delta G = \Delta H - T\Delta S$$

Gi

Energy and spontaneity

The total entropy change that accompanies a process is given by

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= \Delta S + \Delta S_{surr}$$

The subscript sys that refers to the system is dropped hereafter.

Relation between ΔG and ΔS_{total}

According to second law of thermo. for a process to be Spontaneous.

$\Delta S_{total} > 0$.

If ΔH is the enthalpy change accompanying a reaction (system) the enthalpy change of the surrounding is $-\Delta H$ with

$$\Delta S_{surr} = \frac{-\Delta H}{T}$$

Substituting above into

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T}$$

Thus ΔS_{total} is expressed in term of the properties of the system only.
Rearranging

$$T\Delta S_{total} = \Delta H - T\Delta S$$

Substituting

$$\Delta G = -T\Delta S_{total}$$

* $\Delta S_{total} > 0$ and $\Delta G < 0$, the process is spontaneous

* $\Delta S_{total} < 0$ and $\Delta G > 0$, the process is nonspontaneous

* $\Delta S_{total} = 0$ and $\Delta G = 0$, the process is equilibrium.