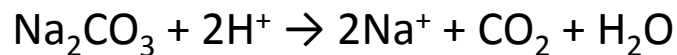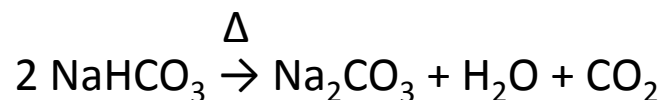## Thermodynamics

Thermochemistry: Laws of Thermochemistry, Enthalpy, Hess's law, Heat of formation, Kirchoff's equations, Heat of neutralization, Heat of reaction

Determination of the enthalpy change of the thermal decomposition of $NaHCO_3$

$$2\ NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

$[NaHCO_3 + H^+ \rightarrow Na^+ + CO_2 + H_2O] \times 2$

$Na_2CO_3 + 2H^+ \rightarrow 2Na^+ + CO_2 + H_2O$

Detail: Please follow class lecture

Born-Haber cycle

Construction of Born-Haber cycle for KCl, NaCl, $MgCl_2$ etc

Scope & limitations of thermodynamics

Thermodynamics, the study of the transformations of energy, enables us to discuss this transformation into heat and work quantitatively and to make useful predictions.

System, surrounding and boundary, kind of processes in a system

A system is the part of the universe, which is under thermodynamic consideration and the rest of the system is surroundings.

The real or imaginary surface separating the system from the surroundings is called the boundary.
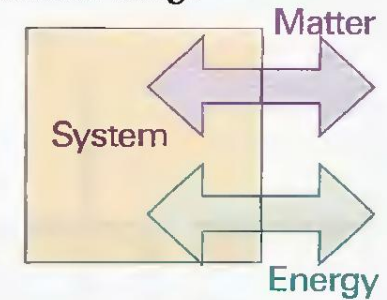
Boundary

System
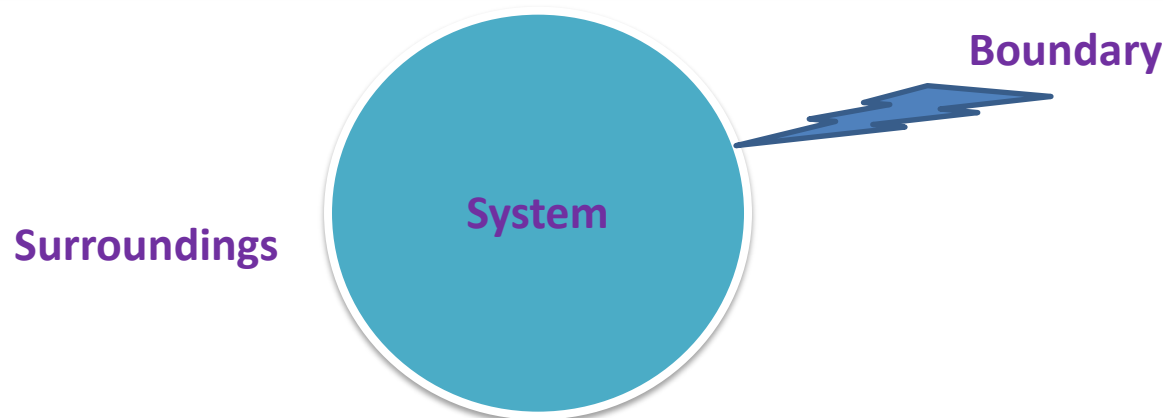
Surroundings

Types of system

Isolated (neither form of matter nor heat can transfer to and from its surroundings; neither mechanical nor thermal contact)
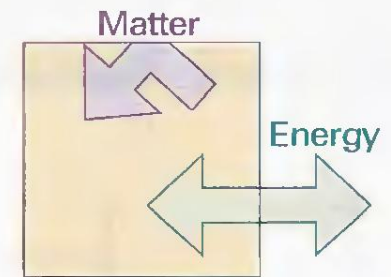
Closed (It can not transfer matter but can transfer energy in the form of heat , work and radiation to and from its surroundings)

Open (Can transfer both matter and heat to and from its surroundings through its boundary)

Surroundings

Matter

System

Energy

(a) Open

Matter

Energy

(b) Closed

Matter

Energy

(c) Isolated

SURROUNDINGS

SYSTEM

BOUNDARY
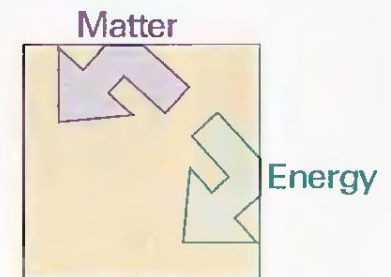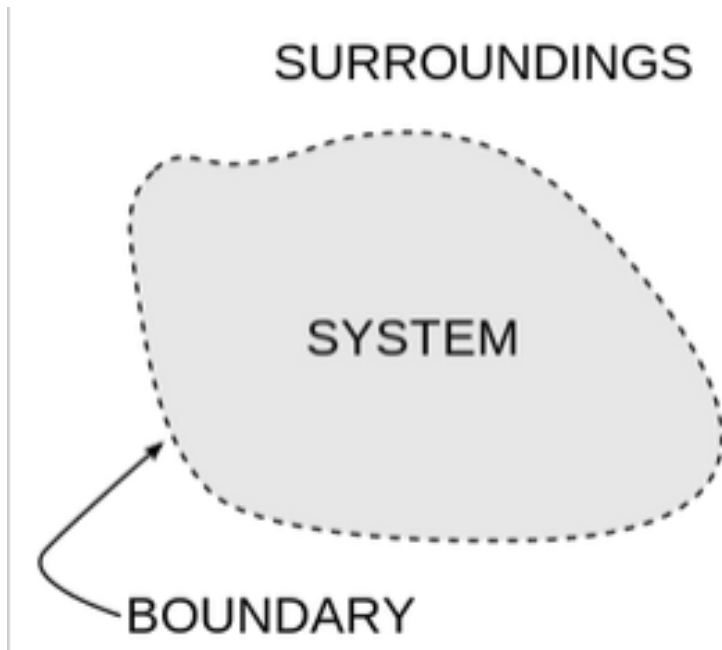
Types of transfers permitted

type of partition	type of transfer		
	Mass and energy	Work	Heat
permeable to matter	✓	✗	✗
permeable to energy but impermeable to matter	✗	✓	✓
adiabatic	✗	✓	✗
adynamic and impermeable to matter	✗	✗	✓
isolating	✗	✗	✗

Properties of system

An extensive property is depends on the amount of substance in the sample. Examples of extensive properties are mass and volume

An intensive property is a property that is independent of the amount of substance in the sample. Examples of intensive properties are temperature, mass density and pressure.

State of a system : A thermodynamic system is said to be in a certain state when all of its properties are fixed. The fundamental properties, which determine the state of a system are pressure (P), Temperature (T), Volume (V), mass (m) and composition

State variables : Independent state variables : P & T
                              Dependent state variables : V

The *IUPAC* sign convention in thermodynamics

If heat is added to the system	*q* **&** ΔU **are positive**

If heat is lost by the system	*q* **&** ΔU **are negative**

If work is done on a system	*w* **&** ΔU **are positive**

If work is done by a system	*w* **&** ΔU **are negative**

Endothermic reaction	ΔH **is positive**

Exothermic reaction	ΔH **is negative**

Zeroth law of thermodynamics

The Zeroth Law of Thermodynamics states that if two bodies are each in thermal equilibrium with some third body, then they are also in equilibrium with each other. Thermal equilibrium means that when two bodies are brought into contact with each other and separated by a barrier that is permeable to heat, there will be no transfer of heat from one to the other.

The most important thing of the Zeroth Law is that it establishes **temperature** is a fundamental and measurable property of matter.
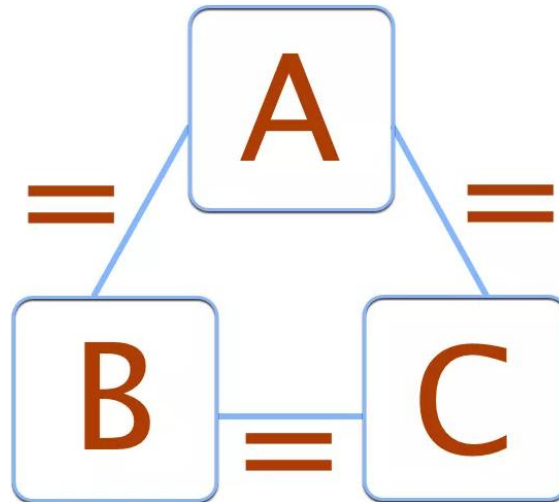
First law of thermodynamics

The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant.

"Heat and work are equivalent ways of changing a system's internal energy"

"It is impossible to build a perpetual motion machine" (Perpetual motion machine is a machine that can produce work without fuel.

"The internal energy of an isolated system is constant"

"The summation of the two inexact differentials can produce an exact differential"

$$\Delta U = \Delta q + \Delta w = \Delta q + P\Delta V$$

Enthalpy and change of state at constant pressure

From first law of thermodynamics and for a isobaric system,

$\Delta U = q_p - P\Delta V$; *work done by the system on surrounding.*

So, $\Delta U = U_f - U_i = q_p - P(V_f - V_i)$

$q_p = (U_f + PV_f) - (U_i + PV_i)$

Since the heat absorbed is given by the two quantities that are functions of the state of the system, a new state function, enthalpy can be defined by,

$H = U + PV$

hence that,

$\Delta H = H_f - H_i$

Therefore,

$q_p = \Delta H$

"Heat absorbed for an isobaric system is equal to the change in enthalpy"
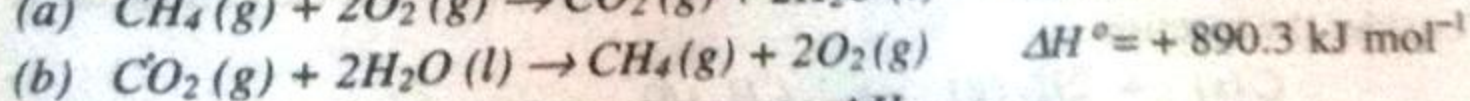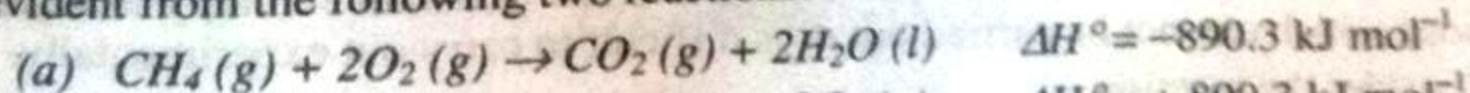
Laws of Thermochemistry

Two laws of thermochemistry are very important in thermochemical calculations. Both the laws preceded the *first law of thermodynamics* (1850). It will, however be shown that the *laws of thermochemistry* are direct consequence of the *first law of thermodynamics*.

Lavoisier and Laplace's law (1782)

This law may be stated in the general form as : *the heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction.*
This is evident from the following two reactions:

This is evident from the following two reactions:

(a) $CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (l)$ $\quad \Delta H° = -890.3$ kJ mol^{-1}

(b) $CO_2 (g) + 2H_2O (l) \rightarrow CH_4(g) + 2O_2(g)$ $\quad \Delta H° = +890.3$ kJ mol^{-1}

Thus, it can be concluded that, $\Delta H_{forward\ reaction} = -\Delta H_{reverse\ reaction}$

Effect of temperature on the heat of the reaction: The Kirchhoff's equation

The heat change accompanying chemical or physical processes generally depends on the temperature at which the process takes place. This dependence is mathematically expressed in the form of what is known as Kirchhoff equation after G. R. Kirchhoff (1858) who first developed this equation. The equation may easily be derived with the help of the first law of thermodynamics.

Consider the process in which the reactants in state A at temperature T_1 are converted into products in state B at temperature T_2. Assume that all operations are carried out at constant pressure. The conversion may be carried out in two ways, but according to Hess's law the total heat change must be the same in both cases.

(1) The reactants in state A at temperature T_1 are heated to a temperature T_2. The heat absorbed is $(\Delta T)(C_p)_A$, where $\Delta T = T_2 - T_1$ and $(C_p)_A$ is the heat capacity of the reactants in the state A. The reaction is now allowed to take place at this temperature and the heat change for the process is $(H_B - H_A)_2 = \Delta H_2$.

The total heat change for the process $= (\Delta T)(C_p)_A + \Delta H_2$.

(2) The reactants in state A at temperature T_1 are converted to products in state B at the same temperature. The heat content change $= (H_B - H_A)_1 = \Delta H_1$. The temperature of the products is then raised from T_1 to T_2 and the heat absorbed is $(\Delta T)(C_p)_B$, where $(C_p)_B$ is the heat capacity of the products.

The total heat change for the process $= (\Delta T)(C_p)_B + \Delta H_1$.

From Hess's law

$$(\Delta T)(C_p)_A + \Delta H_2 = (\Delta T)(C_p)_B + \Delta H_1$$

or
$$\Delta H_2 - \Delta H_1 = [(C_p)_B - (C_p)_A] \times \Delta T$$
$$= (\Delta C_p)(\Delta T)$$

where
$$\Delta C_p = (C_p)_B - (C_p)_A$$

or
$$\frac{\Delta H_2 - \Delta H_1}{\Delta T} = \Delta C_p$$

For an infinitesimally small change in temperature one can write

$$\left[\frac{d(\Delta H)}{dT}\right] = \Delta C_p$$

Similarly, it may be shown that if the process is carried out at constant volume the relationship is

$$\left[\frac{d(\Delta U)}{dT}\right] = \Delta C_v$$

The Joule-Thomson effect

The passage of fixed amount of a gas from higher pressure side to lower pressure side through a porous plug of an insulated adiabatic process produces lower temperature on the low pressure side and the difference being proportional to the pressure differences. This effect is known as Joule-Thompson effect.

It can be proved that the Joule-Thompson process corresponds to an isenthalpic expansion, i.e., the expansion occurs without change of enthalpy. The quantity observed is the temperature change per unit change of pressure. This quantity is called Joule-Thompson co-efficient, μ

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H$$

Limitation of the first law of thermodynamics

1. It does not gives the condition under which energy can be converted into other form.
2. It does not indicate the extent and the direction of such change.
3. Other forms of energy can be completely converted to heat energy

About the first law of thermodynamics

Second law provides the information as to the conditions under which heat can be converted into other forms of energy or work and the limitation that govern such conversion.

Second Law of thermodynamics

This law may be expressed in a variety of equivalent ways. By Kelvin:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

It is impossible to construct a machine functioning in cycles which can convert heat completely into the equivalent amount of work without producing changes elsewhere.

By R. Clausius:

Heat can not of itself, without the intervention of any external agency, pass from a colder to hotter body

Irreversible process generates entropy and reversible process does not.

Spontaneity

1. *Spontaneous process is unidirectional or one-way process. Work has to be done to make it reverse order.*

2. *Spontaneous process is time independent.*

3. *An spontaneous process is accompanied by decrease or increase in internal energy or enthalpy introducing a new term entropy.*

4. *The system tends to attend an equilibrium when $\Delta S = q/T$; external work has to be done to destroy the equilibrium.*