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STATE FUNCTION

- A state function is a property of the system which has definite value for each state and which is independent of the manner in which the state is reached.
- Pressure, volume and temperature are few examples of state functions.

PROPERTIES OF STATE FUNCTION

(I) "By fixing the values of a few state functions the values of other state functions are fixed automatically." If we fix the values of pressure and volume of one mole of ideal gas then value of temperature "T" is fixed automatically.

PV = nRT, Where n = number of moles

PV = RT If n = 1 mole

$\therefore T = \frac{PV}{R}$

(II) The changes in state function of a system depends only on the initial state and final state of the system. It does not depend on how the change in the system is made.

For instance one mole of gas is given in the following initial state :

P_1 = 1 atm, V_1 = 22.4 litre, T_1 = 300 K

Now the gas is changed into final state bearing the values

P_2 = 10.0 atm, V_2 = 4.48 litre, T_2 = 500 K

Thus the change in pressure (ΔP) = P_2 - P_1

= 10 – 1

= 9 atm

The change in volume (ΔV) = V_2 - V_1

= 22.4 – 4.48

= 17.9 litre

The change in temperature $(\Delta T) = T_2 - T_1$

$= 500 - 300$

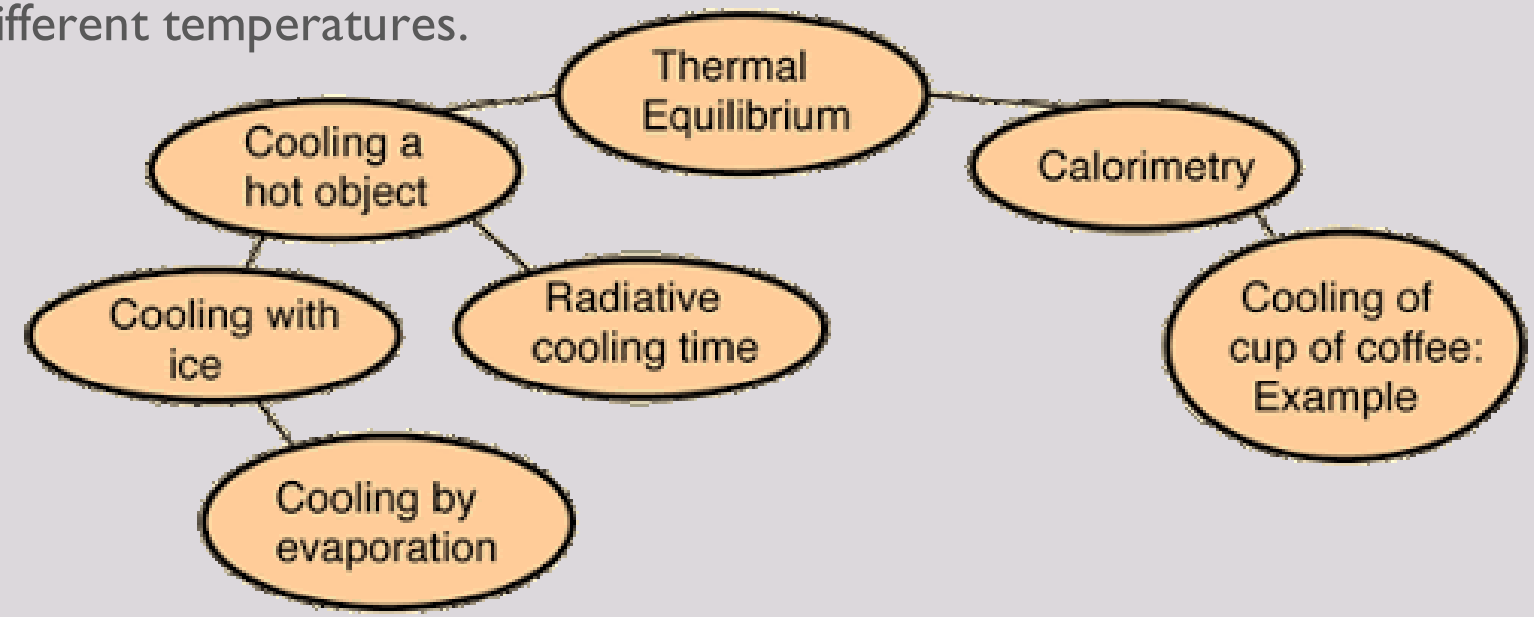
$= 200K$

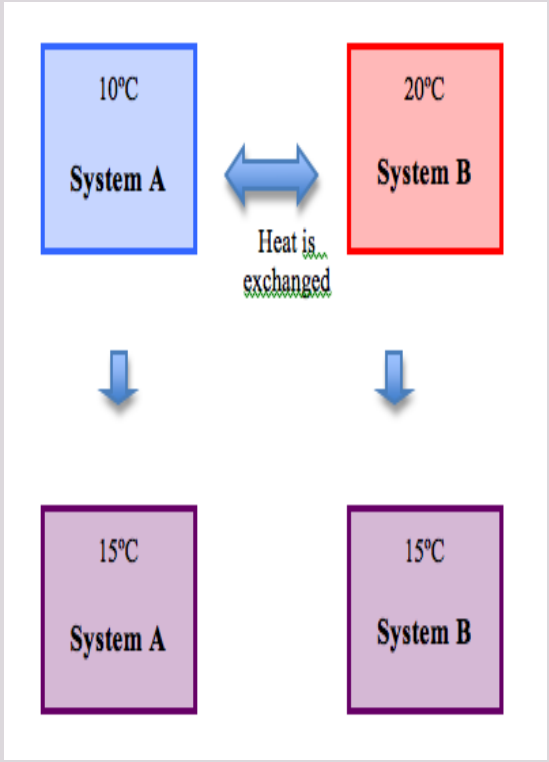
- Here, it is important to remember that 'Δ' (delta) is used to show subtraction of the value of a function in initial state from its final state i.e. ΔV always means $V_{final} - V_{initial}$.

- The change (difference) in each of these state function depends on their value in the initial state and final state of the system and not on the manner in which the change is made.

THERMAL EQUILIBRIUM

- A system is in thermal equilibrium if the temperature remains the same in all parts of the system.
- Systems in thermal equilibrium with each other will have the same temperature (i.e. there is no flow of heat from one part of the system to another) while systems not in thermal equilibrium with each other will have different temperatures.



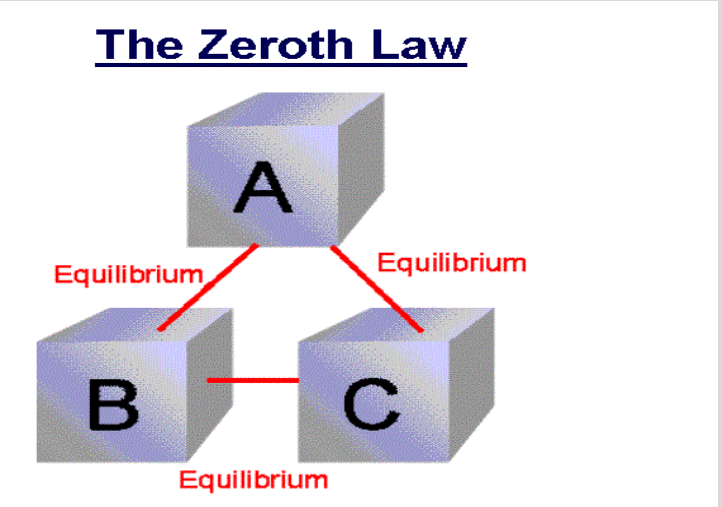


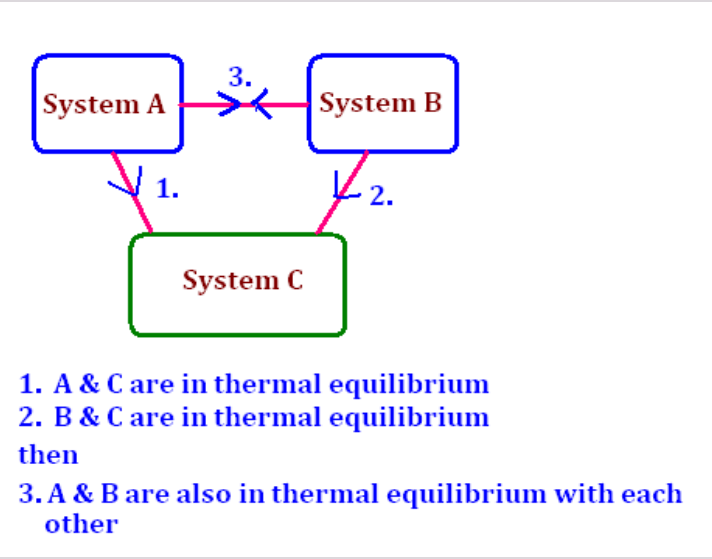
ZEROTH LAW OF THERMODYNAMICS

- We know that temperature is one of the quantities necessary to define the state of a thermodynamic system. In other words, every thermodynamic system must possess a temperature.
- **This law states that;**

If body A is in equilibrium with body C and body B is also in equilibrium with body C, then bodies A and B are in equilibrium with each other.

- Energy manifests itself not only in the form of mechanical work, but also as heat energy, electrical energy and chemical energy. Energy is composed of two factors i.e., intensity factor and capacity factor. The product of these two factors gives the energy.





- Heat energy is measured by the product of temperature (intensity factor) and heat capacity (capacity factor) of the system. The product gives the energy of the system. If a substance of mass m kg and specific heat s kJ per kg is heated through t, the heat energy involved is given by mst kJ.
- The precise experimental basis for this assumption is the law of thermal equilibrium from which it can be shown that in a thermodynamical system for every participants in equilibrium, there exists a certain single valued function 'f' of the state variables, P and V, which have the same values for all participants. It can be expressed as;

$$f_1\ (P_1,V_1) = f_2\ (P_2,V_2) = f_3\ (P_3,V_3) = \ldots\ldots = T$$

where;

f = variable

P = pressure

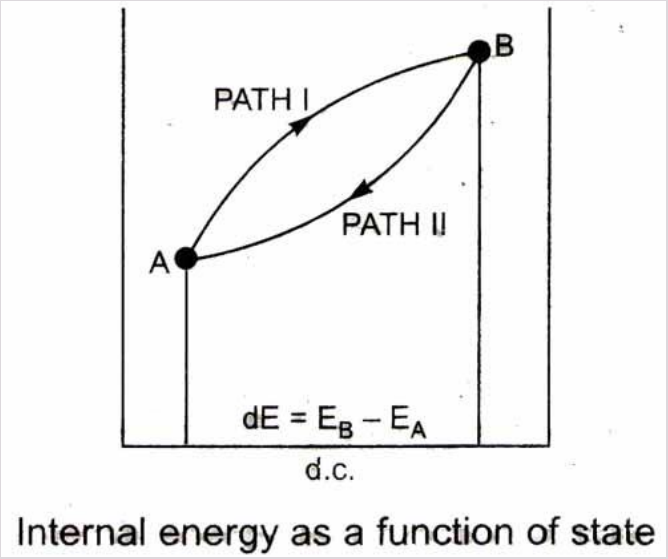
V = volume

T = temperature

Subscripts 1,2,3 = different participants

INTERNAL ENERGY

- The energy possessed by a system due to translational, vibrational and rotational motions of the molecules with the energy of the electrons and nuclei and the energy due to attraction and repulsion amongst nuclei and electrons is known as Internal Energy.
- Internal energy is a state function
- Consider two states A and B. Suppose there are two different paths a and b to connect them, energy given to change the state A to state B along path a is ΔE_a. Energy given to change state A to another state B along path b is ΔE_b. If energy is a state function then; $\Delta E_a = \Delta E_b$.
- Suppose energy is not a state function, then $\Delta E_a \neq \Delta E_b$



Internal energy as a function of state

- Let $\Delta E_b > \Delta E_a$, If we go from state A to state B along path a, energy is ΔE_a. If we come back from state B to state A along path b, we obtain energy equal to ΔE_b. But ΔE_b is greater than ΔE_a. Thus energy is produced. The net energy produced = ΔE_b - ΔE_a. Thus energy can be produced.
- If we repeat this process than we are getting more and more amount of energy. But all attempts to produce the energy have failed. According to law of conservation of energy, " **Energy Can Neither Be Created Nor Be Destroyed** "
- So, ΔE_a must be equal to ΔE_b
- Internal energy depends on initial state and final state and not on path taken. Thus internal energy is a state function.

MEASUREMENT OF ΔE

- Consider reactants to convert as products at a constant temperature.
- These conversions bring changes in state of system.
- Thus there is definite change in the internal energy during chemical reaction.
- Thus ΔE tells us how the internal energy of products differs from the internal energy of reactants.
- When reaction occur under ordinary condition, the system can do work by pressure volume change.

$$\Delta E = q - w \qquad \text{_____(1)}$$

But, $w = -P_{ex} \int_{v_1}^{v_2} dV$

- If we substitute w in equation (1) we get;

$$\Delta E = q - \int_{v_1}^{v_2} P dV$$

- Suppose the reaction are carried out in a closed container, the volume remains constant and changes in volume equal to zero.

$$\therefore \quad \int_{v_1}^{v_2} P dV = 0$$

$$\Delta E = q - 0 \quad \ldots\ldots\ldots \text{(At Constant Volume)}$$

$$\Delta E = q_v$$

- If reaction is carried out at a constant volume, heat absorbed is equal to ΔE i.e. changing in internal energy.
- Thus to measure the ΔE, carry out reaction at constant volume, and measure heat released or absorbed.
- Negative value of ΔE, means heat is released. So the reaction must be exothermic.
- If value of ΔE is positive then heat is absorbed and the reaction must be endothermic.

ENTHALPY (H)

- Most of the chemical reactions are carried out at constant pressure of 1 amt.
- Heat released or absorbed in these conditions is not equal to q_v or ΔE.
- To explain the thermal (heat) effect of reactions carried out at constant pressure, a new state function called enthalpy is defined.
- By definition, enthalpy is;

$$H = E + PV$$

- Enthalpy depends upon the value of E, P and V. But E, P and V are state functions, therefore; H is also a state function. Enthalpy has units of energy.

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = q - w + \Delta(PV) \qquad \{ \therefore \Delta E = q - w \} \qquad \ldots\ldots\ldots\ldots (1)$$

» Now at constant pressure,

$$\Delta(PV) = P\Delta V + V\Delta P$$

$$= P\Delta V + 0 \qquad \{ \therefore \text{ p is constant} \}$$

$$= P\Delta V \qquad \ldots\ldots\ldots\ldots (2)$$

also, $w = -P\Delta V \qquad \ldots\ldots\ldots\ldots (3)$

$\therefore \quad \Delta H = q - P\Delta V + P\Delta V \qquad$ (From 1, 2 & 3)

$$\Delta H = q_p$$

» Thus if reaction is carried out at constant pressure heat released or absorbed is equal to ΔH.

» If ΔH is negative, reaction is exothermic. If ΔH is positive, reaction is endothermic.

DIFFERENCE BETWEEN ΔH AND ΔE

- The difference of volume between solids and liquids is very small. Thus, if only solids and liquids are involved in the reaction.

  $\Delta H = \Delta E$

- This equality is because of a negligible change in $\Delta(PV)$ when solids and liquids are involved.
- Now, $H = E + PV$
- So, $\Delta H = \Delta E + \Delta(PV)$ ..... (1)
- If gases are involved in reaction then,
- For ideal gas, $PV = nRT$
- So, $\Delta PV = \Delta nRT$

» Substituting this value in above equation;

$$\Delta H = \Delta E + \Delta nRT \qquad \text{…….. (2)}$$

» Here Δn is the difference in number of moles of gases.

where, $\Delta n = \Sigma$ no. of moles of gases in final state - Σ no. of moles of gases in initial state

NOTE : When ΔH and ΔE are expressed in calories, the gas constant R must be 1.987 calorie/mole.deg.


THANK
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