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Hons Part II, Paper III, Grp A.

Lecture: (00) Thermodynamics.

Entropy change in ideal gas and mixing of gas. $\rightarrow$

As we know entropy is the measure of degree of randomness or disorderliness of the system. If we calculate change in entropy for ideal gas then, At first we take a cylinder which occupy one mole of ideal gas and the container (cylinder) contains a frictionless, weightless movable piston at constant pressure. Let us suppose the ideal gas is going to expand reversibly from volume V_1 to V_2 . In this process the condition is reversible so the $P_{int} = P_{ext}$ (approx) and the gas is expanding against external pressure at all possible stages. In this condition the maximum work done is PdV .

$$W = PdV.$$

from 1st law of thermodynamics

$$q = E + w$$

$$\text{or } dq = dE + dw \quad \text{--- I}$$

$$\text{We know, } C_v = \frac{dE}{dT}, \text{ so } dE = C_v \cdot dT \quad \text{--- II}$$

$$\& \text{ also } PV = RT, \text{ so, } P = \frac{RT}{V}$$

Now we put the value of dE & P from equation II to I we have

$$dq = C_v \cdot dT + RT \frac{dV}{V} \quad \text{--- III}$$

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Dividing by T to equation 11 we have

$$\frac{dq}{T} = \frac{C_v \cdot dT}{T} + R \frac{dv}{v}$$

We know, $\frac{dq}{T} = ds$

$$\text{So } ds = C_v \cdot \frac{dT}{T} + R \frac{dv}{v}$$

For a fix change from initial state to final state, total change in entropy can be written as Δs .

$$\text{So, } \Delta s = \int_{s_1}^{s_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

$$\Delta s = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad \text{--- IV}$$

For an ideal gas $\frac{v_2}{v_1} = \frac{P_1}{P_2}$ (As $P_1 v_1 = R T_1$)

$$\Delta s = C_v \cdot \ln \frac{T_2}{T_1} + R \cdot \ln \frac{P_1}{P_2} \quad \text{--- V}$$

This is for one mole of gas. But for n mole of gas:

$$\Delta S = C_v \cdot \ln \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1} \quad \text{--- VI}$$

Now change in entropy for ideal gas at ~~no~~ constant volume: -

I At constant volume $V_1 = V_2$, so from eqn VI

$$(\Delta S)_V = n C_V \ln \frac{T_2}{T_1}$$

$$, (\Delta S)_V = 2.303 n C_V \log_{10} \frac{T_2}{T_1}$$

II At constant pressure: -

At constant pressure $P_1 = P_2$

So from

$$(\Delta S)_P = n C_P \ln \frac{T_2}{T_1}$$

$$\text{or } (\Delta S)_P = 2.303 n C_P \log_{10} \frac{T_2}{T_1}$$

III At Isothermal condition: -

At constant temperature (Isothermal) $T_1 = T_2$

$$(\Delta S)_T = n R \ln \frac{V_2}{V_1}$$

$$= n R \ln \frac{P_1}{P_2}$$

$$(\Delta S)_T = 2.303 n R \log_{10} \frac{P_1}{P_2}$$

Physical significance of entropy:-

- i) By the help of value of entropy a state of matter can be identified

$$\Delta S_g > \Delta S_L > \Delta S_s.$$

- ii) The value & sign of ΔS predict the given process or reaction is spontaneous or not.

If $\Delta S = +ve$ the process is spontaneous

Exceptions: i) liquifaction of gas

ii) freezing of water.

- iii) It help to find out the value of free energy

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

the above equation give the relation between ΔH , ΔS & ΔG which are responsible for driving force of spontaneous changes.

