

The first term from R.H.S accounts for ~~the~~ deviation from Joules law $\frac{1}{2}$
 2nd term accounts for deviation from Boyles law for real gas.

For ideal gas both terms on R.H.S of eq reduce to zero. It means ideal gas shows no cooling or heating effect on suffering a throttling process

THERMODYNAMICS POTENTIAL:

The four quantities called thermodynamic potential are used in chemical thermodynamics of reactions and noncyclic process

They are

- (1) Internal energy
- (2) Enthalpy
- (3) Helmholtz
- (4) Gibbs free energy

① INTERNAL ENERGY:

It is defined as energy associated with random, disordered motion of molecules.

It is separated in scale from the macroscopic ordered energy associated with moving objects.

It refers to the invisible microscopic energy on the atomic & molecular scale

① ENTHALPY:

(a) The function enthalpy is defined as

$$H = U + PV \quad \text{--- (1)}$$

where P & V are pressure & volume & U is internal energy

It is precisely a measurable state variable. It is ~~same~~ defined in terms of three other precisely definable state variable.

It is some what parallel to first law of thermodynamic for a constant pressure system.

for an infinitesimal reversible process differentiating eq (1) we have

$$dH = dU + PdV + VdP$$

$$dH = dQ + VdP$$

for isobaric process $P = \text{constant}$ &

$$dP = 0 \quad \text{Hence above eq}$$

$$dH = dQ + V(0)$$

$$dH = dQ_p$$

$$dH = C_p dT$$

Integrating both sides

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p dT$$

$$H_2 - H_1 = \int_{T_1}^{T_2} C_p dT$$

(2) Helmholtz free energy F is defined as $F = U - TS$ where U is internal energy, T is absolute temp & S is entropy.

The internal energy U might be thought of as the energy required to create a system in the absence of changes in temperature or volume. But if the system is created in an environment of temp T then some of energy can be obtained by spontaneous heat transfer from the environment to system.

In amount of the potential energy transfer is TS , where S is the total entropy of system.

For an infinitesimal reversible process

$$dF = dU - TdS - SdT$$

$$= dQ - PdV - TdS - SdT$$

$$= dU - PdV - TdS - SdT$$

putting value of dU in above eq

$$dF = dQ - PdV - TdS - SdT$$

$$= dQ - TdS$$

so

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

for reversible isothermal process
 $T = \text{constant}$ so $dT = 0$

$$dF = -PdV \quad \text{--- (2)}$$

integrating above eq.

$$\int_{F_1}^{F_2} dF = \int_1^2 -PdV$$

$$F_2 - F_1 = - \int_1^2 PdV$$

The change in Helmholtz function is equal to the work done on the system -

for a reversible isothermal and isochoric process $dT = 0$ & $dV = 0$

It gives (in eq (2))

$$dF = f(0) = 0$$

Integrating both sides

$$F = \text{constant}$$

④ GIBB'S FREE ENERGY: G is defined as

$$G = U - TS + PV$$

where U is internal energy, T is absolute temperature, S is final entropy, P is absolute pressure and V is final volume.

The term TS is energy you can get from the system's environment by heating and PV is work which is used to give the system final volume V at constant pressure P .

The Gibbs free energy can also be written as

$$G = H - TS$$

Date: _____

For infinitesimal reversible process
differentiating above eq (1)

$$dG = dH - TdS - SdT$$

as

$$dG = dU + PdV - dU - SdT \quad \left[\begin{array}{l} \text{as } dQ = TdS \\ \text{and } dH = dU + PdV + VdP \\ = dQ + VdP \end{array} \right]$$
$$dG = VdP - SdT$$

for a reversible isothermal and isobaric process
 $dP = 0$ $dT = 0$

so

$$dG = V(0) - S(0)$$

$$dG = 0$$

integrating both sides

$$G = \text{constant}$$

finds application in the processes involving a change of phase such as sublimation, fusion and vaporization which take place isothermally & isobarically