

Thermodynamic potentials

Thermodynamic potentials are extensive state variables of dimension of energy. Their purpose is to allow for simple treatment of equilibrium for systems interacting with the environment. These functions are the energy functions formed by combining the basic thermodynamic variables.

The four fundamental thermodynamic potentials are ;

1. internal energy (U)
2. Enthalpy or total heat function (H)
3. Helmholtz function (F)
4. Gibbs function (G)

Internal Energy (U)

It is the energy of a system possessed due to the kinetic energy and potential energy of the constituents of the system. Kinetic energy refers to energy possessed by the molecules by virtue of its motion and potential energy is due to intermolecular forces.

1. From the first and second laws of thermodynamics

$$T dS = dU + P dV \quad \text{or} \quad dU = T dS - P dV \quad (1)$$

This equation gives the change in internal energy of a system in terms of variables P, V, T and S.

2. From the first law,

$$dQ = dU + PdV$$

Dividing both the sides of the above equation by dT, we get

$$\frac{dQ}{dT} = \frac{dU}{dT} + P \frac{dV}{dT}$$

At constant volume, (dV = 0) the above equation would be

$$\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

Where C_V is the specific heat at constant volume.

Also, for an adiabatic process dQ = 0

Thus $0 = dU + P dV$ or $dU = - P dV$

For an isochoric process, from the above relation, dU = 0

Thus internal energy of a system is a constant in an isochoric - adiabatic process. The potential is also called isochoric - isentropic potential where thermodynamic potential is the internal energy U and the independent variables are Entropy S and volume V .

Enthalpy (H)

Consider two states 1 and 2 of a thermodynamic system. If U_1 and U_2 are the internal energies, then dQ is the heat absorbed by the system, from first law

$$dQ = (U_2 - U_1) + dW$$

If work done is at constant pressure due to change in volume, then

$$dW = P(V_2 - V_1)$$

$$\text{Thus, } (U_2 - U_1) = dQ - P(V_2 - V_1) \text{ or}$$

$$(U_2 + PV_2) - (U_1 + PV_1) = dQ$$

$$\text{Thus } H_2 - H_1 = dQ$$

$$\text{In general } H = U + PV$$

Enthalpy of a system is the total energy of a system given by $H = U + PV$

1. When a system undergoes an infinitesimal process from an initial equilibrium state to final equilibrium state,

$$dH = dU + P dV + V dP \quad (2)$$

$$\text{From first law } dQ = dU + PdV$$

Thus (2) becomes

$$dH = dQ + V dP$$

Dividing both the sides of the equation by dT , we get

$$\frac{dH}{dT} = \frac{dQ}{dT} + V \frac{dP}{dT}$$

At constant pressure ($P=0$) the above equation would be

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$$

Where C_P is the specific heat at constant pressure.

$$\text{Also } dH = TdS + V dP \text{ and } Q = TdS$$

2. Since $dH = dQ + V dP$, the change in enthalpy during isobaric process is the heat transferred. Thus the latent heat is measured during phase transition is

simply the change in enthalpy i.e., $H_f - H_i = Q$ or $H_f - H_i = \int C_p dT$. This indicates isobaric process.

3. For an adiabatic process, $dQ = 0$. Thus for an adiabatic and isobaric process, $dH = 0$. Thus H is constant

The potential is also called **isentropic - isobaric potential**, where independent variables are entropy S and pressure P.

Helmholtz function (F)

From the first and second law of thermodynamics

$$TdS = dU + dW$$

If heat is exchanged between the system and surroundings at constant temperature $TdS = d(TS)$

$$\text{Thus } dU = d(TS) - dW \text{ or } d(U - TS) = -dW$$

Where $U - TS = F$ is called Helmholtz free energy or work function.

The Helmholtz function is defined as **$F = U - TS$**

For an infinitesimal reversible process

$$dF = dU - TdS - SdT$$

From the laws of thermodynamics $TdS = dU + PdV$

Hence $dF = dU - (dU + PdV) - SdT$ or

$$dF = -PdV - SdT$$

Thus for a reversible isothermal process $dF = -PdV$

$$\text{Thus } F_f - F_i = - \int_i^f PdV$$

Hence the change in Helmholtz function during reversible isothermal process equals the work done on the system.

For a reversible isothermal and isochoric process $dF = -PdV = 0$ or $F = \text{constant}$.

Also form

$$dF = -PdV - SdT \left(\frac{\partial F}{\partial V} \right)_T$$

The potential is also called isothermal - isochoric function where independent variables are temperature T and volume V.

Gibbs function (G)

For enthalpy $H = U + PV$.

For an infinitesimal change $dH = TdS + VdP$

If the system is isothermal and pressure is remaining constant, from the above equation $dH = d(TS)$ or $d(H-TS) = 0$. thus $H - TS = \text{constant}$

Where $H - TS = G$ is called Gibb's free energy.

The Gibb's free energy is defined as

$$G = H - TS \text{ or } G = U + PV - TS$$

For an infinitesimal reversible process

$$dG = dH - TdS - SdT \quad \text{also } dH = TdS + VdP$$

Hence $dG = (TdS + VdP) - TdS - SdT$ or

$$dG = VdP - SdT$$

$$\text{Also } \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

For a reversible isothermal and isobaric process $dG = 0$ or $G = \text{constant}$. The potential is also called the **isothermal - isobaric potential** where the independent variables are temperature T and pressure P .

Significance of thermodynamic potentials

A mechanical system is said to be in stable equilibrium if the potential energy of the system is minimum. For example heat flows from higher to lower temperature region till equilibrium is achieved. Also water flows from higher to lower level to achieve minimum potential energy.

As U , H , F and G are all energy functions in thermodynamics, they behave like potential energy in mechanics.

- In an isochoric - adiabatic process, the internal energy tends to minimum.
- In an isobaric - adiabatic process, the enthalpy tends to minimum.
- In an isochoric - isothermal process, the Helmholtz free energy tends to minimum.
- In an isobaric - isothermal process, the Gibbs free energy tends to a minimum.

Chemical potential

- Enthalpy (H), entropy (S), and Gibbs free energy (G) are molal (moles/Kg) quantities.
- Chemical potential is the Gibbs free energy per molal unit.

$$\mu_i = \left(\frac{\partial G}{\partial n} \right)_i$$

- in other words , the chemical potential μ_i is a measure of how much the free energy of a system changes if you add or remove a number dn_i particles of the particle species I while keeping the number of the other particles (and the temperature T and pressure P) constant.

