

③ Helmholtz free energy F is defined as $F = U - TS$ — ①
 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.

The amount of this spontaneous energy transfer is TS , where S is the final entropy of system

for an infinitesimal reversible process
 diff eq ①

$$dF = dU - TdS - SdT$$

$$\text{as } dQ = dU + PdV$$

$$\Rightarrow dU = dQ - PdV$$

putting value of dU in above eq

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

$$\text{as } dQ = TdS$$

so

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

$$dF = -PdV - SdT$$

Important:

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