Lecture notes chapter 8

Wednesday, 6 May 2020 15:19

$$dU = TdS + PdV$$

intensive T and P

extensive S and V

both are canonically conjugate pairs

one thermal, one mechanical variable...

TS

PV

SV

SP

TV

TP

$$dZ = X\,dx + Y\,dy$$

where x, X and y, Y are canonically conjugate pairs

We wish to replace (x, y) by (X, Y)

$$M(X, Y) = Z(x, y) - xX - yY$$

$$dM(X, Y) = -x\,dX - y\,dY$$

$$\frac{\partial Z}{\partial x} = X \qquad \frac{\partial M}{\partial X} = -x$$

$$\frac{\partial Z}{\partial y} = Y \qquad \frac{\partial M}{\partial Y} = -y$$

$$\frac{\partial N}{\partial x} = X \qquad \frac{\partial N}{\partial y} = -Y$$

internal energy $\quad U = U(S, V)$

enthalpy $\quad H = H(S, P)$

Helmholtz function $\quad F = F(T, V)$

Gibbs function $\quad G = G(T, P)$

U, H, F, G are state variables

$$dH = T\,dS + V\,dP$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$F = U - ST$$

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

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$G = U - TS + VP$$

$$dG = dU - TdS - SdT + PdV + VdP = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

$W \leq -\Delta F$ isothermal & reversible

The decrease in Helmholtz function F equals the maximum energy that can be freed in an isothermal process and made available for work.

The condition for equilibrium for a system in thermal contact with a reservoir and kept at constant value is dF = 0.

If contact with the reservoir keeps both temperature and pressure constant, the system goes to the lowest value of the Gibbs function.
Stable equilibrium when dG = 0.
If non-mechanical work is done by the system, then W_nm <= \Delta G (no change in T and P)