HAL FONKSİYONLARININ HAL DEĞİŞKENLERİNE BAĞLILIĞI: TERMODİNAMİK DENKLEMLER (KAPALI SİSTEMLER İÇİN)

$\Delta U = q + W$, $dU = \delta q_{tr} + \delta W_{mak} = TdS - PdV$ 1

$H = U + PV$, $dH = dU + PdV + VdP = TdS - PdV + PdV + VdP = TdS + VdP$ 2

$A = U - TS$, $dA = dU - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$ 3

$G = H - TS$, $dG = dH - TdS - SdT = TdS + VdP - TdS - SdT = VdP - SdT$ 4

Eşitliklerden

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

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

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

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

$dU = TdS - PdV \Rightarrow U = f(S, V)$, $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{..... 1}$$

dH = TdS + VdP $\Rightarrow$ H = f (S, P), $dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$

$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ 2

$dA = -SdT - PdV \Rightarrow$ A = f (T, V), $dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ 3

$dG = -SdT + VdP \Rightarrow$ G = f (T, P), $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$

$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ 4

1, 2, 3 ve 4 Maxwell denklemleri

$\left(\frac{\partial H}{\partial P}\right)_T = ?$

G = H – TS, H = G + TS

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

İdeal gazlar için

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

$= V - T\frac{R}{P} = 0$

V

PV = RT

$\frac{V}{T} = \frac{R}{P}$

$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

$\left(\frac{\partial S}{\partial T}\right)_V = ?$ $\left(\frac{\partial S}{\partial T}\right)_P = ?$

$\left[\frac{\partial (A/T)}{\partial T}\right]_V = ?$

Kimyasal Potansiyel: Molar Serbest Entalpi
(μ) (G)

Molar serbest entalpi fonksiyonuna kimyasal potansiyel denir.

$\mu \equiv G \equiv \frac{g}{n}$, G = f (P, T),

$$dG = -SdT + VdP$$

μ = f (T, P)

(1 atm'de saf ideal gaz için) μ^0: standart kimyasal potansiyel
P^0: standart basınç, 1 atm, 1 bar

$\mu = \mu^0 + RTln\frac{P}{P^0}$ saf gazın kimyasal potansiyeli

Gaz Karışımlarında $\mu_i(T, P_i) = \mu_i^0(T) + RTln\left(\frac{P_i}{P^0}\right)$, $P_i = Py_i$

$\mu_i(T, P, y_i) = \mu_i^*(T, P) + RTlny_i$

Sıvı karışımlarda

$\mu_i = \mu_i^* + RTlnX_i$