

The most important property of the Gibbs free energy is that it is a minimum for a system in equilibrium at constant pressure in thermal contact with a reservoir

$$G \equiv U - \tau\sigma + pV$$

KK Eq. 9.1

Its differential is

$$dG = dU - \tau d\sigma - \sigma d\tau + p dV + V dp$$

constant pressure $\Rightarrow dp = 0$

constant temperature $\Rightarrow d\tau = 0$, so in this situation

$$dG = dU - \tau d\sigma + p dV \quad \text{KK Eq. 9.2}$$

Recall the thermodynamic identity $dU = \tau d\sigma - p dV + \mu dN$

$$dG = \tau d\sigma - p dV + \mu dN - \tau d\sigma + p dV$$

$$dG = \mu dN$$

If $dN = 0$, then $dG = 0$

thus, the number of particles ^{ought to be} constant for G to be a minimum. The "natural variables" are $G(N, \tau, p)$

Again, $dG = dU - \tau d\sigma - \sigma d\tau + p dV + V dp$

(159)

$$dG = \cancel{\tau d\sigma} - \cancel{p dV} + \mu dN - \cancel{\tau d\sigma} - \sigma d\tau + \cancel{p dV} + V dp$$

so $dG = \mu dN - \sigma d\tau + V dp$ KK Eq. 9.5

$$\left(\frac{\partial G}{\partial N}\right)_{\tau, p} = \mu; \quad \left(\frac{\partial G}{\partial \tau}\right)_{N, p} = -\sigma; \quad \left(\frac{\partial G}{\partial p}\right)_{N, \tau} = V$$

and $dG = \left(\frac{\partial G}{\partial N}\right)_{\tau, p} dN + \left(\frac{\partial G}{\partial \tau}\right)_{N, p} d\tau + \left(\frac{\partial G}{\partial p}\right)_{N, \tau} dp$ KK Eq. 9.6

Intensive variables are independent of the size of the system τ, p, μ
 extensive variables scale linearly with the size of the system U, σ, V, F, G

Dividing an extensive quantity by another one yields an intensive one

E.g. $\frac{U(\sigma, V, N)}{N} = u(\sigma/N, V/N, \cancel{N/N})$ ← internal energy per particle independent of N

$$\frac{G(N, p, \tau)}{N} = \phi(\cancel{N/N}, p/N, \tau/N) = \phi(p, \tau)$$

$$\Rightarrow G = N \phi(p, \tau) \quad \text{KK Eq. 9.10}$$

For constant τ, p , $dG = \mu dN$, so

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{\tau, p} = \frac{\partial}{\partial N} N \phi(p, \tau) \Big|_{\tau, p} = \phi(p, \tau)$$

Eq. 9.13

$$G(N, p, \tau) = N\mu(p, \tau)$$

KK Eq. 9.13

160

The chemical potential for a single-component system is equal to the Gibbs free energy per particle

If more than one chemical species, $G = \sum_j N_j \mu_j$

and $dG = \sum_j \mu_j dN_j - \sigma d\tau + Vdp$

For multiple species, $\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P}$

(161)

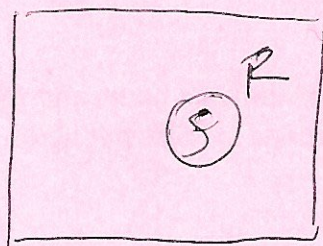
~~126~~

so $G = \sum_j N_j \mu_j$

Using the λ -method $\lambda G(N_1, N_2, \dots) = G(\lambda N_1, \lambda N_2, \dots)$
 $\frac{d}{d\lambda} [\lambda G(N_1, N_2, \dots)] = G(N_1, N_2, \dots) = \frac{d}{d\lambda} G(\lambda N_1, \lambda N_2, \dots)$

Equilibrium in chemical reactions

KK pg. 266



System has fixed T, P ~~determined~~ due to R

Consider reaction $H_2 + Cl_2 \rightleftharpoons 2HCl$

A chemical reaction may be written as

$nu \rightarrow \nu_1 A_1 + \nu_2 A_2 + \dots + \nu_L A_L = 0$ or $\sum_j \nu_j A_j = 0$ Eq. 9.23 Eq. 9.24

$A_1 = H_2$ $\nu_1 = 1$ N_1, N_2, \dots ↑ chemical coefficient species
 $A_2 = Cl_2$ $\nu_2 = 1$ ↑ not conserved
 $A_3 = HCl$ $\nu_3 = -2$ ↑ how many molecules individually

In the real world, chemical reactions occur under constant pressure. For reactions that occur also under ~~given~~ constant temp, the Gibbs free energy is the minimum w.r.t. the proportions of the reactants.

$dG = \sum_j \mu_j dN_j = 0$ Eq. 9.27

so N conserved,
 N_1, N_2, \dots etc. not.

Before we conserved energy but individual energies did vary. Then we allowed the number of particles to vary but total number was conserved. Now

$$dN_j \propto V_j$$

$$dN_j = V_j d\hat{N} \quad \text{Eq. 9.28}$$

\hat{N} is the number of times the reaction occurs

$$\text{So } dG = \left(\sum_j V_j \mu_j \right) d\hat{N} = 0 \Rightarrow \boxed{\sum_j V_j \mu_j = 0} \quad \text{Eq. 9.30}$$

Condition for equilibrium in a transformation of matter

Consider the ideal gas, $\mu_j = \tau \ln \left(\frac{n_j}{c_j} \right)$ with $c_j = \frac{N_Q}{V} Z_{\text{int}} \quad \text{Eq. 9.32}$

9.31

KK 6.44

$$Z_{\text{int}} = \sum_{\text{int}} e^{-\epsilon_{\text{int}}/\tau}$$

(partition function for internal degrees of freedom)

You ~~get~~ derived it in your exam.

It depends on τ but not on $n = \frac{N}{V}$ concentration

$$\sum_j V_j \mu_j = \cancel{\tau} \left[\sum_j V_j (\ln n_j - \ln c_j) \right] = 0$$

$$\Rightarrow \underbrace{\sum_j V_j \ln n_j}_{\text{Eq. 33a}} = \sum_j V_j \ln c_j \Rightarrow \sum_j \ln n_j^{V_j} = \sum_j \ln c_j^{V_j} \quad \text{Eq. 33b}$$

$$\sum_j \ln n_j^{\nu_j} = \ln \prod_j n_j^{\nu_j} \quad \text{Eq. 33c}$$

Eq. 33d

← Equilibrium constant.

Remember Chem 1302

$$\sum_j \ln c_j^{\nu_j} = \ln \prod_j c_j^{\nu_j} \equiv \ln K(\tau)$$

↑ remember quantum

$$K(\tau) = \exp(\ln \prod_j c_j^{\nu_j}) = \prod_j c_j^{\nu_j} \quad \text{concentration is function of } \tau$$

$$\text{So } \exp(\ln K(\tau)) = \exp(\ln \prod_j n_j^{\nu_j}) \Rightarrow \prod_j n_j^{\nu_j} \exp(-\nu_j \bar{F}_j / \tau)$$

since $F = -\tau \ln Z$
 $\bar{F} = -\frac{F}{e}$

~~$$K(\tau) = \prod_j$$~~

$$\prod_j n_j^{\nu_j} = K(\tau)$$

law of mass action.

product of the concentration of reactants is a function of τ only.