

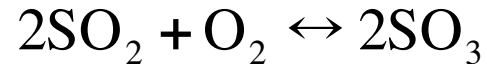
Thermodynamics II

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Chapter 13. Chemical–Reaction Equilibria

- Equilibrium conversion : dependence on T, P, x_i



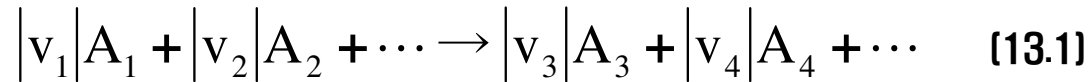
Rate 2 → equilibrium conversion
at 300°C, 90% → at 520°C, 50%

- [**Reaction rate** : not susceptible to thermodynamic treatment
Equilibrium conversion : found by thermodynamic calculation

- **Objective** of chapter : Determine the **effect of T, P, x_i** on the equilibrium conversion of chemical reaction

13.1 The Reaction Coordinate

The general chemical reaction can be written.



where $\left|v_i\right|$: stoichiometric coeff. v_i (+) : for a product
 A_i : chemical formula v_i (-) : for a reactant



$$v_{\text{CH}_4} = -1, \quad v_{\text{H}_2\text{O}} = -1, \quad v_{\text{CO}} = 1, \quad v_{\text{H}_2} = 3$$

=> Changes in the numbers of moles of species $\propto v_i$

$$\frac{dn_2}{v_2} = \frac{dn_1}{v_1}, \quad \frac{dn_3}{v_3} = \frac{dn_1}{v_1}$$

Expansion to
all species

$$\frac{dn_1}{v_1} = \frac{dn_1}{v_1} = \frac{dn_1}{v_1} = \frac{dn_1}{v_1} = \cdots \equiv d\varepsilon \quad (13.2)$$

$$\therefore dn_i = v_i d\varepsilon \quad (13.3) \quad (\varepsilon : \text{reaction coordinate})$$

Integration of eqn (13.3) for initial state ($\varepsilon = 0, n_i = n_{i0}$) to a state after reaction

$$\int_{n_{i0}}^{n_i} dn_i = \int_0^\varepsilon d\varepsilon \quad \Rightarrow n_i = n_{i0} + v_i \varepsilon \quad (13.4)$$

By summation, $n = \sum n_i = \sum n_{i0} + \varepsilon \sum v_i$

$$n = n_0 + v\varepsilon$$

Mole fraction y_i of species i ,
as a function of ε

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \varepsilon}{n_0 + v\varepsilon} \quad (13.5)$$

Multireaction stoichiometry

- Two or more independent simultaneous reaction

use subscript j for the each reaction

=> Stoichiometric number has two subscript (for species , for reaction)

Ex) v_{ij} → stoichiometric number of species i in reaction j

$$dn_i = \sum_j v_{i,j} d\varepsilon_j$$

By integration. $n_i = n_{i0} + \sum_j v_{i,j} d\varepsilon_j$

Summing over all species $n_i = \sum_i n_{i0} + \sum_i \sum_j v_{i,j} \varepsilon_j = n_0 + \sum_j \left(\sum_i v_{i,j} \right) \varepsilon_j$

$$\therefore n = n_0 + \sum_j v_j \varepsilon_j$$

$$\therefore y_i = \frac{n_{i0} + \sum_j v_{i,j} \varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j}$$

Total stoichiometric number for reaction j $\therefore v_j = \sum_i v_{i,j}$

13.2 Application of equilibrium criteria to chemical reaction

- At close system, const T & P $\Delta G^t < 0$
- condition for equilibrium : G^t is minimum
 $\Rightarrow (dG^t)_{T,P} = 0$ [14.68]
 - ※ Any reaction at const T, P lead to decrease of G^t
- Two distinctive feature of the equilibrium state
 - 1) total Gibbs energy G^t is minimum
 - 2) Its differential is $(dG^t)_{T,P} = 0$

13.3 The Standard Gibbs Energy change and the equilibrium constant

Fundamental property relation

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \quad [11.2]$$

If there is **change in the n_i by chemical reaction** $dn_i = v_i d\varepsilon$

$$\therefore d(nG) = (nV)dP - (nS)dT + \sum_i v_i \mu_i d\varepsilon$$

By the exact differential expression

$$\sum v_i \mu_i = \left[\frac{\partial(nG)}{\partial \varepsilon} \right]_{T,P} = \left[\frac{\partial(G^t)}{\partial \varepsilon} \right]_{T,P}$$

$\sum v_i \mu_i$: change of G^t by change of ε (rate of change of G^t by ε)

$\sum_i v_i \mu_i = 0$ (13.8) at equilibrium \Rightarrow another **criteria of chemical reaction equilibrium**

From chap 11, using fugacity of species in solution

$$\overline{G}_i = \mu_i = \Gamma_i(T) + RT \ln \hat{f}_i \quad (11.46)$$

For pure species $G_i = \Gamma_i(T) + RT \ln \hat{f}_i$ at standard state using notation

$$G_i = \Gamma_i(T) + RT \ln f_i^0$$

Difference between μ_i and G_i^0

$$\mu_i - G_i^0 = RT \ln \frac{\hat{f}_i}{f_i^0} \quad (13.9)$$

$$\therefore \mu_i = G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0}$$

$$\sum_i \nu_i (G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0}) = \sum_i \nu_i G_i^0 + RT \sum_i \ln \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = 0$$

$$\Rightarrow \ln \Pi_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = - \frac{\sum_i \nu_i G_i^0}{RT}$$

In exponential for

defining $\prod_i (\hat{f}_i / f_i^0)^{v_i} = K$ (13.10)

where $K = \exp\left(\frac{-\Delta G_i^0}{RT}\right)$, $\ln K = -\frac{\Delta G^0}{RT}$ (13.11)

where $\Delta G^0 \equiv \sum_i v_i G_i^0$

G_i^0 : property of pure species i in its standard state at fixed pressure
=> only function of temperature

K_i : **equilibrium constant for the reaction**

$\sum_i v_i G_i^0 = \Delta G^0$: **standard Gibbs-energy change of reaction**

Difference between G of product and reagent at standard state

In general, standard property changes of reaction for property M_i

$$\Delta M^0 \equiv \sum v_i M_i^0 \quad \text{function of temp only can be related to one another by eqn. similar to property relation}$$

$$\Delta H^0 \equiv \sum v_i H_i^0 \quad \Delta C_p^0 \equiv \sum v_i C_p^0$$

For example,
$$\frac{H}{RT} = -T \left[\frac{\partial(G/RT)}{\partial T} \right]_P \quad (6.39)$$

$$\Rightarrow H_i^0 = -RT^2 \left[\frac{d(G_i^0/RT)}{dT} \right]_P$$

By multiplying v_i and summation over all species

$$\sum_i v_i H_i^0 = -RT^2 \left[\frac{d(\sum_i v_i G_i^0 / RT)}{dT} \right]_P$$

$$\Delta H_i^0 = -RT^2 \frac{d(\Delta G_i^0 / RT)}{dT} \quad (13.13)$$

13.4 Effect of Temperature on the Equilibrium Constant

- standard state temperature = T at equilibrium
=> standard property change of reaction [$\Delta G^\circ, \Delta H^\circ$]

- Dependence of ΔG° on T

$$\Delta H^\circ = -RT^2 \frac{d\left(\frac{\Delta G^\circ}{RT}\right)}{dT} \rightarrow \frac{d\left(\frac{\Delta G^\circ}{RT}\right)}{dT} = \frac{-\Delta H^\circ}{RT^2}$$

since $\ln K = -\frac{\Delta G^\circ}{RT^\circ}$ (13.11) $\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$ (13.14)

=> Show the effect of Temp on the equilibrium constant

Assume that ΔH° is independent of T and integrate from T' to T

$$\ln \frac{K}{K'} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad (13.15)$$

=> Plot of $\ln K$ vs $1/T$ => linear (straight line)

If $\Delta H^\circ < 0$ [exothermic] => $K \downarrow$ as $T \uparrow$

If $\Delta H^\circ > 0$ [endothermic] => $K \uparrow$ as $T \downarrow$

- **Rigorous development** of the effect of T and K
 - Based on the definition of the Gibbs energy

$$G_i^\circ = H_i^\circ - TS_i^\circ \quad (\text{Gibbs energy at standard state})$$

By multiplying v_i and summation over all species

$$\sum v_i G_i^\circ = \sum v_i H_i^\circ - T \sum v_i S_i^\circ$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad \Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT \quad [4.18]$$

$$dH_i^\circ = \Delta C_{p_i}^\circ dT, \quad d\Delta H^\circ = \Delta C_p^\circ dT \quad (T_0 : \text{reference Temp})$$

$$dS_i^\circ = \Delta C_{p_i}^\circ \frac{dT}{T} \quad \rightarrow \quad d\Delta S^\circ = \Delta C_p^\circ \frac{dT}{T}$$

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right) dP \quad [6.21] \quad \Rightarrow \quad \Delta S^\circ = \Delta S_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} \quad [13.17]$$

since $\Delta S_0^\circ = \frac{\Delta H_0^\circ - \Delta G_0^\circ}{T_0}$

$$\therefore \Delta G^\circ = \Delta H_0^\circ + \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT - T\Delta S_0^\circ - RT \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

By division

$$\frac{\Delta G^{\circ}}{RT} = \frac{\Delta C_0^{\circ} - \Delta H_0^{\circ}}{RT_0} + \frac{\Delta H_0^{\circ}}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT - \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} \quad [13.18]$$

$$\frac{\Delta G^{\circ}}{RT} = -\ln K \quad : \text{ know the effect of temperate on K}$$

$$\frac{C_p}{R} = A + BT + CT^2 + DT^2 \quad (\text{temperate dependence of heat capacity})$$

$$\int_{T_0}^T \frac{C_p}{R} dT = AT_0(\tau - 1) + \frac{B}{2} T_0^2(\tau^2 - 1) + \frac{C}{3} T_0^3(\tau^3 - 1) + \frac{D}{T_0} \left(\frac{\tau - 1}{\tau}\right) \quad [4.7]$$

$$\int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT = (\Delta A)T_0(\tau - 1) + \frac{\Delta B}{2} T_0^2(\tau^2 - 1) + \frac{\Delta C}{3} T_0^3(\tau^3 - 1) + \frac{\Delta D}{T_0} \left(\frac{\tau - 1}{\tau}\right) \quad [4.19]$$

$$\Delta A = \sum v_i A_i, \quad \Delta B = \sum v_i B_i, \quad \Delta C = \sum v_i C_i$$

Similarly

$$\int_{T_0}^T \frac{C_p}{R} \frac{dT}{T} = A \ln \tau + [BT_0 + (CT_0^2 + \frac{D}{\tau^2 T_0^2}) \left(\frac{\tau + 1}{2}\right)](\tau - 1) \quad [5.13]$$

$$\int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} = \Delta A \ln \tau + [\Delta B T_0 + (\Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2}) \left(\frac{\tau + 1}{2}\right)](\tau - 1) \quad [13.19]$$

Once, two integrals can be calculated. $\frac{\Delta G^\circ}{RT} = -\ln K$ can be obtained at any temperature

from standard Heat of reaction and standard Gibbs-energy change of reaction at a reference Temp. (usually 298.15)

○ Equation (13.18) can be rearranged and divided into three factors

$$-\frac{\Delta G^\circ}{RT} = \underbrace{-\frac{\Delta G_0^\circ}{RT_0^\circ}}_{(1)} + \underbrace{\frac{\Delta H_0^\circ}{RT_0^\circ} \left(1 - \frac{T_0}{T}\right)}_{(2)} - \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT + \underbrace{\int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}}_{(3)}$$

$$\ln K = (1) + (2) + (3) \quad , \quad K = \exp(1) \times \exp(2) \times \exp(3)$$

Let $K = K_0 K_1 K_2$

$$K_0 \equiv \exp\left(\frac{-\Delta G_0^\circ}{RT_0^\circ}\right) \quad [13.21] \quad K_1 \equiv \exp\left[\frac{\Delta H_0^\circ}{RT_0^\circ} \left(1 - \frac{T_0}{T}\right)\right] \quad [13.22]$$

$$K_2 \equiv \exp\left(-\frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT + \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}\right) \quad [13.23]$$

$$\begin{aligned} &\equiv \exp\left\{\Delta A \left[\ln \tau - \left(\frac{\tau-1}{\tau}\right)\right] + \frac{1}{2} \Delta B T_0^\circ \frac{(\tau-1)^2}{\tau} + \frac{1}{6} \Delta C T_0^{\circ 2} \frac{(\tau-1)^2(\tau+2)}{\tau}\right. \\ &\quad \left. + \frac{1}{2} \frac{\Delta D}{T_0^2} \frac{(\tau-1)^2}{\tau}\right\} \quad [13.24] \end{aligned}$$

K_0 : equilibrium constant at T_0

K_1 : supplies major effect of temperate

K_0K_1 : equilibrium constant of temperate T when ΔH^0 is independent of temperate
(compare with eqn 13.15)

K_2 : consider of temperate influence from change of ΔH

13.6 Relation of Equilibrium Constants to Composition

○ Gas-Phase Reactions

Standard state for a gas : ideal gas state of gas at 1 bar

From eqn (13.10)

$$\begin{aligned} \prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{v_i} &\equiv K & f_i^0 &= P^0 \text{ for each species} \\ \Rightarrow K &= \prod_i \left(\frac{\hat{f}_i}{P^0} \right)^{v_i} & & \text{(13.25)} \end{aligned}$$

K : function of temperature only

\hat{f}_i : reflect **nonideality** of equilibrium mixture and function of T, P, x_i
 \Rightarrow For a fixed temperature, the composition at equilibrium

$$\hat{f}_i = \hat{\phi}_i y_i P \quad (11.52)$$

$$\therefore \prod_i \left(\frac{\hat{\phi}_i y_i P}{P^0} \right)^{v_i} = K \Rightarrow \prod_i (y_i \hat{\phi}_i)^{v_i} = \left(\frac{P}{P^0} \right)^{-v} K \quad (13.26)$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + V_i \varepsilon_e}{n_i + V \varepsilon_e}$$

For fixed temperature

(13.26) : equation relating ε_e with P

○ Liquid-Phase Reactions

$$K = \Pi \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} \quad [13.10]$$

f_i^0 : fugacity of pure liquid i at the temperature of the system and 1 bar

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i} \Rightarrow \hat{f}_i = \gamma_i x_i f_i$$

\therefore **fugacity ratio** $\frac{\hat{f}_i}{f_i^0} = \frac{\gamma_i x_i f_i}{f_i^0} = \gamma_i x_i \left(\frac{f_i}{f_i^0} \right)$

$\frac{f_i}{f_i^0} \Rightarrow 1$: because fugacities of liquid are **weak function of P**

From eqn(11.31) $G_i \equiv \Gamma_i(T) + RT \ln f_i$

- G_i at temperature T and pressure P $G_i = RT \ln f_i$

- G_i at temperature T and standard pressure P^0 $G_i = RT \ln f_i^0$

$$G_i - G_i^0 = RT \ln \frac{f_i}{f_i^0} \quad \text{Since } dG = VdP - SdT = VdP \quad (\text{at const } T)$$

$$G_i - G_i^0 = \int_{P^0}^P V_i dP, \quad RT \frac{f_i}{f_i^0} = \int_{P^0}^P V_i dP$$

V_i is weak function of P for liquid

$$\ln \frac{f_i}{f_i^0} = \frac{V_i(P - P^0)}{RT} \quad (13.30)$$

\therefore Eqn(13.10) becomes

$$\begin{aligned} \Pi \left(\frac{\hat{f}_i}{f_i^0} \right)^{v_i} &= \Pi \left(\frac{\gamma_i x_i f_i}{f_i^0} \right)^{v_i} = \Pi \left[\gamma_i x_i \left(\frac{f_i}{f_i^0} \right) \right]^{v_i} \\ &= \Pi \left(\gamma_i x_i \exp \left(\frac{V_i(P - P^0)}{RT} \right) \right)^{v_i} = K \end{aligned}$$

$$\therefore \Pi (x_i \gamma_i)^{v_i} = K \exp \left[\frac{P^0 - P}{RT} \sum_i v_i V_i \right]^{v_i} \quad (13.31)$$

Except for high pressure, $\Pi (x_i \gamma_i)^{v_i} = K \quad (13.32)$

If the equilibrium mixture is an ideal solution $\gamma_i = 1$

$$\prod_i (x_i)^{\nu_i} = K \quad (13.33)$$

Species present in high concentration ($x_i \rightarrow 1$)

$$\gamma_i \approx 1 \quad \therefore \frac{\hat{f}_i}{f_i} = x_i \quad (\text{Lewis/Randall mole})$$

For species at low concentration

$$\frac{\hat{f}_i}{f_i} \neq x_i \quad \text{Use hypothetical standard state for solute}$$

If the solute obeyed Henry's law up to a **molality m of unity**

$$\hat{f}_i = k_i m_i$$

Hypothetical standard state $m_i^0 = 1$

$$\therefore \hat{f}_i^0 = k_i m_i^0 = k_i \quad \therefore \frac{\hat{f}_i}{\hat{f}_i^0} m_i$$

$$\therefore K = \prod_i (m_i)^{\nu_i}$$

13.7 Equilibrium conversions for single reactions

- Reaction in **homogeneous systems** (only one phase)
composition at equilibrium

$$\Pi(y_i)^{v_i} = \left(\frac{P}{P^0}\right)^{-v} K \quad \text{for ideal gas}$$

$$\Pi(y_i \phi_i)^{v_i} = \left(\frac{P}{P^0}\right)^{-v} K \quad \text{for ideal solution (gas)}$$

$$\Pi(x_i)^{v_i} = K \quad \text{for ideal solution (liquid)}$$

- Reactions in **Heterogeneous systems** (more one phase)

Case) $A(g) + B(l) \Rightarrow C(aq)$: ΔG^0 : mixed standard state
C : ideal 1 molal aqueous solution
B : pure liquid at 1 bar
A : pure ideal gas at 1 bar

$$\Pi\left(\frac{\hat{f}_i}{f_i^0}\right)^{v_i} = K = \frac{\hat{f}_C / f_C^0}{(\hat{f}_A / f_A^0)(\hat{f}_B / f_B^0)} = \frac{m_C}{(\gamma_B X_B)(\hat{f}_A / P^0)} = K$$

15.8 Phase rule & duhem's theorem for reacting system

Phase rule for **non-reacting system** of π phase and N chemical species

$$F = 2 - \pi + N \text{ (phase No - independent eqn)}$$

=> need to be modified to system where chemical reaction occur

F : the number of independent variable that must be fixed to its in its intensive state

○ number of variable : $2 + (N-1)\pi$

○ number of eqn

1) phase-equilibrium eqn ($G_i^\alpha = G_i^\beta = G_i^\gamma \dots$)
[$(\pi - 1)N$]

2) If there are **r independent chemical reaction**

Total independent eqn : $(\pi - 1)N + r$

$$\therefore F = [2 + (N - 1) \pi] - [(\pi - 1) N + r] = 2 - \pi + N - r$$

- How do we determine the number of independent chemical reaction

1) from constituent elements, write chemical eqn

2) eliminate all element not present in the system

The set of r equation by this reduction procedure

=> complete set of independent reactions for the N species

$r \geq$ (No. of compounds presents in the system – No. of constituent elements not present as elements)

If there are special constraints (s)

$$F = 2 - \pi + N - r - s$$

- Duhem's theory ($F = 2$) : F is for reacting as well as non-reacting systems

15.9 Multireaction Equilibria

- When equilibrium state in reacting system depends on two or more independent chemical reaction
- Finding equilibrium composition → extension of the methods for single reaction
 - 1) Determine a set of independent reaction
 - 2) Find reaction coordinate for each independent reaction.
 - 3) Evaluate a separate equilibrium constant for each reaction

$$\prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{v_{ij}} = K_j \quad (13.38) \quad K_j = \exp\left(-\frac{\Delta G_j^0}{RT}\right) \quad (j = 1, 2, \dots, r)$$

For gas-phase reaction $\prod_i \left(\frac{\hat{f}_i}{P^0} \right)^{v_{ij}} = K_j$

If the equilibrium mixture is an ideal gas $\hat{f}_i = y_i P$

$$\prod_i \left(\frac{y_i P}{P^0} \right)^{v_{ij}} = K_j$$

$$\prod_i (y_i)^{v_{ij}} = \left(\frac{P}{P^0} \right)^{-\sum_j v_{ij}} K_j$$

- Alternative method to find **equilibrium composition at multireaction equilibrium**
 => use the fact that **G^t is minimum at equilibrium**

$$(G^t)_{T,P} = g(n_1, n_2, n_3, \dots, N_N)$$

- => find the set { N_i } which minimize G^t for special T, P based on the method of **Lagrange's undetermined multiplier**

1. **Formulate material balance** (total number of atoms of each element is constant)

$$\sum_i n_i a_{ik} = A_K \quad (K = 1, 2, \dots, w) \quad (13.41)$$

A_k : Number of atomic masses of K in the system

a_{ik} : Number of atoms of K per molecules of i

2. **Introduce the Lagrange multipliers** λ_k

$$\lambda_k \left(\sum_i n_i a_{ik} - A_K \right) = 0 \quad (K = 1, 2, \dots, w)$$

Do summation

$$\sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_K \right) = 0$$

3. Define a new function F

$$F = G^t + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_K \right)$$

4. Obtain eqn for $\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = 0$

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1, 2, \dots, N)$$

$$\mu_i = G_i^0 + RT \ln\left(\frac{\hat{f}_i}{f_i^0}\right) = G_i^0 + RT \ln\left(\frac{\hat{f}_i}{P^0}\right) \quad \text{For gas phase reaction}$$

$$G_i^0 = \Delta G_{f_i}^0 \quad (\text{if } G_i^0 = 0 \text{ for all elements})$$

$$\text{For example, } C + O_2 \rightarrow CO_2 \quad G^0 = \sum v_i G_i^0 \quad \Delta G_{CO_2}^0 = G_{CO_2}^0 - G_C^0 - G_{O_2}^0$$

$$\therefore \mu_i = \Delta G_{f_i}^0 + RT \ln\left(y_i \hat{\phi}_i \frac{P}{P^0}\right) + \sum_k \lambda_k a_{ik} = 0$$

$$\therefore \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = \Delta G_{f_i}^0 + RT \ln\left(y_i \hat{\phi}_i \frac{P}{P^0}\right) + \sum_k \lambda_k a_{ik} = 0 \quad (13.43)$$

(13.43) : N equilibrium eqn for chemical species

(13.41) : W material balance eqn for elements

N + W eqn , N + W unknown → can be solved