

Gibbs free energy +

Chemical Equilibrium

$\Delta_{\text{rxn}} G$ - Gibbs free energy of R&N (J)

$\Delta_{\text{rxn}} G^\circ$ - Standard state Gibbs free energy of R&N (J)

$\Delta_{\text{rxn}} H$ - Enthalpy change on Reaction (aka Heat of Reaction) (J)

$\Delta_{\text{rxn}} H^\circ$ - Standard state enthalpy change on R&N

K_a Chemical Equilibrium constant.

K_c Concentration chemical equilibrium ratio

For equilibrium @ constant
 $T, P \rightarrow$

$G \Rightarrow \text{minimum}$

\rightarrow Minimizing G for equilibrium
also applies to chemical Reactions

Basic principle for equilibrium

$$\sum v_i \bar{G}_i = 0$$

v_i = stoichiometric coefficient
for component i

\bar{G}_i : partial molar Gibbs free
energy

Definition: $\bar{G}_i = \left. \frac{\partial G}{\partial x_i} \right|_{x_j \neq i}$

One example problem -

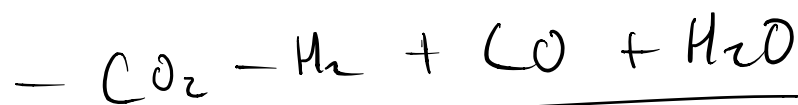


in a closed system,

constant T ,

ideal.

stoichiometric coefficients



-1 -1 1 1

recall $N_i = N_{i,0} + \nu_i \cdot X$ ↖ extent of rxn

↗ $X = \frac{N_i - N_{i,0}}{\nu_i}$

Table of mass balance.

Species	$N_{i,0}$	Final # moles	mole fraction
CO_2	1	$1 - X$	$(1-x)/2$
H_2	1	$1 - X$	$(1-x)/2$
CO	0	X	$x/2$
H_2O	0	X	$x/2$
Totals	2	$2 - X$	\uparrow

Goal: minimize total Gibbs free energy.

$$G = \sum N_i \bar{G}_i(T, P, \underline{y})$$

composition
→ mole fractions

$$G = \sum N_i \bar{G}_i(T, P) + RT \sum_i N_i (\ln y_i)$$

G_i : pure component Gibbs free energy

$$G = (1-x)(\underline{G}_{\text{CO}_2} + \underline{G}_{\text{H}_2}) + x(\underline{G}_{\text{CO}} + \underline{G}_{\text{H}_2\text{O}}) + 2RT[(1-x)\ln\{(1-x)/2\} + x\ln(x/2)]$$

Equilibrium occurs @ minimum

$$\text{at } \left(\frac{\partial G}{\partial x} \right)_{T,P} = 0$$

$$(\underline{G}_{\text{CO}} + \underline{G}_{\text{H}_2\text{O}} - \underline{G}_{\text{CO}_2} - \underline{G}_{\text{H}_2})$$

$$+ 2RT[-\ln\{(1-x^*)/2\} + \ln(x^*/2)] = 0$$

$$\frac{- (\underline{G}_{CO} + \underline{G}_{H_2O} - \underline{G}_{CO_2} - \underline{G}_{H_2})}{RT} = \ln \left[\frac{x^{*2}}{(1-x^*)^2} \right]$$

look @
the Table

replace these
w/ mole fractions

$$\frac{- (\underline{G}_{CO} + \underline{G}_{H_2O} - \underline{G}_{CO_2} - \underline{G}_{H_2})}{RT} = \ln \left[\frac{y_{CO} y_{H_2O}}{y_{CO_2} y_{H_2}} \right]$$

$$\frac{y_{CO} y_{H_2O}}{y_{CO_2} y_{H_2}} = \exp \left(\frac{- (\underline{G}_{CO} + \underline{G}_{H_2O} - \underline{G}_{CO_2} - \underline{G}_{H_2})}{RT} \right)$$

in general:

$$-\frac{\sum_i n_i \underline{G}_i}{RT} = \ln \left[\prod_i \gamma_i^{n_i} \right]$$

means product

↑
typically
Gas

in liquid phase:

$$-\frac{\sum_i n_i \underline{G}_i}{RT} = \ln \left[\prod_i x_i^{n_i} \right]$$

↑
mole fraction
in liquid
phase