Gibb's free energy +
Chemical Equilibrium

$\Delta_{rxn} G$ - Gibb's free energy of RXN (J)

$\Delta_{rxn} G^{\circ}$ - Standard state Gibb's free energy of RXN (J)

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

$\Delta_{rxn} H^{\circ}$ - Standard state enthalpy change on RXN

K_a Chemical Equilibrium constant.

K_c Concentration chemical equilibrium ratio

For equilibrium @ constant
$T, P \rightarrow$

$G \Rightarrow$ minimum

$\rightarrow$ Minimizing G for equilibrium
also applies to chemical Reactions

Basic principle for equilibrium

$$\boxed{\sum \nu_i \bar{G}_i = 0}$$

ν_i = stoichiometric coefficient
for component i

$\bar{G}_i$ = partial molar Gibbs free
energy

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

One example problem.

$$CO_2 + H_2 \rightarrow CO + H_2O$$

in a closed system,

constant T,

ideal.

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stoichiometric coefficients

$-CO_2$	$-H_2$	$+CO$	$+H_2O$
-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~~	

Goal: minimize total Gibbs free energy.

composition
→ mole fractions

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

$$\boxed{G = \sum N_i \underline{G_i}(T, P) + RT \sum_i N_i \ln y_i}$$

$\underline{G}_i$: pure component Gibb's free energy

$$\boxed{G = (1-X)\left(\underline{G}_{CO_2} + \underline{G}_{H_2}\right) + X\left(\underline{G}_{CO} + \underline{G}_{H_2O}\right) + 2RT\left[(1-X)\ln\{(1-X)/2\} + X\ln(X/2)\right]}$$

Equilibrium occurs @ minimum

$$@ \left(\frac{\partial G}{\partial X}\right)_{T,P} = 0$$

$$\left(\underline{G}_{CO} + \underline{G}_{H_2O} - \underline{G}_{CO_2} - \underline{G}_{H_2}\right) + 2RT\left[-\ln\{(1-X^*)/2\} + \ln(X^*/2)\right] = 0$$

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

look @ the Table

replace these w/ mole fractions

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

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

in general:

means product

$$-\frac{\sum_i \nu_i \underline{G_i}}{RT} = \ln\left[\prod_i y_i^{\nu_i}\right]$$

typically gas

in liquid phase:

$$-\frac{\sum_i \nu_i \underline{G_i}^{L}}{RT} = \ln\left[\prod_i x_i^{\nu_i}\right]$$

mole fraction in liquid phase