Reaction Extent

$$\alpha A + \beta B + \gamma C + \cdots \rightarrow \lambda L + \cdots$$

e.g. $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$

algebraically $\sum_{i=1}^{n} \nu_i \vec{R}_i$ $\vec{R}_i$: column vectors w/ number of atoms

e.g. $C_2H_6 = \vec{R}_1 = \begin{bmatrix} 2 \\ 6 \\ 0 \end{bmatrix}$ $O_2 = \vec{R}_2 = \begin{bmatrix} 0 \\ 0 \\ 2 \end{bmatrix}$ $CO_2 = \vec{R}_3 = \begin{bmatrix} 1 \\ 0 \\ 2 \end{bmatrix}$ $H_2O = \vec{R}_4 = \begin{bmatrix} 0 \\ 2 \\ 1 \end{bmatrix}$

order of rows - arbitrary but fixed ; C, H, O in this example.

ν_i : Stoichiometric coefficients, positive (+) for products, negative (-) for reactants
→ can be multiplied by arbitrary constant ←

Reaction progress described by extent "ξ" (ksee)

$$N_i = N_{i,0} + \nu_i \xi$$

$N_{i,0}$: initial amount

ξ: units of mol
→ pure number

Independent Reactions

$$C + O_2 \rightarrow CO_2$$
$$2C + O_2 \rightarrow 2CO$$
$$2CO + O_2 \rightarrow 2CO_2$$

} are these three reactions independent, or can one be written as a combination of others?

Matrix of coefficients $\underline{\underline{M}} = \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1N} \\ \nu_{21} & \nu_{22} & \cdots & \nu_{2N} \\ \vdots & & & \vdots \\ \nu_{K1} & \cdots & & \nu_{KN} \end{bmatrix}$

$$\underline{\underline{M}} = \begin{array}{c} \begin{matrix} C & O_2 & CO_2 & CO \end{matrix} \\ \begin{bmatrix} -1 & -1 & 1 & 0 \\ -2 & -1 & 0 & 2 \\ 0 & -1 & 2 & -2 \end{bmatrix} \end{array} \begin{matrix} \text{rxn 1} \\ \text{rxn 2} \\ \text{rxn 3} \end{matrix}$$

Linear algebra: rank(M) is the number of independent rows or columns

Gaussian elimination to echelon form:

$$\begin{bmatrix} -1 & -1 & 1 & 0 \\ -2 & -1 & 0 & 2 \\ 0 & -1 & 2 & -2 \end{bmatrix} \rightarrow \begin{bmatrix} -1 & -1 & 1 & 0 \\ 0 & 1 & -2 & 2 \\ 0 & -1 & 2 & -2 \end{bmatrix} \rightarrow \begin{bmatrix} -1 & -1 & 1 & 0 \\ 0 & 1 & -2 & 2 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

1st row × −2 add to 2nd

2nd row × 1 add to 3rd

rank(M) = 2 only 2 reactions independent

rank(M) ≤ min(# of rows, # of columns)

∴ # of indep. reactions no more than # of species

Equilibrium Criteria

Consider a single chemical reaction with coefficients $\{\nu_i\}$ at const. T, P

Function being minimized at equil.: $G = U - TS + PV$

$$G = \sum_i N_i \mu_i = \sum_i (N_{i,0} + \nu_i \xi)\mu_i$$

Euler Int.

$$\left.\begin{aligned} dG &= \sum_i \mu_i dN_i \\ dN_i &= \nu_i d\xi \end{aligned}\right\} \Rightarrow dG = \left(\sum_i \nu_i \mu_i\right) d\xi$$

for minimization of G, $dG/d\xi = 0 \Rightarrow$

$$\boxed{\sum_i \nu_i \mu_i = 0} \quad (i)$$

Can be shown to apply to systems under any constraints, not just const. T, P

For r independent reactions, each provides an equilibrium condition:

$$\sum_{i=1}^{n} \nu_{1i}\mu_i = 0 \quad \text{rxn 1}$$

$$\sum_{i=1}^{n} \nu_{2i}\mu_i = 0 \quad \text{rxn 2} \quad \cdots \quad \sum_{i=1}^{n} \nu_{ri}\mu_i = 0 \quad \text{rxn } r$$

Recall definition of fugacity:

$$RT\ln f_i = \mu_i(T, P, \{x\}) - \mu_i^\circ(T, P^\circ, \text{pure } i) \Rightarrow$$

$$\mu_i = RT\ln f_i + \mu_i^\circ \underset{(i)}{\Rightarrow} \sum_i \nu_i \left(RT\ln f_i + \mu_i^\circ\right) = 0 \Rightarrow$$

$$\sum_{i=1}^{n} \nu_i R T \ln \hat{f}_i = -\Delta \underline{G}^{\circ}_{rxn} \qquad (i)$$

where $\Delta \underline{G}^{\circ}_{rxn} \equiv \sum_{i=1}^{n} \nu_i \underline{G}^{\circ}_i(T, P^{\circ}, \text{pure } i)$

is the <u>Standard Gibbs free Energy of Reaction</u>

Defining the Equilibrium "Constant"

$$K(T) \equiv \exp\left(\frac{-\Delta \underline{G}^{\circ}_{rxn}}{RT}\right)$$

A strong function of temperature!

The equilibrium condition is

$$\boxed{\hat{f}_1^{\nu_1} \hat{f}_2^{\nu_2} \cdots \hat{f}_n^{\nu_n} = K(T)}$$

Recall that we are using the convenient, dimensionally inconsistent form of $\hat{f}_i$.

This gives a dimensionally inconsistent expression for $K(T)$.

Correct expression $\left(\frac{\hat{f}_1}{\hat{f}_1^{\circ}}\right)^{\nu_1}\left(\frac{\hat{f}_2}{\hat{f}_2^{\circ}}\right)^{\nu_2} \cdots \left(\frac{\hat{f}_n}{\hat{f}_n^{\circ}}\right)^{\nu_n} = K(T)$

(but $\hat{f}_i^{\circ} = 1$ bar at $P^{\circ} = 1$ bar)