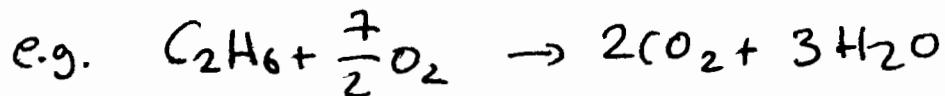
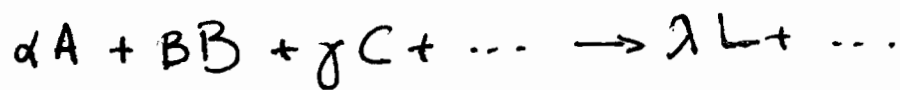
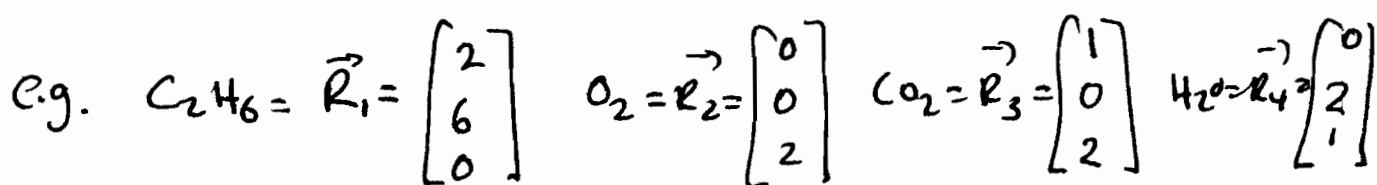


Reaction Extent

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

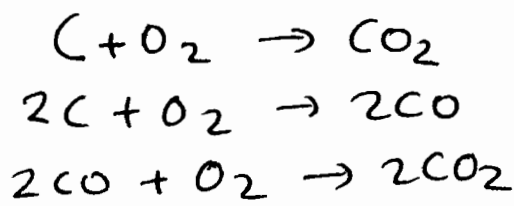


order of rows - arbitrary but fixed; C, H, O  
 in this example.

$\nu_i$ : stoichiometric coefficients, positive (+)  
 for products, negative (-) for reactants  
 → can be multiplied by arbitrary constant ←

Reaction progress described by extent " $\xi$ "  
 (ksee)

$$N_i = \underbrace{N_{i,0}}_{\text{initial amount}} + \underbrace{\nu_i \xi}_{\substack{\text{units of mol} \\ \text{pure number}}}$$

Independent Reactions

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

Matrix of coefficients  $\underline{M} = \begin{bmatrix} v_{11} & v_{12} & \dots & v_{1n} \\ v_{21} & v_{22} & \dots & v_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ v_{k1} & \dots & \dots & v_{kn} \end{bmatrix}$

$$\underline{M} = \begin{array}{cccc|l} & \text{C} & \text{O}_2 & \text{CO}_2 & \text{CO} & \\ \hline & -1 & -1 & 1 & 0 & \text{rxn 1} \\ & -2 & -1 & 0 & 2 & \text{rxn 2} \\ & 0 & -1 & 2 & -2 & \text{rxn 3} \end{array}$$

Linear algebra:  $\text{rank}(M)$  is the number of independent rows or columns

Gaussian elimination to echelon form:

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

$\downarrow$  1st row  $\times -2$  add to 2nd  
 $\downarrow$  2nd row  $\times 1$  add to 3rd

$\text{rank}(M) = 2$  only 2 reactions independent

$$\text{rank}(M) \leq \min(\# \text{ of rows}, \# \text{ of columns})$$

$\therefore$  # of indep. reactions no more than # of species

Equilibrium Criteria

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

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

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

$$\left. \begin{array}{l} \text{Euler Int.} \\ dG = \sum_i \mu_i dN_i \\ dN_i = v_i d\xi \end{array} \right\} \Rightarrow dG = \left( \sum_i v_i \mu_i \right) d\xi$$

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

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

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

For  $r$  independent reactions, each provides an equilibrium condition:

$$\begin{array}{l} \sum_{i=1}^n v_{1i} \mu_i = 0 \quad r_{1n} \quad 1 \\ \sum_{i=1}^n v_{2i} \mu_i = 0 \quad r_{2n} \quad 2 \quad \dots \quad \sum_{i=1}^n v_{ri} \mu_i = 0 \quad r_{2nr} \end{array}$$

Recall definition of fugacity:

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

$$\mu_i = RT \ln f_i + \mu_i^\circ \Rightarrow \sum_i v_i (RT \ln f_i + \mu_i^\circ) = 0 \Rightarrow$$

(i)

$$\sum_{i=1}^n \nu_i RT \ln f_i = - \Delta \underline{G}_{rxn}^{\circ} \quad (i)$$

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

is the Standard Gibbs Free Energy of Reaction

Defining the Equilibrium "Constant"

$$K(T) \equiv \exp\left(\frac{-\Delta \underline{G}_{rxn}^{\circ}}{RT}\right) \quad \text{A strong function of temperature!}$$

The equilibrium condition is

$$\boxed{f_1^{\nu_1} f_2^{\nu_2} \dots f_n^{\nu_n} = K(T)}$$

Recall that we are using the convenient, dimensionally inconsistent form of  $f_i$

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

Correct expression  $\left(\frac{f_1}{f_1^{\circ}}\right)^{\nu_1} \left(\frac{f_2}{f_2^{\circ}}\right)^{\nu_2} \dots \left(\frac{f_n}{f_n^{\circ}}\right)^{\nu_n} = K(T)$

(but  $f_i^{\circ} = 1 \text{ bar}$  at  $P^{\circ} = 1 \text{ bar}$ )