THERMODYNAMICS OF REACTING SYSTEMS

2.1   Introduction

This chapter explains the basics of thermodynamic equilibrium calculations for reacting systems. Reaction stoichiometry, heat and entropy of reaction as well as free energy are considered here. Only single phase systems are considered here. Phase equilibrium will be addressed in the next chapter. Examples and MATLAB calculations of chemical equilibria are provided at the end of this chapter.

2.2   Reaction Stoichiometry

The principle of conservation of each atomic species applied to every well defined chemical reaction leads to reaction stoichiometry. Imagine that we have placed an invisible and impenetrable envelope around a finite mass of reactants and the contents of that envelope are our system. We can count the atoms of each atomic species present in each reactant species in the system initially. A chemical reaction takes place in the system. Upon reaction completion, we recount the number of each atomic species. The total number of atoms of each of the elements present in the remaining reactants and in products formed must remain constant. The principle of conservation of mass applied to each atomic species yields the ratio in which molecules of products are formed and molecules of reactants are reacted.

The representation of chemical species by a chemical formula indicates how many atoms of each species are there in a molecule of the species under consideration. Hence, in a molecule of carbon dioxide (CO_2), there are: one atom of carbon, C, and two atoms of oxygen, O. In a molecule of methane, CH_4, there is one atom of carbon and 4 of hydrogen, etc.

In engineering applications, a mole of the species under consideration is used rather than a chemical formula (e.g., CH_4, O_2, etc.) representing an individual molecule of a particular chemical species. One should recall that a mole is a basic unit of the amount of substance. The SI definition of a mole is: "The mole is the amount of substance of a system that contains as many elementary entities as there are carbon atoms in 0.012 kg of carbon 12." The elementary entity (unit) may be an atom, a molecule, an ion, an electron, a photon, etc. The Avogadro's constant is $L = 6.023 \times 10^{23}$ (mol^{-1}).

To obtain the number of moles of species j, n_j (mol) in our system, we must divide the mass of j in the system m_j (kg), with the molecular weight of j, M_j (g/mol), and multiply the result by 1000.

$$n_j(mol) = \frac{m_j(kg)}{M_j} \times 1000 = \frac{m_j(g)}{M_j} \qquad (1)$$

This is equivalent to dividing the mass of the species j expressed in grams with the molecular weight, as indicated by the second equality in equation (1). So the SI mole is the same amount of substance as the "old" CGS gram-mole that appears in old chemistry and physics texts.

In the US we frequently use a pound-mole (lb mol) as the measure of the amount of substance.

$$n_j^*(lb\ mol) = \frac{m_j(lb)}{M_j} \tag{1a}$$

It is important to note that the molecular weight of a species always has the same numerical value independent of the system of units. For example, the molecular weight of carbon is $M_c = 12$ (g/mol) = 12 (lb /lb mol) = 12 (kg/kmol).

Therefore, 1 (kmol) is thousand times larger than a mole (e.g. 1 (kmol) = 10^3 mol)) and 1 lbmol is 453.4 times larger than a mole, i.e. 1 (lbmol) = 453.4 moles. Accordingly, the Avogadro's constant for a lb mole is L = 2.7308 x 10^{26} (lbmole^{-1}) and for a kmole is L = 6.023 x 10^{26} (kmol^{-1}).

To illustrate how reaction stoichiometry is developed, consider the complete combustion of methane (CH4) to carbon dioxide, CO2. This is a reaction between methane, CH_4, and oxygen, O_2, that creates carbon dioxide, CO_2, and water H_2O by complete combustion.

So we have   at start   at end

               CH4 + O2   CO2 + H2O
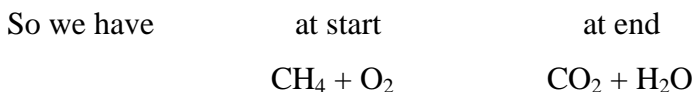
To develop a stoichiometric equation we assume that we start with one mole of methane. This implies that one mole of carbon must be found both on the left hand side and on the right hand side of the stoichiometric equation. So, one mole of CH4 reacted must produce one mole of CO2. Since hydrogen is only contained in methane on the reactant side, and there are 2H2 (two moles of hydrogen) in a mole of methane on the reactant side of the stoichiometric equation, there must be two moles of water formed on the product side in order to balance the amount of hydrogen. Now we have one mole of oxygen (O_2) in the mole of carbon dioxide (CO2) on the product side and another mole of oxygen in two moles of water. Therefore, we must use two moles of oxygen on the reactant side to balance the amount of oxygen. This leads to the following stoichiometric equation for complete combustion of methane:

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O \tag{2}$$

Hence, the requirement to balance out the atomic species, <u>i.e.</u> the application of the principle of conservation of mass of atomic species leads to the establishment of stoichiometric coefficients

(multipliers that multiply the moles of various reactant and product species). The above stoichiometric equation remains unchanged if multiplied with a common multiplier say 1/2:

$$\frac{1}{2}CH_4 + O_2 \Leftrightarrow \frac{1}{2}CO_2 + H_2O \tag{2a}$$

or say 2

$$2CH_4 + 4O_2 \Leftrightarrow 2CO_2 + 4H_2O \tag{2b}$$

Reaction stoichiometry, for a single reaction, such as that of equation (1) can now be represented by:

$$\sum_{j=1}^{S} \nu_j A_j = 0 \tag{3}$$

where

S = total number of species in the system (e.g. 4 in case of reaction 1)

A_j = chemical formula for the j-th species (e.g. CH_4, O_2, CO_2, etc.)

ν_j = stoichiometric coefficient for the j-th species defined as

$\left(\nu_j > 0 \text{ for products}, \quad \nu_j < 0 \text{ for reactants}\right)$

The stoichiometric equation satisfies the overall mass balance for the system

$$\sum_{j=1}^{S} \nu_j M_j = 0 \tag{4}$$

where M_j = molecular weight of species *j*.

For example, for reaction (1) of methane combustion we have

$$\nu_{CH_4} = -1; \quad \nu_{O_2} = -2; \quad \nu_{CO_2} = 1; \quad \nu_{H_2O} = 2$$

If a reaction system can be described by a <u>single reaction,</u> then its generalized stoichiometry is given by eq (3). Alternatively, for a single reaction between two reactants, A and B, and two products, P and S, the stoichiometry can also be represented by:

$$aA + bB = pP + sS \tag{3a}$$

where *A, B, P, S* are chemical species and a,b,p,s are their stoichiometry coefficients, respectively. $\left(A = CH_4, B = O_2, P = CO_2 \text{ and } S = H_2O \text{ in our example}\right)$ Naturally, this implies that molecular weight of species A, B, P, S are such that equation (4) is satisfied with $\nu_A = -1, \nu_B = -2, \nu_p = 1, \nu_s = 2$. This simpler form is convenient for single reactions and also in representing kinetics as discussed later. Single reaction implies that

$$\frac{\left(moles\,of\,A\,reacted\right)}{a} = \frac{\left(moles\,of\,B\,reacted\right)}{b} = \frac{\left(moles\,of\,P\,reacted\right)}{p} = \frac{\left(moles\,of\,S\,reacted\right)}{s} \tag{3b}$$

Hence, a single reaction implies that the ratios of product produced and reactant consumed, or, a ratio of one reactant consumed to the other reactant consumed, are constant e.g.

$$\frac{(moles\ of\ P\ produced)}{(moles\ of\ A\ reacted)} = \frac{p}{a}\ ;\quad \frac{(moles\ of\ A\ reacted)}{(moles\ of\ B\ reacted)} = \frac{a}{b} \tag{3c}$$

If that is not the case, then multiple reactions must be used to describe the system. In a generalized form this can be done as:

$$\sum_{j=1}^{S} v_{ij}\, A_j = 0;\quad i = 1,2...R \tag{5}$$

where

v_{ij} = *stoichiometric coefficient of species j in reaction i*

R = *total number of independent reactions*

For example, if in combustion of carbon, there is also carbon monoxide present, then two reactions are needed to describe the system. They can be as given below:

$$2C + O_2 \Leftrightarrow 2CO \tag{5a}$$

$$2CO + O_2 \Leftrightarrow 2CO_2 \tag{5b}$$

Here, we have a total of S = 4 species (j =1,2,3,4 for $C,\ O_2,\ CO,\ CO_2$, respectively), which are involved in two (R = 2) independent reactions (i = 1,2). If the above combustion reactions involve air instead of oxygen, then nitrogen is the fifth species and hence S = 5, but its stoichiometric coefficient in each reaction is zero ($v_{i5} = 0$ for i=1,2) since nitrogen does not participate in these reactions. Note that the matrix of stoichiometric coefficients (for a system without nitrogen)

$$\begin{pmatrix} -2 & -1 & 2 & 0 \\ 0 & -1 & -2 & 2 \end{pmatrix}$$

has rank two (recall that the rank of a matrix is defined as the size of the largest nonzero determinant). Adding a third reaction

$$C + O_2 \Leftrightarrow CO_2 \tag{5c}$$

would add a third row to the above matrix of stoichiometric coefficients, namely (- 1 - 1 0 1) but the rank of the matrix would remain unchanged at 2.

Clearly, eq (5c) is a linear combination (to be precise the exact sum) of (5a) and (5b). Hence, we do not have a third independent reaction, and the stoichiometry of the system can be described by any choice of two reactions of the above three reactions given by eqns. (5a), (5b) and (5c). Finding the rank of the matrix of stoichiometric coefficients identifies how many independent reactions are needed to characterize the stoichiometry of the system. MATLAB can be used for this purpose..

4

In summary, in any reaction system we should strive to establish the reaction stoichiometry by using the principle of conservation of mass by applying it as conservation of each atomic species (elements). Then, if more than one reaction is present, the number of independent reactions can be established by determining the rank of the matrix of stoichiometric coefficients.

2.3 Measures of reaction progress

Let us consider first a single reaction

$$\sum_{j=1}^{S} \nu_j A_j = 0 \tag{3}$$

occurring either in a batch system (i.e no material flow crosses the boundaries of the system during reaction) or in a continuous flow system at steady state (e.g. no variation in time). If n_j denotes the moles of species j in the batch at some time t, and n_{jo} is the initial number of moles of j at time t_o, then reaction stoichiometry dictates that moles of all species can be related to their initial moles via (molar) extent of reaction X.

$$n_j = n_{jo} + \nu_j X \tag{6a}$$

(moles of j present) = (moles of j originally present) + (moles of j produced by reaction)

Moles of j produced by reaction are given by the product of the stoichiometric coefficient, ν_j, and molar extent of reaction, X, which represents "moles equivalent that participated in reaction". For reactants, $\nu_j < 0$, and moles produced are a negative quantity, hence, they are moles reacted. For products $\nu_j X$ is clearly a positive quantity. Similarly, for a flow system at steady state,

$$F_j = F_{jo} + \nu_j \dot{X} \tag{6b}$$

where F_j, F_{jo} (mol j / s) are molar flow rate of j at exit and entrance, respectively, and $\dot{X}$ (mol/s) is the molar extent of reaction.

Equation (6a) or (6b) indicates that in a single reaction if we can determine the change in moles of one component (say $j = A)$, then the molar extent of reaction can be calculated, (e.g. for eq(6a) by $X = (n_A - n_{Ao})/\nu_A$. Moles of all other species n_j can now be found by applying eq(6a) to all other species j provided their initial moles n_{jo} were given. Equations (6a) and (6b) also indicate that reaction progress, i.e. its extent, is limited by the limiting reactant. The limiting reactant is the one present in amounts less than required by stoichiometry and limits the reaction extent to X_{max} where

$$X_{max} = \left(\frac{n_{jo}}{|v_j|} \right) \text{ smallest value over all } j$$

(7)

Usually, the limiting reactant is denoted by A so that $X_{max} = n_{Ao}/|v_A|$

For multiple reactions

$$\sum_{j=1}^{S} v_{ij} A_j = 0; \quad i = 1,2...R$$

(5)

molar extents X_i (mol) are defined for each independent reaction i so that the moles of j are given by

$$n_j = n_{jo} + \sum_{i=1}^{R} v_{ij} X_i$$

(8)

(moles of j) = (initial moles of j) + $\sum_{all \text{ reactions}}$ *(moles* of j produced by reaction i)

Now, the change in moles of R species must be determined to evaluate the R extents. This involves the solution of R linear algebraic equations. Then the moles of other species can be calculated by eq (8). Maximum extents are now those that yield zero moles of one or more reactants.

Dealing with reaction stoichiometry and reaction progress results in linear algebraic equations to which all rules of linear (matrix) algebra apply. We are interested only in non-negative solutions.

Sometimes other measures of reaction progress are used, such as (molar) extent per unit volume of the system $\xi \left(\frac{mol}{L} \right)$, which has units of concentration, or molar extent per mole which is dimensionless, or extent per unit mass. We will define them as we go along and when we need them.

Often conversion of a limiting reactant is used in single reaction systems to measure progress of reaction

$$x_A = \frac{n_{Ao} - n_A}{n_{Ao}}$$

(9a)

or

$$x_A = \frac{F_{Ao} - F_A}{F_{Ao}}$$

(9b)

The relationship between conversion and extent is readily established

$$n_{Ao} x_A = (-v_A) X \quad \text{or} \quad F_{Ao} x_A = (-v_A) \dot{X}$$

(10)

Hence, in a single reaction moles of all species can be given in terms of conversion, x_A. Note that conversion is unitless while reaction extent has units of moles, <u>i.e.</u> of amount of substance.

2.4   Heat of reaction

Heat of reaction is calculated as the difference between the heat of formation of products and the reactants.

$$\Delta H_{r,i} \;=\; \sum \Delta H_{f(products)} \;-\; \sum \Delta H_{f(reactants)} \tag{11}$$

where $\Delta H_{r,i}$ is the heat of the reaction i.

The products and reactants react proportionally to their stoichiometric coefficients. Therefore, Eqn.(11) can be written as

$$\Delta H_{r,i} \;=\; \sum_{j} \nu_{ij}\; \Delta H_{f,j} \tag{11a}$$

The heat of formation data is usually available at standard conditions of 298 K and 1 atm. Corresponding standard heat of reaction denoted as $\Delta H_{r,i}^{o}$ can be calculated as

$$\Delta H_{r,i}^{\circ} \;=\; \sum_{j} \nu_{ij} \Delta H_{f,j}^{\circ} \tag{12}$$

where $\Delta H_{f,j}^{\circ}$ is the heat of formation of the species j at standard conditions. Tabulated values for some species are shown in Table 1. The extensive database "chemkin" available in the public domain is another source. We will explain later how to use it.

Table 1: Heat of formation, entropy of formation, and Gibbs free energy of formation at standard conditions for selected species. State = gas, temperature T=298K and pressure 1atm.

Gas	$\Delta H^{\circ}\; J/mol$	$\Delta S^{\circ}\; J/mol\,K$	$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}\; J/mol\,K$
Oxygen	0.0		0.0
Water	241,818	-44.3557	-228,600
Methane	-74,520	-79.49	-50,832
Nitric oxide NO	90,250	11.96	86,686
Nitrogen dioxide NO2	33,180	-63.02	51,961
Carbon monoxide	-110,525	89.73	-137.267
Carbon dioxide	393-509	2.84	-394,355
Sulfur dioxide	296,830	11.04	-300,139
Sulfur trioxide	-395,720	-85.16	-370,341
Ozone	142,664	-67.53	162,789

Group contribution methods are also available to predict these quantities for new compounds.

Using the value of standard conditions, the value at any other condition can be calculated using "Hess Law". This states that the enthalpy change is indifferent of the path taken as long as one lands up in the same spot. A reaction carried out at any temperature T is equivalent in terms of energy change to the sum of the energy changes involved in each of the following three paths:

(i)   Cool reactants form T to T_{ref}.

(ii)   Carry out reaction at T_{ref} with an associated enthalpy change of $\Delta H^{\circ}_{r,i}$

(iii)   Heat the products back form T_{ref} to T.

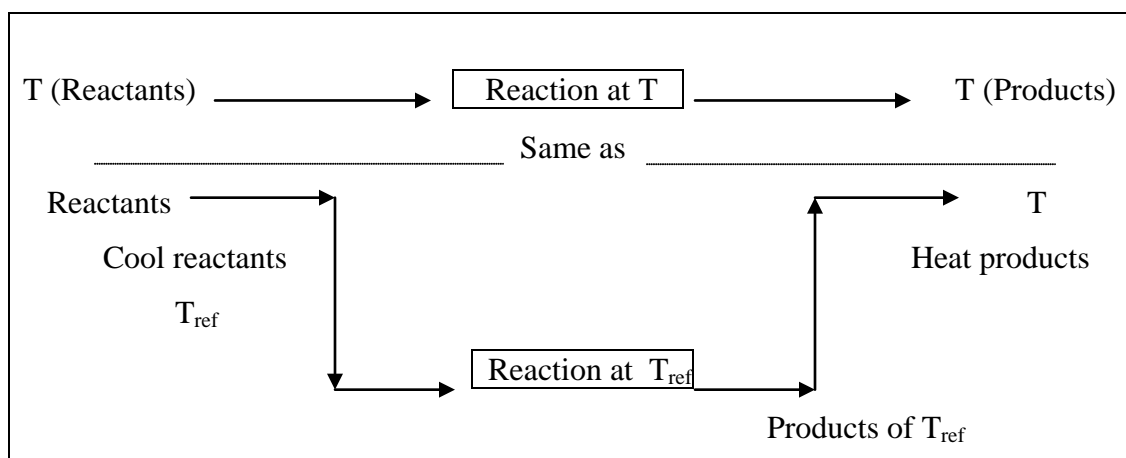The steps are schematically shown in the Figure 1.

Figure 1. Schematics of Hess Law: Enthalpy change is indifferent of the path taken as long as one lands up in the same spot.

Hence, the enthalpy change due to reaction (i.e. the heat of reaction) at temperatures different from the standard temperature can be calculated by equation (13) which adds a temperature correction term to the standard heat of reaction. This temperature correction then is the sum over all species of the algebraic product of the stoichiometric coefficients with the integral of the molar specific heat for each species from the reference (standard!) temperature to the temperature of interest.

$$\Delta H_{r,i} = \Delta H^{\circ}_{r,i} + \sum_{j} [\int_{T_{ref}}^{T} v_{i,j}\ C_{pj}\ dT] \qquad (13)$$

The variation of C_p is usually expressed as a polynomial function of temperature

$$C_{pj} = \sum_{\alpha=0}^{\alpha_{max}} A_{\alpha j}\ T^{\alpha} \qquad (14a)$$

where $A_{\alpha j}$ are the coefficients for species j.

8

or

$$C_p = A + BT + CT^2 + DT^3 \qquad (14b)$$

This is another approximate form of C_p as a function of temperature.

Up to seven constants are used in the "chemkin" database ($\alpha_{max} = 7$) while 4 constants are used as an approximation in many books as shown in (14b).

Substituting eq. (14a) into eq. (13) we find

$$\Delta H_{i,r} = \Delta H^{\circ}_{i,r} + \sum_{j=1}^{s} v_{ij} \sum_{\alpha=0}^{\alpha_{max}} \frac{A_{\alpha j}}{\alpha+1} [T^{\alpha+1} - T_{ref}^{\alpha+1}] \qquad (15)$$

The above expression provides a method for calculation of heat of reaction at any given temperature T in an exact manner. The information needed is the heat of formation of all species at T_{ref} and the coefficients $A_{\alpha j}$ in eq. (14a) for temperature variation of molar specific heat (e.g. heat changes) C_p for each species.

2.5   Entropy change in reaction

ΔS°_r is denoted as the entropy change of reaction at standard condition (T_{ref}) and can be calculated from the entropy of formation $\Delta S^{\circ}_{f,j}$ for each species j participating in the reaction.

$$\Delta S^{\circ}_r = \sum_{j=1}^{s} v_j \, \Delta S^{\circ}_{f,j} \qquad (16)$$

The entropy change at any other temperature T can be calculated as

$$\Delta S_r = \Delta S^{\circ}_r(T_{ref}) + \sum_{j} \int_{T_{ref}}^{T} v_j \frac{C_{pj}}{T} dT \qquad (17)$$

Using the polynomial expression for C_{pj} as a function of temperature and integrating we obtain

$$\Delta S_r = \Delta S^{\circ}_r + \sum_{j=1}^{s} v_j \, A_{0j} \, ln \frac{T}{T_{ref}} + \sum_{j=1}^{S} v_j \sum_{\alpha=1}^{\alpha_{max}} \frac{A_{\alpha j}}{\alpha} [T^{\alpha} - T_{ref}^{\alpha}] \qquad (18)$$

Knowing the entropy and enthalpy change, at any given temperature, the free energy change of reaction is calculated as :

$$\Delta G_r = \Delta H_r - T\Delta S_r \qquad (19)$$

Knowledge of how ΔG_r changes with temperature is important in determining the direction that the reaction will favor. If $\Delta G_r < 0$ reaction to the right or forward reaction is highly favorable, while if $\Delta G_r > 0$ the reverse reaction is more favorable. The temperature at which $\Delta G_r = 0$ is where the transition occurs. For an exothermic reaction, ΔG_r typically increases with temperature.
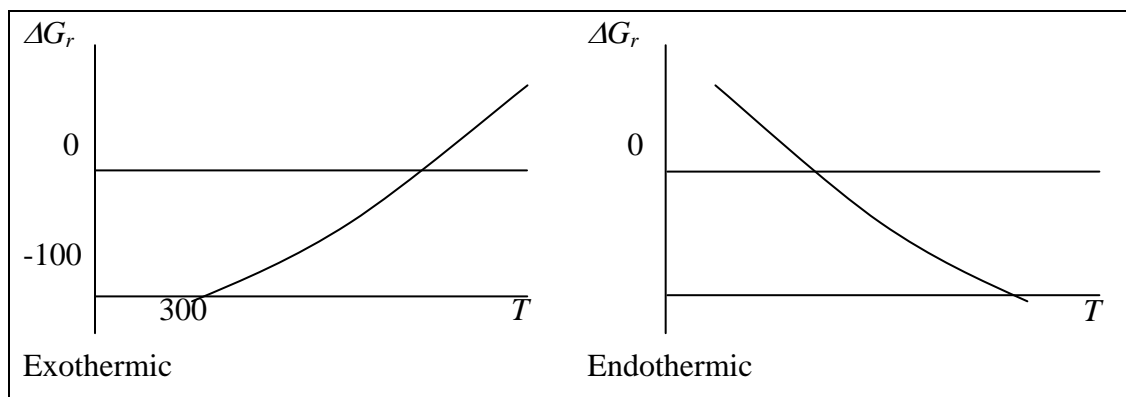
Figure 2: Variations of free energy as a function of temperature for exothermic and endothermic reactions:
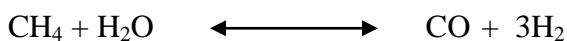
Example:

i)   CO oxidation to CO_2. This is an exothermic reaction.

$$CO + \frac{1}{2}O_2 \longleftrightarrow CO_2$$
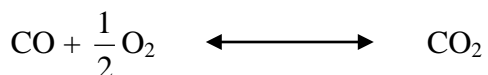
T(K)	ΔH_r (J/mole)	ΔS_r (J/mole K)	ΔG_r (J/mole)
500	-283,866	-88.55	-239,590.8
1500	-282,623	-86.931	-195,692.0
2500	-244,892	-83.71	-110,457
2600	-274,733	-82.33	-60,659

Reaction becomes less favorable at elevated temperature as the reaction is exothermic.

ii)   Steam reforming of methane

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2$$

This is an endothermic reaction

T(K)	ΔH_r (J/mole)	ΔS_r (J/mole K)	ΔG_r (J/mole)
500	215,880	238.2	96,000
700	222,000	248.3	35,700
900	224,700	251.3	-1,762
1000	225,660	252.6	-26,960

Reaction becomes favorable only at higher temperatures. This is always true for an endothermic process. Note that ΔG_r decreases with increasing temperature which is consistent with the trend shown in Figure 2.

2.6   Chemical Thermodynamics: Brief Review of Chemical Equilibria

For simplicity consider an isothermal, single phase system subject to a single reaction.

$$\sum_{j=1}^{s} v_j A_j = 0 \tag{3}$$

The equilibrium state is then defined by the minimum in Gibbs free energy of the system $(\min \sum n_j \tilde{G}_j)$ which can be expressed by

i) $$\sum_{j=1}^{s} v_j \tilde{G}_j = 0 \tag{20}$$

where

ii) $$n_j = n_{jo} + v_j X_e \quad \text{for all } j \tag{21}$$

iii)   appropriate equation of state

$\tilde{G}_j(T, P, x_j)$ is the partial molarGibbs free energy of j and is the function of temperature, pressure and composition. (It is often called chemical potential of j and denoted by μ_j)

In general

$$\tilde{G}_j = G_{\underset{\sim}{j}} + RT \ln a_j \tag{22}$$

where $G_{\underset{\sim}{j}}$ is the molar Gibbs free energy of pure species j (function of temperature only).

a$_j$ is the activity of species j;

nj is moles of j;

n_{jo} is initial moles of j;

v_j is stoichiometric coefficient of j (positive for products, negative for reactants);

T is temperature of the system;

X$_e$ is the equilibrium molar extent of reaction;

Substitution of equation (22) into equation (20) yields

$$\sum_{j=1}^{s} v_j G_{\underset{\sim}{j}} + RT \sum_{j=1}^{s} v_j \ln a_j = 0 \tag{23}$$

Recognizing that $v_j \ell n a_j$ is $\ell n a_j^{v_j}$ and that the sum of logarithms $\sum_{j=1}^{S} \ell n\left(a_j^{v_j}\right)$ is the logarithm of the product $\ell n \prod_{j=1}^{S} a_j^{v_j}$ we get the following equation

$$\ell n \prod_{j=1}^{S} a_j{}^{\upsilon_j} = \frac{-1}{RT} \sum_{j=1}^{S} \upsilon_j \underset{\sim}{G}_j \qquad (23a)$$

We define the standard Gibbs free energy of reaction at temperature T by

$$\Delta G_r = \sum_{j=1}^{s} v_j \underset{\sim}{G}_j \qquad (24)$$

with all $\underset{\sim}{G}_j$ being evaluated at the temperature T of interest.

Then the <u>thermodynamic equilibrium constant,</u> K, which is a function of temperature only, is obtained by taking the anti-logarithm of equation (23a) and is given by:

$$K = \prod_{j=1}^{s} a_j^{\upsilon j} = e^{-\frac{\Delta G_r}{RT}} \qquad (25)$$

where a_j is the activity of species j

In order to calculate the equilibrium reaction extent, X_e, and the equilibrium composition we need to:

a)   Calculate K at the temperature of interest.

b)   Relate the activity of each species, j , a_j , to a measure of composition (e.g. mole fraction) by an appropriate model for the mixture.

c)   Relate the chosen measure of composition to reaction extent using stoichiometric relations   indicated by ii) above.

Since the Gibbs free energy of formation is tabulated for all chemical species at T_{ref} = 298K (25°C) (or can be found from ΔH and ΔS data as shown in the previous section) it is convenient to calculate the Gibbs free energy change due to reaction ΔG_r^o at these standard conditions as:

$$\Delta G_r^o = \sum_{j=1}^{S} v_j \Delta G_{f,j} \qquad (26)$$

The equilibrium constant at standard temperature is then obtained from equation (25) using $T=T_{ref}$ and ΔG_r at standard conditions given by eq. (26).

Van Hoff's equation establishes the rate of change of the equilibrium constant K with temperature:

$$\frac{d\ell n K}{dT} = \frac{\Delta H_r}{RT^2} \qquad (27)$$

$$T = T_o (= 298\,K); K = K_{298} = \exp(-\Delta G_r^o / RT_0) \qquad (28)$$

where ΔH_r is the standard heat of reaction at temperature T (calculated as shown in the previous

section), K_{298} is the equilibrium constant at the standard state temperature of T_O (most often 298K) and ΔG_r^o is the standard Gibbs free energy of reaction at T_O which is obtained from tabulated Gibbs free energies of formation $\Delta G_{f,j}$ of products and reactants.

Now we need to relate activities of various species to the measures of composition in order to determine from the values of K the equilibrium composition and equilibrium extent of recation at various temperature and pressure conditions

For gases (standard state pure gas at 1 atm) we use y_j for mole fraction of j, a_j is the activity of j, p_j is partial pressure of j, P is the total pressure of the system, ϕ_j is the fugacity coefficient of j while $\tilde{f}_j$ is the partial molar fugacity of j.

The needed relations are included below:

$$a_j = y_j P(\frac{\tilde{f}_j}{y_j P})/1atm = p_j(\frac{\tilde{f}_j}{y_j P})/1atm \qquad (30)$$

$$a_j = y_j P \phi_j /1 atm = p_j \phi_j /1 atm \qquad (30a)$$

$$K = \prod_{j=1}^{s} a_j^{v_j} = (\frac{P}{1\,atm})^{\sum v_j} \prod_{j=1}^{s} y_j^{v_j} \prod_{j=1}^{s} \phi_j^{v_j} \qquad (31)$$

$$K = \left(\frac{P}{1atm}\right)^{\sum v_j} K_y K_\phi = \left(\frac{P}{P_0}\right)^{\sum v_j} K_y K_\phi \quad \text{where } P_O = 1 \text{ atm.} \qquad (31a)$$

or

$$K = \prod_{j=1}^{s} a_j^{v_j} = \prod_{j=1}^{s} p_j^{v_j} \prod_{j=1}^{s} \phi_j^{v_j} /(1atm)^{\sum v_j} \qquad (32)$$

$$K = \prod_{j=1}^{s} a_j^{v_j} = K_P K_\phi /(1\,atm)^{\sum v_j} \qquad (32a)$$

The generalized fugacity coefficients ϕ_j, $\phi_j = \left(\dfrac{\tilde{f}_j}{y_j P}\right)$, would have to be evaluated from an

appropriate equation of state. If Lewis-Randall rule is used $\phi_j = \left(\dfrac{f_j}{P}\right)$.

For gases at low pressure $K_\phi \approx 1$

$$K = \left(\frac{P}{1atm}\right)^{\sum v_j} K_y = K_P /(1atm)^{\sum v_j} \qquad (32b)$$

13

For liquids (assuming standard state of unit activity, i.e. the standard state of each component is the pure component state) the following relations hold:

$$a_j = x_j \gamma_j \tag{33}$$

where γ_j is the activity coefficient of j and x_j is the mole fraction of j.

$$K = \prod_{j=1}^{s} a_j^{\upsilon_j} = \prod_{j=1}^{s} \left(x_j \gamma_j \right)^{\upsilon_j} = K_x K_\gamma \tag{34}$$

Since $x_j = C_j / C$

$$K = C^{-\sum \upsilon_j} K_c K_\gamma \tag{35}$$

For an ideal mixture $K_\gamma \approx 1$

Above C_j is the molar concentration of species j and $C = \sum_{j=1}^{s} C_j$ is the total molar concentration.

Example:

Reaction System: $2SO_2 + O_2 = 2SO_3$

Conversion of 99% is desired

Conditions: $T = 600^O C = 873^O K$

$P = 1$ atm

Stoichiometric Feed of Pure Reactants

No Nitrogen

Calculate equilibrium conversion of SO_2 and see if 99% can be reached.

ΔG_f and ΔH_f for various species are given in (kcal/mol) below.

Basis: 2 moles of SO_2.

Total number of species S = 3

$$\sum \upsilon_j = -1$$

$$n_{tot_0} = \sum_{j=1}^{3} n_{jo} = 3$$

$$n_{tot} = \sum n_j = 3 - X$$

Species Name	No.	Stoich. Coeff.	ΔG_f	ΔH_f	n_{jo}	$n_j = n_{jo} + \upsilon_j X$
SO_2	1	-2	-71.7	-70.9	2	$2 - 2X$
O_2	2	-1	0	0	1	$1 - 1X$
SO_3	3	2	-88.6	-94.4	0	$0 + 2X$

Assume ideal gas mixture and write the equilibrium constant in terms of K_y:

$$K = K_y \left(\frac{P}{P_o} \right)^{\sum_{j=1}^{s} \upsilon_j} = K_y \left(\frac{P}{P_o} \right)^{-1} = K_y \left(\frac{P_o}{P} \right)$$

where   (A)

$$K_y = \prod_{j=1}^{3} y_j^{\upsilon_j} = y_1^{-2} y_2^{-1} y_3^{+2} = \frac{y_3^2}{y_1^2 y_2} \left\{ = \frac{y_{SO_3}^2}{y_{SO_2}^2 y_{O_2}} \right\}$$

Evaluate the mole fraction of each species in terms of reaction extent X

$$y_1 = \frac{n_1}{n_{tot}} = \frac{2 - 2X}{3 - X} \quad ; \quad y_2 = \frac{1 - X}{3 - X}; \quad y_3 = \frac{2X}{3 - X}$$

Substitute these mole fractions in the expression for K_y

$$K_y = \frac{\dfrac{4X^2}{(3-X)^2}}{\dfrac{4(1-X)^2(1-X)}{(3-X)^2(3-X)}} = \frac{X^2(3-X)}{(1-X)^3}$$

where $\underline{X = X_e \ = \ \text{equilibrium extent}}$

From (A)

$$K = \frac{X^2(3-X)}{(1-X)^3}\left(\frac{P_0}{P}\right) \hspace{3cm} \text{(B)}$$

Calculate K_{298} at 298°K

$$\Delta G_r^\circ = (-2)x(-71.7)+(-1)x(0)+2x(-88.6) = -33.8\frac{kcal}{mol}$$

$$K_{298} = e^{-\frac{\Delta G_r^\circ}{RT_o}} = e^{-\frac{-33,800}{1.987x298}} = e^{57.08} = 6.17x10^{24}$$

Calculate $\hspace{3cm} \Delta H_r^\circ = (-2)x(-70.9)+(-1)x(0)+2x(-94.4) = -47.0\frac{kcal}{mol}$

Assume for simplicity (in order to find a first estimate for equilibrium conditions) that

$\Delta H_r \approx const \approx \Delta H_r^\circ$

Then

$$\frac{d\ell nK}{dT} = \frac{\Delta H_r^\circ}{RT^2} \quad ; \quad T = T_o = 298 \quad K = K_{298}$$

$$\ell n\left(\frac{K_T}{K_{298}}\right) = \frac{\Delta H_r^\circ}{R}\left(\frac{1}{298}-\frac{1}{T}\right)$$

$$K_T = K_{298}e^{\frac{\Delta H_r^\circ}{R}\left(\frac{1}{298}-\frac{1}{T}\right)}$$

$$K_{873} = e^{57.08 - \frac{47,000}{1.987}\left(\frac{1}{298}-\frac{1}{873}\right)} = e^{4.80}$$

$$\underline{K_{873} = 121.78}$$

Note the dramatic drop in K with temperature due to the exothermicity of the reaction $\left(\Delta H_r < 0\right)$. While equilibrium would have been all the way to the right at 298 K we cannot operate at such conditions because the rate is too low.

Let us see what are the equilibrium limitations at 873 K. Solve equation (B) for K_y expressed in terms of extent (see equation (C))

Solve by trial and error equation (C) for equilibrium extent $X_e = X$.

$$\frac{X^2(3-X)}{(1-X)^3} = K_{873}\left(\frac{P}{P_0}\right) \tag{C}$$

where $K_{873} = 121.78$; $\quad \dfrac{P}{P_o} = 1$. Note that elevated pressure, as predicted by L'Chatelier's principle,

would help move the equilibrium to the right.

.Rearrange equation (C) to use Newton-Raphson procedure

$$\phi(X) = 0 = X^2(3-X) - 121.78(1-X)^3$$

$$D\phi(X) = 3X(2-X) + 365.34(1-X)^2$$

$$X_{n+1} = X_n - \frac{\phi(X_n)}{D\phi(X_n)} \tag{D}$$

Using a starting guess of $X_O = 0.5$ (mol) the Newton Raphson algorithm (D) yields:

Iteration No.	$n = 0$	1	2	3	4	5
Extent (mol)	0.5	0.656	0.742	0.773	0.777	0.777

$X = X_e = 0.777$ (mol)

Conversion of SO_2 is:

$$x_{SO_2} = \frac{n_{SO_{2,0}} - n_{SO_2}}{n_{SO_{2,0}}} = \frac{2 - (2-2X)}{2} = \frac{2X}{2} = X \ (\text{mol})/\ 1 \ (\text{mol})$$

$$x_{SO_{2\,eq}} = 0.777 \ll 0.99$$

Equilibrium conversion of 0.99 required by emission control cannot be reached under these conditions.

Equilibrium extent could be increased by

-        lowering the temperature (but rates are lower)

-        increasing the pressure (some of it can be recovered by running a turbine at the end of reactor as done in the former USSR)

2.7   Solution Thermodynamics

The equilibrium distribution of inorganic compounds in aqueous systems is of great importance in environmental engineering. These calculations are more complex than the gas phase case because of two additional considerations. (i) charge neutrality has to be maintained. (ii) system is often non-ideal. The importance of this in environmental applications is illustrated by a number of examples below.

Example 1:   Heavy metals have toxicological impact and often get incorporated in biota such as fish. The free ion form M^{++} for example, is often the toxic form while the complexes such as MOH^+, $M(OH)_2$ or ligands with SO_4 or other negative ions are considered to be less harmful. The distribution of the metal in various forms is a function of the total concentration and the pH of the solution. Solution thermodynamics provides us with a means of doing such calculations and helps in making judicious policy decisions.

Example 2:   Consider a soil system that has some lead contamination or naturally occurring lead. The question is whether the lead is going to remain there or dissolve in ground water and enter into drinking water. The lead may remain in the solid phase depending on the pH or the presence of other ions (common ion effect described later).

Example 3:   Consider SO_2 generated in a pollutant plume in the gas phase. This is a highly soluble gas and enters the aqueous phase with rain water. It then reacts to form various ionic species such as HSO_3, SO_3^{--} , SO_4^{--} etc. The equilibrium distribution is important in many applications.

Example 4:   Consider mercury, a highly volatile toxic metal, that is highly poisonous. Depending on the pH of the aqueous environment, mercury can be found in various forms such as HgH, Hg, Hg^{++}, Hg_2^{++}, HgO, $HHgO_2$ and $Hg(OH)_2$ forms. When converted to the organic form, monomethyl mercury (CH_3Hg) can be ingested by microorganisms; it becomes lipophyllic and gets accumulated in body fats of fish. Consumption of contaminated fish results in damage to the central nervous system, liver and kidneys and causes impaired child development. In 1950s, 200 people in Minamata Bay in Japan died from mercury poisoned fish.

2.8   STUDY QUESTIONS

What is the significance of the rank of the stoichiometric matrix?

State the measure of progress of reactions for multiple reactions?
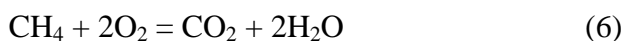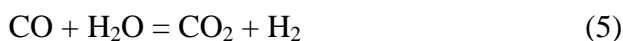
How does the equilibrium constant vary with temperature?

How is K_{eq} and K_y related to each other? Show one example?

2.9   EXERCISES

2.1   The principle of conservation of elements must be applied in order to obtain the stoichiometric coefficients in a single reaction. Assume that there are S chemical species that are either products or reactants in the reaction and there are N elements present as constituents. Let the number of atoms of element i in species j be υ_j^i. Let the yet unknown stoichiometric coefficient of species j be υ_j. Show that the conservation principle above requires $\sum_{j=1}^{S} \upsilon_j \upsilon_j^i = 0$ for all i = 1, 2,.N. Apply this to the reaction of complete combustion of methane and show how to determine the unknown $\upsilon_j's$.

2.2   In a reaction system consisting of methane, oxygen, carbon monoxide, water, hydrogen and carbon monoxide, the following 6 reactions (R'= 6) may occur:

$CH_4 + 3/2\ O_2 = CO + 2H_2O$ (1)
$CO + 1/2\ O_2 = CO_2$ (2)
$CH_4 + H_2O = 3H_2 + CO$ (3)
$H_2 + 1/2\ O_2 = H_2O$ (4)
$CO + H_2O = CO_2 + H_2$ (5)
$CH_4 + 2O_2 = CO_2 + 2H_2O$ (6)

Find the number of independent reactions R.

2.3   Carbon (10 moles initially) is burned with oxygen. At the end of reaction 4 moles of carbon are left and 4 moles of CO are produced. The produced amount of CO_2 is unknown.
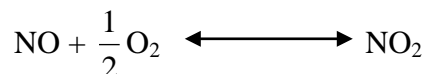
 (i)   Write the stoichiometric matrix with carbon and CO as components (1) and (2)

(ii)   Find the matrix in echelon form.

(iii)   Find the moles of O_2 consumed and CO_2 produced in the process.

2.4   The equilibrium constant for

$$CO_2 \longleftrightarrow CO + \frac{1}{2}O_2 \quad \text{at 1000 K} \quad \text{is } 6.0462*10^{-11}.$$
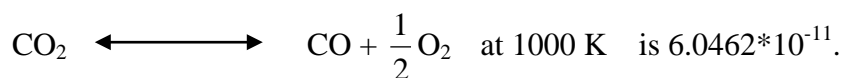
Find the value at 2600 K if the heat of reaction is 282 kj/mole.

2.5   Find the thermodynamic data for the reaction

$$NO + \frac{1}{2}O_2 \longleftrightarrow NO_2$$

Using a suitable database (report which one you used) over a temperature range of 500 to 2500 K, determine at what temperature would you expect a larger NO_2 concentration. Low or high? What is the equilibrium composition?

2.6   What is the effect of pressure on CO formation in a combustion system? At 2600 K, find the CO contents of the exhaust gas if the pressure were 2 atm. Initial composition is the same 18 % CO_2 , 3.3 % O_2,78.7 % N_2 as in the Matlab program example.

2.7   Propane is burned in air with 1.25 times the stoichiometric air. Find the composition of exhaust gases assuming that only CO_2 and H_2O are formed.

2.8   For the composition in Question (2.7) find the equilibrium composition of CO if the combustion takes place at 1800 K and 1 atm pressure.

2.9   Find the equilibrium composition for the above case using the net program.

See APPENDIX for use of MATLAB.

ADDITIONAL READINGS

If you need to refresh your knowledge of chemical thermodynamics consult the books that you are most familiar with. Some of the popular references are:

1. J. M. Smith, H.C. Van Ness and M.M. Abbot , INTROUCTION TO CHEMICAL AND ENGINEERING THERMODYNAMICS. 7th edition. (Textbook used in many chemical engineering curricula for over 50 years).

2. S. I Sandler. CHEMICAL BIOCHEM,ICAL AND ENGINEERING THERMODYNAMICS. 2006. REPLACES OLDER SANDLER'S BOOKS WHICH HAVE BEEN THE MAJOR COMPETITOR TO REFERENCE 1.

3. MIT Open Course Work. Chemical Engineering Thermodynamics. (ocw.mit.edu). Try this or other materials on the web.