2.1 Introduction

This chapter explains the basics of thermodynamic 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 the chemical equilibria are provided at the end of the 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 envelope around a finite mass of reactants and the contents of that envelope are our system in its initial state. We can count the atoms of each atomic species present in each reactant species. 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 remaining reactions and 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$_4$, here 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.

$$n_j (mol) = \frac{m_j (kg)}{M_j} \times 1000 = \frac{m_j}{M_j}$$  \hspace{1cm} (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.

\[
n_j^*(\text{lb mol}) = \frac{m_j(\text{lb})}{M_j}
\]  

(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 lb mol is 453.4 times larger than a mole, i.e. 1 (lb/mol) = 453.4 moles. Accordingly, the Avogadro’s constant for a lb mol is \( L = 2.7308 \times 10^{26} \) (lb mole\(^{-1}\)) and for a kmol is \( L = 6.023 \times 10^{26} \) (kmol\(^{-1}\)).

To illustrate how reaction stoichiometry is developed, consider the complete combustion of methane (\( \text{CH}_4 \)) to carbon dioxide, \( \text{CO}_2 \). This is a reaction between methane, \( \text{CH}_4 \), and oxygen, \( \text{O}_2 \), that creates carbon dioxide, \( \text{CO}_2 \), and water \( \text{H}_2\text{O} \) by complete combustion.

So we have 

\[
\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

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 \( \text{CH}_4 \) reacted must produce one mole of \( \text{CO}_2 \). Since hydrogen is only contained in methane on the reactant side, and there are 2\( \text{H}_2 \) (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 (\( \text{O}_2 \)) in the mole of carbon dioxide (\( \text{CO}_2 \)) 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:

\[
\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}
\]

(2)

Hence, the requirement to balance out the atomic species, i.e. 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:
\[
\frac{1}{2} CH_4 + O_2 \leftrightarrow \frac{1}{2} CO_2 + H_2O
\]  
(2a)

or say 2
\[
2CH_4 + 4O_2 \leftrightarrow 2CO_2 + 4H_2O
\]  
(2b)

Reaction stoichiometry, for a single reaction, such as that of equation (1) can now be represented by:
\[
\sum_{j=1}^{s} \nu_j A_j = 0
\]
(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.)
- \( \nu_j \) = stoichiometric coefficient for the \( j \)-th species defined as
  \( \nu_j > 0 \) for product, \( \nu_j < 0 \) for reactant

The stoichiometric equation satisfies the overall mass balance for the system
\[
\sum_{j=1}^{s} \nu_j M_j = 0
\]
(4)

where \( M_j \) = molecular weight of species \( j \).

For example, for reaction (1) of methane combustion we have
\( \nu_{CH_4} = -1; \ \nu_{O_2} = -2; \ \nu_{CO_2} = 1; \ \nu_{H_2O} = 2 \)

If a reaction system can be described by a single reaction, 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:
\[
aA + bB = pP + sS
\]  
(3a)

where \( A, B, P, S \) are chemical species and \( a, b, p, s \) are their stoichiometry coefficients, respectively.

\( CH_4, B = O_2, P = CO_2 \ and S = H_2O \ in our example \) 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
\[
\frac{\text{moles of } A \text{ reacted}}{a} = \frac{\text{moles of } B \text{ reacted}}{b} = \frac{\text{moles of } P \text{ reacted}}{p} = \frac{\text{moles of } S \text{ reacted}}{s}
\]  
(3b)

Hence, a single reaction implies that the ratio of product produced and reactant consumed, or, a
ratio of one reactant consumed to the other reactant consumed, are constants e.g.
\[
\frac{\text{moles of } P \text{ produced}}{\text{moles of } A \text{ reacted}} = \frac{p}{a}; \quad \frac{\text{moles of } A \text{ reacted}}{\text{moles of } B \text{ reacted}} = \frac{a}{b}
\]
(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:
\[
\sum_{j=1}^{S} \nu_{ij} A_j = 0; \quad i = 1,2...R
\]
(5)
where
\[
\nu_{ij} = \text{stoichiometric coefficient of species } j \text{ in reaction } i
\]
\[
R = \text{total number of independent reactions}
\]

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:
\[
2C + O_2 \leftrightarrow 2CO \quad (5a)
\]
\[
2CO + O_2 \leftrightarrow 2CO_2 \quad (5b)
\]

Here, we have a total of \( S = 4 \) species \( (j=1,2,3,4 \text{ for } C, O_2, CO, CO_2, \text{ respectively}) \), 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 \( (\nu_{i5} = 0) \) 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
\[
C + O_2 \leftrightarrow CO_2 \quad (5c)
\]
would add a third row to the above matrix of stoichiometric coefficients, namely
\[
\begin{pmatrix}
-1 & 1 & 0 & 1
\end{pmatrix}
\]
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 eqs. (5a), (5b) and (5c). Finding the rank
of the matrix of stoichiometric coefficients will always tell how many independent reactions are needed
to characterize the stoichiometry of the system. At the end of the chapter we will show how to find the
rank of a matrix using MATLAB.
In summary, in any reaction system we should strive to establish the reaction stoichiometry by using the principle of conservation of 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

\[ \sum_{j=1}^{s} \nu_j A_j = 0 \]  

(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 \( n_{j0} \) is the initial number of moles of \( j \) at time \( t_0 \), then reaction stoichiometry dictates that moles of all species can be related to their initial moles via (molar) extent of reaction \( X \).

\[ n_j = n_{j0} + \nu_j X \]  

(6a)

\( (\text{moles of } j \text{ present}) = (\text{moles of } j \text{ originally present}) + (\text{moles of } j \text{ produced by reaction}) \)

Moles of \( j \) produced by reaction are given by the product of the stoichiometric coefficient, \( \nu_j \), 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. For a flow system at steady state,

\[ F_j = F_{j0} + \nu_j \dot{X} \]  

(6b)

where \( F_j, F_{j0} \) (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 (6) 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 \( X = (n_A - n_{A0}) / \nu_A \). Moles of all other species \( n_j \) can now be found provided their initial moles \( n_{j0} \) were given. Equation (6) also indicates 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
\[ X_{\text{max}} = \left( \frac{n_{j_0}}{v_j} \right) \text{ smallest value over all } j \] 

(7)

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

For multiple reactions

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

(5)

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

\[ n_j = n_{j_0} + \sum_{i=1}^{R} v_y X_i \] 

(8)

\[(\text{moles of } j \text{ present}) = (\text{moles of } j \text{ initially present}) + \sum_{\text{all reactions}} (\text{moles of } j \text{ produced by reaction } i) \]

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

\[ n_{Ao} x_A = \xi v_A \bar{X} \quad \text{or} \quad F_{Ao} x_A = \xi v_A \bar{X} \]

(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 extent has units of moles, i.e., 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.

\[ \Delta H_{r,i} = \sum \Delta H_{f(\text{products})} - \sum \Delta H_{f(\text{reactants})} \]  

(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

\[ \Delta H_{r,i} = \sum_j v_{ij} \Delta H_{f,j} \]  

(11a)

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

\[ \Delta H_{r}^{o,i} = \sum_j v_{ij} \Delta H_{f}^{o,j} \]  

(12)

where \( \Delta H_{f}^{o,j} \) 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.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \Delta H_{r}^{o} ) J/mol</th>
<th>( \Delta S_{r}^{o} ) J/molK</th>
<th>( \Delta G_{r}^{o} ) =( \Delta H_{r}^{o} - T\Delta S_{r}^{o} ) J/molK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.0</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Water</td>
<td>241,818</td>
<td>-44.3557</td>
<td>-228,600</td>
</tr>
<tr>
<td>Methane</td>
<td>-74,520</td>
<td>-79.49</td>
<td>-50,832</td>
</tr>
<tr>
<td>Nitric oxide NO</td>
<td>90,250</td>
<td>11.96</td>
<td>86,686</td>
</tr>
<tr>
<td>Nitrogen dioxide NO2</td>
<td>33,180</td>
<td>-63.02</td>
<td>51,961</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>-110,525</td>
<td>89.73</td>
<td>-137,267</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>393,509</td>
<td>2.84</td>
<td>-394,355</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>296,830</td>
<td>11.04</td>
<td>-300,139</td>
</tr>
<tr>
<td>Sulfur trioxide</td>
<td>-395,720</td>
<td>-85.16</td>
<td>-370,341</td>
</tr>
<tr>
<td>Ozone</td>
<td>142,664</td>
<td>-67.53</td>
<td>162,789</td>
</tr>
</tbody>
</table>
Group contribution methods are also available to predict these 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 following three paths

(i) Cool reactants form $T$ to $T_{\text{ref}}$.
(ii) Carry out reaction at $T_{\text{ref}}$ with an associated enthalpy change of $\Delta H^o_{r, i}$
(iii) Heat the products back form $T_{\text{ref}}$ to $T$.

The steps are schematically shown in the Figure 1.

![Figure 1](image)

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.

$$\Delta H_{r,i} = \Delta H^0_{r,i} + \sum_j \left[ \int_{T_{r,f}}^{T} v_{r,j} C_{pj} \, dT \right]$$  \hspace{1cm} (13)

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

$$C_{pi} = \sum_{\alpha=0}^{\alpha_{\text{max}}} A_{\alpha j} T^\alpha$$  \hspace{1cm} (14a)

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

8
or

\[ C_p = A + BT + CT^2 + DT^{-2} \]  \hspace{1cm} (14b)

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

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

Substituting we find

\[ \Delta H_{i,r} = \Delta H_{i,r}^0 \left[ j \sum_{j=1}^l \frac{A_{\alpha j}}{T_{\text{ref}} + T} \ln \frac{T_{\text{ref}}}{T} + \sum_{j=1}^l \sum_{\alpha=0}^{\alpha_{\text{max}}} \frac{A_{\alpha j}}{\alpha + 1} \left[ T_{\alpha}^\alpha - T_{\alpha_{\text{ref}}}^\alpha \right] \right] \]  \hspace{1cm} (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 \( T_{\text{ref}} \) and the coefficients \( A_{\alpha j} \) in eq (15a) for temperature variation of molar specific heat (e.g. heat changes) \( C_p \) for each species.

### 2.5 Entropy change in reaction

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

\[ \Delta S^{\circ}_r = \sum_{j=1}^l v_j \Delta S^{\circ}_{f,j} \]  \hspace{1cm} (16)

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

\[ \Delta S_r = \Delta S_r^0(T_{\text{ref}}) + \sum_{j=1}^l \int_{T_{\text{ref}}}^T v_j \frac{C_{pj}}{T} \, dT \]  \hspace{1cm} (17)

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

\[ \Delta S_r = \Delta S_r^0 + \sum_{j=1}^l v_j A_{\alpha j} \ln \frac{T}{T_{\text{ref}}} + \sum_{j=1}^l \sum_{\alpha=0}^{\alpha_{\text{max}}} \frac{A_{\alpha j}}{\alpha + 1} \left[ T_{\alpha}^\alpha - T_{\alpha_{\text{ref}}}^\alpha \right] \]  \hspace{1cm} (18)

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

\[ \Delta G_r = \Delta H_r - T \Delta S_r \]  \hspace{1cm} (19)

Knowledge of how \( \Delta G_r \) 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, \( \Delta G_r \) typically increases with temperature.
**Example:**

i) Thermodynamic calculation for CO oxidation to CO$_2$. This is an exothermic reaction.

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta H_r$ (J/mole)</th>
<th>$\Delta S_r$ (J/mole K)</th>
<th>$\Delta G_r$ (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>-283,866</td>
<td>-88.55</td>
<td>-239,590.8</td>
</tr>
<tr>
<td>1500</td>
<td>-282,623</td>
<td>-86.931</td>
<td>-195,692.0</td>
</tr>
<tr>
<td>2500</td>
<td>-244,892</td>
<td>-83.71</td>
<td>-110,457</td>
</tr>
<tr>
<td>2600</td>
<td>-274,733</td>
<td>-82.33</td>
<td>-60,659</td>
</tr>
</tbody>
</table>

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

ii) Steam reforming of methane

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]

This is an endothermic reaction.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta H_r$ (J/mole)</th>
<th>$\Delta S_r$ (J/mole K)</th>
<th>$\Delta G_r$ (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>215,880</td>
<td>238.2</td>
<td>96,000</td>
</tr>
<tr>
<td>700</td>
<td>222,000</td>
<td>248.3</td>
<td>35,700</td>
</tr>
<tr>
<td>900</td>
<td>224,700</td>
<td>251.3</td>
<td>-1,762</td>
</tr>
<tr>
<td>1000</td>
<td>225,660</td>
<td>252.6</td>
<td>-26,960</td>
</tr>
</tbody>
</table>

Reaction becomes favorable only at higher temperatures. This is always true for an endothermic process. Note that $\Delta G_r$ decreases with increasing the temperature which is consistent with 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.

\[ \sum_{j=1}^{s} \nu_j A_j = 0 \]  

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) \[ \sum_{j=1}^{s} \nu_j \tilde{G}_j = 0 \]  

where

ii) \[ n_j = n_{jo} + \nu_j X_e \]  for all \(j\) \n
iii) appropriate equation of state

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

In general

\[ \tilde{G}_j = G_j + RT \ln a_j \]  

where \(G_j^0\) is the Gibbs free energy of pure species \(j\) (function of temperature only).

\(a_j\) is the activity of species \(j\);
\(n_j\) is moles of \(j\);
\(n_{jo}\) is initial moles of \(j\);
\(\nu_j\) is stoichiometric coefficient of \(j\) (positive for products, negative for reactants);
\(T\) is temperature of the system;
\(X_e\) is the equilibrium reaction molar extent;

Substitution of the second equality of equation (14) for \(\mu_j\) into equation (12) yields

\[ \sum_{j=1}^{s} \nu_j G_j + RT \sum_{j=1}^{s} \nu_j \ln a_j = 0 \]  

Recognizing that \(\nu_j \ell n a_j\) is \(\ell n a_j^{\nu_j}\) and that the sum of logarithms \(\ell n \prod_{j} a_j^{\nu_j}\) is the logarithm of the product \(\ell n \prod_{j=1}^{s} a_j^{\nu_j}\) we get the following equation
We define the standard Gibbs free energy of reaction at temperature $T$ by

$$\Delta G_r = \sum_{j=1}^{s} \nu_j G^0_j$$

with all $G_{-j}$ being evaluated at the temperature $T$ of interest.

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

$$K = \prod_{j=1}^{s} a_j^U = e^{\frac{\Delta G_r}{RT}}$$

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 $T_{ref} = 298$K (25°C) (or can be found from $\Delta H$ and $\Delta S$ data as shown in previous section) it is convenient to calculate the Gibbs free energy change due to reaction $\Delta G_{f_r}$ at these standard conditions as:

$$\Delta G_{f_r} = \sum_{j=1}^{s} \nu_j \Delta G_{f_j}$$

The equilibrium constant at standard temperature is then obtained from equation (25).

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

$$\frac{d\ln K}{dT} = \frac{\Delta H_r}{RT^2}$$

$$T = T_e (= 298$ K); $K_{298} = \exp(-\Delta G_{rT_0} / RT_0)$$

where $\Delta H_r$ is the standard heat of reaction at temperature $T$ (calculated as shown in previous section),
$K_{298}$ is the equilibrium constant at the standard state temperature of $T_0$ (most often 298K) and $\Delta G_{\text{r0}}$ is the standard Gibbs free energy of reaction at $T_0$ which is obtained from tabulated Gibbs free energies of formation $\Delta G_{f_j}$.

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 total pressure of the system, $\phi_j$ is the fugacity coefficient of $j$ while $\tilde{f}_j$ is the partial molal fugacity of $j$.

The needed relations are included below:

$$a_j = y_j P \left( \frac{\tilde{f}_j}{y_j P} \right) / 1 \text{ atm} = p_j \left( \frac{\tilde{f}_j}{y_j P} \right) / 1 \text{ atm}$$

(30)

$$a_j = y_j P \phi_j / 1 \text{ atm} = p_j \phi_j / 1 \text{ atm}$$

(30a)

$$K = \prod_{j=1}^s a_j^{(y_j)} = \left( \frac{P}{1 \text{ atm}} \right) \prod_{j=1}^s y_j^{(y_j)} \prod_{j=1}^s \phi_j^{(y_j)}$$

(31) $K = \left( \frac{P}{1 \text{ atm}} \right) \sum y_j K_j K_{\phi}$ where $P_0 = 1 \text{ atm.}$

(31a)

or

$$K = \prod_{j=1}^s a_j^{(y_j)} = \prod_{j=1}^s p_j^{(y_j)} \prod_{j=1}^s \phi_j^{(y_j) / \text{ atm}} \sum y_j$$

(32)

$$K = \prod_{j=1}^s a_j^{(y_j)} = K_p K_{\phi} / \text{ atm} \sum y_j$$

(32a)

The generalized fugacity coefficients $\phi_j$, $\phi_j = \left( \frac{\tilde{f}_j}{y_j P} \right)$, would have to be evaluated from an appropriate equation of state. If Lewis-Randall rule is used $\phi_j = \left( \frac{\tilde{f}_j}{P} \right)$.

For gases at low pressure, $K_{\phi} \approx 1$

$$K = \left( \frac{P}{1 \text{ atm}} \right) \sum y_j K_p = K_p / \left( 1 \text{ atm} \right) \sum y_j$$

(32b)

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:

$$a_j = x_j \gamma_j$$

(33)

where $\gamma_j$ is the activity coefficient.
\[
K = \prod_{j=1}^{s} a_j = \prod_{j=1}^{s} (k_j \gamma_j)^{v_j} = K_x K_y \tag{34}
\]

Since \( x_j = \frac{C_j}{C} \)

\[
K = C \sum_{j=1}^{c} K_c K_y \tag{35}
\]

For an ideal mixture, \( K_y \approx 1 \)

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

**Example:**

Reaction System: \( 2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3 \)

Conversion of 99% is desired

Conditions: \( T = 600^\circ\text{C} = 873^\circ\text{K} \)

\( P = 1 \text{ atm} \)

Stoichiometric Feed of Pure Reactants

No Nitrogen

Calculate equilibrium conversion of \( \text{SO}_2 \) and see if 99% can be reached.

\( \Delta G_f \) and \( \Delta H_f \) for various species are given in (kcal/mol) below.

**Basis:** 2 moles of \( \text{SO}_2 \).

Total number of species \( S = 3 \)

\[
\sum v_j = -1
\]

\[
n_{tot} = \sum_{j=1}^{3} n_{j0} = 3n_{tot} = \sum n_j = 3 - X
\]

<table>
<thead>
<tr>
<th>Species Name</th>
<th>No.</th>
<th>Stoich. Coeff.</th>
<th>( \Delta G_f )</th>
<th>( \Delta H_f )</th>
<th>( n_{j0} )</th>
<th>( n_j = n_{j0} + v_j X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 )</td>
<td>1</td>
<td>-2</td>
<td>-71.7</td>
<td>-70.9</td>
<td>2</td>
<td>2 - 2X</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1 - 1X</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>3</td>
<td>2</td>
<td>-88.6</td>
<td>-94.4</td>
<td>0</td>
<td>0 + 2X</td>
</tr>
</tbody>
</table>

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

\[
K = K_y \left( \frac{P}{P_0} \right)^{\sum_{j=1}^{s} v_j} = K_y \left( \frac{P}{P_0} \right)^{-1} = K_y \left( \frac{P_0}{P} \right)
\]

where

\[ (A) \]
Evaluate the mole fraction of each species in terms of reaction extent $X$

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

Substitute these mole fractions in the expression for $K_y$

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

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

From (A)

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

Calculate $K_{298}$ at 298°K

$$\Delta G_f = (-2)x(-71.7) + (-1)x(0) + 2x(-88.6) = -3.38 \frac{\text{kcal}}{\text{mol}}$$

$$K_{298} = e^{\frac{-\Delta G_f}{RT_o}} = e^{\frac{-33.800}{1.987x298}} = e^{57.08} = 6.17x10^{24}$$

Calculate

$$\Delta H_f = (-2)x(-70.9) + (-1)x(0) + 2x(-94.4) = -4.70 \frac{\text{kcal}}{\text{mol}}$$

Assume for simplicity (in order to find a first estimate for equilibrium conditions) that $\Delta H_f \approx \text{const} \approx \Delta H_f$

Then

$$\frac{d\ln K}{dT} = \frac{\Delta H_f}{RT^2} ; \quad T = T_o = 298 \quad K = K_{298}$$

$$\ln \left( \frac{K_T}{K_{298}} \right) = \frac{\Delta H_f}{R} \left( \frac{1}{298} - \frac{1}{T} \right)$$

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

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

$$K_{873} = 121.78$$
Note the dramatic drop in K with temperature due to the exothermicity of the reaction \((\Delta H_r < 0)\). 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))

\[
\frac{X^2(3-X)}{(1-X)^3} = K_{873} \left( \frac{P}{P_0} \right)
\]

(C)

where \(K_{873} = 121.78\); \(\frac{P}{P_0} = 1\). 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

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

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

\[
X_{n+1} = X_n - \frac{\phi(X_n)}{D\phi(X_n)}
\]

(D)

Using a starting guess of \(X_0 = 0.5\) (mol) the Newton Raphson algorithm (D) yields:

<table>
<thead>
<tr>
<th>Iteration No.</th>
<th>n = 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent (mol)</td>
<td>0.5</td>
<td>0.656</td>
<td>0.742</td>
<td>0.773</td>
<td>0.777</td>
<td>0.777</td>
</tr>
</tbody>
</table>

\(X = X_e = 0.777\) (mol)

Conversion of \(SO_2\) is:

\[
x_{SO_2} = \frac{n_{SO_2}}{n_{SO_2}} = \frac{2-(2-2X)}{2} = \frac{2X}{2} = X\) (mol)/ 1 (mol)

\(x_{SO_2_{eq}} = 0.777 << 0.99\)

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 \( \text{M}^{++} \) for example, is often the toxic form while the complexes such as \( \text{MOH}^+ \), \( \text{M(OH)}_2 \) or ligands with \( \text{SO}_4 \) 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 \( \text{SO}_2 \) 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 \( \text{HSO}_3^- \), \( \text{SO}_3^- \), \( \text{SO}_4^- \) 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 \( \text{HgH}, \text{Hg}, \text{Hg}^{++}, \text{Hg}_2^{++}, \text{HgO}, \text{HHgO}_2 \) and \( \text{Hg(OH)}_2 \) forms. When converted to the organic form, monomethyl mercury (\( \text{CH}_3\text{Hg} \)) can be inserted 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  Rank and checking linear independence of reactions using MATLAB

To appreciate fully what the MATLAB program does for you look first at Appendix A. In that appendix we describe the procedures involved in obtaining the rank of the matrix and identifying independent reactions.

Consider the carbon dioxide formation considered earlier. The reaction scheme is

\[
\begin{align*}
2C + O_2 & \iff 2CO \\
2CO + O_2 & \iff 2CO_2 \\
C + O_2 & \iff CO_2
\end{align*}
\]

(5a)  (5b)  (5c)

**Step 1:** type in the stoichiometric matrix as follows: Each row is reaction index and each column is the species index. Thus each row represents one reaction in the system. We take carbon, C, to be species 1, oxygen to be 2, carbon monoxide is 3, carbon dioxide is 4. Then the matrix of stoichiometric coefficients is:

\[
v = \begin{bmatrix}
-2 & -1 & 2 & 0 \\
0 & -1 & -2 & 2 \\
-1 & -1 & 0 & 1
\end{bmatrix}
\]

**Step 2:** find the rank by typing the following

```
rank(v)
```

For the above case the answer will be 2 so that there are only two independent reactions. In other words the third reaction is a linear combination of the first two reactions. To find this combination go to step 2a.

**Step 2a:** do this if the rank is less than the number of reactions.

Type

```
rref(v')
```

Note that \( v' \) is the transpose of the stoichiometric matrix and the above command reduces the tranposed matrix to the Echelon form (in this form the main diagonal of the has ones on it). The result will be

\[
\begin{bmatrix}
1.0000 & 0 & 0.5000 \\
0 & 1.0000 & 0.5000 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]
The last column gives the linear combination for the third reaction. Thus reaction (5c) is equal to 0.5 times the first reaction plus 0.5 times the second reaction. In this simple example it is obvious by inspection as well.

**Step 3:** To find the system invariants (these will be relations between moles produces or consumed among various species), type

\[ \text{rref(v)} \]

This reduces the stoichiometric matrix to the echelon form. The result for our example is:

\[
\begin{bmatrix}
1 & 0 & -2 & 1 \\
0 & 1 & 2 & -2 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{bmatrix}
\]

The last two columns here provide the invariants. Thus

\[ \Delta F_3 = -2 \times \Delta F_1 + 2 \times \Delta F_2 \]

and

\[ \Delta F_4 = 1 \times \Delta F_1 - 2 \times \Delta F_2 \]

Here \( \Delta F \) represents the change in molar flow rate between the exit and entrance for species \( I \).

Note that the last row is all zero indicating that the third reaction is redundant and does not contribute to the invariant. (recall that the rank was two).

Let us see what the implication of all this is; the above equations tell us that only two values \( \Delta F_1 \) and \( \Delta F_2 \) are independent. For example, in an experiment suppose we find that 5 mole/sec of carbon has reacted.

Then \( \Delta F_1 = -5 \).

We also find that 4 mole/sec of oxygen is consumed.

\[ \Delta F_2 = -4 \]

Then using the equations above we find

\[ \Delta F_3 = 2 \times 5 \times 4 = 2 \text{ mole/sec is the amount of CO formed.} \]

Also

\[ \Delta F_4 = 5 \times 4 = 3 \text{ mole/sec of CO}_2 \text{ is formed.} \]
If the measurements show otherwise, then either the measurements are in error or some other C bearing species is being formed (not likely here). Hence in this case the measurements would be in error. Thus, the invariants of a reaction are useful in proper bookkeeping of the various species.

2.9 MATLAB PROGRAM FOR CALCULATION OF EQUILIBRIUM COMPOSITION OF A REACTING GAS MIXTURE

The following program calculates the equilibrium composition of a gas mixture. The program is written for the SO\textsubscript{2} example and can be modified easily for other cases. The best way to learn this is for the students to TYPE out the program as it is and execute it on matlab. This way they get familiar with the programming as well. The program also illustrates the use of the solver FSOLVE to solve a set of non-linear algebraic equations. The program is interspaced with some explanation and these statements need to be omitted in the actual program.

PREAMBLE SECTION

% filename gaseq; created on jan 31-03 by P.A.Ramachandran.
% computes the equilibrium composition of a reacting mixture.

% preamble
    global ng ns nr tempin prin ctot xg nu ...
    global keq298 keq delhr
    global rgas
    global n ntot

At this part of the program the number of gas phase species ng and number of reactions nr are to be entered.

% number of species and number of reactions
    ng = 3 ;
    nr = 1 ;

DIMENSIONING THE VECTORS

This is required but no action by user is needed.

% intialize the vectors.
    keq298 = zeros(nr, 1 );
    keq = zeros(nr, 1 );
delhr = zeros(nr, 1);
xg = zeros(ng,1);
nu = zeros ( nr, ng);
zeta = zeros(nr,1) ;

**USER DATA SECTION**

A: REACTIONS

Here the reaction specific variables are entered

These are the stoichiometric matrices and the equilibrium constants for each reaction at 298K and the heat of reaction at 298K. The program assumes that the heat of reaction is independent of temperature. Note that the gas constant rgas must have consistent unit with the heat of reaction.

% provide values for stoichimetry and eq constants.
nu(1,1) = -2. ;
nu(1,2) = -1.
nu(1,3) = 2. ;
keq298(1) = 6.1593E+24 ;
delhr(1) = -47000.0 ; %assumed constant (not a function of T)
rgas = 1.97 ; % gas constant; use consistent units

B: PROCESS CONDITIONS

Here the temperature, pressure and the moles of each species present in the initial mixture are specified.

The user must provide a guess value for the extent of reaction (zeta vector). Try to provide realistic values, for example the conversion of a key component can not be greater than one. This will fix the maximum value for zeta

% provide the feed conditions.
tempin = 873.0;
prin = 1.0e+05;
% initial moles.
xg(1) = 2.0;
xg(2) = 1.0;
xg(3) = 0.0;
% provide initial values for extent of reactions
zeta(1) = 0.4

CALCULATION SECTION
At this stage the matalb takes care of the rest of the calculations
% mtlab function fsolve solver is called to find the roots
% the required equations are programmed in a file fun_eq.m
zeta = fsolve( 'fun_eq', zeta)
% post process the results.
% molar flow rates at exit = TYPE n
% total moles = TYPE ntot

Post processing can be done by typing n which gives the moles of species at
Equilibrium,. The conversion and other required information can be calculated easily on the matlab
command window.

FUNCTION SUBROUTINE
The program requires a function subroutine which calculates the function to be solved. The subroutine is
in a file fun_eq.m and the listing is shown below. No changes in this by user is needed. Students may
want to study how this is written by following this with the text earlier.

function fvec = fun_eq(  zeta)
% filename fun_eq; created on jan 31-03 by P.A.Ramachandra
% Defines the (nr) functions to be solved.

% preamble
   global ng ns nr tempin prin  ctot xg  nu ...
       global keq298 keq delhr
       global n  ntot
       global rgas
fvec = zeros ( nr,1 );

ptotatm = prin /1.0e+05 ;
% find K at the desired conditions
for i = 1: nr
    keq(i)=keq298(i)*exp( delhr(i) /rgas *(1./298-1./tempin)) ;
end

% number of moles of each species for the given extents
% nj0 = 1 for these calculations
for j = 1: ng
    n(j) = xg(j);
    for i=1:nr
        n(j) = n(j) + nu(i,j) * zeta(i);
    end
end
% find ntot
ntot = 0.0;
for j = 1: ng
    ntot = ntot + n(j);
end
% find the mole fractions for each species
pp = n /ntot * ptotatm;

% set up discrepancy function for each reaction
for i = 1: nr
    prod = 1.0;
    for j = 1: ng
        prod = prod * pp(j)^nu(i,j);
    end
    fvec(i) = keq(i) - prod
end

The students should run the program for other cases for example to study the effect of inerts, like nitrogen, pressure or other systems involving multiple reactions.

We will now illustrate use of this program for a combustion application.
Example: Chemical equilibrium sets an upper limit on the composition of combustion gases. Given a mixture of CO, CO$_2$ and O$_2$ we need to find the CO concentration as a function of exhaust gas temperature. Once CO$_2$ is formed, it is unlikely that CO will be formed as the gas cools since the reaction rates are slowed down. Hence the maximum CO in the exhaust gas can be found from the equilibrium calculations.

As an example, consider an exhaust gas mixture with 18%CO$_2$, 3.3%O$_2$ and the rest N$_2$. Temperature of this gas is raised to 1600K. Find the equilibrium composition of this gas assuming the reaction

$$CO_2 \rightleftharpoons CO + 1/2O_2$$

We run the program with 4 species the fourth being inert (N$_2$).

The sample results are as follows:

***** COMPUTED RESULTS *********

Equilibrium constant of reaction 1 is 1.9643907E-05

Heat of reaction 1 is 279958.6 (J/mol)

Free energy change of reaction 1 is 144168.0 (J/mol)

Program converged

The extent of reaction 1 is 1.9459629E-03 (mole)

We use 100 moles total as the input conditions. Moles of CO in the exhaust gas is therefore 1.955E-03% of the total mole or 19.5 ppm (by moles or volume).

Problem for discussion

Predict the effect of temperature (range of 1000 to 2000K) on the CO content of exhaust gas and plot the results. If CO reduction was the only goal, would you operate at high temperature or low temperature

Example: Consider a gas to be 3.3%O$_2$ and rest N$_2$. This presumably simulates and exhaust gas from an internal combustion engine. The following reactions take place

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$NO + 1/2O_2 \rightleftharpoons NO_2$$

Find the concentrations of NO and NO$_2$ at 1800K and 1 atm.
Again we use the fortran program since all these gases are in the chmkin database. We modify the datafile and run the program to find the following results.

Equilibrium constant of reaction 1 is \(1.1928983 \times 10^{-4}\)
Heat of reaction 1 is 181059.9 (J/mole)
Free energy change of reaction 1 is 135194.9
Equilibrium constant of reaction 2 is \(5.1639900 \times 10^{-3}\)
Heat of reaction 2 is -57594.48 (J/mole)
Free energy change of reaction 2 is 78807.43 (J/mole)

program converged
The extent of reaction 1 is \(8.5949510 \times 10^{-2}\) (J/mole)
The extent of reaction 2 is \(1.7736210 \times 10^{-4}\) (J/mole)

\[
\text{NO formed} = 2x_1 - x_2 \\
\text{N}_2\text{O Formed} = x_2
\]
The above are percentages since the total starting moles are assumed as 100. Hence the gas has 172 ppm of NO and 1.77 ppm of NO\(_2\)

2.10 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?
2.11 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 $v_{ij}$. Let the yet unknown stoichiometric coefficient of species j be $v_j$. Show that the conservation principle above requires $\sum_{j=1}^{S} v_{ij} v_j = 0$ for all $i = 1, 2, N$. Apply this to the reaction of complete combustion of methane and show how to determine the unknown $v_j$'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:

\[
\begin{align*}
\text{CH}_4 + 3/2 \text{O}_2 &= \text{CO} + 2\text{H}_2\text{O} \\
\text{CO} + 1/2 \text{O}_2 &= \text{CO}_2 \\
\text{CH}_4 + \text{H}_2\text{O} &= 3\text{H}_2 + \text{CO} \\
\text{H}_2 + 1/2 \text{O}_2 &= \text{H}_2\text{O} \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2 \\
\text{CH}_4 + 2\text{O}_2 &= \text{CO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

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 $\text{CO}_2$ 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 $\text{O}_2$ consumed and $\text{CO}_2$ produced in the process.

2.4 The equilibrium constant for

$$
\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2 \quad \text{at } 1000 \text{ K} \quad \text{is } 6.0462 \times 10^{-11}.
$$

Find the value at 2600 K if the heat of reaction is 282 kj/mole.

2.5 Find the thermodynamic data for the reaction

$$
\text{NO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}_2
$$
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 NO₂ 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 % CO₂, 3.3 % O₂, 78.7 % N₂. 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 CO₂ and H₂O 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.