

STOICHIOMETRIC CHEMICAL EQUILIBRIUM ALGORITHM BY USING SCHEREIBER AND PITZER REAL GAS EOS AND HOMOTOPHY(CONTINUATION) METHOD FOR SOLVING NON-LINEAR SYSTEM OF EQUATIONS

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Abstract In stoichiometric (based on K equilibrium constants) thermodynamic property algorithms, it is usually ideal gas EOS is used. The basic reason for this is simplicity of using ideal gas EOS. Real gas equation of states involves complicated mathematical procedures such as root finding processes, which is time consuming as well as requires long algorithms. Ideal gas based equilibrium calculations are usually satisfies requirements for chemical reactions at atmospheric pressure zone. An equation of state with better accuracy of thermodynamic properties will be required for extreme cases, such as gas turbine combustion chamber. In this study Scheireber-Pitzer real gas equation of state will be used to predict thermodynamic properties of gases. This is a generalised EoS for gases based on Pitzer's acentric factor. Stoichiometric formulations requires equilibrium formulations. Atomic balances gives equilibrium chemical moles as much as number of available atoms, for each additional chemical an additional equilibrium formulations is needed. When equations came together, they created quite a nonlinear system of equation. These set of equation can be solved by linearisation methods. In this study, it is prefer to solve directly in non-linear form by using homotophy(continuation) method. Continuation method is relatively less dependent to initial conditions. It is based on solution of a differential equation system by using a numerical soltion method. 6th degree Runge-Kutta method is used to solve differential equation to obtain non-linear equation solution by continuation method. All the codes are developed in java programming language. The program code are given to interested researchers as free access in www.turhancoban.com adress.

Keywords: Thermodynamic properties of gases, Schereiber-Pitzer EoS, chemical equilibrium, Stochiometric algorithm for chemical equilibrium

1. Formulation of Equation of State

In this paper, We will consider Scheiber-Pitzer equation of states for pure gases. Details of the Scheiber-PitzerEoS is given below.

$$Z = \frac{P}{\rho RT} = 1 + B(T_r, \rho_r)\rho_r + C(T_r, \rho_r)\rho_r^2 + D(T_r, \rho_r)\rho_r^3 + E(T_r, \rho_r)\rho_r^5 + F(T_r, \rho_r)\rho_r^7 + G(T_r, \rho_r)\rho_r^8 + H(T_r, \rho_r)\rho_r^{10} + I(T_r, \rho_r)\rho_r^{12} \quad (1.1)$$

$$B(T_r, \rho_r) = c_1 + \frac{c_2}{T_r} + \frac{c_3}{T_r^2} + \frac{c_4}{T_r^6}$$

$$C(T_r, \rho_r) = c_5 + \frac{c_6}{T_r} + \frac{c_7}{T_r^3} + \frac{c_8}{T_r^4} \exp(-\rho_r^2) = C_1(T_r) + C_2(T_r) \exp(-\rho_r^2)$$

$$D(T_r, \rho_r) = c_9 + \frac{c_{10}}{T_r} + \frac{c_{11}}{T_r^2}$$

$$E(T_r, \rho_r) = \frac{c_{12}}{T_r^2} + \frac{c_{13}}{T_r^3}$$

$$F(T_r, \rho_r) = \frac{c_{14}}{T_r^2} + \frac{c_{15}}{T_r^3}$$

$$G(T_r, \rho_r) = \frac{c_{16}}{T_r^3} + \left(\frac{c_{17}}{T_r^3} + \frac{c_{18}}{T_r^4} \right) \exp(-\rho_r^2) = G_1(T_r) + G_2(T_r) \exp(-\rho_r^2)$$

$$H(T_r, \rho_r) = \left(\frac{c_{19}}{T_r^3} + \frac{c_{20}}{T_r^4} \right) \exp(-\rho_r^2) = H_2(T_r) \exp(-\rho_r^2)$$

$$I(T_r, \rho_r) = \left(\frac{c_{21}}{T_r^3} + \frac{c_{22}}{T_r^4} \right) \exp(-\rho_r^2) = I_2(T_r) \exp(-\rho_r^2)$$

$$c_i = C_{i,0} + C_{i,1}\omega + C_{i,2}\omega^2$$

Where ω in Scheiber-Pitzer equation of states coefficient is called **Pitzer's acentric factor**. This factor is calculated as

$$\omega = -\log_{10} P_{\text{saturated vapor}}(\text{at } T_r = 0.7) - 1 \quad (1.2)$$

Table 1.1 C[i][j] Coefficients of Scheiber-Pitzer EoS

| | j=1 | j=2 | j=3 |
|-------|---------------|---------------|----------------|
| C1,j | 0.4422590000 | 0.7256500000 | 0.0000000000 |
| C2,j | -0.9809700000 | 0.2187140000 | 0.0000000000 |
| C3,j | -0.6111420000 | -1.2497600000 | 0.0000000000 |
| C4,j | -0.0051562400 | -0.1891870000 | 0.0000000000 |
| C5,j | 0.1513654000 | 2.3067060000 | -10.4117400000 |
| C6,j | -0.0438262500 | 4.6960680000 | 15.1414600000 |
| C7,j | 1.1026990000 | 3.1293840000 | -9.5214090000 |
| C8,j | -0.6361056000 | 0.3266766000 | 2.9046220000 |
| C9,j | 0.0087596260 | -3.2040990000 | 8.0023380000 |
| C10,j | 0.3412103000 | 8.8721690000 | -14.4038600000 |
| C11,j | -0.8842722000 | -6.6874710000 | 11.7685400000 |

| | | | |
|-------|---------------|---------------|---------------|
| C12.j | 0.1375109000 | 0.2432806000 | -0.5515101000 |
| C13.j | -0.1443457000 | 1.2869320000 | -2.1809880000 |
| C14.j | -0.0059695540 | 0.0454196100 | 0.0000000000 |
| C15.j | 0.0245053700 | -0.4158241000 | 0.7914067000 |
| C16.j | -0.0041995900 | 0.0910596000 | -0.1786378000 |
| C17.j | 0.0004665477 | -1.2620280000 | -2.8267720000 |
| C18.j | -0.0194510100 | 0.7812220000 | 4.1900460000 |
| C19.j | 0.0408364300 | 1.3988440000 | 0.0000000000 |
| C20.j | -0.0354691700 | -1.4560410000 | 0.0000000000 |
| C21.j | -0.0028779550 | 0.2104505000 | 0.0000000000 |
| C22 | 0.0058962650 | 0.2191255000 | 0.0000000000 |

Derivatives of the equations:

$$\begin{aligned}
\frac{\partial B(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[-\frac{c_2}{T_r^2} - 2\frac{c_3}{T_r^3} - 6\frac{c_4}{T_r^4} \right] \\
\frac{\partial C(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[-\frac{c_5}{T_r^2} - 3\frac{c_7}{T_r^4} - 4\frac{c_8}{T_r^5} \exp(-\rho_r^2) \right] \\
\frac{\partial D(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[-\frac{c_{10}}{T_r^2} - 3\frac{c_{11}}{T_r^4} \right] \\
\frac{\partial E(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[-\frac{c_{12}}{T_r^2} - 3\frac{c_{13}}{T_r^4} \right] \\
\frac{\partial F(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[-2\frac{c_{14}}{T_r^3} - 3\frac{c_{13}}{T_r^4} \right] \\
\frac{\partial G(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[-3\frac{c_{16}}{T_r^4} + \left(-3\frac{c_{17}}{T_r^4} - 4\frac{c_{18}}{T_r^5} \right) \exp(-\rho_r^2) \right] \\
\frac{\partial H(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[\left(-3\frac{c_{19}}{T_r^4} - 4\frac{c_{18}}{T_r^5} \right) \exp(-\rho_r^2) \right] \\
\frac{\partial I(T_r, \rho_r)}{\partial T} &= \frac{1}{T_c} \left[\left(-3\frac{c_{21}}{T_r^4} - 4\frac{c_{22}}{T_r^5} \right) \exp(-\rho_r^2) \right] \quad (1.3)
\end{aligned}$$

Helmholtz energy equation will be used to predict other thermodynamic properties

$$\begin{aligned}
dA &= -SdT - Pdv \quad (1.4) \\
\left. \frac{\partial A}{\partial v} \right|_T &= -P \\
dA &= -Pdv = \frac{P}{\rho^2} d\rho \\
A - A_0 &= \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho = \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{P}{\rho^2} d\rho \\
&= \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho
\end{aligned}$$

The second term (limits between low density ρ_0 and density 0) can be defined as an ideal state case where $P = \rho RT$. Now we can add and subtract ideal gas density term of the equation

$$\begin{aligned}
A - A_0 &= \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho = \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho \\
&\quad - \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho \quad (1.5)
\end{aligned}$$

Considering for real EoS $P = Z\rho RT$ equation becomes

$$\begin{aligned}
A - A_0 &= \int_{\rho_0}^{\rho} \frac{P}{\rho^2} RT [B(T_r, \rho_r)\rho_r + C(T_r, \rho_r)\rho_r^2 + D(T_r, \rho_r)\rho_r^3 \\
&\quad + E(T_r, \rho_r)\rho_r^5 + F(T_r, \rho_r)\rho_r^7 \\
&\quad + G(T_r, \rho_r)\rho_r^9 + H(T_r, \rho_r)\rho_r^{10} \\
&\quad + I(T_r, \rho_r)\rho_r^{12}] d\rho \\
&= \int_{\rho_0}^{\rho} \frac{P}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho \\
&\quad - \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho \quad (1.6)
\end{aligned}$$

$$\begin{aligned}
A - A_0 &= \int_{\rho_0}^{\rho} \frac{Z\rho RT - \rho RT}{\rho^2} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho \\
A - A_0 &= \int_{\rho_0}^{\rho} \frac{RT(Z-1)}{\rho} d\rho + \int_{\rho_0}^0 \frac{\rho RT}{\rho^2} d\rho \\
A - A_0 &= \int_{\rho_0}^{\rho_r} \frac{1}{\rho_r} d\rho_r + \int_{\rho_{r0}}^{\rho_r} \frac{RT}{\rho_r} d\rho_r \\
A - A_0 &= RT \int_{\rho_0}^{\rho_r} [B(T_r, \rho_r) + C(T_r, \rho_r)\rho_r + D(T_r, \rho_r)\rho_r^2 \\
&\quad + E(T_r, \rho_r)\rho_r^4 + F(T_r, \rho_r)\rho_r^6 \\
&\quad + G(T_r, \rho_r)\rho_r^7 + H(T_r, \rho_r)\rho_r^9 \\
&\quad + I(T_r, \rho_r)\rho_r^{11}] d\rho_r + RT \ln \frac{\rho_r}{\rho_{r0}} \quad (1.7)
\end{aligned}$$

Some of the terms in this integration includes terms of exponential and power multiplications. This integrations are carried out as follows:

$$\begin{aligned}
K(m, \rho_r) &= \int_{\rho_0}^{\rho_r} \rho_r^m \exp(-\rho_r^2) d\rho_r = \int_{\rho_0}^{\rho_r} \sum_{n=0}^{\infty} (-1)^n \frac{\rho_r^{2n+m}}{n!} d\rho_r \\
&= \sum_{n=0}^{\infty} (-1)^n \frac{\rho_r^{2n+m+1}}{(2n+m+1)n!} \quad (1.8)
\end{aligned}$$

Handling these terms such as above Taylor series are much easier than taken numerical integration, then Helmholtz departure function becomes:

$$\begin{aligned}
A - A_0 &= RT \left(B\rho_r + C_1 \frac{\rho_r^2}{2} + C_2 K(1, \rho_r) + D \frac{\rho_r^3}{3} + E \frac{\rho_r^5}{5} + F \frac{\rho_r^7}{7} \right. \\
&\quad + G_1 \frac{\rho_r^8}{8} + G_2 K(8, \rho_r) + H_2 K(10, \rho_r) \\
&\quad \left. + I_2 K(12, \rho_r) \right) + RT \ln \left(\frac{\rho_r}{\rho_{r0}} \right) \quad (1.9)
\end{aligned}$$

Entropy departure function:

$$\begin{aligned}
S - S_0 &= - \left. \frac{\partial(A - A_0)}{\partial T} \right|_{\rho} \quad (1.10) \\
S - S_0 &= R \left(B\rho_r + C_1 \frac{\rho_r^2}{2} + C_2 K(1, \rho_r) + D \frac{\rho_r^3}{3} + E \frac{\rho_r^5}{5} + F \frac{\rho_r^8}{8} \right. \\
&\quad + G_1 \frac{\rho_r^9}{9} + G_2 K(8, \rho_r) + H_2 K(10, \rho_r) \\
&\quad \left. + I_2 K(12, \rho_r) \right) \\
&\quad + RT \left(\frac{dB}{dT} \rho_r + \frac{dC_1}{dT} \frac{\rho_r^2}{2} + \frac{dC_2}{dT} K(1, \rho_r) \right. \\
&\quad + \frac{dD}{dT} \frac{\rho_r^3}{3} + \frac{dE}{dT} \frac{\rho_r^5}{5} + \frac{dF}{dT} \frac{\rho_r^8}{8} + \frac{dG_1}{dT} \frac{\rho_r^9}{9} \\
&\quad + \frac{dG_2}{dT} K(8, \rho_r) + \frac{dH_2}{dT} K(10, \rho_r) \\
&\quad \left. + \frac{dI_2}{dT} K(12, \rho_r) \right) + R \ln \left(\frac{\rho_r}{\rho_{r0}} \right)
\end{aligned}$$

Enthalpy departure function:

$$H - H_0 = (A - A_0) + T(S - S_0) + RT(Z - 1) \quad (1.11)$$

Internal energy departure function:

$$U - U_0 = (A - A_0) + T(S - S_0) \quad (1.12)$$

Gibbs energy departure function:

$$G - G_0 = (A - A_0) + RT(Z - 1) \quad (1.13)$$

| i | A _i | B _i | C _i | D _i | T _{hi} K | T _{li} K |
|----|----------------|----------------|----------------|----------------|-------------------|-------------------|
| 0 | 29.4086307829 | -2.2514470327 | -0.0124732186 | 4.5208886188 | 100 | 350 |
| 1 | 27.6461690069 | 0.8823555268 | 0.7700742081 | 4.7644228675 | 350 | 700 |
| 2 | 21.6017064500 | 14.8784143146 | 3.8128084889 | -4.1654669506 | 700 | 1200 |
| 3 | 29.8307659455 | 5.4215607907 | -15.0430960215 | -1.0896138268 | 1200 | 1700 |
| 4 | 35.4767415122 | 0.9735825946 | -42.5476274875 | -0.0974664401 | 1700 | 2200 |
| 5 | 34.9282028043 | 1.3194039653 | -38.1841919451 | -0.1599114820 | 2200 | 2700 |
| 6 | 36.2625256395 | 0.5815001033 | -50.8983620805 | -0.0457311313 | 2700 | 3200 |
| 7 | 35.6573409828 | 0.7661686027 | -34.6659363416 | -0.0598170521 | 3200 | 3700 |
| 8 | 36.4180454205 | 0.4325957723 | -44.1847062013 | -0.0201521727 | 3700 | 4200 |
| 9 | 38.0776880528 | -0.1529603974 | -80.3118075101 | 0.0367938172 | 4200 | 4700 |
| 10 | 37.7602843891 | -0.0499492999 | -73.1011559910 | 0.0277685442 | 4700 | 5200 |
| 11 | 39.9738552178 | -0.8545553355 | -77.5759376892 | 0.1012534665 | 5200 | 6000 |

The fugacity-pressure ratio:

$$\ln \frac{f}{p} = \frac{(A - A_0)}{RT} + \ln \frac{v}{v_0} + (Z - 1) - \ln(Z) \quad (1.14)$$

Data is also needed to solve $C_p(T)$ value. In order to establish that, NIST tables given at the address <https://janaf.nist.gov/> is used. The following partial continuous formulation is taken. the following partial difference curve fitting formula is used

$$C_{pi}(T) = A_i + B_i 10^{-3} T + \frac{C_i 10^5}{T^2} + D_i 10^{-6} T^2 T_{li} \leq T \leq T_{hi} \quad (1.15)$$

As an example case of Partial continuous curve fitting of Cp values Data for Nitrogen is given below.

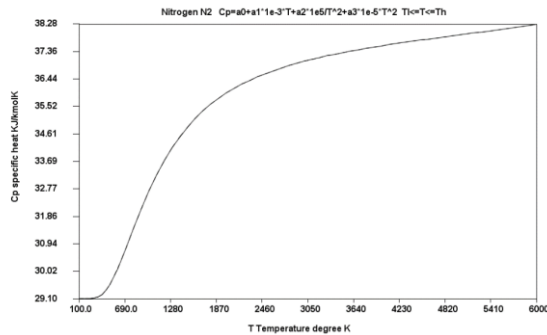


Figure 1.1 Cp of Nitrogen kJ/(kmolK)

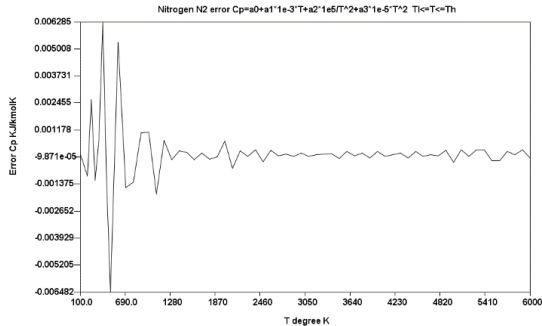


Figure 1.2 Error of Cp in Nitrogen kJ/(kmolK)

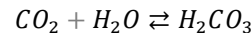
Table 1.2 C_p (kJ/kmol K) partial continuous curve fitting equations for N_2 Nitrogen

| i | A _i | B _i | C _i | D _i | T _{hi} K | T _{li} K |
|----|----------------|----------------|----------------|----------------|-------------------|-------------------|
| 0 | 29.408631 | -2.251447 | -0.012473 | 4.520889 | 100 | 350 |
| 1 | 27.646169 | 0.882356 | 0.770074 | 4.764423 | 350 | 700 |
| 2 | 21.601706 | 14.878414 | 3.812808 | -4.165467 | 700 | 1200 |
| 3 | 29.830766 | 5.421561 | -15.043096 | -1.089614 | 1200 | 1700 |
| 4 | 35.476742 | 0.973583 | -42.547627 | -0.097466 | 1700 | 2200 |
| 5 | 34.928203 | 1.319404 | -38.184192 | -0.159911 | 2200 | 2700 |
| 6 | 36.262526 | 0.581500 | -50.898362 | -0.045731 | 2700 | 3200 |
| 7 | 35.657341 | 0.766169 | -34.665936 | -0.059817 | 3200 | 3700 |
| 8 | 36.418045 | 0.432596 | -44.184706 | -0.020152 | 3700 | 4200 |
| 9 | 38.077688 | -0.152960 | -80.311808 | 0.036794 | 4200 | 4700 |
| 10 | 37.760284 | -0.049949 | -73.101156 | 0.027769 | 4700 | 5200 |
| 11 | 39.973855 | -0.854555 | -77.575938 | 0.101253 | 5200 | 6000 |

For some gases only data is available is in polynomial curve fitting format, for this cases polynomial form is assumed.

2. Stoichiometric chemical equilibrium formulations

Actual products formed in a reaction is not a clear cut concept. The actual products formed in a chemical reactions can only be determined experimentally and as a function of the environmental values such as temperature, pressure and time. When these parameters changed actual products can change as well. One way of estimating what products will be formed is to use equilibrium concept. All physical systems are tend to minimize their energy levels when there are no any external force or energy to the system. For example a bubble takes spherical shape under the influence of surface tension which has the minimal area for the given volume. Chemical reactions when temperature and pressure is constant and long enough time is given, tends to minimize it energy level, specifically gibbs free energy level (or maximize its entropy level). This state is called chemical equilibrium. For example consider a closed system consisting initially of a gaseous mixture of carbon dioxide , oxygen and carbonic acid. A reaction might take place is



At equilibrium the system will consist basically of three components, CO_2 , H_2CO_3 and H_2O , for not all the components gases. This is what is called soda reaction. When soda bottle opened equilibrium condition (pressured in the system) is changed and rection slides to a new equilibrium states, so that some amount of CO_2 and H_2O is formed and amount of carbonic acid is reduced . Changes in the amounts

of these components during the opening of soda bottle:

$$\begin{aligned} dn_{CO_2} &= -dn_{H_2CO_3} \\ dn_{H_2O} &= -dn_{H_2CO_3} \end{aligned} \quad (2.1)$$

where dn denotes the differential change in the representative component.

$$-\frac{dn_{CO_2}}{1} = -\frac{dn_{H_2O}}{1} = \frac{dn_{H_2CO_3}}{1} \quad (2.2)$$

Equilibrium is a condition of balance. When equilibrium is established amount of CO_2 and H_2O and H_2CO_3 tends to be balanced with each other. But when equilibrium is broken and a new conditions arise, like opening of a soda bottle, a new equilibrium will be established. And during these process total gibbs free energy of the system will be minimised.

$$dG(T, P) = 0 \quad (2.3)$$

This amount can be determined from chemical potential changes (see the first chapter for details)

$$\mu_{CO_2} = \frac{\partial G(T, P, n)}{\partial n_{CO_2}} \quad \partial G(T, P, n) = \mu_{CO_2} \partial n_{CO_2}$$

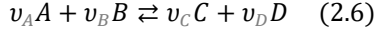
$$\mu_{H_2CO_3} = \frac{\partial G(T, P, n)}{\partial n_{H_2CO_3}} \quad \partial G(T, P, n) = \mu_{H_2CO_3} \partial n_{H_2CO_3}$$

$$\mu_{H_2O} = \frac{\partial G(T, P, n)}{\partial n_{H_2O}} \quad \partial G(T, P, n) = \mu_{H_2O} \partial n_{H_2O}$$

$$dG(T, P) = -1 * \mu_{CO_2} dn_{CO_2} - 1 * \mu_{H_2O} dn_{H_2O} + 1 * \mu_{H_2CO_3} dn_{H_2CO_3} = 0 \quad (2.4)$$

$$dG(T, P) = (-1 * \mu_{CO_2} - 1 * \mu_{H_2O} + 1 * \mu_{H_2CO_3}) dn_{H_2CO_3} = 0 \quad (2.5)$$

This is called the equilibrium reaction. For a more general equilibrium equation such as:



where v 's are stoichiometric coefficients. The following equilibrium case is existed:

$$-\frac{dn_A}{v_A} = -\frac{dn_B}{v_B} = \frac{dn_C}{v_C} = \frac{dn_D}{v_D} = d\varepsilon \quad (2.7)$$

where $d\varepsilon$ is the proportionality factor. From which the following expressions are obtained.

$$\begin{aligned} dn_A &= -v_A d\varepsilon \\ dn_B &= -v_B d\varepsilon \\ dn_C &= v_C d\varepsilon \\ dn_D &= v_D d\varepsilon \end{aligned}$$

(2.8)

For this case the Gibbs free energy equation takes form:

$$dG(T, P) = -v_A * \mu_A - v_B * \mu_B + v_C * \mu_C + v_D * \mu_D = 0 \quad (2.9)$$

For ideal gas mixtures chemical potential can be expressed as specific gibbs free energy as

$$h_{Ti}(T) = h_i(T) - h(298.15) + \Delta h_f(298.15)$$

$$g^0(T) = h_{Ti}(T) - Ts^0(T)$$

$$\mu_i = g_i^0(T) - RT \ln \left(\frac{P_i}{P_{ref}} \right) \quad (2.10)$$

where P_i is the partial pressure of the gas. For an ideal gas, partial pressure can be expressed as a function of components in the total components

$$y_i = \frac{n_i}{n_{total}} \quad P_i = y_i P \quad P_i = \frac{n_i}{n_{total}} P \quad (2.11)$$

Substituting these into the equation gives:

$$\mu_i = g_i^0(T) - RT \ln \left(\frac{n_i}{n_{total}} \frac{P}{P_{ref}} \right) \quad (2.12)$$

For a real gas mixtures chemical potential can be expressed as specific gibbs free energy as

$$h_{Ti}(T, P) = h_i(T, P) - h(298.15, P) + \Delta h_f(298.15) \quad (2.13)$$

$$s(T, P) = s^0(T) - R \ln \left(\frac{f_i}{P_{ref}} \right) \quad (2.14)$$

$$g(T, P) = g^0(T, P) - RT \ln \left(\frac{f_i}{P_{ref}} \right) \quad (2.15)$$

$$g^0(T, P) = h_{Ti}(T, P) - Ts^0(T) \quad (2.16)$$

$$\mu_i = g_i^0(T) - RT \ln \left(\frac{f_i}{P_{ref}} \right) \quad (2.17)$$

Note that $\lim_{P \rightarrow 0} \frac{f_i}{P_i} = 1$ (2.18) therefore $P_{ref} = f_{ref}$

where f_i is the partial fugacity of the gas. For a real gas, partial pressure can be expressed as a function of components in the total components

$$y_i = \frac{n_i}{n_{total}} \quad f_i = y_i f^* \quad f_i = \frac{n_i}{n_{total}} f^* \quad (2.19)$$

Where f^* fugacity that component i would have if the entire gas had that composition at the same temperature and pressure. $f^* = f(T, P)$ (2.20)

Substituting these into the equation gives:

$$\mu_i = g_i^0(T, P) - RT \ln \left(\frac{n_i}{n_{total}} \frac{f^*}{P_{ref}} \right) \quad (2.21)$$

Then the basic Gibbs free energy equation becomes

$$\begin{aligned} dG(T, P) &= -v_A \left[g_A^0(T) - RT \ln \left(\frac{n_A}{n_{total}} \frac{f^*}{P_{ref}} \right) \right] \\ &\quad - v_B \left[g_B^0(T) - RT \ln \left(\frac{n_B}{n_{total}} \frac{f^*}{P_{ref}} \right) \right] \\ &\quad + v_C \left[g_C^0(T) - RT \ln \left(\frac{n_C}{n_{total}} \frac{f^*}{P_{ref}} \right) \right] \\ &\quad + v_D \left[g_D^0(T) - RT \ln \left(\frac{n_D}{n_{total}} \frac{f^*}{P_{ref}} \right) \right] \\ &= 0 \quad (2.22) \end{aligned}$$

Arranging equation:

$$dG^0(T, P) = -v_A g_A^0(T, P) - v_B g_B^0(T, P) + v_C g_C^0(T, P) + v_D g_D^0(T, P)$$

$$dG(T, P) = dG^0(T, P)$$

$$\begin{aligned} &+ RT \left[v_A \ln \left(\frac{n_A}{n_{total}} \frac{f^*}{P_{ref}} \right) \right. \\ &+ v_B \ln \left(\frac{n_B}{n_{total}} \frac{f^*}{P_{ref}} \right) \\ &- v_C \ln \left(\frac{n_C}{n_{total}} \frac{f^*}{P_{ref}} \right) \\ &\left. - v_D \ln \left(\frac{n_D}{n_{total}} \frac{f^*}{P_{ref}} \right) \right] = 0 \quad (2.23) \end{aligned}$$

This equation can be written as:

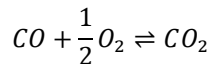
$$\begin{aligned} -\frac{dG^0(T, P)}{RT} &= \left[v_A \ln \left(\frac{n_A}{n_{total}} \frac{f^*}{P_{ref}} \right) + v_B \ln \left(\frac{n_B}{n_{total}} \frac{f^*}{P_{ref}} \right) \right. \\ &\quad - v_C \ln \left(\frac{n_C}{n_{total}} \frac{f^*}{P_{ref}} \right) \\ &\quad \left. - v_D \ln \left(\frac{n_D}{n_{total}} \frac{f^*}{P_{ref}} \right) \right] \quad (2.24) \end{aligned}$$

$$\exp\left(-\frac{dG^0(T,P)}{RT}\right) = \left[\frac{\left(\frac{n_A}{n_{total}} \frac{f^*}{P_{ref}}\right)^{v_A} \left(\frac{n_B}{n_{total}} \frac{f^*}{P_{ref}}\right)^{v_B}}{\left(\frac{n_C}{n_{total}} \frac{f^*}{P_{ref}}\right)^{v_C} \left(\frac{n_D}{n_{total}} \frac{f^*}{P_{ref}}\right)^{v_D}} \right] \\ = \left[\frac{(n_A)^{v_A} (n_B)^{v_B}}{(n_C)^{v_C} (n_D)^{v_D}} \right] \left(\frac{f^*}{n_{total} P_{ref}} \right)^{v_A+v_B-v_C-v_D} \quad (2.25)$$

The left hand side of the equation is called equilibrium constant, which is only function of temperature

$$K(T) = \exp\left(-\frac{dG^0(T,P)}{RT}\right) \quad (2.26)$$

As an example let us evaluate equilibrium constant of the equilibrium reaction



| | CO | O2 | CO2 | b0(reactants) | b1(products) |
|---|-----|-----|-----|---------------|--------------|
| C | 1.0 | 0.0 | 1.0 | 1.0 | 1.0 |
| O | 1.0 | 2.0 | 2.0 | 2.0 | 2.0 |

Equilibrium condition can be solved by solving chemical balance equations together with the equilibrium gibbs free energy minimisation equations. So mass balance is an important part of total set of equations to solve. Mass balance establishes as follows:

$$\sum_{j=1}^{NS} A_{ij} n_j - b_i^0 = 0 \quad (i = 1..na) \quad (2.27)$$

$$b_i = \sum_{j=1}^{NS} A_{ij} n_j \quad (2.28)$$

$$b_i - b_i^0 = 0 \quad (i = 1..na) \quad (2.29)$$

where na is the number of chemical elements. A_{ij} is number of kilogram atoms per kmole of species j.

And b_i^0 is the assigned number of kilogram atoms element i per kmol of total reactants.

In order to explain this equation let us look at an example. If chemicals in the reaction and input moles re given as:

| | |
|------------------|---------|
| CH ₄ | 1 kmol |
| H ₂ O | 10 kmol |
| H ₂ | 0 kmol |
| CO ₂ | 0 kmol |
| CO | 0 kmol |
| O ₂ | 0 kmol |

A_{ij} matrix will be

| atom | CH ₄ | H ₂ O | H ₂ | CO ₂ | CO | O ₂ |
|------|-----------------|------------------|----------------|-----------------|----|----------------|
| H | 4 | 2 | 2 | 0 | 0 | 0 |
| C | 1 | 0 | 0 | 1 | 1 | 0 |
| O | 0 | 1 | 0 | 2 | 1 | 2 |

b_i^0 vector is the multiplication of number of atoms with inlet mole numbers of the molecule

$$b_H^0 = 1*4 + 10*2 + 0*2 + 0*0 + 0*0 + 0*0 = 24$$

$$b_C^0 = 1*1 + 10*0 + 0*0 + 0*1 + 0*1 + 0*0 = 1$$

$$b_O^0 = 0*1 + 10*1 + 0*0 + 0*2 + 0*1 + 0*2 = 10$$

In this case initial matrix will be in the form of:

$$\begin{bmatrix} 4 & 2 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 2 & 1 & 0 \end{bmatrix} \begin{Bmatrix} n_{CH_4} \\ n_{H_2O} \\ n_{CO_2} \\ n_{CO} \\ n_{O_2} \end{Bmatrix} = \begin{Bmatrix} 24 \\ 1 \\ 10 \end{Bmatrix} \quad (2.30)$$

As it is seen from the example mass balance are given us 3 equations, but total number of equations(moles) are 6, remaining equations will be gibbs equations as described above. All together they construct a system of non-linear equations to solve. The results will be equilibrium balance.

In order to solve system of equations continuity method(it is also called homotopy method) is used.

This method is relatively less dependent to initial estimation of the system of equation solution, therefore a good selection for solving the system of non-linear equation. The method details is as follows: When a problem of system of nonlinear equations of the form $F(x)=0$ desired to be solved, assume that solution set to be found is x^* . Consider a parametric function $G(\lambda, x)$ in the form of

$$G(\lambda, x) = \lambda F(x) + (1-\lambda)[F(x) - F(x(0))] \quad (2.31)$$

Where $\lambda=0$ corresponds to initial guess of the solution, $x(0)$, and where $\lambda=1$ value corresponds the actual solution set $x(1)=x^*$

It is desired to be found $G(\lambda, x) = 0$ therefore for $\lambda=0$ equation becomes

$$G(\lambda, x) = G(0, x) = F(x) - F(x(0)) \quad \text{and for } \lambda=1 \quad (2.32)$$

$$0 = G(1, x) = F(x) \quad (2.33)$$

Therefore at $x(1)=x^*$ solution set will be obtained.

If a function $G(\lambda, x)$ satisfies the above equation can be found, it will also find us the solution.

Function G is called a homotopy between the function $G(0, x)$ and $G(1, x)=F(x)$. In order to find such a function, it is assumed to have a function $G(\lambda, x)=0$ is existed and partial derivative of this function with respect to λ and x will also be zero

$$0 = \frac{\partial G(\lambda, x)}{\partial \lambda} + \frac{\partial G(\lambda, x)}{\partial x} x'(\lambda) \quad (2.34)$$

if $x'(\lambda)$ is isolated form this equation, it becomes:

$$x'(\lambda) = - \left[\frac{\partial G(\lambda, x(\lambda))}{\partial x} \right]^{-1} \left[\frac{\partial G(\lambda, x(\lambda))}{\partial \lambda} \right] x'(\lambda) \quad (2.35)$$

If $G(\lambda, x) = \lambda F(x) + (1-\lambda)[F(x) - F(x(0))]$ equation is substituted into the differential equation

$$\left[\frac{\partial G(\lambda, x(\lambda))}{\partial x} \right] = \begin{bmatrix} \frac{\partial f_1(x(\lambda))}{\partial x_1} & \frac{\partial f_1(x(\lambda))}{\partial x_2} & \frac{\partial f_1(x(\lambda))}{\partial x_3} \\ \frac{\partial f_2(x(\lambda))}{\partial x_1} & \frac{\partial f_2(x(\lambda))}{\partial x_2} & \frac{\partial f_2(x(\lambda))}{\partial x_3} \\ \frac{\partial f_3(x(\lambda))}{\partial x_1} & \frac{\partial f_3(x(\lambda))}{\partial x_2} & \frac{\partial f_3(x(\lambda))}{\partial x_3} \end{bmatrix} = J(x(\lambda))$$

(2.36)

Forms a Jacobian matrix. and

$$\left[\frac{\partial G(\lambda, x(\lambda))}{\partial x} \right] = F(x(0)) \quad (2.37)$$

Differential equation becomes

$$x'(\lambda) = \frac{dx(\lambda)}{d\lambda} = -[J(x(\lambda))]^{-1} F(x(0)) \quad 0 \leq \lambda \leq 1$$

(2.38)

It is possible to solve such a differential equation by using initial value problem approaches, solution at $x(1)$ will be given us the roots of the system of equation. Solutions of initial value problems will be given latter chapters in details, but A sixth order Runge-Kutta differential equation solution will be defined here to solve our homotopy problem. If equation

$$\frac{dx(\lambda)}{d\lambda} = f(\lambda, x(\lambda)) \quad (2.39)$$

is given the 6th order Runge-Kutta method to numerically solve this differential equation is defined as:

$$y_{i+1} = y_i + (1/90) * (7k_1 + 32k_3 + 12k_4 + 32k_5 + 7k_6)h$$

$$k_1 = f(x_i, y_i)$$

$$k_2 = f(x_i + 0.25h, y_i + 0.25k_1h)$$

$$k_3 = f(x_i + 0.25h, y_i + 0.125k_1h + 0.125k_2h)$$

$$k_4 = f(x_i + 0.5h, y_i - 0.5k_2h + k_3h)$$

$$k_5 = f(x_i + 0.75h, y_i + (3/16)k_1h + (9/16)k_4h)$$

$$k_6 = f(x_i + h, y_i - (3/7)k_1h + (2/7)k_2h + (12/7)k_3h - (12/7)k_4h + (8/7)k_5h) \quad (2.40)$$

This equation can be given as Butcher tableau as:

| | | | | | |
|-----|------|------|-------|-------|------|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 1/4 | 1/4 | 0 | 0 | 0 | 0 |
| 1/4 | 1/8 | 1/8 | 0 | 0 | 0 |
| 2/4 | 1/4 | -1/4 | 1 | 0 | 0 |
| 3/4 | 3/16 | 0 | 0 | 9/16 | 0 |
| 1 | -3/7 | 2/7 | 12/7 | -12/7 | 8/7 |
| - | 1/90 | 7/90 | 32/90 | 12/90 | 7/90 |

(2.41)

In these equations h is finite difference step size. Solution starts by using the initial value $\lambda=0$, $x(0)$ and adds h into λ in each iteration step. The code given here uses 6th degree Runge-Kutta method to solve homotopy(Continuation problem). It should be note that Homotopy method is less dependent to initial value compare to methods such as Newton-Raphson therefore one possibility is to approach

solution with a relatively rough estimate with homotopy following with a Newton-Raphson type of method, which is quite efficient when the estimation approaches the correct roots.

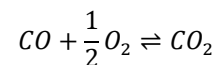
3. Computer code development

In order to calculate thermodynamic properties of gases Schreiber and Pitzer real gas EoS is developed (Gas_SP.java). This equation of state has a subclass to calculate specific heat values as curvefitting values (Gas_Data.java). Equilibrium coefficients are calculated from ChemicalReaction_SP class. System of equations are set together in if_equilibrium_SP class. Continuation method to solve non-linear system of equation is given in class iterative_continuity. And finally equilibrium codes are solve in equilibrium_SP class. In addition to this set an ideal gas equivalent is also prepared for comparison purposes. List of classes and their utilisation areas are given as a table below:

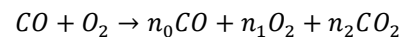
| Program | Utilisation |
|----------------------|--|
| Atom | Calculation atomic balances, atomic properties |
| Gas_Data | Gas data for approximately 600 gases |
| Gas_SP | Schreiber and Pitzer real gas EoS |
| Gas_PG | Perfect Gas EoS |
| ChemicalReaction_SP | Chemical reaction calculator for Gas_SP |
| If_equilibrium_SP | Defines non-linear system of equation for Gas_SP |
| Equilibrium_SP | Stoichiometric Equilibrium calculator for Gas_SP |
| ChemicalReaction_PG | Chemical reaction calculator for Gas_PG |
| If_equilibrium_PG | Defines non-linear system of equation for Gas_PG |
| Equilibrium_PG | Stoichiometric Equilibrium calculator for Gas_PG |
| Iterative_continuity | Continuation(homotopy) method for non-linear system of eqns. |

Sample solutions:

One kmol of CO and one kmol of O_2 established an equilibrium at 3000 K. The equilibrium reaction for this is as follows:



The reaction will be



Find the equilibrium composition. System pressure is $P=101.325$ bar. ($P_{ref}=101.325$ bar)

```
import java.util.*;
import java.awt.*;
import java.applet.Applet;
import java.awt.event.*;
import javax.swing.*;
public class equilibrium_SP
{public double N[][][];
public String s[];
public double result[][];
public double P;
public chemicalReaction_SP r[];
```

```

public if_equilibrium_SP fe;
public equilibrium_SP(String si[],double Ni[][][],double Pi)
{
    N=Ni;
    s=si;
    P=Pi;
    int n=N.length;
    r=new chemicalReaction_SP[n];
    for(int i=0;i<n;i++)
    {r[i]=new chemicalReaction_SP("reaction:"+i,s,N[i]);}
}
public double[][] calculate(double Tproduct,double
Treactant,double P,double n0[],double high[])
{fe=new if_equilibrium_SP(n0,s,r,Treactant,Tproduct,P);
int n_eqn=n0.length;
double low[]=new double[n_eqn];
int n_iteration=10;
iterative_continuity                                itc=new
iterative_continuity(n_iteration,low,high);
result= itc.findContinuityRK4(fe);
return result;
}

public static void main(String arg[])
{
    String s[]={"CO","O2","CO2"};
    double N1[][]={{1.0,0.0},{0.5,0.0},{0.0,1.0}};
    double N[][]={N1};
    double P=101.325; //kPa
    equilibrium_SP eq=new equilibrium_SP(s,N,P);
    double Tproduct=3000;//degree K
    double Treactant=3000;//degree K
    //input moles
    //CO+H2O+N2-->
    double n0[]={1,1,0};
    //output mole first estimates
    double high[]={1.0,1.0,1.0};
    eq.calculate(Tproduct,Treactant,P,n0,high);
    String s1[]={"x initial guess","x","y=f(x)"};
    Text.printT(eq.result,s1,"Newton_continuation");
}
}

```

```

{
    String s[]={"CO","O2","CO2","N2"};
    double
    N1[][]={{1.0,0.0},{0.5,0.0},{0.0,1.0},{1.88,1.88}};
    double N[][]={N1};
    double P=101.325; //kPa
    equilibrium_SP eq=new equilibrium_SP(s,N,P);
    double Tproduct=3000;//degree K
    double Treactant=3000;//degree K
    //input moles
    //CO+H2O+N2-->
    double n0[]={1,1,0,1.88};
    //output mole first estimates
    double high[]={1.0,1.0,1.0,2.0};
    eq.calculate(Tproduct,Treactant,P,n0,high);
    String s1[]={"x initial guess","x","y=f(x)"};
    Text.printT(eq.result,s1,"Newton_continuation");
}

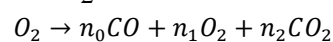
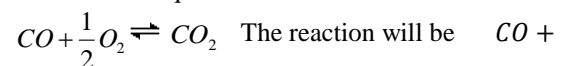
```

| x initial guess | x | y=f(x) |
|--------------------|--------------------|-----------------------|
| 0.4237119081525775 | 0.4237119081525775 | 3.5451650144402436E-6 |
| 0.7118707072048843 | 0.7118707072048843 | 2.302036426371501E-6 |
| 0.5762922534844812 | 0.5762922534844812 | 2.2552501910411138E-7 |
| 1.8799057131256034 | 1.8799057131256034 | 1.6311727337958715E-5 |

To compare the results let us also run equilibrium_PG for the same conditions:

| x initial guess | x | y=f(x) |
|---------------------|---------------------|--------|
| 0.17901996274748555 | 0.42524996056811837 | 0.0 |
| 0.38504904730880185 | 0.7126249802840592 | 0.0 |
| 0.5567586223735005 | 0.5747500394318816 | 0.0 |
| 1.8905350157358185 | 1.88 | 0.0 |

For T=3000 K and P=1000 kPa, if N2 is added to the reaction. Equilibrium reaction is still the same:



| x initial guess | x | y=f(x) |
|--------------------|--------------------|-------------------------|
| 0.1471735996531205 | 0.1471735996531205 | 1.2957901418531037E-... |
| 0.5735924677072117 | 0.5735924677072117 | -6.902536369146617E-6 |
| 0.8528203359640902 | 0.8528203359640902 | -2.799026342037436E-6 |

To compare the results let us also run equilibrium_PG for the same conditions:

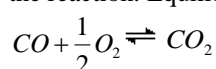
| x initial guess | x | y=f(x) |
|-----------------|---------------------|--------|
| 0.0 | 0.14799227192627473 | 0.0 |
| 0.0 | 0.5739961359631375 | 0.0 |
| 0.0 | 0.8520077280737253 | 0.0 |

| x initial guess | x | y=f(x) |
|--------------------|--------------------|-----------------------|
| 0.3406696157029702 | 0.3406696157029702 | 4.222021930511133E-6 |
| 0.6703472942504498 | 0.6703472942504498 | 1.3546075638970478E-7 |
| 0.6593266528142379 | 0.6593266528142379 | 1.327369465564665E-5 |

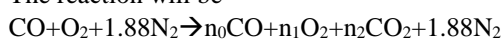
To compare the results let us also run equilibrium_PG for the same conditions:

| x initial guess | x | y=f(x) |
|----------------------|--------------------|--------|
| 0.049084885297797864 | 0.3421068814833881 | 0.0 |
| 0.41740161356657407 | 0.671053440741694 | 0.0 |
| 0.5199888966313939 | 0.657893118516612 | 0.0 |

For T=3000 K and P=1.01325 bar, if N2 is added to the reaction. Equilibrium reaction is still the same:



The reaction will be



Find the equilibrium composition.

```
public static void main(String arg[])
```

Equilibrium Chemical Reaction

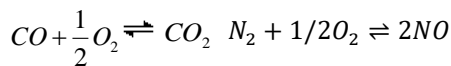
Treactant = 3000.0 degree K
Tproduct = 3000.0 degree K
P = 101.325 bar

=====
Equilibrium Reaction : CO + 0.5 O2 = CO2
Equilibrium constant K = 3.054925273465477
Equilibrium constant lnK = 1.1167551319202988
=====
Equilibrium Reaction : CO + H2O = CO2 + H2
Equilibrium constant K = 5.5591404532168915E-5
Equilibrium constant lnK = -9.7974819634039
=====

| name | n0 mole in | x0 mole ratio in | n mole out | x mole ratio out |
|-------|------------|------------------|----------------|------------------|
| CO | 1.0 | 0.5 | 0.992611081... | 0.496302593... |
| H2O | 1.0 | 0.5 | 0.992587331... | 0.496290718... |
| CO2 | 0.0 | 0.0 | 0.007388918... | 0.003694437... |
| H2 | 0.0 | 0.0 | 0.007412668... | 0.003706312... |
| O2 | 0.0 | 0.0 | 1.187503614... | 5.937482819... |
| total | 2.0 | 1 | 2.000011875... | 1 |

Example case:

For T=3000 K and P=101.325 kPa, if N2 is added to the reaction. Equilibrium reaction is still the same:



The reaction will be $CO + O_2 \rightarrow n_0CO + n_1O_2 + n_2CO_2 + n_3N_2 + n_4NO$

Sample program:

```
import java.util.*;
import java.awt.*;
import java.applet.Applet;
import java.util.*;
import java.awt.*;
import java.applet.Applet;
import java.awt.event.*;
import javax.swing.*;
public class equilibrium1_SP
{ public static void main(String arg[])
{ chemicalReaction_SP r[]=new chemicalReaction_SP[2];
String s[]={ "CO","O2","CO2","N2","NO"};
double
N1[][]={{1.0,0.0},{0.5,0.0},{0.1},{0.0,0.0},{0.0,0.0}};
r[0]=new chemicalReaction_SP("r0",s,N1);
double
N2[][]={{0.0,0.0},{1.0,0.0},{0.0,0.0},{1.0,0.0},{0.0,2.0}};
r[1]=new chemicalReaction_SP("r1",s,N2);
double Tproduct=3000.0;//degree K
double Treactant=3000.0;//degree K
double n0[]={1.0,1.0,0.0,1.88,0.0};
double P=101.325;//kPa
if_equilibrium_SP fe=new
if_equilibrium_SP(n0,s,r,Treactant,Tproduct,P);
double n[]={0.51,0.52,0.53,0.54,0.55};
//double r1[]={} r1=
continuity.continuationRK6(fe,n,4);
double r1[]={} r1=
continuity.newton_continuationRK6(fe,n);
```

4. Results and conclusion

Stoichiometric chemical equilibrium algorithm is developed by using Schreiber and Pitzer real gas EoS. Schreiber and Pitzer EoS is relatively

```
String
ss[]={ "nCO","nH2O","nCO2","nH2","nO2"};
String ss1="Equilibrium reaction
CO+"+"\u00BD"+"O2"+"+\u21C4"+" CO2 \n";
ss1+="CO"+"+"at T="+Tproduct+" K ";
fe.equilibrium_print(r1);
}}
```

Equilibrium Chemical Reaction

Treactant = 3000.0 degree K
Tproduct = 3000.0 degree K
P = 101.325 bar

=====
Equilibrium Reaction : CO + 0.5 O2 = CO2
Equilibrium constant K = 3.0553054547259464
Equilibrium constant lnK = 1.1168795728057161
=====
Equilibrium Reaction : O2 + N2 = 2.0 NO
Equilibrium constant K = 0.014983741237240755
Equilibrium constant lnK = -4.2007895832606374
=====

| name | n0 mole in | x0 mole ratio in | n mole out | x mole ratio out |
|-------|------------|------------------|----------------|------------------|
| CO | 1.0 | 0.257731958... | 0.434849576... | 0.120878017... |
| O2 | 1.0 | 0.257731958... | 0.650927268... | 0.180942564... |
| CO2 | 0.0 | 0.0 | 0.565150423... | 0.157098607... |
| N2 | 1.88 | 0.484536082... | 1.813502480... | 0.504111298... |
| NO | 0.0 | 0.0 | 0.132995039... | 0.036969512... |
| total | 3.88 | 1 | 3.597424788... | 1 |

To compare the results let us also run equilibrium1_PG (Perfect gas) for the same conditions:

Equilibrium Chemical Reaction

Treactant = 3000.0 degree K
Tproduct = 3000.0 degree K
P = 101.325 bar

=====
Equilibrium Reaction : CO + 0.5 O2 = CO2
Equilibrium constant K = 3.0346607625094837
Equilibrium constant lnK = 1.1100996431437236
=====
Equilibrium Reaction : O2 + N2 = 2.0 NO
Equilibrium constant K = 0.014924103484176143
Equilibrium constant lnK = -4.2047776895695295
=====

| name | n0 mole in | x0 mole ratio in | n mole out | x mole ratio out |
|-------|------------|------------------|----------------|------------------|
| CO | 1.0 | 0.257731958... | 0.436381569... | 0.121278052... |
| O2 | 1.0 | 0.257731958... | 0.651780644... | 0.181141213... |
| CO2 | 0.0 | 0.0 | 0.563618430... | 0.156639395... |
| N2 | 1.88 | 0.484536082... | 1.813589859... | 0.504028265... |
| NO | 0.0 | 0.0 | 0.132820281... | 0.036913073... |
| total | 3.88 | 1 | 3.598190784... | 1 |

unknown equation of states that generalised gas relations by using Pitzer coefficients. Equilibrium calculations are based on atomic mass balances and minimisation of gibbs energy. Stoichiometric

chemical equilibrium concepts is used in calculations, required equilibrium equations are defined as an input parameter, and chemical equilibrium coefficients are calculated by using only temperature dependent components of gibbs energy. In order to compare the results, perfect gas base calculations are also carried out. The most notable

difference of ideal gas based calculations and real gas based calculations are that ideal gas equations are based on pressure while real gas equations are based on fugacity. Results seems not deviates much,

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therefore one of the conclusion is that for atmospheric reactions ideal gas approach will be sufficient for evaluation of chemical reactions. Several example cases runs with both EoS'. The complete codes for this analysis is given in internet site www.turhancoban.com as zip fie SCO1.rar. Further analysis for direct gibbs free energy minimisation without Stoichiometric equations are also studied by our group. It will be presented as sperate papers.

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6. Nomenclature

| | |
|-------------|------------------------------------|
| Z | Compressibility factor |
| P | Pressure |
| ρ | density |
| R | Gas constant |
| T | Temperature |
| B,C,D,E,F,G | Schreiber-Pitzer EoS constants |
| T_r | Reduced pressure |
| T_c | Critical temperature |
| A | Helmholts energy |
| H, h | Enthalpy |
| G,g | Gibbs free energy |
| S,s | Entropy |
| f | Fugacity |
| v | Specific volume |
| C_p | Specific heat at constant pressure |
| μ | Chemical potential |
| A_{ij} | Atom matrix |
| λ | Homotopy(continuity) variable |
| n | Mole numbers |
| M | Molecular weight |