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STOICHIOMETRIC CHEMİCAL EQUILIBRİUM ALGORİTHM BY USİNG 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 athmospheric 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 equlibrium formulations. Atomic balances gives equalibrium chemical moles as much as number of available atoms, for each additional chemical an additional equiibrium 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.

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

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

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

$$=C_1(T_r)+C_2(T_r)\exp(-\rho_r^2)$$

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

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

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

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

$$=G_1(T_r)+G_2(T_r)\exp(-\rho_r^2)$$

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

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

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

Where ωin Scheiber-Pitzer equation of states coefficient is called **Pitzer's accentric factor**. This factor is calculated as

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

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:

$$\frac{\partial B(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[-\frac{c_2}{T_r^2}-2\frac{c_3}{T_r^3}-6\frac{c_4}{T_r^7}\right]$$
$$\frac{\partial C(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[-\frac{c_5}{T_r^2}-3\frac{c_7}{T_r^4}-4\frac{c_8}{T_r^5}\exp(-\rho_r^2)\right]$$
$$\frac{\partial D(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[-\frac{c_{10}}{T_r^2}-3\frac{c_{11}}{T_r^4}\right]$$
$$\frac{\partial E(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[-\frac{c_{12}}{T_r^2}-3\frac{c_{13}}{T_r^4}\right]$$
$$\frac{\partial F(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[-2\frac{c_{14}}{T_r^3}-3\frac{c_{13}}{T_r^4}\right]$$
$$\frac{\partial G(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[-3\frac{c_{16}}{T_r^4}+\left(-3\frac{c_{17}}{T_r^4}-4\frac{c_{18}}{T_r^5}\right)\exp(-\rho_r^2)\right]$$
$$\frac{\partial H(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[\left(-3\frac{c_{19}}{T_r^4}-4\frac{c_{18}}{T_r^5}\right)\exp(-\rho_r^2)\right]$$
$$\frac{\partial I(T_r,\rho_r)}{\partial T}=\frac{1}{T_c}\left[\left(-3\frac{c_{21}}{T_r^4}-4\frac{c_{22}}{T_r^5}\right)\exp(-\rho_r^2)\right]\quad(1.3)$$

Helmholtz energy equation will be used to predict other thermodynamic properties

$$dA=-SdT-Pdv\quad(1.4)$$
$$\left.\frac{\partial A}{\partial v}\right|_T=-P$$
$$dA=-Pdv=\frac{P}{\rho^2}d\rho$$
$$A-A_0=\int_{\rho_0}^{\rho}\frac{P}{\rho^2}d\rho=\int_0^{\rho}\frac{P}{\rho^2}d\rho+\int_{\rho_0}^{0}\frac{P}{\rho^2}d\rho$$
$$=\int_0^{\rho}\frac{P}{\rho^2}d\rho+\int_{\rho_0}^{0}\frac{\rho RT}{\rho^2}d\rho$$

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 substract ideal gas density term of the equation

$$A-A_0=\int_{\rho_0}^{\rho}\frac{P}{\rho^2}d\rho=\int_0^{\rho}\frac{P}{\rho^2}d\rho+\int_{\rho_0}^{0}\frac{\rho RT}{\rho^2}d\rho+\int_0^{\rho}\frac{\rho RT}{\rho^2}d\rho$$
$$-\int_0^{\rho}\frac{\rho RT}{\rho^2}d\rho\quad(1.5)$$

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

$$A-A_0=\int_{\rho_0}^{\rho}\frac{P}{\rho^2}RT[B(T_r,\rho_r)\rho_r+C(T_r,\rho_r)\rho_r^2+D(T_r,\rho_r)\rho_r^3$$
$$+E(T_r,\rho_r)\rho_r^5+F(T_r,\rho_r)\rho_r^7$$
$$+G(T_r,\rho_r)\rho_r^8+H(T_r,\rho_r)\rho_r^{10}$$
$$+I(T_r,\rho_r)\rho_r^{12}]d\rho$$
$$=\int_0^{\rho}\frac{P}{\rho^2}d\rho+\int_{\rho_0}^{0}\frac{\rho RT}{\rho^2}d\rho+\int_0^{\rho}\frac{\rho RT}{\rho^2}d\rho$$
$$-\int_0^{\rho}\frac{\rho RT}{\rho^2}d\rho\quad(1.6)$$
$$A-A_0=\int_0^{\rho}\frac{Z\rho RT-\rho RT}{\rho^2}d\rho+\int_{\rho_0}^{\rho}\frac{\rho RT}{\rho^2}d\rho$$
$$A-A_0=\int_0^{\rho}\frac{RT(Z-1)}{\rho}d\rho+\int_{\rho_0}^{\rho}\frac{\rho RT}{\rho^2}d\rho$$
$$A-A_0=\int_0^{\rho_r}\frac{1}{\rho_r}d\rho_r+\int_{\rho_{r0}}^{\rho_r}\frac{RT}{\rho_r}d\rho_r$$
$$A-A_0=RT\int_0^{\rho_r}[B(T_r,\rho_r)+C(T_r,\rho_r)\rho_r+D(T_r,\rho_r)\rho_r^2$$
$$+E(T_r,\rho_r)\rho_r^4+F(T_r,\rho_r)\rho_r^6$$
$$+G(T_r,\rho_r)\rho_r^7+H(T_r,\rho_r)\rho_r^9$$
$$+I(T_r,\rho_r)\rho_r^{11}]d\rho_r+RTln\frac{\rho_r}{\rho_{r0}}\quad(1.7)$$

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

$$K(m,\rho_r)=\int_0^{\rho_r}\rho_r^m\exp(-\rho_r^2)d\rho_r=\int_0^{\rho_r}\sum_{n=0}^{\infty}(-1)^n\frac{\rho_r^{2n+m}}{n!}d\rho_r$$
$$=\sum_{n=0}^{\infty}(-1)^n\frac{\rho_r^{2n+m+1}}{(2n+m+1)n!}\quad(1.8)$$

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

$$A-A_0=RT\Bigg(B\rho_r+C_1\frac{\rho_r^2}{2}+C_2K(1,\rho_r)+D\frac{\rho_r^3}{3}+E\frac{\rho_r^5}{5}+F\frac{\rho_r^7}{7}$$
$$+G_1\frac{\rho_r^8}{8}+G_2,K(8,\rho_r)+H_2K(10,\rho_r)$$
$$+I_2K(12,\rho_r)\Bigg)+RTln\left(\frac{\rho_r}{\rho_{r0}}\right)\quad(1.9)$$

Entropy departure function:

$$S-S_0=-\left.\frac{\partial(A-A_0)}{\partial T}\right|_{\rho}\quad(1.10)$$
$$S-S_0=R\Bigg(B\rho_r+C_1\frac{\rho_r^2}{2}+C_2K(1,\rho_r)+D\frac{\rho_r^3}{3}+E\frac{\rho_r^5}{5}+F\frac{\rho_r^8}{8}$$
$$+G_1\frac{\rho_r^9}{9}+G_2,K(8,\rho_r)+H_2K(10,\rho_r)$$
$$+I_2K(12,\rho_r)\Bigg)$$
$$+RT\Bigg(\frac{dB}{dT}\rho_r+\frac{dC_1}{dT}\frac{\rho_r^2}{2}+\frac{dC_2}{dT}K(1,\rho_r)$$
$$+\frac{dD}{dT}\frac{\rho_r^3}{3}+\frac{dE}{dT}\frac{\rho_r^5}{5}+\frac{dF}{dT}\frac{\rho_r^8}{8}+\frac{dG_1}{dT}\frac{\rho_r^9}{9}$$
$$+\frac{dG_2}{dT}K(8,\rho_r)+\frac{dH_2}{dT}K(10,\rho_r)$$
$$+\frac{dI_2}{dT}K(12,\rho_r)\Bigg)+Rln\left(\frac{\rho_r}{\rho_{r0}}\right)$$

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_{li} K	T_hi 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

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

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

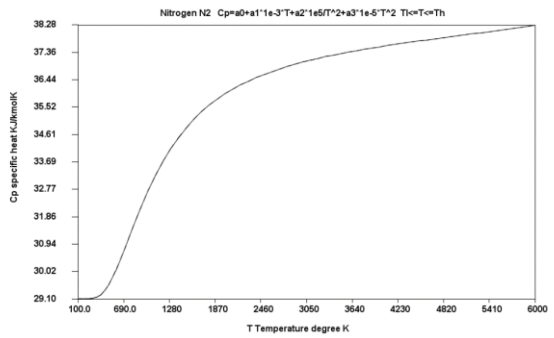


Figure 1.1 Cp of Nitrogen kJ/(kmolK)

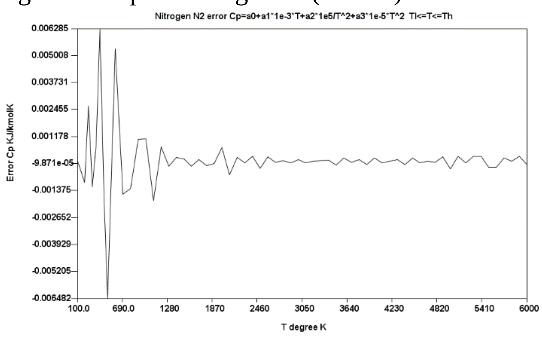


Figure 1.2 Error of Cp in Nitrogen kJ/(kmolK)

Table 1.2 Cp (kJ/kmol K) partial continious curve fitting equations for N_2 Nitrogen

i	A_i	B_i	C_i	D_i	T_{li} K	T_hi 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 carbondioxide , oxygen and carbonic acid. A reaction might take place is

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

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 equailibrium condition (pressured in the system) is changed and rection slides to a new equilibrium states, so that some omount 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:

$$dn_{CO_2} = -dn_{H_2CO_3}$$
$$dn_{H_2O} = -dn_{H_2CO_3} \quad (2.1)$$

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)

$$\mu_{CO_2} = \frac{\partial G(T,P,n)}{\partial n_{CO_2}} \qquad \partial G(T,P,n) = \mu_{CO_2}\partial n_{CO_2}$$
$$\mu_{n_{H_2CO_3}} = \frac{\partial G(T,P,n)}{\partial n_{H_2CO_3}} \qquad \partial G(T,P,n) = \mu_{H_2CO_3}\partial n_{H_2CO_3}$$
$$\mu_{H_2O} = \frac{\partial G(T,P,n)}{\partial n_{H_2O}} \qquad \partial G(T,P,n) = \mu_{H_2O}\partial n_{H_2O}$$
$$dG(T,P) = -1 * \mu_{CO_2}dn_{CO_2} - 1 * \mu_{H_2O}dn_{H_2O} + 1 * \mu_{H_2CO_3}dn_{H_2CO_3} = 0 \quad (2.4)$$
$$dG(T,P) = \left(-1 * \mu_{CO_2} - 1 * \mu_{H_2O} + 1 * \mu_{H_2CO_3}\right)dn_{H_2O} = 0 \quad (2.5)$$

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

$$\upsilon_A A + \upsilon_B B \rightleftarrows \upsilon_C C + \upsilon_D D \quad (2.6)$$

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

$$-\frac{dn_A}{\upsilon_A} = -\frac{dn_B}{\upsilon_B} = \frac{dn_C}{\upsilon_C} = \frac{dn_D}{\upsilon_D} = d\varepsilon \quad (2.7)$$

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

$$dn_A = -\upsilon_A\, d\varepsilon$$
$$dn_B = -\upsilon_B\, d\varepsilon$$
$$dn_C = \upsilon_C\, d\varepsilon$$
$$dn_D = \upsilon_D\, d\varepsilon$$

(2.8)

For this case the Gibbs free energy equation takes form:

$$dG(T,P) = -\upsilon_A * \mu_A - \upsilon_B * \mu_B + \upsilon_C * \mu_C + \upsilon_D * \mu_D = 0 \quad (2.9)$$

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

$$h_{Ti}(T) = h_i(T) - h(298.15) + \Delta h_f(298.15)$$
$$g^0(T) = h_{Ti}(T) - Ts^0(T)$$
$$\mu_i = g_i^0(T) - RTln\left(\frac{P_i}{P_{ref}}\right) \quad (2.10)$$

where P_i is the partial pressure of the gas. For and 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:

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

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

$$h_{Ti}(T,P) = h_i(T,P) - h(298.15,P) + \Delta h_f(298.15) \quad (2.13)$$
$$s(T,P) = s^0(T) - Rln\left(\frac{f_i}{P_{ref}}\right) \quad (2.14)$$
$$g(T,P) = g^0(T,P) - RTln\left(\frac{f_i}{P_{ref}}\right) \quad (2.15)$$
$$g^0(T,P) = h_{Ti}(T,P) - Ts^0(T) \quad (2.16)$$
$$\mu_i = g_i^0(T) - RTln\left(\frac{f_i}{P_{ref}}\right) \quad (2.17)$$

Note that $\lim_{P\to 0}\frac{f_i}{P_i} = 1$ (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:

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

Then the basic Gibbs free energy equation becomes

$$dG(T,P) = -\upsilon_A\left[g_A^0(T) - RTln\left(\frac{n_A}{n_{total}} \quad \frac{f^*}{P_{ref}}\right)\right] - \upsilon_B\left[g_B^0(T) - RTln\left(\frac{n_B}{n_{total}} \quad \frac{f^*}{P_{ref}}\right)\right] + \upsilon_C\left[g_C^0(T) - RTln\left(\frac{n_C}{n_{total}} \quad \frac{f^*}{P_{ref}}\right)\right] + \upsilon_D\left[g_D^0(T) - RTln\left(\frac{n_D}{n_{total}} \quad \frac{f^*}{P_{ref}}\right)\right] = 0 \quad (2.22)$$

Arranging equation:

$$dG^0(T,P) = -\upsilon_A g_A^0(T,P) - \upsilon_B g_B^0(T,P) + \upsilon_C g_C^0(T,P) + \upsilon_D g_D^0(T,P)$$
$$dG(T,P) = dG^0(T,P) + RT\left[\upsilon_A ln\left(\frac{n_A}{n_{total}} \quad \frac{f^*}{P_{ref}}\right) + \upsilon_B ln\left(\frac{n_B}{n_{total}} \quad \frac{f^*}{P_{ref}}\right) - \upsilon_C ln\left(\frac{n_C}{n_{total}} \quad \frac{f^*}{P_{ref}}\right) - \upsilon_D ln\left(\frac{n_D}{n_{total}} \quad \frac{f^*}{P_{ref}}\right)\right] = 0 \quad (2.23)$$

This equation can be written as:

$$-\frac{dG^0(T,P)}{RT} = \left[\upsilon_A ln\left(\frac{n_A}{n_{total}} \quad \frac{f^*}{P_{ref}}\right) + \upsilon_B ln\left(\frac{n_B}{n_{total}} \quad \frac{f^*}{P_{ref}}\right) - \upsilon_C ln\left(\frac{n_C}{n_{total}} \quad \frac{f^*}{P_{ref}}\right) - \upsilon_D ln\left(\frac{n_D}{n_{total}} \quad \frac{f^*}{P_{ref}}\right)\right] \quad (2.24)$$

$$exp\left(-\frac{dG^0(T,P)}{RT}\right)=\left[\frac{\left(\frac{n_A}{n_{total}}\quad\frac{f^*}{P_{ref}}\right)^{\upsilon_A}\left(\frac{n_B}{n_{total}}\quad\frac{f^*}{P_{ref}}\right)^{\upsilon_B}}{\left(\frac{n_C}{n_{total}}\quad\frac{f^*}{P_{ref}}\right)^{\upsilon_C}\left(\frac{n_D}{n_{total}}\quad\frac{f^*}{P_{ref}}\right)^{\upsilon_D}}\right]$$

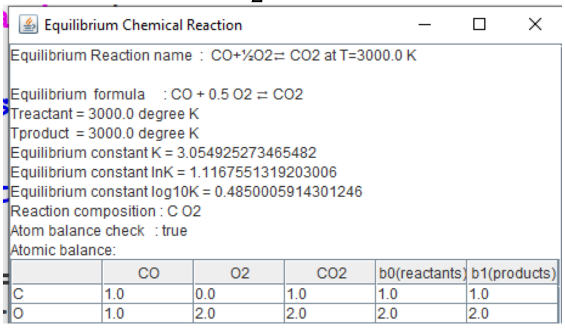
$$=\left[\frac{(n_A)^{\upsilon_A}(n_B)^{\upsilon_B}}{(n_C)^{\upsilon_C}(n_D)^{\upsilon_D}}\right]\left(\frac{f^*}{n_{total}P_{ref}}\right)^{\upsilon_A+\upsilon_B-\upsilon_C-\upsilon_D} \quad (2.25)$$

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

$$CO+\frac{1}{2}O_2 \rightleftharpoons CO_2$$


Equilibrium Chemical Reaction

Equilibrium Reaction name : CO+½O2⇌ CO2 at T=3000.0 K

Equilibrium formula : CO + 0.5 O2 ⇌ CO2
Treactant = 3000.0 degree K
Tproduct = 3000.0 degree K
Equilibrium constant K = 3.054925273465482
Equilibrium constant lnK = 1.1167551319203006
Equilibrium constant log10K = 0.4850005914301246
Reaction composition : C O2
Atom balance check : true
Atomic balance:

	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_2O	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_2O	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:

$$\begin{bmatrix}4&2&2&0&0&0\\1&0&0&1&1&0\\0&1&0&2&1&0\end{bmatrix}\begin{Bmatrix}n_{CH_4}\\n_{H_2O}\\n_{H_2}\\n_{CO_2}\\n_{CO}\\n_{O_2}\end{Bmatrix}=\begin{Bmatrix}24\\1\\10\end{Bmatrix} \quad (2.30)$$

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 togetger 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 homotophy 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(λ,x) in the form of

G(λ,x) = λF(x) + (1-λ)[F(x) - F(x(0))] (2.31)

Where λ=0 coresponds to initial guess of the solution , x(0) ,and where λ=1 value corresponds the actual solution set x(1)= x*

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

G(λ,x) =G(0,x) = F(x) - F(x(0)) and for λ=1 (2.32)

0=G(1,x) = F(x) (2.33)

Therefore at x(1)=x* solution set will be obtained. If a function G(λ,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(λ,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'(λ) is isolated form this equation, it becomes:

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

(2.35)

If G(λ,x) = λF(x) + (1-λ)[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

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

Differential equation becomes

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

(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

$\frac{dx(\lambda)}{d\lambda}=f(\lambda,x(\lambda))$ (2.39)is given the 6th order Runge-Kutta method to numerically solve this differential equation is defined as:

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

$k_1=f(x_i,y_i)$

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

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

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

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

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

This equation can be given as Buthcher tableu as:

$$\begin{array}{c|ccccc} 0 & 0 & 0 & 0 & 0 & 0\\ 1/4 & 1/4 & 0 & 0 & 0 & 0\\ 1/4 & 1/8 & 1/8 & 0 & 0 & 0\\ 2/4 & 1/4 & -1/4 & 1 & 0 & 0\\ 3/4 & 3/16 & 0 & 0 & 9/16 & 0\\ 1 & -3/7 & 2/7 & 12/7 & -12/7 & 8/7\\ \hline & 1/90 & 7/90 & 32/90 & 12/90 & 7/90 \end{array}$$

(2.41)

In these equations h is finite difference step size. Solution starts by using the initial value λ=0 , x0(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 Homotophy 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 homotophy 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 termodynamic properties of gases Schereiber 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 ChemicalRaction_SP class. System of equations are set together in if_equilibrium_SP class. Continuatio 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	Schereiber and Pitzer real gas EoS
Gas_PG	Perfect Gas EoS
ChemicalReaction_SP	Chemical reaction calculater 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 calculater for Gas_PG
If_equilibrium_PG	Defines non-linear system of equation for Gas_PG
Equilibrium_PG	Stoichiometric Equilibrium calculator for Gas_SP
Iterative_continuity	Continuation(homotophy) method for non-linear system of eqns.

Sample solutions:

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

$$CO+\frac{1}{2}O_2 \rightleftharpoons CO_2$$

The reaction will be

$$CO+O_2 \rightarrow n_0CO+n_1O_2+n_2CO_2$$

Find the equilibrium composition. System pressure is P=101.325 bar. (Pref=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");
 }

}
```

Newton_continuation

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 equlibrium_PG for the same conditions:

Newton_continuation

x initial guess	x	y=f(x)
0.049084885297797864	0.3421068814833881	0.0
0.4174016135657407	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:

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$$

The reaction will be

$CO+O_2+1.88N_2 \rightarrow n_0CO+n_1O_2+n_2CO_2+1.88N_2$

Find the equilibrium composition.

```
public static void main(String arg[])
 {
    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");
 }
```

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 equlibrium_PG for the same conditions:

Newton_continuation

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:

$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$ The reaction will be $CO + O_2 \rightarrow n_0CO + n_1O_2 + n_2CO_2$

Newton_continuation

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 equlibrium_PG for the same conditions:

Newton_continuation

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

```
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:

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2 \quad N_2 + 1/2O_2 \rightleftharpoons 2NO$$

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[]=fe.func(n);
          //double              []              r1=
continuity.continuationRK6(fe,n,4);
          double              []              r1=
continuityi.newton_continuationRK6(fe,n);
          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 equlibrium1_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

4. Results and conclusion

Stoichiometric chemical equilibrium algorithm is developed by using Schereiber and Pitzer real gas EoS. Schereiber and Pitzer EoS is relatively 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 equilibrum 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 calulations are that ideal gas equations are based on pressure while real gas equations are based on fugacity. Results seems not deviates much, therefore one of the conclution 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 presenrted as sperate papers.

5. References

1. The International Association for the Properties of Water and Steam, Revised Relase on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam, Lucerne, Switzerland, August 2007, IAPWS R7(2012)
2. J.R. Cooper, R. B. Dooley, The International Association for the Properties of Water and Steam, Guideline on an Equation of State for Humid Air in Contact with SeaWater and Ice, Consistent with the IAPWS Formulation 2008 for the Thermodynamic Properties of SeaWater
3. Robert C. Reid, John M. Prausnitz, Bruce E. Poling, The Properties of Gases & Liquids, Fourth Edition, McGraw-Hill ISBN 0-07-051799-1
4. Bruce E. Poling, John M Prausnitz, John P. O'connel, The Properties of Gases & Liquids, 5th edition, 2004, McGraw-Hill ISBN 0-07-051799-1, ISBN-10: 0070116822
5. Numerical Thermodynamics, M. Turhan Coban, www.turhancoban.com
6. Ian H. Bell, Jorrit Wronski, Sylvain Quailin, and Vincent Lemort, Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp, Ind Eng Chem Res 2014 Feb 12;53(6) 2498-2508 DOI 10.1021/ie4033999
7. Simeen Sattar, Thermodynamics of Mixing Real Gases, Jornal of Chemical Education Vol. 77 No 10 October 2000
8. Pitzer, Kenneth S., J. J. Am. Chem. Soc., 77:3427 (1955)
9. Schreiber, Donald R. and Pitzer, Kenneth S., Selected equation of State in the Acentric Factor System, International Journal of Thermodynamics, Vol 9, No. 6, 1988
10. M. Turhan Çoban, Numerical Thermodynamics, http://www.turhancoban.com/kitap/NUMERICAL%20THERMODYNAMICS.pdf

6. Nomenclature

Z	Compressibility factor
P	Pressure
ρ	density
R	Gas constant
T	Temperature
B,C,D,E,F,G	Schereiber-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	Homotophy(continuity) variable
n	Mole numbers
M	Molecular weight