EVALUATION OF METHODS TO CALCULATE CHEMICAL EQUILIBRIUM IN GASEOUS SYSTEMS

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Key words: Equilíbrio químico, reação de equilíbrio, métodos computacionais.

INTRODUCTION

The separation of fluid mixtures is an aspect of chemical process design. To accomplish it, thermodynamic models are required to describe or estimate chemical and phase equilibria between these fluids.

Computation of chemical equilibrium in multi-reaction systems can be done by using the following methods: free energy minimization, Brinkley’s method and Series reactor method (or Relaxation method). With the first cited, it is possible to determine the mixture reaction to the final composition without knowledge of stoichiometric reactions involved, therefore it is called the nonstoichiometric method. The others are known as stoichiometric methods, that is...
to say, they are applied when stoichiometric reactions are already known.

Early work referred to as the stoichiometric method, such as that for Brinkley (1947), concentrated on solving the set of nonlinear algebraic equations. Sanderson and Chien (1973) solved these equations using Marquardt's method (1963) after reformulating the problem. Xiao et al. (1989) improved the algorithm of Sanderson and Chien by modifying the procedure with the inner and outer interaction loops are solved. Smith and Missen's book (1982) provides a completely review and exposition of the work in this area.

For many chemical engineering applications the Gibbs free energy can be minimized. White et al. (1958) were the first to solve the problem using optimization techniques. They considered ideal mixtures only and tested two methods, one of which was steepest descent method while the other relied on techniques of linear programming. Gautam and Sieder (1979) and White and Seider (1981) solved chemical equilibrium problems where some of the reactions may not be taken at equilibrium. Lucia and Xu (1990) investigated issues of reliability and efficiency for Quasi-Newton and Newton methods for several chemical process applications. Castier et al. (1989) presented an algorithm that uses a stoichiometric formulation which automatically selects the independent chemical reactions. A review of these contributions is given by McDonald and Floudas (1995).

This work wants to explore and evaluate the existing methods to calculate the chemical equilibrium in gaseous systems. The gaseous phase was modeled by at least two equations: The Peng-Robinson equation and Virial equation. The influence of these equations in the results were discussed. Heat capacity equations to calculate the standard Gibbs free energy were tested. The evaluation was done applying the methods for some industrial examples found in literature. The results demonstrated that care must be taken in finding equilibrium solutions for a variety of problems.

**THEORY**

2.1. Methods of formulating solutions for multireaction equilibrium.

2.1.1. The method of Brinkley (BRK)

Brinkley (1947) concentrated on solving the set of non-linear algebraic equations based on the equilibrium constant expressions and the material balance equations. This stoichiometric method comprises seven steps, as follows:

1. Select the chemical species that may be present at equilibrium;
2. Determine the number of independent components;
3. Choose a set of independent components from among the species present;
4. Write a set of chemical reaction equations;
5. Write the chemical equilibrium equation of each of these reactions;
6. Write the material balances on the individual chemical elements;
7. The equilibrium equations of step 5 and the element balances of step 6 make up a system that is solved for the composition of the equilibrium mixture.

A solution by successive approximation is employed and requires a starting estimate of the composition. The Newton-Raphson method was used to solve the problem.

2.1.2. The relaxation method (The series reactor method)

The series reactor method (RCT) adopts a hypothetical system of reactors equal in number to the independent stoichiometric equations present at equilibrium. Each reactor operates batchwise and forces equilibrium of the reaction with the same number as the reactor. The process is started by charging the original mixture into the first reactor, where the reaction one

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reaches equilibrium. That product is then charged into the second reactor, and so on. The last stream must be returned to the first reactor. The feed to each reactor is the equilibrium product from the preceding one and only one reaction occurs in each vessel. The process is continued until the effluent composition from any reactor becomes constant. One equation needs to be solved for each reactor. The convergence is attained in accordance with the adopted criteria.

2.1.3. Minimization of Gibbs Energy (GEM)\textsuperscript{6,10,11,18,19,20.}

In this method, stoichiometric analysis is not required, simply a list of the chemical species expected at equilibrium. The problem consists in minimizing the Gibbs free energy (G) of the reaction system given by:

\[ G = \sum_{i=1}^{N} \sum_{k=1}^{n_k} n_k \mu_k = \sum_{i=1}^{N} \sum_{k=1}^{n_k} n_k \Delta G_k \]  \hspace{1cm} (1)

where \( n_k \) is the number of moles of component \( k \) in phase \( i \) which must be obtained in the calculations, \( \mu_k \) is the associated chemical potential, \( N \) is the total number of components, \( \Delta G_k \) is the partial molar Gibbs free energy and \( \pi \) is the number of phases at equilibrium. Chemical potential is expressed in terms of Gibbs free energy of formation (\( \Delta G_{i} \)) and partial fugacity of component \( i \) in phase \( j \) (\( \phi_i \)) that is represented as a function of partial fugacity coefficient for each component (\( \hat{\phi}_i \)). Two different equations for heat capacity were employed to calculate \( \Delta G_{i} \) for each component and also, two PVT (Pressure-Volume-Temperature) equations represented the gaseous phase.

To evaluate the methods for solving chemical equilibrium problems and the effect of the equations used the initial conditions were established when necessary. Some examples involving single phase were taken from literature\textsuperscript{17,23,22.}

2.2. Basic equations

For a multicomponent and multiphase system, the Gibbs free energy function is expressed as follows:

\[ G = \sum_{i=1}^{N} n_i \left( \Delta G_{i,0} + RT \ln \hat{\alpha}_i \right) \]  \hspace{1cm} (2)

Where: \( n_i \) is the number of moles of species \( i \), \( R \) is the universal gas constant and \( \hat{\alpha}_i \) is the activity for the component in the mixture that is written in the form:

\[ \hat{\alpha}_i = \frac{f_i}{f_i^*} = \frac{\hat{\phi}_i y_i P}{\hat{\phi}_i P \left( \frac{n_i}{n} \right)} \]  \hspace{1cm} (3)

Where the fugacity coefficients described by \( \hat{\phi}_i \) depend on the temperature, pressure and composition \( y_i \) of the system. The standard state for the vapor phase was taken as an ideal gas at unit fugacity at the system temperature where this quantity is usually equal to 1 atm.

The vapor-phase fugacity coefficients were calculated from the Peng-Robinson equation\textsuperscript{25}.

\[ P = \frac{RT}{V-b} - \frac{a}{(V+b)(V-b)} \]  \hspace{1cm} (4)

The mixture parameters \( a, b \) used in equation (4) are defined by the mixing rules,

\[ a = \sum_{i} \sum_{j} y_i y_j (1-k_{ij}) \sqrt{a_i a_j} \]  \hspace{1cm} (5)

\[ b = \sum_{i} y_i b_i \]  \hspace{1cm} (6)

with binary interaction parameters \( k_{ij} \) considered equal zero. The virial equation truncated at the second member \( B \)\textsuperscript{25},
\[ \frac{PV}{RT} = 1 + \frac{B}{V} \]  

(7)

The equation (7) was employed with,

\[ B = \sum_i \sum_j y_i y_j B_{ij} \]  

(8)

where each \( B_{ij} \) is a function of temperature. For phase and chemical equilibria where reaction does occur, the conservation of chemical elements must be satisfied:

\[ b_j = \sum_i a_{ij} n_i = 0 \]  

(9)

Where: \( a_{ij} \) represents the number of grams-atoms of element \( i \) in component \( j \). \( b \) is the total number of grams-atoms of element \( i \) in the system, \( M \) is the number of elements and \( C \) the number of components.

To solve the chemical equilibrium problem using any method described it is necessary to know the Gibbs free energy of formation for the components that take part in the reaction at system temperature. Therefore, the Gibbs-Helmholtz equation was used\(^{17,18} \), thus with reference values represented by \( \Delta G^r \), \( \Delta H^r \) and \( T_\circ \).

\[ \int_{\Delta G^r / T_\circ} d\left( \frac{\Delta G}{T} \right) = - \int_{T_\circ}^{T} \left( \frac{\Delta H}{T^2} \right) dT \]  

(10)

The Equation (10) is solved if one equation for the molar heat capacity, \( C_r(T) \), is known. In this manner, the molar enthalpy change as a function of the temperature yields:

\[ \Delta H = \Delta H^0 + \int_{T_\circ}^{T} C_r(T) dT \]

The heat capacity, for each component, can be represented as a function of temperature by means the equation (11) found in Reid et al. 1987\(^{24} \).

\[ Cp = A + BT + CT^2 + DT^3 \]  

(11)

and by the following equation (12) that is presented in Smith et al. 1996\(^{22} \):

\[ Cp = A + BT + CT^2 + DT^{-2} \]  

(12)

Empirical constants \( (A, B, C \text{ and } D) \) were adjusted between 300-1800K for equation (12). There was no mention about temperature range for the constants in the equation (11).

**RESULTS AND DISCUSSIONS**

The application of the methods to single-phase multireactional systems is now considered. Some illustrative examples were selected from the literature and they are presented. Systems containing one, two or three or more reactions were chosen at the range of pressure between 1 atm to 40 atm, for the temperature range from 358K and 2200 K. The methods were compared for the Examples 1, 2 and 3. Examples 4 and 5 were solved for the (GEM) and (BRK) only.

The examples chosen to demonstrate the application of the methods are:

**EXAMPLE 1:** Esterification reaction (\( T: \) 358K; \( P: \) 1 atm)\(^{25} \):

\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_4\text{C}_2\text{O}_2 \rightarrow \text{H}_8\text{C}_4\text{O}_2 + \text{H}_2\text{O} \]

**EXAMPLE 2:** Production of \( \text{CS}_2 \) (\( T: \) 1000K; \( P: \) 1.5 atm)\(^{5} \):

\[ \text{CH}_4 + \text{S}_2 \rightarrow \text{CS}_2 + 2\text{H}_2 \text{H}_2 + \frac{1}{2}\text{S}_2 \rightarrow \text{H}_2\text{S} \]

**EXAMPLE 3:** Combustion reaction (\( T: \) 2200K, \( P: \) 40 atm)\(^{9} \):

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

\[ \text{CO}_2 + \frac{1}{2}\text{N}_2 \rightarrow \text{CO} + \text{NO} \]

\[ \text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2 \]
EXAMPLE 4: Cracking of C₂H₆
(T: 1000 K; P: 1 atm)²⁶:

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2 \]
\[ \text{C}_2\text{H}_6 + \frac{7}{2} \text{O}_2 \rightleftharpoons 2\text{CO}_2 + 3\text{H}_2\text{O} \]
\[ \text{C}_2\text{H}_6 + \frac{3}{2} \text{O}_2 \rightleftharpoons 2\text{CO} + 3\text{H}_2\text{O} \]
\[ \text{C}_2\text{H}_6 + \text{H}_2\text{O} \rightleftharpoons 2\text{CH}_4 + \frac{1}{2} \text{O}_2 \]
\[ \text{C}_2\text{H}_6 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_2 + 3\text{H}_2 \]
\[ \text{C}_2\text{H}_6 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2 \]

The equation can be found in Silva, 2002 ²¹. In tables, the mole fraction, \( Y^m \), represents the value published by literature. The results given in table 1 were obtained using the equation (11) otherwise table 2 shows the ones obtained working with equation (12) to compute the Gibbs free energy of formation for each component.

### Table 1. Mole fraction calculated by all methods. Compared results for example 1.

<table>
<thead>
<tr>
<th>COMP</th>
<th>Y⁰⁰</th>
<th>Y⁰⁰₁</th>
<th>ΔY⁰⁰₁</th>
<th>YBRK</th>
<th>ΔYBRK</th>
<th>YECT</th>
<th>ΔYECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{C}_2\text{H}_5\text{OH}</td>
<td>0.0753</td>
<td>0.0675</td>
<td>0.0078</td>
<td>0.0679</td>
<td>0.0170</td>
<td>0.0675</td>
<td>0.0078</td>
</tr>
<tr>
<td>\text{H}_2\text{C}_2\text{O}_4</td>
<td>0.0753</td>
<td>0.0675</td>
<td>0.0078</td>
<td>0.0679</td>
<td>0.0170</td>
<td>0.0675</td>
<td>0.0078</td>
</tr>
<tr>
<td>\text{C}_4\text{H}<em>8\text{O}</em>{2}</td>
<td>0.4247</td>
<td>0.4325</td>
<td>0.0079</td>
<td>0.4321</td>
<td>0.0200</td>
<td>0.4325</td>
<td>0.0078</td>
</tr>
<tr>
<td>\text{H}_2\text{O}</td>
<td>0.4247</td>
<td>0.4325</td>
<td>0.0079</td>
<td>0.4321</td>
<td>0.0200</td>
<td>0.4325</td>
<td>0.0078</td>
</tr>
<tr>
<td>ΔYm</td>
<td>0.0078</td>
<td>20 iter.</td>
<td>0.0185</td>
<td>2 passes</td>
<td>0.0078</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( T = 358 K; P = 1 \text{ atm}; C_e \text{ equation from Reid et al., 1987} \)

### Table 2. Mole fraction calculated by all methods. Compared results for example 1.

<table>
<thead>
<tr>
<th>COMP</th>
<th>Y⁰⁰</th>
<th>Y⁰⁰₁</th>
<th>ΔY⁰⁰₁</th>
<th>YBRK</th>
<th>ΔYBRK</th>
<th>YECT</th>
<th>ΔYECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{C}_2\text{H}_5\text{OH}</td>
<td>0.0753</td>
<td>0.1063</td>
<td>0.0310</td>
<td>0.0649</td>
<td>0.0170</td>
<td>0.1184</td>
<td>0.0431</td>
</tr>
<tr>
<td>\text{H}_2\text{C}_2\text{O}_4</td>
<td>0.0753</td>
<td>0.1063</td>
<td>0.0310</td>
<td>0.0649</td>
<td>0.0170</td>
<td>0.1184</td>
<td>0.0431</td>
</tr>
<tr>
<td>\text{C}_4\text{H}<em>8\text{O}</em>{2}</td>
<td>0.4247</td>
<td>0.3937</td>
<td>0.0310</td>
<td>0.4351</td>
<td>0.0200</td>
<td>0.3817</td>
<td>0.0430</td>
</tr>
<tr>
<td>\text{H}_2\text{O}</td>
<td>0.4247</td>
<td>0.3937</td>
<td>0.0310</td>
<td>0.4351</td>
<td>0.0200</td>
<td>0.3817</td>
<td>0.0430</td>
</tr>
<tr>
<td>ΔYm</td>
<td>0.0310</td>
<td>37 iter.</td>
<td>0.0185</td>
<td>2 passes</td>
<td>0.0430</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( T = 358 K; P = 1 \text{ atm}; C_e \text{ equation from Smith et al., 1998} \)

Tables 1 and 2 show the effective influence of the \( C_e \) equation through the average deviations (ΔYm) obtained. The prediction of equilibrium composition did not change by taking into account the method employed. Tables 3 and 4 show the results for example 2 using the same sequence of equations as in the last example.

### Table 3. Mole fraction calculated by all methods. Compared results for example 2.

<table>
<thead>
<tr>
<th>COMP</th>
<th>Y⁰⁰</th>
<th>Y⁰⁰₁</th>
<th>ΔY⁰⁰₁</th>
<th>YBRK</th>
<th>ΔYBRK</th>
<th>YECT</th>
<th>ΔYECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CH}_4</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0003</td>
<td>0.0000</td>
</tr>
<tr>
<td>\text{S}_2</td>
<td>0.0153</td>
<td>0.0160</td>
<td>0.0007</td>
<td>0.0160</td>
<td>0.0007</td>
<td>0.0160</td>
<td>0.0007</td>
</tr>
<tr>
<td>\text{CS}_2</td>
<td>0.3281</td>
<td>0.3279</td>
<td>0.0002</td>
<td>0.3278</td>
<td>0.0003</td>
<td>0.3279</td>
<td>0.0002</td>
</tr>
<tr>
<td>\text{H}_2\text{S}</td>
<td>0.6270</td>
<td>0.6248</td>
<td>0.0022</td>
<td>0.6249</td>
<td>0.0021</td>
<td>0.6249</td>
<td>0.0021</td>
</tr>
<tr>
<td>\text{H}_2</td>
<td>0.0293</td>
<td>0.0310</td>
<td>0.0017</td>
<td>0.0310</td>
<td>0.0003</td>
<td>0.0309</td>
<td>0.0016</td>
</tr>
<tr>
<td>ΔYm</td>
<td>0.0010</td>
<td>74 iter.</td>
<td>0.0007</td>
<td>3 passes</td>
<td>0.0010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( T = 1000 K; P = 1.5 \text{ atm}; C_e \text{ equation from Reid et al., 1987} \)
Table 4. Mole fraction calculated by all methods. Compared results for example 2.

<table>
<thead>
<tr>
<th>COMP.</th>
<th>Y^GEM</th>
<th>Y^GEM</th>
<th>ΔY^GEM</th>
<th>Y^BRK</th>
<th>ΔY^BRK</th>
<th>Y^RECT</th>
<th>ΔY^RECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0002</td>
<td>0.0001</td>
<td>0.0003</td>
<td>0.0000</td>
</tr>
<tr>
<td>S2</td>
<td>0.0153</td>
<td>0.0160</td>
<td>0.0007</td>
<td>0.0150</td>
<td>0.0003</td>
<td>0.0160</td>
<td>0.0007</td>
</tr>
<tr>
<td>CS2</td>
<td>0.3281</td>
<td>0.3279</td>
<td>0.0002</td>
<td>0.3282</td>
<td>0.0001</td>
<td>0.3279</td>
<td>0.0002</td>
</tr>
<tr>
<td>H2S</td>
<td>0.6270</td>
<td>0.6248</td>
<td>0.0022</td>
<td>0.6273</td>
<td>0.0003</td>
<td>0.6249</td>
<td>0.0021</td>
</tr>
<tr>
<td>H2</td>
<td>0.0293</td>
<td>0.0310</td>
<td>0.0017</td>
<td>0.0292</td>
<td>0.0001</td>
<td>0.0309</td>
<td>0.0016</td>
</tr>
<tr>
<td>ΔYm</td>
<td>0.0010</td>
<td></td>
<td></td>
<td>63 iter.</td>
<td>0.0002</td>
<td>3 passes</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

(T = 1000 K; P = 1.5 atm, Cp equation from Smith et al. 1996).

Finally, for the system setting three reactions, the results are shown in tables 5 and 6.

Table 5. Mole fraction calculated by all methods. Compared results for example 3.

<table>
<thead>
<tr>
<th>COMP.</th>
<th>Y^GEM</th>
<th>Y^GEM</th>
<th>ΔY^GEM</th>
<th>Y^BRK</th>
<th>ΔY^BRK</th>
<th>Y^RECT</th>
<th>ΔY^RECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>0.1080</td>
<td>0.1064</td>
<td>0.0016</td>
<td>0.1064</td>
<td>0.0016</td>
<td>0.1038</td>
<td>0.0042</td>
</tr>
<tr>
<td>N2</td>
<td>0.7389</td>
<td>0.7381</td>
<td>0.0008</td>
<td>0.7381</td>
<td>0.0008</td>
<td>0.7376</td>
<td>0.0013</td>
</tr>
<tr>
<td>H2O</td>
<td>0.1472</td>
<td>0.1469</td>
<td>0.0003</td>
<td>0.1469</td>
<td>0.0004</td>
<td>0.1451</td>
<td>0.0021</td>
</tr>
<tr>
<td>CO</td>
<td>0.0029</td>
<td>0.0044</td>
<td>0.0015</td>
<td>0.0044</td>
<td>0.0016</td>
<td>0.0074</td>
<td>0.0045</td>
</tr>
<tr>
<td>O2</td>
<td>0.0013</td>
<td>0.0019</td>
<td>0.0007</td>
<td>0.0019</td>
<td>0.0006</td>
<td>0.0013</td>
<td>0.0000</td>
</tr>
<tr>
<td>NO</td>
<td>0.0010</td>
<td>0.0014</td>
<td>0.0004</td>
<td>0.0015</td>
<td>0.0005</td>
<td>0.0048</td>
<td>0.0038</td>
</tr>
<tr>
<td>H2</td>
<td>0.0007</td>
<td>0.0008</td>
<td>0.0001</td>
<td>0.0008</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0006</td>
</tr>
<tr>
<td>ΔYm</td>
<td>7.7E-4</td>
<td>154 iter.</td>
<td>0.0008</td>
<td>6 passes</td>
<td>0.0024</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(T = 2200 K; P = 40 atm, Cp equation from Reid et al. 1987).

Table 6. Mole fraction calculated by all methods. Compared results for example 3.

<table>
<thead>
<tr>
<th>COMP.</th>
<th>Y^GEM</th>
<th>Y^GEM</th>
<th>ΔY^GEM</th>
<th>Y^BRK</th>
<th>ΔY^BRK</th>
<th>Y^RECT</th>
<th>ΔY^RECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>0.1080</td>
<td>0.1084</td>
<td>0.0004</td>
<td>0.1078</td>
<td>0.0010</td>
<td>0.1043</td>
<td>0.0037</td>
</tr>
<tr>
<td>N2</td>
<td>0.7389</td>
<td>0.7378</td>
<td>0.0011</td>
<td>0.7388</td>
<td>0.0001</td>
<td>0.7355</td>
<td>0.0034</td>
</tr>
<tr>
<td>H2O</td>
<td>0.1472</td>
<td>0.1439</td>
<td>0.0034</td>
<td>0.1471</td>
<td>0.0001</td>
<td>0.1459</td>
<td>0.0013</td>
</tr>
<tr>
<td>CO</td>
<td>0.0029</td>
<td>0.0024</td>
<td>0.0004</td>
<td>0.0031</td>
<td>0.0002</td>
<td>0.0064</td>
<td>0.0035</td>
</tr>
<tr>
<td>O2</td>
<td>0.0013</td>
<td>0.0025</td>
<td>0.0013</td>
<td>0.0015</td>
<td>0.0002</td>
<td>0.0017</td>
<td>0.0004</td>
</tr>
<tr>
<td>NO</td>
<td>0.0010</td>
<td>0.0012</td>
<td>0.0001</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0046</td>
<td>0.0036</td>
</tr>
<tr>
<td>H2</td>
<td>0.0007</td>
<td>0.0038</td>
<td>0.0031</td>
<td>0.0008</td>
<td>0.0001</td>
<td>0.0017</td>
<td>0.0010</td>
</tr>
<tr>
<td>ΔYm</td>
<td>0.0014</td>
<td></td>
<td></td>
<td>0.0002</td>
<td>0.0024</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(T = 2200 K; P = 40 atm, Cp equation from Smith et al. 1996).

In this case, the series reactors model was not so suitable as the other. It seems that it is not recommended when the number of reactions is increased. Along with the tables it is easy to note the influence of the Cp equation in the final composition. All the authors cited were not selective, employing any equation at random.

The effect of EOS was small and can be illustrated in the graphics of absolute deviation (A.D. or ΔY) versus mole fraction of component i in the mixture, as follows:

$$\text{A.D. or } \Delta Y = \left| Y_i^{\text{calc.}} - Y_i^{\text{literature}} \right|$$  (13)

We plotted the results (Graphics 1 to 5) for all absolute deviations obtained with the five systems last reported. The notation is defined thus:

PR**; PR*: Results reached by using the PR EOS and Eq.(12;11).

VR**; VR*: Results reached by using virial equation and Eq.(12;11).

Figure 1. Comparative results by Brinkley's method.

Figure 2. Comparative results by Relaxation method.

Figure 3. Comparative results by using different EOS.

Figure 4. Comparative results by GEM method.

Taking into account the illustrative examples studied, the results showed that equilibrium composition did not change using any equation for the vapor phase to calculate the fugacity coefficients. In the case of the $C_p$ equation, the results indicated that the simulation of chemical equilibrium requires some reliable experimental data to confirm what the best equation should be used to integrate the van't Hoff equation.

**CONCLUSIONS**

The chemical equilibrium calculations for systems in the gaseous phase could be made by non-stoichiometric as by stoichiometric methods regarding the systems studied here.

The effect of two different heat capacity equations to calculate the Gibbs free energy was evaluated in the results. Their influence in the final results was confirmed.

There was no influence of the EOS equation for most systems which can be modelled on the equations mentioned above.

Some examples were presented which demonstrated the effective influence of the $C_p$ equation in solving chemical equilibrium problems. Experimental data will be necessary to guarantee the reliability of the methods and equations.

**REFERENCES**


