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Equation-of-State Calculations of Chemical Reaction Equilibrium in Nonideal Systems

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In order to calculate accurately chemical-reaction equilibria of a system over a wide range of temperatures and pressures, one must account for the nonidealities of the system. In this work, a method is developed to predict accurately chemical-reaction equilibria and phase equilibria of a system using an equation of state to account for the nonidealities. The general formalism for a multicomponent system with multiple reactions is presented. Three widely used cubic equations of state are used to calculate the physical properties of the species. The proposed method is applied to the water-gas shift reaction, to the decomposition of methylcyclohexane, and to the reaction of carbon monoxide with hydrogen sulfide over a wide range of temperatures and pressures.

KEY WORDS: chemical-reaction equilibria; equation of state; phase equilibria.

1. INTRODUCTION

Chemical-reaction equilibria usually are calculated in terms of the equilibrium constant. In general, the equilibrium constant, which is defined in terms of the change in Gibbs free energy at the standard state and hence is a function of temperature only, is equated to the ratio of the activities of the products over the activities of the reactants of the system. However, calculation of the activity of a specific compound requires an accurate estimation of the nonidealities of the system, and in most cases this is not a trivial problem. In order to obtain quantitative information for the extent of reaction, several simplifications are made [1–4]. Usually, the mixture is

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assumed to be ideal and so the activity is estimated from the concentration of the compound. However, this approximation is not correct at conditions of high pressure and thus leads to erroneous results.

In this work, we developed a method to calculate the activity of a compound over the entire temperature and pressure range using an equation of state. This method has been used widely to calculate thermodynamic properties and phase equilibria of associating fluids [5–9]. In this approach, the fugacity coefficient, which is a measure of the nonideality of the system, is expressed in terms of the equation of state. The advantage of this method is that it calculates accurately the extent of reaction, and at the same time it allows prediction of the phase equilibria for the system.

The technique presented is general for multireaction equilibria for any equation of state. Three cubic equations of state are presented here. The Redlich–Kwong–Soave (RKS) [10] and the Peng–Robinson (PR) [11] equations of state are the most popular cubic equations of state for thermodynamic and phase equilibria calculations. A cubic equation of state developed recently by Elliott et al. [8], the Elliott–Suresh–Donohue (ESD) equation of state, is presented also. The ESD was derived based on molecular simulation studies and so it has a semitheoretical basis. The method is applied to the water-gas shift reaction using the RKS and PR equations of state to calculate the extent of reaction as a function of temperature and pressure. More importantly, the method is able to predict condensation of water for a wide range of temperatures and pressures. In addition, the proposed method is applied to the decomposition of methylcyclohexane, which is a strong function of temperature and pressure. Finally, the method is used to calculate the extent of the reaction of carbon monoxide with hydrogen sulfide forming carbonyl sulfide and hydrogen.

2. DEVELOPMENT OF THE MODEL

A simple chemical reaction is expressed in terms of the following expression:

$$A + B \rightleftharpoons C \tag{1}$$

where A and B denote the reactants and C is the product. For more complicated reactions, more than one product may exist. In this section we present our chemical-reaction equilibrium model for the general case of a multireaction equilibrium. For the case where M chemical reactions occur simultaneously, the following equations describe these reactions:[4]

$$\sum_k \nu_{k,j} R_k \rightleftharpoons \sum_l \nu_{l,j} P_l \qquad (j = 1,\ldots, M) \tag{2}$$

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[4] For an explanation of all the symbols, see Nomenclature, at the end of the paper.

where R_k denotes reactant k, P_l denotes product l, and $v_{i,j}$ stands for the stoichiometric coefficient of species i in reaction j. At equilibrium, the following equation results from classical thermodynamics [2]:

$$\sum_i v_{i,j}\mu_i = 0 \qquad (j = 1,\ldots, M) \tag{3}$$

where μ_i is the chemical potential of species i and the summation is over all the reactants and products. In Eq. (3) and in all the subsequent equations, the stoichiometric coefficients $v_{i,j}$ have positive values for the products and negative values for the reactants. The chemical potential of a component i can be written as [13]:

$$\mu_i = g_i^0 + RT \ln \hat{a}_i \tag{4}$$

where g_i^0 is the standard Gibbs free energy of component i in the system and $\hat{a}_i$ is the activity of component i. Substituting Eq. (4) to Eq. (3), one obtains

$$\ln \prod_i \hat{a}_i^{v_{i,j}} = -\frac{\sum_i v_{i,j} g_i^0}{RT} \qquad (j = 1,\ldots, M) \tag{5}$$

By definition, the equilibrium constant of the jth reaction is given by the expression

$$K_j = \exp\left(-\frac{\sum_i v_{i,j} g_i^0}{RT}\right) = \exp\left(-\frac{\Delta g_j^0}{RT}\right) \qquad (j = 1,\ldots, M) \tag{6}$$

where Δg_j^0 is the standard Gibbs free energy of the jth reaction, and so

$$K_j = \prod_i \hat{a}_i^{v_{i,j}} \tag{7}$$

In applying Eq. (6), one has to define the standard state. We take as standard state of component i the ideal-gas state of pure i at unity pressure. In this case, the activity of i is equal to the fugacity of i and

$$\hat{f}_i = x_i \phi_i P \tag{8}$$

where $\hat{f}_i$ is the fugacity of component i, x_i the mole fraction of i, and ϕ_i the fugacity coefficient of i. Therefore, Eq. (6) can be written as

$$K_j = \prod_i (x_i \phi_i P)^{v_{i,j}} = \left(\prod_i x_i^{v_{i,j}}\right)\left(\prod_i \phi_i^{v_{i,j}}\right) P^{\sum_i v_{i,j}} \qquad (j = 1,\ldots, M) \tag{9}$$

For the case of an ideal mixture, the fugacity coefficients are unity and so Eq. (9) simplifies considerably. However, for the case of nonideal mixtures, the fugacity coefficients are not unity and they must be evaluated from classical thermodynamics as shown later. For each reaction j, the extent of reaction ε_j is a measure of the progress of the reaction. A simple material balance for component i at equilibrium gives

$$n_i = n_i^0 + \sum_j \nu_{i,j}\varepsilon_j \tag{10}$$

where n_i is the number of moles of i and superscript 0 denotes the initial value of the variable. The mole fraction x_i is accordingly

$$x_i = \frac{n_i}{\sum_i n_i} = \frac{n_i}{n} \tag{11}$$

The fugacity coefficient of component i is calculated from classical thermodynamics according to the expression

$$\ln \phi_i = \int_V^{\infty} \left[\frac{1}{RT} \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{1}{V} \right] dV - \ln Z \tag{12}$$

where Z is the compressibility factor. In order to evaluate the integral in Eq. (12), an equation of state is needed. In general, any equation of state can be written as

$$Z = \frac{PV}{nRT} = 1 + Z^{\text{rep}} + Z^{\text{att}} \tag{13}$$

where Z^{rep} and Z^{att} are the repulsive and the attractive parts of the equation of state. The fugacity coefficient is evaluated using Eq. (13), and the following expression results:

$$\phi_i = \frac{1}{Z} \exp\left(\int_V^{\infty} \Omega_i \, dV \right) \tag{14}$$

where

$$\Omega_i = \frac{1}{V} \left(Z^{\text{rep}} + Z^{\text{att}} + n \left(\frac{\partial (Z^{\text{rep}} + Z^{\text{att}})}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \tag{15}$$

Substituting Eqs. (14) and (15) back to Eq. (9), one obtains the following expression:

$$K_j = \left(\prod_i x_i^{\nu_{i,j}} \right) \left(\frac{nRT}{V} \right)^{\sum_i \nu_{i,j}} \times \left(\prod_i \exp\left(\int_V^{\infty} (\nu_{i,j} \Omega_i) \, dV \right) \right) \qquad (j = 1, \ldots, M) \tag{16}$$

Equation (16) can also be expressed in terms of the concentrations of the compounds:

$$K_j=\left(\prod_i (c_i RT)^{\nu_{i,j}}\right)\left(\prod_i \exp\left(\int_V^{\infty} (\nu_{i,j}\Omega_i)\, dV\right)\right) \quad (j=1,\dots, M) \tag{17}$$

where c_i is the concentration of component i. The equilibrium constant K_j is a known function of temperature T and so Eq. (16) [or Eq. (17)] defines a system of M nonlinear algebraic equations with M unknowns which are the ε_j extent of reaction for each of the M reactions.

The expressions derived so far are independent of the equation of state used to calculate the physical properties of the reacting species and can be applied in both the vapor and the liquid phases. Next three cubic equations of state are presented that can be used in the general formalism developed. For fugacity calculations, the RKS and PR equations of state are the most accurate cubic equations [12]. The RKS equation of state developed by Soave [10] is a modification of the Redlich–Kwong equation and is given from the expression

$$Z=\frac{v}{v-b}-\frac{a\alpha}{RT(v+b)} \tag{18}$$

Peng and Robinson [11] developed an accurate cubic equation of state that has the form

$$Z=\frac{v}{v-b}-\frac{a\alpha v}{RT(v^2+2bv-b^2)} \tag{19}$$

In Eqs. (18) and (19), a, b, and α are characteristic parameters calculated from the critical properties, the reduced temperature, and acentric factor. The actual expressions for these parameters can be found in most thermodynamics or phase equilibria textbooks (see, e.g., Ref. 12) and are not given here.

Elliott et al. [8] presented a cubic equation that fits molecular simulation data for repulsive and attractive interactions well and it is suitable for spherical and chain molecules. The ESD equation of state is

$$Z=1+\frac{4c\eta}{1-1.9\eta}-\frac{9.49q\eta Y}{1+1.7745\eta Y} \tag{20}$$

where c and q are shape factors for the repulsive and attractive interactions, η is the reduced density, and Y is an energy parameter. These parameters are correlated against the critical properties of the components [8].

Table I. Z^{rep} and Z^{att} from the Redlich–Kwong–Soave (RKS), Peng–Robinson (PR), and Elliott–Suresh–Donohue (ESD) Equations of State

Equation of state	Z^{rep}	Z^{att}
RKS	$\frac{b}{v-b}$	$\frac{-a\alpha}{RT(v+b)}$
PR	$\frac{b}{v-b}$	$\frac{-a\alpha v}{RT(v^2+2bv-b^2)}$
ESD	$\frac{4c\eta}{1-1.9\eta}$	$\frac{-9.49q\eta Y}{1+1.7745\eta Y}$

In Table I, the expressions for Z^{rep} and Z^{att} for the three cubic equations of state are presented. For mixture calculations, appropriate mixing rules should be applied to calculate the mixture parameters. For the RKS and PR equations of state, the usual Berthelot mixing rules can be used for a and b [13]. For the ESD equation of state, Elliott and co-workers suggested mixing rules for groups of parameters, and not for each parameter individually. For example, a quadratic mixing rule is proposed for the $c\eta$ term, and not for each of the c and η separately.

3. APPLICATIONS

3.1. The Water-Gas Shift Reaction

In this section, we apply the proposed method to a simple chemical reaction, that is, the water-gas shift reaction. This chemical reaction is described by the expression

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{21}$$

The water-gas shift reaction is an industrially important reaction and, among others, is used for hydrogen production [14]. The equilibrium constant is calculated using the procedure described by Sandler [2] based on the heats of formation and the specific heat of the reactants and the products. The equilibrium constant for this reaction is calculated from the expression

$$\begin{aligned}\ln K = {} & 11.51 - 1.0861 \ln\left(\frac{T}{298}\right) \\ & + 3.263\times10^{-3}(T-298) - 9.4028\times10^{-7}(T^2-298^2) \\ & + 1.2437\times10^{-10}(T^3-298^3) + 4870.55\left(\frac{1}{T}-\frac{1}{298}\right)\end{aligned} \tag{22}$$

In the water-gas shift reaction there is no stoichiometric change, that is, two molecules react to form another two molecules, and so

$$\sum_i \nu_i = 0 \tag{23}$$

Therefore if one ignores the effect of pressure and density on the system and assumes that the fugacity coefficients are unity, the extent of reaction becomes pressure independent and is only a function of temperature. This result is realistic only for low pressures or high temperatures.

We performed calculations for the water-gas shift reaction using both the RKS and the PR equations of state to account for the physical properties of the components. In Fig. 1, the extent of reaction is shown as a function of temperature and pressure. The initial amounts of the species were assumed to be $n^0_{CO}=1$, $n^0_{H_2O}=1$, $n^0_{H_2}=0$, $n^0_{CO_2}=0$. At low temperatures (room temperature), the reaction goes almost to completion. Since the reaction is exothermic, at higher temperatures the conversion decreases. At low pressures, the reaction is independent of pressure. At pressures higher than 100 bar, the nonidealities of the system have a significant effect on the equilibrium of the mixture. It is interesting to note that at low temperatures, the pressure effect is higher, since at these temperatures intermolecular forces are strong and highly nonideal. As the temperature increases to higher than 1000 K, the intermolecular forces are weak com-

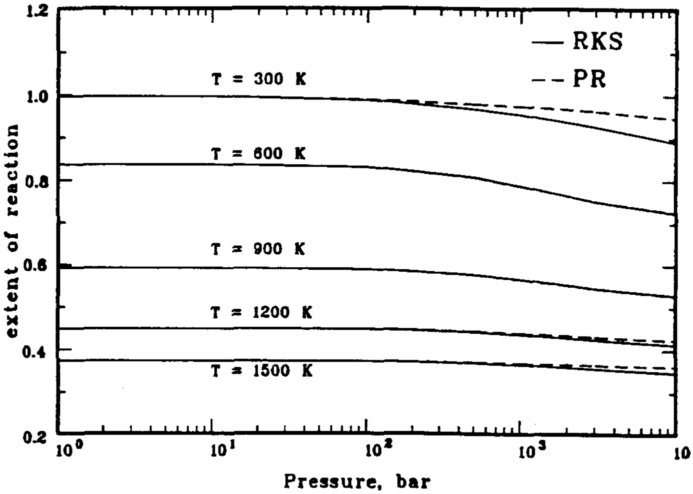

Fig. 1. Extent of the water-gas shift reaction from the RKS and the PR equations of state. Initial amounts of components: $n^0_{CO}=1$, $n^0_{H_2O}=1$, $n^0_{H_2}=0$, and $n^0_{CO_2}=0$.

pared to the thermal energy of the molecules and so the molecules behave almost ideally at both high and low pressures. It should be mentioned that for the calculations presented here no binary interaction parameters were used, and these results are strictly predictions. There is good agreement between the two equations of state except at 300 K, where the RKS predicts a larger decrease in the extent of reaction as the pressure increases compared to the PR.

The water-gas shift reaction takes place in the vapor phase. However, at temperatures below the critical temperature of water ($T_c = 647$ K), water condensation might occur. In industrial processes, it is very important to know whether the mixture forms one or more phases. A condensed phase might cause significant problems and decrease the efficiency of the process. For the water-gas shift reaction, water condensation would cause problems to compressors, to the catalyst, and to the reactor. Although it is often assumed that the water-gas shift reaction is an ideal-vapor phase reaction ignoring any water condensation [14], there is a need for a method capable of predicting the phase equilibria of the system simultaneously with the chemical equilibria.

The method proposed in this work is applicable in both the liquid and the vapor phases and also can be used to calculate simultaneously chemical and phase equilibria of the system. We developed an iterative algorithm

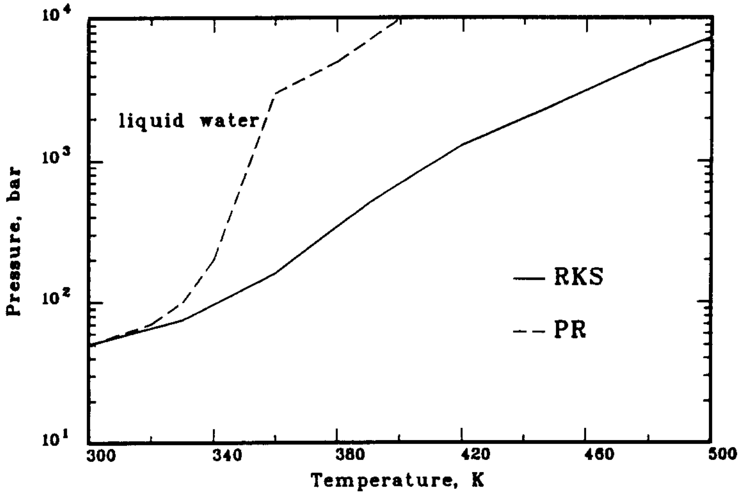

Fig. 2. Phase-equilibria predictions for the water-gas shift reaction from the RKS and the PR equations of state. At high pressures and low temperatures, water condenses. Initial amounts of components: $n^0_{CO} = 1$, $n^0_{H_2O} = 1$, $n^0_{H_2} = 0$, and $n^0_{CO_2} = 0$.

based on phase equilibria fundamentals [13] that takes into account the constraints imposed by the chemical reaction. The equation of state is used to calculate the fugacities of the components in each of the phases. In Fig. 2, the region of temperature and pressure where water condenses for the water-gas shift reaction is shown. Each of the two lines, corresponding to the predictions from the RKS and PR equations of state, divides the temperature–pressure space into two areas. For temperatures and pressures in the upper left part of the figure, liquid water forms, whereas at lower temperatures and pressures, all the compounds are in the vapor phase. As the temperature increases, the boundary pressure for liquid formation increases, and eventually only one vapor phase exists over the entire pressure range. Although the predictions from RKS and PR agree qualitatively, the boundary pressure predicted from the PR has a much higher slope than the boundary pressure predicted from the RKS equation.

In order to force the equilibrium toward hydrogen production, an excess of water is used for the water-gas shift reaction in industrial processes [14]. In Fig. 3, the extent of reaction is shown as a function of temperature and pressure for initial amounts of species: $n^0_{CO} = 1$, $n^0_{H_2O} = 2$, $n^0_{H_2} = 0$, and $n^0_{CO_2} = 0$. The pressure effect on the equilibrium becomes important at high pressures and is higher at low temperatures. These results are similar to the results shown in Fig. 1. However, calculations concerning the formation of a liquid phase predict that water is forming at low pressure over a wide range of temperatures. In Fig. 4, these predictions

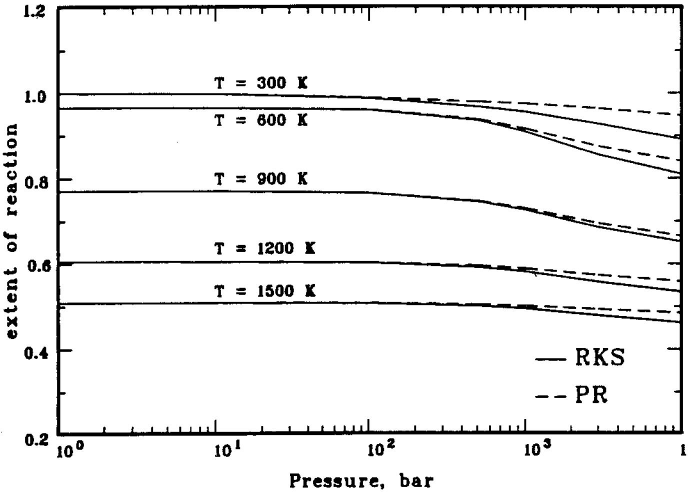

Fig. 3. Extent of the water-gas shift reaction from the RKS and the PR equations of state. Initial amounts of components: $n^0_{CO} = 1$, $n^0_{H_2O} = 2$, $n^0_{H_2} = 0$, and $n^0_{CO_2} = 0$.

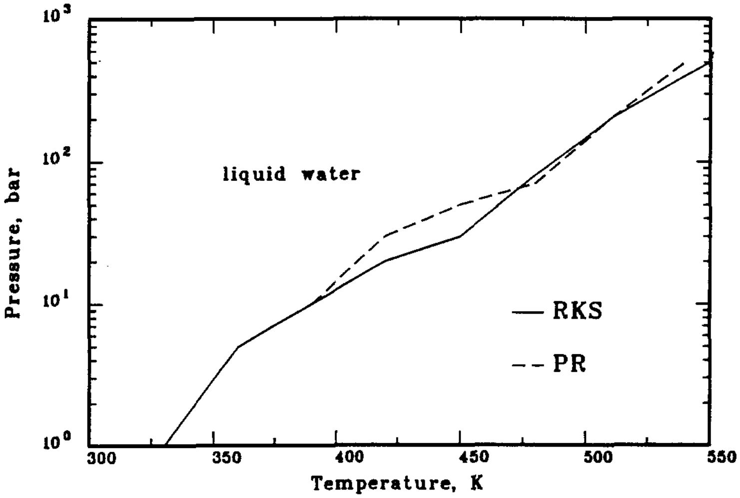

Fig. 4. Phase-equilibria predictions for the water-gas shift reation from the RKS and the PR equations of state. At high pressures and low temperatures, water condenses. Initial amounts of components: $n^0_{CO}=1$, $n^0_{H_2O}=2$, $n^0_{H_2}=0$, and $n^0_{CO_2}=0$.

are shown for the initial ratio $H_2O:CO=2:1$. Since the water is in excess in the beginning of the process, at most only half of the initial amount of water would react, and therefore the mixture at equilibrium would have a significant amount of water. Thus, water condenses at even moderate pressures. The boundary pressure where water condensation occurs is almost two orders of magnitude lower than the corresponding pressure in Fig. 2, where equal initial amounts of water and carbon monoxide were used.

3.2. Methylcyclohexane Decomposition

Methylcyclohexane decomposes at elevated temperatures as

$$C_7H_{14} \rightleftharpoons C_7H_8 + 3H_2 \tag{24}$$

An expression for the equilibrium constant of this reaction is proposed based on the procedure described by Sandler [2]:

$$\begin{aligned}\ln K = & -38.35 + 13.15 \ln\left(\frac{T}{298}\right) \\ & - 1.334\times10^{-2}(T-298) + 2.295\times10^{-6}(T^2-298^2) \\ & - 2.051\times10^{-10}(T^3-298^3) - 21784.9\left(\frac{1}{T}-\frac{1}{298}\right)\end{aligned} \tag{25}$$

According to Eq. (24), there is stoichiometric change in the decomposition of methylcyclohexane, so that

$$\sum_i \nu_i = 3 \tag{26}$$

As a result, even in the case of the ideal-gas assumption, the extent of reaction would be a strong function of pressure based on the stoichiometric change [Eq. (9)] as shown in Fig. 5. At constant temperature, the extent of methylcyclohexane decomposition decreases at higher pressure. On the other hand, temperature increase has a favorable effect on this reaction. In Fig. 5, calculations are shown also for the cases where the ideal-gas assumption is relaxed and the PR and RKS equations of state are used to calculate the fugacity coefficients of the species. Calculation of the nonidealities of the system has a significant effect only at pressures higher than 30 bar as shown in Fig. 5. Nevertheless, using an equation of state to calculate the nonideal behavior of the system, one is able to calculate the phase equilibria as well.

For the system under consideration, pure methylcyclohexane is in the liquid phase. As the extent of reaction increases, generation of hydrogen will cause the formation of a vapor phase. These phase equilibria cannot be calculated based on the ideal-gas assumption solely but can be easily

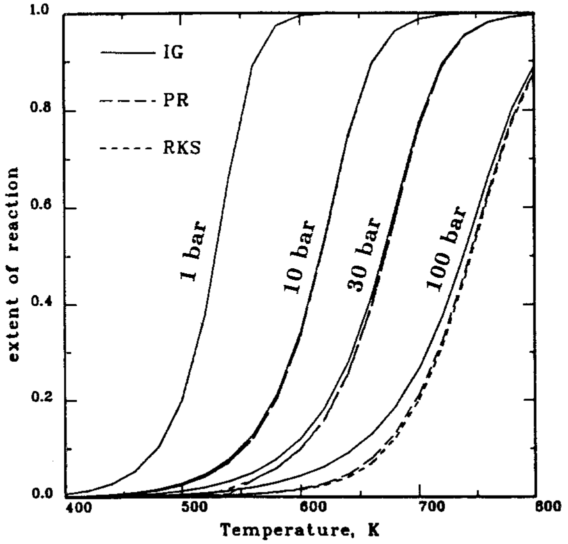

Fig. 5. Methylcyclohexane decomposition. Calculations based on the ideal-gas assumption (IG) and predictions from the PR and RKS equations of state.

calculated using the method proposed in this work. Phase-equilibria calculations for the ternary mixture hydrogen–toluene–methylcyclohexane show that there is a region of vapor–liquid equilibrium at pressures higher than 20 bar and temperatures up to 570 K. This phase equilibrium does not affect the chemical equilibrium considerably since the extent of reaction at the condition where vapor–liquid equilibrium occurs is low.

3.3. Carbon Monoxide and Hydrogen Sulfide Reaction

Carbon monoxide and hydrogen sulfide react to form carbonyl sulfide and hydrogen according to the reaction

$$CO + H_2S \rightleftharpoons COS + H_2 \tag{27}$$

The equilibrium constant for this reaction is calculated from the expression [2]

$$\begin{aligned}\ln K = {} & 0.324 - 0.313 \ln\left(\frac{T}{298}\right) \\ & + 0.286 \times 10^{-2}(T - 298) - 1.029 \times 10^{-6}(T^2 - 298^2) \\ & + 1.539 \times 10^{-10}(T^3 - 298^3) + 1440.7\left(\frac{1}{T} - \frac{1}{298}\right)\end{aligned} \tag{28}$$

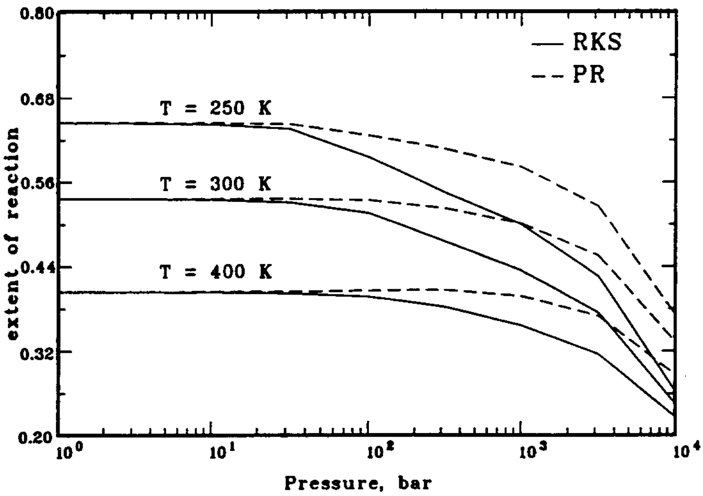

Fig. 6. Extent of the carbon monoxide and hydrogen sulfide reaction to form carbonyl sulfide and hydrogen.

In this reaction there is no stoichiometric change, and therefore in the ideal-gas assumption the extent of reaction is independent of pressure. However, if one applies the method developed in this work, one will obtain that the extent of reaction varies considerably with pressure especially at moderate and high pressures.

In Fig. 6, the extent of reaction is plotted as a function of pressure for three temperatures, namely, 250, 300, and 400 K. For low pressures up to approximately 10 bar, the extent of reaction is almost independent of pressure. However, as the pressure increases, the extent of reaction decreases at constant temperature. For example, at 250 K the extent of reaction at low pressure and in the ideal-gas approximation is 0.645. The predicted values for the extent of reaction using the RKS equation of state are 0.596 at 100 bar and 0.500 at 1000 bar. At the same time, the values obtained from the PR equation of state are 0.627 at 100 bar and 0.582 at 1000 bar. Although the results obtained from the two cubic equations of state agree with each other qualitatively, there is a considerable difference in the absolute predictions. It should be pointed out here again that no binary-interaction parameters were used for the calculations and the results are pure predictions.

4. SUMMARY

A method that combines chemical-reaction equilibria and phase equilibria is proposed in order to calculate the equilibrium of a multicomponent mixture. The method is applicable in any fluid or condensed phase and over a wide range of temperatures and pressures. The general formalism is presented. To illustrate the applicability of the new method, the chemical and phase equilibria for the water-gas shift reaction are calculated using the Redlich–Kwong–Soave and the Peng–Robinson equations of state. In addition, the extent of methylcyclohexane decomposition and the reaction of carbon monoxide and hydrogen sulfide are calculated as a function of temperature and pressure.

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NOMENCLATURE

a	Molecular parameter in RKS and PR equations of state
a	Activity
b	Molecular parameter in RKS and PR equations of state
c	Shape parameter in ESD equation of state
c_i	Concentration of i
f	Fugacity
g	Molar Gibbs free energy
K	Equilibrium constant
M	Total number of reactions
n	Total number of moles
n_i	Number of moles of i
P	Pressure
P_l	Product component l
q	Shape parameter in ESD equation of state
R	Gas constant
R_k	Reactant component k
T	Temperature
V	Total volume
v	Molar volume
x	Mole fraction
Y	Energy parameer for the ESD equation of state
Z	Compressibility factor

Greek Letters

ε_j	Extent of chemical reaction j
η	Reduced density
μ_i	Chemical potential of component i
$\nu_{i,j}$	Stoichiometric coefficient of component i in reaction j
ϕ_i	Fugacity coefficient of component i
Ω_i	Expression defined in Eq. (15)

Subscripts

i	Component i
j	Chemical reaction j

Superscripts

att	Attractive
0	Reference state

0	Initial value
rep	Repulsive
^	Property of component in the mixture

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