

## The System Carbon Dioxide-Water and the Krichevsky-Kasarnovsky Equation

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*The system carbon dioxide water has been studied often. However, there is some controversy about the thermodynamic description of the behavior of this system. Some researchers indicate that the system CO<sub>2</sub>-H<sub>2</sub>O is accurately modeled by the Krichevsky-Kasarnovsky equation. Others say that it is not. This paper investigates this controversy. As a part of this study an overview of Henry's law and a discussion of the limitations of the Krichevsky-Kasarnovsky equation are presented. From the analysis presented in this paper, it must be concluded that for temperatures lower than about 100°C, the system CO<sub>2</sub>-H<sub>2</sub>O is accurately modeled by the Krichevsky-Kasarnovsky equation. On the other hand, at 100°C and higher, it is not. In order to arrive at this conclusion, four models of the solubility were investigated. Using these models, it is clearly demonstrated that the activity coefficients are not negligible and hence the Krichevsky-Kasarnovsky equation is not applicable at high temperatures.*

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**KEY WORDS:** Henry's law; solubility; Krichevsky equation; carbon dioxide-water.

### 1. Introduction

Although the system carbon dioxide-water is important to many branches of science and engineering, there remains much controversy about the high pressure phase equilibrium in this system. It is the purpose of this paper to examine one of these controversies - the use of the Krichevsky-Kasarnovsky equation for modeling the solubility of CO<sub>2</sub> in water. Many investigators have addressed this problem, but, as will be shown later, their conclusions differ significantly.

Henry's law is an often used approach for modeling the solubilities of gases in liquids. Included in this paper is an overview of Henry's law and how it is related to Krichevsky analysis. Some of the

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difficulties with Krichevsky analysis are also discussed.

## 2. Henry's Law

The condition for phase equilibrium in a closed system is that each component must have the same chemical potential in all phases. Equivalently, the fugacities of each component must also be the same in all phases. For a two component system consisting of two phases, the equality of fugacities is

$$\hat{f}_i^L = \hat{f}_i^V \quad i = 1, 2 \quad (1)$$

where all of the symbols are defined at the end of the paper.

One approach to modeling phase equilibrium is the "two-fluid model." In this method different reference states are used for calculating the fugacities of the two phases.

For binary systems where the liquid phase is dilute in one component, it is convenient to use a combined Henry's law-Raoult's law approach to correlate the composition of co-existing phases. This method is a two-fluid model. A rigorous treatment, based on Raoult's law, yields the following equation for the solvent

$$\gamma_1 x_1 P_1^0 \phi_1^0 \exp[\nu_1(P - P_1^0)/RT] = y_1 P \hat{\phi}_1 \quad (2)$$

For the solvent, the reference fugacity is the fugacity of the pure liquid under its own vapor pressure at the temperature of the system. At low temperatures,  $\phi_1^0 = 1$ , but often this is assumed to be the case regardless of the temperature. It is often stated that the reference fugacity for the solvent is the vapor pressure of the pure solvent, which is not strictly accurate.

A similar treatment for the solute, based on Henry's law, results in the following equation

$$\gamma_2 x_2 H_{21} \exp[\bar{\nu}_2^\infty(P - P_1^0)/RT] = y_2 P \hat{\phi}_2 \quad (3)$$

For the solute, the reference fugacity at infinite dilution is the Henry's constant. In Eqs. (2, 3) the exponential terms are the Poynting correction for the effect of pressure on the reference fugacity. It is assumed that  $\nu_1$  and  $\bar{\nu}_2^\infty$  are independent of pressure, which are the only assumptions in the derivation of Eqs. (2, 3).

The activity coefficients express the effect of composition on the fugacity. The method presented here uses the unsymmetric convention for activity coefficients

$$\lim_{x_1 \rightarrow 1} \gamma_1 = 1 \quad (4)$$

$$\lim_{x_2 \rightarrow 0} \gamma_2 = 1 \quad (5)$$

Thus at infinite dilution of the solute, the activity coefficients of both the solvent and the solute are unity.

For a binary system containing water and a light gas this approach is often used. Yet, Eqs. (2, 3) are rarely used as given. Often some assumptions are made that result in a simplified set of equations. These assumptions should be justified by experimental measurements.

### 2.1. Henry's Constant

In Eq. (3),  $H_{21}$  is the Henry's constant. The strict definition of Henry's law states that the solubility of a gas in a liquid is proportional to its partial pressure. The proportionality constant implied by this definition is called the Henry's constant. A better definition of Henry's constant is<sup>(1)</sup>

$$\lim_{x_2 \rightarrow 0} \hat{f}_2/x_2 = H_{21} \quad (6)$$

Or, from l'Hôpital's rule

$$\lim_{x_2 \rightarrow 0} d\hat{f}_2/dx_2 = H_{21} \quad (7)$$

Thus, Henry's constant is the slope of the fugacity against mole fraction at infinite dilution. Unfortunately, these definitions are difficult to apply directly to a set of experimental data.

### 2.2. Krichevsky Analysis

To obtain Henry's constants from solubility data, especially at high pressure, the method of Krichevsky is often used. The Krichevsky-Kasarnovsky<sup>(2)</sup> (KK) equation is

$$\ln(\hat{f}_2/x_2) = \ln H_{21} + \bar{v}_2^\infty (P - P_1^\circ)/RT \quad (8)$$

This equation can be derived from the rigorous equilibrium expression [Eq. (3)]. The derivation assumes that the concentration of the solute is sufficiently small that the activity coefficients are unity. It is further assumed that  $\bar{v}_2^\infty$  is independent of pressure. Therefore a plot of

$$\ln(\hat{f}_2/x_2) \text{ vs. } (P - P_1^0)$$

should yield a straight line with an intercept of  $\ln H_{21}$  and a slope of  $\bar{v}_2^\infty/RT$ . The liquid phase composition as a function of pressure at constant temperature is obtained from experiments and the fugacity is calculated using an equation of state. Usually it is the fugacity of the components in the gas that is calculated, but theoretically, the fugacity of the liquid could also be calculated.

If there is a significant deviation of the activity coefficients from unity, then they must be incorporated into the model. A simple, yet often realistic, model for activity coefficients is the two-suffix Margules equation. For the solvent

$$RT \ln \gamma_1 = Ax_2^2 \quad (9)$$

and for the solute  $RT \ln \gamma_2 = A(x_1^2 - 1)$  (10)

where  $A$  is an empirical parameter. Equation (8) becomes

$$\ln(\hat{f}_2/x_2) = \ln H_{21} + A(x_1^2 - 1)/RT + \bar{v}_2^\infty(P - P_1^0)/RT \quad (11)$$

This equation is called the Krichevsky-Iiinskaya<sup>(3)</sup> (KI) equation. Equation (11) has three unknown quantities:  $H_{21}$ ,  $A$  and  $\bar{v}_2^\infty$ . Even with experimental data of high accuracy it may not be possible to obtain accurate values of  $A$ ,  $H_{21}$  and  $\bar{v}_2^\infty$  from this equation. Competing effects are almost impossible to separate. The usual approach to implementing the KI equation is to use a value of  $\bar{v}_2^\infty$  obtained from volumetric measurements.<sup>(4)</sup> Then a plot of

$$\ln(\hat{f}_2/x_2) - \bar{v}_2^\infty(P - P_1^0)/RT \text{ vs. } (x_1^2 - 1)$$

is constructed. If this transformed version of Eq. (11) applies, then the intercept is  $\ln H_{21}$  and the slope is  $A/RT$ . This approach requires  $\bar{v}_2^\infty$ , which is often not known, especially for high temperature and pressure.

The Krichevsky approach should be used with caution. Just because the KK plot is linear does not mean that the activity coefficients are unity nor that the slope is the actual partial molar volume at infinite dilution. Competing effects may cancel each other.

Figure 1 shows a hypothetical system where the activity coefficient of the solute is a decreasing function of composition (and, since solubility increases with increasing pressure, a decreasing function of pressure). The Poynting term, the effect of pressure on the reference

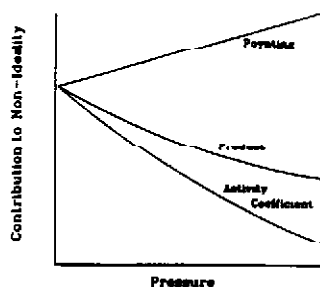


Fig. 1. Liquid phase non-idealities for a hypothetical binary mixture.

fugacity, is an increasing function of pressure since  $\bar{v}_2^\infty$  is positive. The product of the two represents the overall non-ideality in the liquid phase. Note how this product can be approximately linear. A KK plot for such a system would be nearly linear and result in a negative slope. An erroneous, but often made, assumption is that  $\bar{v}_2^\infty$  is negative. A similar discussion is given by Mathias and O'Connell.<sup>(5)</sup> Another problem with this approach is the calculation of the fugacities. This is discussed in detail in the next section.

Finally, the two suffix Margules equation, applicable to non-electrolytes, but not to electrolytes, is a very simple model for activity coefficients. It should not be expected to be applicable over a wide range of concentration. Theoretically, other activity coefficient models could be used instead, but the resulting equations would be very difficult to use or interpret.

It is worth noting that the KK equation is an important tool for the analysis of high pressure solubility data, but it should be used with caution. Interpretation of the slope and intercept of such plots should reflect judgment on the part of the investigator and not just blind belief.

### 2.3. Calculation of the Fugacities

The calculation of the fugacities is a weak link in Krichevsky analysis. Problems are associated with the calculation of the fugacity for both the liquid and the vapor phases.

Ideally, an equation of state that can be used to accurately calculate the fugacities of components in the liquid phase, without empirical modification, is highly desirable. Such an equation does not exist. Indeed, if such an equation did exist, there would be no need to perform Krichevsky analysis or for that matter to use Henry's law. All equations of state require some type of empirical modification, based on experimental data, such that they can be used to calculate accurately the liquid phase fugacities. If the experimental data must be used to obtain

the fugacities, then the fugacities are not independent of the data that are being examined.

On the other hand, fugacities of components in the vapor are more easily calculated. Then using the criterion for equilibrium [Eq. (1)], the fugacity of the component in the liquid can be obtained. Equations of state can be used, with reasonable accuracy, for gaseous mixtures without resorting to empirical modifications. Highly accurate calculations require empirical modification, which has the shortcomings noted for the liquid phase. However, in order to do so requires the composition of the vapor in equilibrium with the solution. Often the vapor compositions are not reported with solubility measurements. In these cases some assumption must be made. Typically two assumptions are made: (1) use a form of Raoult's law to estimate the amount of solvent in the vapor (for example, the partial pressure of the solvent is equal to its vapor pressure) or (2) assume that the fugacity of the solute in the gaseous solution is equal to the fugacity of the pure component at the same temperature and pressure (the Lewis-Randall rule).

### 3. Comments on Previous Work

Many researchers have applied the KK equation to the system carbon dioxide-water. The results of these studies yield conflicting conclusions. Some of the limitations of the previous studies will be discussed in this section.

King<sup>(6)</sup> demonstrated that the experimental data of Wiebe and Gaddy<sup>(7)</sup> at 40°C followed the KK equation up to 40.5 MPa. To calculate the fugacities, King<sup>(6)</sup> assumed that the vapor was pure CO<sub>2</sub>. Although he does not show it graphically, he claims that the 75 and 100°C isotherms of Wiebe and Gaddy<sup>(7)</sup> also follow the KK equation. King<sup>(6)</sup> also notes that other data deviate from the KK equation and concludes that these data are probably in error. Such a claim is not justified. The KK equation is *not* a test for thermodynamic consistency. Failure to follow the KK equation is not a sufficient reason to reject experimental data. Significant discrepancy between sets of data is, however, a good reason.

Weiss<sup>(8)</sup> came to a similar conclusion as King,<sup>(6)</sup> except that Weiss<sup>(8)</sup> examined the isotherms of Wiebe and Gaddy<sup>(7)</sup> from 12 to 40°C and pressures to 50 MPa. Weiss<sup>(8)</sup> used the Benedict-Webb-Rubin (BWR) equation of state to calculate the fugacity of carbon dioxide and he assumed that the vapor was pure carbon dioxide. Equation of state parameters for CO<sub>2</sub> were taken from Bishnoi and Robinson.<sup>(9)</sup> However, the stated range of applicability of the constants given by Bishnoi and

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Robinson<sup>(9)</sup> is  $P < 34.5$  MPa and  $38 < t < 204^\circ\text{C}$ . Only one isotherm presented in the discussion of Weiss<sup>(8)</sup> is in this temperature range and several solubilities are for pressures greater than 34.5 MPa. Although this may not be a major problem, difficulties often arise when the BWR equation is used outside its stated range. A more important point is that several data points used by Weiss<sup>(8)</sup> to construct his KK plot are not vapor-liquid equilibrium points but liquid-liquid. There is no noticeable effect of this phase transition on the slope of his curves whereas one would definitely be expected.

On the other hand, Parkinson and De Nevers<sup>(10)</sup> and Gibbs and Van Ness<sup>(11)</sup> show that the system CO<sub>2</sub>-H<sub>2</sub>O does not follow the KK equation. Both studies used smoothed values from Houghton *et al.*<sup>(12)</sup> for the solubilities and fugacities over the range of temperature 0 to 50°C. Note, the solubility data from Houghton *et al.*<sup>(12)</sup> are based almost solely on the measurements of Zelvenskii.<sup>(13)</sup> Houghton *et al.*<sup>(12)</sup> used the Beattie equation of state to calculate the fugacity of CO<sub>2</sub>. A problem with both Houghton *et al.*<sup>(12)</sup> and Zelvenskii<sup>(13)</sup> is that at 0°C "solubility" values are reported for pressures up to 3.24 MPa. However, CO<sub>2</sub> forms a hydrate at 0°C and 1.26 MPa.<sup>(14)</sup> These solubility values represent at best a metastable equilibrium and at worst could be totally erroneous. Either way, they should not have been included in this kind of analysis. Also, many isotherms given by Houghton *et al.*<sup>(12)</sup> are interpolations. Since the values of Houghton *et al.*<sup>(12)</sup> are smoothed, the question must be asked, "Does the fact that the smoothed values of Houghton *et al.*<sup>(12)</sup> are not fit by the KK equation just reflect the model that they used for smoothing or is this a reason to question the applicability of the KK equation?" A more logical explanation is that Houghton *et al.*<sup>(12)</sup> used a model other than the KK approach for their correlation.

Finally, other authors have just assumed that the KK equation applies to the system CO<sub>2</sub>-H<sub>2</sub>O. For example, Nighswander *et al.*<sup>(15)</sup> refer to the KK equation as the "definition" of the Henry's constant. It is important to state that the KK equation is *not* the definition of Henry's constant. The proper definition was presented earlier in this paper [Eq. (6)]. Assuming that the KK equation applies to a system is incorrect. It cannot be stated *a priori* that the KK equation will apply to any given system - this can only be determined by examining experimental results.

#### 4. Krichevsky Analysis of the Solubility of Carbon Dioxide in Water

A set of data for the solubility of carbon dioxide in water was selected for this analysis. Data were selected only if compositions for

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Table I. Source of Experimental Data for the System Carbon Dioxide-Water

Source (Ref.)	Temperature (°C)	Pressure (MPa)	Number of Points
7	50-75	2.5-40.5	12
16	50-200	20-50	8
17	150-200	10-50	10
19	200	19.6	1
20	50-75	10.1-15.2	4
21	100-200	0.3-8.1	48

both the vapor and the liquid were reported. The upper temperature was somewhat arbitrarily limited to 200°C. At higher temperatures there is a large discrepancy between the experimental values (especially between Tödheide and Franck<sup>(16)</sup> and Takenouchi and Kennedy<sup>(17)</sup>). There is also a significant disagreement among the data at very high pressure. Hence pressures were limited to about 50 MPa. Also, only experimental values were used; compilations such as Houghton *et al.*<sup>(12)</sup> were excluded from this investigation. Table I summarizes the data used here. The data base used here does not include all the data in the reported studies, only those that meet the criteria outlined above. Thus some studies may appear to be incomplete as described in Table I.

Gas fugacities were calculated using the Redlich-Kwong<sup>(18)</sup> (RK) equation of state. The fugacities are calculated based solely on pure component parameters and in no way rely on the experimental equilibrium data. This is both a blessing and a curse as the fugacities are not as accurate as perhaps they could be, but they are not impaired by their reliance on the data under examination.

Muller *et al.*<sup>(21)</sup> provide a rather complete set of data from 100 to 200°C at moderate pressures. Figure 2 shows the Krichevsky plots based on those data. Table II summarizes the least squares regression of these data. With many isotherms, the point at the lowest concentration deviates significantly from the trend exhibited by the other points. This observation can be seen clearly for the 120, 160 and 180°C isotherms. This is not unexpected since the lowest solubilities tend to be more difficult to measure and thus they have a somewhat larger absolute error. Eliminating these points from the three isotherms has a significant effect on the KK analysis. However, the  $\bar{v}_2^\infty$  are still different from the expected value. The regressions without the lowest concentration points



Table II. Results of Krichevsky-Kasarnovsky Analysis

Temp. (°C)	NP	Slope	$\bar{v}_2^{\infty}$	Inter- cept	H <sub>21</sub> (MPa)	r <sup>2</sup>
50	11	0.01307	35.1	5.635	280	0.995
75	7	0.01075	31.1	5.996	402	0.970
100 <sup>b</sup>	6	-0.01049	-32.5	6.231	508	0.369
100	8	0.00923	28.6	6.206	496	0.989
120 <sup>b</sup>	7	0.02820	92.1	6.304	547	0.427
120 <sup>c</sup>	6	0.00467	15.3	6.240	572	0.421
140 <sup>b</sup>	7	0.02055	70.6	6.372	585	0.925
150	7	0.00937	33.0	6.254	520	0.977
160 <sup>b</sup>	7	0.01462	52.6	6.340	567	0.210
160 <sup>c</sup>	6	0.03074	110	6.309	549	0.913
180 <sup>b</sup>	7	0.03425	122	6.200	493	0.825
180 <sup>c</sup>	6	0.02419	91.1	6.237	511	0.974
200 <sup>b</sup>	14	-0.00496	-19.5	6.347	571	0.031
200	22	0.00244	9.6	6.311	551	0.250

<sup>a</sup> Units: cm<sup>3</sup>·mol<sup>-1</sup>. <sup>b</sup> Data of Müller *et al.* only. <sup>c</sup> Data of Müller *et al.*, point of lowest concentration removed; other isotherms contain data from at least two sources.

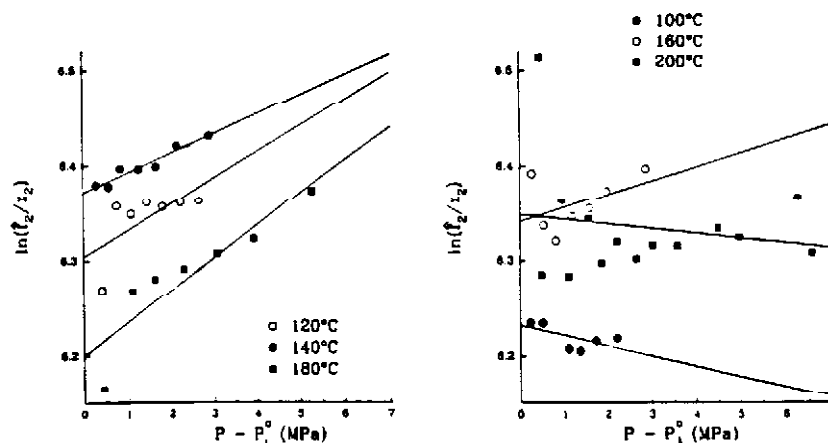


Fig. 2. Krichevsky-Kasarnovsky plots for the data of Müller *et al.*  
(a) 120, 140 and 180°C. (b) 100, 160 and 200°C.

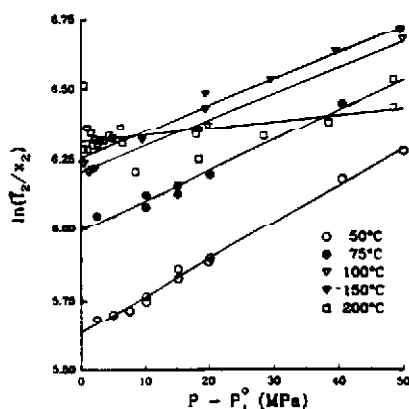


Fig. 3. Krichevsky-Kasamovsky plots for the combined data set.

are also included in Table II.

The remainder of the data, which met the criteria outlined above, were combined into a single set. The regression of these data is also presented in Table II and Krichevsky plots are given in Figure 3.

For 50 and 75°C, we must conclude that the system CO<sub>2</sub>-H<sub>2</sub>O is accurately modeled by the KK equation. The plots are linear and the slopes have values that are approximately what was expected. The  $\bar{v}_2^\infty$  obtained from the KK plots are in excellent agreement with the value of  $33.9 \pm 0.4 \text{ cm}^3\text{-mol}^{-1}$  (at 25°C), which was obtained volumetrically by Moore *et al.*<sup>(22)</sup> Although the calculated and experimental values were obtained at different temperatures, it is reasonable to expect that  $\bar{v}_2^\infty$  is a weak function of temperature over this range.

For 100°C and above, the results are not as conclusive. For example the curves based on the data from Müller *et al.*<sup>(21)</sup> at 100 and 200°C have negative slopes. Even at these temperatures,  $\bar{v}_2^\infty$  for CO<sub>2</sub> in water is not negative. For the other temperatures, the slopes from the Müller *et al.*<sup>(21)</sup> data seem to be too large. The inclusion of the two points from Tödheide and Franck<sup>(16)</sup> at 100°C exerts a large influence on the regression since they are for much higher pressure than those of Müller *et al.*<sup>(21)</sup> The two points dramatically change the slope of the line from an unreasonable  $-32.5 \text{ cm}^3\text{-mol}^{-1}$  to a very reasonable  $28.6 \text{ cm}^3\text{-mol}^{-1}$ . On the other hand, the two points change the Henry's constant by only about 2.5%.

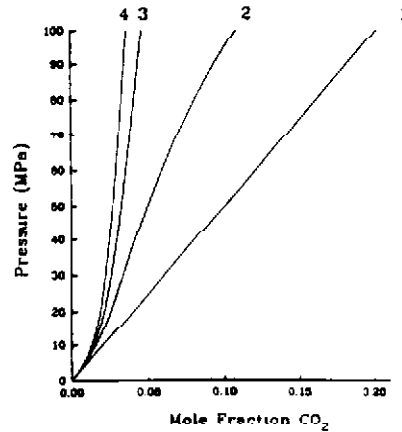


Fig. 4. Predicted solubility of CO<sub>2</sub> in water at 100°C from the four models (see text for description of models).

### 5. Modeling the Solubility

Since the Krichevsky analysis was less than conclusive, four models were postulated to calculate the solubility of CO<sub>2</sub> in water. The first of these, Model #1, is the strict Henry's law where the solubility is proportional to the partial pressure of the solute

$$x_2 H_{21} = y_2 P \quad (12)$$

The second, Model #2, is an extension of the strict Henry's law, where non-idealities in the vapor phase are included

$$x_2 H_{21} = y_2 P \hat{\phi}_2 \quad (13)$$

This approach was used successfully to model the solubility of CO<sub>2</sub> in water for pressure up to about 1 MPa.<sup>(23)</sup> The third, Model #3, includes the vapor phase non-ideality and the Poynting correction. This is equivalent to the KK equation.

$$x_2 H_{21} \exp[\bar{v}_2^\infty (P - P_1^\circ) / RT] = y_2 P \hat{\phi}_2 \quad (14)$$

If the system CO<sub>2</sub>-H<sub>2</sub>O is accurately modeled by the KK equation, then it follows that we should expect this equation to correlate accurately the solubility. Finally, Model #4 is essentially the rigorous formulation of Henry's law. The activity coefficients are calculated using the two-suffix Margules equation. This is basically the KI equation.

$$\exp[A(x_1^2 - 1) / RT] x_2 H_{21} \exp[\bar{v}_2^\infty (P - P_1^\circ) / RT] = y_2 P \hat{\phi}_2^\circ \quad (15)$$

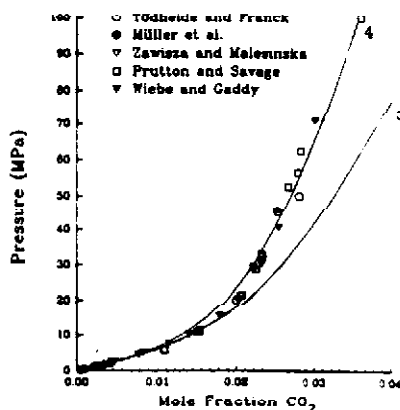


Fig. 5. The solubility of  $\text{CO}_2$  in water at  $100^\circ\text{C}$  from models #3 and #4 and some experimental data.

An appropriate model for the solvent depended upon the equation used for the solute.

Figure 4 shows the solubility of  $\text{CO}_2$  at  $100^\circ\text{C}$  calculated using the four models. The following parameters were used:  $H_{21} = 495.6$  MPa and  $\bar{v}_2^\infty = 28.6 \text{ cm}^3\text{-mol}^{-1}$ , which were taken from the KK equations in the previous section of this paper, and  $P_1^\circ = 0.101325$  MPa and  $v_1 = 18.8 \text{ cm}^3\text{-mol}^{-1}$ , which were taken from the steam tables.<sup>(24)</sup> The fugacity coefficients were calculated using the RK equation of state. Finally  $A = -11 \text{ kJ-mol}^{-1}$  was obtained by fitting the experimental data. Figure 5 shows a comparison between Models #3 and #4 along with the experimental data of Tödheide and Franck<sup>(16)</sup> and Müller *et al.*<sup>(21)</sup> (both of which were used in the KK analysis, except the point at 100 MPa), Wiebe and Gaddy,<sup>(7)</sup> Prutton and Savage<sup>(25)</sup> and Zawisza and Malesinska.<sup>(26)</sup> The last three sources were not used in the KK analysis since vapor compositions were not reported. Figure 4 demonstrates that there is a significant difference between the four models and Figure 5 shows that Model #4 provides an excellent fit of the experimental data. On the other hand, Model #3 overestimates the solubility and the error increases with increasing pressure. From this approach, one must conclude that for this temperature ( $100^\circ\text{C}$ ), the system  $\text{CO}_2\text{-H}_2\text{O}$  is not accurately modeled by the KK equation.

Figure 6 shows the calculated vapor phase composition that is in equilibrium with the aqueous  $\text{CO}_2$  solution. The data of Tödheide and Franck,<sup>(16)</sup> Coan and King<sup>(27)</sup> and Müller *et al.*<sup>(21)</sup> are also shown. Models #3 and #4 predict essentially the same vapor composition. Al-

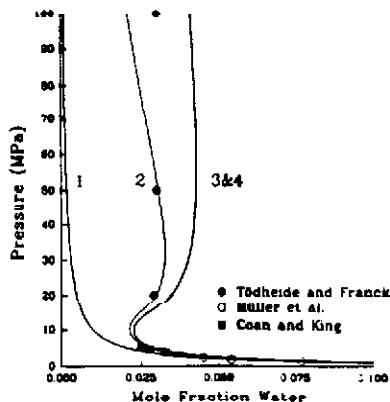


Fig. 6. Vapor phase composition for CO<sub>2</sub>-H<sub>2</sub>O at 100°C from the four models and some experimental data (see text for description of models).

though Model #4 is not the best fit of the vapor composition, it is a reasonable prediction. Note, that this is a true prediction, because, in this case, the experimental vapor phase compositions were not used in these models.

## 6. Concluding Remarks

From this analysis, the system CO<sub>2</sub>-H<sub>2</sub>O is and is not accurately modeled by the KK equation, depending on the temperature. For temperatures below 100°C, the KK equation is accurate, but above that temperature it is not.

As was noted in this paper, all the previous investigations had some shortcomings. This paper is a significant improvement over the previous attempts in two respects: (1) only experimental data were considered (smoothed values were not used) and (2) no assumption was made about the composition of the vapor in equilibrium with the liquid. Although the fugacities calculated based on the experimental compositions were not as accurate as one might like, they were not further impaired by an assumption about the vapor.

Finally, the solubility was modeled using four formulations of Henry's law including those analogous to both the KK and KI equations. As a result of modeling the solubility using different forms of Henry's law, more data can be incorporated into the analysis. This allows us to conclude that at 100°C the system CO<sub>2</sub>-H<sub>2</sub>O is not accurately modeled by the KK equation. For pressures up to about 10 MPa (or solubilities of about 2 mol%), there is essentially no difference between the two approaches. However, at higher pressure (and hence

larger solubility), deviations from the KK approach become significant. Since this deviation is small, it may be possible that it is due to the effect of pressure on  $\bar{v}_2^\infty$ . This effect has not been examined in detail.

### Nomenclature

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Roman	
$A$	Margules constant
$\hat{f}$	fugacity of a component in a mixture
$H_{21}$	Henry's constant for solute 2 in solvent 1
NP	number of points
$P$	total pressure
$P^\circ$	vapor pressure
$R$	gas constant
$r^2$	correlation coefficient
$T$	absolute temperature
$t$	Celsius temperature
$v$	molar volume
$\bar{v}^\infty$	partial molar volume at infinite dilution
$x$	mole fraction in liquid
$y$	mole fraction in vapor
Greek	
$\gamma$	activity coefficient
$\phi^\circ$	fugacity of pure, saturated component
$\hat{\phi}$	fugacity coefficient for component in mixture
Superscripts	
L	liquid phase
V	vapor phase
Subscripts	
$i$	component $i$
1	component 1, solvent, water
2	component 2, solute, carbon dioxide

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