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Empirical Partitioning of CO_2 in H_2O-CO_2 Mixtures

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ABSTRACT

It is presented an empirical method to estimate the partial mass fractions of both components inside H_2O-CO_2 mixtures at moderate and relatively high temperatures and pressures. This method is based both on the thermodynamic theory of vapor-liquid equilibrium and on the mathematical and statistical processing of the available experimental data. The developed algorithm allows the estimation of the specific enthalpy of such mixtures in the two-phase region. Limits of the method are just established by the ranges of temperature and pressure comprised on the experimental works. In addition, a numerical example is included in order to describe the whole process involved. The main application of this methodology is in the geothermal industry, in the areas of reservoir and production engineering.

1. INTRODUCTION

The binary system H_2O-CO_2 is one of the fundamental geological and geochemical binary systems (Malinin, 1959; Takenouchi and Kennedy 1964), which is important not only in the industry but also in the processes of capture and storage of CO_2 (García, 2001). This system has been considered as one of the more complex systems to be thermodynamically characterized (Harvey, 2002, Aasen et al., 2017), and there are several papers reporting the results of experimental studies on the H_2O-CO_2 system (Wiebe and Gaddy, 1937; Malinin, 1959; Ellis and Golding, 1963; Tödheide and Franck, 1963; Takenouchi and Kennedy 1964; Zel'venski, 1974; Sawisza and Malesiňska, 1981). These experimental results have been used to compute related and derived parameters, such as partial molar volume (Malinin, 1974; Akinfiev and Diamond, 2003), fugacity and fugacity coefficient (Spycher and Reed, 1988), equation of state (Pritchett et al, 1981; Ándersen et al. 1992; Duan et al. 1992; Aasen et al., 2017), and the Henry's constant (Plyasunov, 1991; Crovetto and Wood, 1992; Harvey, 1996).

In addition, the theoretical basis related to the vapor-liquid equilibrium (VLE) applicable to this binary system has also been described (Sánchez-Upton and Santoyo, 2002). However, the most relevant experimental works on VLE of the H_2O-CO_2 system are those by Tödheide and Franck (1963) and Takenouchi and Kennedy (1964).

This paper starts by presenting in especial plots the mentioned experimental data of the H_2O-CO_2 system, selecting the most reliable and representative data related to the VLE. This was carried out by ordering and processing the available mathematical-statistical data. The data processing included the fitting of all the sets of data mainly by polynomials of different degree. Afterwards, the different equations used to describe the VLE are reviewed, and an equation, similar to the Krichevsky-Kasarnovsky one is proposed, to define the equilibrium conditions of these systems. As the whole two-phase region of these systems is limited by the almost all liquid-phase (VLE condition) state and the all vapor-phase state, it is necessary to implement an adequate algorithm that allows to estimate the continuous thermodynamic states along the CO_2 iso-concentrations. This process is described in the following sections of this paper. Finally, an example with the logical steps of the procedure is presented.

2. DATA COLLECTION-PROCESSING AND REVIEW

The mentioned works of Tödheide and Franck (1963) and a Takenouchi and Kennedy (1964) could be considered as complete in the sense that they report both the solubility of CO_2 in the liquid-phase, and the molar fraction of CO_2 in the vapor phase, as well as pressures and temperatures. Both works are also important because of the great amount of experimental data of the VLE of the H_2O-CO_2 system reported. Most of the subsequent works do not report the molar fractions of CO_2 in the vapor phase.

Fig. (1), contains the first plots of data regarding the solubility of CO_2 in H_2O (liquid-phase), obtained from the mentioned works for temperatures between 110 and 260 °C, while Fig. 2 shows the same plots for temperatures between 270 and 360 °C. It is possible to note that both results about solubility are similar up to temperature of 300 °C and along the partial pressure of CO_2 of the comparison intervals. The largest differences of this parameter are noticed at 350 °C (Fig. 2).

On the other hand, the results obtained for the vapor part disagree almost totally throughout the partial pressure of CO_2 intervals (Fig.3). However, the best approximations are mainly noted at low and relatively low partial pressure of CO_2.

The information reported by Takenouchi and Kennedy (1964), corresponding to the vapor phase, was easier for processing. Thus, it was decided to use just these results to complete this paper.

The more time consuming of the different tasks comprised in this study, was the fit of the various sets of data by polynomial functions. The reliable regression model that allows the best fittings was a segmented-polynomial, of the following form:

$$P_{CO_2,i} = k_{i,1}Ж_{2,i} + k_{i,2}\left(Ж_{2,i} - \lambda_{i,1}\right)^2 + k_{i,3}\left(Ж_{2,i} - \lambda_{i,1}\right)^3 + k_{i,4}\left(Ж_{2,i} - \lambda_{i,2}\right)^3 \qquad (1)$$

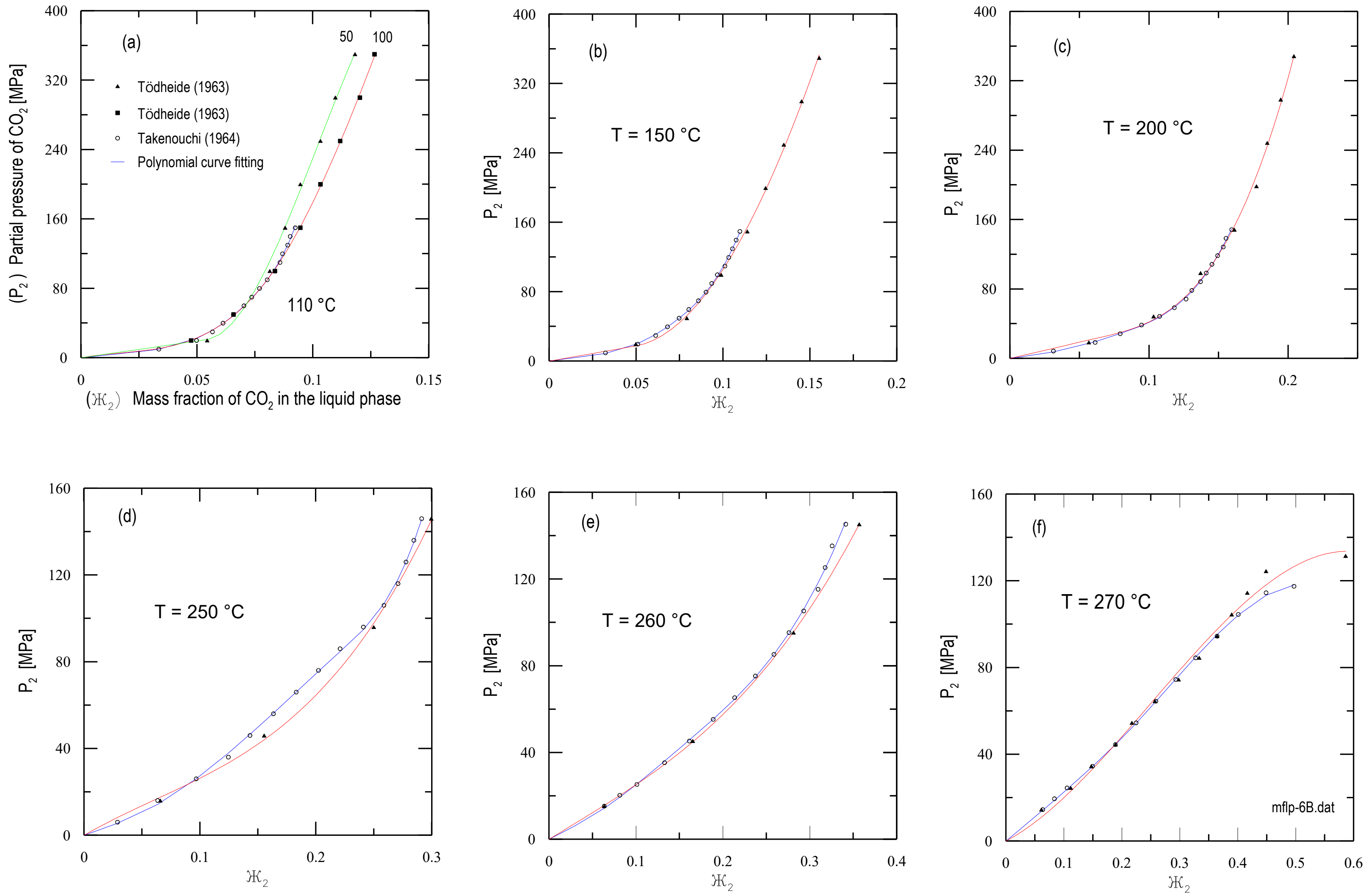

Figure 1: Distribution of the mass fraction of CO_2 in the liquid phase ($Ж_2$) as a function of the partial pressure of CO_2 $(P_2 = P_{CO_2})$ for temperatures 110-260 °C . Experimental data taken from Tödheide und Franck (1963) and Takenouchi and Kennedy (1964).

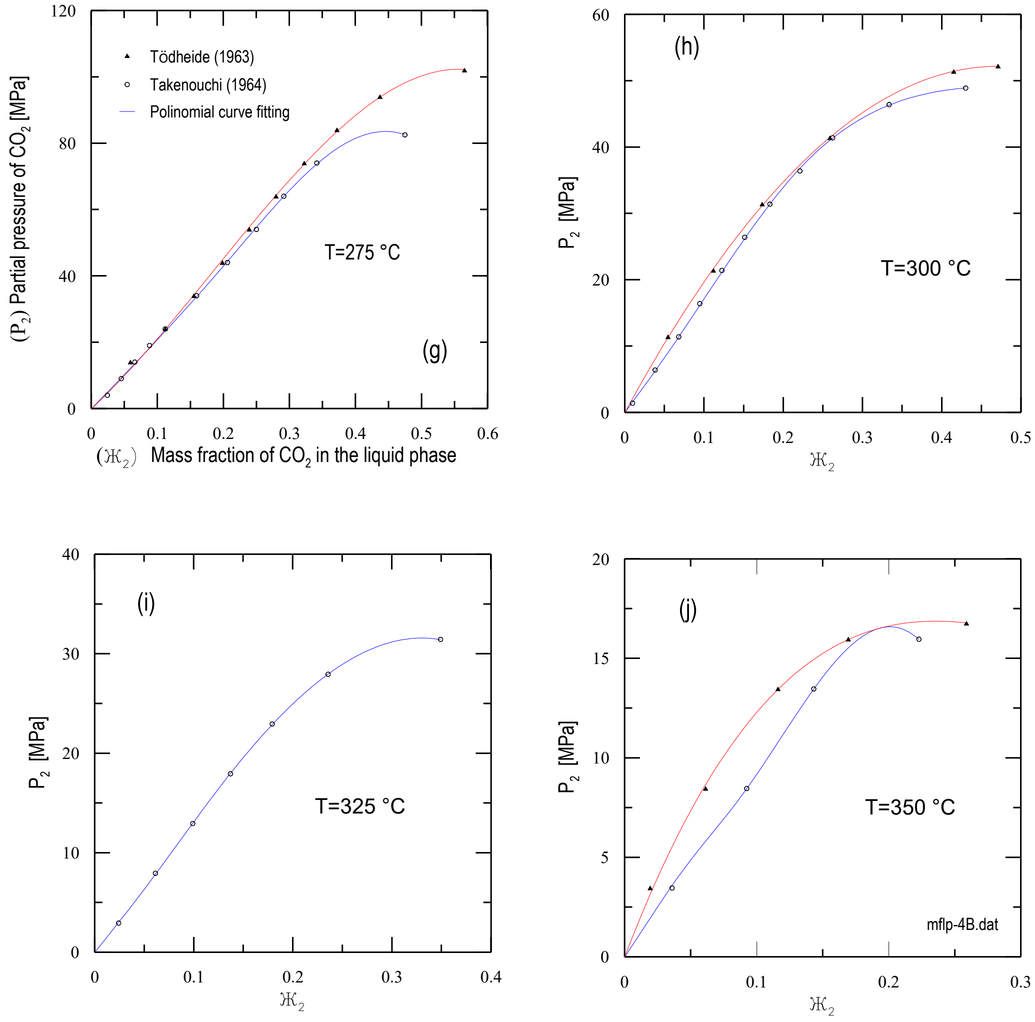

Figure 2: Distribution of the mass fraction of CO_2 in the liquid phase ($Ж_2$) as a function of the partial pressure of CO_2 $(P_2 = P_{CO_2})$ for temperatures 270-350 °C . Experimental data taken from Tödheide und Franck (1963) and Takenouchi and Kennedy (1964).

where P_{CO_2} is the partial pressure of CO_2; $Ж_2$ is the mass fraction of CO_2 in the liquid phase; k's are the polynomial coefficients, λ's are the nodes that links the segments; and subscript i refers to the i-th isotherm. Table 1 presents the coefficients of the 10 different isotherms.

The vapor phase data were also fitted through segmented polynomials in a similar way, but now, graphing Π_2 vs. P_{CO_2} (Fig. 3). The different polynomial regressions give values of R_D^2 (coefficient of determination) superior to 0.99.

However, it was observed during the study that

$$\Pi_2 \, P \approx P_{CO_2} \tag{2}$$

where Π_2 is the mass fraction of CO_2 in the vapor phase, and P is the total pressure. This observation was earlier reported by Sutton (1976) and used by Pritchett et al. (1981) too.

Eq. (2) seems to be valid at low and relatively low pressures. In order to improve this observation, we introduce the $Я$ factor as follows:

$$Я \, \Pi_2 \, P \approx P_{CO_2} \tag{3}$$

where $Я$ is an improvement factor. The improvement factor depends on temperature and pressure, and it can be computed with the following equation:

$$Я_j = k_{j,1} + k_{j,2}P + k_{j,3}P^2 \tag{4}$$

where subscript j stands for the jth isotherm. $Я$ has the following pressure restrictions:

$$Я = \begin{cases} = 1; & 0 < P < P_{Lo} \\ = f(T,P); & P_{Lo} \le P \le P_{Hi} \end{cases} \tag{5}$$

Table 2 shows the three coefficients used in Eq. (4) along with the corresponding low (P_{Lo}) and high (P_{Hi}) values of pressure.

Table 2: Polynomial coefficients that fit the experimental data (liquid phase) from the 10 isotherms reported by Takenouchi and Kennedy (1964). In the polynomials $\lambda_{i,1} = 0.03$.

i	T [°C]	Coefficients of the polynomials				$\lambda_{i,2}$	R^2 [%]
		$k_{i,1}$	$k_{i,2}$	$k_{i,3}$	$k_{i,4}$		
1	110	0.2845D+03	0.1662D+05	0.1941D+06	0.3659D+07	0.076952	99.9634
2	150	0.2734D+03	0.1411D+05	0.7727D+04	0.5944D+06	0.074723	99.9848
3	200	0.2402D+03	0.5917D+04	-0.3879D+05	0.1865D+06	0.079175	99.9848
4	250	0.1915D+03	0.1978D+04	-0.4273D+04	0.8952D+05	0.220913	99.9857
5	260	0.2084D+03	0.1077D+04	-0.2837D+04	0.9709D+04	0.161339	99.9747
6	270	0.2233D+03	0.1161D+02	0.5072D+03	-0.2329D+04	0.224598	99.9869
7	275	0.2055D+03	0.4494D+02	0.1217D+03	-0.1780D+04	0.205987	99.9754
8	300	0.1633D+03	0.2482D+03	-0.1195D+04	0.1693D+04	0.220913	99.9905
9	325	0.1254D+03	0.2108D+03	-0.1307D+04	0.9064D+03	0.136963	99.9992
10	350	0.1006D+03	-0.5096D+03	0.4726D+04	-0.9643D+04	0.092385	99.9954

Table 2: Polynomial coefficients used in the equations of the improve factor $(Я_j)$.

j	T [°C]	Coefficients of the polynomials			P_{Lo} [MPa]	P_{Hi} [MPa]	R^2 [%]
		$k_{j,1}$	$k_{j,2}$	$k_{j,3}$			
1	110	0.98651589D+00	0.12232099D-02	-0.29625914D-05	**10**	150	99.1795
2	150	0.98413121D+00	0.17113731D-02	-0.47588785D-05	**10**	150	99.7585
3	200	0.95661136D+00	0.26633583D-02	-0.82894783D-05	**10**	150	99.9401
4	250	0.89448452D+00	0.53268841D-02	-0.16772141D-04	10	150	99.8813
5	260	0.88106487D+00	0.58890192D-02	-0.17620137D-04	20	150	99.9201
6	270	0.10159235D+01	-0.69310759D-03	0.57455851D-04	20	123	96.9272
7	275	0.97026987D+00	-0.27820558D-02	0.13619637D-03	10	88.5	91.3836
8	300	0.93055981D+00	-0.10836005D-01	0.44426020D-03	10	57.5	92.7045
9	325	0.17992911D+01	-0.89322552D-01	0.21125852D-02	15	43.5	92.3803
10	350	0.71478225D+01	-0.56040487D+00	0.12469666D-01	20	32.5	94.0048

Fig. (4) illustrates three different mathematical expressions that can be used to estimate P_{CO_2} inside the vapor phase, for a mixture at 250 °C. The commonest form is based on a mol basis $\left(y_{CO_2}P\right)$, as chemists usually do, whereas the second form is based on a mass basis $\left(\Pi_{CO_2}P\right)$. Figure 4 shows that the term that includes Π_{CO_2} (mass fraction of CO_2 in the vapor phase) approaches better to the values of P_{CO_2}. This approximation is excellent at low and relatively low P_{CO_2} [see Fig. (4)], but gradually deviates as P_{CO_2} increases. In order to reduce the differences between $\Pi_{CO_2}P$ and P_{CO_2} we introduce the improvement factor $(Я)$ defined by Eqs. (4) and (5). This factor, as mentioned before, is represented by a common second degree polynomial and depends on temperature and total pressure. The corresponding polynomial is able to reduce (almost to zero) the error involved.

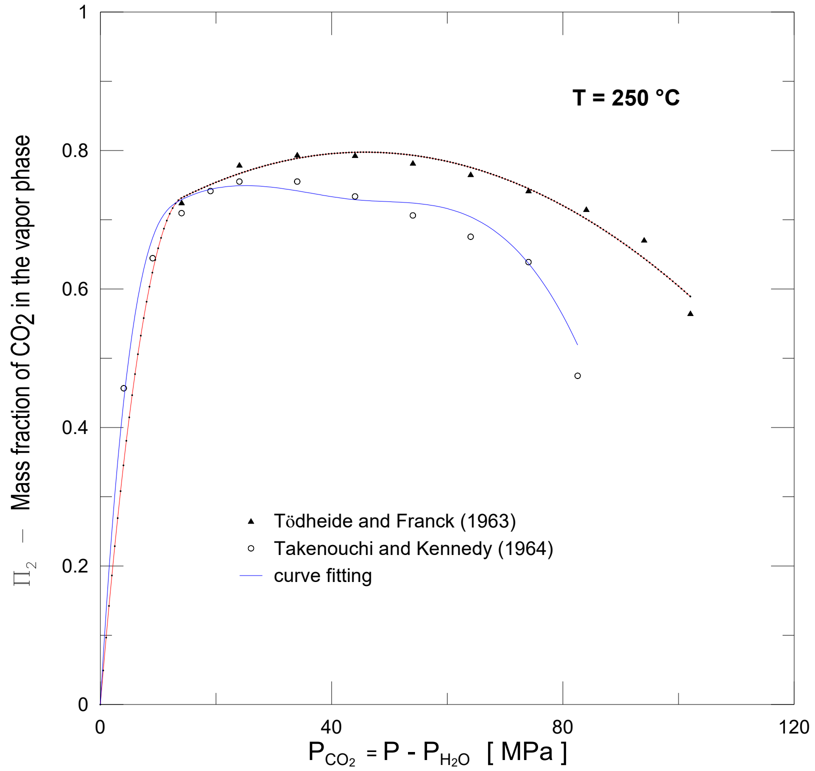

Figure 3: Mass fraction of CO_2 in the vapor phase (Π_2) as a function of the partial pressure of CO_2 (P_{CO_2}).

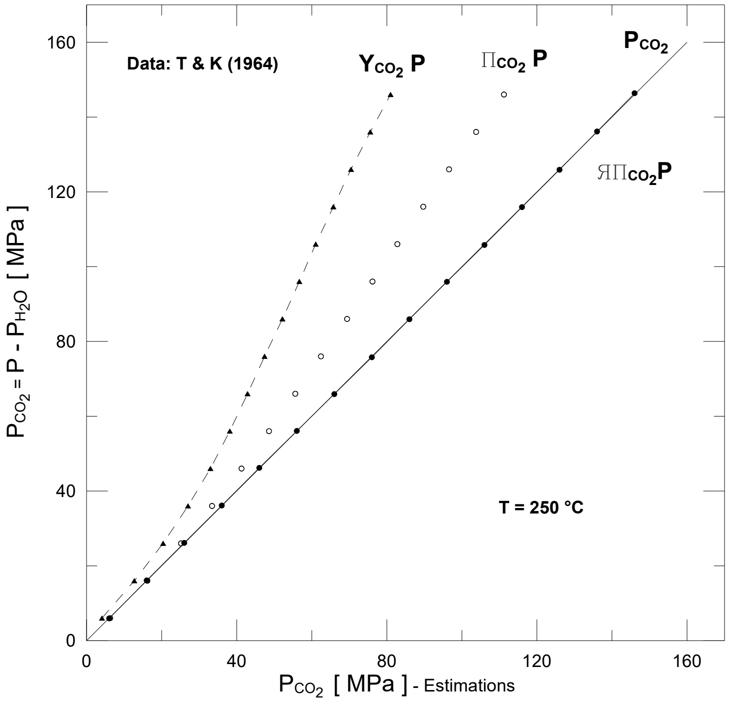

Figure 4: Comparison of three different estimators of the partial pressure of CO_2, for the gas phase.

3. FUNDAMENTAL THEORY ON GAS-LIQUID EQUILIBRIUM

"It may be asserted that every liquid is capable of taking up every gas, and therewith to form a homogeneous liquid or solution" (Ostwald, 1891), but the relative quantity depends on the similarity or dissimilarity of the components. However, the quantity of a gas dissolved by a specified quantity of a liquid at some temperature is proportional to the pressure of the gas.

The gas-liquid equilibrium theory starts assuming that for any component i the fugacities in both phases must be the same (Pausnitz et al. 1999). The simplest form to represent the anterior idea is the Raoult's law, which is:

$$p_i = x_i P_i^S \tag{6}$$

where P_i is the partial pressure of component i in the gas phase, x_i is the mole fraction (solubility) of i, and P_i^S is the saturation pressure of pure (frequently hypothetical) liquid i at the temperature of the solution. The ideal solubility (Eq. 1) gives correct order of magnitude, providing that the partial pressure of the gas is small enough and sufficiently below the critical temperature of the solvent and not too above the critical temperature of the gaseous solute.

An improvement to the anterior observation is described through the Henry´s law

$$p_i = y_i P = k x_i \tag{7}$$

where y_i is the mole fraction of component i in the gaseous phase, and k is a constant of proportionality depending only on the temperature. This equation provides a good approximation when the solubility and the partial pressure of the solute are small and when the temperature is also well below the critical temperature of the solvent (Pausnitz et al. 1999).

One of the most "complete" equations on gas-liquid solubility is the commonly known Krichevsky-Kasarnovsky equation (Prousnitz et al., 1999; Sánchez-Upton and Santoyo, 2002), this is:

$$ln\left(\frac{f_i}{x_i}\right) = ln\left(\frac{\phi_i y_i P}{x_i}\right) = ln\left(H_{i,solvent}^{p^r}\right) + \frac{\int_{p^r}^{P} \bar{v}_i^{\infty} dP}{RT} \tag{8}$$

where f_i is the fugacity of component i; ϕ_i is the coefficient of fugacity of component i; $H_{i,solvent}^{p^r}$ is Henry's constant evaluated at an arbitrary reference pressure p^r, $\bar{v}_i^{\infty}$ is the partial molar volume of component i at infinite dilution, R is the universal gas constant (8.314 MPa cm^3 mol^{-1} K^{-1}), and T is the absolute temperature of the mixture. The second term at the right of Eq. (8) is called the Poynting factor which is added to the Henry's law to take into account the pressure effect.

Based on observation and easiness, we propose a little-different version of the Krichevsky-Kasarnovsky equation but on a mass basis, to estimate the VLE condition, this is:

$$ln\left(\frac{\text{Я}(P,T)\ \text{П}_2\ \text{P}}{\text{Ж}_2}\right) = ln(H) + \frac{\bar{v}_i^{\infty}(P,T) f(P,T)}{2.303\, R\, T}\ (P - P_1^S) \tag{9}$$

where Я is the improvement factor; П_2 is the mass fraction of CO_2 (solute) in the gaseous phase; Ж_2 is the mass fraction of CO_2 in the liquid phase; f is a scale factor (Sánchez-Upton and Santoyo, 2002) and P_1^S is the partial pressure of H_2O (solvent). П_2 and Ж_2 are defined in the following sections.

4. AUXILIARY EQUATIONS

In this section, a group of auxiliary equations are derived to be used for solving the problem of CO_2 partitioning in mixture, which are located inside the two-phase region, this is, between the all vapor-phase state and the all liquid-phase state, and follows an iso-concentration path.

First, it is necessary to define the mass fraction of CO_2in the liquid phase (Ж_2), as follows:

$$\text{Ж}_2 = \frac{m_{2,f}}{m_f} \Rightarrow m_f = \frac{m_{2,f}}{\text{ж}_2} \tag{10}$$

where $m_{2,f}$ is the mass of component 2 (solute) in liquid phase; and m_f is the total mass of liquid. We also define the mass fraction of CO_2 in the vapor phase (П_2), as:

$$\text{П}_2 = \frac{m_{2,g}}{m_g} \Rightarrow m_g = \frac{m_{2,g}}{\text{п}_2} \tag{11}$$

where $m_{2,g}$ is the mass of component 2 (solute) in the gas phase; and m_g is the total mass of vapor. Then, it is necessary to define as well the mass fraction of CO_2 in the mixture, this is:

$$f_{2,m} = \frac{m_2}{m} \tag{12}$$

where $f_{2,m}$ is the mass fraction of CO_2 in the mixture; m_2 is the total mass of CO_2 in the mixture; and m is the total mass of the mixture.

Now, by adding Eq. (10) and Eq. (11), we get:

$$m_f + m_g = \frac{m_{2,f}}{\text{Ж}_2} + \frac{m_{2,g}}{\text{П}_2} \tag{13}$$

reminding that $m = m_f + m_g$ and $m_{2,g} = m_2 - m_{2,f}$, Eq. (13) can be rewritten as:

$$m = \frac{m_{2,f}}{\text{Ж}_2} + \frac{m_2 - m_{2,f}}{\text{П}_2} \tag{14}$$

After arranging:

$$\frac{m_{2,f}}{m} = \frac{\text{Ж}_2\left(\text{П}_2 - \frac{m_2}{m}\right)}{\text{П}_2 - \text{Ж}_2} \Rightarrow m_{2,f} = \frac{\text{Ж}_2\left(\text{П}_2 - f_{2,m}\right)}{\text{П}_2 - \text{Ж}_2} m \tag{15}$$

It simply follows that:

$$m_{2,g} = m_2 - m_{2,f} \tag{16}$$

On the other hand, the enthalpy or energy equation can be written as:

$$mh = m_{1,f}h_{1,f} + m_{2,f}\left(h_{2,gP} + h_{2,Sol}\right) + m_1 h_{1,g} + m_2 h_{2,gP_p} \tag{17}$$

The first pair of terms on the right side of Eq. (17) corresponds to the enthalpy of the liquid-phase, and the second pair on the same side to the enthalpy of the vapor-phase. Eq. (17) can be rewritten in the following form:

$$m_{1,f} = \frac{m_1 h_{1,g} + m_2 h_{2,gP_p} + m_{2,f}\left[\left(h_{2,gP} + h_{2,Sol}\right) - h_{2,gP_p}\right] - mh}{h_{1,g} - h_{1,f}} \tag{18}$$

where $m_{1,f}$ is the mass of component 1 (H_2O) in the liquid phase; m_1 is the total mass of H_2O in the mixture; $h_{1,g}$ is the specific enthalpy of saturation of steam at the temperature of the mixture (T); h_{2,gP_p} is the enthalpy of CO_2 at the partial pressure of CO_2 (P_2) and(T); $h_{2,gP}$ is the enthalpy of CO_2 at the total pressure $(P = P_1^s + P_2)$ and (T); $h_{2,Sol}$ is the specific enthalpy of solution of CO_2 at (T); $h_{1,f}$ is the specific enthalpy of liquid at (P,T); h is the specific enthalpy of the mixture; and P_1^s is the saturation pressure of H_2O at T.

It also follows that:

$$m_{1,g} = m_1 - m_{1,f} \tag{19}$$

Eqs. (15) and (18) are the two main auxiliary equations used to solve the problem of the partitioning of CO_2.

A numerical example is presented at the end part of this work, in order to show the different steps in a common problem related to the partitioning of CO_2 in mixtures located inside the two-phase region. This example uses a three-input-variables set, which are: $T - h - f_{mCO_2}$, but could be any other.

5. CONCLUSIONS

1. The procedure presented in this study seems to be applicable for determine the partitioning of CO_2 in $H_2O - CO_2$ mixtures. It is easy to use and does not depend of derived parameters such as fugacity and/or activity coefficients, or partial molar volumes.
2. This algorithm can be extended, through the whole ranges of temperature and pressure comprised in experimental works, by using an interpolation subroutine such as that developed by Sánchez-Upton (2020).
3. The modified version of the Krichevsky-Kasarnovsky equation is useful for determining the approximate value of the partial molar volume of CO_2 at infinite dilution. It neither depends on the fugacity or activity coefficients.
4. The equations developed by Pritchett et al., (1981) to compute the specific enthalpies of CO_2 (enthalpies of gas and of solution) are useful enough inside its ranges of pressure and temperature of application (up to 60 MPa and 350 °C).

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ADDENDUM 1. EXAMPLE

Following is an example to describe the logical procedure to determine the mass fractions of H_2O and CO_2 of a mixture at certain temperature. The example departs from three independent variables T, h and f_{mCO_2}, and the problem consists in determining the CO_2 partitioning in a $H_2O - CO_2$ mixture of unitary mass (1 kg) at the following conditions:

Mass fraction of CO_2	Temperature [°C]	Specific enthalpy [kJ/kg]
0.15	250	1500

The first step is to establish the two limit conditions of the mixture. These conditions are the all liquid-phase state and the all vapor-phase, both computed at the same concentration of CO_2 $\left(f_{mCO_2}\right)$.

All liquid-phase

In this case, the mass fraction of CO_2 $\left(f_{mCO_2}\right)$ is equal to the mass fraction of CO_2 in the liquid-phase.(Ж_2). Thus, the partial pressure of CO_2 $\left(P_{CO_2}\right)$ can be computed by using Eq. (1) and the coefficient given in Table 1 for $T = 250\ °C$, this is:

$$P_{CO_2} = 191.5\,\text{Ж}_2 + 1978\,(\text{Ж}_2 - 0.03)^2 - 4273(\text{Ж}_2 - 0.03)^3 \tag{A-1}$$

Substituting the value of $\text{Ж}_2 = 0.15$ into Eq. (A-1) gives $P_{CO_2} = 49.82\ MPa$.

On the other hand, the saturation pressure of pure H_2O at $T = 250\ °C$ is $P_{H_2O} = 3.98\ MPa$. Therefore, the mixture would be at the total pressure of $P_T^L = P_{H_2O} + P_{CO_2} = 53.8\ MPa$. The specific enthalpies of both components are as follows:

for H_2O (Schmidt, 1979)

$$P_T^L = 53.8\left\{h_{1,f} = 1094.80\right. \tag{A-2}$$

and for CO_2 (Pritchett et al. 1981):

$$P_T^L = 53.8\begin{cases} h_{2,g} = 470.82 \\ h_{2,Sol} = 217.77 \end{cases} \tag{A-3}$$

then the specific enthalpy of the mixture is:

$$h_m^L = \frac{1}{m}\left\{m_{1,f}\,h_{1,f} + m_{2,f}\left(h_{2,g} + h_{2,Sol}\right)\right\} \tag{A-4}$$

After substituting corresponding values, the specific enthalpy of the liquid mixture (h_m^L) is

$$h_m^L = 1033.87 \tag{A-5}$$

Therefore, the specific enthalpy of the mixture at this condition is equal to $1033.87\ [J/g]$, which is very close to the specific enthalpy of the mixture at the equilibrium condition because of the vapor phase is presumed to be too small.

All vapor-phase

In this case f_{mCO_2} is equal to the mass fraction of CO_2 in the vapor-phase $(\Pi_2 = 0.15)$. Thus, P_{CO_2} can be computed from Eq. (3), this is:

$$P_{CO_2} = \frac{P_{H_2O}}{\frac{1}{\text{Я}\Pi_2} - 1} \tag{A-6}$$

Replacing respective values, $P_{CO_2} = 0.7$, assuming that $\text{Я} = 1$ (this equation, with $\text{Я} = 1$, seems to be especially valid at low pressures). Then, $P_T^V = 4.68$. The specific enthalpies of both components are as follows:

For H_2O (Schmidt, 1979)

$$P_{H_2O} = 3.98\left\{h_{1,g} = 2800.43\right. \tag{A-7}$$

For CO_2 (Pritchett, 1981)

$$P_{CO_2} = 0.7\left\{h_{2,g} = 523.67\right. \tag{A-8}$$

Then the specific enthalpy of the mixture is:

$$h_m^V = \frac{1}{m}\{m_{1,g}\,h_{1,g} + m_{2,g}h_{2,g}\} \tag{A-9}$$

After substituting corresponding values, the specific enthalpy of the liquid mixture (h_m^V) is

$$h_m^V = 2458.92 \tag{A-10}$$

Thus, the specific enthalpy of the mixture at this condition is equal to 2458.92 $[J/g]$.

As we can see, the specific enthalpy of the mixture in this example, is between the enthalpies of the cases of all liquid-phase and all vapor-phase.

Two-phase mixture

If the specific enthalpy of the mixture is between the enthalpies of the all liquid-phase and all vapor-phase cases, this would mean that the mixture is located inside the two-phase region. In this way, it is expected that the value of the total pressure of any mixture be into the interval of pressures of the two cases before computed. Thus, the total pressure of the mixture can be estimated through the following linear interpolation equation:

$$P_m^T = P_T^L + \frac{P_T^V - P_T^L}{(h_m^V - h_m^L)}(h - h_m^L) \tag{A-11}$$

after the substitution of corresponding values, it results:

$$P_m^T = 53.8 + \frac{4.68 - 53.8}{(2458.92 - 1033.87)}(1500 - 1033.87) = 37.73 \tag{A-12}$$

Thus, the CO_2 partial pressure is 33.75 MPa, and the H_2O partial pressure is 3.98 MPa. Therefore, the specific enthalpies of both components are as follows:

for H_2O (Schmidt, 1979)

$$P = P_m^T = 37.73\,\{h_{1,f} = 1089.22\,;\; P_{H_2O} = 3.98\,\{h_{1,g} = 2800.43 \tag{A-13}$$

and for CO_2 (Pritchett et al. 1981)

$$P = P_m^T = 37.73\begin{cases} h_{2,gL} = 468.1 \\ h_{2,Sol} = 217.77 \end{cases};\; P_{CO_2} = 33.75\,\{h_{2,gG} = 467.99 \tag{A-14}$$

In order to start the solution process, we use the value of the mass fraction of CO_2 in the liquid phase at $P_{CO_2} = 33.75$, this is $Ж = 0.1151$ (just proposed as initial value). Also, the mass fraction of CO_2 in the vapor phase can be calculated with:

$$П_2 = \frac{P_{CO_2}}{Я\,P} \tag{A-15}$$

the improvement factor $(Я)$ is computed through:

$$Я = 0.89448452 + 0.53268841 \text{ x } 10^{-2}\text{ P} - 0.16772141 \text{ x } 10^{-4}\text{ P}^2 \tag{A-16}$$

thus, $Я = 1.0716$, and $П_2 = 0.8347$.

On the other hand, the mass of CO_2 in the liquid phase can be computed with:

$$m_{2,f} = \frac{Ж_2\,(П_2 - f_{mCO_2})}{П_2 - Ж_2}\,m = \frac{0.1151(0.8347 - 0.15)(1)}{0.8347 - 0.1151} = 0.1096 \tag{A-17}$$

This implies that $m_{2,g} = 0.0404$ $[kg]$. The mass of liquid H_2O can be computed with:a version of the energy or enthalpy equation, this is:

$$m_{1,f} = \frac{m_1h_{1,g} + m_2h_{2,gG} + m_{2,f}\{(h_{2,gL} + h_{2,Sol}) - h_{2,gG}\} - mh}{h_{1,g} - h_{1,f}} \tag{A-18}$$

Substituting the corresponding values previously given, one has:

$$m_{1,f} = \frac{0.85(2800.43) + 0.15(467.99) + 0.1096\{(468.1 + 217.77) - 467.99\} - 1(1500)}{2800.43 - 1089.22} \tag{A-19}$$

After solving the anterior equation, $m_{1,f} = 0.5694$, therefore $m_{1,g} = 0.2806$. Other quantities necessary in the calculus are: the mass of the liquid phase $(m_f = 0.6793)$; and the mass of the vapor phase $(m_g = 0.3206)$.

The following step includes the recalculation of the mass fractions of CO_2 in the liquid and vapor phases, this is:

$$\text{Ж}_2 = \frac{m_{2,f}}{m_f} = 0.1613; \; \Pi_2 = \frac{m_{2,g}}{m_g} = 0.1261 \qquad \text{(A-20)}$$

With this new pair of values, we again have to compute $m_{2,f}$, $m_{1,f}$, and so on. This process should be repeated twice or thrice, until the values of the variables do not change. The final results are presented in the following table:

Table A-1 . Results obtained through the partitioning process

$m_{1,f}$	0.5698	$m_{1,g}$	0.2802	$(m_{1,g} + m_{2,g})/m$	0.3207
$m_{2,f}$	0.1096	$m_{2,g}$	0.0404	$Ж_2$	0.1612
m_f	0.6793	m_g	0.3207	Π_2	0.1261

Finally, in order to revise the functionality (appropriateness) of Eq. (9), we construct a graph of $ln(\text{Я}\ \Pi_2\ \text{P}/\text{Ж}_2)$ vs $(P - P_1^S)$, by using the experimental data at 250 °C (Takenouchi and Kennedy, 1964). This is Fig. A-1.

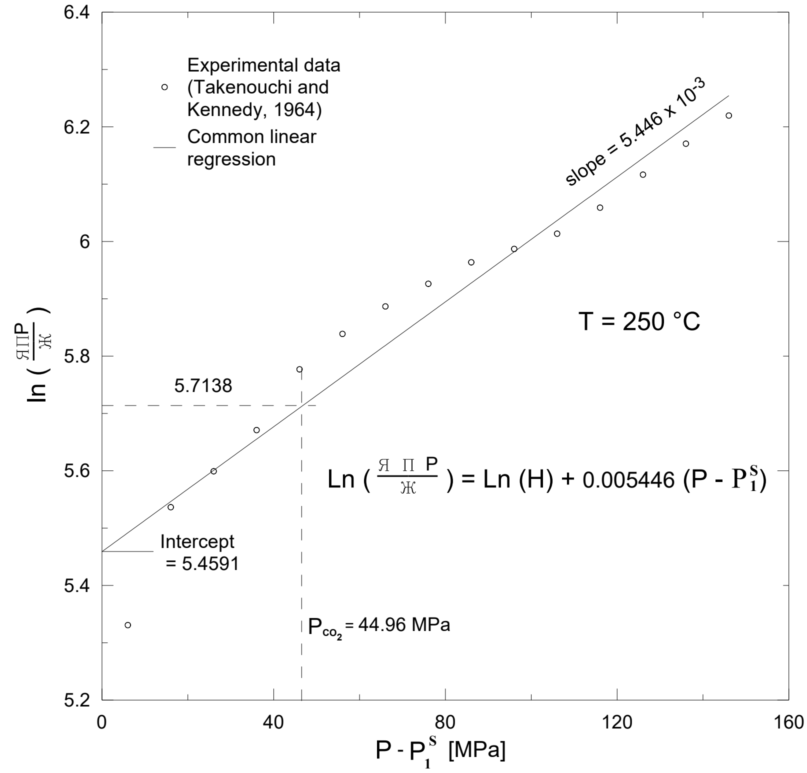

Fig. A-1. Graph of $ln\left(\frac{Я\,\Pi_2\,P}{Ж_2}\right)$ vs $(P - P_1^S)$ using the experimental data at 250 °C, after Takenouchi and Kennedy (1964)

Then, the experimental data is fitted through a current straight line, without the elimination of any point considered as outlier. As we can see, the interception of this straight line with the $ln(\text{Я}\ \Pi_2\ \text{P}/\text{Ж}_2)$ axis is $ln(H) = 5.4591$.

On the other hand, the slope of this straight line is $s = 5.446\ x\ 10^{-2}$. Now, Eq. (9) can be arrange as follows

$$ln(\text{Я}\ \Pi_2\ \text{P}) = ln(H\text{Ж}_2) + \frac{\bar{v}_2^{\infty} f}{2.303\,R\,T}\,(P - P_1^S) \qquad \text{(A-21)}$$

Reminding that $P_2 = Я\,\Pi_2\,P = P - P_1^S$, and according to Sánchez-Upton and Santoyo (2002), $\bar{v}_2^{\infty} = 54.29$ cm^2 mol^{-1} and $f = 1$. Therefore Eq. (A-21) becomes:

$$ln(\text{P}_2) = 3.562 + 0.00542\ (\text{P}_2) \qquad \text{(A-22)}$$

Solution to Eq. (A-22) can be obtained by using a numerical method such as Newton-Raphson. After solving, the result is $P_2 \approx 44.96\ [MPa]$. Therefore the value of the total pressure through this method is $P_T = P_1 + P_2 = 3.98 + 44.96 = 48.94\ [MPa]$.

It can be noted that the value of $\bar{v}_2^{\infty} f/2.303\, R\, T = 5.42\, x\, 10^{-3}$ is similar to the slope of the straight line used to fit the experimental data. In addition, the absolute error between the two methods used here to compute the total pressure at the vapor-liquid equilibrium, is of the order of 9%.