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Phase equilibria for the oxygen–water system up to elevated temperatures and pressures

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Abstract

A new thermodynamic model was presented to calculate the phase equilibria for the oxygen–water system. The modified Redlich–Kwong equation of state with a new correlated cross-interaction parameter was used to calculate fugacity coefficients for the vapor phase. The dissolved oxygen followed Henry's law. A new expression was correlated from the experimental data to calculate Henry's constant of oxygen. The calculated results of equilibrium composition were compared with the available experimental data and those calculated by other models with different parameters. The comparison revealed that the new model is suitable for calculating both liquid and vapor compositions while the empirical method is only suitable for estimating the liquid composition. Furthermore, compared to the model proposed by Rebenovich and Beketov, the calculated results of the vapor composition with the new model are better.

Keywords: Oxygen; Water; Equation of state; Vapor–liquid equilibrium; Henry's constant

1. Introduction

Many natural and industrial processes occur in aqueous environments that involve or are affected by dissolved oxygen. Such processes range from biological and synthesis reactions to the corrosion and oxidation of materials. A detailed knowledge of temperature and pressure effects on oxygen solubility enables the related processes to be modelled more accurately and controlled more effectively. In previous literature, oxygen solubility in water was determined experimentally, and Henry's constant of oxygen in water was correlated from partial pressure [1,2] or total pressure [3–5] in which an equation of state (EOS) was used to calculate fugacity coefficients for the vapor phase. However, none of the used EOS was verified by the available experimental data. It may be reasonable to calculate the liquid composition, but the vapor composition cannot be calculated reliably, especially at high pressures.

Meanwhile, thermodynamic properties (humidity, enthalpy and entropy) in the vapor phase for the oxygen–water system are of importance [6]. Saturated vapor composition is often needed in order to calculate saturated properties. Based on virial EOS, Rabinovich and Beketov [6] proposed a model to calculate thermodynamic properties including saturated vapor composition for the studied system. Because of the scarcity of the experimental data, the cross-interaction parameter between molecular oxygen and water was estimated from theory and the calculated results of saturated vapor composition were verified by comparing with the experimental data of the nitrogen–water system. The calculated results of the saturated composition and other properties in the vapor phase are questionable, and liquid composition cannot be calculated since the liquid phase was assumed to be pure water.

In this paper, phase equilibria of the oxygen–water system were studied. Fugacity coefficients of the components in the vapor phase were calculated with the modified Redlich–Kwong (RK) EOS [7]. The dissolved oxygen in the liquid phase followed Henry's law. Available experimental data were collected and analyzed to obtain a reasonable Henry's constant and to investigate the existing

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cross-interaction parameter in the modified RK EOS. Calculated results in this paper were compared with experimental data and those of other models in the literature.

2. Thermodynamic model

The thermodynamic condition for liquid–vapor equilibrium is

$$\phi_i y_i P = f_i^0 x_i \gamma_i \tag{1}$$

ϕ_i is calculated with the modified RK EOS developed by de Santis et al. [7] and

$$\ln \phi_i = \ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - 2\cdot\frac{\sum_j y_j a_{ij}}{RT^{1.5}b}\cdot\ln\left(\frac{v+b}{v}\right) + \frac{ab_i}{RT^{1.5}b^2}\cdot\left[\ln\left(\frac{v+b}{v}\right) - \frac{b}{v+b}\right] - \ln\left(\frac{Pv}{RT}\right) \tag{2}$$

where a and b are parameters with the mixing rule [7] and

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{3}$$

$$a_{ii} = a_{ii}^0 + a_{ii}^1(T) \tag{4}$$

$$a_{ij} = a_{ji} = (a_{ii}^0 a_{jj}^0)^{0.5} \tag{5}$$

$$b = \sum_i y_i b_i \tag{6}$$

The temperature-independent parameters of gaseous oxygen, a_{ii}^0 and b_i, were taken from Wark [8] and those for water vapor were taken from de Santis et al. [7]. The temperature-dependent parameter, a_{ii}^1, is zero for gaseous oxygen. For water vapor, a_{ii}^1 was taken from de Santis et al. [7]. Because the modified RK EOS has not been verified yet for the oxygen–water system, it was investigated in the following text.

The liquid phase reference fugacity of water f_w^0 is calculated with Eq. (7). Properties of pressure and volume were calculated from the industrial standard IAPWS-IF97 [9], the calculation formula and parameters are shown in Appendix A. For the part of $\phi_w^V(T, P_w^s)$, since the formula cannot be obtained directly for our programming from the source of IAPWS-IF97 [9], we calculated it by using Aspen Plus with STEAMNBS model [10] because of its better results compared with other models, such as Peng-Robinson and modified RK EOSs, and correlated with the polynomial equation (8). The calculated results of liquid phase reference fugacity of water f_w^0 in this paper were compared with those calculated from the software SUPCRT92 [11]. The calculated results are almost the same when the temperature is higher than 373.15 K. At lower temperature (<373.15 K), there are some deviations because in the SUPCRT92 it was assumed that the pressure is to be 1 bar

$$f_w^0 = \phi_w^V(T, P_w^s) P_w^s(T) \exp\left[\frac{1}{RT}\int_{P_w^S}^{P} v_w^L(T, P)\,\mathrm{d}P\right] \tag{7}$$

$$\phi_w^V(T, P_w^s) = 1.30259 - 3.73088\times10^{-3}T + 1.6357\times10^{-5}T^2 - 2.91522\times10^{-8}T^3 + 1.6073\times10^{-11}T^4 \tag{8}$$

The dissolved oxygen follows Henry's law, and f_i^0 of oxygen is equal to H (Henry's constant). The Henry's constant of oxygen in water can be taken from literature [1–5,12,13] or calculated from Helgeson EOS with Eq. (9) [11,14] or re-correlated from the available experimental data. It was studied carefully as described as follows.

$$H = 55.51 \exp\left(\frac{\Delta G_{O_2,g}^0(T, P)_m - \Delta G_{O_2,aq}^0(T, P)_m}{RT}\right) \tag{9}$$

Activity coefficients were assumed to be unity because the dissolved gas is small.

2.1. Adjustment of the modified RK EOS

For the model described above, parameters in the modified RK EOS are often correlated from the experimental data in the vapor phase. For the studied system, most of the experimental data are oxygen solubilities in the liquid phase. Although Zoss [15] determined the vapor composition up to high temperatures and pressures, it was proved that there are experimental errors [16]. Subsequently, the modified RK EOS has not been verified yet for the oxygen–water system.

Recently, Wylie and Fisher [17] determined the enhancement factor from 298.15 to 348.15 K and 20–140 bar for the oxygen–water system. Saturated vapor compositions were calculated from this group of experimental data [17] and used to investigate the modified RK EOS in this paper.

Henry's constant of oxygen in water is also needed in order to calculate the saturated vapor composition. For the first try, the Henry's constant was calculated with the Helgeson EOS from Eq. (9). The calculated results of water vapor composition were compared with the experimental data [17]. Comparison is shown in Fig. 1. Obviously, the higher the pressure and the lower the temperature, the higher the deviation between the calculated results and the experimental data of Wylie and Fisher [17]. The deviation is about 15% at 298.15 K and 140.85 bar.

The deviation may be due to two factors, the parameters in the modified RK EOS and the Henry's constant calculated with the Helgeson EOS. At low temperature (<100 °C), parameters in the Helgeson EOS were correlated from experimental data of Benson et al. [12] in which the Henry's constant of oxygen in water was correlated from the accurate oxygen solubility with a semi-empirical method. Therefore, we can conclude that the Henry's constant calculated with the Helgeson EOS should be correct in the low temperature range. Wylie and Fisher [17] also stated that the effect

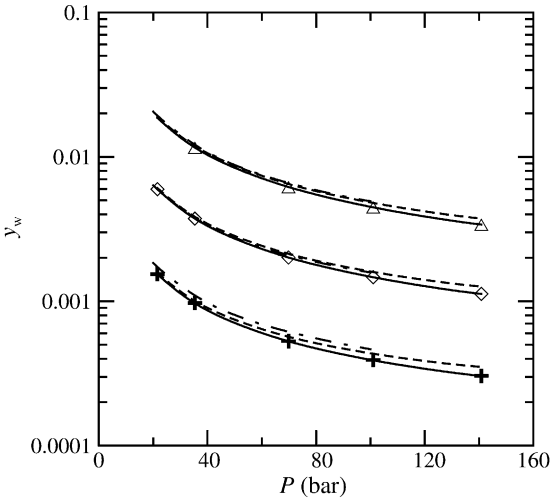

Fig. 1. Comparison of the water vapor composition. +, ◇ and Δ, experimental data of Wylie and Fisher [17] at 298.15, 323.15 and 348.15 K, respectively. (- - -) and (—) calculated results of the modified RK EOS with the original and new correlated parameters, respectively; (- - -) calculated results of Rabinovich and Beketov [6].

of oxygen on the concentration of water vapor with liquid water is mainly caused by intermolecular forces in the gas phase. The Poynting effect is about one-third compared to intermolecular forces of gas, and the Raoult effect is much less compared to intermolecular forces of gas and the Poynting effect. In other words, the effect of Henry's constant on the vapor composition is small. Therefore, the deviation is due to the parameters in the modified RK EOS.

In this paper, an adjustable parameter k was added in order to calculate the cross-interaction parameter as shown in Eq. (10). k was correlated from experimental data of Wylie and Fisher [17]. The correlation result is also shown in Eq. (10):

$$a_{ij} = a_{ji} = k(a_{ii}^0 a_{jj}^0)^{0.5} = 0.783(a_{ii}^0 a_{jj}^0)^{0.5} \quad (10)$$

2.2. Correlation of the Henry's constant of oxygen in water (H)

The correlation of Henry's constant of oxygen in water was performed in two steps:

1. the calculation of H of each experimental data point with Eq. (1) by iterative calculation, and
2. the correlation of the expression of H to describe the effects of temperature and pressure.

2.2.1. Correlation of H for each experimental data point

The Henry's constant of oxygen in water has been correlated from solubility data which have been determined experimentally [1–5,14]. In some of these studies [1,2,14], the partial pressure of oxygen, which was estimated by subtracting the vapor pressure of water from the total pressure, was used. When a gas dissolves in water, the partial pressure of water will deviate from the saturated pressure of pure water, especially at high pressure. It indicates that the estimated partial pressure of oxygen in the literature is unreasonable. In other studies [3–5], total pressure was used and an equation of state was used to calculate fugacity coefficient for the vapor phase, but none of them was investigated by the available experimental data in the vapor phase.

In this paper, the Henry's constant of oxygen in water was correlated from the solubility data at the experimental temperature and total pressure [12,13,18–21]. Since the total pressure was not reported in the work of Cramer [1], we have not included the data of Cramer [1] in our correlation. It was proved that the solubility values of Zoss [15] are more than an order of magnitude high at low temperature, therefore, they were not considered in the correlation and their experimental errors were checked in the later text. The data of Stephan et al. [13] covered the data of Pray and Stephan [20], so the data of Pray and Stephan [20] were excluded in the correlation. The data of Rettich et al. [21] were also not considered because the temperature range is within that of Benson et al. [12], and the deviation between them is small.

Henry's constant was correlated for each experimental data point with the Newton's method. However, for the data of Benson et al. [12], Henry's constant for each experimental data point has been correlated, and it was used directly in this paper.

2.2.2. Correlation of the expression of $H = f(T, P)$

Krichevsky–Kasarnovsky equation is often used to describe the pressure effects at lower temperature (<373.15 K). Since the studied temperature is up to 623.15 K, and with increasing pressure the H obtained in the first step may increase or almost keep a constant at the same temperature, an appropriate expression, Eq. (11), was chosen for the expression of H in this paper.

The errors of the available experimental data have not been estimated in previous studies. In order to obtain reasonable correlation results, each experimental data point has an equivalent weight in our correlation. But in this case a large error in one group will cause a large deviation in the correlation. In order to avoid this, each group of data were correlated first with Eq. (11). Since the number of the data of Pray et al. [19] is less than that of parameters in the correlation expression, the data cannot be checked in this step. The correlation results for other groups are listed in Table 1.

Table 1
Correlation results for each group of data and multi-groups of data

No.	Data source	R^2
1	[12]	>0.9999
2	[13]	0.9972
3	[18]	0.9999
4	Case A	0.9917
5	Case B	0.9970

Case A, four groups of data [12,13,18,19] were used in the correlation; Case B, three groups of data [12,13,18] were used in the correlation.

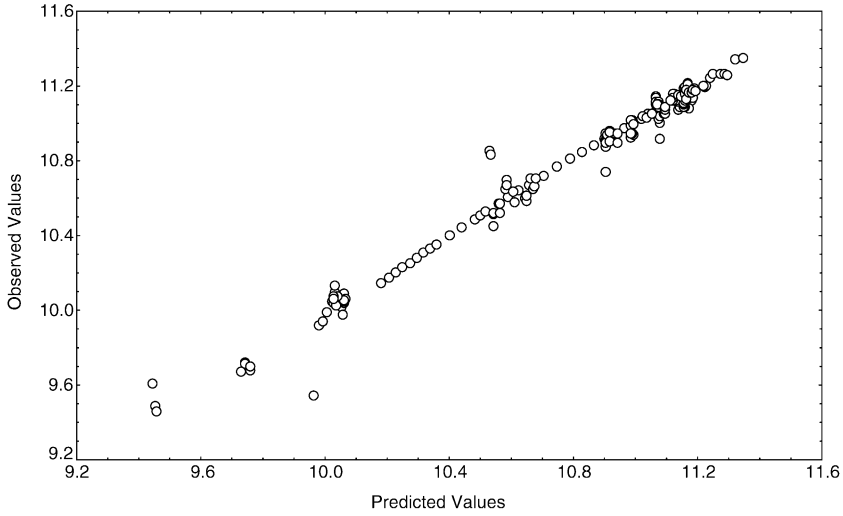

Fig. 2. Observed vs. predicted values ($\ln H$) with Eq. (11) when four groups of data (case A) were used to correlate the expression.

$$\ln H = Q_1 + Q_2 P + Q_3 P^2 + (Q_4 + Q_5 P + Q_6 P^2)T + (Q_7 + Q_8 P + Q_9 P^2)T^2 + (Q_{10} + Q_{11} P + Q_{12} P^2) \ln T \quad (11)$$

As shown in Table 1, the random experimental error for each group of data is small (No. 1 to No. 3). Therefore, all of them combined with the data of Pray et al. [19] (case A) were used to correlate the parameters in Eq. (11). The correlation results are listed in Table 1 (No. 4) and Fig. 2. From the correlation results shown in Fig. 2, it is clear that some experimental data caused large deviations. The data of Pray et al. [19] may be responsible because they had not been checked separately before correlation. In order to verify this conclusion, three groups of data [12,13,18] (case B) were used to correlate the parameters in Eq. (11). The correlation results are also listed in Table 1 (No. 5) and shown in Fig. 3. The value of R^2 of case B is near to that of case A, but the distribution of the deviation of case B is much better than that of case A as shown in Figs. 2 and 3. Therefore, the correlation results of case B are reasonable and the corresponding correlation results for each parameter are listed in Table 2.

3. Comparison and discussion

3.1. Direct comparison of the Henry's constant

Since an empirical expression, instead of Krichevsky–Kasarnovsky equation, was used, the extrapolation to the infinite-dilution may introduce error. In order to verify the

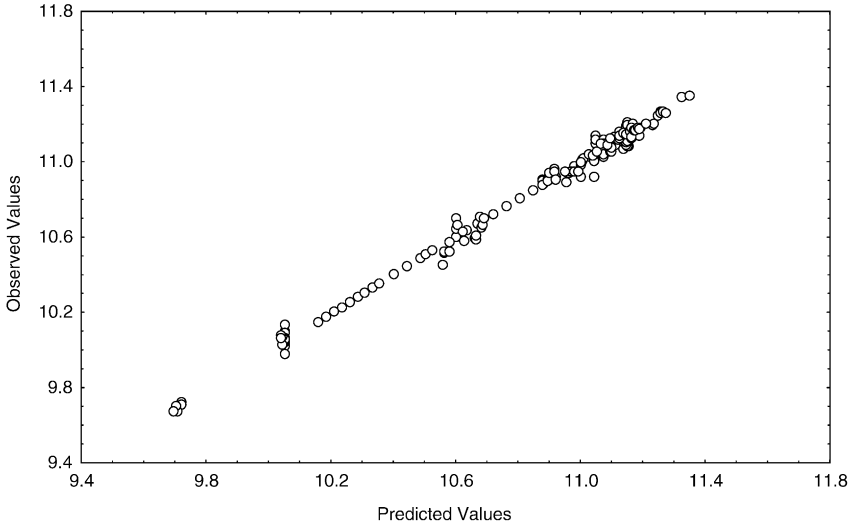

Fig. 3. Observed versus predicted values ($\ln H$) with Eq. (11) when three groups of data (case B) were used to correlate the expression.

Table 2
Coefficients in Eq. (11) for calculating the Henry's constant of oxygen

Symbol	Value
Q_1	-2.10973×10^{2}
Q_2	2.32745×10^{0}
Q_3	-1.19186×10^{-2}
Q_4	-2.02733×10^{-1}
Q_5	2.45925×10^{-3}
Q_6	-1.21107×10^{-5}
Q_7	9.77301×10^{-5}
Q_8	-1.43857×10^{-6}
Q_9	6.84983×10^{-9}
Q_{10}	4.79875×10^{1}
Q_{11}	-5.14296×10^{-1}
Q_{12}	2.61610×10^{-3}

reliability of our expression, the correlation results at saturated water vapor pressure was compared with those determined by others [1,2,12]. From the comparison shown in Fig. 4, it is clear that the correlation results in this paper are consistent with those in the literature at saturated water vapor pressure.

Fig. 5 shows the pressure effect on Henry's constant at 373.15 K. At pressure below 150 bar, the effect of pressure on Henry's constant can be neglected. When the pressure is high, the value of Henry's constant increases obviously. In this case, it is necessary to consider the pressure impact in order to obtain reliable results. Correlation results of Tromans [2] are also plotted as a dashed line in Fig. 5. Obviously, the results in this paper are much better than those of Tromans [2] at high pressure.

In the former text, the Henry's constant of oxygen in water was calculated first from Helgeson EOS with Eq. (9)

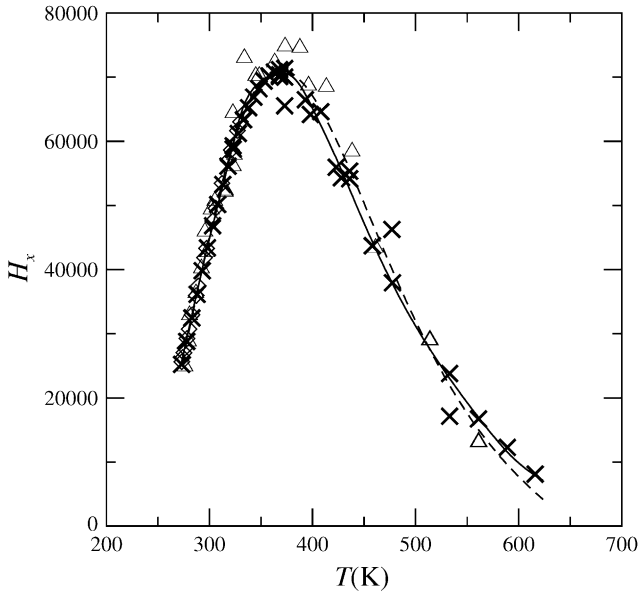

Fig. 4. Comparison of Henry's constant at the saturated pressure of water. Δ, × and ◇, experimental data of Cramer [1], Tromans [2] and Benson et al. [12], respectively. (—) Correlation results in this paper; (- - -) calculated results from the Helgeson EOS.

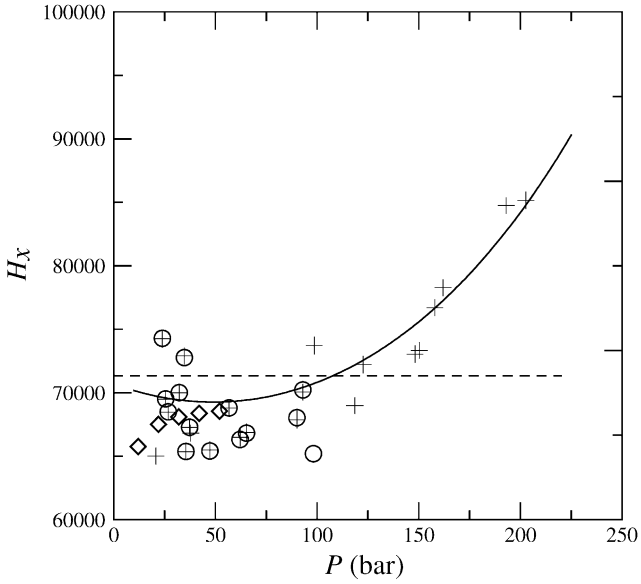

Fig. 5. Comparison of Henry's constant at 373.15 K. +, ◇ and ○, experimental data of Stephan et al. [13], Brodén and Simonson [18] and Pray and Stephan [20], respectively. (—) Correlation results of this paper; (- - -) correlation results of Tromans [2].

in order to correlate the cross-interaction parameter in the modified RK EOS. Therefore, it is necessary to check the calculated results of Helgeson EOS. The Henry's constant at the saturated pressure of water was calculated with Eq. (9) and compared with those correlated in this paper. The comparison results are depicted in Fig. 4 as a dashed line. At low temperature (<400 K), results from Helgeson EOS are very close to those correlated in this paper since these two studies are all based on the results of Benson et al. [12] at low temperature. This also implies that the correlation of the cross-interaction parameter for the oxygen–water system in the modified RK EOS is reasonable.

When the temperature is high, there is some deviation between the calculated results of this paper and those calculated with the Helgeson EOS. This is explained by the following text. In the Helgeson EOS [11,14], the parameter of the effective Born coefficient (w_e) for the neutral species ($O_{2,aq}$) was correlated from the equilibrium constant. The equilibrium constant was calculated from the solubility data in which the partial pressure was estimated by subtracting vapor pressure of water from total pressure [13]. The deviation of the estimated partial pressure caused the deviation in the Henry's constant. This also indicates that it is necessary to make a further study on how to improve and correct the parameter of the Helgeson EOS.

3.2. Comparison of the composition

Composition was calculated here with two methods, thermodynamic and empirical ones, in order to understand the effects of Henry's constant and the method on the equilibrium composition. In the thermodynamic method,

the partial pressure of water was calculated when each component satisfied the conditions for phase equilibria. In the empirical method, the partial pressure of water is the saturated pressure of pure water.

In both of these two methods, the Henry's constant of oxygen in water was needed. The Helgeson EOS [11,14] can be used to calculate the Henry's constant at a certain temperature and pressure. Tromans [2] correlated the Henry's constant from 273 to 613 K and the partial pressure up to 60 bar. In this paper, a new expression for Henry's constant was correlated. Therefore, the Henry's constant was calculated or taken from these three studies respectively to calculate the composition for comparison.

In addition, in the thermodynamic method, fugacity coefficient in the vapor phase was calculated by the modified RK EOS with the existing parameter and the new parameter correlated in this paper, respectively.

Based on the above discussion, five cases were calculated in this paper:

- Case 1, thermodynamic method, the Henry's constant was calculated from the correlation expression in this paper and the fugacity coefficients were calculated by the modified RK EOS with the new parameter correlated in this paper.
- Case 2, thermodynamic method, the Henry's constant was calculated from the Helgeson EOS and the fugacity coefficients were calculated by the modified RK EOS with the new parameter correlated in this paper.
- Case 3, thermodynamic method, the Henry's constant was calculated from the Helgeson EOS and the fugacity coefficients were calculated from the modified RK EOS with the existing parameter in the literature [14].
- Case 4, empirical method, $x_{O_2} = P_{O_2}\phi_{O_2}(T, P)/H$, $y_w = P^s_w/P \cdot \phi_{O_2}$ was calculated by the modified RK EOS with the existing parameter. The Henry's constant was calculated from the Helgeson EOS.
- Case 5, empirical method, $x_{O_2} = P_{O_2}/H$, $y_w = P^s_w/P$. The Henry's constant was taken from Tromans [2].

Calculated results at 560.93 K and different pressures were shown as an example. The calculated results of the oxygen solubility in water (x_{O_2}) were compared with experimental data of Stephan et al. [13]. However, experimental data in the vapor phase have not been determined at this temperature. In order to show the difference between different methods, the calculated results of this paper (Case 1) were used as reference data because their accuracy has been checked in the previous text. The calculation and comparison results are shown in Table 3.

In cases 1 and 2, the Henry's constant was taken from different studies. The water vapor in different cases is nearly the same. The maximum deviation is about 0.06%. However, the calculated results of oxygen solubilities in case 1 are much better than those in case 2 by comparing with the experimental data. This implies that the effect of the Henry's constant on liquid composition is obvious while its effect on vapor composition is small enough to be neglected.

In cases 2 and 3, fugacity coefficients were calculated from the modified RK EOS with the new correlated and existing parameters, respectively. Comparing the calculated results of these two cases, one conclusion can be drawn. The effects of the parameter in the modified RK EOS on liquid and vapor compositions are visible.

In cases 4 and 5, the composition of water vapor was calculated by the empirical method. Comparing the calculated results of water vapor in these two cases with those in case 1, the deviation is large and the maximum value is up to 20%. However, the calculated results of liquid composition in these two cases are better than those in case 3. It implies that the empirical method is suitable for calculating the liquid composition.

Based on the above comparison, we can conclude that the thermodynamic method is better than the empirical method. Furthermore, with the new parameter in the modified RK EOS and the Henry's constant correlated in this paper, the calculated results for both liquid and vapor compositions are better than other models.

Table 3
Equilibrium composition for the oxygen (1)–water (2) system at 560.93 K[a] calculated with different methods and parameters

P (bar)	$10^4 x_{1exp}$	Thermodynamic method						Empirical method			
		Case 1		Case 2		Case 3		Case 4[b]		Case 5	
		$10^4 x_1$	y_{2r}	$10^4 x_1$	y_2	$10^4 x_1$	y_2	$10^4 x_1$	y_2	$10^4 x_1$	y_2
103.7	18.4	18.22	0.7715	19.30	0.7714	18.96	0.7731	18.10	0.6972	18.78	0.6972
105.7	19.5	19.42	0.7606	20.49	0.7605	20.08	0.7630	21.55	0.6840	19.98	0.6840
135.4	38.5	37.51	0.6308	37.63	0.6308	36.85	0.6368	39.44	0.5340	37.74	0.5340
138.8	39.5	39.61	0.6189	39.50	0.6189	38.69	0.6254	41.40	0.5209	39.77	0.5209
171.2	61.2	59.96	0.5264	56.91	0.5267	55.72	0.5368	59.57	0.4223	59.15	0.4223
172.6	61.9	60.85	0.5231	57.73	0.5234	56.25	0.5336	60.42	0.4189	59.98	0.4189
Maximum (%)		2.57	–	7.01	0.06	9.13	2.01	10.51	19.92	3.34	19.92
Average (%)		1.33	–	4.33	0.02	5.07	1.09	4.07	15.10	2.27	15.10

Maximum $= \max(|x_1 - x_{1exp}|/x_{1exp})_i$ or $= \max(|y_2 - y_{2r}|/y_{2r})_i$ $(i = 1, 6)$, Average $= (1/6)\sum_{i=1}^{6}(|x_1 - x_{1exp}|/x_{1exp})_i$ or $= (1/6)\sum_{i=1}^{6}(|y_2 - y_{2r}|/y_{2r})_i$.

[a] The saturated pressure P^s_w is 73.3 bar at 560.93 K.

[b] If the second point was excluded, Maximum = 4.81%, Average = 2.79%.

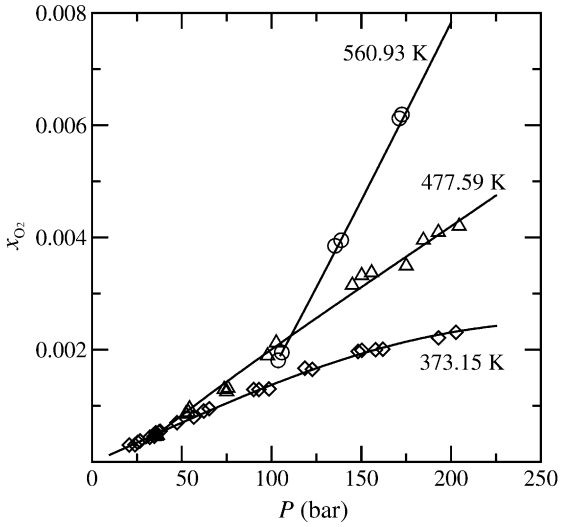

Fig. 6. Comparison of the calculated results of the liquid composition for the oxygen–water system in this paper with the experimental data of Stephan et al. [13].

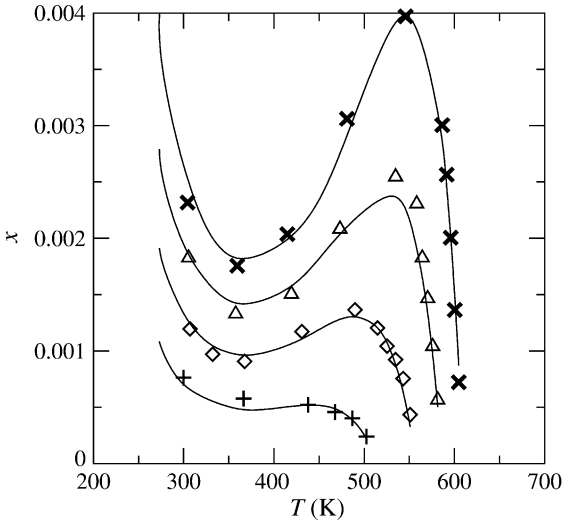

Fig. 7. Comparison of the calculation results of liquid composition of water with experimental data of Zoss [15]. +, ◇, Δ, and ×, experimental data at 34.5, 68.95, 103.4 and 137.9 bar, respectively; (—) calculated results in this paper.

To show the comparison at other temperatures and pressures, the calculated results of this paper were compared with the experimental data of Stephan et al. [13] in Fig. 6. Obviously, our calculated results agree well with experimental data throughout the whole comparison range.

3.3. Comparison with the model proposed by Rabinovich and Beketov [6]

Rabinovich and Beketov [6] calculated and tabulated saturated vapor composition from 200 to 400 K and 1–100 bar. In order to investigate the calculated results of this model, data at 298.15, 323.15 and 348.15 K were interpolated from 20 to 100 bar and compared with the experimental data of Wylie and Fisher [17]. The comparison results are shown in Fig. 1. The calculated results of Rabinovich and Beketov [6] are higher than the experimental data of Wylie and Fisher [17]. The lower the temperature and the higher the pressure, the larger the deviation.

The calculated results of the new model with the new correlated parameters are also shown in Fig. 1 for comparison. From 298.15 to 348.15 K, the average deviation of the calculated results in this paper from the experimental data [17] is within 0.3%, and the maximum deviation is only 0.5%. It implies that the correlation is reasonable, and the calculated results of this paper are much better than those of Rabinovich and Beketov [6].

3.4. Investigation of the data of Zoss [15]

Vapor and liquid compositions were determined experimentally by Zoss [15]. However, it was stated that the data of liquid composition are more than an order of magnitude high at low temperature. In the literature [15], it was also proved that the solubility data at the higher temperatures appears to be reliable. We made a comparison of the calculated results with the data of Zoss [15]. Fig. 7 gives the comparison results for the liquid composition. At high temperatures and pressures, the calculated results agree with the experimental data of Zoss [15].

Table 4 shows the comparison of the water vapor composition calculated in this paper with the experimental data of Zoss [15]. The experimental data of Zoss [15] are much higher than the calculated results in this paper. Because our calculated results have been evaluated by the experimental

Table 4
Comparison of the calculation results of water vapor composition (y_{wcal}) in this paper with the experimental data of Zoss [15] (y_{wexp})

T (K)	68.95 bar		T (K)	103.4 bar		T (K)	137.9 bar	
	y_{wexp}	y_{wcal}		y_{wexp}	y_{wcal}		y_{wexp}	y_{wcal}
307.0	0.137	8.81E−4	305.4	0.273	5.76E−4	304.3	0.155	4.35E−4
355.9	0.133	8.55E−3	360.4	0.248	7.12E−3	358.2	0.090	5.13E−3
369.8	0.203	1.45E−2	417.6	0.427	4.54E−2	413.7	0.338	3.16E−2
429.3	0.594	9.00E−2	472.0	0.731	1.70E−1	484.8	0.719	1.72E−1
489.3	0.882	3.55E−1	534.8	0.917	5.41E−1	547.6	0.910	5.18E−1

data of Wylie and Fisher [17] from 298.15 to 348.15 K and 140 bar, there might be some errors in the experimental data of Zoss [15].

4. Conclusions

Phase equilibria for the oxygen–water system were studied by the thermodynamic method in which the modified Redlich–Kwong EOS with a new correlated parameter was used to calculate fugacity coefficients for the vapor phase and the dissolved gas followed Henry's law. A reliable expression was obtained to calculate fugacity coefficient of pure saturated water accurately, and a new Henry's constant of oxygen in water was correlated from the experimental data. Furthermore, the investigation of the Henry's constant of oxygen in water calculated with the Helgeson EOS shows that there are some deviations at high temperatures and pressures, which means that new parameters in Helgeson EOS are to be re-correlated.

Equilibrium compositions were calculated by the new model with the parameters suggested in this paper and compared with experimental data and those calculated by other models with different parameters. The comparison revealed that the new model is reliable for calculating liquid and vapor compositions, and the calculated results of the vapor composition are much better than those in the study of Rabinovich and Beketov [6], while the empirical method is only suitable for estimating the liquid composition. Meanwhile, there might be some errors in the experimental data of Zoss [15].

List of symbols

a, b	coefficients in the modified RK EOS
f^0	liquid phase reference fugacity
ΔG^0	Gibbs free energy
H	Henry's constant of oxygen in water
k	adjustable parameter in the modified RK EOS
P	total pressure (bar)
Q_1–Q_{12}	coefficients in Eq. (11)
R	the gas universal constant
T	temperature (K)
v	specific volume
x	liquid composition
y	vapor composition

Greek letters

γ	activity coefficients in the liquid phase
ϕ	fugacity coefficients in the vapor phase

Subscripts

i, j	component
m	molality basis
w	water

Superscript

s	saturated state

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Appendix A

A.1. Saturated pressure of pure water

From 273.15 to 623.15 K, the value of saturated pressure of water was calculated from industrial standard IAPWS-IF97 [9]. The expression is

$$P_w^s(T) = \left[\frac{2C}{-B + (B^2 - 4AC)^{0.5}}\right]^4 \text{(MPa)},$$
$$A = \nu^2 + n_1\nu + n_2,\ B = n_3\nu^2 + n_4\nu + n_5,$$
$$C = n_6\nu^2 + n_7\nu + n_8,\ \nu = \frac{T}{T^*} + \frac{n_9}{T/T^* - n_{10}},$$
$$T^* = 1\,\text{K} \qquad \text{(A.1)}$$

where n_1 to n_9 are the parameters. Their values are listed in the following table.

i	n_i
1	$0.11670521452767 \times 10^4$
2	$-0.72421316703206 \times 10^6$
3	$-0.17073846940092 \times 10^2$
4	$0.12020824702470 \times 10^5$
5	$-0.32325550322333 \times 10^7$
6	$0.14915108613530 \times 10^2$
7	$-0.48232657361591 \times 10^4$
8	$0.40511340542057 \times 10^6$
9	-0.23855557567849
10	$0.65017534844798 \times 10^3$

A.2. Volume for pure water

From 273.15 to 623.15 K, the value of pressure and temperature dependence on volume for pure water was calculated from industrial standard IAPWS-IF97 [9]. The expression is

$$v(P,T) = \frac{RT}{P^*}\sum_{i=1}^{24}(-n_i I_i)(7.1-\pi)^{(I_i-1)}(\tau - 1.222)^{J_i} \times (\text{m}^3\,\text{kg}^{-1}),$$
$$\pi = \frac{P}{P^*},\ P^* = 16.53\,\text{MPa}, \tau = \frac{T^*}{T},$$
$$T^* = 1386\,\text{K},\ R = 0.461526\,(\text{kJ}\,\text{kg}^{-1}\,\text{K}^{-1}) \qquad \text{(A.2)}$$

The coefficients n_i and exponents I_i and J_i are listed in the following table.

i	I_i	J_i	n_i	i	I_i	J_i	n_i
1	0	−2	0.14632971213167	18	2	3	$-0.44141845330846 \times 10^{-5}$
2	0	−1	−0.84548187169114	19	2	17	$-0.72694996297594 \times 10^{-15}$
3	0	0	$-0.37563603672040 \times 10^{1}$	20	3	−4	$-0.31679644845054 \times 10^{-4}$
4	0	1	$0.33855169168385 \times 10^{1}$	21	3	0	$-0.28270797985312 \times 10^{-5}$
5	0	2	−0.95791963387872	22	3	6	$-0.85205128120103 \times 10^{-9}$
6	0	3	0.15772038513228	23	4	−5	$-0.22425281908000 \times 10^{-5}$
7	0	4	$-0.16616417199501 \times 10^{-1}$	24	4	−2	$-0.65171222895601 \times 10^{-6}$
8	0	5	$0.81214629983568 \times 10^{-3}$	25	4	10	$-0.14341729937924 \times 10^{-12}$
9	1	−9	$0.28319080123804 \times 10^{-3}$	26	5	−8	$-0.40516996860117 \times 10^{-6}$
10	1	−7	$-0.60706301565874 \times 10^{-3}$	27	8	−11	$-0.12734301741641 \times 10^{-8}$
11	1	−1	$-0.18990068218419 \times 10^{-1}$	28	8	−6	$-0.17424871230634 \times 10^{-9}$
12	1	0	$-0.32529748770505 \times 10^{-1}$	29	21	−29	$-0.68762131295531 \times 10^{-18}$
13	1	1	$-0.21841717175414 \times 10^{-1}$	30	23	−31	$0.14478307828521 \times 10^{-19}$
14	1	2	$-0.52838357969930 \times 10^{-4}$	31	29	−38	$0.26335781662795 \times 10^{-22}$
15	2	−3	$-0.47184321073267 \times 10^{-3}$	32	30	−39	$-0.11947622640071 \times 10^{-22}$
16	2	0	$-0.30001780793026 \times 10^{-3}$	33	31	−40	$0.18228094581404 \times 10^{-23}$
17	2	1	$0.47661393906987 \times 10^{-4}$	34	32	−41	$-0.93537087292458 \times 10^{-25}$

References

[1] S.D. Cramer, Ind. Eng. Chem. Process Des. Develop. 19 (1980) 300–305.
[2] D. Tromans, Hydrometallurgy 48 (1998) 327–342.
[3] R.F. Prini, R. Crovetto, J. Phys. Chem. Ref. Data 18 (1989) 1231–1243.
[4] A.H. Harvey, AIChE J. 42 (1996) 1491–1494.
[5] R.F. Prini, J.L. Alvarez, A.H. Harvey, J. Phys. Chem. Ref. Data 32 (2003) 903–916.
[6] V.A. Rabinovich, V.G. Beketov, Moist gases, thermodynamic properties, House, Begell, 1995.
[7] R. de Santis, G.J.F. Breedveld, J.M. Prausnitz, Ind. Eng. Chem. Process Des. Devlop. 13 (1974) 374–377.
[8] K. Wark, Advanced Thermodynamics for Engineers, McGraw-Hill, Inc., Singapore, 1995.
[9] W. Wagner, A. Kruse, Properties of Water and Steam, Springer, New York, 1998.
[10] Aspen Plus, UserGuide, Aspen Tech. Inc., Cambridge, MA, 1999.
[11] J.W. Johnson, E.T. Oelkers, H.C. Helgeson, Comput. Geosci. 18 (1992) 899–947.
[12] B.B. Benson, D. Krause, M.A. Peterson, J. Solu. Chem. 8 (1979) 655–690.
[13] E.F. Stephan, N.S. Hatfield, R.S. Peoples, H.A.H. Pray, The solubility of gases in water and in aqueous uranyl solutions at elevated temperature and pressure, BMI, 1067, 54, Battelle Mem. Inst., Columbus, OH, 1956.
[14] E.L. Shock, H.C. Helgeson, D.A. Sverjensky, Geochim. Cosmochim. Acta 53 (1989) 2157–2183.
[15] L.M. Zoss, Oxygen and Ozoner, IUPAC Solubility Data Series 7, Pergamon Press, Oxford, 1952.
[16] R. Battino, Oxygen and Ozoner, IUPAC Solubility Data Series 7, Pergamon Press, Oxford, 1981.
[17] R.G. Wylie, R.S. Fisher, J. Chem. Eng. Data 41 (1996) 175–180.
[18] Å. Brodén, R. Simonson, Svensk Parrerstidning 81 (1978) 541–544.
[19] H.A. Pray, C.E. Schweickert, B.H. Minnich, Ind. Eng. Chem. 44 (1952) 1146–1151.
[20] H.A. Pray, E.F. Stephan, Oxygen and Ozoner, IUPAC Solubility Data Series 7, Pergamon Press, Oxford, 1953.
[21] T.R. Rettich, R. Battino, E. Wilhelm, J. Chem. Thermodyn. 32 (2000) 1145–1156.