===== **THERMOPHYSICAL PROPERTIES** =====
OF MATERIALS

The Calculation of Liquid-Vapor Phase Equilibrium in H_2O–H_2O_2 Two-Component System

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Abstract—The dependences of total pressure and equilibrium composition of vapors on temperature and mole fraction of hydroperoxide in solution are calculated for a water–hydroperoxide two-component two-phase system. It is assumed that the relaxation to concentration equilibrium in gas at the surface of solution is attained quite rapidly compared to the half-life of hydroperoxide. Three independent approximate methods are used to calculate the total pressure. The ideal gas approximation for the gas phase is not used in two of these methods. Approximation formulas are suggested, which explicitly express the dependence of pressure and composition of gas on relative concentration of hydroperoxide in solution and on temperature. The accuracy of the methods and the range of their validity are discussed.

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INTRODUCTION

The difficulties of calculation of liquid–vapor phase equilibrium at high temperatures and corresponding high pressures are associated with the theoretically unsolved problem on the equation of state for liquids and dense gases. The lack of exact solutions is compensated in part by the available approximate semiempirical methods and formulas with fitting parameters, which enable one to calculate the activity coefficients of components and other functions of equilibrium two-phase mixtures given adequate experimental data for the determination of fitting parameters [1–3]. Unfortunately, no general approximate method is available that would be optimal for all two-component systems and problems. The choice of one or another approximate method depends on concrete problem, on the physicochemical properties of components, and on the available experimental data.

Several methods are known of approximate calculation of the activity coefficients as functions of the composition of the liquid phase (mole fraction of one of the components of the liquid phase x) and of temperature T using a limited set of experimental data. Among these data are, for example, the data on total pressure of saturated vapors $P(x, T)$, which is relatively easy to measure. Moreover, if the total pressure in the entire range of values of x from zero to unity is determined on the isotherms experimentally or by some theoretical method, the composition of the gas phase and the activity coefficients on each such isotherm may be exactly calculated in the ideal gas approximation (relative to the preassigned distribution of total pressure) [2–4].

Given in Section 1 of this paper are analytical formulas obtained by us for lines of phase equilibrium of

$P(T)$ of individual components, namely, water and hydroperoxide, which are required for the calculation of total pressure $P(x, T)$ in H_2O–H_2O_2 equilibrium two-component two-phase system.

Three approximate analytical relations for $P(x, T)$ in the entire range of values of x from zero to unity are given in Section 2. The first relation was obtained using direct and indirect data on the boiling temperature of solution $T_b(x, P)$ on isobars at low and high pressures. Such data for aqueous solutions of hydroperoxide were published in [5, 6]. The second relation was obtained using the method of Redlich and Kister [7–10] and a limited set of low-temperature experimental data on the total pressure of a two-component system. The third relation was obtained proceeding from the closeness of the thermodynamic properties of water and hydroperoxide: the $P(x, T)$ function was determined using formulas for lines of phase equilibrium of $P(T)$ of individual components. Unlike the first and third relations, the use of the second relation in the field of high temperatures (and pressures) must be treated as extrapolation.

In Section 3, comparison is made of the results of calculations of $P(x, T)$ on isotherms for the H_2O–H_2O_2 system using three derived relations. In addition, approximation formulas are given for the calculation of the activity coefficients of the components.

1. LINES OF PHASE EQUILIBRIUM FOR SYSTEM COMPONENTS

In solving practical problems, semiempirical thermodynamic relations are often employed, which are valid on some characteristic lines, for example, on phase equilibrium line, on the line of isobaric depen-

The error of formula (1) for water and hydroperoxide as individual substances

T, K	P, atm (1)	P, atm [13], [9]	$|\Delta P/P(T)|$, %
Water			
373.15	1.0364	1.0332	0.31
423.15	4.8616	4.854	0.16
473.15	15.760	15.857	0.62
523.15	40.326	40.56	0.58
573.15	87.641	87.61	0.03
623.15	169.15	168.63	0.31
633.15	190.72	190.42	0.16
638.15	202.25	202.21	0.02
643.15	214.31	214.68	0.17
647.30	224.72	225.65	0.41
Hydroperoxide			
423.15	1.012	0.994	1.8
473.15	4.069	4.004	1.6
523.15	12.06	11.99	0.6
573.15	29.19	29.19	0
623.15	61.17	61.23	0.1
673.15	115.2	115.2	0
723.15	199.8	199.9	0.03
430.15	214.66	214	0.3

dence of temperature on the composition of mixture, and so on. Such relations are often also valid in the region of thermodynamic parameters, in which the properties of the gas phase are significantly different from those of ideal gas. Moreover, in the case of notation using certain variables, these relations may be quite simple and convenient for calculations. Among useful relations of this type is the two-parameter dependence of pressure on temperature on the line of phase equilibrium for an individual component [11, 12],

$$P(T) = [(T/\alpha)^{1/8} - A]^8, \text{ atm}, \tag{1}$$

where α and A are parameters. Approximation (1) is highly accurate at relatively high pressures (for water, at $P > 0.2$ atm), including the critical point. This approximation differs to advantage from other known representations of the $P(T)$ line, first of all, by its simplicity and, second, by the existence of as simple an inverse function [11, 12],

$$T(P) = \alpha[Z + A]^8, \quad Z \equiv (P/P_0)^{1/8}, \quad P_0 = 1 \text{ atm}. \tag{2}$$

By its simplicity, approximation (1) is comparable with the known exponential approximation $P = C\exp(-D/RT)$; however, in the region of relatively high pressures, which includes the critical point as well, the latter approximation is much less accurate. For more detail about approximation (1), see [11, 12] and references cited there.

Because approximation (1) will be used in what follows, we will give the values of parameters α and A for both components of the H_2O–H_2O_2 system [12, 7],

$$\alpha_w = 3.4679 \times 10^{-7} \text{ K}, \quad A_w = 12.4575 \tag{3}$$

for water (subscript w) and

$$\alpha_h = 3.7642 \times 10^{-7} \text{ K}, \quad A_h = 12.5302 \tag{4}$$

for hydroperoxide (subscript h). The error ($|\Delta P/P|$) of approximation (1) with parameters (3) and (4) relative to the reference data for water and hydroperoxide at pressures from ~$0.0028P_c$ to critical pressure P_c is comparable with the error of reference data and amounts, as a rule, to hundredths or even tenths of a percent (see table).

2. APPROXIMATE METHODS OF CALCULATION OF TOTAL PRESSURE

Given in this section are three approximate analytical methods of calculating the total pressure $P(x, T)$ in the H_2O–H_2O_2 system in the entire range of values of x from zero to unity.

Method 1

Relations (1) for water and hydroperoxide may be used for the calculation of isothermal dependence of the total pressure of a two-component two-phase mixture on its composition given the boiling temperature of the mixture T_b as a function of composition (mass fraction x_m or mole fraction x of hydroperoxide in solution) at constant pressure P. For the H_2O–H_2O_2 system, the dependences $T_b(x_m, P)$ and $T_b(x, P)$ at pressures of ~0.10–1 atm are close to linear dependences [5] (Figs. 1a and 1b). Note that, at atmospheric pressure, the temperature on the saturation line for hydroperoxide is close to 150°C.

In [7], the results of processing of the data of [6] on the boiling of superheated aqueous solutions of hydroperoxide were used to obtain the dependence of temperature of equilibrium boiling T_b on isobars on mass fraction of hydroperoxide in solution x_m, i.e., $T_b(x_m, P)$. Unlike [7], Fig. 2 gives the dependence of temperature of equilibrium boiling of aqueous solutions of hydroperoxide on mole fraction of hydroperoxide x. In addition to high-temperature isobars [7], Fig. 2 gives two low-temperature isobars obtained in independent experiments [5] (see Fig. 1).

The incompleteness of the data of [6] and possible systematic errors of these data prevent one from getting a single-valued notion of the true function $T_b(x, P)$. However, within the error of measurement, the isobaric dependences of T_b on x in Fig. 2 may be replaced by straight lines. Note that a similar assumption was made in [7] for isobaric dependences of T_b on x_m. Judging by the data of [5, 6], it does not appear possible to answer the question of which one of these approximations is
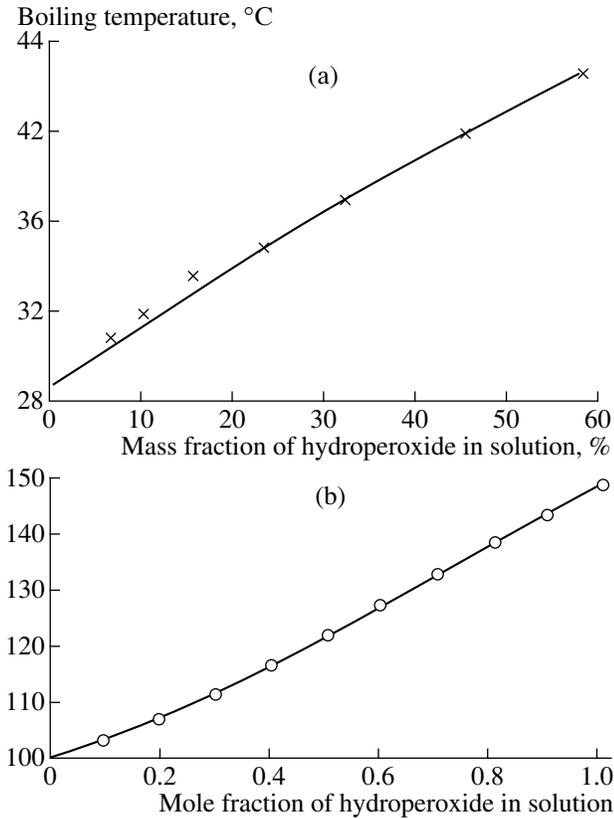
Fig. 1. Experimentally obtained dependences of boiling temperature on the composition of aqueous solution of hydroperoxide on isobars [5]: (a) $P = 4$ kPa, (b) $P = 0.1$ MPa.

Fig. 2. Isobars for aqueous solutions of hydroperoxide according to the data of [5]: (*1*) 0.004 MPa, (*2*) 0.1; and [7]: (*3*) 2.6 MPa, (*4*) 3.8, (*5*) 5.0, (*6*) 6.2, (*7*) 7.5, (*8*) 8.7, (*9*) 9.9, (*10*) 11.1, (*11*) 12.4, (*12*) 13.6, (*13*) 14.8, (*14*) 16.0, (*15*) 17.3, (*16*) 18.5, (*17*) 19.7, (*18*) 20.9, (*19*) 21.5, (*20*) 22.7.

more accurate without invoking additional reasoning and results of other independent studies. Nevertheless, as distinct from [7], we will proceed, in what follows, from the linear approximation of boiling temperature by the mole (rather than mass) fraction of hydroperoxide in solution. The mole concentration as thermodynamic variable appears to be physically more informative. One can expect that, at higher temperatures, where the differences between the thermodynamic properties of liquid and dense gas on the line of phase equilibrium decrease, the isobaric dependence of boiling temperature on x does not become more complex and differs only slightly from linear dependence.

We take the function $T_b(x, P)$ to be linear with respect to x and represent it in the form

$$T_b(x, P) = T_w(P)(1 - x) + T_h(P)x, \qquad (5)$$

where $T_w(P)$ and $T_h(P)$ are pressure-dependent (according to (2)) temperatures on the saturation lines for water and hydroperoxide, respectively. We substitute explicit expressions (2) for $T_w(P)$ and $T_h(P)$ into Eq. (5) and derive the equation which relates the boiling temperature T_b, the total pressure P, and the mole fraction of hydroperoxide x. Then we assume the boiling temperature $T_b = T$ and derive the transcendental equation
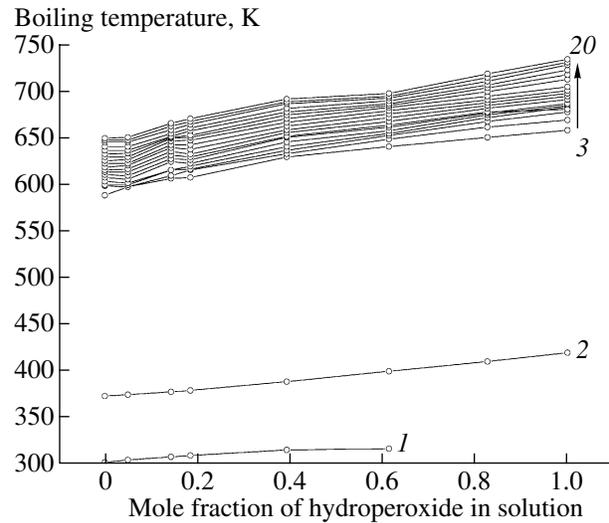
which implicitly defines the dependence of total pressure on temperature and composition of solution,

$$T = \alpha_w[Z + A_w]^8(1 - x) + \alpha_h[Z + A_h]^8 x,$$
$$Z \equiv (P/P_0)^{1/8}, \quad P_0 = 1 \text{ atm}. \qquad (6)$$

It is significant that the assumption of ideality of the gas phase was not used in deriving Eq. (6). Solutions (6) on isotherms are approximated with high accuracy (tenths of a percent or better) by decreasing exponents. The results of such approximations for a number of isotherms are given below ($P(x)$ is in atm),

isotherm $T = 373$ K:
$$P(x, T) = -0.02548 + 1.02916\exp(-x/0.56804); \qquad (7)$$

isotherm $T = 423$ K:
$$P(x, T) = -0.09725 + 4.80366\exp(-x/0.68164); \qquad (8)$$

isotherm $T = 473$ K:
$$P(x, T) = -0.223 + 15.4784\exp(-x/0.77931); \qquad (9)$$

isotherm $T = 523$ K:
$$P(x, T) = -0.33182 + 39.36297\exp(-x/0.86531); \qquad (10)$$

isotherm $T = 573$ K:
$$P(x, T) = -0.21453 + 85.03652\exp(-x/0.94177); \qquad (11)$$

isotherm $T = 623$ K:
$$P(x, T) = 0.5471 + 163.15932\exp(-x/1.0102); \qquad (12)$$

isotherm $T = 643$ K:
$$P(x, T) = 1.1658 + 206.23992\exp(-x/1.03568). \qquad (13)$$

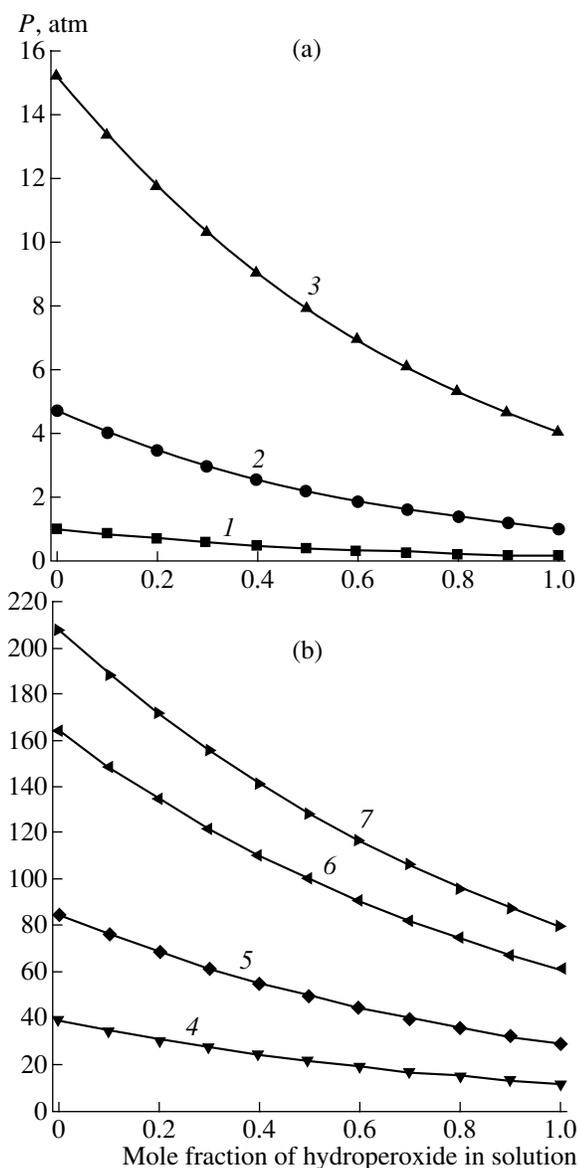Graphs of functions $P(x, T)$ are given in Fig. 3.

Fig. 3. Predicted dependences of pressure on mole fraction of hydroperoxide in aqueous solution on isotherms: (a)—(1) $T = 373$ K, (2) 423 K, (3) 473 K; (b)—(4) $T = 523$ K, (5) 573 K, (6) 623 K, (7) 643 K.

Method 2

The Redlich–Kister approximation exists in application to aqueous solutions of hydroperoxide [7–10]. The Redlich–Kister method is based on limited low-temperature experimental data on total pressure in the H_2O–H_2O_2 two-component two-phase system and on the relation between total pressure and activity coefficients of components in the system. In so doing, the gas phase, which is at equilibrium with solution, is taken to be ideal gas. Therefore, in the region of high pressures (and temperatures), the results of calculations by the Redlich–Kister method must be regarded as extrapola-

tion. The Redlich–Kister formulas for the activity coefficients of water γ_w and hydroperoxide γ_h have the form

$$\gamma_w = \exp\{x^2/(RT) \times [B_0 + B_1(1 - 4X) + B_2(1 - 2X)(1 - 6X)]\}, \quad (14)$$

$$\gamma_h = \exp\{X^2/(RT) \times [B_0 + B_1(3 - 4X) + B_2(1 - 2X)(5 - 6X)]\}, \quad (15)$$

where T is the temperature in K, R is the gas constant, and $X = 1 - x$ is the mole fraction of water in solution. For aqueous solutions of hydroperoxide, we have

$$B_0 = -1017 + 0.97T; \quad B_1 = 85; \quad B_2 = 13^1. \quad (16)$$

The total pressure is expressed by the sum

$$P(x, T) = \gamma_h P_h(T)x + \gamma_w P_w(T)X, \quad (17)$$

where $P_h(T)$ and $P_w(T)$ denote the saturated vapor pressure over pure components, namely, hydroperoxide and water, respectively (see Eqs. (1), (3), and (4)).

The mole fractions of components in the vapor phase and solution are related by the relations $y = \gamma_h x$ and $Y = \gamma_w X$. Therefore, for better understanding of the meaning of formula (17), we rewrite this formula as

$$P(x, T) = P_h(T)y + P_w(T)Y. \quad (18)$$

Formula (18) expresses the Dalton law for ideal gas. However, it is often employed for mixtures of real gases as well, in spite of the fact that the saturated vapor pressures over pure components $P_h(T)$ and $P_w(T)$ may strongly differ from ideal gas pressures at high pressures (and temperatures), especially, in the vicinity of critical points. In the general case, approximation (18) is one of the forms of additivity of pressures. According to Dodge ([2], p. 248—Russ. transl.), this approximation may be referred to as the Barlett law of additivity of pressures, because the law was apparently first used by Barlett and associates. One can judge the degree (accuracy) with which this law and the Redlich–Kister approximation may be applied to aqueous solution of hydroperoxide in the region of high temperatures (above 373–423 K) and corresponding high pressures (from 1 atm to critical pressure of water) by comparing

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[1] We found that, at temperatures $T > 373$ K, the total pressure defined by formulas (14)–(17) is independent of coefficient B_2 within 0.1% in the entire range of concentrations of solution, and the respective terms in the exponents of (14) and (15) may be omitted. This remark refers also to the accuracy of calculation of the activity coefficients proper, less the small neighborhood ($\Delta x \approx 0.1$) of point $X = 0$ for γ_h and of point $X = 1$ for γ_w, where the inclusion of terms with coefficient B_2 causes a variation of the values of γ_h and γ_w by approximately 1–1.5%. However, this results in a very minor variation (≈ 0.001) of mole fractions of the components of the gas phase, because the respective concentrations of solution components in the neighborhood of the foregoing end points are low (water at $X \longrightarrow 0$ and hydroperoxide at $x \longrightarrow 0$). This is qualitatively explained by the relative smallness of coefficient B_2 and by the fact that the contribution by terms with B_2 in the exponents of (14) and (15) goes to zero in the middle of segment $0 < X < 1$ and in the neighborhood of its edges.
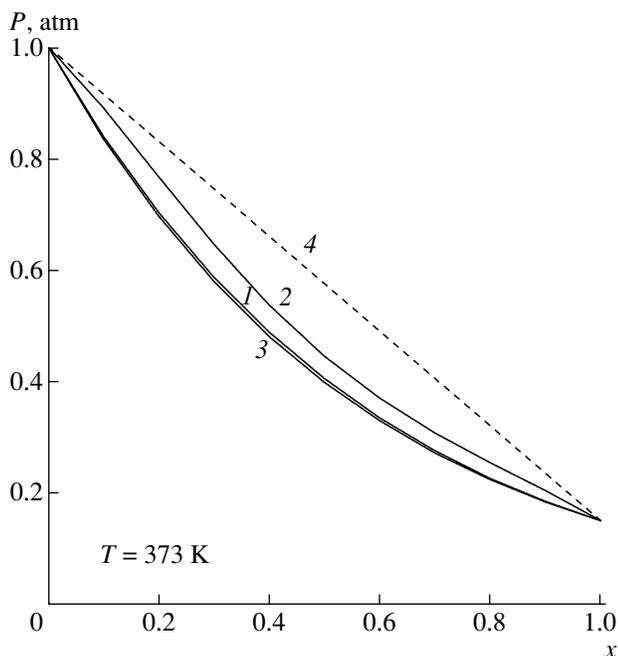
Fig. 4. Predicted dependences of total pressure on mole fraction of hydroperoxide in solution at a temperature of 373 K: (*1*) method 1, (*2*) method 2, (*3*) method 3, (*4*) ideal solution approximation.
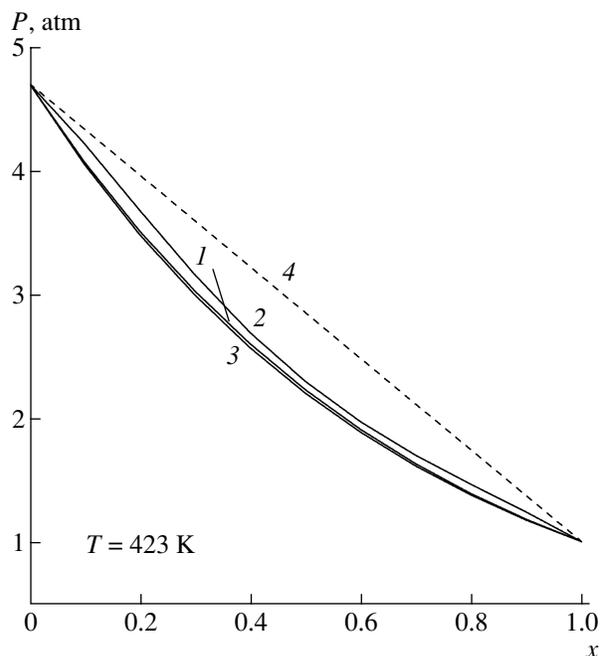

Fig. 5. Ditto (as in Fig. 4) at a temperature of 423 K.

the total pressure calculated by formulas (14)–(17) with that obtained independently of the latter formulas by formulas (7)–(13).

Such comparison is given in Figs. 4–9, where the calculations by formulas (7)–(13) and (14)–(17) correspond to curves *1* (method 1) and *2* (method 2). Curves *4* in Figs. 4–9 correspond to the ideal solution approximation expressed by formula (17) with the activity coefficients in this formula substituted by unity. Curves *3* in Figs. 4–9 correspond to yet another approximation (method 3) suggested by us (see below).

Method 3

The values of parameters α and A in formula (1) turn out to be close for individual substances of similar thermodynamic properties, for example, for C_nH_{2n+2} n-alkanes with close values of number n or for water and hydroperoxide. Indeed, for n-heptane ($n = 7$) and n-octane ($n = 8$), the values of α and A differ by approximately 10% and 2.5% [14] and for water and hydroperoxide—by 8.5 and 0.6%, respectively (see Eqs. (3) and (4)). Formula (1) may be assumed to be approximately valid for two-component mixtures of such substances as well if the parameters α and A are treated as linear combinations,

$$\alpha(x) = \alpha_1(1-x) + \alpha_2 x, \quad A(x) = A_1(1-x) + A_2 x \quad (19)$$

where the subscripts 1 and 2 indicate components with concentrations $1 - x$ and x, respectively. In approximation (19), formulas (1)–(4) define the isothermal depen-

dence of pressure and isobaric dependence of temperature of the mixture on mole fractions of components in the mixture. We apply formulas (1)–(4) and (19) to aqueous solution of hydroperoxide to derive the following expression for total pressure:

$$P(x, T) = [(T/\alpha(x))^{1/8} - A(x)]^8, \text{ atm}, \quad (20)$$

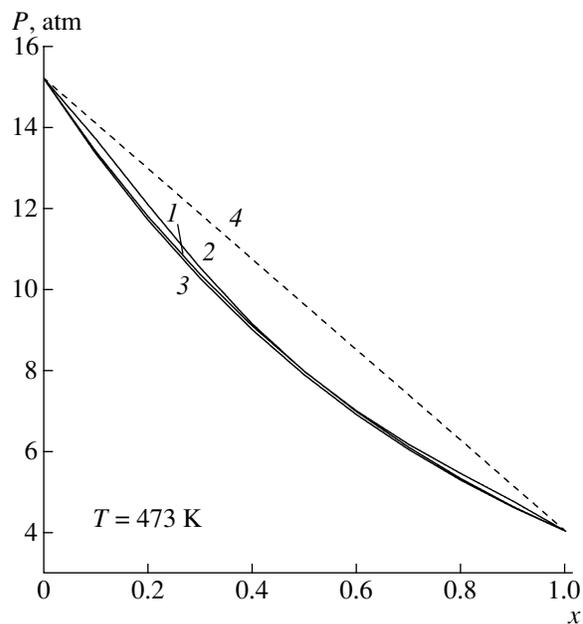$$\alpha(x) = \alpha_w(1-x) + \alpha_h x, \quad A(x) = A_w(1-x) + A_h x. \quad (21)$$
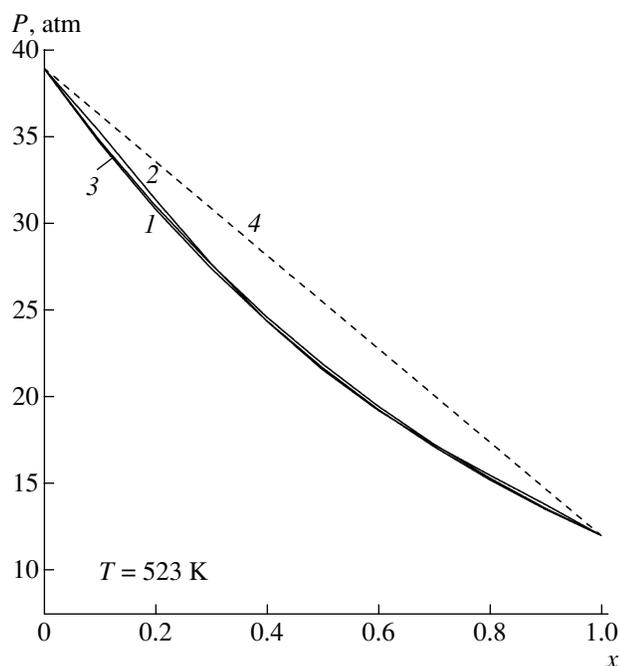

Fig. 6. Ditto (as in Fig. 4) at a temperature of 473 K.

Fig. 7. Ditto (as in Fig. 4) at a temperature of 523 K.

Fig. 8. Ditto (as in Fig. 4) at a temperature of 573 K.

3. DISCUSSION OF THE RESULTS

One can see in Figs. 4–9 that curves *1–3*, which correspond to calculations by methods 1–3, significantly deviate from straight line *4* for ideal solution (the solution is nonideal), but little differ from one another. A more detailed consideration of the calculation results reveals that the maximal differences between the values of total pressure obtained by formulas (7)–(13) and (14)–(17) are observed at $x \approx 0.3$–0.4 on each isotherm and decrease with increasing temperature. In so doing, the maximal differences between predicted values of total pressure on the isotherms $T = 373, 423, 473, 523, 673$, and 723 K amounted to 18%, 16%, 3%, 0.9%, 0.7%, and 0.6%, respectively. Therefore, one can assume that the results of calculations of the activity coefficients by formulas (14) and (15) likewise exhibit a small error. Yet another consideration counts in favor of this assumption. As the temperature increases, the differences between the properties of liquid and gas on saturation lines decrease, and the values of the activity coefficients approach unity. As a result, the possible error of their calculation decreases as well.

Small deviations of curves *1–3* from one another in Figs. 4–9 imply that any of three approximations (methods 1–3) may be used for the calculation of total pressure $P(x, T)$ in the H_2O–H_2O_2 system. Possible maximal errors of calculations are given above. The simplest method for the calculation of total pressure is method 3. However, in view of the fact that the activity coefficients need to be known in case of applications, the Redlich–Kister method is to be regarded as the most preferred one: this m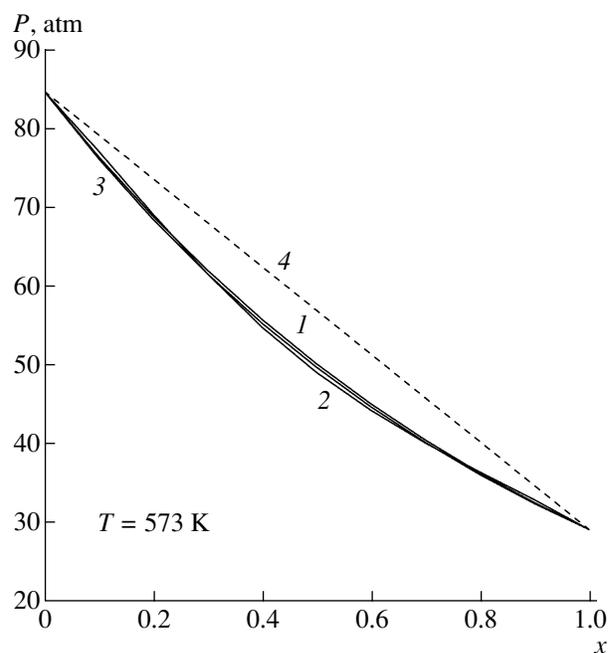ethod enables one to calculate both the activity coefficients and the total pressure (formulas (14)–(17)). Without the coefficient B_2 (see Footnote 1), formulas (14)–(16) may be written in a simplified form,

$$\gamma_w = \exp\{x^2/(RT)[B_0 + B_1(1 - 4X)]\}, \qquad (22)$$

$$\gamma_h = \exp\{X^2/(RT)[B_0 + B_1(3 - 4X)]\}, \qquad (23)$$

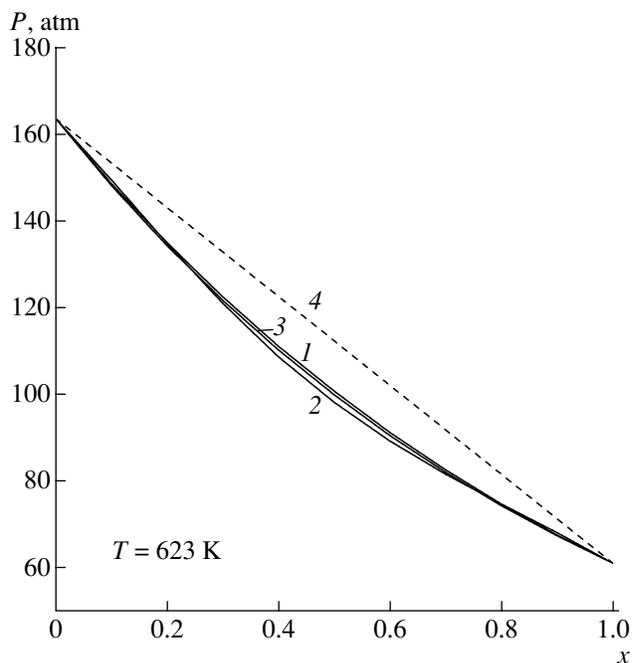$$B_0 = -1017 + 0.97T; \quad B_1 = 85. \qquad (24)$$

Fig. 9. Ditto (as in Fig. 4) at a temperature of 623 K.

In view of the foregoing results of calculations of total pressure, we estimate the error of calculation of coefficients γ_w and γ_h by formulas (22) and (23) to be approximately 7% on the average over the entire range of concentrations of solution and to be one-and-a-half or two times higher for compositions of low concentration of hydroperoxide or water, i.e., at $x \ll 1$ for γ_h and at $X \ll 1$ for γ_w.

CONCLUSIONS

Three approximate methods are suggested for the calculation of total pressure for a water-hydroperoxide equilibrium two-component two-phase system at high pressures and temperatures up to the critical point. The first method is based on the use of direct and indirect literature data on the boiling temperature of aqueous solutions of hydroperoxide on isobars at low and high pressures. The second method is the extrapolation of the Redlich–Kister relations describing a limited set of low-temperature experimental data on total pressure to the high-temperature region. The third method is based on the closeness of the thermodynamic properties of water and hydroperoxide; this made it possible to determine the total pressure using formulas for lines of phase equilibrium of individual components. It was assumed in all cases that the relaxation to concentration equilibrium in gas at the surface of solution was attained quite rapidly compared to the half-life of hydroperoxide. The results of calculation of total pressure by all suggested independent methods agree quite well with one another; this may be regarded as the indication of validity of the assumptions made. Approximation formulas were suggested, which explicitly express the dependence of pressure and composition of gas on relative concentration of hydroperoxide in solution and on temperature. The accuracy of the methods and the range of their validity were discussed.

ACKNOWLEDGMENTS

REFERENCES

1. Reid, R.C., Prausnitz, J.M., and Sherwood, T.K., *The Properties of Gases and Liquids*, New York: McGraw-Hill, 1977. Translated under the title *Svoistva gazov i zhidkostei: Spravochnoe posobie*, Leningrad: Khimiya, 1982.

2. Dodge, B.F., *Khimicheskaya termodinamika* (Chemical Thermodynamics), Moscow: Izd. Inostrannoi Literatury, 1950 (Russ. transl.).

3. *Spravochnik po ravnovesiyu mezhdu zhidkost'yu i parom v binarnykh i mnogokomponentnykh sistemakh* (Handbook on Equilibrium between Liquid and Vapor in Binary and Multicomponent Systems), Kafarov, V.V., Ed., Leningrad: Gosudarstvennoe Nauchno-Tekhnicheskoe Izd. Khimicheskoi Literatury, 1957.

4. Krichevskii, I. and Kazarnovskii, Ya., *Zh. Fiz. Khim.*, 1934, vol. 5, issue 9, p. 1222.

5. *Khimiya i tekhnologiya perekisi vodoroda* (The Chemistry and Technology of Hydrogen Peroxide), Seryshev, G.A., Ed., Leningrad: Khimiya, 1984.

6. Nikitin, E.D., Pavlov, P.A. and Popov, A.P., *Teplofiz. Vys. Temp.*, 1992, vol. 30, no. 3, p. 508.

7. Kuznetsov, N.M. and Frolov, S.M., *Teplofiz. Vys. Temp.*, 2006, vol. 44, no. 1, p. 50 (*High Temp.* (Engl. transl.), vol. 44, no. 1, p. 47).

8. Redlich, O. and Kister, A.K., *Ind. Ing. Chem.*, 1948, vol. 40, p. 345.

9. Scatchard, G., Kavanagh, G.M., and Ticknor, L.B., *J. Am. Chem. Soc.*, 1952, vol. 74, p. 3715.

10. Schumb, W.C., Satterfield, C.N., and Wentworth, R.L., *Hydrogen Peroxide*, New York: Reinhold Publishing Corporation, 1955.

11. Kuznetsov, N.M., *Dokl. Akad. Nauk SSSR*, 1981, vol. 257, no. 4, p. 858.

12. Kuznetsov, N.M., *Dokl. Akad. Nauk SSSR*, 1982, vol. 266, no. 3, p. 613.

13. Vukalovich, M.P., *Termodinamicheskie svoistva vody i vodyanogo para* (The Thermodynamic Properties of Water and Steam), Moscow: Mashgiz, 1950.

14. Kuznetsov, N.M., Aleksandrov, E.N., and Davydova, O.N., *Teplofiz. Vys. Temp.*, 2002, vol. 40, no. 3, p. 395 (*High Temp.* (Engl. transl.), vol. 40, no. 3, p. 359).