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**THERMOPHYSICAL  
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## **The Pressure–Temperature–Concentration Correlation for Aqueous Solutions of Hydroperoxide**

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Received November 16, 2004

**Abstract**—The results of analysis of available experimental data on the pressure dependence of temperature of nonequilibrium boiling of rapidly heated aqueous solutions of hydroperoxide are used to determine the pressure( $P$ )–temperature( $T$ )–concentration( $x$ ) correlation. This correlation is obtained for a solution under conditions of phase equilibrium (saturation surface in three-dimensional space of variables  $P$ ,  $T$ , and  $x$ ) in a wide range of states, including the critical line. The obtained surface is used to calculate the equilibrium composition of gas over the solution as a function of  $x$  and  $T$  by solving the Duhem equation.

### INTRODUCTION

A concentrated aqueous solution of hydroperoxide is regarded as a promising component for two-propellant pulsed detonation jet engines (PDE) [1, 2]. The intrachamber mixing of liquid jets of standard aviation fuel and aqueous solution of hydroperoxide makes it possible to significantly reduce the energy of initiation of detonation in a PDE [3]. An adequate concentration of vapors of fuel and hydroperoxide must be provided in the PDE chamber for reliable initiation of detonation in a multicomponent two-phase mixture. While quite a few data are available (see, for example, [4]) for the pressure of vapors of individual hydrocarbons on the saturation line, hardly any thermodynamic data are available for the saturation line of hydroperoxide and its aqueous solutions.

Unlike numerous other solutions, for which tabular or graphic data are available on the dependence of pressure on isotherms or of temperature on isobars on the concentration of solution in a wide range of temperatures and pressures, the data for aqueous solutions of hydroperoxide are limited to temperatures  $t \leq 105$  °C [5]. This is associated with the rapid disintegration of hydroperoxide and explosion hazard of its solutions at high temperatures. In the case of shortage or absence of direct results on the thermodynamic properties of aqueous solutions of hydroperoxide at high temperatures, any indirect results are important which may be used to obtain necessary information

with the aid of thermodynamic or kinetic transformations.

In this respect, experiments in explosive boiling of water and aqueous solutions of hydroperoxide appear to be of interest [6, 7]. In these experiments, the temperature of superheated liquid at the instant of boiling and the frequency of emergence of vapor bubbles depending on the degree of superheating were measured at a preassigned pressure of gas (argon) over the liquid. Superheated states of liquid were obtained by rapid pulsed electric heating of a platinum wire immersed in the liquid being investigated. The wire temperature was determined by its electric resistance. The boiling temperature of liquid in contact with the wire surface corresponded to the temperature at which a perturbation of its monotonic increase was observed. In experiments with pure water under conditions of rapid heating of wire (the time of heating to the boiling point was varied from 10 to 1000  $\mu$ s), the observed boiling temperature  $T_b(P)$  at different preassigned values of pressure  $P$  was higher than the temperature of boiling under equilibrium conditions, i.e., than the temperature on the saturation line  $T_{eq}(P)$ .

We use the results of measurements of  $T_b(P)$  to calculate the dependences of pressure and equilibrium composition of vapor over an aqueous solution of hydroperoxide. The first one of these dependences was obtained in a wide temperature range including the neighborhood of the critical line, and that for the

equilibrium composition of vapor was obtained at temperatures up to 250 °C.

In our study (Sections 1–3), the data of [7] on the superheating of pure water and aqueous solution of hydroperoxide are analyzed, and the degree of superheating of pure hydroperoxide as a function of pressure is estimated. This analysis results in determining the approximate correlation of temperature, pressure, and concentration of the solution on the saturation surface (this latter term is used by analogy with the “liquid-vapor” saturation line for single-component systems). This correlation of three thermodynamic variables is expressed in relation to temperature (Section 2) and pressure (Section 3). Section 4 gives the formula and results of calculations for the critical line of aqueous solutions of hydroperoxide. The saturation surface (Section 5) represented in the form of concentration dependence of saturating pressure on isotherms is used to find the equilibrium composition of vapor over the aqueous solution of hydroperoxide by way of integration of the Duhem equation. The calculation of the composition of vapor at temperatures above 250 °C is discussed in Section 6.

## 1. DEGREE OF SUPERHEATING OF PURE WATER AS A FUNCTION OF PRESSURE

In order to calculate the difference  $T_b(P) - T_{eq}(P)$ , the function  $T_{eq}(P)$  was determined using two-parameter approximation [8],

$$T_{eq}(P) = \alpha[Z + A]^8, \quad Z \equiv (P/P_0)^{1/8}, \quad (1)$$

$$P_0 = 1 \text{ atm},$$

which is highly accurate at relatively high pressures (for water at  $P > 0.2$  atm), including the critical point. Relation (1) differs from other approximations of the  $T(P)$  line, which are known for a number of systems and contain a large number of parameters, by its simplicity and by the existence of a similarly simple analytical inverse function,

$$P(T) = [(T/\alpha)^{1/8} - A]^8, \text{ atm.} \quad (2)$$

Another known simple exponential approximation  $P = C \exp(-D/RT)$  in the region of relatively high pressures, including the critical point, produces results which are much less accurate compared to Eq. (2).

Relation (1) was initially derived for water [9] using the Clausius–Clapeyron equation and experimental data on specific energies and phase volumes on the line of water–vapor equilibrium. It was later found that this relation is valid with high accuracy for

other liquid–vapor systems [10], including saturated hydrocarbons from methane to eicosane ( $C_{20}H_{42}$ ). The physical meaning of relation (1) with the exponent of eight was treated in [10]. Following are the values of parameters  $\alpha$  and  $A$  necessary for further analysis. For water,

$$\alpha_w = 3.4679 \times 10^{-7} \text{ K}, \quad A_w = 12.4575^1, \quad (3)$$

and for hydroperoxide,

$$\alpha_H = 3.7642 \times 10^{-7} \text{ K}, \quad A_H = 12.5302. \quad (4)$$

The parameters  $\alpha_w$  and  $A_w$  for water were determined previously [8, 9] using thermodynamic tables [10] (see [8, 9] for details regarding the approximation). The values of  $\alpha_H$  and  $A_H$  for hydroperoxide were obtained by the method of nonlinear regression (Mathcad 6.0 PLUS) for eight points on the  $P(T)$  line. The function  $P(T)$  was approximated by the known relation [5]

$$\log P \text{ (mm)} = 44.5760 - 4025.3/T - 12.996 \log T + 0.0046055 T \quad (5)$$

with a uniform temperature step of 40 K from 423 K to 703 K (i.e., in the pressure range from  $\sim 1$  to  $\sim 162$  atm). The error ( $|\Delta P/P|$ ) of approximation by Eq. (2) of the reference data for water at pressures from  $\sim 0.0028P_c$  to the critical pressure  $P_c$  is comparable to the error of the reference data proper and amounts, as a rule, to hundredths or tenths of a percent. Relation (2) agrees with approximation (5) with approximately the same accuracy. In calculating the difference  $T_b(P) - T_{eq}(P)$ , we used the data on  $T_b(P)$  [7] obtained under conditions of rapid heating, i.e., at values of the time of heating close to the minimal values from the range identified above (10 to 1000  $\mu$ s). In this case, the variation of the concentration of solution of hydroperoxide in the process of heating may be ignored.

One can see in Table 1 that the difference  $T_b(P) - T_{eq}(P)$ , i.e., the degree of superheating, depends on pressure and decreases with increasing pressure.

<sup>1</sup>The values of  $\alpha_w$  and  $A_w$  given here differ somewhat from those obtained in [8] ( $\alpha_w = 3.3564 \times 10^{-7}$  K and  $A_w = 12.5085$ ), which is associated with the different units of measurement of pressure in formula (1) compared to [8] where the pressure was in  $\text{kg/cm}^2$ .

**Table 1.** Comparison of temperatures  $T_b(P)$  and  $T_{eq}(P)$  for water

No.	$P$ , MPa	$T_b(P)$ , K [7]	$T_{eq}(P)$ , K	$T_b(P) - T_{eq}(P)$ , K
1	2.6	588	499.6	88
2	3.8	598	520.8	77
3	5.0	599	537.3	62
4	6.2	603	551.0	52
5	7.5	607	563.7	43
6	8.7	610	574.0	36
7	9.9	613	583.3	30
8	11.1	615	591.7	23
9	12.4	618	600.0	18
10	13.6	622	607.2	15
11	14.8	625	613.9	11
12	16	629	620.2	8.8
13	17.3	632	626.6	5.4
14	18.5	636	632.2	3.8
15	19.7	640	637.6	2.4
16	20.9	645	642.7	2.3
17	21.5	647	645.1	1.9
18	22.0	649	647.14	1.86

**Table 2.** Comparison of temperatures  $T_b(P)$  and  $T_{eq}(P)$  for hydroperoxide

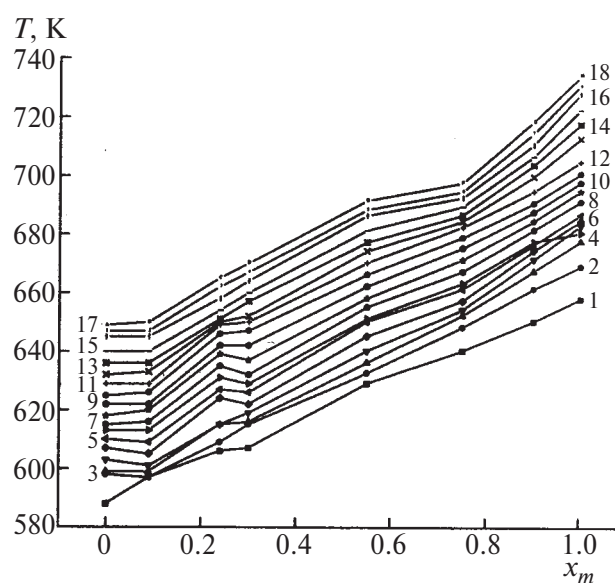
No.	$P$ , MPa	$T_b(P)$ , K	$T_{eq}(P)$ , K	$T_b(P) - T_{eq}(P)$ , K
1	2.6	657.5	565.2	92.3
2	3.8	668.5	589.2	79.3
3	5.0	677	607.8	69.2
4	6.2	682.5	623.2	59.3
5	7.5	684	637.5	46.5
6	8.7	686	649.0	37
7	9.9	688	659.4	28.6
8	11.1	690.5	668.9	21.6
9	12.4	694	678.4	15.6
10	13.6	697	686.4	10.6
11	14.8	700	693.9	6.1
12	16	704	701.0	3
13	17.3	712	708.2	3.8
14	18.5	717	714.5	2.5
15	19.7	722	720.5	1.5
16	20.9	727.5	726.2	1.3
17	21.5	730.3	729.0	1.3
18	22.7	733.5	730.19	3.2

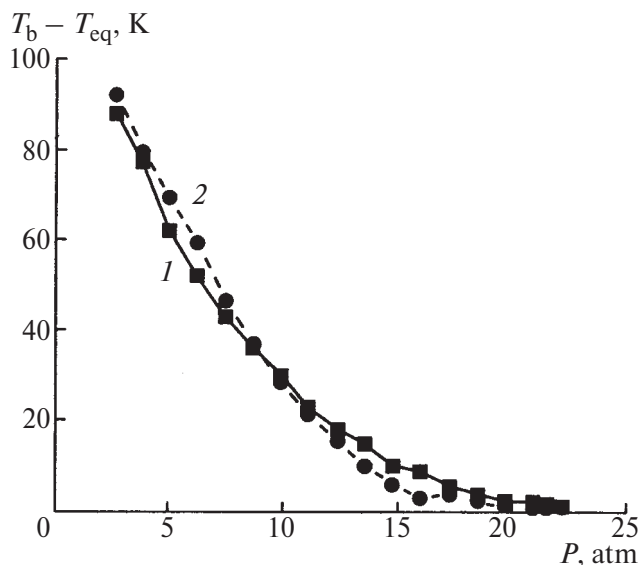
## 2. DEGREE OF SUPERHEATING OF PURE HYDROPEROXIDE. CALCULATION OF DEPENDENCE $T(x_m, P)$ ON THE SATURATION SURFACE

Within the error of measurement, the isobaric dependences of the temperature of boiling of solution  $T_b(x_m, P)$  on its mass concentration  $x_m$ , including the extreme point  $x_m = 0$  (pure water), are close to straight lines (see Fig. 1). These lines may be extrapolated within  $\sim 1\text{--}5$  K from the last experimental point of concentrated solution (the mass and molar concentrations at this point  $x_m$  and  $x$  are equal to 0.9 and 0.827, respectively) to the point  $x_m = x = 1$ .

The points in Fig. 1 correspond to the data of [7] at a heating rate at which the time from the beginning of heating to the instant of boiling amounts to 15  $\mu\text{s}$ . Zero and negative gradients  $\partial T/\partial x$  in Fig. 1 are apparently associated with the systematic errors of experiment [7]. However, it is possible that the kinks on the lines in Fig. 1 are defined by real effects. More detailed experimental investigations are required for clearing up this question. In the absence of relevant data, a linear approximation appears to be a permissible and most natural approximation. The extrapola-

tion results are given in the second column of Table 2. Their comparison with the respective values of temperature on the saturation line  $T_{eq}(P)$  for pure hydroperoxide (see the third and fourth columns in Table 2) leads one to conclude that the  $T(P)$  distribu-

**Fig. 1.** Isobars for aqueous solutions of hydroperoxide [7]. The number of curve corresponds to the number of line in Table 2.



**Fig. 2.** The degrees of superheating for (1) water and (2) hydroperoxide in experiments [7].

tions are qualitatively similar to the behavior of the function  $T(P)$  for water (see Table 1).

The approximate linear dependence of isobars  $T_b(x_m, P)$  may be represented in the form

$$T_b(x_m, P) = (1 - x_m)T_b(0, P) + x_m T_b(1, P), \quad (6)$$

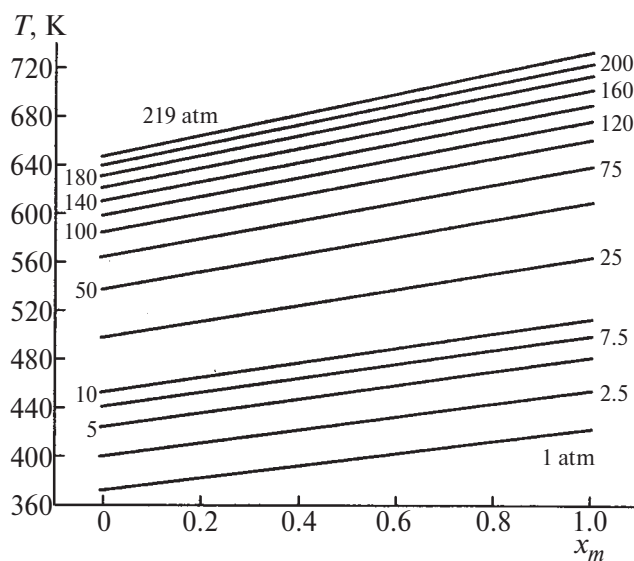
where  $T_b(0, P) \equiv T_b(P)$  for water and  $T_b(1, P) \equiv T_b(P)$  for hydroperoxide.

Comparison of the data on  $T_b(P) - T_{eq}(P)$  in Tables 1 and 2 reveals that the degrees of superheating of water and hydroperoxide on each isobar (i.e., at equal pressures) may be taken to be the same within the experimental error (see also Fig. 2). This fact, together with the observed monotonic or nearly monotonic dependence of the temperature of boiling of solution  $T_b(x, P)$  on the molar concentration  $x$  (Fig. 1), leads one to assume that the boiling of solution in [7] for all concentrations occurs in the superheated state, and the degree of superheating  $T_b(x, P) - T_{eq}(x, P)$  is independent or almost independent of  $x$ . This assumption makes it possible to determine the phase equilibrium temperature  $T_{eq}(x, P)$  on the plane of variables  $x_m$  and  $P$  as the difference between known quantities

$$T_{eq}(x_m, P) = T_b(x_m, P) - \Delta T(P), \quad (7)$$

when

$$\begin{aligned} \Delta T(P) &= T_b(0, P) - T_{eq}(0, P) = \\ &= T_b(1, P) - T_{eq}(1, P). \end{aligned} \quad (8)$$



**Fig. 3.** Calculated isobars for aqueous solutions of hydroperoxide.

In accordance with Eq. (8), we have identically

$$\begin{aligned} \Delta T(P) &= (1 - x_m)[T_b(0, P) - T_{eq}(0, P)] + \\ &+ x_m[T_b(1, P) - T_{eq}(1, P)]. \end{aligned} \quad (9)$$

We express the terms on the right-hand side of Eq. (7) in the form of (6) and (8) to derive

$$T_{eq}(x_m, P) = (1 - x_m)T_{eq}(0, P) + x_m T_{eq}(1, P). \quad (10)$$

Here,

$$T_{eq}(0, P) \equiv T_{eq, w}(P), \quad T_{eq}(1, P) \equiv T_{eq, H}(P),$$

and  $T_{eq, w}(P)$  and  $T_{eq, H}(P)$  denote the temperature on the saturation lines for water and hydroperoxide, respectively, determined by formulas (1), (3), and (4). In what follows, the temperature is used only as a parameter of equilibrium solutions (with equilibrium rather than superheated state of liquid). Therefore, the subscript "eq" with temperature will be omitted. We substitute expressions (1), (3), and (4) into (10) to derive the equation which relates the temperature of equilibrium boiling  $T(x_m, P)$ , the mass concentration of hydroperoxide  $x_m$ , and the pressure,

$$\begin{aligned} T(x_m, P) &= 3.4679 \times 10^{-7}[Z + 12.4575]^8(1 - x_m) + \\ &+ 3.7642 \times 10^{-7}[Z + 12.5302]^8 x_m, \end{aligned} \quad (11)$$

$$Z \equiv (P/P_0)^{1/8}, \quad P_0 = 1 \text{ atm}.$$

Figure 3 gives examples of isobars calculated by formula (11).

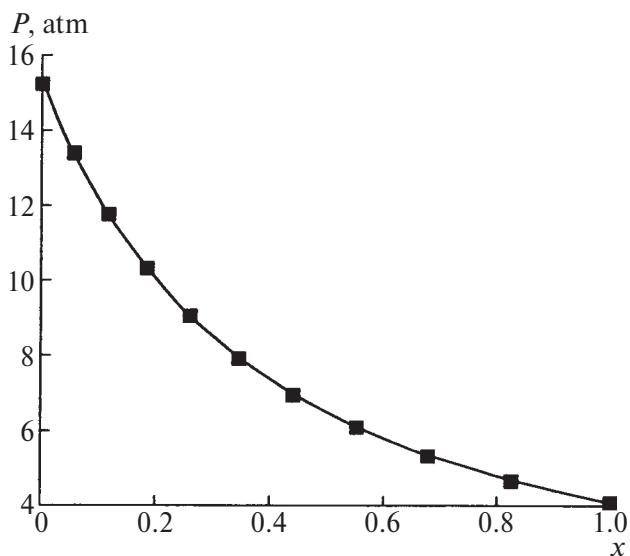


Fig. 4. Calculated dependences of pressure on molar concentration of hydroperoxide in aqueous solution on isotherm  $t = 200\text{ }^\circ\text{C}$ .

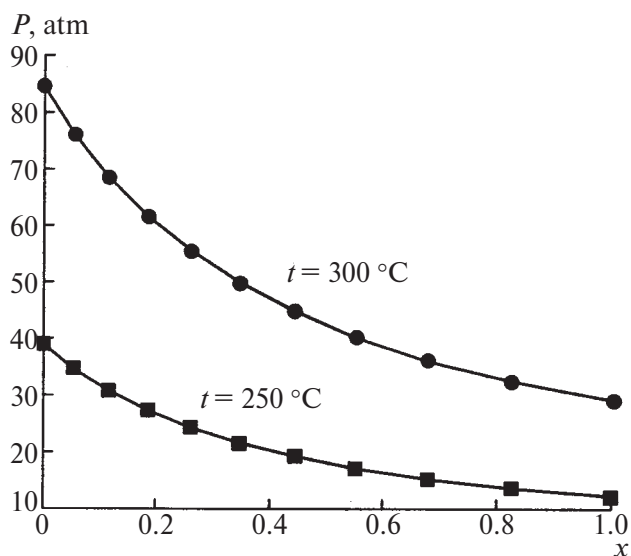


Fig. 5. Calculated dependences of pressure on molar concentration of hydroperoxide in aqueous solution on isotherms  $t = 250$  and  $300\text{ }^\circ\text{C}$ .

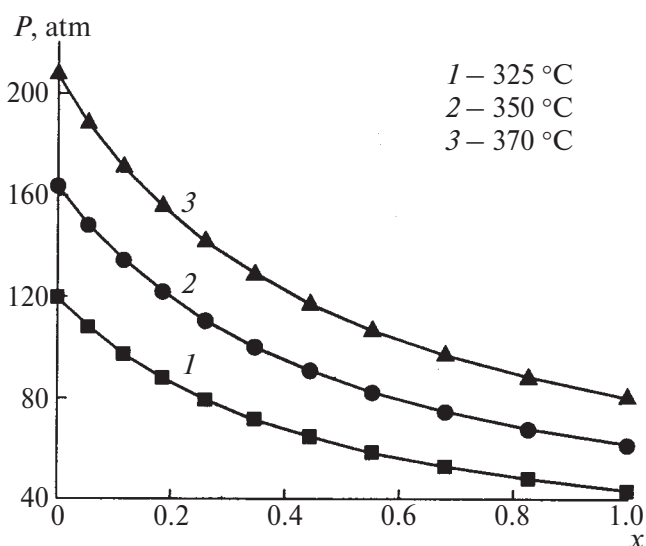


Fig. 6. Calculated dependences of pressure on molar concentration of hydroperoxide in aqueous solution on isotherms  $t = 325, 350,$  and  $370\text{ }^\circ\text{C}$ .

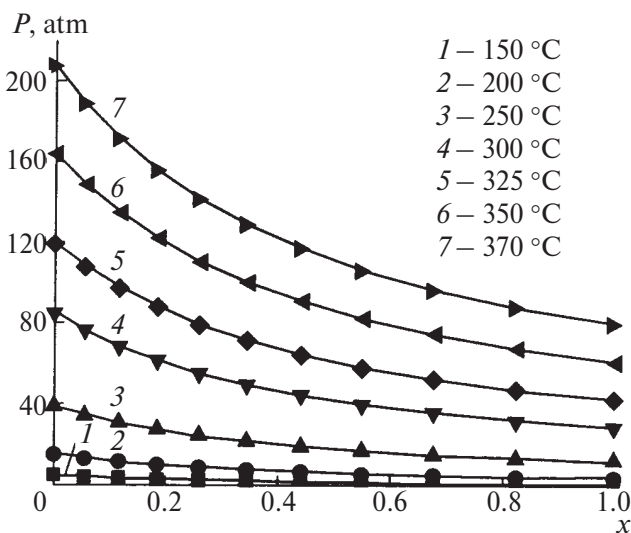


Fig. 7. Calculated dependences of pressure on molar concentration of hydroperoxide in aqueous solution on different isotherms.

### 3. CONCENTRATION DEPENDENCE OF PRESSURE ON ISOTHERMS: CALCULATION RESULTS AND ANALYTICAL APPROXIMATION

The correlation between three variables  $T$ ,  $P$ , and  $x_m$ , defined by Eq. (11), may be treated as an implicit transcendental dependence of pressure on temperature and concentration of solution. Figures 4–7 give the results of calculation of pressure on isotherms as a

function of the molar concentration of solution, obtained by way of numerical solution of Eq. (11) and transition from mass to molar concentration of solution.

The isotherms given in Figs. 4–7 are approximated with high accuracy by the following relations:

$$P(x) = 2.0419 + 5.16891 \exp\left(-\frac{x}{0.20106}\right) + 8.03636 \exp\left(-\frac{x}{0.71524}\right) \text{ at } t_1 = 200\text{ }^\circ\text{C}, \quad (12)$$

**Table 3.** Accuracy of approximation (12) for isotherm  $t = t_1 = 200\text{ }^\circ\text{C}$ 

$x$	0	0.05556	0.11688	0.18493	0.26087	0.34615	0.44262	0.55263	0.67925	0.82653	1
$P(x)$ , atm (11)	15.254	13.39	11.75	10.31	9.042	7.925	6.943	6.080	5.321	4.654	4.069
$P(x)$ , atm (12)	15.247	13.399	11.757	10.308	9.034	7.919	6.942	6.084	5.327	4.657	4.063
$ \delta P(x) /$ $P(x),\%$	0.05	0.07	0.06	0.02	0.09	0.08	0.01	0.07	0.1	0.06	0.1

$$P(x) = 10.42579 + 28.29054 \exp\left(-\frac{x}{0.37625}\right)$$

at  $t_2 = 250^\circ\text{C}$ , (13)

$$P(x) = 18.67143 + 18.7893 \exp\left(-\frac{x}{0.19134}\right) +$$

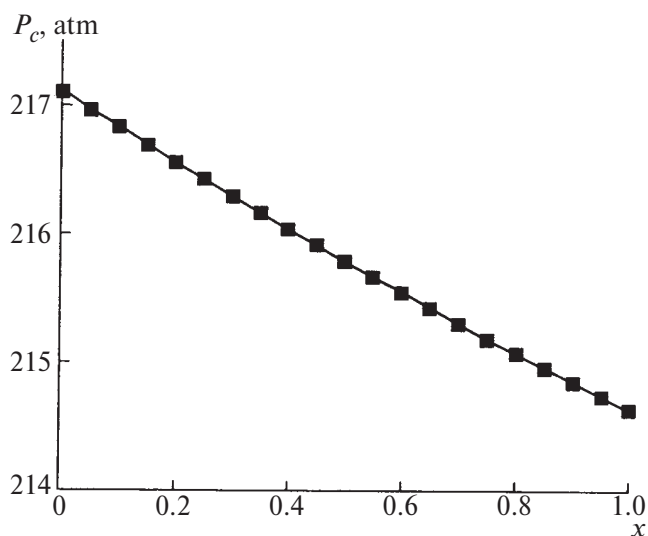
$$+ 47.35864 \exp\left(-\frac{x}{0.66065}\right) \text{ at } t_3 = 300^\circ\text{C}, (14)$$

$$P(x) = 40.18836 + 33.92112 \exp\left(-\frac{x}{0.19585}\right) +$$

$$+ 89.59737 \exp\left(-\frac{x}{0.68441}\right) \text{ at } t_4 = 350^\circ\text{C}, (15)$$

$$P(x) = 52.86407 + 41.88883 \exp\left(-\frac{x}{0.1973}\right) +$$

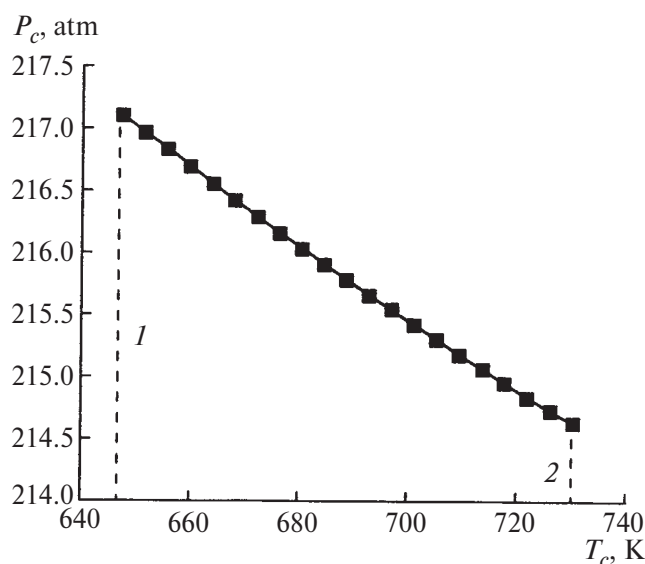
$$+ 112.65555 \exp\left(-\frac{x}{0.69219}\right) \text{ at } t_5 = 370^\circ\text{C}. (16)$$

**Fig. 8.** Calculated dependence of critical pressure in a water–hydroperoxide system on molar concentration of hydroperoxide in aqueous solution.

The accuracy of approximations (12)–(16) is illustrated in Table 3 using approximation (12) as an example.

#### 4. CRITICAL LINE

In addition to measuring the boiling temperature  $T_b(x_m, P)$ , Nikitin *et al.* [7] obtained data on the concentration dependence of critical temperature and pressure. Because of absolute instability of superheated liquid in the neighborhood of the critical point and, accordingly, of almost instantaneous phase relaxation, the obtained results apply directly to thermodynamically equilibrium (non-superheated) states. Nikitin *et al.* [7] note that the critical temperature is measured with a lower error than the pressure. The dependence of critical temperature on mass concentration of hydroperoxide in solution  $T_c(x_m)$  given in [7] is approximated by a straight line,

**Fig. 9.** Calculated critical line for a water–hydroperoxide system. Dashed line 1 corresponds to the critical point for water, and line 2 – to critical point for hydroperoxide.

$$T_c(x_m) = 648 + 78.9x_m, \text{ K.} \quad (17)$$

The set of equations (11) and (17) with substitution of  $T = T_c(x_m)$  in (11) defines implicitly the concentration dependence of critical pressure  $P_c(x_m)$ . Figures 8 and 9 give the results of numerical solution of this set of equations in the  $P$ - $x_m$  and  $P$ - $T$  coordinates. Following is an analytical approximation of these results,

$$P_c = 217.10279 - 2.81814x + 0.35008x^2, \quad 0 \leq x \leq 1,$$

$$P_c = 260.37706 - 0.09978T_c + 5.08604 \times 10^{-5}T_c^2,$$

$$647.14 \leq T_c \leq 730.19 \text{ K,}$$

where  $P_c$  is in atm, and  $T_c$  is in K.

### 5. DETERMINATION OF EQUILIBRIUM COMPOSITION OF GAS OVER LIQUID SOLUTION FOR GIVEN EQUILIBRIUM DEPENDENCE $P(X, T)$

For relatively low temperatures  $t \leq (200-250)^\circ\text{C}$ , the gas phase over an aqueous solution of hydroperoxide may be approximately treated as ideal gas. At  $t > 200^\circ\text{C}$ , the correction for nonideality of gas to pressure on the saturation line for water increases rapidly. For example, at  $t = 210^\circ\text{C}$ , this correction is 9%, and at  $t = 250^\circ\text{C}$  - 20%. Because the critical temperature for hydroperoxide is much higher than that for water (by approximately 83 K), the respective correction for hydroperoxide is somewhat smaller. In the ideal gas approximation, one can use the Dalton law and calculate the composition of the gas phase using the obtained equilibrium dependence  $P(x, t)$  without previously calculating the activity coefficient. For this purpose, we will write the Duhem equation [11-13],

$$d \ln P / dy = (y - x) / [y(1 - y)], \quad (18)$$

in which  $x$  and  $y$  are molar fractions of one and the same component in solution and in gas phase, respectively.

Note that the thermodynamic Duhem equation (18) is applied to an equilibrium rather than metastable system using the equilibrium dependence  $P(x, T)$ . This property of the dependence  $P(x, T)$  follows from the fact that this dependence is calculated by solving Eq. (11). If the pressure on the isotherm is known and has the form  $P(y)$ , the Duhem equation (18) reduces to an algebraic or transcendental equation which relates the concentrations of  $y$  and  $x$  on the isotherm. However, the pressure is usually measured in experiments as a function of the composition of solution, i.e., of  $x$ .

The foregoing equation (11) and formulas (12)-(16) likewise define the pressure as a function of  $x$ . In this case, we replace an independent variable to derive a first-order ordinary differential equation from Eq. (18),

$$\begin{aligned} dy/dx &= y(1 - y)/(y - x)z(x, T), \\ z(x, T) &\equiv (\partial \ln P / \partial x)_T. \end{aligned} \quad (19)$$

The sought integral curve  $y = y(x)$  is defined by Eq. (19) and by preassignment of the coordinates of some single point  $(x_0, y_0)$  on this curve. Such a point may be any of two points at the ends of segment  $0 \leq x \leq 1$ , where the concentrations of one of the components in solution and gas are zero. In so doing, the right-hand part of Eq. (19) will contain an uncertainty of the form 0/0 and, therefore, the boundary points are singular points of Eq. (19). Prior to numerical integration of the equation, it is necessary to clear up the pattern of these singular points. It is known (see, for example, [14]) that the point  $x = 0, y = 0$  in Eq. (19) is a node if  $z(0, T) < 0$ , and a saddle singular point if  $z(0, T) > 0$ .

We apply Eq. (19) to an aqueous solution of hydroperoxide and take into account the foregoing notation for the concentration of components in the liquid and gas phases ( $x, y$  for hydroperoxide and  $X, Y$  for water) to represent Eq. (19) in the form

$$\begin{aligned} dY/dX &= Y(1 - Y)/(Y - X)Z(X, T), \\ Z(X, T) &\equiv -z(x, T) \equiv (\partial \ln P / \partial X)_T. \end{aligned} \quad (20)$$

In aqueous solutions of hydroperoxide, the pressure on isotherms decreases with increasing  $x$  and, accordingly, increases with increasing  $X$ . In particular, the following inequalities are valid:

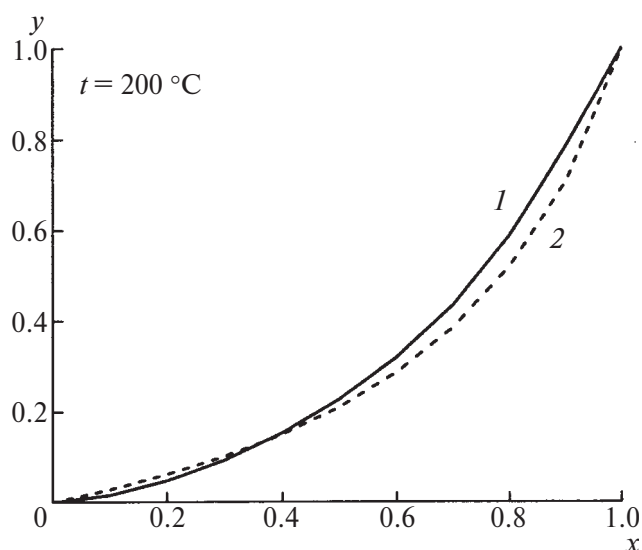
$$z(0, T) < 0, \quad Z(0, T) > 0. \quad (21)$$

One can see from Eqs. (21) and from the inequalities given above for singular points that the point  $x = 0, y = 0$  is a node, and the point  $X = 0, Y = 0$  corresponding to nonaqueous hydroperoxide is a saddle singular point. Hence follows that numerical integration of Eq. (20) must be performed from the point  $X = 0, Y = 0$ . The sought integral curve is one of two separatrices of the saddle singular point, the tangent to which at this point satisfies the equation

$$Y = k_2 X, \quad k_2 \equiv 1 + Z(0, T). \quad (22)$$

At  $X \ll 1$ , this separatrix coincides with tangent (22) within  $O(X^2)$ . The tangent equation (22) is a concrete expression of the Henry law, which corresponds





**Fig. 10.** Calculated dependence of molar concentration of hydroperoxide in the gas phase on its molar concentration in aqueous solution on isotherm  $t = 200\text{ }^{\circ}\text{C}$ . Curve 1 corresponds to solution of Duhem equation (20), and curve 2 – to ideal solution approximation.

to the preassigned value  $Z(0, T)$  of the isothermal pressure gradient.

The entire integral curve of Eq. (20) is represented as

$$Y(X) = (1 + Z(0, T))X, \quad 0 \leq X \leq X_1,$$

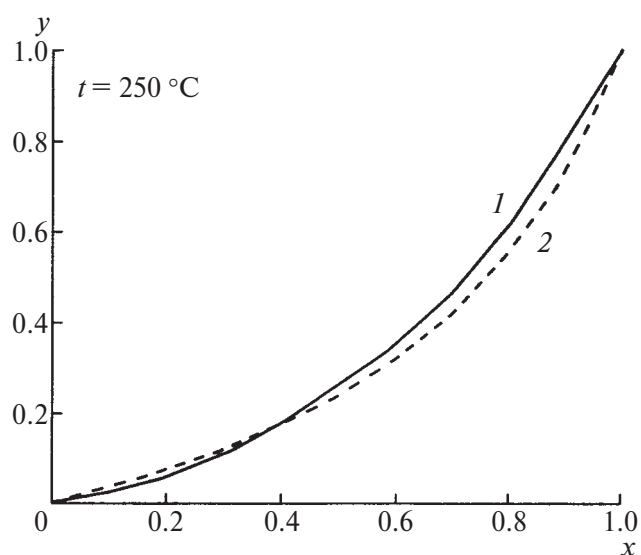
$$Y(X) = Y_{\text{int}}(X), \quad X_1 < X \leq 1,$$

where  $X_1$  is any sufficiently low value of  $X$  (for example, 0.001), and  $Y_{\text{int}}(X)$  is the result of numerical integration of Eq. (20) with the initial data  $X = X_1$ ,  $Y = (1 + Z(0, T))X_1$ . The solid curves in Figs. 10–14 represent the results of calculation of the function  $Y(X)$  on isotherms. Section 6 gives the results of analysis of the dependences given in Figs. 12–14.

In the method being treated, the activity coefficients are not required for determining the composition of gas. However, they may be of interest in comparing the results of calculation of equilibrium composition of vapors over solution by different methods. After calculation of the function  $Y(X)$ , the activity coefficient  $\gamma_i$  may be calculated by the formula

$$y_i = \gamma_i P_i(T) x_i / P.$$

Here,  $i = 1, 2$  denotes the component numbers,  $x_1 = X$ ,  $y_1 = Y(X)$ ,  $x_2 = 1 - x_1$ ,  $y_2 = 1 - Y_1$ ,  $P_i(T)$  denotes pressures on the saturation line for components (see



**Fig. 11.** Calculated dependence of molar concentration of hydroperoxide in the gas phase on its molar concentration in aqueous solution on isotherm  $t = 250\text{ }^{\circ}\text{C}$ ; (1, 2) as in Fig. 10.

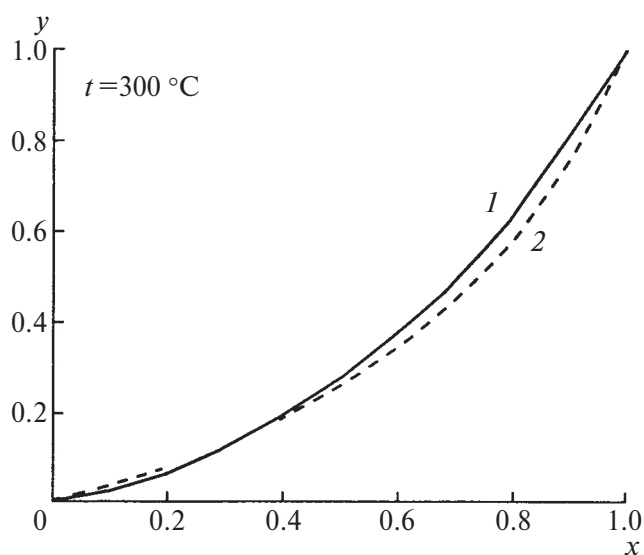
Eqs. (2)–(4)), and  $P$  is the total pressure. The values of  $\gamma_i = 1$  correspond to the ideal solution approximation.

## 6. CALCULATION OF THE COMPOSITION OF WATER–HYDROPEROXIDE TWO-PHASE MIXTURE AT TEMPERATURES $T > 250\text{ }^{\circ}\text{C}$

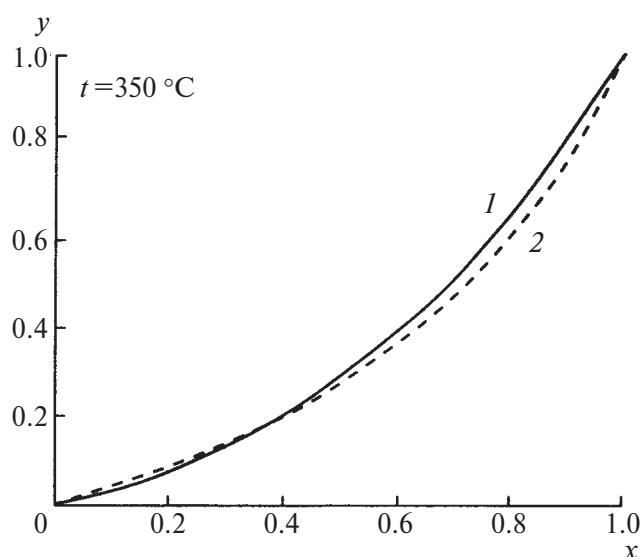
As was noted above, Eq. (19) and the equivalent equation (20) were derived in the ideal gas approximation; as a result, Eqs. (19) may be solved in the water–hydroperoxide system only for temperatures  $t \leq 250\text{ }^{\circ}\text{C}$ . Formally, solutions of Eqs. (19) exist at higher temperatures as well (and, accordingly, high pressures) up to critical states; however, the error of thermodynamic parameters in this region is not known and may be high. This, in particular, is true of the results given in Figs. 12–14. They are a far extrapolation of low-temperature approximation to high temperatures and pressures. It will be interesting to compare these data with the results of more correct calculations performed in view of thermodynamic properties of dense gases and their mixtures.

At high temperatures ( $t > 250\text{ }^{\circ}\text{C}$ ) and, accordingly, higher pressures and densities of gas, including the neighborhood of the critical line, the function  $P(x, T)$  may be used for determining the equilibrium composition of gas over solution at preassigned temperature and composition of solution. For this purpose one more equation is required, because the Dalton law of partial pressures is invalid for a dense mixture of gas-





**Fig. 12.** Calculated dependence of molar concentration of hydroperoxide in the gas phase on its molar concentration in aqueous solution on isotherm  $t = 300\text{ }^\circ\text{C}$ ; (1, 2) as in Fig. 10.



**Fig. 13.** Calculated dependence of molar concentration of hydroperoxide in the gas phase on its molar concentration in aqueous solution on isotherm  $t = 350\text{ }^\circ\text{C}$ ; (1, 2) as in Fig. 10.

es; consequently, the Duhem equation (19) is invalid. The missing equation may be provided by the Gibbs–Duhem equation [12, 13] which will be represented for the gas phase as

$$y_1 d\mu_1 + (1 - y_1) d\mu_2 = 0. \quad (23)$$

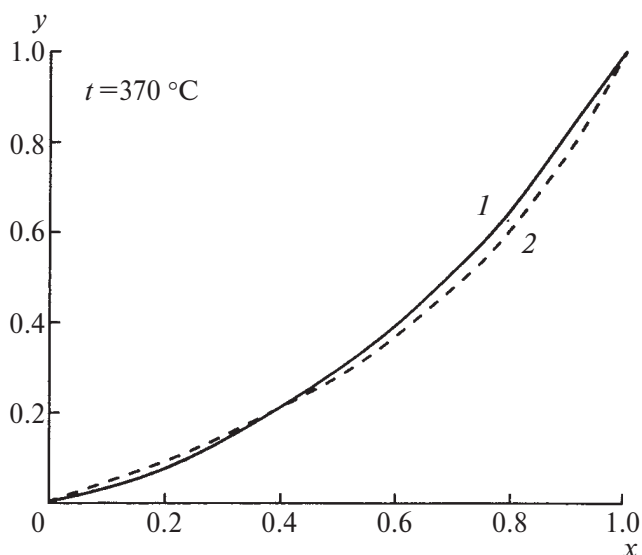
Here,  $\mu_1$  and  $\mu_2$  are the chemical potentials of components in the gas phase, which should be expressed as functions of  $T$ ,  $P$ , and  $y_1$ . The general conditions of phase equilibrium could have been used instead of the function  $P(x, T)$  and Eq. (23), namely, the equality of the chemical potentials of each component in liquid solution and in gas phase,

$$\mu_{l1} = \mu_{g1}, \quad \mu_{l2} = \mu_{g2}.$$

For doing this, however, one needs to know the dependence of chemical potentials of components on  $T$  and  $P$  and on the composition of both the gas and liquid phases. Such dependences for aqueous solutions of hydroperoxide at high temperatures are not known. Setting up the equations which define the composition of solutions being treated presents an independent problem falling outside of the scope of this paper. It follows from the foregoing that the solution of this problem is simplified somewhat when the obtained function  $P(x, T)$  is used, because this enables one to do without the chemical potentials of the liquid phase. The solution of this problem will be given in the next paper.

## CONCLUSIONS

The results of analysis of experimental data on the boiling temperature of superheated aqueous solutions of hydroperoxide have been used to obtain the dependence of pressure of equilibrium saturated vapors over solution on composition of solution and temperature  $P(x, T)$  at high pressures, including the



**Fig. 14.** Calculated dependence of molar concentration of hydroperoxide in the gas phase on its molar concentration in aqueous solution on isotherm  $t = 370\text{ }^\circ\text{C}$ ; (1, 2) as in Fig. 10.

critical line. In so doing, no assumptions were made of the ideality of the gas phase such as equations of state for gas components, the concept of partial pressures, and the Dalton law on their sum. The obtained function  $P(x, T)$  was used to calculate the equilibrium composition of vapor over solution as a function of  $x$  and  $T$  by solving the Duhem equation at temperatures up to 250 °C. At higher temperatures ( $t > 250$  °C) and, accordingly, higher pressures and densities of gas, including the neighborhood of the critical line, one can use  $P(x, T)$  for determining the equilibrium composition of vapor over solution at preassigned temperature and composition of solution given the chemical potential of components of the gas phase as a function of  $T$ ,  $P$ , and composition of the gas phase.

### ACKNOWLEDGMENTS

This study was supported by the International Scientific-and-Technical Center (project no. 2740).

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