Determination of the degree of electrolytic dissociation of perchloric acid by vapor pressure

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Analysis of the published data on the vapor pressure and degree of electrolytic dissociation of perchloric acid revealed that the molar fraction of nondissociated $HClO_4$ is determined by the Raoult—Henry law in a wide range of acidimetric concentrations and temperatures. The degree of dissociation of perchloric acid was calculated from its thermodynamic activity. The results of calculations agree satisfactorily with the known spectroscopic data.

Key words: perchloric acid, electrolytic dissociation, vapor pressure, hydrogen bond.

The properties of perchloric acid and its aqueous solutions have been studied[1—6] in detail by the methods of analytical chemistry, physicochemical analysis, vibrational spectroscopy, and NMR. The chemical shift of the signal in ^{1}H NMR spectrum and the viscosity of aqueous solutions of perchloric acid have previously been established[6] to change similarly with a change in the acid concentration.

In this work, we found a spectral thermodynamic correlation between the molar fraction of nondissociated perchloric acid and a relative decrease in the partial vapor pressure (activity of $HClO_4$). A satisfactory agreement with other methods was also obtained when the thermodynamic activity was recalculated to the degree of dissociation of $HClO_4$.

Results and Discussion

Anhydrous perchloric acid is characterized by a noticeable volatility even at room temperature. The vapor pressure above anhydrous perchloric acid and its aqueous solutions was measured[7] with a small concentration steps in the temperature interval from 0 to 50 °C with an accuracy of ±0.01 Torr. We calculated the partial pressure of $HClO_4$ (P_{HClO_4}) from the chemical and spectroscopic data on the vapor composition.[1,8] The $HClO_4$—H_2O vapor mixtures behave as an ideal gas at comparatively low pressures[8] (<1 atm), which justifies the application of Dalton´s law. In order to determine the total vapor pressure (P) and then to calculate the partial pressure at temperatures >50 °C, the published data[7] were extrapolated to the region of high temperatures using a linear plot in the $\log P$—$1/T$ coordinates

$$\log P = A/T + B,$$

where A and B are constants.

The data for the 20—200 °C temperature interval were thus obtained. The diagram of partial pressures for the 50 °C isotherm is presented in Fig. 1.

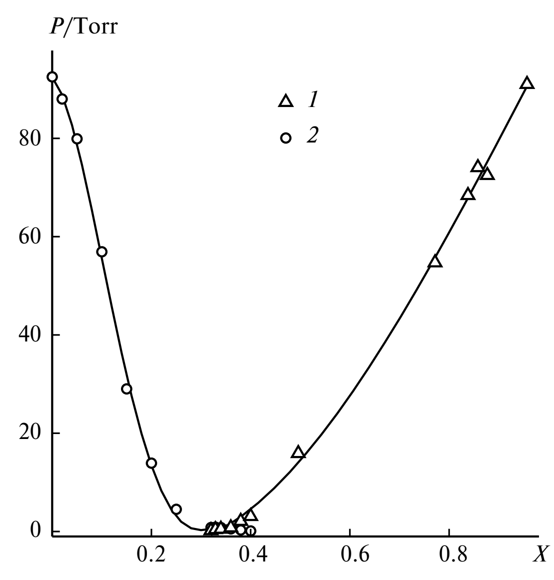

Fig. 1. Diagram of the partial pressures (P) of $HClO_4$ (*1*) and H_2O (*2*) for aqueous solutions of perchloric acid at 50 °C (X is the acidimetric concentration of $HClO_4$ expressed in molar fractions).

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The partial pressure of $HClO_4$ above anhydrous perchloric acid is equal to the total pressure minus the partial pressure of Cl_2O_7. Perchloric anhydride is formed[1,9] by the reaction

$$3\,HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4 \cdot H_2O. \qquad (1)$$

The equilibrium constant of this reaction

$$K_c = \frac{[Cl_2O_7] \cdot [HClO_4 \cdot H_2O]}{[HClO_4]^3} \qquad (2)$$

was determined by three methods[1]: (1) at −10 °C, using the data of measurements of the viscosity in the Cl_2O_7—$HClO_4$ system; (2) at +20 °C, from the composition of the gas mixture above anhydrous acid; (3) at +70 °C, by the kinetics of thermal decomposition of anhydrous $HClO_4$.

The first method was used to find $K_c = 0.80 \cdot 10^{-4}$ L mol^{-1}, whereas $K_c = 1.30 \cdot 10^{-4}$ L mol^{-1} and $K_c = 1.94 \cdot 10^{-4}$ L mol^{-1} were determined by the second and third methods, respectively. According to the data,[1] the temperature plot of the equilibrium constant obeys the equation

$$\ln K_c = -1960/RT - 5.633. \qquad (3)$$

Taking into account ionization of $HClO_4$, the expression for the equilibrium constant takes the form

$$K = \frac{[Cl_2O_7] \cdot [H_3O^+] \cdot [ClO_4^-]}{[HClO_4]^3}. \qquad (4)$$

The authors of the work[10] determined K at 20 °C by two methods: conductometric and volumetric. The first method was used to find $K = 0.68 \cdot 10^{-6}$, and $K = 0.72 \cdot 10^{-6}$ was obtained by the second method. It should be noted that $K = K_c \cdot [Cl_2O_7]$ determined[1] at 20 °C differs by an order of magnitude from K obtained in Ref. 10.

Expressions (2) and (4) can be transformed into Eqs. (5) and (6), respectively

$$K_c = \eta_0^2/[9C^0_{HClO_4}(1 - \eta_0)^3], \qquad (5)$$

$$K = \eta_0^3/[27(1 - \eta_0)^3], \qquad (6)$$

where η_0 is the degree of conversion (disproportionation) of anhydrous $HClO_4$, and $C^0_{HClO_4}$ is its initial concentration (mol L^{-1}). According to the known data,[11] $\eta_0 = 0.06 \pm 0.01$ at 20 °C. Substituting η_0 into Eqs. (5) and (6), we find $K_c = (2.8 \pm 1.0) \cdot 10^{-5}$ L mol^{-1} and $K = (1.0 \pm 0.5) \cdot 10^{-5}$. In the calculation of K_c we used $C^0_{HClO_4} = 17.62$ mol L^{-1}. We believe that these η_0, K, and K_c values are most exact. The measurement of η_0 was carried out by NMR from a change in the ^{1}H chemical shift, which is caused by the transition of partially deuterated anhydrous liquid perchloric acid from the nonequilibrium to equilibrium state.[11] Nonequilibrium perchloric acid is a chemically individual substance without admixtures of the disproportionation products, Cl_2O_7 and H_3OClO_4. This acid is condensed in a trap cooled by dry ice or liquid nitrogen during vacuum distillation from the H_3OClO_4 melt.[2,12] The IR spectra of nonequilibrium liquid $HClO_4$ and $DClO_4$ contain no absorption bands of Cl_2O_7 characteristic of the equilibrium form.[2]

A noticeable difference in the K and K_c values calculated by the published data[11] and measured[1,10] suggests that, in one case,[1] the samples contain Cl_2O_7 in some excess and, in another case,[10] in a deficiency.

Assuming that the Cl_2O_7 excess in the samples under study affected only the absolute value of the equilibrium constant but had no substantial effect on the character of the temperature plot, we used Eq. (3) for the determination of the refined K_c values at $T \neq 20$ °C. The K_c value was calculated by the formula

$$\ln K_c = -1960/RT - 7.105.$$

The calculation of the Cl_2O_7 concentration using Eqs. (5) and (6) give close results (Table 1). The calculated equilibrium concentration of Cl_2O_7 expressed in molar fractions ($x_{Cl_2O_7}$) is 0.02 (0.35 mol L^{-1}) at 20 °C, and the published values are 0.698 [1] and 0.155 mol L^{-1}.[10]

Hydrogen bonds between the $HClO_4$ and Cl_2O_7 molecules in the liquid phase are very weak. The concentration of Cl_2O_7 in anhydrous $HClO_4$ is low (see Table 1). Therefore, in this case, the estimation of the partial pressure of Cl_2O_7 ($P_{Cl_2O_7}$) using the Raoult—Henry law is quite appropriate. The saturated vapor pressure of Cl_2O_7 ($P^0_{Cl_2O_7}$) was calculated by the equation[13]

$$\log P_{Cl_2O_7} = 7.796 - 1770/T.$$

Table 1. Molar fractions (x) of nondissociated $HClO_4$, Cl_2O_7, H_3O^+, and ClO_4^- in equilibrium anhydrous perchloric acid at different temperatures

T /°C	Calculation by Eq. (5)			Calculation by Eq. (6)			
	x_{HClO_4}	$x_{Cl_2O_7}$	$x_{H_3OClO_4}$	x_{HClO_4}	$x_{Cl_2O_7}$	$x_{H_3O^+}$	$x_{ClO_4^-}$
20	0.96	0.020	0.020	0.94	0.020	0.020	0.020
25	0.96	0.020	0.020	0.93	0.021	0.021	0.021
50	0.95	0.025	0.025	0.93	0.023	0.023	0.023
100	0.94	0.027	0.027	0.92	0.027	0.027	0.027
200	0.93	0.035	0.035	0.90	0.033	0.033	0.033

Note. Accepting that $C^0_{HClO_4} \approx C_{HClO_4}$, the following data were used in calculation by Eq. (5):

T/°C	0	20	25	50	100	200
d/g cm^{-3}	1.8077	1.7703	1.7587	1.7098	1.61*	1.40*
C/mol L^{-1}	—	17.62	17.51	17.02	16.0	14.0

* Result of extrapolation.

Table 2. Total vapor pressure (P) and partial pressures of $HClO_4$ (P_{HClO_4}) and Cl_2O_7 ($P_{Cl_2O_7}$) above equilibrium anhydrous perchloric acid at different temperatures

T/°C	P	$P_{Cl_2O_7}$	P_{HClO_4}
	Torr		
20	29.4	1.1	28.3
25	32.1	1.6	30.5
50	96	5.0	91
100	440*	30	410
200	3550*	390	3160

* These values were obtained by extrapolation to the region of high temperatures.

The results of calculation by the expression $P_{Cl_2O_7} = x_{Cl_2O_7} \cdot P^0{}_{Cl_2O_7}$ using the $x_{Cl_2O_7}$ values from Table 1 and the partial pressures calculated by the equation

$$P_{HClO_4} = P - P_{Cl_2O_7} \quad (7)$$

are presented in Table 2. The typical values of the total pressure P above equilibrium anhydrous $HClO_4$ were calculated by the equation[7]

$$\log P = 6.947 - 1607/T.$$

The enthalpy of evaporation of the anhydrous acid in the temperature interval from 0 to 25 °C determined from this equation is ΔH_{vap} = 30.9±0.4 kJ mol^{-1}. According to other data, ΔH_{vap} = 43.5,[1] 38.4±0.6,[13] 37.0,[14] and 39.7±1.3 [15] kJ mol^{-1}. We prefer the data in the work[7] because of the high accuracy of measurements of the pressure (±0.01 Torr) and temperature (±0.05 °C). The average concentration of the samples of perchloric acid was 99.98±0.03 wt.%, and 15 points of the measurements fit smoothly on a straight line in the log$P$—1/T coordinates. In the work,[1] the pressure was measured with an accuracy of ±0.4 Torr in the temperature interval from 5 to 25 °C, the average concentration of 14 samples of perchloric acid was 99.96±0.20 wt.%, and the accuracy of temperature measurement was not indicated.

It is most difficult to estimate a probable contribution of the systematic error in the determination of the total vapor pressure above the anhydrous acid, because the composition of anhydrous $HClO_4$ can change depending on the conditions of preparation: due to enrichment in perchloric anhydride upon distillation and hydration by contacting with humid air or spontaneous decomposition. Therefore, the measurements of the total vapor pressure[7] above 100% $HClO_4$, probably, differ noticeably from the data of other authors.[1,10]

T/°C	P/Torr	Ref.
20	29.4	7
	21.1	1
	22.9	10
25	32.1	7
	27.5	1
	30.8	10

The extrapolation of the data[1,10] results in relatively small deviations of P from the known data[7] at 50 °C (from 5 to 26%). However, discrepancies become intolerable at 100 (from 40 to 140%) and 200 °C (from 140 to 490%), although we cannot doubt in the reliability of these data.[7]

The vapor composition above aqueous solutions of $HClO_4$ is known[1,8] not for all necessary values of the acidimetric concentration of perchloric acid (X) and T (the X value will be expressed in molar fractions). The total vapor pressure P at temperatures >50 °C was not measured.[7] Therefore, to use the equation $P_{HClO_4} = P - P_{H_2O}$ for calculations, we have to apply interpolations and extrapolations in some cases. At X = 0.50—0.74 the vapor phase consists of the $HClO_4$ molecules, whereas at X = 0.77—1.0 it consists of the $HClO_4$ and Cl_2O_7 molecules. At $X \geq 0.77$, the partial pressure of $HClO_4$ was determined by Eq. (7). The $P_{Cl_2O_7}$ value was estimated using Raoult´s law, calculating preliminarily the molar fraction of Cl_2O_7 in a solution for the corresponding temperature and X values from K and K_c.

The results of experiments on acidimetric determination of the vapor composition in the $HClO_4$—H_2O system confirm the reliability of calculations of the partial pressure of the anhydride. In particular, at $X = 0.76$ $x_{Cl_2O_7} \approx 0$, at X = 0.9 $x_{Cl_2O_7}$ = 0.04±0.02, and at X = 1 $x_{Cl_2O_7}$ = 0.11±0.03. For $X < 0.76$ at temperatures 50 and 100 °C, analogous data of acidimetric determination of the vapor composition are presented in the work[8] (as a table), and for $X \to 1$ at 20 °C the data are given as a plot.[1] As indicated in the monograph,[1] for the vapor above anhydrous perchloric acid at 20 °C, $x_{Cl_2O_7} = 0.114$ and $x_{HClO_4} = 0.886$ (x_{HClO_4} is the equilibrium concentration of nondissociated perchloric acid in the liquid phase expressed in molar fractions). The $x_{Cl_2O_7}$ value indicated[1] for X = 1 exceeds 3.7-fold that calculated by us. However, as we have shown above in refinement of the K and K_c values by η = 0.06, the samples of perchloric acid used[1] for acidimetric determination of $x_{Cl_2O_7}$ contained, probably, some excess of perchloric anhydride. Thus, the results of our calculations do not contradict, most likely, the known data on the content of perchloric anhydride in the gas phase.

The pressures of saturated $HClO_4$ vapor ($P^0{}_{HClO_4}$) for different temperatures were found by the extrapolation of lines by the points with the coordinates (P_{HClO_4}, x_{HClO_4}): $P_{HClO_4} \to P^0{}_{HClO_4}$ at $x_{HClO_4} \to 1$. The x_{HClO_4} values were calculated from the data of spectroscopic measurements[3,5] of the degree of electrolytic dissociation of perchloric acid (α); in addition, the x_{HClO_4} values from Table 1 were used.

T/°C	20	25	50	100	200
$P^0_{HClO_4}$/Torr	29	33	97	440	3400

Estimating $P^0_{HClO_4}$ by the square extrapolation of the curvilinear $P_{HClO_4}(X)$ plot in the interval $0.33 < X < 0.77$, we obtained the values close to the results at $X \to 1$.

As a whole, the $P^0_{HClO_4}$ values slightly differ from the total vapor pressure above the equilibrium anhydrous acid. A decrease in the $HClO_4$ pressure caused by acid disproportionation is likely compensated, to a great extent, by volatility of Cl_2O_7.

The thermodynamic activities (a) of perchloric acid

$$a_{HClO_4} = P_{HClO_4}/P^0_{HClO_4},$$

calculated for several concentrations X = 0.33—0.74 and 0.77—0.99 at different temperatures are presented in Table 3. The most exact a_{HClO_4} values refer to an interval of 20—50 °C, and less exact values lie in the 100—200 °C interval. The calculation indicates some relation of a_{HClO_4} to X and temperature.

The a_{HClO_4} and x_{HClO_4} values for nondissociated perchloric acid in an aqueous solution are compared in Table 4. The probable error of a_{HClO_4} determination is 5% in the temperature interval from 20 to 50 °C and 15% in an interval of 100—200 °C. The x_{HClO_4} values were calculated by the degree of electrolytic dissociation (α) measured by IR [3] and ¹H NMR [5] methods. Determination of the α values by the proton shift of resonance frequency in the NMR spectrum depends on the choice of the proton hydration model. The results obtained in both works are close. The measurements[5] were carried out in the concentration interval X = 0.55—1.0, and in the whole other interval the α values were obtained by interpolation. The corresponding points are not included in the table.

Table 3. Calculated thermodynamic activities of perchloric acid (a_{HClO_4}) in an aqueous solution for different acidimetric concentrations (X) and temperatures

X*	a_{HClO_4}				
	20 °C	25 °C	50 °C	100 °C	200 °C
0.33	0.0034	0.0032	0.0044	0.0045	0.011
0.34	0.0044	0.0043	0.0053	0.0077	0.014
0.36	0.0090	0.0076	0.0080	0.0084	—
0.38	0.017	0.013	0.022	0.029	0.043
0.40	0.033	0.027	0.032	0.033	0.038
0.409	0.036	—	—	—	—
0.417	—	0.037	—	—	—
0.496	—	—	0.16	—	—
0.71	—	0.52	—	—	—
0.74	0.56	—	—	—	—
0.772	0.56	0.58	0.56	0.56	—
0.838	0.60	0.68	0.71	0.80	—
0.858	0.68	0.70	0.76	0.88	—
0.877	0.74	0.74	0.75	0.78	—
0.986	0.94	0.92	0.90	0.96	—
1	0.98	0.92	0.94	0.93	0.93

* Expressed in molar fractions.

Table 4. Comparison of the molar fractions of nondissociated $HClO_4$ (x_{HClO_4}) and thermodynamic activities of $HClO_4$ (a_{HClO_4})

X	T/°C	x_{HClO_4}	a_{HClO_4}
1.0	20	0.95[a]	0.98
	25	0.95[a]	0.92
	50	0.94[a]	0.94
	100	0.93[a]	0.93
	200	0.91[a]	0.93
0.986	25	0.97[b]	0.92
	50	0.97[b]	0.90
0.877	25	0.76[b]	0.74
	50	0.77[b], 0.89[c]	0.75
0.858	25	0.72[b]	0.70
	50	0.73[b], 0.86[c]	0.76
0.838	25	0.68[b]	0.68
	50	0.70[b], 0.83[c]	0.71
0.772	25	0.57[b]	0.58
	50	0.57[b], 0.70[c]	0.56
0.74	20	—	0.56
0.71	25	0.59[b]	0.52
0.50	50	0.15[c]	0.16
0.40	50	0.029[c]	0.032
0.36	50	0.004[c]	0.008
0.33	25	>0[d]	0.0036
	50	0[d]	0.0044
0.29	200	0.005[e]	0.005

[a] Calculated using the η_0 value.
[b] Estimated from the data in Ref. 5.
[c] Estimated from the α—C_{HClO_4} plot.[3]
[d] Estimated from the data in Ref. 1.
[e] Estimated from the α value presented in Ref. 4.

Taking into account that the accuracy of photometric measurements on a commercial IR spectrophotometer is not too high, we can accept that the error of x_{HClO_4} estimation is ~5%. The authors of the work[3] used anhydrous $HClO_4$ as a reference with α = 0, neglecting disproportionation by Eq. (1). Since in fact $\alpha = \eta_0 = 0.06$,[11] the error increases to 20%. In addition, the plots of α *vs.* C_{HClO_4} and molar ratio of components of the perchloric acid—water system ($[H_2O]/[HClO_4] = n$) at 50 °C are presented.[3] In the case of $n = 0$ ($X = 1$), this plot contains the inexact value C_{HClO_4} = 17.6 mol L^{-1} (instead of correct 17.0 mol L^{-1}). Therefore, the n scale and the scale of molar-volume concentrations begin to diverge. Thus, one should not overestimate the reliability of the published data[3] in the region of $X \to 1$. Note that the divergence between the data in Refs. 3 and 5 are especially high precisely in this concentration region. Due to this evident uncertainty, we plotted a_{HClO_4} *vs.* x_{HClO_4} for X = 0.772, 0.838, 0.858 (50 °C) using only the x_{HClO_4} values, which were determined from the α value taken from the work.[5]

Comparison of the x_{HClO_4} and a_{HClO_4} values indicates that they are proportional. These parameters, as follows from the data in Table 4, coincide within the error at all studied concentrations and temperatures: $a_{HClO_4} = \gamma \cdot x_{HClO_4}$, where $\gamma = 1.00 \pm 0.05$.

Aqueous $HClO_4$—H_2O solutions differ from ideal solutions by the violation of the Raoult—Henry law, *i.e.*, for them

$$P_{HClO_4}/P^0_{HClO_4} = a_{HClO_4} \neq X.$$

The curve of vapor pressure above an $HClO_4$—H_2O solution has an extreme,[7] and negative deviations from Raoult´s law are observed due to the ionization of an aqueous solution. Negative deviations have also been found for H_2O—HCl [16,17] and H_2O—HNO_3 [17—19] solutions. At the same time, in fact

$$P_{HClO_4}/P^0_{HClO_4} = x_{HClO_4}. \quad (8)$$

Equality (8) makes it possible to estimate the molar fraction of the nondissociated acid in an aqueous medium by the known relative vapor pressure. The determination of molecules in a solution from the vapor pressure gives reasonable results at different concentrations. Raoult´s law has previously been used for similar purposes, for example, to determine molar fractions of a nondissociated substance in H_2O—HCl [16,20,21] and H_2O—HNO_3 [22] solutions. The molar fractions of free water in an H_2O—$HClO_4$ solution were also estimated to determine the number of ion hydration[7]; however, independent data confirming validity of this approach were not presented.

Equality (8) is not commonly accepted. Therefore, we have to understand why this equation is fulfilled in this case. The composition of the $HClO_4$—H_2O liquid-phase system has been studied in detail by the methods of analytical chemistry, physicochemical analysis, vibrational spectroscopy, and ^{1}H NMR spectroscopy.[1—12] Based on the available information, we can present the material balance equation in the form

$$x_{HClO_4} + x_{Cl_2O_7} + x_{H_2O} + x_+ + x_- = 1,$$

where x_{HClO_4}, $x_{Cl_2O_7}$, x_{H_2O}, x_+, and x_- are the molar fractions of perchloric acid, perchloric anhydride, water, positive ions, and negative ions, respectively. The ultimate concentrated solutions for which $X > 0.74$ have $x_{Cl_2O_7} \neq 0$.[1] At $X < 0.74$ $x_{Cl_2O_7} \approx 0$. Then

$$x_{HClO_4} + x_{H_2O} + x_+ + x_- = 1. \quad (9)$$

Assume that some number of the $HClO_4$ molecules (n_s) is bound to the cations and anions in the solvate shell, and some number of the H_2O molecules (n_h) is bound to the cations and anions in the hydrate shell. The ion-molecular bonds are much stronger than the intermolecular bonds. Then the equilibrium concentrations of ions and molecules are functions of the X, α, n_s, and n_h variables, whose specific form can be found from the condition of normalization of the sum of concentrations (9)

$$x_{HClO_4} = X(1 - \alpha - \alpha \cdot n_s)/[1 + \alpha \cdot X(1 - n_s - n_h)],$$
$$x_{H_2O} = (1 - X - \alpha \cdot X \cdot n_h)/[1 + \alpha \cdot X(1 - n_s - n_h)],$$
$$x_+ = x_- = (\alpha \cdot X)/[1 + \alpha \cdot X(1 - n_s - n_h)].$$

Further we will show that $x_{H_2O} \approx 0$ for $0.33 < X < 0.74$ and $x_{HClO_4} \approx 0$ for $0 \le X < 0.33$. In the case of $x_{H_2O} \approx 0$, we have

$$x_{HClO_4} + x_+ + x_- = 1,$$
$$x_+ = x_- = \alpha/[1 + \alpha(1 - n_s)],$$
$$x_{HClO_4} = (1 - \alpha - \alpha \cdot n_s)/[1 + \alpha \cdot (1 - n_s)], \quad (10)$$
$$n_h = (1 - X)/\alpha X = n/\alpha, \quad (11)$$

where the n number characterizes the molar ratio of water to acid in the starting (nonequlibrium) $HClO_4$—H_2O system. Using Eq. (10), one can present n_s as a function of α and x_{HClO_4}

$$n_s = 1/\alpha - (1 + x_{HClO_4})/(1 - x_{HClO_4}). \quad (12)$$

The author of the work[5] calculated the degree of ionization of water (α_w) in perchloric acid at $X > 0.32$. Note that $n_h = 1/\alpha_w$.

In the case of $0 \le X < 0.33$, we have

$$x_{H_2O} + x_+ + x_- = 1,$$
$$x_+ = x_- = X/[1 + X(1 - n_h)],$$
$$x_{H_2O} = (1 - X - X \cdot n_h)/[1 + X(1 - n_h)]. \quad (13)$$

Based on Eq. (13), we can write the expression for n_h in the form

$$n_h = 1/X - (1 - x_{H_2O})/(1 + x_{H_2O}). \quad (14)$$

In a particular case, at $n_s = 0$, Eq. (12) can be reduced to the form

$$\alpha = (1 - x_{HClO_4})/(1 + x_{HClO_4}), \quad (15)$$

or

$$x_{HClO_4} = (1 - \alpha)/(1 + \alpha). \quad (16)$$

Expressions (15) and (16) coincide with the commonly accepted equations, which relate the degree of conversion to the molar fraction of a substance for the chemical reaction.[17]

At $n_h = 0$, Eq. (14) is reduced to the correlation

$$x_{H_2O} = (1 - X)/(1 + X),$$

which is a standard formula for recalculation of the molar fraction of $HClO_4$ to the molar fraction of H_2O in the nonequilibrium $HClO_4$—H_2O system without decomposition of $HClO_4$ to the ions.

Taking into account Eq. (8), we replace the variables in Eq. (12): $x_{HClO_4} = a_{HClO_4} = P_{HClO_4}/P^0{}_{HClO_4}$. Then

$$n_s = 1/\alpha - (1 + a_{HClO_4})/(1 - a_{HClO_4}). \quad (17)$$

The equation relative in sense can also be obtained by the similar replacement of the variables in Eq. (14): $x_{H_2O} = a_{H_2O} = P_{H_2O}/P^0{}_{H_2O}$

$$n_h = 1/X - (1 + a_{H_2O})/(1 - a_{H_2O}). \quad (18)$$

Equation (18) was earlier presented[7] without a derivation.

The conditions $x_{H_2O} \approx 0$ (at $X > 0.33$) and $x_{HClO_4} \approx 0$ (at $X < 0.33$) follow directly from the estimation of the partial vapor pressure and results of the spectroscopic study of the gas and liquid phases of the $HClO_4$—H_2O system. An azeotrope with a very low vapor pressure is formed in the boundary concentration region ($X \approx 0.33$). In particular, according to the published data,[7] P = 0.26 Torr at 20 °C and X = 0.3185. The P_{HClO_4} and P_{H_2O} branches of the diagram of partial vapor pressure intersect in the immediate vicinity of the concentration axis (see Fig. 1). The curve of total vapor pressure in the $HClO_4$—H_2O system passes through a minimum, and the extreme point is almost tangent to the abscissa[7] at 50 °C. Therefore, the diagram of partial pressures as if consists of two parts, as well as the diagram of total vapor pressure. The azeotrope composition varies under different external conditions, leading to some diffusion of the boundary region (X = 0.32—0.34). At a pressure of 5.7 Torr, the composition exactly corresponds to the chemical formula $HClO_4 \cdot 2H_2O$.[1,23] The low vapor pressure means that the azeotrope is formed due to the ionization of the majority of the $HClO_4$ and H_2O molecules in a solution. The IR and Raman spectra of the liquid phase, whose composition is close to that of the azeotrope, contain maxima of cation and anion concentrations and do not contain maxima of neutral molecules.[3,4] Gaseous $HClO_4$—H_2O mixtures are ideal at low pressures, which is indicated by the IR spectroscopic data.[8] It has been found by IR spectroscopy[3,4,8] that the $HClO_4$ molecules without H_2O appear in the liquid phase at $X > 0.33$, whereas at $X < 0.33$ the H_2O molecules appear virtually without $HClO_4$. In addition, $P_{H_2O} \approx 0$ in the first case, and $P_{HClO_4} \approx 0$ in the second case. The low partial pressure implies that the number of neutral molecules of water or perchloric acid in a solution is insignificant. Substituting the tabulated a_{HClO_4} and α values from the published data[3,5] into Eq. (17), we find $n_s = 0$. However, the spectroscopic data show that $n_s \neq 0$: the $HClO_4$ molecule is associated with the ClO_4^- anion through the hydrogen bond. Thus, a contradiction appears but can simply be explained. The bond energy of $HClO_4$ with ClO_4^- in an $HClO_4$—H_2O solution differs slightly from the energy of the intermolecular bond in anhydrous perchloric acid. According to the spectroscopic data, the energy of the intermolecular hydrogen bond in anhydrous $HClO_4$ is ~13 kJ mol^{-1}, and the ClO_4^-...$HClO_4$ bond energy in liquid perchlorate monohydrate is 15—19 kJ mol^{-1}. Therefore, equality (8) is fulfilled due to a small difference between the energies of intermolecular and anion-molecular hydrogen bonds.

The data in Table 3 indicate some increase in a_{HClO_4} with temperature. Such a behavior corresponds to that expected in the case of $a_{HClO_4} = x_{HClO_4}$. The degree of dissociation of $HClO_4$ decreases, in fact, with temperature, which is indicated, for example, by the appearance of the ν(Cl—O) line of the nondissociated acid in the Raman spectrum of an $HClO_4 \cdot 2.44H_2O$ solution at 200 °C.[4] The temperature plot of a_{HClO_4} in the case of anhydrous $HClO_4$ is more complicated. The degree of disproportionation of the anhydrous acid with temperature does not decrease but, on the contrary, increases.[1]

The substitution of $n_s = 0$ into Eq. (17) or $x_{HClO_4} = a_{HClO_4}$ into Eq. (15) gives

$$\alpha = (1 - a_{HClO_4})/(1 + a_{HClO_4}). \quad (19)$$

The $\alpha = f(X)$ function plotted for T = 50 °C from the data in Table 3 recalculated by Eq. (19) is shown in Fig. 2. For comparison, the plot also contains points measured by IR spectroscopy[3] and ^{1}H NMR spectroscopy.[5] The points obtained from the IR spectroscopic data[3] in the region of high concentrations lie below the curve obtained by us. This deviation is reasoned by an incorrect value of the perchloric acid density used in Ref. 3 for plotting a similar function of the molar-volume concentration. Remarkably, different methods of α determination (by the data of IR spectroscopy, Raman spectroscopy, and tensimetry) give close results. The results of NMR measurements depend on the choice of the proton hydration

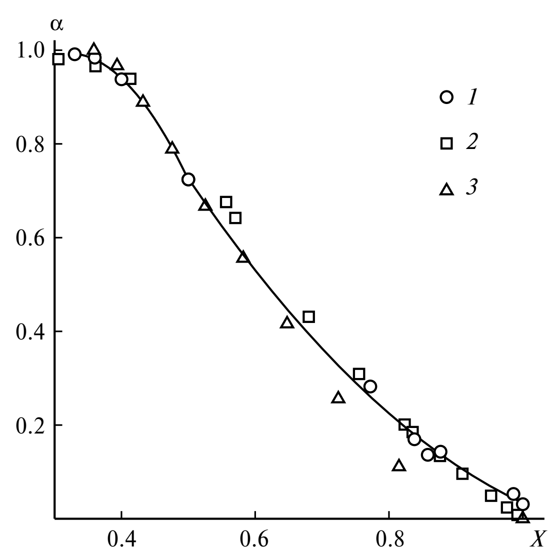

Fig. 2. Degree of dissociation of perchloric acid (α) at 50 °C as a function of the acidimetric concentration (X): calculated by the vapor pressure[7] (*1*), by the data in Ref. 5 (*2*), and by the data in Ref. 3 (*3*).

model. When IR spectroscopy or tensimetric data are used, this model becomes unnecessary. It is most likely that the tensimetric method provides more exact results at low X.

The existence of the $P_{HClO_4}/P^0_{HClO_4}$—x_{HClO_4} linear correlation follows directly from analysis of the published data,[3,5,7] first, for the concentration interval X = 0.33—0.76 and temperatures 20—50 °C. It was necessary to calculate the equilibrium constant of reaction (1) and related partial pressures of perchloric anhydride and perchloric acid mainly to refine $P^0_{HClO_4}$ and to find several P_{HClO_4} points at $X > 0.76$. The corresponding a_{HClO_4} values at these X depend weakly on the accuracy of determination of the Cl_2O_7 content in the gas phase, which consists mainly of the $HClO_4$ molecules. The assumption that the partial pressure of Cl_2O_7 is proportional to the molar fraction in the liquid anhydrous acid is not too rough and has been used previously.[1]

Thus, this correlation is observed when the experimental data are used in an interval of 20—50 °C. We also present similar data for higher temperatures, because the equality $a_{HClO_4} = x_{HClO_4}$ is satisfactorily fulfilled. However, validity of the linear extrapolation of the log$P$—1/T plot in a wide temperature interval needs comments. The problem is that we have no other criteria except for the published error of evaporation enthalpy determination. The corresponding data for $HClO_4$ are presented above.

For Cl_2O_7 the authors[13] present ΔH = 33.9±0.4 kJ mol^{-1} in the –5—15 °C temperature interval, while ΔH = 34.7 kJ mol^{-1} in the –29—30 °C interval is given[1] without an error. The scatter of the ΔH values makes it possible to estimate the error of P determination as 3—5% for perchloric acid and perchloric anhydride. At the same time, a possible influence of an ignored systematic error should be taken into account. In this case, extrapolation to the region of high temperatures could increase the error by several times. In fact, as shown by the results presented in Tables 1, 3, and 4, the values at higher temperatures agree with those determined more correctly for the 20—50 °C temperature interval. In our opinion, this result can be explained by the mutual compensation of both random and systematic errors in the calculation of the $P_{HClO_4}/P^0_{HClO_4}$ ratio.

The dissociation of $HClO_4$ results in high negative deviations from the law of ideal solutions. At the same time, analysis of the data shows a linear correlation between the relative vapor pressure (thermodynamic activity) and molar fraction of nondissociated perchloric acid in an aqueous solution. The molar fraction of the nondissociated acid equals its activity with an accuracy to 5%, *i.e.*,

$$x_{HClO_4} = a_{HClO_4} = P_{HClO_4}/P^0_{HClO_4}. \quad (20)$$

Based on the a_{HClO_4} values, recalculating to the degree of electrolytic dissociation, can produce the $\alpha = f(X)$ function similar to that known from the spectroscopic data.

Equation (19) is likely valid either when the energies of anion-molecular (ClO_4^-...$HClO_4$) and intermolecular ($HClO_4$...$HClO_4$) hydrogen bonds coincide, or when these energies differ slightly. In the case of formation of a strong anion-molecular bond but a weak intermolecular hydrogen bond, more general equation (17) should be used instead of Eq. (15).

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