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DEVELOPMENT OF A MATHEMATICAL MODEL OF THE ELECTRICAL CONDUCTIVITY OF FEED WATER IN TPS

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Abstract: *The article deals with the development of mathematical model of electric conductivity of thermal power station TPS process waters. The ranges of possible temperatures of heat carrier (water) samples are given. The plots of empirical expressions in the range of temperatures from 0 to 120 °C and at higher temperatures are analyzed. The results obtained by these formulas for the temperature range from 0 to 100 °C are practically the same. The figures indicate changes in calculated limit motions of H^+ and OH^- ions depending on temperature. The calculated equation of reduction of specific electrical conductivity to the value at 25 °C for pure water is obtained.*

Key words: *water-chemical regime, electrical conductivity, ion, chemical and technological process, desalted water, alkalinity.*

Reliable constant supply is essential for mathematical models representing the chemical-technological processes at thermal power station (TPS). Various values of the same type are also provided in the reference literature. The ionic product of water and the equivalent electrical conductivity of ions in extremely dilute solutions (demineralized water, turbine condensate and feed water) are especially sensitive to such a constant supply, mathematical models of diagnostic systems and monitoring the state of the water-chemical regime or simulating the operation of the main equipment of TPS. In them it is necessary to precisely define these constants in a wide range of temperatures - from 10 to 350 $^o C$, and in the reference literature their values are given only in a narrow range.

The most significant measure, from an electrochemical point of view, is the ionic component of water and its temperature dependency. This indicator determines the concentrations of ions of hydroxonium and hydroxyl:

$$2H_2O \leftrightarrow H_3O^+ + OH^-,$$
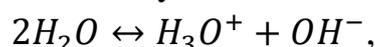
Or in simplified expression, hydrogen and hydroxyl ions:

$$H_2O \leftrightarrow H^+ + OH^-.$$
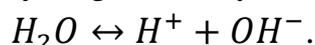
The quantitative relationship of K_2 with the concentrations of ions H^+ and OH^- (in the formula of the activity) is expressed by the equation

$$K_w = a_{H^+} + a_{OH^-}.$$

We learn various forms of empiric dependences to evaluate the K_w meaning based on the temperature.

Therefore, according to Bouskvita formula we have [1].

$$pK_w(T) = \frac{484,51}{T} + \frac{362,5}{T^2} + 8,2902 \tag{1}$$

The book by H. Harned and B. Owen [2] contains the following dependencies:

$$pK_w(T) = \frac{484,51}{T} + 35,3944 - 0,00853 * T - 11,8261 * lgT; \tag{2}$$

$$lgK_w = -\frac{6013,79}{T} - 23,6521 * lgT + 64,7013 \tag{3}$$

$$lgK_w = -\frac{4780,13}{T} - 0,0176 * T + 6,0875 \tag{4}$$

By the formula used in the calculations by V.F. Ochkov [3],

$$pK_w = -\frac{4780,13}{T} + 0,019559 * T - 7,856. \tag{5}$$

According to the Holzapfel formula [4, 5] in a wide range of temperatures and densities we have

$$⟦pK_w(\rho, T) = -2\left[7,5 + \frac{2\rho}{\rho_0}\right] * lg\frac{2\rho}{\rho_0} - lg[K_w(\rho_0, T)],$$

Where ρ_0 - water density under standard conditions, $\frac{kg}{m^3}$ $\left(\rho = 1000 \frac{kg}{m^3}\right)$.

In [6] the dependence for a wide range of temperatures and pressures is given:

$$lgK_w = \left(13,957 - \frac{1262,3}{T} + \frac{856410}{T^2}\right)lg\rho - 4,096 - \frac{3245,2}{T} + \frac{23020}{T^2} - \frac{3,984*10^7}{T^3}.$$

From the theoretical point of view, the equilibrium constant can be defined as the first approximation of the Gaber equation [7].

$$\ln K_p = -\frac{\Delta_r * H_{298}^o}{RT} + \frac{\Delta S_{298}^o}{R}, \tag{6}$$

Where $\Delta_r * H_{298}^o$ - entropy of chemical reaction at 298.15 K $\frac{J}{mol}$; ΔS_{298}^o - entropy of reaction $\frac{J}{mol*K}$.

For the case of the ionic product of water dependence (6), using the reference data [7], can be written as follows

$$lnK_w(T) = -\frac{6716}{T} - 9,701.$$

A related formula (3) is contained in the literature [3], but the third element is supplied with a misprint. Dependence (6) gives the most accurate calculation results at temperatures close to 25 °C. However, at temperatures above 100 ° C, its use is unacceptable, as the change in enthalpy, entropy and heat capacity of substances depending on temperature is not taken into account. It is of interest to consider three temperature ranges:

1) The spectrum of potential temperatures of the heat carrier (water) in the condensate and feed path and boiler water of the power unit: 25-350 °C:

2) The range of possible temperatures of the coolant samples taken at the atmospheric pressure: 15-100 °C;

3) Temperature range of coolant samples received in sample preparation devices for analysis by automatic chemical control devices: 15-40 °C.

The first range provides diagnostics of the coolant (water) and its impurities behavior directly in the process conditions. The second and third ranges meet the capabilities of working with samples of cooled coolant at atmospheric pressure.

Fig.1 indicates graphs of dependencies (1) - (5) in a wide range of temperatures.
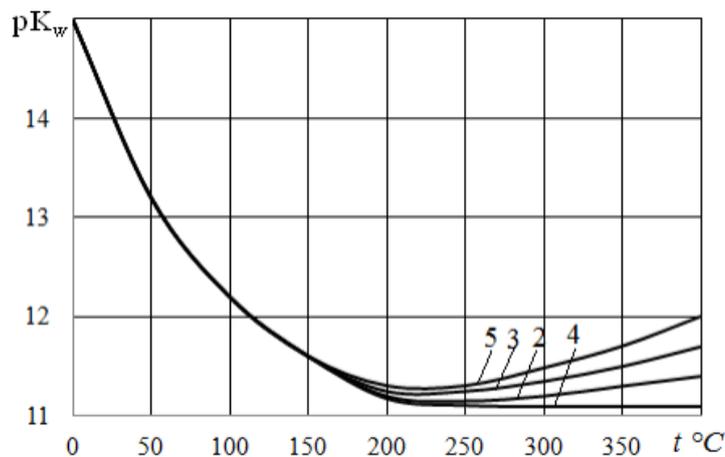
Fig.1. Results of calculating K_w using empirical formulas depending on temperature.

Analysis of the empiric model charts by approximation (1)-(5) reveals that all these dependencies give essentially the same results in the temperature range from 0 to 75 °C. Above 75 °C dependence (1) should not be used for calculations, because in these conditions it has an unacceptable error, which increases sharply with increasing temperature. The graphs of dependencies (2) - (5) in the temperature range from 0 to 120 °C practically coincide, and at higher temperatures they differ significantly. The choice of the most adequate ones is complicated by the fact that in the reference literature the K_w values differ greatly depending on the temperature. Analysis of the curves indicates that they have the following minimum points: dependence (2) 265,6 °C. (3) 312,3 °C, (4) – 238,8 °C, (5) 221,2 °C. One can agree that the empirical formula (2) most adequately describes the temperature dependence, which is noted in the book by H. Harned, B. Owen [2]. Variation in the limit mobility of ions in dependence on temperature is described by the following empirical formula; the book by L.I. Antropov [8] gives the dependence:

$$\lambda_{0,i}(t) = \lambda_{0,i}^{25}[1 + \alpha_i(t - 25) + 0,0163(\alpha_i - 0,0174)(t - 25)^2], \quad (7)$$

Where α_i is the temperature coefficient of electrical conductivity of the ion
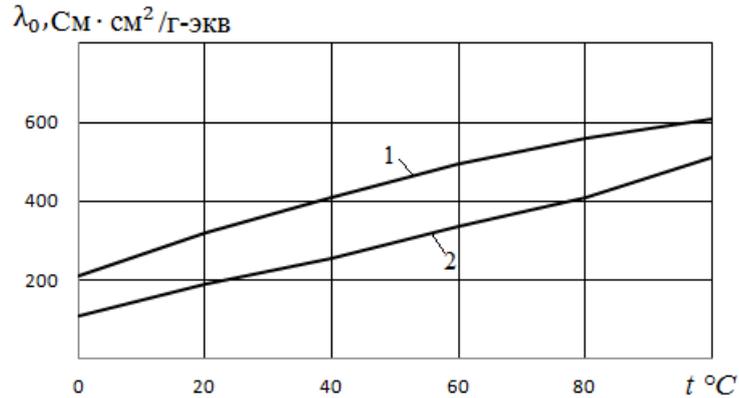
$$\alpha_{H^+} = 0{,}0142; \ \alpha_{Na^+} = 0{,}0208; \ \alpha_{OH^-} = 0{,}0196; \ \alpha_{Cl^-} = 0{,}0194.$$

In the book of H. Harned and B. Owen [2]

$$\lambda_{0,i}(t) = \lambda_{0,i}^t + a_i(t - 25) + b_i(t - 25)^2 + c_i(t - 25)^3 \tag{8}$$

Where a, b and c are the coefficients.

The results obtained by these formulas for the temperature range from 0 to 100 °C are almost identical. Changes in calculated limit motions of H^+ and OH^- ions depending on temperature are indicated in Fig. 2.

Fig.2. Dependence of the limiting mobility of ions H^+ (1) and OH^- (2) on temperature

The specific electrical conductivity of absolutely pure water at sample temperature can be written down according to the electrical conductivity equation in the form of

$$1000\chi_{H_2O}^t = \lambda_{0,H^+}^t[H^+] + \lambda_{0,OH^-}^t[OH^-], \tag{9}$$

Where λ_{0,H^+}^t, λ_{0,OH^-}^t are the limits of mobility H^+ and OH^- at water temperature See* $\dfrac{cm^2}{g-eqv}$.

For absolutely pure water, equality is fair.

$$H^+ = OH^-,$$

Then we will get

$$1000\chi_{H_2O}^t = \left(\lambda_{0,H^+}^t + \lambda_{0,OH^-}^t\right)\sqrt{K_w(T)}. \tag{10}$$

Changes in the specific electrical conductivity of absolutely pure water as a function of temperature are indicated in the figure. 3. The small discrepancy between the reference data [9, 10] and the calculated data can be explained by the use of various calculation formulas, with the largest deviation being 17.9 % at 10 °C and with temperature increase decreasing to 4.6 % at 50 °C.
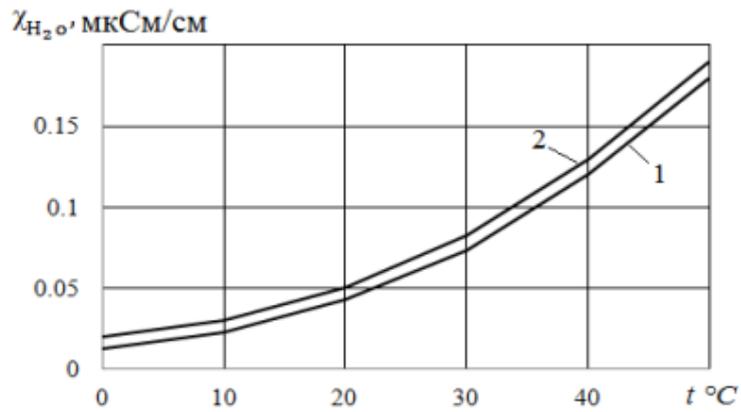
Fig.3. Specific electrical conductivity of absolutely pure water depending on temperature (range from 0 to 50 •*C*): 1 - calculated dependence; 2 - reference data [10, 11].

Comparison of the calculated data on equation (10) with the experimental ones [13] in the whole range of considered temperatures is presented in Fig. 4 and indicated identical dependencies at large experimental values for all χ_{H_2O} temperatures. Excess of the experimental information over the calculated in this case are determined by insufficient "purity" of water in the experience and dissolution of structural materials, as evidenced by the mismatch of the "forward motion" with the "backward motion".
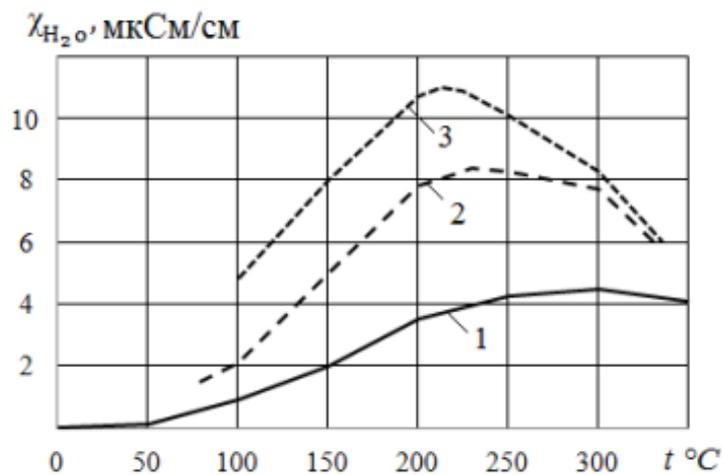
Fig.4. Specific electrical conductivity of absolutely pure water as a function of temperature (range from 0 to 350 ° C): 1 - calculated dependence; 2 - experimental "forward motion" data 3 - experimental "backward motion" data.

Due to the fact that the value of the ion product K_w changes with temperature, the hydrogen pH of water also depends on the temperature and for pure water can be recorded in the form:

$$pH(t) = -0{,}5 lg K_w(t) \qquad (11)$$

Changes in pH of absolutely pure water depending on temperature are indicated in the Fig.5.

Under the conditions of automatic chemical control of the coolant quality of the TPS and NPP units the indicator χ_{25} - specific electrical conductivity of the water sample reduced to the standard temperature of 25 $°C$ is taken.

The calculated equation of reduction of specific electrical conductivity to the value at 25 $°C$ for pure water is obtained in the form:

$$\chi_{H_2O}^{25} = \frac{\chi_{H_2O}^t}{(0,596+0,016t)} \sqrt{\frac{K_W^{25}}{K_W^t}} \tag{12}$$
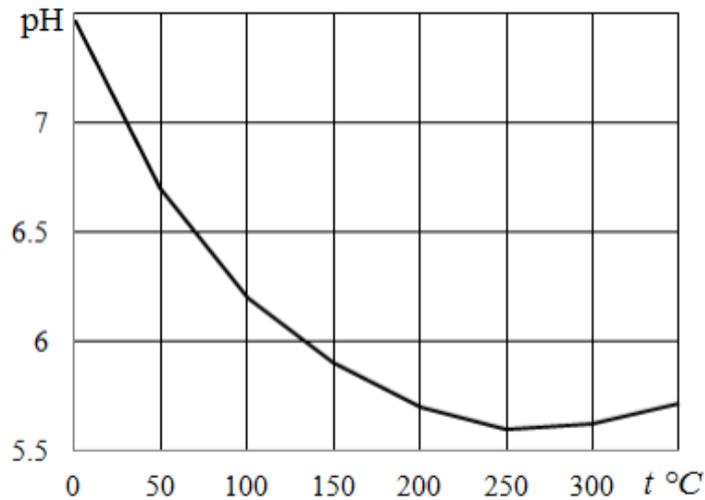
Fig.5. Change in pH value of abstractly pure water as a function of temperature

In the case of extremely diluted aqueous solution of electrolytes, which is the feed water of the power units, it is recommended that the task of reducing the changed specific electrical conductivity of the coolant sample at a temperature reduced to 25 $°C$ be addressed by the formula [14]:

$$\chi^{25} = \frac{\chi^t}{1+0,02(t-25)}. \tag{13}$$

In relation to formula (10) and (12), only the first portion of the approximation sequence is used here, which restricts the temperature spectrum to 25 ± 10 $°C$. For practical purposes, automatic chemical control of the coolant is sufficient. However, even in this temperature range (15 - 40 $°C$) the specific electrical conductivity of pure water changes nonlinearly and more intensively than the specific electrical conductivity of salt. Therefore, with the measured electrical conductivity values $\chi_{изм} < 0,15$ $mkCm/cm$ (feed water of supercritical pressure units), it is reasonable to separate the conversion to standard temperature for salt and water based on the law of additivity of electrical conductivity:

$$\chi_{изм}^t = \chi_{соли}^t + \chi_{H_2O}^t \tag{14}$$

The basic electrical conductivity calculated at temperature t can then be reduced to a value of 25 °C for water by equation (12) and salt by equation (13).

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