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DENSITY DEPENDENCE OF HEAT CONDUCTIVITY OF AQUEOUS HYDRAZINE SOLUTIONS WITHIN WIDE RANGES OF TEMPERATURE AND PRESSURE

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Equations are obtained that establish dependence of heat conductivity of hydrazine on density and concentration of water at various values of temperature and pressure.

Measurements of the density of aqueous hydrazine solutions were carried out using hydrostatic weighing [1]. Heat conductivity was measured using a cylindric bicalorimeter of the regular thermal regime [2]. The density of aqueous hydrazine solutions was studied within the range of temperatures of 292.3–561.1 K and within the range of pressures of 0.101–98.1 MPa. The general relative error of the density measurements does not exceed 0.1%.

Measurements of the heat conductivity of aqueous hydrazine solutions were carried out using the method of the cylindric bicalorimeter of the regular thermal regime along isotherms within the range of temperatures of 292–547.3 K and within the range of pressures of 0.101-49.0 MPa. The thickness of the layer under investigation was 0.65 mm. Variations of the temperature on the boundary of the layer under investigation were from 1.31 to 0.65 K. The general relative error of measurements of heat conductivity is 4.5%.

It is found that heat conductivity of the solutions under investigation is first increased with an increase in temperature to ~413 K, and then is decreased, and is increased with an increase in pressure.

The density of the solutions under investigation is decreased with increasing temperature according to a linear law and is increased with increasing pressure. In order to establish a relationship between the heat conductivity and density of aqueous hydrazine solutions at atmospheric pressure and various temperatures the following functional dependence was used:

$$\frac{\lambda}{\lambda_1} = f\left(\frac{\rho}{\rho_1}\right), \tag{1}$$

where λ and λ_1 are the heat conductivities of aqueous hydrazine solutions at temperatures T and T_1, respectively; ρ and ρ_1 are the corresponding densities of the solutions at temperatures T and T_1; $T_1 = 293$ K.

Fulfilment of the condition (1) has shown that the experimental points fit the common curve well. The equation of this curve is as follows:

$$\lambda = \left[-68.32\left(\frac{\rho}{\rho_1}\right)^2 + 130.2\left(\frac{\rho}{\rho_1}\right) - 60.87\right]\lambda_1 . \tag{2}$$

Knowing experimental values of the density of aqueous hydrazine solutions as a function of temperature [3], one can calculate by Eq. (2) the temperature dependence of heat conductivity of solutions at atmospheric pressure with an error of 1–2%, provided the value λ_1 is known.

It would be interesting to connect λ_1 in Eq. (2) with the molar concentration of water n_{H_2O}. For the solutions under investigation this dependence is described by the equation

$$\lambda_1 = 1.03\cdot 10^{-5}\eta_{H_2O}^2 + 2.84\cdot 10^{-4}\eta_{H_2O} + 0.325\,, \quad W/(m\cdot K)\,. \tag{3}$$

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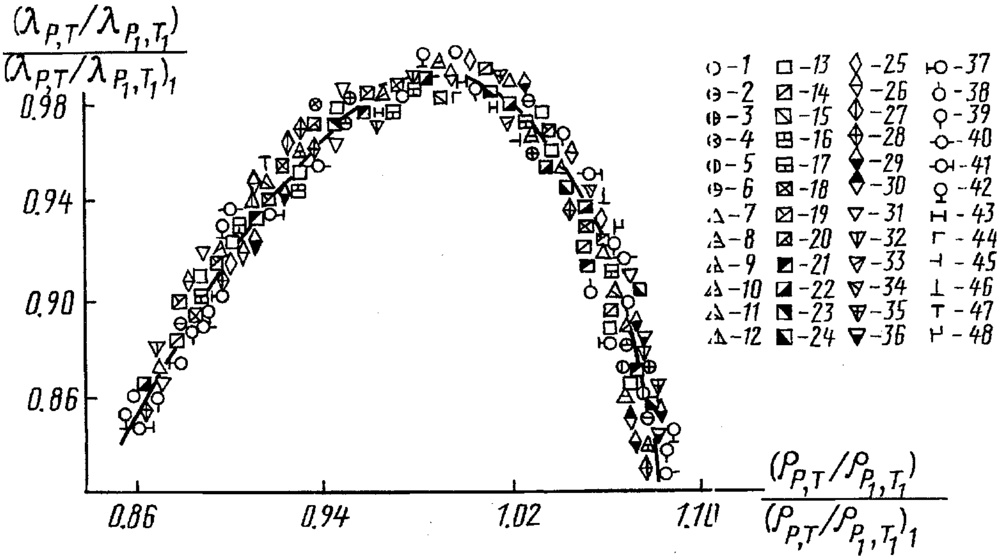


Fig. 1. Dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})/(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ on $(\rho_{P,T}/\rho_{P_1,T_1})$ / $(\rho_{P,T}/\rho_{P_1,T_1})_1$ of aqueous hydrazine solutions within wide ranges of temperatures and pressures: 1-6) 90% N_2H_4 + 10% H_2O; 7-12) 80% N_2H_4 + 20% H_2O; 13-18) 70% N_2H_4 + 30% H_2O; 19-24) 60% N_2H_4 + 40% H_2O; 25-30) 50% NH_4 + 50% H_2O; 31-36) 40% N_2H_4 + 60% H_2O; 37-42) 30% N_2H_4 + 70% H_2O; 43-48) 20% N_2H_4 + 80% H_2O.

From Eqs. (2) and (3) we obtain

$$\lambda = \left[-68.32\left(\frac{\rho}{\rho_1}\right)^2 + 130.2\left(\frac{\rho}{\rho_1}\right) - 60.87\right]\left(1.03\cdot 10^{-5}\eta_{H_2O}^2 + 2.84\cdot 10^{-4}\eta_{H_2O} + 0.325\right). \quad (4)$$

Knowing n_{H_2O} and the temperature dependence of the density, one can calculate using Eq. (4) the heat conductivity at atmospheric pressure of aqueous hydrazine solutions previously not studied experimentally with an error of 1.5–3%.

In order to establish a relationship between the heat conductivity and density of aqueous hydrazine solutions at high parameters of state we used the following functional dependence based on the thermodynamic similarity theory

$$\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right) \Big/ \left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1 = f\left[\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right) \Big/ \left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1\right], \quad (5)$$

where $\lambda_{P,T}$ is the heat conductivity at pressure P and temperature T; λ_{P_1,T_1} is the heat conductivity at pressure P_1 and temperature T_1; $(\lambda_{P,T}/\lambda_{P_1,T_1})$ are the values of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ at $(\rho_{P,T}/\rho_{P_1,T_1})$; $(\rho_{P,T}/\rho_{P_1,T_1})_1 = 1.09$; $P_1 = 4.9\cdot 10^6$ Pa and $T_1 = 473$ K.

The fulfilment of the condition (5) for all acqueous hydrazine solutions is shown in Fig. 1, from which is clear that the experimental points fit the common curve well. The equation of this curve is as follows:

$$\frac{(\lambda_{P,T}/\lambda_{P_1,T_1})}{(\lambda_{P,T}/\lambda_{P_1,T_1})_1} = \sqrt{\left(-21.34\left[\left(\frac{\rho_{P,T}}{\rho_{P_1,T_1}}\right) \Big/ \left(\frac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)_1\right]^2 + 41.68\left[\left(\frac{\rho_{P,T}}{\rho_{P_1,T_1}}\right) \Big/ \left(\frac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)_1\right] - 19.36\right)}. \quad (6)$$

Using Eq. (6) one can calculate the heat conductivity $\lambda_{P,T}$ of aqueous hydrazine solutions as a function of density $\rho_{P,T}$ [3], provided the values λ_{P_1,T_1}, ρ_{P_1,T_1}, and $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ are known.

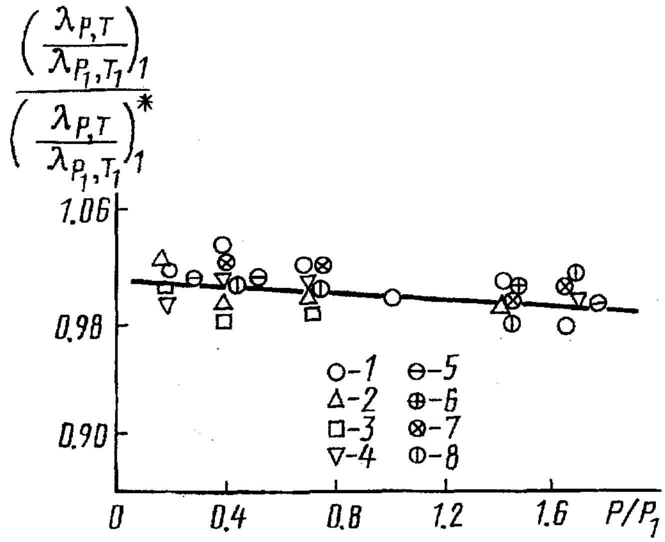


Fig. 2. Dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1/(\lambda_{P,T}/\lambda_{P_1,T_1})_1^*$ on the relative pressure P/P_1 for the solutions under investigation: 1) 90% N_2H_4 + 10% H_2O; 2) 80% N_2H_4 + 20% H_2O; 3) 70% N_2H_4 + 30% H_2O; 4) 60% N_2H_4 + 40% H_2O; 5) 50% N_2H_4 + 50% H_2O; 6) 40% N_2H_4 + 60% H_2O; 7) 30% N_2H_4 + 70% H_2O; 8) 20% N_2H_4 + 80% H_2O.

Verification of the dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ on pressure has shown that the experimental data for individual solutions fit the different straight lines.

In order to obtain a unique straight line for all aqueous hydrazine solutions the experimental data were approximated by the following functional dependence:

$$\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1 \Big/ \left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1^* = f\left(\frac{P}{P_1}\right), \tag{7}$$

where $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ are the values of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1^*$ at pressure P_1; $P_1 = 29.43\cdot 10^6$ Pa. The accuracy of the approximation can be judged from Fig. 2. Experimental data for all solutions are described by the equation

$$\frac{(\lambda_{P,T}/\lambda_{P_1,T_1})_1}{(\lambda_{P,T}/\lambda_{P_1,T_1})_1^*} = 1.135 - 8.75\cdot 10^{-2}\frac{P}{P_1}. \tag{8}$$

The dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1^*$ for the objects under investigation on the molar concentration of water is as follows:

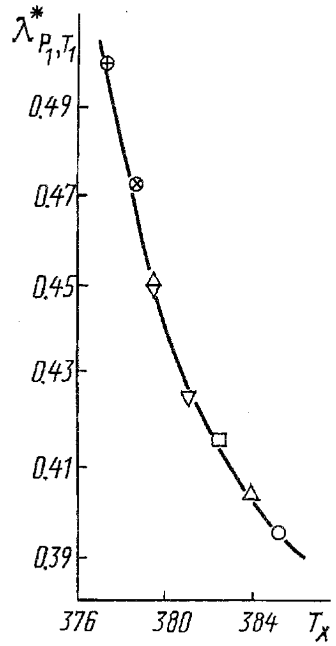
$$(\lambda_{P,T}/\lambda_{P_1,T_1})_1^* = -\,2.798\cdot 10^{-5}\eta_{H_2O}^2 + 1.656\cdot 10^{-3}\eta_{H_2O} + 1.035\,. \tag{9}$$

From Eqs. (8) and (9) we obtain

$$(\lambda_{P,T}/\lambda_{P_1,T_1})_1 = \left(1.135 - 8.75\cdot 10^{-2}\frac{P}{P_1}\right)\left(-\,2.798\cdot 10^{-5}\eta_{H_2O}^2 + 1.656\cdot 10^{-3}\eta_{H_2O} + 1.035\right). \tag{10}$$

For λ_{P_1,T_1} and ρ_{P_1,T_1} of the aqueous hydrazine solutions under investigation the following dependences were used:

$$\frac{\lambda_{P_1,T_1}}{\lambda_{P_1,T_1}^*} = f\left(\frac{P}{P_1}\right); \quad \frac{\rho_{P_1,T_1}}{\rho_{P_1,T_1}^*} = f\left(\frac{P}{P_1}\right), \tag{11}$$



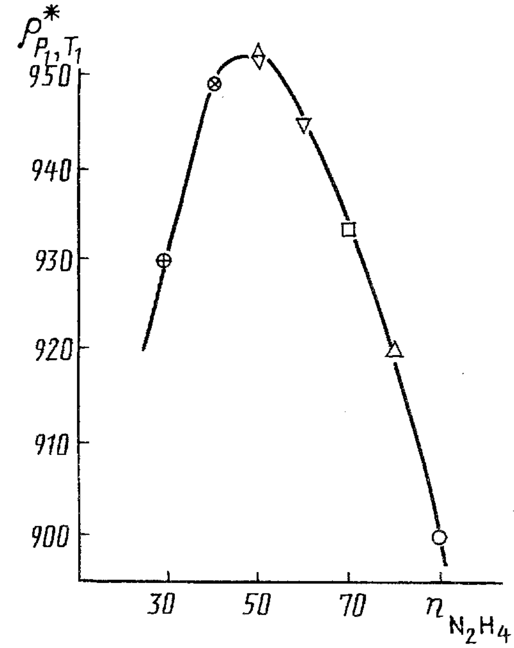


Fig. 3. Dependence of $\lambda^*_{P_1,T_1}$, W/(cm·K) on the boiling temperature T_x^{boil} of the solutions. The notation is the same as in Fig. 2.

Fig. 4. Dependence of $\rho^*_{P_1,T_1}$, kg/m^3 on the mass concentration of hydrazine $n_{N_2H_4}$, %. The notation is the same as in Fig. 2.

where $P_1 = 29.43 \cdot 10^6$ Pa.

The particular forms of these dependences are straight lines:

$$\frac{\lambda_{P_1,T_1}}{\lambda^*_{P_1,T_1}} = 8.33 \cdot 10^{-2} \frac{P}{P_1} + 0.917 \,; \quad \frac{\rho_{P_1,T_1}}{\rho^*_{P_1,T_1}} = 3.417 \cdot 10^{-2} \frac{P}{P_1} + 0.965 \,. \tag{12}$$

Analysis of the data on $\lambda^*_{P_1,T_1}$ and $\rho^*_{P_1,T_1}$ has shown that they are functions of T_x, K, and the molar concentration of hydrazine $n_{N_2H_4}$, where $T_x = x_1 T_{N_2H_4} + x_2 T_{H_2O}$ is the boiling temperature of the solution.

The fulfilment of the dependences $\lambda^*_{P_1,T_1} = f(T_x)$ and $\rho^*_{P_1,T_1} = f(n_{N_2H_4})$ is shown in Figs. 3 and 4. These curves are described by the equations

$$\begin{aligned} \lambda^*_{P_1,T_1} &= -\,8.052 \cdot 10^{-5}\, T_x^2 + 4.943 \cdot 10^{-2}\, T_x - 6.7 \,, \quad \mathrm{W/(m \cdot K)} \,; \\ \rho^*_{P_1,T_1} &= -\,3.369 \cdot 10^{-8} \eta^2_{N_2H_4} + 3.475 \eta_{N_2H_4} + 859.3 \,, \quad \mathrm{kg/m^3} \,. \end{aligned} \tag{13}$$

We write Eqs. (12) in terms of (13) in the following form:

$$\begin{aligned} \lambda_{P_1,T_1} &= \left(8.33 \cdot 10^{-2} \frac{P}{P_1} + 0.917 \right) \left(-\,8.052 \cdot 10^{-5}\, T_x^2 + 4.943 \cdot 10^{-2}\, T_x - 6.7 \right) ; \\ \rho_{P_1,T_1} &= \left(3.417 \cdot 10^{-2} \frac{P}{P_1} + 0.965 \right) \left(-\,3.369 \cdot 10^{-2} \eta^2_{N_2H_4} + 3.475 \eta_{N_2H_4} + 859.3 \right) . \end{aligned} \tag{14}$$

Substituting (8), (9), (17), and (18) into (6) we obtain the following relationship for calculations of heat conductivity of aqueous hydrazine solutions as a function of temperature and pressure

$$\lambda_{P_1,T_1} = (1.135 - 2.973 \cdot 10^{-9} P)\,(-\,2.798 \cdot 10^{-5} \eta^2_{H_2O} + 1.656 \cdot 10^3 \eta_{H_2O} + 1.035) \times$$

$$\times (2.824 \cdot 10^{-9} P + 0.917)(-8.052 \cdot 10^{-5} T_x^2 + 4.943 \cdot 10^{-2} T_x - 6.7) \times$$

$$\times \sqrt{-17.96 \rho_{P,T}^2 / D^2 + 38.2 \rho_{P,T} / D - 19.36}\,, \qquad (15)$$

where $D = \left[(1.161 \cdot 10^{-9} P + 0.965)(-3.369 \cdot 10^{-2} \eta_{N_2H_4}^2 + 3.475 \eta_{N_2H_4} + 859.3) \right]^2$.

Equation (15) establishes a relationship between the heat conductivity and the density of aqueous hydrazine solutions at various temperatures, pressures, and molar concentrations.

Using Eq. (15) with experimental values of the density of solutions at various temperatures and pressures [3], one can calculate their heat conductivity within the temperature range of 293-500 K and within the range of pressures of 0.101–98.1 MPa with an error of 2–4%; for certain points, however, this error is as much as 8%.

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