# THERMAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AT 20-340°C

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The experimental apparatus is described. Experimental data are given on the thermal conductivity of aqueous solutions of potassium chloride at concentrations 1% and 3% by mass and at temperatures 20-340°C.

For more extensive utilization of geothermal energy, it is necessary to study the thermophysical properties of aqueous solutions of electrolytes, as the main components of geothermal waters, in a wide range of temperatures and pressures. There is no information in the reference literature on the thermal conductivity of an aqueous solution of KCl at high temperatures and pressures. Our investigations of the thermal conductivity of an aqueous solution of KCl cover the temperature range 20-340°C, the pressure range 2-14 MPa, and concentrations 1% and 3% by mass. We chose the method of a plane layer to make the measurements, and we set up the experimental apparatus in Sirota's scheme [1].

The apparatus consists of a constant-temperature vessel containing the measurement unit, relieved of pressure, and a system for producing and measuring pressure. In Fig. 1 we give a schematic diagram of the measurement unit, which consists of a hot plate 2 and a cold plate 17, connected together by a metal ring. The investigated substance fills the gap between the measuring plates. The measurement unit is made of 1Kh18N10T steel and the protective plate 5 is made of copper. The upper plate 2, the protective ring 21, and the connector 18 between them, with a thickness 0.2 mm, are made from a single steel blank. Along the periphery of the ring 21 and the lower plate 17 there are thin flanges with a thickness 0.5 mm, which are welded together by an argon weld through the gasket 19. The working surfaces of the plates were preliminarily lapped and polished. The gap between the working plates is set and fixed by three washers 11, with a diameter 4 mm, made of 1Kh18N10T steel. The set of washers was ground and polished preliminarily using a well-defined technology. From the set of finished washers we selected specimens whose thickness differed by no more than 0.001 mm. The thickness of the washers and the cleanness of their finish were monitored and measured with a UIM-21 microscope. For the measurement unit we selected three washers with a thickness 1.342 ± 0.001 mm. Annular grooves were made in the lower plate around the contact points 12 with the washers to reduce the heat flow. The grooves are used simultaneously for the supply and removal of the investigated substance in the working gap of the unit. The substance was supplied through the axis of the lower plate, the channel 23, and removed through a capillary (not shown in Fig. 1). Such a flow-through system permits the rapid and reliable filling of the working section with the investigated substance. The cup 8 fixes the entire assembly of the constant-temperature, high-pressure vessel 9. To relieve the load and eliminate deformation or destruction of the working section of the measurement unit, the vessel is filled with nitrogen at the same pressure as the working substance in the gap between the plates. The low thermal conductivity of the gas minimizes heat leaks from the hot plate. The model of conductive heat transfer in the plane-parallel layer of the investigated substance is implemented by the heat flux directed from the hot upper plate to the cold lower plate. For this purpose, concentric grooves are cut into the hot plate, in which a nichrome heater is located. Heat leaks from the main heater 1 are compensated for by protective heaters 6 and 7, located in the protective ring 21 and the plate 5. The coils of the main and protective heaters 10, made of wire 0.1 mm in diameter, were specially treated with organic silicate materials, which ensured their reliable electrical insulation when operating in the high-temperature range. The gaps 22 between the main working section of the hot plate 2 and the protective zones 21 were filled with quartz wool, preventing the development of uncontrolled convective thermal gas flows. The heaters

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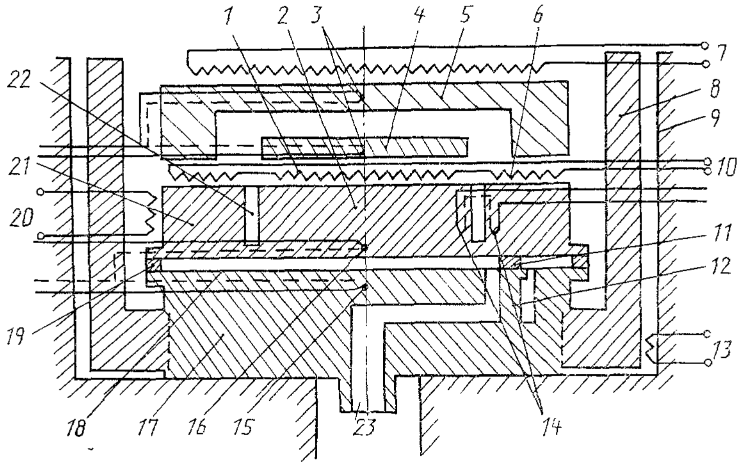

Fig. 1. Schematic diagram of the measurement unit.

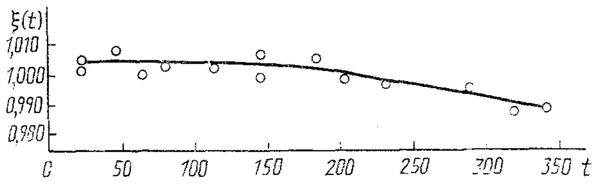

Fig. 2. Temperature dependence of the instrument constant. t, °C.

13 and 20 are designed to equalize the temperature field and achieve isothermal conditions in the working section for measuring the thermal conductivity of the liquid. The temperature difference between the plates was measured with thermocouples 15 and 16 located in radially drilled channels. Heat fluxes from the working heater in the axial direction are compensated for with a three-junction differential thermocouple 3, placed in plates 4 and 5, and those in the radial direction are compensated for with a nine-junction differential thermocouple 14, placed uniformly on both sides of the connector 18. The main and protective thermocouples were made of copper and Copel wires 0.2 mm in diameter and were specially treated.

The measurement unit is placed in a high-pressure vessel inside a vessel of constant-temperature liquid. The automatic regulation system maintains a constant working temperature to within ±0.01°C. The thermocouple and heater leads are brought out from the zone of high temperatures and pressures by means of a system of special rings that are insulated from each other. To eliminate possible errors associated with stray thermal emf, the entire set of leads is placed in a vessel of constant-temperature oil. The temperature of the constant-temperature system of the measurement unit is determined with a PTS-10 standard platinum resistance thermometer. Pressure in the apparatus is produced and maintained by gas heated in thermal compressors. The system of separated vessels makes possible the automatic equalization of the pressures of the gas and the investigated liquid. The allowable pressure drop between the liquid and gas is monitored with a sensitive differential manometer. The gas pressure is measured with an MP-600 load-piston manometer. Before each test run, the "zero readings" of the thermocouples were taken with the heaters of the unit turned off. During the main measurements, the power of the protective heaters was set so that the readings of the protective thermocouples were equal to the "zero readings."

The thermal conductivity coefficient for the plane layer of investigated liquid is determined from the equation

$$\lambda = \frac{Q\delta}{F\Delta T} = \frac{q\delta}{\Delta T}. \tag{1}$$

The fraction of the radiative component of the heat flux increases with increasing temperature. If heat transfer by conduction and radiation in a light-absorbing medium is assumed to be additive, then the specific heat flux between plates of infinite size can be expressed by the well-known relationship [2]

$$q = \frac{\lambda \Delta T}{\delta} + \frac{4\sigma_0 n^2 T^3 \Delta T}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1 + \frac{3}{4}\tau}. \tag{2}$$

The effective thermal conductivity is determined by the expression

$$\lambda_e = \lambda + \frac{4\sigma_0 n^2 T^3 \delta}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1 + \frac{3}{4}\tau}, \quad \lambda_e = \lambda + \Delta\lambda_{rad} \tag{3}$$

A number of papers have been devoted to the theoretical solution of the problem of combined radiative—conductive heat transfer in a plane layer of gray medium [3-5].

According to Andrianov [5], the correction for the radiative component of thermal conductivity is

$$\Delta\lambda_{rad} = A_e 4\sigma_0 T^3 \delta. \tag{4}$$

The quantity $A_e$ is determined from Andrianov's diagram [5]. In this case, the thermal conductivity of the investigated substance will be

$$\lambda = \frac{q\delta}{\Delta T} - \Delta\lambda_{rad} \tag{5}$$

Calculation of the corrections for the influence of the boundary conditions and the isothermicity of the temperature field in the working section of the measurement unit is complicated. When a relative method is used to measure the thermal conductivity of aqueous solutions of electrolytes, these corrections can be taken into account by calibration to a standard substance. Water serves as such a standard in our investigations. Water is the solvent in the investigated solutions, and its thermophysical properties have been investigated in detail in a wide range of pressures and temperatures. To determine the constant of the measurement unit, we used reference data on the thermal conductivity of water [6] and calibrated the instrument against deaerated, distilled water in the temperature range 20-350°C and the pressure range 0.1-20 MPa. The instrument constant was determined from the equation

$$\xi(t) = \frac{\lambda_w^{[6]}}{\lambda_w}, \tag{6}$$

where $\lambda_w = q\delta/\Delta T_w - \Delta\lambda_{rad.w}$.

The temperature dependence of the instrument constant is given in Fig. 2.

The thermal conductivity of the investigated solution is determined from the equation

$$\lambda_{sol} = \xi(t)\left(\frac{q\delta}{\Delta T_{sol}} - \Delta\lambda_{rad.sol}\right). \tag{7}$$

The calibration of the instrument and the subsequent measurements were carried out

TABLE 1. Experimental Data on the Thermal Conductivity of an Aqueous Solution of Potassium Chloride

| p, MPa | S = 1% by mass | | S = 3% by mass | |
|---|---|---|---|---|
| | $t$, °C | $\lambda$, $10^3$ W/m·deg | $t$, °C | $\lambda$, $10^3$ W/m·deg |
| 5 | 31,98 | 618 | 23,25 | 603 |
| | 61,20 | 650 | 60,85 | 646 |
| | 83,79 | 667 | 84,04 | 665 |
| | 104,25 | 676 | 103,74 | 673 |
| | 123,62 | 679 | 123,23 | 676 |
| | 144,12 | 680 | 139,80 | 678 |
| | 173,77 | 676 | 166,19 | 675 |
| | 197,33 | 664 | 196,83 | 661 |
| | 234,61 | 631 | 237,49 | 630 |
| 10 | 261,13 | 608 | 257,49 | 604 |
| | 288,74 | 566 | 281,01 | 577 |
| 12 | 317,32 | 515 | 305,26 | 540 |
| 14 | 339,6 | 465 | 334,03 | 484 |

TABLE 2. Thermal Conductivity of Water [6] and of Aqueous Solutions of Potassium Chloride, λ, $10^3$ W/m·deg, on the Saturation Line

| $t$, °C | KCl concentration, mass % | | | $t$, °C | KCl concentration, mass % | | |
|---|---|---|---|---|---|---|---|
| | 0[6] | 1 | 3 | | 0[6] | 1 | 3 |
| 20 | 599 | 597 | 593 | 200 | 663 | 661 | 657 |
| 40 | 628 | 625 | 621 | 220 | 648 | 646 | 642 |
| 60 | 649 | 646 | 641 | 240 | 628 | 626 | 623 |
| 80 | 664 | 661 | 656 | 260 | 605 | 603 | 600 |
| 100 | 676 | 672 | 666 | 280 | 577 | 575 | 573 |
| 120 | 682 | 679 | 673 | 300 | 544 | 542 | 539 |
| 140 | 684 | 681 | 676 | 320 | 507 | 505 | 503 |
| 160 | 680 | 678 | 674 | 340 | 464 | 463 | 462 |
| 180 | 674 | 672 | 667 | | | | |

with allowance for the conditions of the development of convection in the plane layer. The observance of strict isothermicity of the measurement plates, achieved by the system of compensating heaters, prevents the development of convective flows in the layer of investigated liquid. In the course of the measurements, we monitored for convection by measuring the effective thermal conductivity with different temperature drops in the working layer of liquid. Independence of the thermal conductivity on the temperature drop indicated an absence of convective heat transfer. In our measurements, the Rayleigh numbers at t = 300°C reached Ra = 2100.

To prepare the KCl aqueous solutions, we used salt of analytical purity and twice-distilled water. The concentration of the solutions was monitored with a pycnometer. The thermal conductivity of the water and the KCl aqueous solutions was measured at the same heat fluxes in the working section at the 5, 10, 12, and 14 MPa isobars. Upon reaching a steady state, the experiment was conducted at different fixed heat fluxes, and the resulting thermal conductivity was determined from these measurement data. Experimental values of the thermal conductivity of an aqueous solution of potassium chloride are given in Table 1. The relative rms error in measuring the thermal conductivity coefficient was 1.3-1.6% at the confidence level p = 0.95, and the maximum error was 1.4-2.0%.

In [7, 8] it was shown that the influence of pressure on the thermal conductivity of water and aqueous solutions of electrolytes within the limits of the measured pressures is slight, and we can take

$$\left(\frac{\partial\lambda}{\partial p}\right)_{\text{w}} = \left(\frac{\partial\lambda}{\partial p}\right)_{\text{sol}} .$$

In this case, the thermal conductivity of a solution on the saturation line will be

$$\lambda_{\text{sol.sat}} = \lambda_{\text{sol.p}} - \left(\frac{\partial\lambda}{\partial p}\right)_{\text{sol}} (p - p_{\text{s}}).$$

An analysis of Table 2 shows that in the entire investigated range of temperatures, the thermal conductivity of the solution relative to the thermal conductivity of water decreases with increasing concentration, which is due to the polarizability of dissolved ions and the degree of destruction of the water structure.

## NOTATION

Q, heat flux; δ, thickness of the liquid layer; F, plate area; ΔT, temperature drop in the liquid layer; q, specific heat flux; $\sigma_0$, Boltzmann constant; n, index of refraction of the investigated medium; $\varepsilon_1$ and $\varepsilon_2$, emissivity of the plates; τ, optical depth of the medium; T, absolute temperature of the hot plate; λ, molecular thermal conductivity; $\Delta\lambda_{\text{rad}}$, correction for radiative heat transfer; $A_{\text{e}}$, generalized reduced emissivity; $\lambda_{\text{sol.p}}$, thermal conductivity of the solution at the pressure p; $\lambda_{\text{sol.sat}}$, thermal conductivity of the solution at the saturation pressure $p_{\text{s}}$.

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# STUDY OF POROUS-SUBLIMATIONAL COOLING

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A nonmonotonic change in the temperature of the cooled surface and a nonmonotonic increase in the heat-transfer coefficient with an increase in the thermal load are observed in porous-sublimational cooling, and an explanation is offered for these events. The theory is compared with experimental data.

Porous-sublimational cooling [1-3] has several advantages over other methods of cooling that use solid cryogens [4]. Porous-sublimational cooling makes it possible to avoid using mechanical devices to press the solid cryogen to the surface being cooled by contact cooling [4]. This appreciably simplifies the design of the cooling unit and improves the reliability of cryosublimation systems. Experiments in [2] showed that heat transfer between the cryogen and the object being cooled is considerably more intense in porous-sublimational cooling than in other types of cooling which employ solid cryogens. However, the authors of [2] used a porous body composed of copper grids. Here, the thermal conductivity of the porous skeleton of the body was relatively low, and its thermal contact with the surface being cooled was unsatisfactory. In addition, the fact that the temperature and pressure fields in the body were not unidimensional made it impossible to compare the theory [1-3] with the experiment [2].

1. Description of Experiment. In the present investigation, we study the accumulation and sublimation of a solid cryogen in a porous specimen 1 (Fig. 1) having a porosity $\varepsilon_s$ = 0.62. The specimen was obtained by sintering powdered copper of grade PMS-N (GOST 460-75). The cylindrical porous specimen 1 was sintered with a disk 2 of monolithic copper containing a sensor 3 (germanium thermal converter) to measure the temperature of the surface 4 being cooled. Mounted on the disk 2 is an electric heater 5 made of a constantin wire connected to a stabilized current source. The foam plastic housing 6 provides thermal insulation from the surrounding cryogen 7, the temperature of which $T_L$ is measured with sensor 8. The lateral surface of the specimen 1 is impermeable to gases (being coated with a layer of vacuum lubricant), so the vapor from the cryogen can leave only through the evacuation surface 9. The entire cold accumulator (Fig. 1) is placed in a transparent cryostat connected to an AVZ-20D vacuum pump. Measurements of the temperatures and power of the heater were made automatically with an SM-4 computer [2, 5].

Experiments were conducted in the following manner. Liquid cryogen (nitrogen or hydrogen) was poured into the cavity of the cryostat so that the cold accumulator (Fig. 1) would be "frozen" into the solid state after solidification of the liquid. We then pumped out the

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