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Thermal Conductivity of Aqueous Solutions of NaCl and KCl at High Pressures

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This paper presents new experimental measurements of the thermal conductivity of aqueous solutions of NaCl and KCl at high pressures. The measurements were made with a parallel-plate apparatus. The temperatures covered the range from 293 to 473 K at pressures up to 100 MPa and concentrations from 0.025 to 0.25 mass fraction of NaCl and KCl. The measurements included 6 isobars at pressures from 0.1 to 100 MPa at intervals of 20 MPa, 10 isotherms at temperatures from 293 to 473 K at intervals of 20 K, and 6 isopleths at concentrations from 0.025 to 0.25 mass fraction of NaCl and KCl at intervals of 0.05. The precision of the measurements was ±1.6%. The thermal conductivity obtained for $NaCl + H_2O$ and $KCl + H_2O$ was compared with data of other authors, with satisfactory agreement. The viability of the technique was confirmed and the essential features of a high-precision instrument were established.

KEY WORDS: aqueous solutions; high pressures; KCl; NaCl; thermal conductivity.

1. INTRODUCTION

NaCl and KCl are important primary salts in seawater and most other natural waters and in many industrially important fluids. Thermal-conductivity data on electrolyte aqueous solutions are required in the development and utilization of many industrial energy systems. For example, data on geothermal brines and seawater; which can be considered as mixtures of aqueous solutions of NaCl and KCl, are needed for geothermal and ocean thermal-energy utilization devices and for desalination of seawater. In addition, there is considerable interest in the transport properties of

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$NaCl + H_2O$ and $KCl + H_2O$ from the standpoint of the theory of ionic solutions. There are many interesting differences between ionic and nonionic fluids [1, 2]. However, measurements of the thermal conductivity of these fluids have so far been restricted to limited ranges of temperature, pressure, and concentration. We have developed a parallel-plate apparatus for making precise measurements of the thermal conductivity of electrically conducting liquids. In this study, we measured the thermal conductivity of aqueous NaCl and KCl solutions from 293 to 473 K and at pressures up to 100 MPa and concentrations from 0.025 to 0.25 mass fractions of NaCl and KCl. The experiments were made in the liquid-phase region.

Previously the thermal conductivity of aqueous solutions of NaCl and KCl has been investigated by a number of authors [3–13, 17]. Table I identifies the selected primary data sets, indicating their individual pressure, temperature, and concentration ranges and the method of measurement. In the literature, a considerable amount of data is available

Table I. Measurements of the Thermal Conductivity of Aqueous NaCl and KCl Solutions

First author [Ref. No.]	Year	System	Method	Temperature range (K)	Maximum pressure (MPa)	Concentrations (mass fraction)
Riedel [3]	1951	$NaCl + H_2O$ $KCl + H_2O$	Coaxial cylinder Parallel-plate	293	0.1	0.05–0.25 0.05–0.20
Kapustinskii [4]	1955	$NaCl + H_2O$ $KCl + H_2O$	Parallel-plate	293	0.1	0.02–0.25 0.02–0.25
Vargaftik [5]	1956	$NaCl + H_2O$ $KCl + H_2O$	Hot wire	293–303	0.1	0–0.20 0–0.20
Davis [6]	1971	$NaCl + H_2O$ $KCl + H_2O$	Hot wire	288–318	0.1	0.03–0.15 0.03–0.15
Yusufova [7]	1975	$NaCl + H_2O$	Parallel-plate	293–603	2	0.02–0.25
Nagasaka [9]	1983	$NaCl + H_2O$	Hot wire	273–353	40	0.055–0.226
Nagasaka [13]	1984	$NaCl + H_2O$ $KCl + H_2O$	Hot wire	273–473	50	0.05–0.23
Eldarov [8]	1986	$NaCl + H_2O$	Hot wire	293–473	30	0.05–0.30
Magomedov [11]	1989	$NaCl + H_2O$ $KCl + H_2O$	Parallel-plate	293–603	100	0.15–0.23
Ganiev [17]	1990	$NaCl + H_2O$	Coaxial cylinder	293–673	100	0.0–0.19
Safronov [10]	1990	$KCl + H_2O$	Coaxial cylinder	293–473	100	0.05–0.10

for thermal conductivity of $NaCl + H_2O$ and $KCl + H_2O$ at atmospheric pressure [3–7], but there are only a limited amount of data at higher pressures [8–11, 13, 17]. Most of the these measurements were carried out with a hot-wire technique.

2. EXPERIMENTS

The thermal conductivity of aqueous NaCl and KCl solutions was measured with a parallel-plate apparatus otiginally developed by Amirkhanov and Adamov [14] and further improved by Magomedov [12]. This apparatus is suitable for measuring the thermal conductivity of liquids and gases at pressures up to 200 MPa and temperatures up to 500 K. The thermal-conductivity cell is shown in Fig. 1. The cell has a cylindrical form with a 21-mm height and 90-mm outer diameter. The cell is made from a stainless-steel 12X18H10T. The thermal conductivity cell consists of three plates: guard plate (1), upper plate (2), and lower plate (6). The guard plate is surrounded by guard heater (4). The thickness *d* of the gap between the upper and the lower plate is fixed by supports (11).

The upper plate has a diameter of 68.05 mm. The lower plate has a thickness of 9 mm. The cell is located in a high-pressure vessel made of high-strength steel. The fluid surrounds the cell and fills the gaps between the upper and the lower plates. Both the lower surface of the upper plate and the upper surface of the lower plate are highly polished to decrease heat transfer by radiation. The gap between the upper and the lower plates is $d = 0.3010 \pm 0.0001$ mm. The gap between the guard plate and the upper plate is 1 mm and is filled with glass fiber.

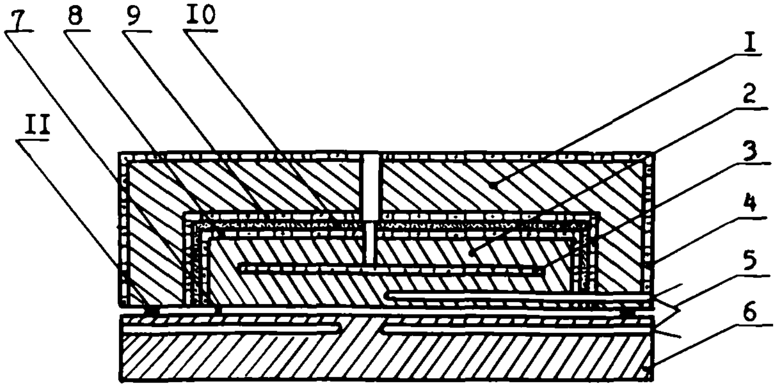

Fig. 1. Parallel-plate thermal conductivity cell: 1, guard plate; 2, upper plate; 3, inner heater; 4, guard heater; 5, differential thermocouple; 6, lower plate; 7, fluid layer; 8 and 9, arms of Wheatstone bridge; 10, glass-fiber layer; 11, support.

Table II. Experimental Results for the Thermal Conductivity of Aqueous Solutions of NaCl

	$\lambda(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$ at $P(\mathrm{MPa})$					
$T(\mathrm{K})$	0.1–2	20	40	60	80	100
			$x = 0.025$ mass fraction of NaCl			
293	594	603	611	619	629	639
313	624	634	645	654	663	673
333	650	659	668	679	690	700
353	669	678	689	700	712	722
373	680	690	701	713	725	737
393	687	697	707	719	731	744
413	687	699	709	723	737	749
433	680	694	707	720	735	747
453	673	687	700	714	727	743
473	658	672	696	700	715	730
			$x = 0.05$ mass fraction of NaCl			
293	591	598	607	616	625	633
313	620	630	640	649	659	669
333	647	655	665	675	685	695
353	665	674	686	696	706	718
373	677	686	698	709	721	731
393	681	693	704	718	728	739
413	684	695	706	719	730	742
433	678	690	704	716	728	741
453	670	681	696	709	724	737
473	655	669	683	695	711	725
			$x = 0.10$ mass fraction of NaCl			
293	588	592	600	608	616	624
313	615	625	633	641	650	660
333	640	650	658	668	677	686
353	649	670	677	689	696	707
373	668	678	690	700	710	721
393	676	685	696	707	717	727
413	677	686	698	710	721	732
433	672	682	696	707	718	730
453	663	674	687	700	712	724
473	649	661	674	685	697	712

Table II. *(Continued)*

	$\lambda(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$ at $P(\mathrm{MPa})$					
T(K)	0.1-2	20	40	60	80	100
			$x = 0.15$ mass fraction of NaCl			
293	580	586	593	601	610	617
313	611	620	625	637	641	650
333	635	643	650	659	668	677
353	655	660	670	680	689	696
373	663	672	682	692	700	708
393	670	680	687	697	707	717
413	670	680	690	701	711	722
433	666	677	689	699	708	719
453	657	667	680	690	701	713
473	643	654	665	675	687	700
			$x = 0.20$ mass fraction of NaCl			
293	574	579	585	593	600	605
313	604	610	618	624	630	638
333	627	633	642	650	657	664
353	645	654	661	668	677	685
373	658	664	672	680	690	698
393	664	671	679	690	697	705
413	665	674	682	691	700	708
433	658	668	678	687	697	706
453	650	658	669	678	690	700
473	637	646	656	666	678	690
			$x = 0.25$ mass fraction of NaCl			
293	566	573	578	584	590	597
313	597	602	610	616	623	628
333	621	625	633	640	647	653
353	640	645	652	661	665	673
373	650	656	664	673	678	688
393	654	662	670	677	686	696
413	657	663	671	680	688	698
433	651	660	670	678	685	694
453	643	650	660	670	678	688
473	630	640	647	657	666	678

Table III. Experimental Results for the Thermal Conductivity of Aqueous Solutions of KCl

	$\lambda(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$ at P(MPa)					
T(K)	0.1-2	20	40	60	80	100
$x = 0.025$ mass fraction of KCl						
293	590	598	610	618	628	637
313	624	629	641	651	662	669
333	647	656	666	678	689	698
353	666	675	686	699	710	720
373	676	689	697	711	722	732
393	684	696	703	718	729	742
413	684	697	707	720	731	744
433	679	691	705	719	729	742
453	670	685	698	712	725	738
473	657	670	685	700	714	729
$x = 0.05$ mass fraction of KCl						
293	588	595	605	613	620	629
313	617	625	635	646	653	662
333	641	650	660	671	680	690
353	659	670	680	690	700	711
373	672	680	692	702	714	724
393	678	688	700	710	722	733
413	678	689	702	713	726	737
433	675	685	698	710	722	735
453	665	677	691	701	715	730
473	650	665	678	691	705	718
$x = 0.10$ mass fraction of KCl						
293	576	584	591	600	607	613
313	607	614	625	630	640	649
333	631	638	647	657	665	674
353	647	657	666	675	686	696
373	660	670	680	689	700	710
393	666	675	686	696	706	718
413	668	676	688	700	711	722
433	662	672	684	694	706	718
453	652	665	675	688	702	715
473	641	652	662	676	687	701

Table III. *(Continued)*

	λ(mW · m^{-1} · K^{-1}) at P(MPa)					
T(K)	0.1-2	20	40	60	80	100
			$x = 0.15$ mass fraction of KCl			
293	567	571	580	586	594	601
313	600	605	612	621	629	636
333	620	628	635	645	652	658
353	638	646	654	662	672	678
373	650	656	666	674	684	694
393	654	664	673	683	693	703
413	657	665	675	685	695	706
433	652	660	670	680	691	701
453	642	652	662	672	683	693
473	630	640	650	661	671	683
			$x = 0.20$ mass fraction of KCl			
293	557	561	568	574	582	588
313	587	593	600	607	615	622
333	600	612	623	630	637	644
353	626	633	640	650	659	666
373	635	645	654	659	666	676
393	641	650	660	667	675	683
413	642	653	661	670	680	689
433	640	647	656	665	675	687
453	630	640	650	658	670	680
473	617	627	637	645	657	667
			$x = 0.25$ mass fraction of KCl			
293	544	552	558	564	570	575
313	574	580	587	593	599	603
333	596	604	610	615	621	627
353	612	620	627	633	640	648
373	622	630	638	644	650	658
393	628	635	642	650	658	666
413	630	636	645	652	659	667
433	624	633	640	650	658	664
453	616	624	632	643	652	658
473	605	613	619	627	637	645

Table IV. Dependence of the Cell Constant on Temperature

T (K)	d/S (m^{-1})
298	0.082765
323	0.082737
348	0.082270
373	0.082675
398	0.082634
423	0.082604
448	0.082570
473	0.082541

Differential thermocouples are used for the measurement of the temperature difference between the upper and the lower plates. This temperature difference can be determined with a precision of approximately ±0.0015 K. The thermocouples are made from chromel–copel wire with a double insulation of silk and are 0.2 mm in diameter. They are insulated and fitted into stainless-steel sheaths, which slide into the pressure tubes fitted in the cell. The thermocouples are located at a distance of 0.5 mm from the surface of the liquid layer. The temperature of the upper and the lower plates is measured with a chromel–copel thermocouple with a precision of ±0.02 K.

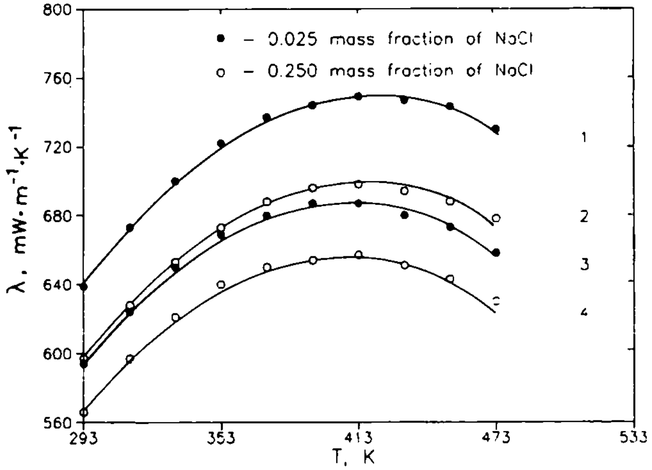

Fig. 2. Dependence of the thermal conductivity of aqueous solutions of NaCl on temperature at a number of pressures and concentrations: 1 and 2, 100 MPa; 3 and 4, 0.1 MPa.

The thermocouples were calibrated against a platinum resistance thermometer. The cell described above was used in conjunction with an automatic Wheatstone bridge.

The pressure vessel is placed in the thermostat, which maintains the operating temperature within ±0.01 K. The desired temperature is reached in 10 h. Before filling, the vessel is heated to 423 K and evacuated during 5 h.

The wires of the electrical system are led outside the bath, protected by a tube of stainless steel. The thermostat mixture consists of 45% KNO_3 and 55% $NaNO_3$. The melting temperature of this mixture is 388 K. The thermostat mixture is intensly stirred with a circulator. At the lower temperatures ($T \leqslant 423$ K) an oil-bath thermostat is used. The thermal conductivity of the aqueous NaCl and KCl solutions is deduced from the relation

$$\lambda = \frac{Qd}{S \Delta T} \tag{1}$$

where Q is the power transferred from the upper plate to the lower plate by conduction through the liquid layer, $S = 36.38 \pm 0.01$ cm^2 the effective area of the upper plate, and ΔT the temperature difference across the liquid layer. The experiments were performed with a temperature difference ΔT about 1 K.

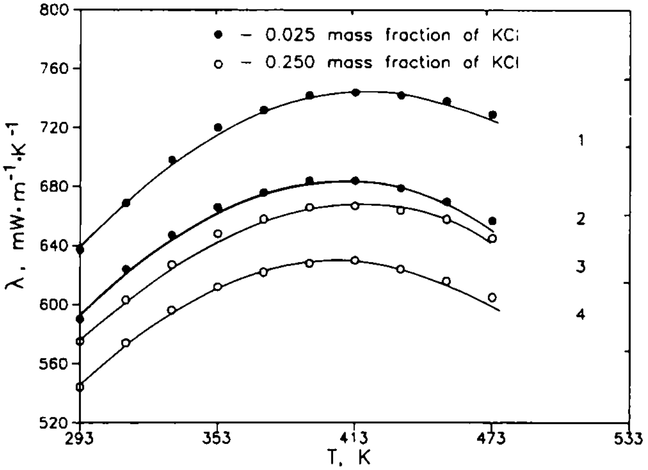

Fig. 3. Dependence of the thermal conductivity of aqueous solutions of KCl on temperature at a number of pressures and concentrations: 1 and 3, 100 MPa; 2 and 4, 0.1 MPa.

The thermal conductivity is calculated from the measured temperature difference ΔT and the measured power Q supplied to the upper plate with the aid of Eq. (1). The dependence of the cell constant d/S on temperature for the present instrument is given in Table II. The pressure effects on the cell constant are negligibly small. The power Q_{exp} in the electrical heater could be measured with an accuracy of 0.08%; Q_{exp} has been corrected for parasitic heat flow through the guard plate. The correction for radiation was negligibly small. The correction for parasitic heat flow was of the order of 0.03%. Considering all sources of possible error, we estimate the total uncertainty in the thermal-conductivity determination to be about $\pm 2\%$.

The pressure of the liquid is transferred to oil via a mercury piston and the oil pressure is measured with a deadweight gauge. The pressure was determined with an uncertainty of $\pm 0.05\%$. This apparatus has previously been tested with ordinary water [15] and heavy water [16]. The solutions were prepared gravimetrically from ion-exchanged distilled water and reagent-grade NaCl and KCl (purity, 99.5%).

3. RESULTS AND DISCUSSION

Experimental thermal-conductivity data were obtained as a function of pressure at 10 isotherms covering a range of temperatures from 293 to 473 K for each concentration, namely, 0.025, 0.05, 0.10, 0.15, 0.20, and 0.25 mass fractions of NaCl and KCl. The experimental results are presented in Tables III and IV. The experimental behavior of the thermal conductivity

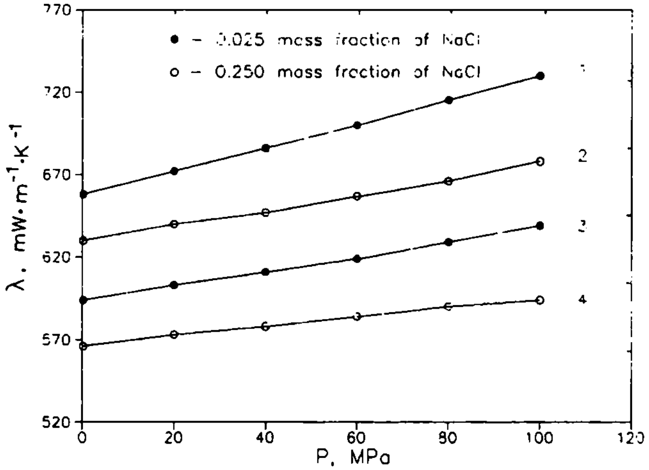

Fig. 4. Dependence of the thermal conductivity of aqueous solutions of NaCl on pressure at different temperatures and constant concentrations: 1 and 2, 473 K; 3 and 4, 293 K.

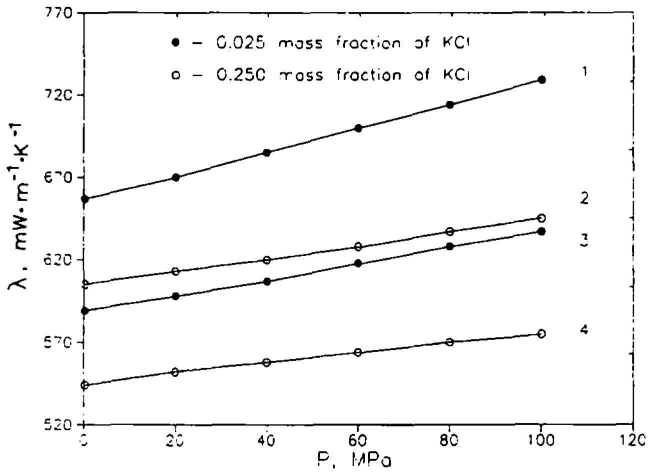

Fig. 5. Dependence of the thermal conductivity of aqueous solutions of KCl on pressure at different temperature and constant concentrations: 1 and 2, 473 K; 3 and 4, 293 K.

of the aqueous NaCl and KCl solutions is shown in Figs. 2–6. It is evident that along each isobar a given concentration shows the thermal-conductivity maximum at temperatures about 413 K. The maxima occur for both systems. Figure 7 is a plot of the thermal conductivity of NaCl solution as a function of temperature and includes the results of earlier measurements

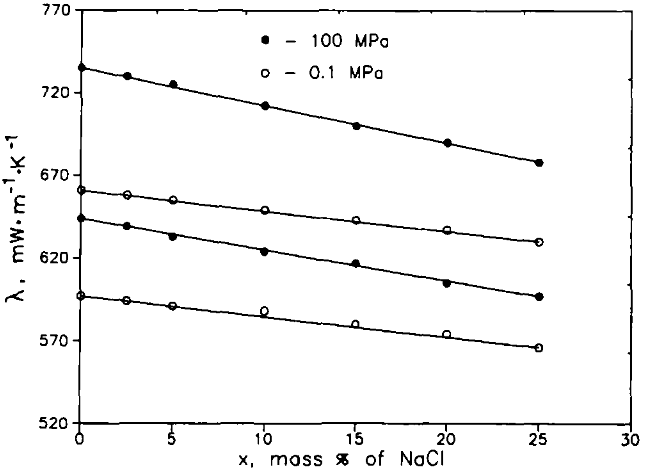

Fig. 6. Dependence of the thermal conductivity of aqueous solutions of NaCl on concentration at a constant temperature and different pressures: 1 and 2, 473 K; 3 and 4, 293 K.

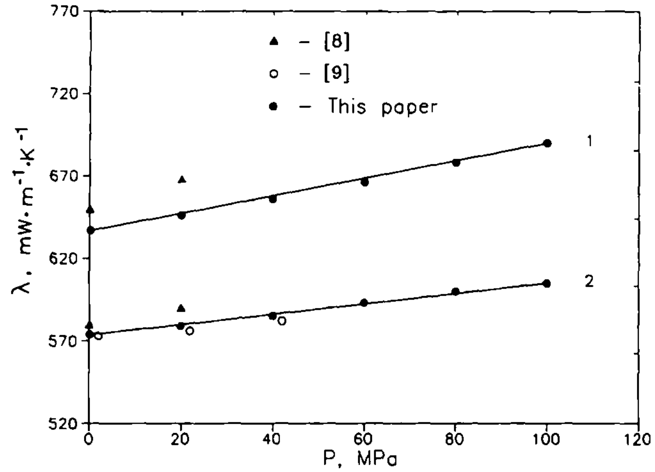

Fig. 7. A comparison between the thermal conductivity data for NaCl + H_2O reported in this paper and those obtained earlier [8, 9] at $x = 0.2$ mass fraction of NaCl: 1, 473 K; 2, 293 K.

for the same solutions by Eldarov [8] and Nagasaka et al. [9], who used a hot-wire technique. The deviation from the present data is 0.5% for Ref. 9 and 3% for Ref. 8. The results obtained by Safronov et al. [10] for KCl + H_2O are compared with the data from the present work in Fig. 8. In the range up to 60 MPa there is very good agreement with the data of

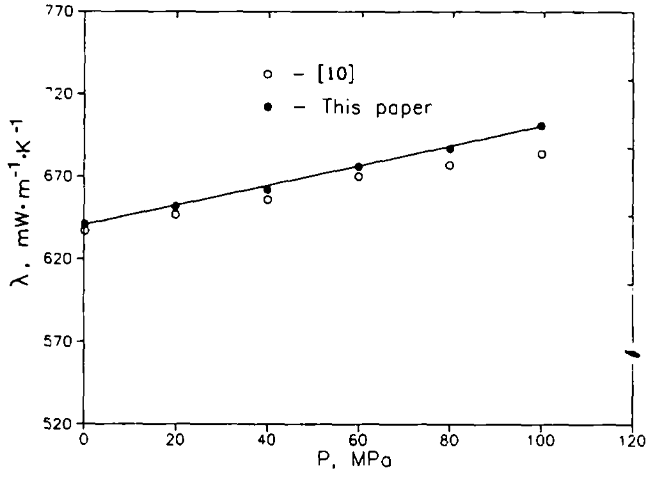

Fig. 8. Comparison between our experimental values for the thermal conductivity of the KCl + H_2O system at 473 K and $x = 0.1$ mass fraction of KCl and the values proposed in Ref. 10.

Safronov et al. [10], with deviations of no more than 0.3%. At pressures above 60 MPa the deviations increase to 3%. Their values are higher than the present results. Riedel [3], Kapustinskii and Ruzavin [4], Vargaftik and Osminin [5], and Davis et al. [6] have reported measurements at one atmosphere and at different temperatures. These data agree within ±0.3% with the results of the present investigation.

A comparison of the present results for $NaCl + H_2O$ and $KCl + H_2O$ with earlier work indicates that the instrument yields satisfactory results within its estimated uncertainty of ±2%.

4. CONCLUSION

The thermal conductivity of aqueous solutions of NaCl and KCl was measured in the temperature range from 293 to 473 K and in the pressure range up to 100 MPa, with an uncertainty of better than ±2%.

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