Electrical Conductance of Single Molten Lithium Halides

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The specific conductivities and densities of molten LiCl, LiBr and LiI have been investigated as a function of temperature. A comparison between the data in literature and the present data has been made and the reliability of the different data is discussed.

The electrical conductance is perhaps the most extensively studied property of molten salts. Nevertheless, for many salts there is a large scatter of the published data and for others the experimental data are scarce. Both these are true for the lithium halides. We therefore have reinvestigated their electrical conductances and also their densities.

Experimental

Apparatus. The resistance measurements were carried out with a Wayne-Kerr autobalance precision bridge, model B 331, with a precision of ±0.01%, at a fixed frequency of 1592 Hz (the internal operating frequency of the bridge). The influence of the frequency on the measured resistance was investigated in a separate set of experiments when the bridge was adjusted to operate with an external signal generator up to 20 kHz. The observed variations in resistance were within experimental errors for all studied cases.

U-shaped, previously described[1], silica capillary cells were used. Their constants were of 500 – 700 cm^{-1}, as determined with a 1 N KCl solution at $25^\circ \pm 0.01$. Due to the low thermal expansion of silica, no correction for the high temperatures was necessary. The cell constant was systematically redetermined after every 3d or 4th run.

During the experiment the conductance cell was placed in a vertical furnace so built as to ensure a temperature gradient of 0.5° over a 10 cm length zone, where the capillary was situated.

The temperature was measured with a Pt-Pt 10% Rh calibrated thermocouple attached to the capillary wall.

The density measurements were made with a precision of 0.2% by a hydrostatic method[1], provided to ensure a carefully controlled atmosphere.

Chemicals. The lithium halides used were p. a. grade reagents. Because of their high hygroscopicity, special care was taken to remove all compounds formed by hydrolysis within the salt upon heating.

The LiCl and LiBr salts were recrystalized twice from distilled water and dried for 24 h at 150°. Then they were melted in a special silica cell[2] while argon gas, saturated with CCl_4 and $CHBr_3$ vapours, respectively, was bubbled through the melt. The obtained solid pellets were kept under liquid CCl_4 and $CHBr_3$, respectively. They were transferred into the conductance cell or density crucible in a dry box and were remelted by steadily increasing the temperature while a carefully dried argon gas was bubbled through the cell. Any CCl_4 or $CHBr_3$ trace was thus removed before melting.

Considerable difficulties were encountered in preparing and maintaining anhydrous LiI melts.

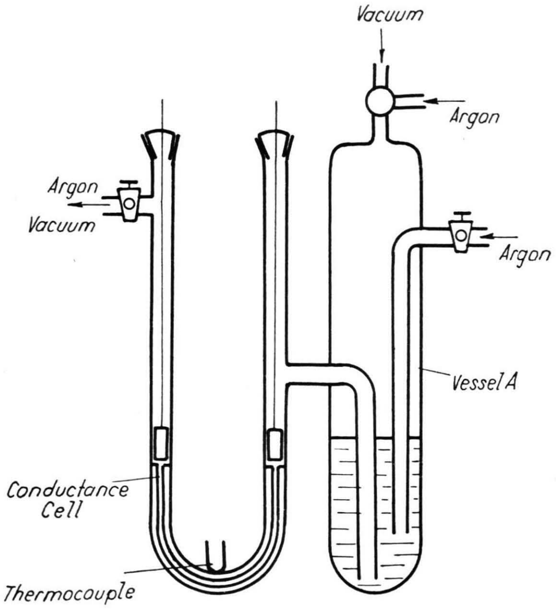

Fig. 2. Conductivity cell for LiI.

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The most suitable method proved to be direct melting into the conductance cell. For this purpose, to the conductance cell an additional vessel for LiI pretreatment was attached (Figure 1).

Commercially available LiI (p. a. grade, yellowish crystals) was heated in a separate vessel at 80° for $5-6$ h in vacuum in order to remove the crystallization water. The white LiI crystals obtained were then introduced into the vessel A and were dryed under a vacuum of $10^{-3}-10^{-4}$ torr for 80 h while the temperature was steadily raised (3° per hour). After melting, a carefully dried HI gas was passed through the melt for $6-8$ h, followed by argon gas for 2 h. Finally the melt, free of $HI + I_2$ traces, was transferred into the conductance cell by an argon overpressure. In the density measurements the LiI melts were prepared in the same way.

Each melt was checked for alkalinity (with phenolphtalein) before and after runs. Only results obtained with consistently neutral melts were considered.

Results and Discussions

The specific conductance[5] of the melts was measured over temperature ranges of at least 100° both at increasing and decreasing temperature. The experimental results are given in Table 1. They were obtained in $5-6$ different runs for each salt. The densities were measured within the same temperature ranges. They are presented as linear functions of temperature in Table 2.

A detailed statistical analysis of the presently obtained data for the electrical conductances was performed in the Molten Salts Data Center[3] TROY. The experimental data were least squares fitted to both a polynomial and an Arrhenius equation:

specific conductance: $k = a + b\,t - c\,t^2$,
$k = A_k \exp\{-E_k/R\,T\}$;
equivalent conductance: $\lambda = a + b\,t - c\,t^2$,
$\lambda = A_\lambda \exp\{-E_\lambda/R\,T\}$.

The equations in Table 2 are the results of this calculation. For each equation the standard error of estimate (S.E.E.) and the percent S.E.E. is also tabulated.

Figure 2 shows the percent departure of the present data from the recommended data reported by Janz et al. in the NBS circular[4]. We note here that the percent difference is calculated as:

$$100\left[\frac{\text{our value} - \text{recommended value}}{\text{recommended value}}\right].$$

Table 1. Specific conductivity of lithium halides.

LiCl		LiBr		LiI	
t^0	k ohm^{-1} cm^{-1}	t^0	k ohm^{-1} cm^{-1}	t^0	k ohm^{-1} cm^{-1}
627	5.977	650	4.757	489	3.968
629	5.994	567	4.798	493	3.996
637	6.020	570	4.807	502.5	4.035
638	6.038	582	4.894	505.5	4.043
644	6.041	588	4.926	518	4.114
650	6.092	590	4.927	525	4.141
652.5	6.095	606	4.993	533	4.183
663	6.153	608	5.012	535	4.194
667	6.175	615.5	5.033	547	4.252
668	6.183	618	5.066	562	4.313
671	6.202	626	5.090	567	4.340
681	6.229	628	5.089	578.5	4.379
682	6.250	637	5.125	585	4.413
690	6.261	646	5.168	598.5	4.472
703	6.352	647	5.183	602	4.476
710	6.385	659	5.216	616	4.538
721	6.414	662	5.250	622	4.551
724	6.435	668	5.260	637	4.619
739.5	6.516	675	5.286		
743.5	6.517	680.5	5.310		
748	6.546	690.5	5.370		
768	6.603	694	5.383		
781	6.666	698	5.398		
792.5	6.680	704	5.425		
802	6.720	719.5	5.476		
		727	5.503		
		731	5.504		
		749.5	5.571		

As seen in the figure, our data for LiCl are by $2-3\%$ higher than the recommended data which are based on the combined values of Van Artsdalen and Yaffe[5] and Edwards et alias[6]. However, the temperature dependence is similar in both cases.

For LiBr, the data obtained in the present work, indicate a lower temperature dependence than the recommended ones[7]. There is excellent agreement between the two sets of data (departure of $\pm 0.2\%$) in the $560-625°$ temperature range, but at higher temperatures the departure increases to -2.4% at the upper temperature limit.

As it can be seen in Fig. 2, a close agreement exists between our data for LiI and the recommended values based on the work of Johnson[8]. The minimal deviation is of -0.02% and the maximal one of -0.46%.

A survey[9] of the studies carried out prior to the present one indicates a total of twenty investigations[5, 6, 10–27] for k_{LiCl}, four[7, 18, 28, 29] for k_{LiBr} and three[7, 8, 30] for k_{LiI}. Generally, there is a marked disagreement among various investigators. Thus for

Table 2. Equations relating density and electrical conductivity of lithium halides to temperature.

Salt	Equations	Temperature range	S.E.E.
LiCl	$d = 1.7562-0.4243\cdot10^{-3}\,t$	660– 830°	
	$k = 0.156958+13.1442\cdot10^{-3}\,t-6.17769\cdot10^{-6}\,t^2$	627– 802°	$1.08\cdot10^{-2}$ (0.17%)
	$k = 12.51056\exp\{-1319.94/RT\}$	900–1075 K	$1.39\cdot10^{-2}$ (0.22%)
	$\lambda = -7.74227+0.363762\,t-1.28426\cdot10^{-4}\,t^2$	627– 802°	$3.17\cdot10^{-1}$ (0.17%)
	$\lambda = 485.040\exp\{-1875.80/RT\}$	900–1075 K	$3.32\cdot10^{-1}$ (0.18%)
LiBr	$d = 2.9793-0.7893\cdot10^{-3}\,t$	630– 840°	
	$k = 0.439475+1.03164\cdot10^{-2}\,t-4.61953\cdot10^{-6}\,t^2$	560– 749.5°	$1.02\cdot10^{-2}$ (0.20%)
	$k = 11.1694\exp\{-1406.6/RT\}$	833–1022.5 K	$1.14\cdot10^{-2}$ (0.22%)
	$\lambda = 6.48563+0.333174\,t-9.50247\cdot10^{-5}\,t^2$	560– 749.5°	$3.72\cdot10^{-1}$ (0.20%)
	$\lambda = 526.414\exp\{1938.97/RT\}$	833–1022.5 K	$3.73\cdot10^{-1}$ (0.20%)
LiI	$d = 3.4830-0.8172\cdot10^{-3}\,t$	560– 790°	
	$k = 0.339401+9.76840\cdot10^{-3}\,t-4.79905\cdot10^{-1}\,t^2$	489– 637°	$4.60\cdot10^{-3}$ (0.11%)
	$k = 10.0741\exp\{-1409.1/RT\}$	762– 910 K	$5.72\cdot10^{-3}$ (0.13%)
	$\lambda = 7.47451+0.407843\,t-1.44780\cdot10^{-4}\,t^2$	489– 637°	$2.03\cdot10^{-1}$ (0.11%)
	$\lambda = 557.629\exp\{-1778.69/RT\}$	762– 910 K	$2.05\cdot10^{-1}$ (0,11%)

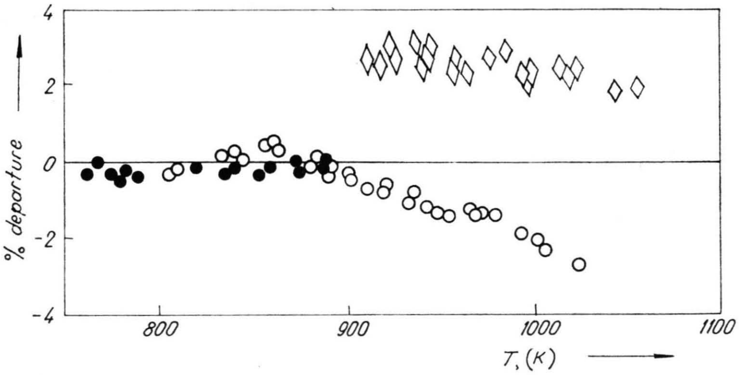

Fig. 2.
Departure from recommended values [4] for lithium halides.
◇ – LiCl; ○ – LiBr; ● – LiI.

LiCl, the percent departure from the recommended values [5, 6] is amazingly scattered, ranging from about +16% to about −6%. The present data agree fairly well with those given by Duke and Bissel [19] (±0.2%), Bloom and Knaggs [14] (+0.4%) and Emons and Brautigam [26] (+0.1 − 0.7%). The recommended values [7] for LiBr agree very well with those of Bizouard's [18], while the other two sets of data [28, 29] differ by as much as +1.5 and −5% respectively. The drawback of all these papers is the scarcity of the experimental points (2 − 4 points over 200° temperature range). As a matter of fact, the present study is the most extensive one so far. As already stated, our data for k_{LiI} are in excellent agreement with Johnson's [8]. The other two studies quoted [7, 30] are by −5% to −7% and −7% to −10% lower, respectively.

In concluding, we consider that taking into account the satisfactory precision of usual resistance bridges, the scattering of the published data accuses either the purity of the salts or the type of conductance cell employed. Thus, the parasitic conductance encountered when dealing with dipping silica capillary cells immersed in melts consisting of small cations (as Na^+ and Li^+) was already discussed [31]. According to our experience, in the case of U-shaped capillary cells in an air bath an important source of error (reaching a few percents) could be the inadequate control of the temperature gradient along the capillary.

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