[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

# The Heat Capacity of Lithium Chloride from 15 to 325 Degrees Kelvin[1a]

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The heat capacity of lithium chloride has been measured in the temperature range 15–325° K. The data are analyzed in terms of an optical branch model and found to agree qualitatively but not quantitatively with this model. A relationship derived from this model between heat capacity and elastic constants is found to be obeyed roughly by several alkali halides. For LiCl, $S_{298.15}$ is $-14.17 \pm 0.02$ gibbs/mole.

Simple theoretical considerations[1c] suggest that the phonon spectrum of a diatomic lattice of the sodium chloride structure should consist of an optical branch, associated with the unlike atoms vibrating against each other, and an acoustical branch. If the ionic masses are quite different, the frequency of the optical branch will not change strongly with wave number, changing only from $\omega\alpha\mu^{-1/2}$ to $\omega\alpha m^{-1/2}$, where $\mu$ and $m$ are the reduced mass and the mass of the smaller ion, respectively. Then to a first approximation the heat capacity may be represented by a combination of three isochromatic Einstein functions for the optical branch plus a Debye function for the acoustical branch.[2] The present research was undertaken to determine how accurately this model represents the heat capacity in a nearly ideal case.

The most obvious manifestation of an optical branch is a maximum in the function $C_V/T^3$ at low temperatures. This maximum is essentially due to the optical branch, since $C_V/T^3$ approaches constancy at low temperatures on the Debye model. Lithium chloride was chosen for this investigation because the ionic masses are enough different for the optical branch model to be applicable, while both ions are light enough for the maximum in $C_V/T^3$ to lie well within the temperature range of hydrogen calorimetry.

## Experimental

The sample was "Bakers Analyzed" reagent, lot number 90941, supplied with the percentage analysis:

| | |
|---|---|
| Assay (LiCl) | 99.1 |
| Loss on drying | 0.2 |
| Insoluble matter | .005 |
| Alkalinity | .006 |
| Nitrate | .0005 |
| Sulfate | .005 |
| Barium | .0002 |
| Calcium | .002 |
| Heavy metals | .00005 |
| Potassium | .03 |
| Sodium | .06 |

Since lithium chloride is extremely hygroscopic, it was felt that the figure for "loss on drying" did not represent the total water content. Three samples were fused and were found to decrease in weight by 0.74 ± 0.02%.

The sample was further purified by several recrystallizations and fused. It was cooled in a desiccator, and the calorimeter was filled in a dried gloved box. A finely powdered sample in an open bottle in the gloved box did not gain weight during the time when the calorimeter was being filled. The sample which was used consisted of crystals of dimensions in the range 0.1–1.0 mm. The weight of lithium chloride was 188.033 g. *in vacuo*.

The heat capacity measurements were made with the copper calorimeter used by Papadopoulos and Giauque.[3] The heat capacity of the calorimeter was remeasured during the course of the present work. The temperature was measured by a gold resistance thermometer–heater which was compared with Laboratory Standard Thermocouple No. 105 before and after each heating period. The thermocouple was compared with the triple (13.94° K.) and boiling points (20.36° K.) of hydrogen and the triple (63.15° K). and boiling points (77.34° K.) of nitrogen. 0° was taken as 273.15° K. and 1 defined calorie was taken equal to 4.1840 absolute joules.

## Results

The experimental heat capacities are listed in Table I. The data in Series II were taken because a faulty contact within the potentiometer made the resistance thermometer calibration in Series I incomplete below 100°K.

Most of the experimental points showed deviations of considerably less than 0.1% from a smooth curve through the data. The deviations were very small in the liquid nitrogen temperature range, the ideal region for this type of calorimetry, and of the order of 0.1% at the lowest and highest temperatures. The accuracy was 0.1% above 30°K., deteriorating to about 1% below 20°K. because of the decreasing sensitivity of the resistance thermometer.

In Table II are collected smoothed values of the thermodynamic properties at convenient temperatures. The entropy $S_{298.15}^{\circ} = 14.17 \pm 0.02$ gbs./mole.[4] This may be compared with the value 13.9 ± 0.5 gbs./mole obtained by Kelley from the heat and free energy of formation.[5]

## Discussion

For purposes of comparison with theoretical heat capacity functions, the experimental values of $C_p$ were converted to $C_v$ using the thermodynamic relationship

$$C_p - C_v = -VT\frac{\alpha^2}{\beta} \qquad (1)$$

The volume expansion data which were used were those of Henglein[6] and of Straumanis and Ievins,[7]

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[1] (a) This work was supported by National Science Foundation Grant G-3014. (b) National Science Foundation Predoctoral Fellow, 1955–1958. (c) See, for example, C. Kittel, "Introduction to Solid State Physics," 2nd Ed., 1956, pages 109 ff.

[2] See, for example, K. S. Pitzer, "Quantum Chemistry," 1953, p. 306–316.

[3] M. N. Papadopoulos and W. F. Giauque, THIS JOURNAL, **77**, 2740 (1955).

[4] 1 gbs. (gibbs) = 1 defined calorie/defined degree Kelvin. See W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *ibid.*, **82**, 62 (1960).

[5] K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy," XI, 60 (1948). (U. S. Bureau of Mines Bulletin 477).

[6] F. A. Henglein, *Z. physik. Chem.*, **117**, 275 (1925).

[7] M. Straumanis and A. Ievins, *Z. anorg. u. allgem. Chem.*, **238**, 175 (1938).

TABLE I

HEAT CAPACITY OF LITHIUM CHLORIDE

| $T$, °K. | $C_p$, gbs./mole | $T$, °K. | $C_p$, gbs./mole |
|---|---|---|---|
| Series I | | 212.60 | 10.531 |
| 16.65 | 0.07464 | 219.84 | 10.650 |
| 19.07 | .1159 | 227.52 | 10.769 |
| 21.64 | .1799 | 235.07 | 10.865 |
| 24.40 | .2721 | 242.55 | 10.939 |
| 27.49 | .4145 | 246.90 | 10.996 |
| 30.59 | .5921 | 249.94 | 11.035 |
| 33.81 | .8012 | 255.11 | 11.056 |
| 37.37 | 1.0672 | 263.92 | 11.185 |
| 41.70 | 1.4341 | 272.31 | 11.258 |
| 46.58 | 1.8862 | 280.78 | 11.350 |
| 51.39 | 2.3573 | 290.11 | 11.400 |
| 56.60 | 2.8800 | 299.64 | 11.484 |
| 62.36 | 3.4728 | 309.77 | 11.545 |
| 68.53 | 4.0884 | 320.42 | 11.625 |
| 74.98 | 4.6886 | Series II | |
| 81.43 | 5.2512 | 13.77 | 0.03691 |
| 88.01 | 5.7732 | 15.42 | .05554 |
| 95.08 | 6.3009 | 17.54 | .08496 |
| 102.03 | 6.7694 | 20.38 | .14440 |
| 109.30 | 7.2094 | 23.03 | .2247 |
| 116.72 | 7.6216 | 25.84 | .3351 |
| 124.12 | 8.0110 | 29.27 | .5060 |
| 131.52 | 8.3291 | 32.67 | .7173 |
| 138.83 | 8.6401 | 36.36 | .9856 |
| 146.06 | 8.9202 | 40.83 | 1.4541 |
| 153.34 | 9.1630 | 46.05 | 1.8386 |
| 160.92 | 9.4061 | 51.94 | 2.4015 |
| 168.45 | 9.6014 | 58.29 | 3.0468 |
| 175.72 | 9.7770 | 64.71 | 3.7037 |
| 182.99 | 9.9583 | 71.80 | 4.4009 |
| 190.21 | 10.106 | 80.03 | 5.1198 |
| 197.56 | 10.264 | 88.52 | 5.8057 |
| 204.91 | 10.404 | 97.03 | 6.4289 |

and the compressibility data were those of Slater.[8] The values of $C_p - C_v$ for several temperatures are listed in Table III. It should be noted that uncertainties in $\alpha$ and $\beta$ introduce a considerable error into the calculation of $C_v$ at high temperatures, while the total correction is only 0.2% at 50° and 1.2% at 100°K.

The expected maximum in $C_v/T^3$ occurs at 33°K. In Fig. 1 $C_v/T^3$ is plotted against $T$, along with several theoretical curves. It is clear that the optical branch model is qualitatively correct for lithium chloride, although a good fit of the data is not obtainable.[9]

During the course of this work the thermal data of Berg and Morrison[10] on several other alkali halides became available. By considering these, one can made a systematic comparison of the thermal properties of alkali halides with the optical branch model. First we note that it is customary to plot $\theta_D$ derived from heat capacity measurements against $T$. The parameter $\theta_D$ then exhibits a minimum at a temperature $T_M$ which may be attributed to the optical branch, and in fact this minimum corresponds very closely to the maximum in the functions $C_v/T^3$. If $C_v(T_M/T)^3$ is plotted against $T/T_M$ as in Fig. 2, it is apparent that the behavior of this function is again qualitatively what would be expected on the optical branch model. As would be expected the maximum is more pronounced for LiCl and NaI, where the masses are quite different, than for KCl, KBr and KI, where the masses are more nearly equal.

TABLE II

THERMODYNAMIC PROPERTIES OF LITHIUM CHLORIDE IN GIBBS MOLE$^{-1}$

| $T$, °K. | $C_p$ | $S_T^0$ | $-(F^0 - H_0^0)/T$ | $(H^0 - H_0^0)/T$ |
|---|---|---|---|---|
| 15 | 0.0504 | 0.0186 | 0.0055 | 0.0131 |
| 20 | .1356 | .0434 | .0115 | .0319 |
| 25 | .2978 | .0896 | .0221 | .0675 |
| 30 | .5538 | .1652 | .0391 | .1261 |
| 35 | .8834 | .2745 | .0645 | .2100 |
| 40 | 1.284 | .4181 | .0994 | .3187 |
| 45 | 1.737 | .5951 | .1380 | .4571 |
| 50 | 2.214 | .8027 | .1939 | .6088 |
| 55 | 2.712 | 1.037 | .260 | .777 |
| 60 | 3.227 | 1.295 | .335 | .960 |
| 70 | 4.231 | 1.868 | .512 | 1.356 |
| 80 | 5.126 | 2.493 | .721 | 1.772 |
| 90 | 5.926 | 3.144 | .953 | 2.191 |
| 100 | 6.637 | 3.806 | 1.206 | 2.600 |
| 110 | 7.250 | 4.468 | 1.472 | 2.996 |
| 120 | 7.794 | 5.122 | 1.794 | 3.373 |
| 130 | 8.267 | 5.765 | 2.033 | 3.732 |
| 140 | 8.686 | 6.394 | 2.322 | 4.072 |
| 150 | 9.057 | 7.006 | 2.614 | 4.392 |
| 160 | 9.374 | 7.601 | 2.907 | 4.694 |
| 170 | 9.651 | 8.178 | 3.201 | 4.977 |
| 180 | 9.893 | 8.736 | 3.493 | 5.243 |
| 190 | 10.106 | 9.277 | 3.783 | 5.494 |
| 200 | 10.310 | 9.800 | 4.071 | 5.729 |
| 210 | 10.494 | 10.308 | 4.356 | 5.952 |
| 220 | 10.655 | 10.800 | 4.638 | 6.162 |
| 230 | 10.794 | 11.276 | 4.916 | 6.360 |
| 240 | 10.915 | 11.738 | 5.191 | 6.547 |
| 250 | 11.035 | 12.186 | 5.462 | 6.724 |
| 260 | 11.144 | 12.621 | 5.729 | 6.892 |
| 270 | 11.240 | 13.044 | 5.992 | 7.052 |
| 280 | 11.323 | 13.454 | 6.251 | 7.203 |
| 290 | 11.403 | 13.853 | 6.506 | 7.347 |
| 298.15 | 11.470 | 14.170 | 6.712 | 7.458 |
| 300 | 11.487 | 14.241 | 6.758 | 7.483 |
| 310 | 11.557 | 14.619 | 7.005 | 7.614 |
| 320 | 11.622 | 14.986 | 7.249 | 7.737 |
| 325 | 11.680 | 15.166 | 7.369 | 7.797 |

TABLE III

$C_p - C_v = -VT\dfrac{\alpha^2}{\beta}$ FOR LITHIUM CHLORIDE

| $T$, °K. | $C_p - C_v$, gbs./mole |
|---|---|
| 25 | 0.0000 |
| 50 | .003 |
| 75 | .032 |
| 100 | .076 |
| 150 | .237 |
| 200 | .411 |
| 250 | .573 |
| 300 | .738 |

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(8) J. C. Slater, *Phys. Rev.*, **23**, 488 (1924).

(9) Note that M. H. Norwood and C. V. Briscoe [*Phys. Rev.*, **112**, 45 (1958)] have used infrared and elastic constant data to derive the heat capacities of the potassium halides.

(10) W. T. Berg and J. A. Morrison, *Proc. Roy. Soc.* (*London*), **A242**, 467 (1957).

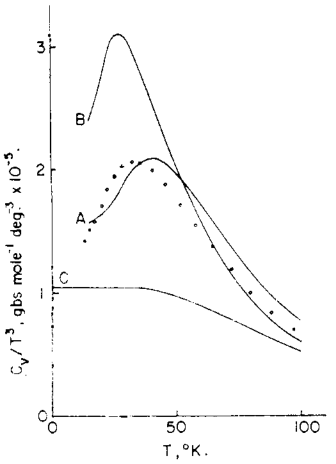

Fig. 1.—$C_v/T^3$ *vs.* $T^3$ for lithium chloride. The circles represent the experimental data. The curves are based on (A) the optical branch model with $\theta_D = 310$, $\theta_E = 250$ chosen empirically, (B) a calculation due to Karo (footnote 11) and (C) a Debye function with $\theta_D = 450$.

TABLE IV

| Substance | $T_M$, °K. | $10^2\sqrt{ac_{11}/\mu}$[11] cgs. units × (moles)$^{1/2}$ | $T_M/\sqrt{ac_{11}/\mu}$ |
|---|---|---|---|
| LiCl | 33 | 4.94 | 6.7 |
| NaI | 12 | 2.28 | 5.3 |
| KCl | 17 | 2.86 | 5.9 |
| KBr | 12 | 2.30 | 5.2 |
| KI | 9.5 | 2.00 | 4.7 |

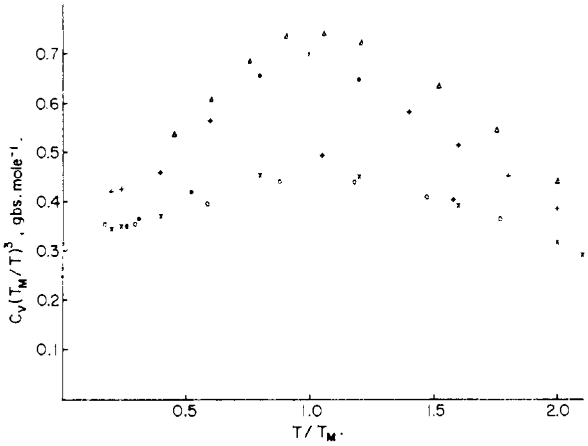

Fig. 2.—A reduced plot of $C_v(T_M/T)^3$ for several alkali halides(○, KCl; ×, KBr; +, NaI; ●, KI; △, LiCl).

One further correlation which may be made consists of comparing $T_M$ with the quantity $\sqrt{(ac_{11})/\mu}$. According to the model

$$T_M \; \alpha\omega\alpha \; \sqrt{ac_{11}/\mu} \qquad (2)$$

The results are collected in Table IV. While the ratio is not constant within experimental error, there is a strong correlation, considering the range of the parameters.

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[11] The values of $c_{11}$ were obtained from A. M. Karo, reported in University of California Radiation Laboratory Report UCRL 5525 (1959), and from ref. 9.

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# Properties, Interaction and Esterification of Methylphosphonic Dihalides

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The mechanism of the formation of Sarin by the esterification of methylphosphonic dihalides with 2-propanol has been elucidated from physicochemical considerations, and evidence for the extent and rate of metathesis of an equimolar mixture of methylphosphonic dichloride and methylphosphonic difluoride is presented. The densities, viscosities, molar polarizations, dipole moments, refractive indexes, vapor pressures, freezing points and infrared spectral data of the dihalides were obtained, as well as the solid-liquid phase relations of the dichlor-difluor system.

The final step in the synthesis of isopropyl methylphosphonofluoridate (Sarin) involves the reaction of 2-propanol with an equimolar mixture of methylphosphonic dichloride and methylphosphonic difluoride (hereafter termed dichlor and difluor, respectively). The over-all reaction is

$$CH_3P(O)Cl_2 + CH_3P(O)F_2 + 2(CH_3)_2CHOH \longrightarrow 2CH_3P(O)(F)OCH(CH_3)_2 + 2HCl \qquad (1)$$

Studies of the mechanism of this reaction were made in Germany after the initial preparation of Sarin by Schrader and also in England and in this country after World War II. Based on observations of the ease of reaction and of the nature and relative quantities of products formed in reactions of derivatives of methylphosphonic acid, Perry[1] postulated a sequence of reactions

$$CH_3P(O)Cl_2 + (CH_3)_2CHOH \longrightarrow CH_3P(O)(Cl)OCH(CH_3)_2 + HCl \qquad (2)$$

$$CH_3P(O)F_2 + (CH_3)_2CHOH \xrightarrow{HCl} CH_3P(O)(F)OCH(CH_3)_2 + HF \qquad (3)$$

$$CH_3P(O)(Cl)OCH(CH_3)_2 + HF \longrightarrow CH_3P(O)(F)OCH(CH_3)_2 + HCl \qquad (4)$$

These are accompanied by the side reaction

$$CH_3P(O)(Cl)OCH(CH_3)_2 + (CH_3)_2CHOH \longrightarrow CH_3P(O)[OCH(CH_3)_2]_2 + HCl \qquad (5)$$

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[1] B. J. Perry, Ministry of Supply, U.K., unpublished report.