PHYSICAL REVIEW VOLUME 119, NUMBER 6 SEPTEMBER 15, 1960

Behavior of the Principal Elastic Moduli and Specific Heat at Constant Volume of KCl at Elevated Temperatures*

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(Received January 25, 1960; revised manuscript received April 25, 1960)

Measurements of the adiabatic elastic constants of potassium chloride (KCl) have been made in the region 300°K to the melting point (1043°K) by a dynamical method developed by Balamuth. Recently determined values of the specific heat at constant pressure (C_p) have been used to calculate the isothermal values of the compressibility. Values of the specific heat at constant volume (C_v) have been obtained, using recent values of the coefficient of thermal linear expansion (α), the above mentioned values of C_p, and the isothermal compressibilities. The results indicate that there is a slight rise in C_v above the Dulong-Petit value above 725°K. This rise is not significant, since the estimated error interval incloses the Dulong-Petit value, and consequently the D-P law is most likely valid up to the melting point.

INTRODUCTION

ELASTIC constants of crystals and their temperature variation not only are of interest in themselves, but provide much information concerning the interatomic forces in solids and the equations of state of solids. They are also necessary for a complete thermodynamical description of solids and are a necessary adjunct to the reduction of the specific heat at constant pressure (C_p) to constant volume (C_v). The measurements on potassium chloride were undertaken initially to be used for the reduction of recent specific heat data, since reliable data for temperatures near the melting point could not be found in the literature. These data, on the temperature variation of the elastic constants obtained in this research, enable one to calculate the variation of the compressibility (β) with temperature, which is then used for the conversion of the specific heats at constant pressure (C_p) to specific heats at constant volume (C_v). One very important parameter, the coefficient of linear thermal expansion (α), was also remeasured[1] since "preliminary" work indicated that the values of the coefficient of linear expansion at elevated temperatures, as quoted in the literature,[2] were in error.[3]

The behavior of C_v in the neighborhood of the melting point is of considerable interest, since Eucken and Dannöhl[4] have obtained values of C_v for sodium chloride, using their own values of α and values of the compressibility that were extrapolated from room-temperature values of Slater and Bridgman, which indicate that C_v drops below the Dulong-Petit value at elevated temperatures. Hunter and Siegel's[5] results also indicated that C_v dropped slightly below the D-P value near the melting point, but they doubted the validity of this drop due to the unreliability of the high-temperature values of α and C_p used for the reduction. A drop in C_v would seem to indicate that the energy required to raise a sample through a temperature interval is decreasing instead of remaining constant at the higher temperatures. This would be contrary to the Debye high-temperature limit of $3R$, the Dulong-Petit value.

These values of C_v are also used to check the behavior of the quantity γ defined by the equation

$$\gamma = 3V\alpha / C_v\beta_{\text{is}},$$

which Grüneisen,[6] in developing an equation of state of metals, on the assumption of central-force interaction of atoms, found should be independent of temperature.

THEORY AND EXPERIMENTAL METHOD

Balamuth[7] and Rose[8] have described methods for measuring Young's modulus and the rigidity modulus corresponding to any chosen direction in a solid crystalline substance. The method utilized the properties of a separately excited composite piezoelectric oscillator constructed by cementing an X-cut quartz cylinder to one end of a cylinder of the specimen material. This method was employed with success at the lower temperatures, but due to the fact that the piezoelectric quartz driver has an $\alpha \rightarrow \beta$ transformation at 846°K, it is not feasible to use simply a two-part oscillator, in which the quartz crystal is maintained at the same temperature as the KCl specimen. The extension of the three-part oscillator was made by Rose,[8] and Hunter and Siegel[5]; who have checked the accuracy of the three-part data by comparing it with Durand's[9] two-part data. The agreement of the two sets of data established the validity of the three-part method. Two types of three-part oscillators are used—one for longi-

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* The majority of this work was supported by the Office of Naval Research.

[1] D. Engle and K. Marks, Masters thesis, Franklin and Marshall College, 1957 (to be published).

[2] A. Eucken and W. Dannöhl, Z. Electrochem. **40**, 814 (1934).

[3] F. D. Enck, Final Technical Report No. 11, Contract Nonr 60200, Project No. NR-017-206, University of Maryland, 1955 (unpublished).

[4] A. Eucken and W. Dannöhl, Z. Electrochem. **40**, 789 (1934).

[5] L. Hunter and S. Siegel, Phys. Rev. **61**, 84 (1942).

[6] E. Grüneisen [see *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1926)], Vol. X, for a survey of his work).

[7] L. Balamuth, Phys. Rev. **45**, 715 (1934).

[8] F. C. Rose, Phys. Rev. **49**, 50 (1936).

[9] M. Durand, Phys. Rev. **50**, 453 (1938).

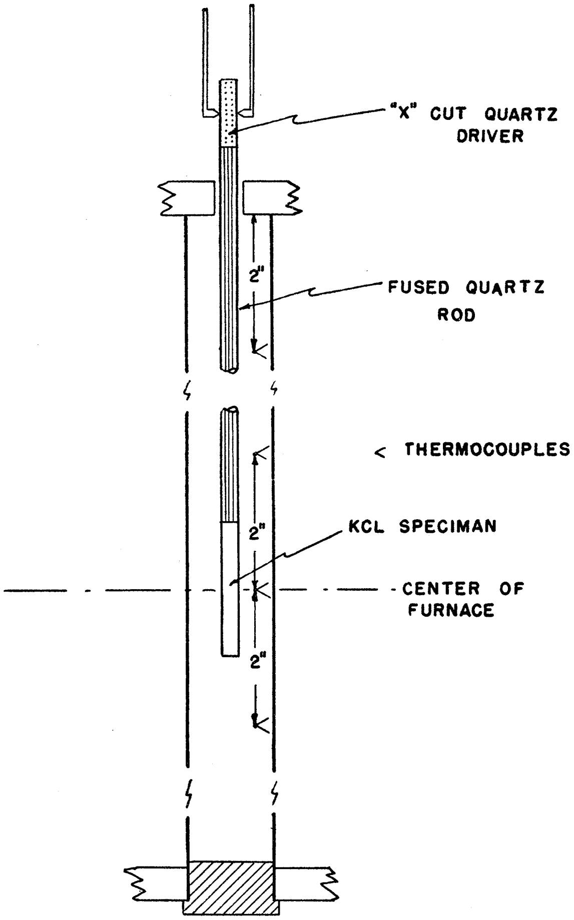

FIG. 1. Three-part longitudinal oscillator in position in the furnace.

tudinal, and one for torsional vibrations. The longitudinal oscillator consists of a X-cut quartz crystal, an intermediate fused quartz rod, and the bar or cylindrical shaped KCl specimen. The torsional oscillator consists of a Y-cut quartz crystal, an intermediate fused quartz rod, and the cylindrical KCl specimen. The oscillator is suspended vertically on the axis of a tube furnace, with the KCl specimen at the center of the furnace, maintained at the desired elevated temperature. The quartz crystal is situated above the end of the furnace, and is maintained essentially at room temperature by circulating air around it.

The furnace used was wound with platinum-rhodium windings on a cylindrical core 18 in. long and $1\frac{1}{2}$ in. inside diameter. To further facilitate maintaining a low-temperature gradient in the central part of the furnace, two separate end windings were also used. The temperature inside the furnace was read with four platinum-rhodium thermocouples which had been calibrated at the National Bureau of Standards. Three of these thermocouples were mounted at 2-in. intervals near the center of an inconel tube mounted snugly inside the furnace core. The fourth was mounted about 2 in. from the top of the furnace, and was used as a sensing element to control the current in the upper furnace winding in order to maintain a constant temperature gradient between the center and upper end of the furnace. This constant gradient was established in order that the conditions under which all runs were made are entirely similar. Figure 1 is a diagram of the core of the furnace, showing the three-part oscillator and the location of the thermocouples. A Leeds and Northrup Wenner precision potentiometer was used to measure the voltage of the thermocouples.

The theory of such a three-part oscillator has been developed by Rose.[8] The resonance frequency of the two- and three-part longitudinal or torsional oscillator is measured by observing the variation of the electrical impedance of the piezoelectric oscillator with the frequency of the applied voltage. The Young's modulus or the rigidity modulus of the KCl specimen for the particular crystallographic orientation is calculated from the above-mentioned resonant frequencies and other measurable quantities.

Four elastic moduli were calculated: Young's modulus in the (100) and the (110) directions, E and E', respectively; and the rigidity modulus in the (100) and the (110) directions, G and G', respectively. Formulas which relate Young's modulus and the rigidity modulus for any direction in a cubic crystal to the elastic constants are given by Voigt.[10] A cubic crystal has three independent elastic constants, S_{11}, S_{12}, and S_{44}. These are related to the measured elastic moduli by the formulas

$$\begin{aligned} 1/E&=S_{11},\\ 1/E'&=S_{11}'=\tfrac{1}{2}(S_{11}+S_{12}+\tfrac{1}{2}S_{44}),\\ 1/G&=S_{44}, \end{aligned} \tag{1}$$

and

$$1/G'=S_{44}'=(S_{11}-S_{12}+\tfrac{1}{2}S_{44}).$$

The compressibility (β) can be obtained from the elastic constants using the relationship

$$\beta=3(S_{11}+2S_{12}). \tag{2}$$

Furthermore, it can be readily shown that the relations between the elastic moduli and elastic constants are

$$\begin{aligned} C_{11}&=(S_{11}+S_{12})/(S_{11}-S_{12})(S_{11}+2S_{12}),\\ C_{12}&=-S_{12}/(S_{11}-S_{12})(S_{11}+2S_{12}),\\ C_{44}&=1/S_{44}. \end{aligned} \tag{3}$$

In accordance with the theory of Voigt,[11] the adiabatic and isothermal constants and moduli are related by the formulas

$$(S_{11})_{\mathrm{ad}}-(S_{11})_{\mathrm{is}}=(S_{12})_{\mathrm{ad}}-(S_{12})_{\mathrm{is}}=-T\alpha^2/\rho C_p, \tag{4}$$

$$(C_{11})_{\mathrm{ad}}-(C_{11})_{\mathrm{is}}=(C_{12})_{\mathrm{ad}}-(C_{12})_{\mathrm{is}}=T\alpha^2/(\rho C_p)(S_{11}+2S_{12})^2, \tag{5}$$

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[10] W. Voigt, Lehrbuch der Kristall Physik, B. Teubner, 739 (1910).

[11] W. Voigt, Lehrbuch der Kristall Physik, B. Teubner, 789 (1910).

where T is the absolute temperature, α is the coefficient of thermal linear expansion, C_p is the specific heat at constant pressure, and ρ is the density. The adiabatic and isothermal S_{44} and C_{44} are the same.

PREPARATION OF THE KCl SPECIMENS

The specimens used in this research were cut from KCl crystal blanks obtained from the Harshaw Chemical Company. The KCl blanks were cleaved into two blanks approximately 5 cm×5 cm×0.5 cm in size. One of these blanks was used for the (100) cuts and the other used for the (110) cuts. The reason for this is to ensure that both the (110) and the (100) cuts are, respectively, cut from as close to proximal positions in the crystal as possible.[12]

A few rough (110) specimens were cut from one blank, and a few rough (100) specimens cleaved from the other. These were then ground, on a lathe, to a circular cross section using a tool post grinder.[13] Each specimen measured approximately 3.5 mm in diameter and from 3 to 5 cm in length. The diameter of the specimen was made to match that of the fused quartz rod, since area matching is extremely critical in the torsional case. The adhesive used to cement the KCl specimens to the fused quartz rod was Sauereisen thinner No. 14. Many adhesives were tried, and Sauereisen thinner was found to be superior to all those tested. The cement will hold, in most cases, for several days at temperatures up to 650°C, and for a period of at least 36 hours at temperatures up to 800°C.

RESULTS

In all 40 individual temperature runs were made on about 10 different crystals. For each elastic constant measured a smooth curve was drawn to fit, as well as possible, all data on that elastic constant. Values of the elastic constant were then read from this curve at 25° intervals. The values of the elastic constants (S_{11}, S_{11}', S_{44}, and S_{44}') were then used to calculate the elastic constant S_{12} using the second and fourth equations of Eqs. (1). The values of S_{12} obtained by each method of calculation had a spread of as much as 5%, when the coefficient of linear expansion (α) as quoted by Eucken and Dannöhl,[2] was employed in the original calculations. However, α has since been remeasured[1] and these new values have been incorporated in the results quoted in this paper. Employment of these values of α reduced the variation of S_{12}, as calculated by each method, to an average deviation of 1% and a maximum deviation of 2%.

TABLE I. The adiabatic elastic constants and moduli of KCl.

Temperature °C	Adiabatic constants $\times 10^{13}$ cm²/dyne					Adiabatic moduli $\times 10^{-11}$ dynes/cm²			
	S_1	S_{44}	S_{11}'	S_{44}'	$-S_{12}$	C_{11}	C_{12}	C_{44}	$(C_{11}-C_{12})$
25	26.00	158.6	51.15	108.4	2.85	3.95	0.487	0.631	3.47
50	26.47	159.7	51.63	109.5	3.07	3.89	0.511	0.626	3.39
75	27.00	160.9	52.08	111.0	3.30	3.83	0.534	0.622	3.30
100	27.62	162.0	52.55	112.48	3.55	3.76	0.555	0.617	3.21
125	28.30	163.1	52.96	113.96	3.80	3.69	0.572	0.613	3.12
150	29.00	164.3	53.50	115.48	4.08	3.62	0.592	0.609	3.02
175	29.71	165.4	54.01	117.08	4.34	3.54	0.606	0.605	2.94
200	30.52	166.5	54.52	118.62	4.64	3.46	0.621	0.601	2.84
225	31.35	167.6	55.08	120.2	4.94	3.39	0.634	0.597	2.76
250	32.21	168.7	55.63	121.84	5.26	3.32	0.647	0.593	2.67
275	33.10	169.9	56.20	123.60	5.58	3.24	0.658	0.589	2.59
300	34.04	171.1	56.78	125.40	5.92	3.17	0.667	0.584	2.50
325	35.03	172.27	57.33	127.30	6.30	3.10	0.680	0.580	2.42
350	36.25	173.50	58.06	129.32	6.75	3.02	0.690	0.576	2.33
375	37.40	174.65	58.72	131.60	7.20	2.94	0.700	0.573	2.24
400	38.60	175.95	59.39	133.81	7.66	2.87	0.711	0.568	2.16
425	39.90	177.28	60.17	136.40	8.12	2.79	0.712	0.564	2.07
450	41.25	178.62	60.96	139.90	8.63	2.73	0.721	0.560	2.01
475	42.70	180.00	61.80	141.8	9.11	2.65	0.718	0.556	1.93
500	44.30	181.36	62.62	144.5	9.65	2.57	0.712	0.551	1.86
525	45.95	182.80	63.52	147.3	10.25	2.50	0.717	0.547	1.78
550	47.60	184.26	64.39	150.4	10.86	2.43	0.718	0.543	1.71
575	49.35	185.71	65.34	153.7	11.53	2.36	0.720	0.538	1.64
600	51.20	187.22	66.28	157.0	12.24	2.30	0.723	0.534	1.58
625	53.10	188.74	67.28	160.5	12.94	2.23	0.719	0.530	1.52
650	55.10	190.00	68.30	164.0	13.63	2.17	0.712	0.526	1.46
675	57.10	191.90	69.38	167.9	14.36	2.11	0.721	0.521	1.39
700	59.20	193.60	70.54	171.8	15.10	2.05	0.701	0.517	1.35
725	61.40	195.30	71.72	175.8	15.86	1.99	0.692	0.512	1.29
750	64.05	197.24	73.02	180.0	16.80	1.92	0.682	0.507	1.24
755	64.90	197.72	73.30	181.0	17.11	1.90	0.680	0.506	1.22
760	65.70	198.10	73.50	182.0	17.65	1.90	0.697	0.504	1.20

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[12] As suggested by R. L. Quimby, Columbia University.

[13] For a detailed description of the preparation of the oscillators see: F. D. Enck, Ph.D. thesis, University Microfilms, Publication No. 23 264 (unpublished).

TABLE II. Values of the isothermal moduli at 30°C as reported by different observers.

Observer	Elastic modulus S_{11}	$-S_{12}$	S_{44}
Durand[a]	26.26	3.7	158.9
Voigt[b]	27.37	1.4	156.0
Bridgman[c]	29.4	5.3	127
Enck	26.09	2.89	158.8

[a] See reference 9.
[b] See reference 10.
[c] P. W. Bridgman, Proc. Amsterdam Acad. 64, 19 (1929).

The temperature variation of the adiabatic elastic constants S_{11}, S_{12}, and S_{44} are tabulated in Table I. The elastic moduli C_{11}, C_{12}, and C_{44} are obtainable from the S_{ik}'s by the linear relationships given in Eqs. (3). From these one may construct pure shear moduli, C_{44}, $C_{11}-C_{12}$, and a pure dilation constant β, the compressibility. These quantities are also tabulated in Table I.

The percentage variation of the elastic moduli for different samples was as much as 2%, but the variation of the elastic moduli on different runs using the same crystal was always less than 0.2%. This variation of the elastic moduli from sample to sample could be due to the nonuniformity of the specimen cylinders, a slight area miss-match between the specimen and the silica rod, or due to the variation of crystal impurity. The case for crystal impurity is quite strong, since much smaller variations of the elastic moduli were observed if the samples were cut from proximal positions in the crystal. For the particular KCl sample used in this research the percentage of error involved in the determination of S_{11}' and S_{44}' is less than 0.3% over the entire temperature range. Thus the reliability of S_{12} is about 1%, the adiabatic compressibility about 3%, the isothermal compressibility about 3.2%, and C_v about 3%. The results are considered somewhat more reliable above 200°C, since a more consistant temperature gradient could be maintained above that temperature, thereby assuring better reproducibility. Values of the isothermal elastic moduli at 30°C reported by different observers are given in Table II.

Referring to Table I, it is apparent that the isotropy relation

$$(C_{11}-C_{12})=2C_{44}$$

is not satisfied anywhere in the temperature range from room temperature to the melting point. However, the agreement becomes better near the melting point. The results (Table I) also indicate that the Cauchy relation

$$C_{12}=C_{44}$$

is not very well satisfied over the temperature range employed in this investigation. C_{12} is about 23% below C_{44} at 25°C, equal to C_{44} at 175°C, and rises to about 27% above C_{44} near the melting point.

From Fig. 2 it is apparent that the compressibility increases monotonically to within a few degrees of the melting point. However, the drop observed in the compressibility in the last 5° before the melting point is believed to be real. This reduction seems to imply that the lattice becomes harder to compress in the immediate neighborhood of the melting point. It should be stated, however, that Fig. 2 is a plot of the adiabatic compressibility and not the isothermal compressibility. The isothermal compressibility is larger by the amount $9\alpha^2VT/C_p$. Since there is no reliable data available for the coefficient of linear expansion (α) in the immediate neighborhood of the melting point, the coefficient of linear expansion might increase quite rapidly near the melting point. Thus the isothermal compressibility might possibly increase monotonically up to the melting point.

SPECIFIC HEAT AT CONSTANT VOLUME

The present results for the compressibility, and the newly determined values of C_p[14] and α[1] can be used to determine, more reliably than had been hitherto possible, the behavior of the specific heat at constant volume at elevated temperatures. The specific heat at constant volume can be calculated using the thermodynamic relation

$$C_v=C_p-9\alpha^2VT/\beta.$$

The calculated values of C_v are tabulated in Table III, and are displayed graphically in Fig. 3. They indicate that C_v reaches the D-P value at about 450°C, and rises to a value of about 12.3 cal/mole°C near the melting

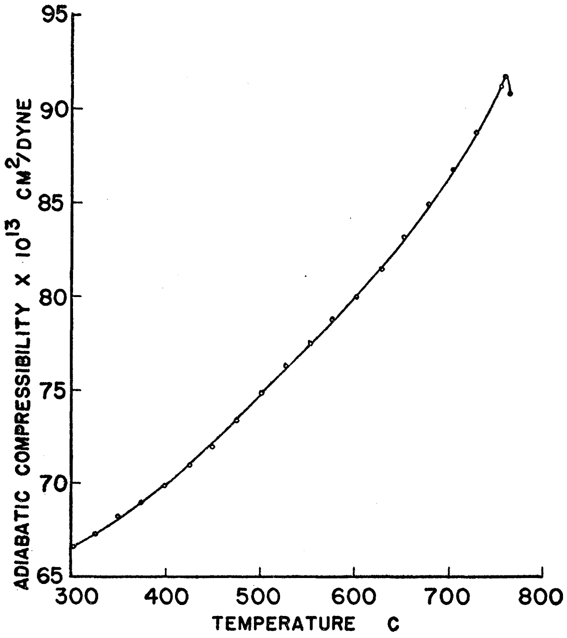

FIG. 2. Variation of the adiabatic compressibility with temperature.

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[14] C. Cooper, Final Technical Report No. 11, Nonr 60200, Project No. NR-017-206, University of Maryland, January, 1955 (unpublished).

point. This rise above the D-P value is not significant (in the usual sense of the word) since the D-P value lies within the experimental error interval of ±0.37 cal/mole°C (3%).

It is of interest to note that previous attempts to determine the behavior of C_v at elevated temperatures for a different alkali halide (NaCl) indicated that C_v dropped below the D-P value. Eucken and Dannöhl[4] reported that C_v of NaCl dropped to about 10 cal /mole°C at the melting point. This result may be discarded in favor of the more recent work of Hunter and Siegel.[5] Their results indicate a drop of about 0.5 cal/mole°C near the melting point. However, they did not consider this drop significant, due to the rather uncertain values of α and C_p used in the calculations, and surmised that C_v maintained the D-P value up to the melting point. α plays an important role in the calculation of the elastic moduli from the frequency data, and in the conversion of β_{ad} to β_{is}, and C_p to C_v. In fact, the author observed a similar drop in C_v for KCl, as that quoted by Hunter and Siegel for NaCl, when the values of α as reported by Eucken and Dannöhl were used in the calculations. The author, substantiated by Glover,[15] suspected that Eucken and Dannöhl's values of α were systematically high above 400°C. Consequently, α was remeasured at this institution.[1] When these values of α were used in the calculations of the elastic moduli, β_{is}, and C_v, the D-P value was inclosed by the error interval of C_v, as mentioned above. These new values of α also decreased the variation of S_{12}, obtained from Eqs. (1), from 5% to an average deviation of 1%, as mentioned previously.

TABLE III. Values of the compressibility, specific heat, and Grüneisen's constant at elevated temperatures.

Temperature °C	Compressibility $\times 10^{13}$ cm²/dyne β_{ad}	β_{is}	Specific heat cal/mole-degree $(C_p)^a$	C_v	Grüneisen's constant γ
300	66.60	73.55	13.125	11.884	1.393
325	67.29	74.88	13.256	11.913	1.405
350	68.25	76.51	13.383	11.939	1.411
375	69.00	78.01	13.509	11.949	1.425
400	69.84	79.51	13.635	11.954	1.447
425	70.98	81.34	13.756	12.005	1.426
450	71.97	83.00	13.877	12.003	1.419
475	73.44	85.20	13.995	12.063	1.409
500	75.00	87.54	14.113	12.091	1.397
525	76.35	89.66	14.229	12.120	1.388
550	77.64	91.71	14.345	12.144	1.380
575	78.87	93.80	14.461	12.159	1.376
600	80.16	95.99	14.577	12.173	1.371
625	81.66	98.43	14.688	12.186	1.364
650	83.52	101.25	14.802	12.210	1.350
675	85.14	103.87	14.913	12.223	1.341
700	87.00	106.77	15.028	12.245	1.329
725	89.04	109.89	15.140	12.278	1.313
750	91.35	113.23	15.252	12.304	1.294
755	92.04	114.13[b]	15.275	12.318[b]	1.289[b]
760	91.20	113.45[b]	15.30	12.229[b]	1.310[b]

[a] See reference 14.
[b] α extrapolated from 750°C.

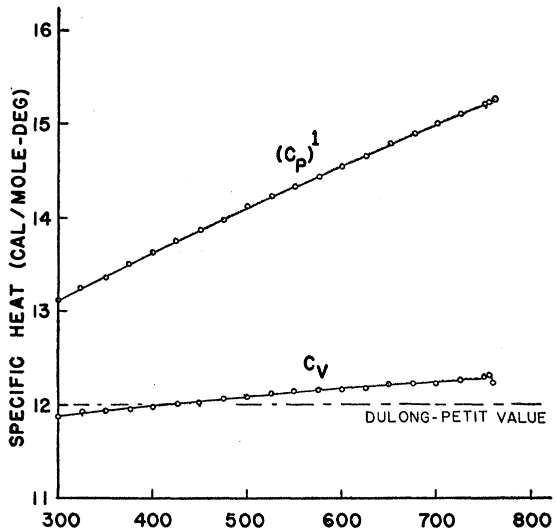

FIG. 3. Specific heat at constant pressure and constant volume for KCl at elevated temperatures.

The values of γ (Table III), defined by the equation

$$\gamma = 3\alpha V / C_v \beta_{is},$$

(a result deduced by Grüneisen from his equation of state of solids) tend to support his deductions that it should be practically independent of temperature.

In conclusion, there appears to be no important discrepancy between the D-P law and the present results for KCl. Currently, a literature search is in progress to obtain more recent values of α and C_p, in order to determine which parameter is mainly responsible for the "abnormal" behavior of C_v for NaCl as reported by Eucken and Dannöhl, and Hunter and Siegel.

ACKNOWLEDGMENTS

It is a real pleasure to acknowledge the invaluable advice, council, and guidance of Dr. Ralph D. Myers, and the aid and data supplied by many others, among them are: Dr. C. B. Cooper, K. Marks, D. Engle, and J. Ainsworth. The author also wishes to thank the Office of Naval Research, and the University of Maryland for the financial support of this work.

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[15] R. E. Glover, III, Z. Physik 138, 222 (1954).