The Heat Capacities of Molecular Lattices III. Some Simple Molecular Solids

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The experimental heat capacity data for crystalline Cl_2, CO_2, SO_2, SCO, N_2O, C_2N_2, C_6H_6, C_2H_4, and CH_3Br have been compared with the results of calculations made employing a semi-theoretical method suggested by Lord, Ahlberg, and Andrews and amplified by Lord. Good agreement between the calculated and experimental results is obtained.

THE purpose of this paper is to examine the experimental heat capacity data for a number of simple molecular solids in terms of the theoretical views advanced by Andrews[1a] and Lord, Ahlberg, and Andrews[1b] and more recently by Lord.[2] According to this point of view the heat capacity of a molecular solid at constant pressure C_p is representable by an equation of the form

$$C_p = C_v + [aC_{v(L)} + bC_{v(I)}]^2 T, \qquad (1)$$

with $C_v = C_{v(L)} + C_{v(I)}$, a and b being constants assumed independent of T. Here $C_{v(L)}$ represents the contribution of the translational and rotational modes of vibration of the molecules, acting as units, to the heat capacity of the solid at constant volume. This is given by $C_{v(L)} = nD(\theta/T)$, where n is the number of rotational and translation degrees of freedom possessed by the molecule in the gas state, and $D(\theta/T)$ is the usual Debye heat capacity function. The contribution of the internal vibration of the molecules to the heat capacity (at constant volume) is given by $C_{v(I)} = \sum_i E(\theta_i/T)$, where i represents the number of such internal degrees of freedom per molecule and $E(\theta/T)$ the Einstein heat capacity function, θ_i being calculated from spectroscopically determined internal frequencies of the molecule in the gas state.

In the absence of theoretical means of determining θ, a, and b at the present time we have contented ourselves with an examination of the validity of Eq. (1) by making an analysis of the experimental heat capacity data for a number of simple molecular solids in terms of the above-mentioned point of view. The molecular solids chosen for analysis were Cl_2, CO_2, SO_2, SCO, N_2O, C_2N_2, C_6H_6, C_2H_4, and CH_3Br. These molecules have been chosen because the requisite vibrational analyses have been carried out for the gas state and also precise studies of the heat capacities of the solid state have been made.

METHOD OF COMPARISON

A. Chlorine

As an illustration of the technique employed in obtaining values for θ, a, and b in Eq. (1) from the experimental heat capacity data and known internal frequencies of the molecule we shall consider solid chlorine in some detail.

Clearly there are three desiderata: (1) a temperature range in which $C_p - C_v$ and $C_{v(I)}$ are both very small or zero; (2) a temperature range in which $C_p - C_v$ and $C_{v(L)}$ are large while $C_{v(I)}$ is small; (3) a temperature range in which $C_p - C_v$ and $C_{v(I)}$ are large while $C_{v(L)}$ has very nearly reached a value approaching its upper limit. The first temperature range permits the determination of θ, the second a, and the third b. In any actual case these conditions will not be entirely fulfilled and it will usually be necessary to find an *approximate* value of a in order to obtain a value for θ.[3]

The heat capacity of solid chlorine has been

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[1a] D. H. Andrews, Proc. Roy. Acad. Amsterdam 29, 744 (1926); [1b] Lord, Ahlberg, and Andrews, J. Chem. Phys. 5, 649 (1937).

[2] R. C. Lord, J. Chem. Phys. 9, 693 (1941). Paper I of this series.

[3] Such an approximate value may be found by using the Nernst-Lindemann melting point equation $C_p - C_v = 0.0214 C_p^2 T/T$ (m.p.). Zeits. f. Elektrochemie 17, 817 (1911).

measured by Giauque and Powell[4] with good accuracy from 15°K to almost the melting point (172°K), and the frequency of vibration of the molecule in the gas state is also known.[5]

Since $C_{v(I)}$ for Cl_2 below 60°K is 0.001 cal./mole/deg. or less we may use this range to evaluate θ. The Lindemann melting point formula[3] gives an approximate value for $a = 1.1 \times 10^{-2}$ cal.$^{-\frac{1}{2}}$. Employing this value of a to obtain $(C_p - C_v)$, we have calculated θ_D (using $n = 5$) using the experimental values of C_p (interpolated from a smooth curve) in the range 15–50°K. The resulting θ values show a temperature trend increasing from approximately 141 at 15° to 146 at 50°. In terms of the analysis made in a previous paper[2] this observed upward trend of θ with increasing temperature is to be interpreted as meaning that the ratio of the Debye θ's for rotation and translation is not unity but nearer to 1.5, and that the apparent θ will reach a limiting value of about 150. This value ($\theta \doteq 150$) was then chosen for calculating $C_{v(L)}$ throughout the entire temperature range (15–170°K) in Eq. (1).

The more exact calculation of a may then be carried out by choosing a temperature such that the term $aC_{v(L)}$ is large compared to the term $bC_{v(I)}$. This usually requires that $C_{v(I)}$ be small compared to $C_{v(L)}$ since in practice we find a and b to be of the same order of magnitude. Choosing $T = 100°K$ with C_p (observed) $= 10.10$

cal. deg.$^{-1}$ mole^{-1}, $C_v = C_{v(L)} + C_{v(I)} = 8.92 + 0.04$ we obtain $a = 1.2 \times 10^{-2}$ cal.$^{-\frac{1}{2}}$.

Having obtained a value for a we may evaluate the constant b. Here we desire $C_{v(I)}$ to be as large as possible. Selecting $T = 160°$, where $C_{v(I)} = 0.315$ cal. deg.$^{-1}$ mole^{-1}, we solve Eq. (1) directly to obtain $b = 5.9 \times 10^{-2}$ cal.$^{-\frac{1}{2}}$.

These values of θ, a, and b have been used to calculate C_p throughout the temperature range 15–170°K. Table I summarizes the calculation. The next to last column shows $\Delta = C_p$ (observed) $- C_p$ (calc.) for various temperatures. The agreement, on the whole, is quite good. The chief discrepancy lies in the temperature range 15–50°K. This is due, of course, to the choice of $\theta = 150$ as a value to be used at all temperatures. Clearly one may improve the general fit of the experimental data by using a somewhat lower value for θ, say $\theta = 148$. Since $C_{v(L)}$ has reached 85 percent of its maximum value at 80°K such a change in θ will leave a and b virtually unchanged while improving the fit at low temperatures. This is shown in the last column of Table I where $\Delta^* = C_p$ (obs.) $- C_p$ (calc.) and the parameters $\theta = 148°$, $a = 1.2 \times 10^{-2}$ cal.$^{-\frac{1}{2}}$, and $b = 6 \times 10^{-2}$ cal.$^{-\frac{1}{2}}$ have been used.

TABLE I.

T	$C_{v(L)}$	$C_{v(I)}$	$C_p - C_v$	C_p (calc.)	C_p (obs.)	Δ	Δ^*
°K	$\theta = 150$			$\theta = 150$		$\theta = 150$	$\theta = 148$
15	0.75		0.00	0.75	0.89	+0.14	+0.11
20	1.61		.01	1.62	1.87	.25	.20
25	2.64		.03	2.67	2.90	.23	.18
30	3.66		.06	3.72	3.97	.25	.17
40	5.37		.17	5.54	5.73	.19	.11
50	6.58		.31	6.89	6.99	.10	.02
60	7.42		.47	7.89	8.00	.11	.05
70	7.99	.002	.64	8.63	8.68	.05	.00
80	8.38	.007	.82	9.21	9.23	.02	−0.02
90	8.68	.019	1.00	9.70	9.71	.01	.02
100	8.90	.037	1.19	10.13	10.10	−0.03	.06
110	9.06	.064	1.39	10.52	10.47	.05	.08
120	9.19	.10	1.54	10.83	10.87	.04	.08
130	9.30	.14	1.87	11.31	11.29	.02	.05
140	9.38	.20	2.15	11.73	11.73	.00	.03
150	9.45	.25	2.48	12.18	12.20	+0.02	.00
160	9.50	.32	2.81	12.63	12.68	.05	+0.02
170	9.55	.38	3.19	13.12	13.17	.05	.02

The numerical results listed in Tables I and III are expressed in calories. One calorie (15°) = 4.183 international joules. The gas constant R was taken to be 1.986 cal. deg.$^{-1}$ mole^{-1}.

[4] W. F. Giauque and T. M. Powell, J. Am. Chem. Soc. 61, 1970 (1939).
[5] A. Elliott, Proc. Roy. Soc. London A127, 638 (1930).

TABLE II.

Molecule	n	θ Deg.	a Cal.$^{-\frac{1}{2}}$	b Cal.$^{-\frac{1}{2}}$	Source of data	
					Heat capacity	Frequency assignment
CO_2	5	171	0.0110	0.030	(1)	(12)
SO_2	6	172	0.0098	0.049	(2)	(13)
SCO	5	131	0.0122	0.020	(3)	(14)
N_2O	5	160	0.0118	0.034	(4)	(15)
C_6H_6	6	150	0.0090	0.0057	(5), (6), (7)	(16)
C_2N_2	5	150	0.0093	0.007	(8)	(17)
CS_2	5	125	0.0115	0.012	(9)	(18)
C_2H_4	6	170	0.0141	—	(10)	(19)
CH_3Br	6	150	0.0095	0.01	(11)	(20)

[1] Giauque and Egan, J. Chem. Phys. 5, 45 (1937).
[2] Giauque and Stephenson, J. Am. Chem. Soc. 60, 1389 (1938).
[3] Kemp and Giauque, J. Am. Chem. Soc. 59, 79 (1937).
[4] Blue and Giauque, J. Am. Chem. Soc. 57, 991 (1935).
[5] Ahlberg, Blanchard, and Lundberg, J. Chem. Phys. 5, 539 (1937).
[6] Huffman, Parks, and Daniels, J. Am. Chem. Soc. 52, 1547 (1930).
[7] Nernst, Ann. d. Physik 36, 395 (1911).
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[9] Brown and Manov, J. Am. Chem. Soc. 59, 500 (1937).
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[11] Egan and Kemp, J. Am. Chem. Soc. 60, 2097 (1938).
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[13] Badger and Bonner, Phys. Rev. 43, 305 (1933).
[14] Bartunek and Barker, Phys. Rev. 48, 516 (1935).
[15] Plyler and Barker, Phys. Rev. 38, 1827 (1931); 41, 369 (1932).
[16] Langseth and Lord, Kgl. Danske Vid. Sels. Math-Fys. Medd. 16, 75, No. 6 (1938), Table 18. The missing frequencies in this Table, Nos. 14 and 15, make only a trifling contribution to C_v. They have been estimated to be 1600 and 1160 cm^{-1}, respectively.
[17] Woo and Badger, Phys. Rev. 39, 932 (1932). See also Burcik and Yost, J. Chem. Phys. 7, 1114 (1939); Stitt, ibid. 1115 (1939).
[18] Dennison and Wright, Phys. Rev. 38, 2077 (1931).
[19] Bonner, J. Am. Chem. Soc. 58, 34 (1936).
[20] The frequencies used by Egan and Kemp (reference 11) to compare the thermal and spectroscopic entropies were used. See also Stevenson and Beach, J. Chem. Phys. 6, 25, 108 (1938).

TABLE III.

T °K	CO₂ C_p(obs)	C_p(calc)	Δ	SO₂ C_p(obs)	C_p(calc)	Δ	SCO C_p(obs)	C_p(calc)	Δ	N₂O C_p(obs)	C_p(calc)	Δ
15	0.54	0.52	+0.02	0.83	0.61	+0.22	1.37	1.10	+0.27	0.67	0.63	+0.04
20	1.23	1.16	.07	1.68	1.37	.31	2.61	2.21	.40	1.50	1.38	.12
25	2.14	2.01	.13	2.72	2.39	.33	3.78	3.43	.35	2.46	2.34	.12
30	3.08	2.95	.13	3.79	3.49	.30	4.84	4.56	.28	3.45	3.33	.12
40	4.69	4.70	−0.01	5.78	5.59	.19	6.62	6.35	.27	5.13	5.13	.00
50	6.10	6.11	.01	7.36	7.28	.08	7.70	7.61	.09	6.52	6.52	.00
60	7.18	7.17	+0.01	8.62	8.55	.07	8.48	8.49	−0.01	7.56	7.57	−0.01
70	7.97	7.98	−0.01	9.57	9.52	.05	9.08	9.14	.06	8.32	8.35	.03
80	8.58	8.61	.03	10.32	10.29	.03	9.62	9.66	.04	8.95	8.97	.02
90	9.11	9.12	.01	10.93	10.91	.02	10.09	10.12	.03	9.44	9.47	.03
100	9.53	9.54	.01	11.49	11.45	.04	10.53	10.54	.01	9.90	9.94	.04
110	9.92	9.93	.01	11.97	11.95	.02	10.95	10.96	.01	10.32	10.37	.05
120	10.30	10.28	+0.02	12.40	12.43	−0.03	11.40	11.39	+0.01	10.77	10.79	.02
130	10.67	10.62	.05	12.83	12.88	.05	11.85	11.85	.00	11.25	11.24	+0.01
140	11.04	10.99	.05	13.31	13.36	.05				11.72	11.70	.02
150	11.39	11.36	.03	13.82	13.84	.02				12.19	12.20	−0.01
160	11.77	11.75	.02	14.33	14.33	.00				12.71	12.73	.02
170	12.17	12.17	.00	14.85	14.85	.00				13.30	13.28	+0.02
180	12.61	12.60	.01	15.42	15.38	+0.04				13.98	13.87	.11
190	13.07	13.05	.02	16.02	15.93	.09						

T °K	C₂N₂ C_p(obs)	C_p(calc)	Δ	CS₂ C_p(obs)	C_p(calc)	Δ	C₆H₆ C_p(obs)	C_p(calc)	Δ	C₂H₄ C_p(obs)	C_p(calc)	Δ	CH₃Br C_p(obs)	C_p(calc)	Δ
15	0.86	0.75	+0.11	1.64	1.24	+0.40	0.92	0.91	+0.01	0.68	0.63	+0.05	1.54	0.90	+0.64
20	1.76	1.62	.15	2.82	2.44	.38	1.84	1.94	−0.10	1.52	1.42	.10	2.56	1.94	.62
25	2.82	2.65	.17	3.92	3.71	.21	3.00	3.20	.20	2.54	2.46	.08	3.60	3.18	.42
30	3.78	3.70	.08	4.97	4.84	.13	4.24	4.46	.22	3.56	3.62	−0.06	4.54	4.44	.10
40	5.57	5.52	.05	6.65	6.59	.06	6.47	6.58	.11	5.67	5.81	.14	6.37	6.55	−0.18
50	7.02	6.94	.08	7.83	7.79	.04	8.14	8.15	.01	7.39	7.63	.24	7.93	8.18	.25
60	8.20	8.11	.09	8.62	8.62	.00	9.32	9.28	+0.04	8.92	9.05	.13	9.16	9.33	.17
70	9.13	9.08	.05	9.28	9.26	.02	10.16	10.20	−0.04	10.18	10.18	.00	10.02	10.14	.12
80	9.97	9.94	.03	9.89	9.83	.06	10.85	10.90	.05	11.55	11.11	+0.44	10.79	10.79	.00
90	10.71	10.73	−0.02	10.49	10.35	.14	11.44	11.53	.09	13.29	11.84	1.45	11.42	11.31	+0.11
100	11.41	11.45	.04	11.07	10.86	.21	11.98	12.16	.18	17.05	12.52	4.53	11.92	11.73	.19
110	12.08	12.12	.04	11.61	11.37	.24	12.61	12.77	.16				12.34	12.09	.27
120	12.73	12.77	.04	12.09	11.89	.20	13.32	13.36	.04				12.67	12.43	.24
130	13.35	13.39	.04	12.52	12.42	.10	14.02	14.03	.01				12.96	12.76	.20
140	13.91	13.99	.08	12.92	12.94	−0.02	14.76	14.73	+0.03				13.21	13.05	.16
150	14.47	14.58	.11	13.28	13.48	.20	15.53	15.48	.05				13.44	13.37	.07
160	15.02	15.14	.12	13.63	14.01	.38	16.31	16.28	.03				13.66	13.69	−0.03
170	15.58	15.69	.11				17.10	17.14	−0.04				13.88	14.00	.12
180	16.20	16.23	.03				18.01	18.05	.04						
190	16.82	16.77	+0.05				18.99	19.05	.06						
200	17.45	17.29	.16				20.07	20.10	.03						
210	18.11	17.79	.32				21.21	21.25	.04						
220	18.82	18.29	.53				22.30	22.38	.08						
230	19.54	18.78	.76				23.52	23.56	.04						
240	20.27	19.27	1.00				24.80	24.80	.00						
250							26.13	26.10	+0.03						
260							27.75	27.44	.31						
270							29.55	28.83	.72						

For the molecular solids studied in this paper we have always adjusted the θ to give a good fit at low temperatures in the manner described above.

B. Other Molecules

The other molecular solids whose heat capacities have been analyzed in the above manner are listed in Table II together with the source of the heat capacity data and frequency assignments employed in making the comparisons. In addition, Table II presents the values used for n (the number of translational and rotational degrees of freedom of the molecule) θ, a, and b for each solid. These have been used to make the

calculations of C_p listed in Table III. In all tables the experimental C_p values listed have been obtained from a smooth curve through the data given in the reference cited.

DISCUSSION OF RESULTS

An examination of Tables I and III shows that Eq. (1) does indeed represent the experimental heat capacity data with good accuracy, especially for the molecules Cl_2, CO_2, N_2O, and C_6H_6, where the disagreement is of the same order of magnitude as the experimental errors in C_p. In all the molecular solids studied the agreement is poorest for very low temperatures (below 30°K). As has already been pointed out this disagreement is to be expected, since, in general, the arbitrary choice of a single Debye function to represent both the translational and torsional motions of the molecules is certainly inadmissible in this temperature range. That the agreement can be quite good to temperatures as low as 4°K has been shown by Lord, Ahlberg, and Andrews[1] for benzene.

It should be pointed out that the good agreement between the calculated and experimental values of C_p for these molecular solids is very dependent upon the correct choice of n (Table II). Thus, good agreement between the calculated and experimental values of C_p for crystalline SCO is obtained only if the molecule is assumed to be linear $(n=5)$. This choice is in agreement with the conclusion of Eucken and Schaefer[6] that an angular model[7] for the SCO molecule is incompatible with ultrasonic measurements of the heat capacity of the gas.

The discrepancies which arise for C_2N_2 and C_2H_4 in the neighborhood of the melting point are probably to be attributed to the fact that as melting becomes imminent the motion of the molecules comprising the solid is no longer harmonic, their amplitudes becoming very large. An analysis of the heat capacity data for crystalline SiH_4, CF_4, SF_6, and CCl_4 exhibited similar disagreements in the neighborhood of the melting or transition temperatures.[8]

From Table II it may be seen that the values of the constants a and b are of the same order of magnitude. Due to the fact that the solid usually melts before the contribution of the internal molecular vibrations to C_p becomes large the constant b is less accurately determined than a.

ACKNOWLEDGMENT

The authors wish to acknowledge the help and continued interest of Dr. R. C. Lord, Jr., who suggested this problem to us.

[6] A. Eucken and K. Schaefer, Chem. Abst. **36**, 2767 (1942).

[7] J. Wagner, Zeits. f. physik. Chemie **B48**, 309 (1941).

[8] A. Eucken, Zeits. f. Elektrochemie **45**, 126 (1939), has carried out a somewhat different analysis of the experimental C_p data and has concluded that the rapid increase of C_p at the higher temperatures is due to the character of the torsional motion of the molecules in the lattice.

Erratum: Contact Angles at Liquid-Liquid-Air Interfaces

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EQUATION (3) should read

$$d\sigma_{an,w} = \sigma_{w,A}\left[\frac{\sin(\theta+\phi)}{\cos\phi}\right]d\theta - \left[\frac{\cos(\theta+\phi)}{\cos\phi}\right]d\sigma_{w,A} - \frac{d\sigma_{an,A}}{\cos\phi},$$

instead of

$$d\sigma_{an,w} = -\sigma_{w,A}\left[\frac{\sin(\theta+\phi)}{\cos\phi}\right]d\theta - \left[\frac{\cos(\theta-\phi)}{\cos\phi}\right]d\sigma_{w,A} - \left[\frac{\cos 2\phi}{\cos\phi}\right]d\sigma_{an,A}.$$