[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Heat Capacities of Cis and Trans Dichloroethylenes

BY A. R. OLSON AND F. W. BRITTAIN

In an investigation of *cis-trans* reactions which is in progress in this Laboratory, the heat capacities of the two forms of gaseous dichloroethylene were needed. No data for these substances were found in the literature, and so we determined them by the velocity of sound method. Eucken and Mücke[1] and Kneser[2] have discussed objections to the use of high frequency sound waves for heat capacity determinations. As will be seen later, these objections, apparently, do not apply to the dichloroethylenes in the temperature range in which we worked.

Briefly the method consists in determining the wave length of sound waves in the gas to be investigated. These waves are produced by a quartz crystal which is responding to an alternating current of known frequency. For an ideal gas the equation connecting heat capacity with the velocity of sound, W, is

$$C_v = \frac{R}{(MW^2/RT) - 1} = \frac{R}{\gamma - 1} \tag{1}$$

For a gas obeying van der Waals equation we can write

$$C_v = R/(\gamma - 1 + \phi) \tag{2}$$

in which

$$\phi = \frac{2aP}{(RT)^2} - \gamma\frac{2bP}{RT} \tag{3}$$

if we neglect higher order terms. Since the correction due to first order terms is small, this procedure is justified.

The van der Waals constants a and b have not been determined, and so they were estimated by two different methods. In the first method the average effect of substituting a chlorine for a hydrogen was determined for six substances for which the a's and b's were known, and then twice this correction was made in the constant for ethylene. In the second method, the average percentage change in the constants due to replacing two hydrogens bound to carbon by a carbon–carbon double bond was determined for five substances, and this reduction was made in the constants for ethylene dichloride. By the first method $a = 0.0319$ and $b = 0.00455$ and by the second method $a = 0.0303$ and $b = 0.00437$. The average values, $a = 0.031$ and $b = 0.0045$ are probably accurate to about 10%. This uncertainty in a and b corresponds to an uncertainty of 0.05 calorie/deg. in the heat capacity and this is less than the average experimental error.

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(1) A. Eucken and O. Mücke, *Z. physik. Chem.*, **18B**, 167 (1932).

(2) Kneser, *Ann. Physik*, **11**, 777 (1931). Also by personal communication of as yet unreported results.

Apparatus.—Electrical circuits for sonic interferometers have been described so often in the literature[3] that the description of the circuit is here limited to the wiring diagram in Fig. 1. The variation of the current through the microammeter due to sonic interference was from 20 to 100 microamperes, depending on the distance separating the reflector from the crystal.

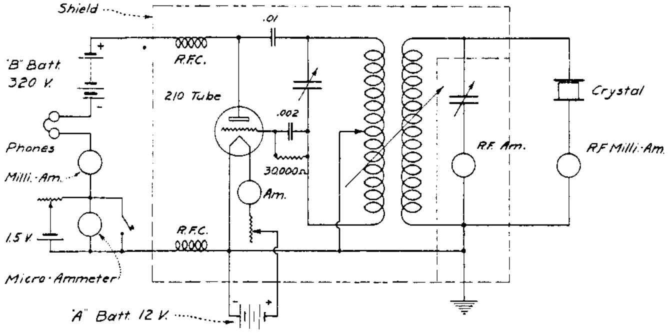

Fig. 1.—Wiring diagram for the sonic interferometer.

The quartz crystal was 28 × 23 × 22 mm. It was cut so that the 28 mm. axis was inclined about 18.5° away from the optic axis toward the mechanical axis, so as to get a vibration perpendicular to the face which was parallel to the reflector, as shown by Wright and Stuart.[4] The vibration frequency of the crystal was determined at various pressures and temperatures, not only directly by a General Radio standard wave meter, but also by checking by harmonic bracketing against several local broadcasting stations. The error in the frequency is estimated to be not more than 0.1%.

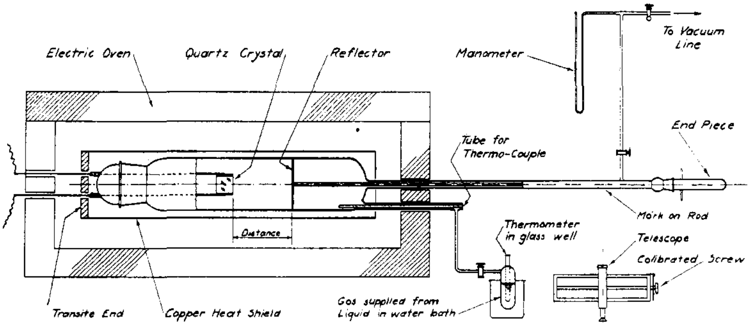

Fig. 2.—Assembly for measuring the velocity of sound.

The glass cylinder shown in Fig. 2 is about 70 mm. by 350 mm. The crystal mounting is depicted in Fig. 3. The reflector could be moved parallel to itself by turning the end piece. Positions of the reflector were read to 0.01 mm. The lubricant recommended by Meloche and Fredrick[5] was used on the joints exposed to the dichloroethylene. The gas pressure was determined by the temperature of liquid dichloroethylene

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(3) See G. W. Pierce, *Am. Acad. Arts Sci.*, **60**, 271 (1925); C. D. Reid, *Phys. Rev.*, **35**, 814 (1930).

(4) R. B. Wright and D. M. Stuart, *Bureau Standards Research Paper*, No. 356 (1931).

(5) C. C. Meloche and W. G. Fredrick, THIS JOURNAL, **54**, 3264 (1932).

in the side-tube. The temperature of the gas in the cylinder was measured by a thermocouple. The temperature measurements are probably accurate to about 0.25°.

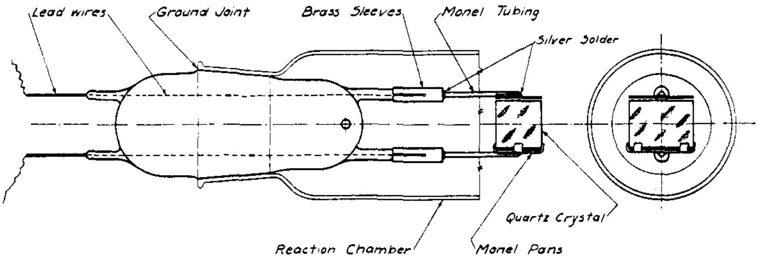

Fig. 3.—Mounting for quartz crystal.

The temperature of the gas between the oscillating crystal and the reflector was higher than the ambient gas due to the energy in the sound waves. This was checked not only by experiments on air at atmospheric pressure where all the data for computing the temperature from $w^2 = RT/M\ (C_p/C_v)$ are known, but also by inserting an alcohol thermometer in the path of the sound waves. For the crystal we used, a current through the crystal of 3.3 m. a. produced an increase of 0.3 degree in air at atmospheric pressure. By keeping the gas pressure and the current low enough, we were able to make this temperature correction unimportant.

Experimental Procedure

A new sample of gas was introduced into the reaction chamber for each run. The chamber was pumped out and filled with gas several times to eliminate air. The final pumping was run several hours at a pressure less than 10^{-3} mm. The pressure of the

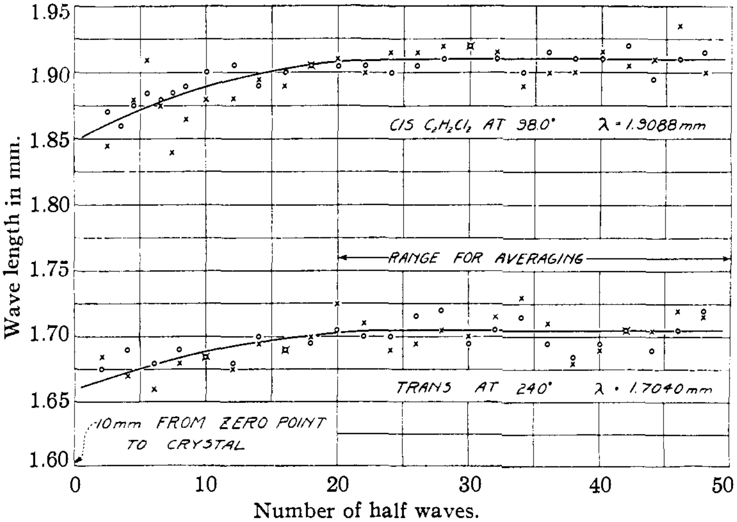

Fig. 4.—Typical curves of wave length as a function of the number of half waves separating the reflector from the crystal.

gas was taken as that corresponding to the temperature of the liquid and checked by the manometer. For the runs with the oven at room temperature the liquid was about

10° for the *cis* and at 0° for the *trans*. For runs at higher temperature the liquid was at room temperature for the *cis* and 8 to 10° for the *trans*. The oven, meanwhile, was heated to near the desired temperature and was allowed to stand for at least one hour to come to temperature equilibrium. The gas was allowed to stand in the reaction chamber with the crystal oscillating for at least half an hour before the run to ensure steady operation. For the runs, the reflector was set either 1 or 3 cm. away from the crystal and the first peak called the 0 or 20 half-wave position to correspond. The reflector was moved out and readings of distance taken for every other peak to the fiftieth peak and then repeated as the reflector was moved toward the crystal. The manometer, thermometers and other instruments were read before, at the middle and at the end of each run.

Typical readings of the wave length as a function of the number of half-wave lengths separating the reflector from the crystal are shown in Fig. 4. Due to the obvious trend in the wave length at small distances, only the sixteen readings between the twentieth and the fiftieth nodes were used for averaging. The average wave length was computed from $[(A + B \ldots N) - (a + b + \ldots n)]/N^2$ where $A, B \ldots N$ are the first eight readings and $a, b \ldots n$ are the second series of eight readings. From the two separate averages obtained as the reflector was moved in or out, a final average reading was computed for the runs. These final average wave lengths agreed within 0.1%.

TABLE I

SUMMARY OF RUNS OF *Cis* DICHLOROETHYLENE

Temp., °C.	Press., mm. Hg, p	Wave length, λ	Freq. kcy., f	Vel. sound, W	$\gamma = MW^2/RT$	C_v ideal gas[a]	Corr. term, ϕb	C_v actual gas[b]
22.1	112	1.6965	100.80	171.00	1.1549	12.82	0.0064	12.31
71.9	161	1.8427	100.70	185.60	1.1641	12.11	.0065	11.64
97.7	168	1.9089	100.65	192.11	1.1605	12.38	.00575	12.02
98.1	168	1.9088	100.65	192.08	1.1589	12.50	.00575	12.06
140.2	181	2.0141	100.45	202.32	1.1547	12.84	.0048	12.46
162.3	180	2.0697	100.35	207.70	1.1576	12.60	.00450	12.25
163.7	180	2.0834	100.35	209.07	1.1667	11.91	.00450	11.60
192.9	173	2.1455	100.15	214.91	1.1556	12.76	.00345	12.58
240.5	180	2.2697	99.95	226.86	1.1713	11.80	.00300	11.60

[a] See Equation (1). [b] See Equations (2) and (3).

TABLE II

SUMMARY OF RUNS OF *Trans* DICHLOROETHYLENE

Temp., °C.	Press., mm. Hg., p	Wave length, λ	Freq. kcy., f	Vel. sound, W	$\gamma = MW^2/RT$	C_v ideal gas[a]	Corr. term, ϕb	C_v actual gas[b]
24.0	124	1.7040	100.80	171.76	1.1578	12.59	0.0070	12.05
54.9	180	1.7861	100.75	179.95	1.1511	13.15	.0082	12.48
79.2	182	1.8577	100.70	187.07	1.1582	12.56	.0070	12.02
123.8	180	1.9763	100.70	198.70	1.1598	12.43	.0053	12.03
150.5	178	2.0395	100.40	204.77	1.1541	12.89	.0045	12.52
181.2	193	2.1149	100.25	211.98	1.1532	12.97	.0041	12.62
197.4	179	2.1607	100.15	216.39	1.1604	12.38	.0035	12.12
243.7	171	2.2735	99.90	227.12	1.1638	12.13	.0027	11.92

[a,b] See footnotes for Table I.

Results and Conclusions

The data and the computed values of C_v are summarized in Tables I and II and are shown on curves on Figs. 5 and 6. It is interesting to note the decrease of 1 to 2% in the wave length close to the crystal which occurred consistently in all tests whereas Pierce and Reid[3] working with air and carbon dioxide found an increase.

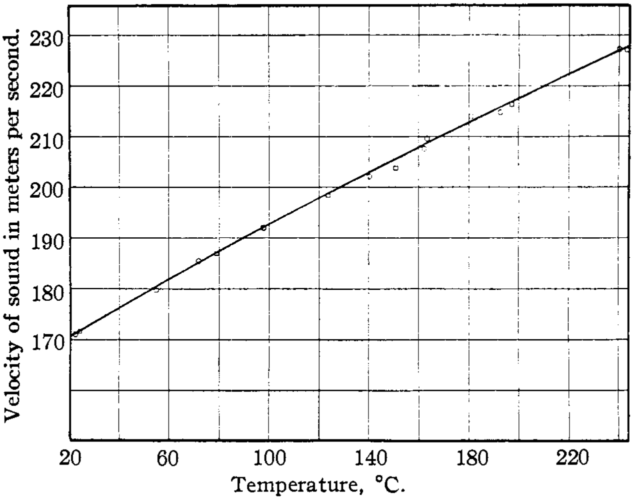

Fig. 5.—Velocity of sound in *cis*- and *trans*-dichlorethylene: ○, *cis*-dichloroethylene; □, *trans*-dichlorethylene.

The accuracy of the final results suffers from the nature of the equation, for the errors in measuring the velocity of sound are increased some fifteen times in computing C_v due to the fact that the velocity is squared and that γ (about 1.16) is so nearly equal to 1. Frequency and wave length were each measured to about 0.1%. This corresponds to an error of about 0.25 calorie in the heat capacity, agreeing with an average deviation of about 0.26 calorie for the individual experimental values.

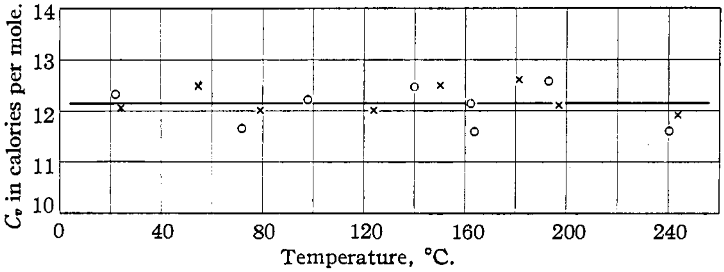

Fig. 6.—Heat capacity of *cis*- and *trans*-dichloroethylene: ○, *cis*-dichloroethylene; ×, *trans*-dichloroethylene.

Referring to Fig. 6, the data may be interpreted by assuming that C_v is the same for both gases and is constant over the whole range of temperatures with an average value of 12.14 ± 0.26 calories per mole.

Eucken and Mücke point out that with too high a frequency, the velocity of sound experiments on air and similar gases measures only a part of the vibrational energy. Kneser states that following a small and sudden change of pressure, each of the internal degrees of freedom, rotational and vibrational, requires a certain length of time to establish equilibrium with the translational degrees and that this time interval is a function of $h\nu/RT$. For a given temperature there is a critical frequency (or range of frequencies) below which the half period is relatively large and the particular internal degree is measured and above which the half period is too small for the degree to respond. For a given frequency and temperature, the internal degrees of freedom with relatively low $h\nu$ values will be measured and those with a relatively high $h\nu$ value will fail to respond. Due to the constancy of C_v over such a large temperature range, it appears to be quite likely that both forms of dichloroethylene have three vibration degrees of freedom of such low frequencies that they respond fully, and that the other nine vibrations have such high frequencies that they do not contribute appreciably to the heat capacity below 250°.

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The Activity Coefficients of Hydrochloric Acid in Aqueous Solutions Containing Either Sodium or Potassium Perchlorate

BY STUART J. BATES AND JOSEPH W. URMSTON

Recent investigations,[1] both theoretical and experimental, have emphasized the fact that except in very dilute solutions, activity coefficients of strong electrolytes cannot be accurately calculated from theoretical considerations alone.

The original Debye–Hückel development of the ion attraction theory showed that in dilute solution the activity coefficient is chiefly determined by the ionic strength. Its dependence upon other factors was later taken into account and more accurate formulas derived. These involve constants whose numerical values must be determined from the data themselves.[1d] One of these constants "A" is related to the ionic diameters. By making certain assumptions regarding its value in mixtures of electrolytes,

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[1] (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); (b) Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924); (c) Noyes, *ibid.*, **46**, 1080, 1098 (1924); (d) Hückel, *Physik. Z.*, **26**, 93 (1925).