

of  $\lambda$  was calculated from the data of Watkins and Jones<sup>10</sup> on the equivalent conductance of potassium ferricyanide at various temperatures, and the values given by Johnston<sup>7</sup> for the equivalent ionic conductance of the potassium ion at various temperatures.

### Discussion

Cottrell<sup>2</sup> has shown in a linear diffusion experiment on zinc sulfate that the quantity  $i\sqrt{t}$  remained constant to  $\pm 5\%$  for a period of over two days, but made no theoretical calculation of the value of the constant obtained.

It is evident from the data given in Table I that in our experiments the extreme limits of fluctuation in  $i\sqrt{t}$  were only  $\pm 0.5\%$  from the average value, in 26 readings over a period of twenty minutes. In other experiments a constancy was obtained over a period of several hours, but in general a slight drift toward higher values with very long periods of time was observed, due to unavoidable vibrations.

The data given in Table II show that the observed values for the quantity  $i\sqrt{t}$  show a deviation from those calculated from the equivalent ionic conductances at infinite dilution of  $-1.5$ ,  $-2.9$  and  $+1.5\%$  for the ferrocyanide, ferricyanide, and silver ions, respectively. These data

(10) C. Watkins and H. C. Jones, *THIS JOURNAL*, **37**, 2626 (1915).

are in essential agreement with those of Lingane and Kolthoff<sup>6</sup> on diffusion currents with the dropping mercury electrode.

The observed values of the temperature coefficient of  $i\sqrt{t}$  are in good agreement with the calculated values over the same temperature range, as is evident from the data given in Table III. The agreement is probably within the experimental error, since the measurements were made only over a temperature range of ten degrees.

### Summary

1. Current-time curves with various shapes of electrodes and diffusion fields in the electro-oxidation of ferrocyanide ions were determined, and the condition under which theoretical diffusion conditions can be obtained are discussed. Theoretical conditions were not obtained with spherically symmetrical diffusion in aqueous solution, but were approached in 3% agar and in 4% gelatin gels.

2. With linear diffusion in such a direction as to produce a density gradient in the downward direction, the quantity of  $i\sqrt{t}$  was found to be constant to  $\pm 0.5\%$  over a period of twenty minutes.

3. The temperature coefficient of the quantity  $i\sqrt{t}$  was found to be in agreement with the calculated value.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

## The Specific Heat of Some Ethylene Halides<sup>1</sup>

BY WILFORD E. RAILING<sup>2</sup>

The problem whether there is free or restricted rotation about the carbon-carbon bond in ethane and its derivatives has led to considerable research upon the 1,2-disubstituted ethanes. Of these, the chloro and bromo derivatives have received the greatest attention. Time-temperature heating curves made by White and Morgan<sup>3</sup> revealed a transition or hump in the specific heat curve in 1,2-dibromoethane at  $-23^\circ$ . Since the dielectric constant is only minutely affected by the transition, it is likely that the change of state does not affect the polarity of the molecule. Since these

(1) Part of a dissertation presented to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Master of Arts.

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(3) White and Morgan, *J. Chem. Phys.*, **6**, 655 (1937).

transitions are most effectively studied by means of heat capacity measurements, the heat capacities of 1,2-dibromoethane (ethylene bromide), 1,2-dichloroethane (ethylene chloride), and 1,2-bromochloroethane (ethylene chlorobromide) have been determined in the range  $90$ – $320^\circ\text{K}$ .

### Apparatus and Procedure

The calorimeter employed was the same calibrated conduction calorimeter and the procedure was the same as employed by Stull.<sup>4</sup>

### Materials

**Benzene.**—J. T. Baker c. p. thiophene-free material was distilled through a five-foot (1.5 m.) column packed with glass helices similar to those described by Young and Jasaitis.<sup>5</sup> The middle fraction was then fractionally

(4) Stull, *THIS JOURNAL*, **59**, 2729 (1937).

(5) Young and Jasaitis, *ibid.*, **58**, 377 (1936).

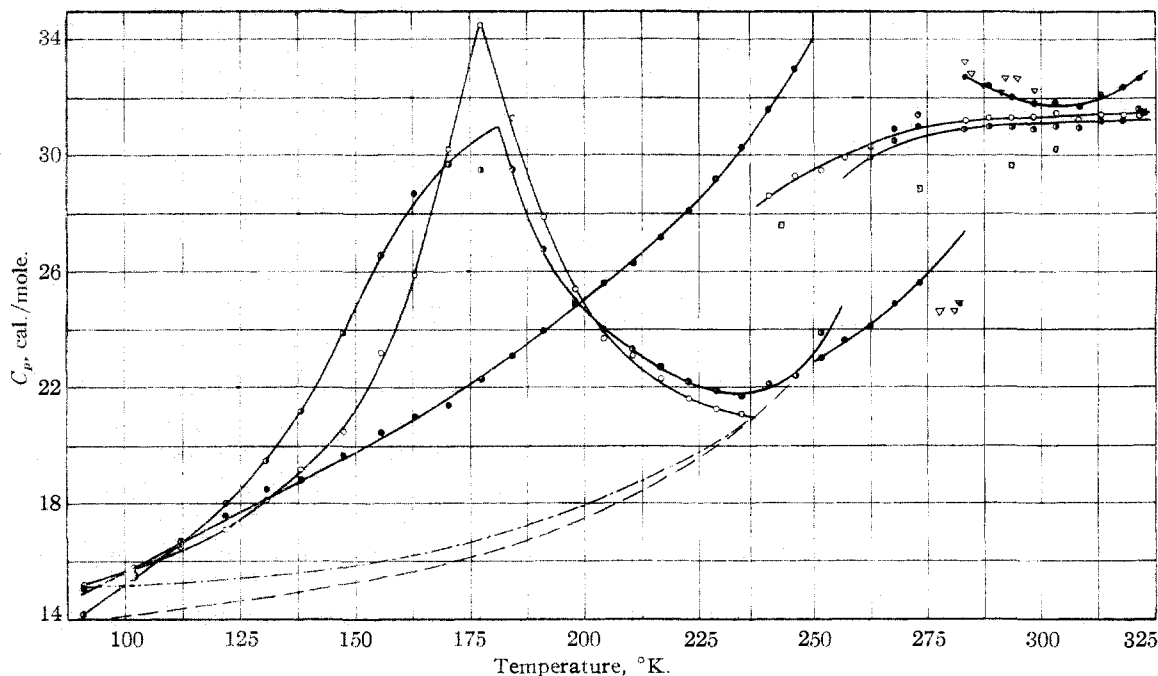


Fig. 1.—Molal heat capacities:  $\circ$ , 1,2-dichloroethane, mol. wt. 98.97; moles in sample, 0.0358;  $\bullet$ , 1,2-dibromoethane, mol. wt., 187.88; moles in sample, 0.0328;  $\odot$ , 1,2-bromochloroethane, mol. wt., 143.42; moles in sample, 0.0343. ---, extrapolated "Normal" heat capacity for dichloroethane. — —, extrapolated "Normal" heat capacity for bromochloroethane.  $\Delta$ , Previously published values for dibromoethane.  $\square$ , Previously published values for dichloroethane.  $0^{\circ}\text{C.} = 273.10^{\circ}\text{K.}$ ; 1 calorie = 4.1850 abs. joules.

crystallized six times, about one-fifth of the material being discarded each time. This was again distilled through the column and a fraction boiling over a  $0.02^{\circ}$  range was obtained. This material was used in all the calibration runs. The amount of premelting indicated a purity of 99.997 mole per cent.

**Ethylene Chloride.**—Eastman Kodak Co. material was distilled twice through a five-foot column, a fraction with a boiling range of  $0.02^{\circ}$  being obtained. This fraction was fractionally crystallized twice and given a final distillation before using; b. p.  $83.8^{\circ}$ , m. p.  $-35.5^{\circ}$ . The amount of premelting indicated a purity of 99.96 mole per cent.

**Ethylene Chlorobromide.**—Eastman Kodak Co. material was distilled twice through a 40-cm. Vigreux column, and a  $0.2^{\circ}$  fraction was obtained. This fraction was recrystallized six times, and given a final distillation before using; m. p.  $-16.7^{\circ}$ . The amount of premelting indicated a purity of 99.8 mole per cent.

**Ethylene Bromide.**—Eastman Kodak Co. material was given the same treatment that was given the chlorobromide; m. p.  $9.93^{\circ}$ . The amount of premelting indicated a purity of 99.92 mole per cent.

### Experimental Results

The accuracy of averaged determinations obtained with this calorimeter has been placed within 0.75–1.25% of the true values by Stull.<sup>4</sup> It is the author's opinion that a better value for the accuracy would be 1–2%. The heats of fusion are

probably accurate to 1% or better, instead of Stull's estimate of 3–4%.

The thermocouples used in this work had been calibrated by Stull,<sup>4</sup> and were used about a year after his research. Comparison of the melting and transition points of several materials with the literature values showed that the calibration had not changed appreciably.

The experimental specific heat values were plotted against the temperature, and a smooth curve drawn through the points. These smooth curves together with the experimental values are sketched in Fig. 1. The values of the experimental points may be read off the figure within the limit of the accuracy (1–2%).

It will be seen that the chlorobromide and chloride exhibit humps of considerable magnitude in the specific heat curve for the solid. To calculate the increase in heat content represented by these humps, the course of the "normal" heat capacity curve was charted as shown by the broken lines in the diagrams. The values of the special increments of heat content estimated in this manner are probably within 10% of the correct values. These values, together with the other transition and heats of fusion data, are presented in Table I.

TABLE I  
HEATS OF TRANSITION AND FUSION DATA IN CALORIES PER MOLE AND °C.

	Fusion, This Research	Transition, This Research	Fusion, Demerliac	Fusion, Petersson
1,2-Dichloroethane	2090 at -35.5°	680	....	...
1,2-Dibromochloroethane	2300 at -16.7°	740	....	...
1,2-Dibromoethane	2590 at 9.93°	450 at -22.5°	2540 at 9.55°	2440 at 8.0°

together with the results obtained by other observers. The error in the heat of transition of the bromide is probably less than 2%. The heats of fusion have been corrected for premelting, and represent the heat of fusion for a 100% pure compound. The specific heat values for the solids just below the melting point have also been corrected for premelting.

The previously published data of the specific heats of these compounds<sup>6</sup> disagree somewhat with the values presented here, as can be ascertained from Fig. 1. It should be noted, however, that except for one set (Leblanc and Mobius),<sup>6</sup> the data are from forty to seventy-five years old. The values of Leblanc and Mobius for the bromide agree well with our results in the liquid state, but their values for the solid are about 3% lower than those presented here. No heat capacity data could be found in the literature for ethylene chlorobromide.

The heat of fusion of the bromide is about 2% higher than any previously observed values.<sup>7</sup> This may be due to the fact that a correction for premelting has been included in the data presented here. The melting point of Demerliac's sample (9.55°) is almost 0.4° lower than our value (9.93°). Premelting may have influenced Demerliac's determination. The other reported value,<sup>8</sup> was measured on a sample whose melting point (8°) indicated such an impure material that its heat of fusion is undoubtedly too low. These results will be found in Table I.

Early in this experimental investigation it was found that series of heat capacity determinations made successively on the same sample of ethylene chloride displayed systematic disagreements which could not be attributed to the functioning of the calorimeter. The disagreement was most noticeable in the liquid state. Calibration runs made with benzene checked with their usual accuracy, proving that the fault was not with the calorime-

ter. It became apparent that the observed heat capacity depended upon the thermal history of the sample. Determinations were then made in the liquid state upon an "annealed" sample, *i. e.*, a sample which had been liquid for a considerable time. Care was taken not to freeze any of this sample when it was cooled down. Determinations carried out upon these annealed samples agreed very well. Determinations made on solid samples that were frozen more slowly than they were melted during the run agreed well; but the measurements upon the liquid made immediately after melting did not agree with those made upon the annealed liquid. The type of results obtained can be seen from Fig. 2, where it can be seen that there are humps in the curves obtained from the recently thawed samples. The magnitude of this hump varied somewhat from run to run. The heat capacity values all approached the values of the annealed liquid at higher temperatures.

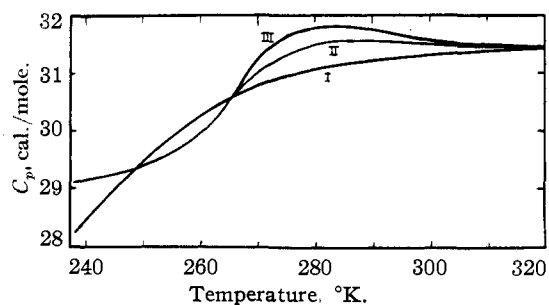


Fig. 2.—1,2-Dichloroethane: I, unfrozen sample; II, rapidly frozen sample; III, slowly frozen sample.

It was also observed that the more rapidly the sample was frozen, the smaller were the specific heat values of the solid in the region of the transition. The greatest variance was about 1 cal./mole/°C.

Effects similar to these were observed in the chlorobromide, though of a lesser magnitude. The heat capacity values in Table I for these two compounds were obtained upon the annealed liquid and the slowly frozen solid. No such effects were noticed in the case of the bromide. However, a slight, constant deviation, not exceeding the limits of experimental error, was noticed in the case of the liquid, depending upon whether the sample had been frozen rapidly or slowly.

(6) Demerliac, *J. Phys. Radium*, **7**, 591 (1898); "International Critical Tables," Vol. V; Landolt-Börnstein-Roth-Scheel, "Physikalische-chemische Tabellen," J. Springer, Berlin, 1927; Leblanc and Mobius, *Ber. Sachs. Akad. Wiss. Leipzig, Math. Phys. Klasse*, **85**, 75 (1933); Regnault, *Mem. Ak. Roy. Inst. (France)*, **26**, 262 (1862).

(7) Demerliac, *loc. cit.*

(8) Petersson, *Ber.*, **27**, 6 (1894).

### Discussion

It is now widely believed that rotation about the carbon-carbon bond in ethane and its derivatives is not free but restricted by an energy barrier of appreciable magnitude. This amounts to more than 5 kg. cal./mole in the case of the halogen derivatives studied here, according to Beach and co-workers.<sup>9</sup> Dielectric constant, dipole moment and Raman spectra measurements indicate that while the solid is almost entirely in the *trans* configuration, considerable rotatory oscillation about the carbon-carbon bond takes place in the liquid state or in solvents. These measurements indicate that the motion is much more pronounced in ethylene chloride and chlorobromide than in the bromide.

Kohlrausch<sup>10</sup> interpreted his Raman spectral studies as indicating the existence of *cis-trans* isomers. Stuart<sup>11</sup> considers that the mutual repulsion of the chlorine atoms would prevent a stable *cis* form. Mizushima and Morino<sup>12</sup> suggest that there may be a potential minimum other than the *trans* configuration. Beach and co-workers,<sup>9</sup> however, interpret their electron diffraction patterns as indicating no other such potential minimum. Their measurements were carried out upon the gaseous phase. In the liquid phase the molecules, due to their greater proximity, may influence each other in such a manner as to render stable such a position of potential minimum.

If it is assumed that a configuration of minimum energy exists other than the *trans* configuration, the data and observations reported above may be explained in the following manner:<sup>13</sup>

1. There exists a dynamic equilibrium between the *cis* and *trans* configurations of the material. In the liquid state, there is a considerable amount of the *cis* form present, while the solid contains very little, if any. This is supported by the Raman spectra measurements of Mizushima and Morino<sup>14</sup> on the solid ethylene halides, in which the line attributed by them to the *cis* form is absent. It is further assumed that it

(9) Beach and co-workers, *J. Chem. Phys.*, **6**, 639 (1938); *This Journal*, **61**, 303 (1939).

(10) Kohlrausch, *Z. phys. Chem.*, **B18**, 61 (1932).

(11) Stuart, *Physik. Z.*, **32**, 793 (1931).

(12) Mizushima and Morino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 188 (1936).

(13) For convenience, the other minimum energy configuration will be called the *cis* configuration to differentiate it from the *trans* form, but this is not intended to imply that this other stable position necessarily involves rotation of 180° from the *trans* form.

(14) Mizushima and Morino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **26**, 1 (1934).

takes an appreciable time for a quantity of one isomer to change into the other.

2. When a sample of an ethylene halide is frozen rapidly, insufficient time is allowed for all of the molecules to assume the *trans* form, and an appreciable amount of the *cis* configuration is frozen in.

White and Morgan<sup>8</sup> suggest that the transition in ethylene bromide might mark the onset of a rotation about the zigzag Br-C-C-Br axis. Probably only the *trans* configuration could undergo this transition, as too much space would be necessary for the *cis* form to rotate. The transitions in ethylene chloride and chlorobromide may be of the same type, in which only the *trans* configuration might be expected to take part.

If an ethylene chloride sample is frozen so rapidly that some of the *cis* form is frozen into the solid, then the heat capacity values in the region of the transition might be smaller than if only *trans* molecules were present, since the *cis* form would not be expected to undergo this zigzag rotation. This was observed experimentally in the case of the chloride and the chlorobromide.

3. A sample that was frozen slowly, upon melting, would consist almost entirely of *trans* molecules, since the normal crystal lattice accommodates only *trans* molecules. But if a rapidly melted sample of the normal solid were heated, *trans* molecules would have to isomerize to the *cis* modification, in order to establish the equilibrium state stable at a temperature just above the melting point. Since the *cis* form would be expected to have a higher energy content than the *trans* form, due to dipole interaction, etc., this isomerization might be expected to absorb heat, thereby increasing the apparent heat capacity of the sample. As the isomerization proceeds and equilibrium is approached, the heat capacities should approach the normal values. As Fig. 2 shows, this is what was observed experimentally. The peak is not so high for a rapidly frozen sample, since some *cis* is already present in the solid state, and therefore less isomerization occurs.

As has already been mentioned, the difference in heat capacity in the liquid state of ethylene bromide between a recently frozen sample and an annealed sample was noticeable, but very slight, being within the limits of experimental error. Mizushima and Morino,<sup>15</sup> as a result of their dipole moment and Raman spectra measurements,

(15) Mizushima and Morino, *ibid.*, **25**, 159 (1934).

concluded that less deviation from the *trans* position occurs in the bromide than in the chloride and chlorobromide. Therefore, to obtain equilibrium in the liquid state of the recently thawed bromide, fewer of the *trans* molecules need isomerize and the effect upon the heat capacity would be considerably less.

The transition in the bromide has been observed by White and Morgan.<sup>3</sup> They explain it as being due to the setting in of rotation about the zigzag Br-C-C-Br axis rather than a rotation about the carbon-carbon bond, since the dielectric constant through the transition was only minutely affected. Raman spectra measurements show that upon solidification, rotation of one halogen with respect to the other is greatly restricted. Since the heat of transition is small, compared to the heat of fusion, this is a plausible explanation of the transition.

However, the transition is of the sharp or fusion type, rather than the gradual or rotational type, and may be just a phase transition. The transitions in the chloride and the chlorobromide are of the hump or rotational type, and may well be attributed to zigzag rotation about the X-C-C-X

axis, since the dielectric constant of the chloride was unaffected in the region of the hump. Further information upon these transitions is necessary to establish this point.

While heating through the transition in the bromide, it was noticed that the sample superheated, sometimes as much as 0.35°. The same effect was noticed by White and Morgan.<sup>3</sup>

**Acknowledgment.**—The author is greatly indebted to Drs. W. T. Ziegler and E. R. Blanchard, whose assistance in carrying out this work and writing this paper was invaluable.

### Summary

1. The heat capacities of 1,2-dibromoethane, 1,2-dichloroethane, and 1,2-bromochloroethane have been measured over the range 90–320°K.

2. Heats of fusion and transition have been measured for these compounds.

3. Certain phenomena in connection with the thermal history of these compounds and its effect upon the specific heat have been interpreted in the light of restricted intramolecular rotation in these compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DICKINSON COLLEGE]

## The Viscosity of Solutions of Sulfur Dioxide in Organic Liquids

BY S. B. CUPP AND H. E. ROGERS

This paper is a continuation of the work begun by Lewis<sup>1</sup> and Adams and Rogers<sup>2</sup> on the viscosity of solutions of sulfur dioxide in organic liquids. The present paper includes data concerning the effect of dissolved sulfur dioxide on the viscosity of *n*-propyl bromide, *i*-propyl bromide and *n*-butyl bromide.

### Experimental Part

*n*-Propyl bromide, *i*-propyl bromide and *n*-butyl bromide were each washed four to six times with concentrated sulfuric acid, followed by a solution of sodium carbonate, dried over calcium chloride and distilled.

	B. p., °C.	$d_{25}^4$	$n_D^{25}$
<i>n</i> -Propyl bromide	70.9	1.3430	1.4313
<i>i</i> -Propyl bromide	59.6	1.3060	1.4220
<i>n</i> -Butyl bromide	101.6	1.2689	1.4373

The apparatus and procedure were the same as described in the earlier paper.<sup>2</sup>

(1) J. R. Lewis, *THIS JOURNAL*, **47**, 626 (1925).

(2) H. E. Adams and H. E. Rogers, *ibid.*, **61**, 112 (1939).

### Discussion

Density data for solutions of sulfur dioxide in *n*-propyl bromide, *i*-propyl bromide, and *n*-butyl bromide are found in Table I. Each liquid shows an expansion, in volume, when sulfur dioxide is dissolved in it. In the case of the *n*-propyl bromide solutions, mixtures from 0 to 60% sulfur dioxide have almost the same density as the pure *n*-propyl bromide.

In Fig. 1, the viscosity data in Table II are plotted. The viscosity is plotted against weight % and each curve is concave upward. Similar curves are obtained when the viscosity is plotted against volume %. The viscosity curves in Fig. 1 appear to be typical. The *n*-butyl bromide shows the greatest sag, as is to be expected. The difference between the viscosities of the pure sulfur dioxide and the pure *n*-butyl bromide is greater than it is for the other two liquids; consequently