shown in equation 5. The hydrolysis of these compounds would account for all of the observed products.

Since no products containing nitrogen linked to nitrogen have been obtained by the interaction of either phenyl or ethyl azide and fuming sulfuric acid, the possibility that diazene or its homologs might be formed by the interaction of hydrogen azide and the fuming acid seems rather remote under the prevailing conditions. The mechanism already suggested for this reaction[3] is confirmed by the behavior of phenyl azide toward the fuming acid.

Summary

1. The action of fuming sulfuric acid upon phenyl azide apparently results in the formation of phenylaminomonopersulfuric acid *m*-sulfonic acid, which on hydrolysis yields *p*-aminophenol *o*-sulfonic acid.

2. The action of fuming sulfuric acid upon ethyl azide results in the formation of products which on hydrolysis yield sulfuric acid and a mixture of acetaldehyde, formaldehyde, ammonia and methylamine.

3. A useful method for the separation of formaldehyde and acetaldehyde has been described.

4. No compounds containing nitrogen linked to nitrogen were obtained as products of either reaction. The analogy between these reactions, particularly that of the phenyl azide, and that of hydrogen azide and fuming sulfuric acid has been noted.

NORTHAMPTON, MASS. RECEIVED OCTOBER 30, 1939

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

The Heat Capacities, Heats of Transition and Fusion, and Entropies of Ethylene Dichloride and Ethylene Dibromide

BY KENNETH S. PITZER

Internal rotation in ethylene dichloride and ethylene dibromide has been studied by dielectric constant[1] measurements, electron diffraction,[2] and Raman spectra.[3] Although it has been proved that the rotation is considerably restricted, many aspects are yet to be worked out. With this in mind, the low temperature heat capacities, heats of fusion, and heats of transition for both substances have been measured, leading of course to entropy values. Work is in progress on the heat capacities of these substances in the gas phase.

These substances are also interesting because of the transitions they undergo as solids. Ethylene dibromide shows a sharp transition at 249.54° K., while ethylene dichloride has a large peak in its heat capacity curve near 177°K.

Apparatus and Materials.—The vacuum calorimeter used in this investigation already has been described.[4] The value 273.10°K. was taken for the ice point, and the defined calorie, 4.1833 International joules, was used throughout.

The calorimetric samples were purified by washing with water, drying, and repeatedly fractionating. The impurity in each case was estimated from the rise in heat capacity below the melting point, and found to be 0.058% in the case of ethylene dichloride and 0.26% in ethylene dibromide. Although impurities of this magnitude make the true heat capacity below the melting point uncertain, they do not appreciably affect the final entropy values.

Melting and Transition Temperatures.—The melting points were observed for different fractions melted and were corrected for impurities. The transition temperature in ethylene dibromide was similarly measured. The results are presented in Table I together with the values obtained by other observers.

Heat Capacities.—The heat capacities were measured by the usual method and are listed in Tables II and III shown graphically in Fig. 1. The temperature increments employed can be judged by the spacing of the reported results. In the anomaly in ethylene dichloride small increments were necessary to show that the true curve is rounded at the peak. This special series of measurements is included at the end of Table II. The results of other special measure-

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(1) Beach and Stevenson, *J. Chem. Phys.*, **6**, 635 (1939); Zahn, *Phys. Rev.*, **40**, 291 (1932); **38**, 521 (1931).

(2) Beach and Turkevich, THIS JOURNAL, **61**, 303 (1939); Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

(3) Ta-You Wu, *ibid.*, **7**, 965 (1939), who gives additional references.

(4) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928); Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).

TABLE I

MELTING AND TRANSITION TEMPERATURES FOR ETHYLENE DIBROMIDE AND DICHLORIDE (0°C. = 273.10°K.)

M. p. of $C_2H_4Cl_2$	M. p. of $C_2H_4Br_2$	Trans. temp. of $C_2H_4Br_2$	Observer
237.6	283.10		Timmermans and Martin[a]
240.6			Hammick and Howard[b]
	283.07		LeBlanc and Möbius[c]
	282.3	249	White and Morgan[d]
		248.4	Morino[e]
237.2 ± 0.1	283.0 ± 0.2	249.54 ± 0.1	This research

[a] Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926); *ibid.*, **25**, 411 (1928). [b] Hammick and Howard, *J. Chem. Soc.*, 2915 (1932). [c] LeBlanc and Möbius, *Ber. Verhandl. sächs. Akad. Wiss., Leipzig, Math.-phys. Klasse*, **85**, 75 (1933). [d] White and Morgan, *J. Chem. Phys.*, **5**, 655 (1937). [e] Morino, *J. Chem. Soc. Japan*, **60**, 222 (1939).

ments indicated slow thermal equilibrium near the peak, but no detectable hysteresis.

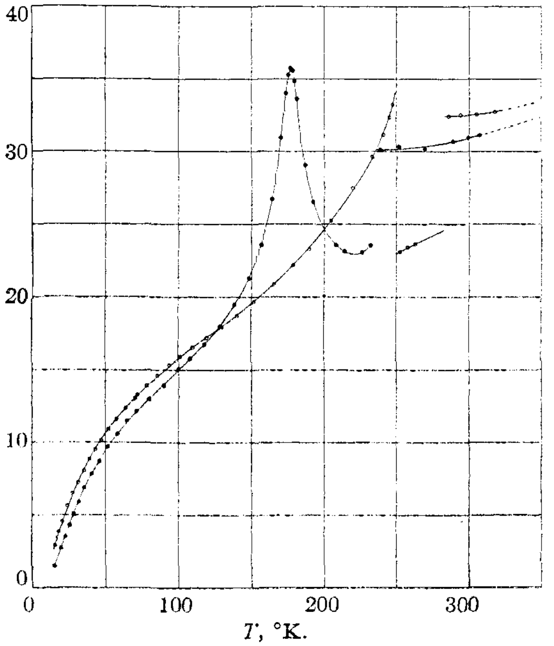

Fig. 1.—The molal heat capacity of ethylene dichloride (solid circles) and ethylene dibromide (open circles) in cal. per degree.

The error in the heat capacities is probably less than 0.2% under optimum conditions. At the highest temperatures rapid heat exchange by radiation is troublesome, while at the lowest temperatures the resistance thermometer is less sensitive. Just below the melting point, the premelting effect obscures the true heat capacity curve. The listed results have been corrected for this effect on the basis of Raoult's law, which may not be followed accurately. This uncertainty is greater in the ethylene dibromide, due to both the larger impurity and the proximity of the transition to the melting point. The observed heat capacities above the transition fit the following expression within experimental error: $C_p = A + BT + C/(T_{\text{M.P.}} - T)^2$. In this expression the first two terms represent the true heat capacity, assumed to vary linearly with temperature over this short range, and the third term the "Raoult's law" premelting. Since a series of six evenly spaced observations was available, as compared to three constants, the agreement is real evidence for the correctness of this treatment. It cannot be regarded as conclusive, however, and only the three measurements farthest from the melting point are included in Table III.

While the presence of small impurities renders the heat capacity uncertain just below the melting point, any appreciable error in this region is compensated in the heat of fusion, so that the

TABLE II

THE MOLAL HEAT CAPACITY OF ETHYLENE DICHLORIDE, $C_2H_4Cl_2$, MOL. WT. 98.966

T, °K.	C_p	T, °K.	C_p
15.12	1.432	170.48	30.91
19.85	2.676	176.15	35.16
22.41	3.488	181.50	33.54
25.10	4.201	186.99	28.96
28.35	4.990	192.46	26.46
31.94	5.823	199.99	24.89
35.92	6.791	208.30	23.50
40.69	7.768	214.23	23.06
45.71	8.621	226.32	23.00
51.83	9.595	232.01	23.48
58.39	10.51	liquid	
64.83	11.41	238.68	30.01
71.49	12.06	252.27	30.24
80.07	12.93	269.98	30.08
90.10	13.87	289.23	30.61
99.92	14.98	299.88	30.86
108.20	15.75	307.53	31.04
118.16	16.71	peak of anomaly	
128.43	17.93	174.13	33.93
138.94	19.43	175.92	35.19
148.25	21.21	177.18	35.63
156.78	23.49	178.44	35.52
164.21	26.66	179.69	34.82

TABLE III

THE MOLAL HEAT CAPACITY OF ETHYLENE DIBROMIDE, $C_2H_4Br_2$, MOL. WT. 187.88

T, °K.	C_p	T, °K.	C_p
15.25	2.851	129.71	17.90
17.94	3.792	140.49	18.69
20.28	4.502	152.12	19.66
23.78	5.605	165.53	20.82
27.59	6.460	178.99	22.13
31.49	7.209	189.94	23.24
35.20	8.019	204.98	25.20
39.08	8.820	219.72	27.42
43.10	9.471	232.93	29.62
47.36	10.10	241.58	31.15
52.11	10.86	245.23	32.37
57.59	11.55	247.83	33.22
63.87	12.31	transition	
70.54	13.04	252.69	23.09
71.78	13.25	257.79	23.35
78.08	13.87	262.86	23.58
85.48	14.58	melting point	
93.84	15.29	286.48	32.41
101.37	15.89	294.38	32.48
110.05	16.53	305.47	32.56
119.54	17.18	318.04	32.71

total entropy or heat content is not seriously altered.

Heats of Fusion and Transition.—Table IV contains the observed heats of fusion and transition. The temperature intervals and times of heating are also listed. In each heat of fusion a correction was made for the amount "premelted" at the initial temperature. It is believed that the uncertainties given in Table IV are sufficient to cover any calorimetric errors. However, a failure of the premelting effect to even approximate Raoult's law might possibly lead to errors about five times those listed. As stated above, the total entropy is not rendered uncertain by this latter possibility.

TABLE IV

HEATS OF FUSION AND TRANSITION

Temp. interval, °K.	Time of heat input, min.	$\Delta H°$ cal./mole
Fusion of $C_2H_4Cl_2$ at 237.2°K.		
229.22–244.45	24	2112.1
229.88–248.33	33	2112.0
		Av. value 2112.0 ± 2
Fusion of $C_2H_4Br_2$ at 283.0°K.		
275.62–294.51	24	2617.1
272.47–294.05	25	2614.5
		Av. value 2615.8 ± 5
Transition of $C_2H_4Br_2$ at 249.54°K.		
247.17–258.64	14	465.5
248.97–258.96	10	462.3
247.17–250.29	14	463.7
		Av. value 463.8 ± 2

Entropies.—The entropies were calculated by the usual graphical integrations, together with extrapolations to the absolute zero based on the Debye theory. The heat capacity does not fit a single Debye function (three degrees of freedom) satisfactorily for either substance, but does fit twice a Debye function (corresponding to six degrees of freedom). This latter assumption is consistent with the idea that the tendency of the molecules to oscillate torsionally leads to torsional waves similar to the more common compressional waves. Lord, Ahlberg and Andrews[5] found this assumption very successful in the case of benzene and discussed its justification in greater detail.

Measurements are now in progress on the heats of vaporization of both substances, and on heat capacities as gases. Consequently, it seems best to postpone calculations and discussions of the entropies of gaseous ethylene dichloride and dibromide until these data are available.

Discussion of Transitions.—Some comment seems worth while on the nature of the transition in ethylene dibromide and the gradual transition or anomaly in the chloride. Measurements of the dielectric constant by White and Morgan[6] show only small changes in passing through these regions. The dielectric constant becomes large only above the melting point for either substance. This probably means that the molecules retain configurations of small dipole moment until they melt. Rotation of whole molecules about their long axis might set in, however, without allowing internal rotation. The internal rotation is considerably restricted even in the gas phase.[1,2]

If this explanation is accepted, the results for either substance by itself would seem reasonable, since similar thermal effects have been observed for the beginning of rotation within other crystals. However, the difference seems very great for two such similar compounds. The following explanation is offered as plausible but by no means proved.

If the coöperative or coupling effect between the rotation of one molecule and its neighbors is relatively small, then the whole curve for the chloride becomes understandable and the rather

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[5] Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937).

[6] See note d, Table I.

TABLE V

MOLAL ENTROPY OF ETHYLENE DICHLORIDE

0–15.0°K.	Debye extrapolation	0.505
15.0–237.2	Graphical–solid	33.500
237.2	Fusion (2112.0/237.2)	8.904
237.2–298.1	Graphical–liquid	6.935
	Entropy of liquid at 298.1°K.	49.84 ± 0.15 cal./deg.

TABLE VI

MOLAL ENTROPY OF ETHYLENE DIBROMIDE

0–15.00°K.	Debye extrapolation	1.106
15.00–249.54	Graphical–solid II	36.490
249.54	Transition (463.8/249.54)	1.859
249.54–283.0	Graphical–solid I	2.989
283.0	Fusion (2615.8/283.0)	9.243
283.0–298.1	Graphical–liquid	1.688
	Entropy of liquid at 298.1°K.	53.37 ± 0.2 cal./deg.

gradual rise in the bromide curve from 150 to 250°K. is also to be expected. Above 250°K. some fundamentally different crystal structure, based on rotating molecules, becomes more stable for the ethylene dibromide, and a sharp interphase transition of the usual sort occurs. If one considers lattices comprising points which represent only the centers of gravity of the molecules, then the writer proposes that the lattice for ethylene dichloride will be essentially the same above and below the peak or "transition." Probably the lattice for ethylene dibromide below the transition is also similar; however, it is suggested that above the transition the ethylene dibromide lattice is quite different. The marked similarity of the heat capacity curves below 100°K. gives some confirmation to the suggestion that the low temperature lattices are similar. Also a comparison of the extra entropy associated with the peak in ethylene dichloride (about 2.8 cal. per deg.) with that in the abnormal rise and the transition in ethylene dibromide (about 3.7 cal. per deg.) is in reasonable agreement with this picture. The latter might be expected to be somewhat larger because it includes a change in lattice in addition to molecular rotation. Thus the observations are accounted for in a general way, although x-ray studies would be needed to prove that these ideas are correct.

Since submitting this paper for publication, Railing[7] has published results of a somewhat similar investigation. His measurements do not extend below 90°K. and he did not attempt to make an entropy calculation. A comparison of certain results is presented.

		Railing	This Research
Melting point, °K.	$C_2H_4Cl_2$	237.6	237.2 ± 0.1
	$C_2H_4Br_2$	283.03	283.0 ± 0.2
Transition temp., °K.	$C_2H_4Br_2$	250.6	249.54 ± 0.1
Heat of fusion, cal.	$C_2H_4Cl_2$	2090 ± 21	2112.0 ± 2
	$C_2H_4Br_2$	2590 ± 26	2615.8 ± 5
Heat of transition, cal.	$C_2H_4Br_2$	450 ± 9	463.8 ± 2

For the greater part, the heat capacity results agree well within the 1–2% error suggested by Railing. However, near the transitions, melting points, or other irregularities, appreciable discrepancies arise, particularly with the dichloroethane. This is not too surprising when one considers the method of measurement employed by Railing, as described by Stull.[8] Briefly, this involves continuous introduction of energy with temperature measurements at the same time. Under these conditions, temperature gradients certainly exist, and a thermometer reading may not correspond to the temperature which would be attained at thermal equilibrium with the same heat content. In most regions, the error in temperature should remain almost constant, leading to correct heat capacities. However, near transitions, melting points, etc., these temperature gradients may change rapidly, leading to considerable error in the heat capacity results. Since, with the method used in this research, temperatures are measured only when thermal equilibrium has been essentially attained, the results of the present investigation are not subject to this error.

In this connection the writer is not convinced as to the reality of the variation of heat capacity depending on thermal history, which was found by Railing for liquid ethylene dichloride. He reports that one curve is obtained "immediately after melting" and another with liquid which has been cooled to just above the melting point. Presumably, in the first case the introduction of energy is not stopped after the fusion is completed and the liquid heat capacity measurements begin with the thermal gradients that existed under the conditions of melting. These gradients may differ considerably from those of the

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[7] Railing, THIS JOURNAL, **61**, 3349 (1939).

[8] Stull, THIS JOURNAL, **59**, 2726 (1937).

recently cooled liquid. The observed differences, depending on rate of freezing, can similarly be explained as arising from differences in heat conductivity within the sample, which depends on the size of crystals among other factors.

The results of the present investigation neither support nor definitely disprove these effects reported by Railing. They do, however, offer strong evidence against the slow *cis–trans* isomerization suggested by him in explanation. The presence of *cis* and *trans* isomers would be expected to produce variations in the melting point and other peculiar effects which were definitely not observed. Also, according to Railing's suggestions, absorption of heat and apparent cooling would be expected after melting the material. No such cooling effect was observed in the heat of fusion experiments.

Summary

The thermal behavior of ethylene dichloride and ethylene dibromide was investigated from 15°K. to room temperature, for which range values of the heat capacities are given. The following melting points (0°C. = 273.10°K.) and heats of fusion were determined: $C_2H_4Cl_2$, 237.2 ± 0.1°K., 2112.0 ± 2 cal./mole; $C_2H_4Br_2$, 283.0 ± 0.2°K., 2615.8 ± 5.0. The following temperature and heat of transition values were determined: $C_2H_4Br_2$, 249.54 ± 0.10°K., 463.8 ± 2.0 cal./mole. From these data, the following values of entropy at 298.1°K. were calculated: $C_2H_4Cl_2$(l), 49.84 ± 0.15 cal./deg. mole; $C_2H_4Br_2$(l), 53.37 ± 0.20 cal./deg. mole.

Ethylene dichloride shows no sharp transition but has a peak in the heat capacity curve near 177°K. which may correspond partially to the transition in ethylene dibromide. A possible explanation of the transitions is offered.

BERKELEY, CALIF. RECEIVED NOVEMBER 21, 1939

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Solutions of Electrolytes as a Function of the Concentration. VI. Potassium Bromide and Lanthanum Chloride

BY GRINNELL JONES AND ROBERT ELIOT STAUFFER

The general objective of this paper and of the others of this series is a study of the viscosity of solutions of electrolytes as a function of the concentration, temperature and nature of the salt. The earlier papers[1] should be consulted for a more detailed theoretical discussion and for a description of the experimental technique.

The potassium bromide used in this work was prepared by S. Baeckström.[2]

The lanthanum chloride was originally purified from other rare earths by the late Professor Charles James and had been used in previous investigations in this Laboratory[3] and recovered by precipitation as the oxalate. The oxalate was ignited to the oxide, dissolved in a solution of hydrochloric acid in ethyl alcohol, filtered through a sintered glass filter, chilled with ice and hydrogen chloride gas passed into the solution until the lanthanum chloride was precipitated. The salt was dried by centrifugal drainage and reprecipitated from alcohol in the same manner. The use of ethyl alcohol instead of water gives better yields. A suitable quantity for each solution was placed in a platinum boat inside of a quartz tube and heated to 600° for four hours in a stream of hydrogen chloride gas without fusion. The salt was cooled in an atmosphere of hydrogen chloride gas and then the acid gas replaced by dried air and the boat put into a weighing bottle by the use of a Richards bottling apparatus. The solutions were then made up by weight.

The solutions prepared from the salt dried in this manner had a *p*H of about 6.0 when tested with brom thymol blue, which agrees with the earlier work of Kolthoff and Elmquist,[4] and of Jacques[5] and of Jones and Bickford.[6] No corrections were applied for this slight hydrolysis. Erratic results were obtained at first and the cause was traced to a slight deposit of lanthanum hydroxide in the capillary tube of the viscometer. However, it was found that the deposit was formed during the rinsing of the viscometer with hot water after a series of measurements, which in-

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[1] Grinnell Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1935); **58**, 619 (1936); **60**, 1683 (1938); Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936); **59**, 1630 (1937); Grinnell Jones and S. M. Christian, *ibid.*, **59**, 484 (1937); Grinnell Jones and E. Ferrell, *J. Chem. Soc.*, 325 (1939).

[2] Grinnell Jones and S. Baeckström, THIS JOURNAL, **56**, 1519 (1934).

[3] Grinnell Jones and C. F. Bickford, *ibid.*, **56**, 602 (1934); Grinnell Jones and L. T. Prendergast, *ibid.*, **58**, 1376 (1936).

[4] I. M. Kolthoff and R. Elmquist, THIS JOURNAL, **50**, 959 (1928).

[5] A. G. Jacques, Dissertation, Harvard University, 1931, p. 344.

[6] Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 605 (1934).