[CONTRIBUTION NO. 73 FROM THE CRYOGENIC LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

The Heat Capacities from 10.9°K., Heats of Transition, Fusion and Vaporization, Vapor Pressures and Entropy of Pentafluorochloroethane, the Barrier Hindering Internal Rotation[1]

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The heat capacities of pentafluorochloroethane from 10.9°K. to the normal boiling point are tabulated. Temperatures of a rotational transition and the triple point are tabulated as well as vapor pressures, heats of transition, fusion and vaporization. The calorimetric entropy of the vapor at the normal boiling point when compared with a value calculated from spectroscopic data yields a barrier of 5300 cal. mole^{-1} hindering internal rotation.

Introduction

The barrier hindering internal rotation[2] in ethyl chloride is 4700 cal. mole^{-1} while that in ethane is 2750 cal. mole^{-1}.[3] The barrier is 4350 cal. mole^{-1} in perfluoroethane[4] so that one would place the barrier in pentafluorochloroethane as somewhat above 5000 cal. mole^{-1}.

The present investigation describes the thermal data necessary for the determination of the third law entropy at the normal boiling point to be used in a comparison with the entropy calculated from spectroscopic data leading to a barrier near 5000 cal. mole^{-1}. The calculation of the entropy from these data together with a calculation of the spectroscopic entropy has already been given in a note for purposes of expediency.[5]

Experimental

The Material.—The sample used had less than 0.01 mole per cent. impurity. It was supplied by the Jackson Laboratory of E. I. du Pont de Nemours and Company through the courtesy of A. F. Benning and needed no further purification. It was weighed in a small high pressure cylinder.

The Apparatus.—Calorimeter C[6] was used. Standard thermocouple S-7 was used as primary temperature standard with occasional checks against S-4 which showed no changes in calibration greater than 0.05° since the last comparison of both with hydrogen and oxygen vapor pressures in 1944.

The Heat Capacities.—The molal heat capacities are tabulated at rounded temperatures in Table I and graphed in Fig. 1 which is constructed in such a way that the experimental points may be obtained within experimental error by interpolation from the table and addition of the deviation of the point from the curve representing the data of Table I.

With the exception of the points below 40°K., near 80°K. and near 150°K. the accuracy is about 0.2%. Below 45°K. the error may fall to over 1% due to the insensitivity of the thermocouples and the changing resistance thermometer derivatives. Near 80°K. and near 150°K. changes in resistance thermometer derivative limit the accuracy to about 0.4%.

The values of the solid immediately below the melting point have been corrected for premelting based on 0.008 mole per cent. impurity. The values in the liquid near the normal boiling point have been corrected for vaporization into the filling line assuming the vapor to be a perfect gas and using heats of vaporization calculated from the vapor pressure equation on the same assumption. This assumption produces negligible error.

TABLE I

MOLAL HEAT CAPACITY OF C_2F_5Cl AT INTEGRAL TEMPERATURES

Mole wt. 154.477; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	4.22	70	15.40	160	28.55
16	4.70	75	16.16	165	29.15
17	5.22	80.24	17.13 Solid I	170	29.80
18	5.76	80.24	23.00	173.72	30.33
19	6.26	85	23.18	Fusion at 173.72	
20	6.675	90	23.37	173.72	31.13 log
21	7.02	95	23.58	175	31.18
22	7.34	100	23.81	180	31.36
23	7.65	105	24.07	185	31.57
24	7.945	110	24.36	190	31.80
25	8.23	115	24.67	195	32.07
30	9.58	120	25.00	200	32.38
35	10.68	125	25.35	205	32.71
40	11.57	130	25.72	210	33.04
45	12.31	135	26.11	215	33.38
50	12.96	140	26.53	220	33.73
55	13.56	145	26.99	225	34.08
60	14.15	150	27.48	230	34.44
65	14.75	155	28.00	234.04	34.72

The Transition and Melting Points.—The equilibrium temperatures for certain fractions transformed during transition and melting are given in Table II along with the deduced transition and melting temperature and mole per cent. impurity deduced in the customary manner.

TABLE II

TRANSITION AND MELTING POINTS OF PENTAFLUOROCHLOROETHANE

0°C. = 273.16°K.

Temp., °K.	% Transformed	Temp., °K.	% Melted (x)	$1/x$
80.243	27	173.681	31	3.2
80.233	46	173.692	62	1.61
80.237	65	173.726	86	1.16
80.24 K. (transition point)		173.72		1.00 (extrap.)
		173.71		0.00 (extrap.)

Melting point (triple point) 173.71°K.
Impurity: 0.008 mole %

The Heats of Transition and Fusion.—Tables III and IV summarize the data and average values. The penultimate column in Table IV gives the correction to the heat of fusion for material already melted at the start of the determination.

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[1] This research was carried out in part on Contract N6-ONR-269, T. O. III of the Office of Naval Research.

[2] J. Gordon and W. F. Giauque, THIS JOURNAL, **70**, 1506 (1948).

[3] G. B. Kistiakowsky, J. R. Lacher and Fred Stitt, *J. Chem. Phys.*, **7**, 289 (1939).

[4] E. L. Pace and J. G. Aston, THIS JOURNAL, **70**, 566 (1948).

[5] J. G. Aston and R. P. Zolki, *ibid.*, **77**, 804 (1955).

[6] (a) J. G. Aston and G. H. Messerly, *ibid.*, **58**, 2354 (1936); (b) G. H. Messerly and J. G. Aston, *ibid.*, **62**, 886 (1940).

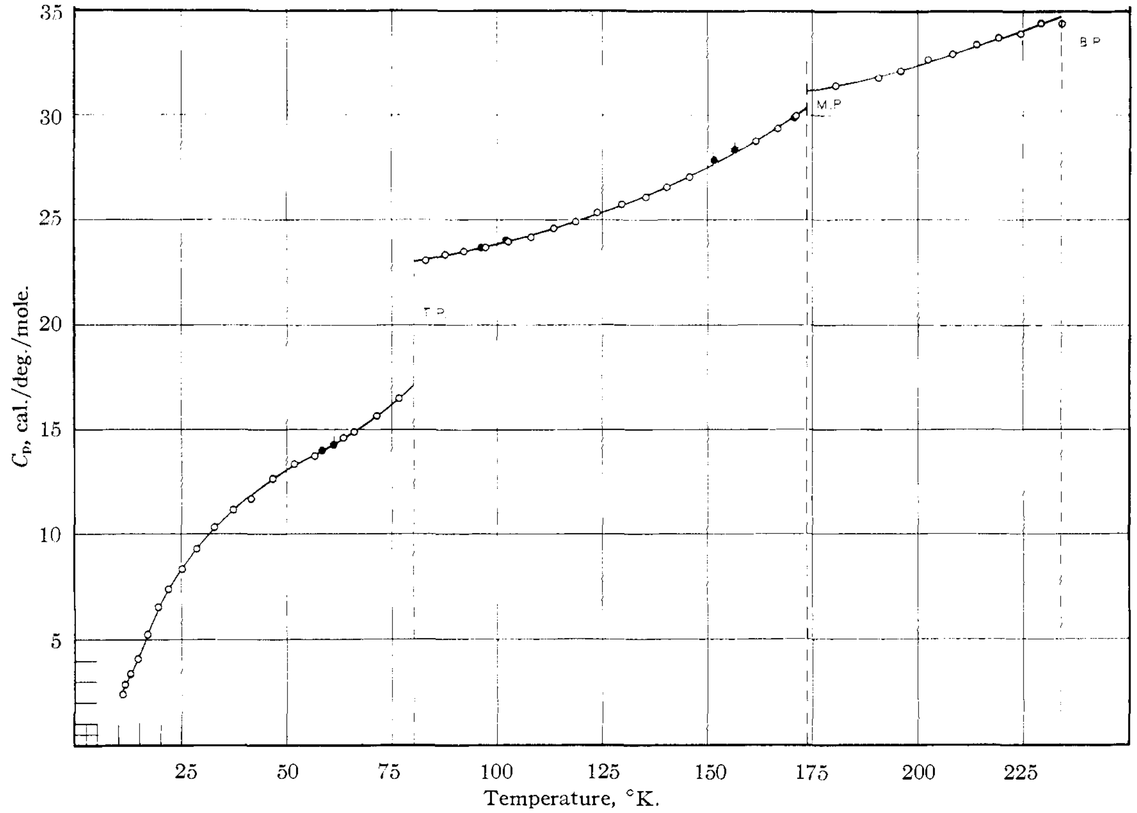

Fig. 1.—Plot of data: (a) ○, points of a continuous run; (b) ●, check points; (c) ●, (a) on top of (b).

Table III

Heat of Transition of C_2F_5Cl at 80.24°K.

Mol. wt. 154.477; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp. interval, °K.	Heat input, cal. mole^{-1}	$\int C_p dt$, cal. mole^{-1}	ΔH transition, cal. mole^{-1}
79.287–80.967	679.561	− 54.806	624.75
78.973–83.902	797.4814	−166.872	630.61
79.041–83.144	768.852	−141.277	627.57
79.087–83.148	767.507	−140.082	627.43

Mean ΔH = 627.6 ± 1.5

Table IV

Heat of Fusion of C_2F_5Cl at 173.71°K.

Mol. wt. 154.477; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp. interval, °K.	Heat input, cal. mole^{-1}	$\int C_p dt$, cal. mole^{-1}	Pre-melting, cal. mole^{-1}	ΔH fusion, cal. mole^{-1}
172.383–175.293	582.42	−138.36	+3.3	447.4
172.875–175.207	557.34	−111.13	+4.2	450.4
172.393–175.223	580.27	−134.54	+3.3	449.0

Mean ΔH = 448.9 ± 1

Table V

Vapor Pressures of Pentafluorochloroethane

0°C. = 273.16°K.; normal boiling point, 234.04°K.; g for State College = 980.124.

T, °K.	$P_{\text{obsd.}}$, international mm.	$P_{\text{calcd.}}$, international mm.	$T_{\text{obsd.}} - T_{\text{calcd.}}$, °K.[a]
177.838	23.45	23.44	+0.004
182.830	35.415	35.40	+ .006
190.728	64.47	64.53	− .008
208.066	200.26	200.22	+ .003
217.131	332.74	332.80	− .003
225.342	506.08	506.08	.000
233.303	735.32	735.34	− .001
233.925	756.20	756.18	+ .001

[a] Calculated from equation 1.

$$\log p_{\text{mm}} = \frac{-1823.225}{T} - 11.51021 \log T + 0.007503762T + 36.185941 \quad (1)$$

The Vapor Pressures and Heats of Vaporization.—The vapor pressure data leading to the equation given at the foot of the Table V are summarized in Table V along with pressures calculated from this equation and deviations of the observed from the calculated temperatures. The heats of vaporization determinations are summarized in Table VI. These were taken by adding energy to vaporize, first into an auxiliary weighed bulb cooled in liquid air while adjusting a sensitive valve until a constant pressure and temperature were attained. The vapor was then directed into a second weighed bulb by a two-way stopcock. The energy was counted from this time until the stopcock was again directed into the auxiliary bulb, the pressure and temperature being held constant during the period. Heat leak correction was made on the basis of temperature readings on the top, bottom and sides of the calorimeter and the shield.

At the foot of Table VI is given a value of ΔH, calculated from equation 1 and thermodynamics using a modified Berthelot equation to calculate the volume of the gas. The critical constants and liquid volume were those furnished by J. J. Martin. The excellent agreement justifies the method of correction used below for obtaining the gaseous entropy in the ideal gas state. The equation of state of Martin leads to a value 22 cal. higher, but his experimental data extend only to 2 atm.

Calculated Entropies.—A summary of the calculation of the entropies has already been given.[5] The values for the liquid and gas at the normal boiling point (234.04°K.) are, respectively, 59.28 ± 0.13 and 79.10 ± 0.17 e.u. The entropy of the ideal gas at this same temperature is calculated from the modified Berthelot equation and critical data

TABLE VI

HEATS OF VAPORIZATION OF C_2F_5Cl

Mol. wt. 154.477; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules

Vaporized, mole	Mean temp. of vapor, °K.	ΔH, T, °K., cal. mole^{-1}	ΔH, real gas 234.04°K. cal. mole^{-1}
0.019965	233.982	4649	4648
.013234	234.032	4643	4643
.021347	234.359	4624	4627
.021094	234.365	4634	4637
		Av.	4639 ± 10

Value calcd. from eq. 1 with T_c = 353.1° K., P_c = 30.8 atm. Berthelot corrn. = −212 cal. mole^{-1} (liq. vol. corrn. = −24 cal. mole^{-1}) 4634

Value calcd. from eq. 1 and Martin data of state 4663

furnished by Dr. J. J. Martin to be 79.28 ± 0.20 e.u. (The critical temperature is 353.1°K. and the critical pressure is 30.8 atm.) The potential barrier hindering internal rotation which must be assumed to bring the entropy[5] into agreement with a "spectroscopic" entropy calculated from the Raman and infrared[7] is 5300 cal. mole^{-1}. A doubtful Raman line at 75 cm.$^{-1}$, which is possibly due to the hindered rotation, has been observed by Professor R. C. Taylor.[8] This corresponds to a barrier of 4500 cal. mole^{-1}. The entropy at 234.04°K. calculated on this basis is 79.47 e.u. The entropy at 298.16°K. calculated from the spectroscopic data using the barrier of 4500 cal. mole^{-1} as derived from the Raman line at 75 cm.$^{-1}$ is 85.47 e.u. We prefer this value to that calculated on the basis of the empirical barrier of 5300 cal. mole^{-1}, because assuming the assignment of the 75 cm.$^{-1}$ to the torsion to be valid, any errors in the calorimetric data are avoided.

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[7] J. Rud Nielson, E. Y. Liany, R. M. Smith and D. C. Smith, *J. Chem. Phys.*, **21**, 383 (1953).

[8] Professor R. C. Taylor, Department of Chemistry, University of Michigan, private communication.

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

The Vibrational Spectrum, Associative and Thermodynamic Properties of Acetic Acid Vapor

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The infrared spectrum of acetic acid vapor (CH_3COOH and CH_3COOD) has been measured down to 300 cm.$^{-1}$ at 25 and 175°, and vibrational assignments are made for both the monomer and hydrogen-bonded dimer molecules. Two bands appearing at low frequencies at the higher temperature are attributed to the O–H out-of-plane bending in the *cis* and *trans* forms of the monomer. The heat capacity of the vapor has been measured between 95 and 270° and at pressures of approximately $^1/_3$, $^2/_3$ and 1 atm. The major contribution to the heat capacity at the lower temperatures in this region is that due to absorption of heat for the dissociation of dimer molecules. It is found, contrary to most other work, that only monomer and dimer molecules (no higher polymers) are present, and the derived dissociation constants are approximately in agreement with those determined by Taylor from low pressure vapor density measurements. At 100° the heat content and entropy change in the dissociation of one mole of dimer are 15.05 cal./mole and 36.3 cal./mole deg., respectively. The potential barrier hindering internal rotation of the CH_3 group is found to be 2500 ± 700 cal./mole. The thermodynamic properties of the two molecular species are tabulated, but only an inconclusive comparison of the experimental and calculated entropies at 25° can be made, because accurate values of the heat of vaporization at that temperature and of the energy difference between *cis* and *trans* isomers in the monomer are lacking.

The unusual hydrogen-bonded dimer which acetic acid forms has made it the subject of numerous investigations. Several of these investigations have been concerned with the measurement of vapor densities[2–4] and the derivation of the stability of the dimer, and perhaps higher polymers, in the vapor phase. To these may be added measurements of the infrared spectra of the associated and unassociated molecules,[5] low temperature heat capacity measurements,[6] and determination of the molecular structures by electron diffraction.[7] The resulting data are usually sufficient to establish the vibrational assignment and thermodynamic properties of a molecule. In this case, however, because of the complexity of the vapor state, and also the question of residual entropy, the problem has not been satisfactorily solved.[8]

In this paper there is reported the vapor heat capacity of acetic acid over a range of temperature and pressure. It is found that this physical property is very sensitive to the concentrations of the molecular species present in the vapor and to the equilibria existing between them. In fact, one is able to eliminate those results obtained from vapor density measurements which propose the presence of

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[1] Department of Chemistry, Harvard University, Cambridge, Mass.

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[8] See, however, J. O. Halford, *J. Chem. Phys.*, **9**, 859 (1941); **10**, 582 (1942).