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The Heat Capacity, Heat of Transition, Vaporization, Vapor Pressure and Entropy of 1,1,1-Trichloroethane

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Introduction.—The work of Kemp, Pitzer and other investigators has[2] established the existence of barriers hindering the rotation of methyl groups in ethane and a number of other molecules containing methyl groups. 1,1,1-Trichloroethane, CH_3CCl_3, is another molecule of this class, and it seemed important to determine the height of its barrier since one of the rotating groups is a completely substituted methyl group. The height of the barrier was found to be 2700 ± 350 calories per mole, a value almost equal to that for the ethane molecule. It is of considerable interest that the magnitude of the barrier is but little affected by the substitution of chlorine for hydrogen in ethane.

An additional interesting property of 1,1,1-trichloroethane is that dipole moment studies[3] indicate that its molecules begin to rotate in the solid at a temperature of 224.3°K. The heat capacity data reported here establish the existence of a transition at this temperature.

Material.—Eastman Kodak Co. "methyl chloroform" was purified by fractional distillation and subsequent repeated fractional crystallization. The corrected boiling range of the fraction which was to be recrystallized was 73.8–74.0°. After four recrystallizations the material was dried by passing its vapor over anhydrous calcium sulfate. It is believed that the purity of the final fraction used in the heat capacity measurements is easily 99.7%, high enough for the purposes of the present investigation.

Heat Capacity Measurements.—The heat capacity of solid and liquid 1,1,1-trichloroethane was determined with the adiabatic calorimeter (Gold-plated copper calorimeter I, and a strain-free resistance thermometer CT-2) described elsewhere.[4]

The experimental data are presented in Table I. They are expressed in terms of the defined calorie equal to 4.1833 international joules. The value 273.16°K. was taken for the ice point.

The temperature interval of each heat capacity measurement given in Table I may be estimated from the spacing of the mean temperatures, since there were no gaps between measurements in any series. The data are shown plotted in Fig. 1; the measurements were reproducible at all of the temperatures where the various series of measurements overlap. The deviations of the data from a smooth curve are within 0.2%; the probable accuracy of the measurements is about 1% at a temperature of 15°K. and 0.2% above 25°K. Thermal equilibrium was easily attained even for measurements taken at temperatures in the immediate neighborhood of the peaks shown in Fig. 1.

TABLE I

THE MOLAL HEAT CAPACITY OF 1,1,1-TRICHLOROETHANE

0°C. = 273.16°K.; molecular weight = 133.415; 1.7383 moles in the calorimeter.

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
Series 1		Series 4		Series 8	
82.58	13.81	207.17	31.61	245.40	33.35
86.17	14.22	212.28	33.19	251.61	33.47
93.33	14.90	216.96	40.10	257.80	33.57
101.84	15.76			263.81	33.72
109.86	16.48	Series 5		269.77	33.61
117.74	17.29	227.80	35.86	275.85	33.91
125.73	18.12	231.91	43.38	281.85	34.07
133.84	18.89	234.98	96.3	287.70	34.23
141.86	19.66			293.71	34.35
157.05	21.26	Series 6		299.59	34.49
164.26	22.01	190.22	24.87	Series 9	
171.27	22.62	195.29	25.98	12.29	1.40
178.08	23.42	199.19	27.47	13.33	1.90
		202.84	31.57	14.37	2.34
Series 2		206.18	34.98	15.68	2.86
177.23	23.24	209.51	31.32	17.50	3.52
183.83	24.04	212.88	33.94	19.61	4.29
190.24	24.92	216.01	38.09	21.68	4.98
196.43	26.28	218.81	45.16	24.04	5.706
				27.02	6.686
Series 3		Series 7		30.36	7.461
183.64	24.03	226.13	34.70	33.83	8.175
189.98	24.84	228.91	37.60	37.75	8.853
196.13	26.13	230.82	40.70	42.43	9.517
201.88	29.93			47.60	10.22
207.03	35.28			53.40	10.89
211.99	33.02			59.56	11.49
				65.83	12.13
				73.22	12.86
				81.09	13.69
				89.59	14.55
				98.57	15.44

The peak at 206°K. is believed to be due to an eutectic resulting from the presence of a small amount of impurity, since similiar data taken with another sample of 1,1,1-trichloroethane by

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[2] J. D. Kemp and K. S. Pitzer, THIS JOURNAL, **59**, 276 (1937). See E. Bright Wilson, *Chem. Rev.*, **27**, 17 (1940), for a summary of references to this work.

[3] A. Turkevich and C. P. Smyth, THIS JOURNAL, **62**, 2468 (1940).

[4] Don. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, *ibid.*, **63**, 3488 (1941).

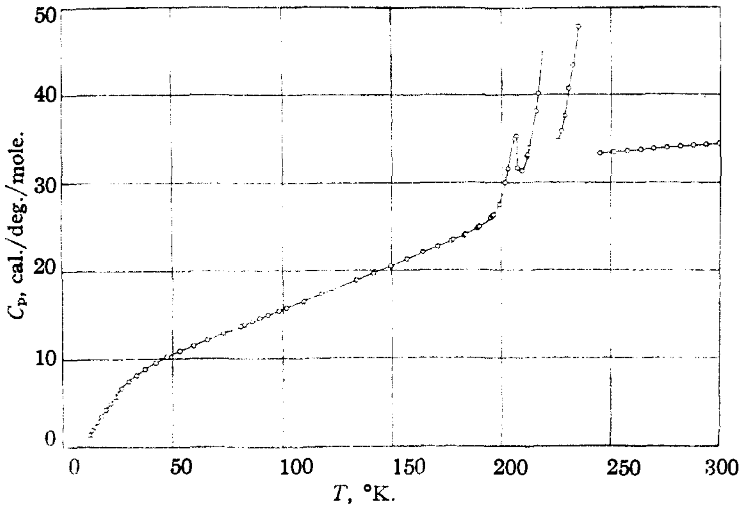

Fig. 1.—The molal heat capacity of 1,1,1-trichloroethane.

Professor E. A. Long showed no such maximum.[5]

Immediately below the melting point, premelting effects obscure the course of the true heat capacity curve. It is obvious that the effect is large for relatively little impurity, since the heat of fusion is small. A correction based on Raoult's law applied in a manner given by Pitzer[6] could not be made, because of the close proximity of the transition temperature to the melting point.

Transition Temperature and Melting Point.—The transition temperature and melting point were carefully measured, and the results are presented in Table II, together with the values obtained by other observers. The melting point value is an extrapolated one, corresponding to a completely melted system in which the mole fraction of dissolved impurities is small.

TABLE II

MELTING AND TRANSITION TEMPERATURES FOR 1,1,1-TRICHLOROETHANE

0°C. = 273.16°K.

Melting point, °K.	Transition temperature, °K.	Observer
240.5	224.3	Turkevich and Smyth[3]
241.0	...	Van de Vloed[7]
242.8		Henne and Hubbard[8]
240.2 ± 0.5	224.20 ± 0.03	This Research

Heats of Transition and Fusion.—The heat of transition of 1,1,1-trichloroethane was observed to be 1785 cal./mole and 1787 cal./mole from measurements over a temperature range of 214.785–225.716°K. and 210.983–227.301°K., respectively; the average value is 1786 ± 2 cal./mole. Each value of the heat of transition contains a correction for the normal heat capacity of the solid obtained by extrapolating the heat capacity curve below 206°K. to the transition temperature. The uncertainty in the heat of transition given includes all calorimetric errors, but errors in the extrapolated heat capacity values at temperatures above 206°K. may increase this uncertainty fivefold. The total entropy and heat content are not affected appreciably by this latter possibility, since errors in the extrapolated heat capacity values are compensated almost completely by the resulting errors in the heat of transition.

An accurate value of the heat of fusion was not determined because of the errors in the heat capacity of the solid just above the transition point. A rough value for the heat of fusion of 1,1,1-trichloroethane of 450 ± 300 calories per mole was calculated from the total heat absorbed over the melting range and from the estimated heat capacity of the solid; it was assumed that the latter were about equal to the heat capacity of the liquid.

Neither this rough value of the heat of fusion nor the melting point given above is used in the calculation of the total entropy, and uncertainties in these quantities do not affect the uncertainty in the total entropy.

Heat of Vaporization.—The heat of vaporization of 1,1,1-trichloroethane was determined in a Giauque type calorimeter fitted with a strain-free platinum resistance thermometer.[4] The usual corrections were made for the heat lost by the calorimeter to its surroundings by radiation and the heat carried off by the vapor. A constant measured pressure was maintained for every determination in a manner described elsewhere.[4] The temperatures of vaporization were calculated from the pressure data using the vapor pressure equation given below.

The observed molal heat of vaporization of 1,1,1-trichloroethane at 284.34°K. and a pressure of 6.899 cm. was 7988 cal./mole and at 286.53°K. and 7.686 cm. was 7969 cal./mole. These values when corrected to 286.53°K. and 7.686 cm. become 7955 and 7969 cal./mole, respectively, with an average value of 7962 ± 12 cal./mole. The correction to 286.53°K. was made using (a) the heat capacity of the gas from spectroscopic data, (b) the heat capacity of the liquid from this research and (c) Berthelot's equation with reasonable estimates for the critical constants of T_c = 533°K. and P_c = 50 atm.

Vapor Pressure.—The vapor pressure of 1,1,1-trichloroethane at various temperatures is given in Table III together with pressures calculated from the derived vapor pressure equation presented below. The temperature of the liquid was measured in the Giauque type calorimeter

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(5) E. A. Long, private communication.

(6) K. S. Pitzer, THIS JOURNAL, **62**, 331 (1940).

(7) Van de Vloed, *Bull. Soc. Chim. Belg.*, **48**, 229 (1940).

(8) A. L. Henne and D. M. Hubbard, THIS JOURNAL, **58**, 404 (1936).

used for determining the heat of vaporization. The pressure was measured with a mercury manometer by means of a Gaertner meter bar and a Henson cathetometer. Corrections for the capillary depression were made from the measured height of the menisci and the data of Cawood and Patterson.[9]

TABLE III

THE VAPOR PRESSURE OF 1,1,1-TRICHLOROETHANE

0°C. = 273.16°K., pressures in int. cm.

T, °K.	P, obs., cm.	P,[a] calcd., cm.	P, calcd. − P, obs.
267.796	2.88	2.91	+0.03
272.943	3.87	3.85	− .02
278.269	5.05	5.09	+ .04
284.464	6.93	6.95	+ .02
290.083	9.12	9.12	− .00

[a] $\log_{10} P_{\text{cm.}} = -(1729/T) + 6.92013$.

Vapor pressure values were not determined above 17°C. since in this region condensation of vapor in the manometer would result. The uncertainty in any of the pressure values is estimated to be ±0.05 cm. It was not deemed essential, in this case, to measure the vapor pressures with high precision.

The Entropy of 1,1,1-Trichloroethane.—The entropy from the calorimetric data is summarized in Table IV. The entropy of the solid below a temperature of 15°K. was calculated by a Debye extrapolation with three degrees of freedom and $\Theta_D = 78°$; the entropy over the temperature interval from 224.20°K. to 241.00°K., was calculated by graphical evaluation of $\int C_p \, d \ln T$ from 224.20°K. to a known intermediate temperature (about 236°K.). Above this temperature the function $\Sigma \frac{Q}{T_{\text{max.}}}$ was used to calculate the rest of the entropy in the interval ending at 241.00°K.; ΣQ is the total energy absorbed over the latter temperature interval, and $T_{\text{max.}}$ is the temperature of maximum heat capacity, in this interval (equal to about 240.1 ± 0.2°K.). The imperfect gas correction was made assuming a Berthelot equation of state and the estimated critical data.

TABLE IV

THE MOLAL ENTROPY OF 1,1,1-TRICHLOROETHANE FROM CALORIMETRIC DATA

0°C. = 273.16°K.; molecular weight = 133.415

	Entropy, cal./deg./mole
0–15°K. Debye extrapolation, Θ_D = 78.0°	0.851
15–224.20°K. graphical (solid)	33.852
Eutectic at 206°K.	0.150
Transition, 1786/224.20	7.967
224.20–241.00°K., graphical (fusion range)	4.319
241.00–286.53°K., graphical (liquid)	5.828
Vaporization 7962/286.53	27.788
Entropy of real gas at 286.53°K. and 7.686 cm.	80.755 ± 0.16
Gas imperfection[a]	0.002
Correction to 1 atm.	− 4.553
Entropy of ideal gas at 286.53°K. and 1 atm.	76.22 ± 0.16
Entropy of ideal gas at 298.16°K. and 1 atm.	76.97 ± 0.16
Entropy of liquid at 298.16°K.	54.37 ± 0.12

[a] S (ideal) − S (real) = $\frac{27RT_c^3P}{32T^3P_c}$, P_c = 50 atm., T_c = 533°K.

An accurate value cannot be given for the mole percentage impurity present, mainly because a precise value of the freezing point and heat of fusion is not known. A rough estimate of an upper limit of 0.3 mole per cent. may be made from the data available. It may be remarked that this estimate is not unreasonable because large premelting effects are to be expected for small amounts of impurities present in substances having a low heat of fusion. The final entropy value is not affected to a significant extent by concentrations of impurity of this order of magnitude.

The Entropy from Molecular Data.—The calculated entropy for 1,1,1-trichloroethane from the molecular data is given in Table V.

The vibrational frequencies were taken to be harmonic. The fundamental frequencies, of which all are active in the Raman spectrum except the torsional one around the C–C axis, are: 345 (1), 523 (1), 977 (1), 1471 (1), 2939 (1), 241 (2), 340 (2), 713 (2), 1086 (2), 1450 (2) and 3000 (2). The numbers in the parentheses adjoining the frequencies are their degeneracies as assigned by us from rough polarization measurements. The frequency 340 (2) which overlaps 345 (1) is not certain. It corresponds to a bending vibration of the CH_3 and CCl_3 groups about the C–C bond. A more complete discussion of the spectrum will be given elsewhere. The moments of inertia for the rigid molecule were calculated from the following data of Beach and Stevenson[10]: C–Cl distance, 1.76Å.; C–C distance, 1.54Å.;

TABLE V

THE MOLAL ENTROPY OF GASEOUS 1,1,1-TRICHLOROETHANE AT 286.53°K. AND 1 ATM. FROM MOLECULAR DATA

	Entropy in cal./deg./mole
Translational	40.38
Rotational (free rotator)	28.85
Vibrational	8.24
Total for free rotator	77.47 ± 0.10
Calorimetric	76.22 ± 0.16
Difference	1.25 ± 0.16
Diff. calcd. for a potential of 2700 ± 350 cal./mole	1.26 ± 0.16

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[9] W. Cawood and N. S. Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).

[10] J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **61**, 2643–2651 (1939).

C–H distance, 1.09Å.; C–C–H angle, 109°28′; and the Cl–C–C angle 110°. The symmetry number for the rigid molecule was taken as three.

The following natural constants, given by Birge,[11] were used in the calculations: 0°C. = 273.16°K., R = 1.9870 cal./deg./mole, r, the Boltzmann constant, = 1.3805 × 10^{-16} erg/deg., N = 6.023 × 10^{23} and h = 6.624 × 10^{-27} erg sec.

The difference between the calorimetric entropy value and the one calculated using molecular constants is 1.25 calories per mole, and this corresponds to a barrier of 2700 calories per mole. This value was calculated using the tables of Pitzer and Gwinn.[12] The reduced moment of inertia of the methyl group of the molecule was taken to be 5.26 × 10^{-40} c. g. s. units.

We wish to thank Professor Alexander Goetz for supplying us with liquid hydrogen.

Summary

The heat capacity of 1,1,1-trichloroethane has been measured from 14°K. to room temperature. There is a transition point in the solid at 224.20°K. The heat of transition is 1786 ± 2 cal./mole. An approximate value for the melting point is 240.2 ± 0.5°K., and a rough value for the heat of fusion is 450 ± 300 cal./mole. The heat of vaporization is 7962 ± 12 cal./mole at 286.53°K. The entropy of the ideal gas at 286.53°K. and 1 atm. is 76.22 ± 0.16 cal./deg./mole, and 76.97 ± 0.16 cal./deg./mole at 298.16°K. and 1 atm. The entropy of the liquid at 298.16°K. is 54.37 ± 0.11 cal./deg./mole. A comparison of the statistical and calorimetric values of the entropy indicates a barrier of 2700 ± 350 cal./mole.

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(11) R. T. Birge, *Rev. Modern Phys.*, **13**, 233 (1941).

(12) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Ternary System: Dioxane–Benzene–Water

BY ROBERT J. BERNDT AND CECIL C. LYNCH

Several ternary liquid systems have been examined by Hand[1] for dineric distribution between conjugate phases. Bancroft and Hubbard[2] have recently presented a new method of determining dineric distribution in such systems and have examined two ternary systems in some detail.

The object of this work has been to study the ternary liquid system dioxane–benzene–water, in which the dioxane is the consulate liquid, for dineric distribution between the conjugate phases at 25°. Because of the extensive region of immiscibility in the system, we have employed both the method of Bancroft and an analytical method for determining the composition of conjugate phases.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Co. was purified by the method described by Eigenberger.[3] The product was kept over metallic sodium, from which it was distilled when needed; density d^{25}_{4} 1.0276, n^{25}_{D} 1.4197.

Benzene.—Thiophene-free benzene was dried with calcium oxide, from which it was fractionally distilled. It was kept in bottles protected from moisture with suitable drying tubes.

Freshly boiled redistilled water was used also in all mixtures.

Experimental Method

Mixtures were prepared in glass-stoppered flasks by direct weighing and were allowed to reach equilibrium in a water thermostat (25 ± 0.05°). The conjugate phases were sampled with pipets; for the lower layer, the tips of the pipets used were drawn off and sealed. These tips were broken off under the lower layer for sampling to avoid any contamination with the upper layer. Densities of all solutions were determined with 25-cc. or 10-cc. pycnometers to a precision of ± 0.0001 unit. All refractive indicex measurements were made with an Abbe refractometer to a precision ± 0.0002 unit.

The Binodal Curve.—The binodal curve for the 25° isotherm was determined by titration of binary mixtures of benzene and dioxane with water and of mixtures of dioxane and water with benzene to the first indication of immiscibility. In the overlapping portions from the two sets of titrations, these data were found to agree within ±0.2%. The data for the binodal curve are given in Table I, and the plot in Fig. 1.

TABLE I

DATA FOR THE BINODAL CURVE OF THE SYSTEM: DIOXANE–BENZENE–WATER AT 25°

% Dioxane	% Water	% Benzene	% Dioxane	% Water	% Benzene
10.24	89.66	0.10	9.97	0.14	89.89
20.38	79.49	.13	19.89	.26	79.85
30.10	69.73	.17	30.53	.58	68.89
39.76	59.98	.26	40.80	.84	58.36
50.21	49.10	.69	50.11	1.34	48.55
58.39	39.90	1.71	58.81	2.09	39.10
64.53	32.08	3.39	63.43	2.70	33.87
67.58	27.69	4.73	67.79	3.73	28.48
70.21	23.05	6.74	69.69	4.34	25.97
72.50	18.24	9.26	71.66	5.09	23.25
71.51	20.33	8.16	73.23	6.06	20.71
73.60	15.44	10.96	74.21	7.43	18.36
74.45	13.31	12.24	74.59	12.43	12.98
74.86	8.33	16.81	73.37	15.78	10.85
72.92	5.71	21.37			
75.01	10.24	14.75			

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(1) Hand, *J. Phys. Chem.*, **34**, 1961 (1930).

(2) Bancroft and Hubbard, THIS JOURNAL, **64**, 347 (1942).

(3) Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).