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The Entropy of the Compound Formed between Cyclopentane and 2,2-Dimethylbutane at 0°K.[1]

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The heat capacities from 14 to 298°K., melting points and heats of fusion of two cyclopentane–2,2-dimethylbutane solutions (66.6 and 69.3 mole % cyclopentane) have been measured. Values for the temperatures and entropies of the rotational transitions which are of second or higher order have been determined. The heat of vaporization of the 66.6 mole % cyclopentane solution at 298.16°K. has been determined experimentally and that of the 69.3 mole % cyclopentane solution has been estimated. From these data the entropy of the solutions at the absolute zero has been determined. The zero point entropies have been interpreted to indicate that a compound or complex consisting of two units of cyclopentane and one of 2,2-dimethylbutane exists in five isomeric forms randomly arranged at the absolute zero.

Introduction

A maximum in the solid–liquid phase diagram[2a] of cyclopentane–2,2-dimethylbutane solutions at 66.7 mole % cyclopentane indicates compound formation at this composition. A maximum in the liquid–vapor diagram[2b] at the same composition shows that a constant boiling solution exists. Nuclear magnetic resonance measurements[3] have shown that a rotational transition occurs at 65°K. for the 66.7 mole % cyclopentane solution.

The present work was undertaken to determine whether this cyclopentane–2,2-dimethylbutane solution behaves as a compound or complex as it is cooled to 0°K. or as a solid solution of the individual components.

This paper presents the results of a calorimetric study of the 66.7 mole % cyclopentane solution leading to a value of the entropy of the system with this composition at 0°K.

In addition, the results of a calorimetric study of a 70 mole % cyclopentane solution, which are useful in determining the effects of excess cyclopentane on the entropy at 0°K., are presented and discussed.

Experimental

Apparatus.—Platinum calorimeter G of this Laboratory was used in this work. Temperatures were measured with platinum resistance thermometer Pt-G 10. This calorimeter together with its cryostat and temperature scale were previously described.[4]

The Cyclopentane and 2,2-Dimethylbutane Samples.—The cyclopentane and 2,2-dimethylbutane samples were "reagent grade" specimens obtained from the Phillips Petroleum Company. The purity of a sample of each was determined calorimetrically by observing equilibrium temperatures of solid and liquid with increasing fractions of the sample melted.[5] By this procedure it was found that the cyclopentane was 99.99 mole % pure and the 2,2-dimethylbutane 99.98 mole % pure, assuming no solid solution. The observed melting points were 179.62 and 174.28°K., respectively, showing excellent agreement with previously reported values.[6-9]

Preparation of the Solution Samples.—After degassing by consecutive freezing of the sample, evacuation and melting three times, 31.011 g. of cyclopentane was sealed under vacuum in a glass bulb equipped with an inner "break off" seal. The weighed sample bulb was sealed to a glass manifold leading to the calorimeter filling tube. After evacuation, the break off seal was broken and the sample was distilled into the calorimeter. A 16.859-g. sample of 2,2-dimethylbutane was similarly prepared and distilled into the calorimeter. After transfer of the solution components to the calorimeter, the mixture (69.327 mole % cyclopentane) was frozen and melted three times, and held just above the melting point overnight in each case to ensure thorough mixing. Thermal measurements on this sample which we shall refer to as Composition A, were then made.

After completing measurements on composition A, the composition of the solution in the calorimeter was altered. An additional 2.249 g. of 2,2-dimethylbutane was transferred to the calorimeter, and measurements on the resulting 66.602 mole % cyclopentane, which shall be referred to as composition B, were made after mixing by the process described above.

The Heat Capacity Measurements.—Smoothed values of the heat capacities of the two solutions at integral temperatures taken from the best curves through the experimental points are given in Table I except in the vicinity of the rotational transition (60°K.). From 60 to 85°K. the experimental values of the heat capacity are given at the experimental temperatures. The experimental values are indicated in Fig. 1 by appropriately designated points. The curves below the melting point are the best curves through the experimental points. The curves above the melting point are those calculated from the heat capacities of the components above their melting points. Values indicated in both Table I and Fig. 1 are for one mole of solution (75.048 g. of solution of composition A and 75.485 g. of solution of composition B) which is the unit used throughout this paper. Results of nuclear magnetic resonance measurements[3] on a 66.7 mole % cyclopentane solution are also indicated in Fig. 1.

The precision of the liquid heat capacities and the solid heat capacities from 85 to 125°K. is 0.1%. From 125°K. to the melting point of the samples the precision is 0.2% due to the premelting which is accentuated by the small heat of fusion. From 45 to 80°K. the uncertainty is 0.2% and below 45°K. the error may rise to as much as 2% due to difficulty in obtaining equilibrium conditions. Above the melting point the accuracy is about 0.2% at all temperatures.

The Solid Transitions.—Abnormal rises in the heat capacities of the solutions beginning at 62.5 and 65.0°K., respectively, for the 66.602 and 69.327 mole % cyclopentane compositions indicate onset of second order transitions. The temperatures at which these transitions are complete (*i.e.*, all material converted to the higher energy state) were determined by measuring equilibrium temperatures at various fractions of the solid in the higher state. Values of 83.200 and 83.150°K. for the 66.602 and 69.327 mole %

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(1) Aided in part by contract N6onr-269, T.O. III of the Office of Naval Research. Reproduction in whole or in part is permitted for any purposes of the United States Government.

(2) (a) H. L. Fink, M. R. Cines, Q. E. Frey and J. G. Aston, THIS JOURNAL, **69**, 1501 (1947); (b) A. S. Carney, Ph.D. Dissertation, The Pennsylvania State University, 1955.

(3) J. G. Aston, B. Bolger, R. Trambarulo and H. Segall, *J. Chem. Phys.*, **22**, 460 (1954).

(4) J. G. Aston, J. L. Wood and T. P. Zolki, THIS JOURNAL, **75**, 6202 (1953).

(5) J. G. Aston, H. L. Fink, J. W. Tooke and M. R. Cines, *Ind. Eng. Chem.*, **19**, 218 (1947).

(6) J. E. Kilpatrick and K. S. Pitzer, THIS JOURNAL, **68**, 1066 (1946).

(7) J. G. Aston, H. L. Fink and S. C. Schumann, *ibid.*, **65**, 341 (1943).

(8) D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 1704 (1946).

(9) D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 173 (1946).

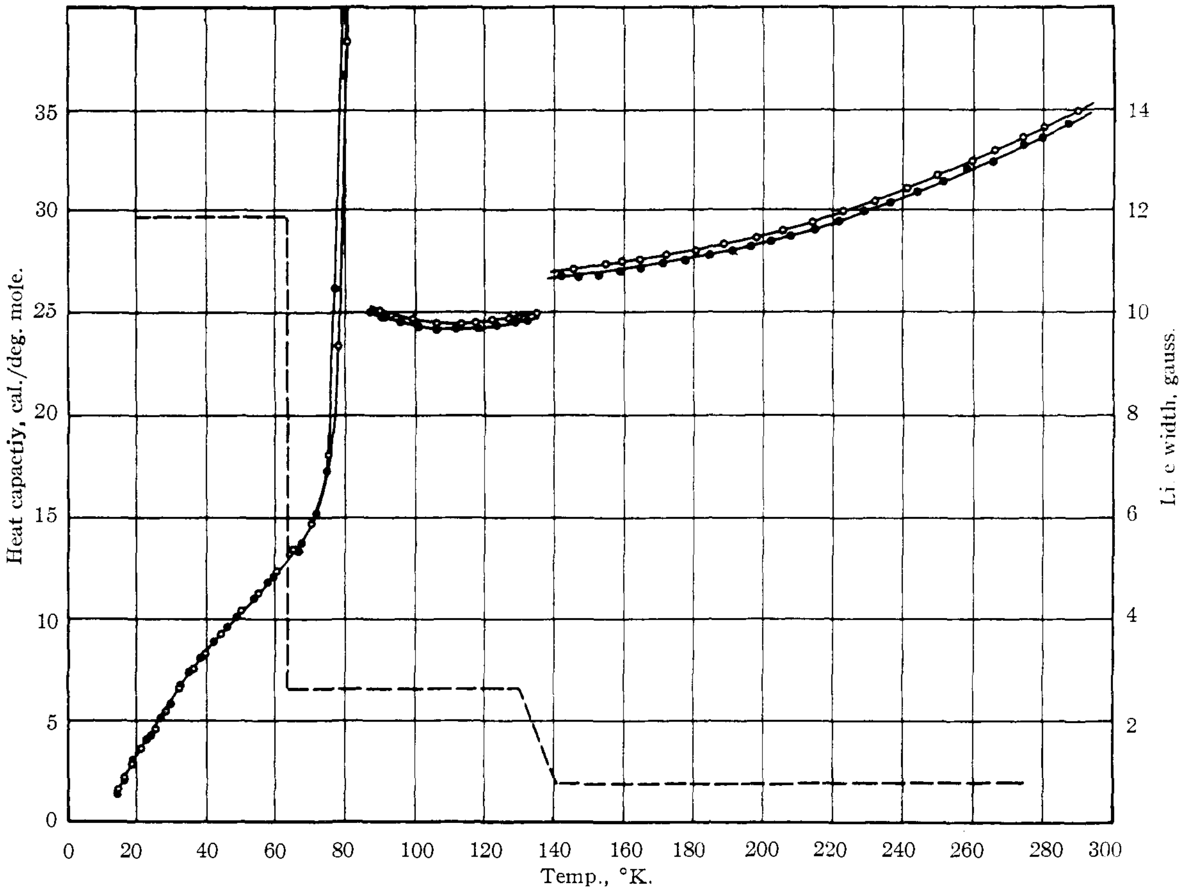

Fig. 1.—Heat capacities of the mixtures: 0.66602 mole of cyclopentane; 0.33398 mole of 2,2-dimethylbutane and 0.69327 mole of cyclopentane; 0.30673 mole of 2,2-dimethylbutane and nuclear magnetic resonance data for a 66.7 mole % cyclopentane, 33.3 mole % 2,2-dimethylbutane mixture: ○, 0.66602–0.33398 mixture; ●, 0.69327–0.30673 mixture; ---, n.m.r. data.

cyclopentane solutions, respectively, were obtained. The data for the complex (composition B) are given in Table II. Those for composition A are similar.

Values for the heats of transition of the solutions were obtained by assuming that the values of heat capacities observed from the onset of the transition (62.50 and 65.00°K. for the 66.602 and 69.327 mole % cyclopentane compositions, respectively) to the completion of the transitions (83.200 and 83.150°K., respectively) can be separated into a part due to transition and a part due to normal heat capacity. The latter are those obtained by extrapolation of the heat capacities from temperatures below onset of the transitions to temperatures corresponding to completion of the transitions along curves they would be predicted to follow if the transitions did not occur. The former are obtained by assuming that all heat input in excess of $\int C_{p_{extrap}}\, dT$ is due to heat of transition. The total heat capacities are, of course, independent of any assumption. Values obtained by this method for composition B are given in Table III. The average value of the heat of transition for composition B is 328.92 ± 0.61 cal. mole^{-1}. Similar data for composition A gives an average value of 349.68 ± 0.35 cal. mole^{-1}.

The Melting Points and Heats of Fusion.—Equilibrium temperatures of solid and liquid were observed for both solutions with increasing fractions of the samples melted. The melting points of the 66.602 and 69.327 mole % cyclopentane compositions, corrected for 0.06 and 0.14 mole % liquid soluble solid-insoluble impurity, respectively, were found to be 137.710 and 137.691°K. Data are given in Table IV for composition B.

Results of heat of fusion measurements are summarized in Table V for the solution of composition B. The usual corrections[10] for premelting and for heat capacity of solid and liquid have been applied. The value for solution A, obtained in the same manner is 191.81 ± 0.72 cal. mole^{-1} at 137.69°K.

The Entropy of the Cyclopentane–2,2-Dimethylbutane Solutions in the Liquid State at 298.16°K.—Calculations of the entropies of the 66.602 and 69.327 mole % cyclopentane solutions in the liquid state at 298.16°K. are summarized in Table VI and VII, respectively. Values for the entropies of the solid state transitions were calculated by dividing the measured heat capacities from the onset of the transitions to their completion into "normal" and transition contributions as described earlier and performing the appropriate graphical integrations

$$\Delta S_{trans} = \int (C_{p_{meas}} - C_{p_{extrap}})\, dT/T \qquad (1\text{-a})$$

Equation 1-a gives the transition entropy. The entropy values which are calculated are based on one total mole of solution components.

The Vapor Pressure of the 66.602 Mole % Cyclopentane.—Since composition B has been shown to be a constant boiling solution,[2b] the vapor pressures were measured in the usual way.[7] Absolute temperatures were measured with the calorimeter resistance thermometer. The data obtained are given in Table VIII. Column three of the table gives the difference between the observed pressure and that calculated from the equation

$$\log p_{mm} = 8.0624 - \frac{1817.6}{T + 29.21} \qquad (2)$$

The heat of vaporization at 298.16°K. calculated from this equation is 6744 cal. mole^{-1} of composition B. The Berthelot correction (155 cal. mole^{-1}) was calculated as a linear combination of those of the components.

The Heat of Vaporization of the 66.602 Mole % Cyclopentane Solution (Composition B) from Calorimetric Measure-

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[10] J. G. Aston and G. J. Szasz, THIS JOURNAL, **69**, 3108 (1947).

Table I

Molal Heat Capacity of Two Cyclopentane–2,2-Dimethylbutane Solutions Containing (A) 69.327 Mole % Cyclopentane and (B) 66.602 Mole % Cyclopentane

0°C. = 273.16°K., 1 cal. = 4.1833 int. joules

T, °K.	C_p (cal. deg.$^{-1}$ mole^{-1}) Soln. A (75.048 g.)	C_p (cal. deg.$^{-1}$ mole^{-1}) Soln. B (75.485 g.)
14	1.50	1.50
15	1.78	1.78
16	2.06	2.06
17	2.35	2.35
18	2.63	2.63
19	2.91	2.91
20	3.19	3.19
22	3.75	3.75
24	4.31	4.31
26	4.86	4.86
28	5.41	5.40
30	5.94	5.94
35	7.19	7.19
40	8.32	8.31
45	9.34	9.28
50	10.25	10.25
55	11.13	11.20
60.077	...	12.20
60.216	12.14	...
65.185	...	13.37
67.231	13.66	...
70.285	...	14.66
71.651	15.16	...
74.751	17.15	...
75.222	...	18.00
77.357	26.16	...
78.627	...	38.47
79.393	36.61	...
	Transition	
87.548	25.00	...
87.741	...	25.42
88	24.98	25.26
90	24.88	25.11
95	24.63	24.85
100	24.45	24.66
105	24.32	24.52
110	24.26	24.46
115	24.24	24.45
120	24.48	24.51
125	24.36	24.60
130[a]	24.47	24.69
135[a]	24.58	24.80
	Fusion	
140	26.59	27.05
150	26.80	27.23
160	27.04	27.43
170	27.29	27.66
180	27.58	27.97
190	27.93	28.30
200	28.33	28.67
210	28.78	29.12
220	29.31	29.68
230	29.93	30.28
240	30.58	30.89
250	31.26	31.56
260	31.92	32.29
270	32.62	33.07
280	33.43	33.90
290	34.33	34.78
300	35.27	35.70

[a] Corrected for premelting.

Table II

Temperature of Completion of the Second-order Transition for the 66.602 Mole % Cyclopentane, 33.398 Mole % 2,2-Dimethylbutane Solution

0°C. = 273.16°K., 1 cal. = 4.1833 int. joules

Temp., °K.	1/fraction in higher energy state
81.577	11.95
82.733	4.35
82.938	2.11
83.030	1.38
83.200 (extrapolated)	1.00

Table III

Molal Heat of the Second-order Transition for a Mixture of 0.66602 Mole of Cyclopentane 0.33398 Mole of 2,2-Dimethylbutane (Composition B)

$T_{\text{transition}}$ = 83.200°K., 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules; 1 mole = 75.485 g.

Temp. interval (°K.)	Heat input A (cal. mole^{-1})	$\int C_{p_{\text{normal}}}\,dT$ B (cal. mole^{-1})	$\Delta H_{\text{transition}}$ (62.50 – 79.785°K.) C (cal. mole^{-1})	$\Delta H_{\text{transition}}$ A – B + C (cal. mole^{-1})
79.785–83.998	376.81	78.82	31.54	329.53
79.785–85.244	407.47	110.70	31.54	328.31

Av. ΔH (per mole of component) = 328.92 ± 0.61 cal. mole^{-1}

Table IV

Melting Point of the Solution; 66.602 Mole % Cyclopentane, 33.398 Mole % 2,2-Dimethylbutane (Composition B)

Temp., °K.	1/fraction melted
136.017	9.75
136.891	4.76
137.375	2.51
137.534	1.52
137.597	1.07
137.600 (extrapolated)	1.00
137.710 (extrapolated)	0

Table V

Molal Heat of Fusion of the Solution; 0.66602 Mole of Cyclopentane, 0.33398 Mole of 2,2-Dimethylbutane (Composition B)

M.p. = 137.71°K., 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules; 1 mole = 75.485 g.

Temp. interval, °K.	Heat input A (cal. mole^{-1})	$\int C_p\,dT$ B (cal. mole^{-1})	Pre-melting ΔH C (cal. mole^{-1})	ΔH fusion A – B + C (cal. mole^{-1})
129.079–138.634	439.51	238.66	0.00	200.85
134.257–142.734	411.58	221.58	9.68	199.68

Av. ΔH_{fusion} = 200.27 ± 0.59 cal. mole^{-1}

Table VI

The Entropy of the Mixture: 0.66602 Mole Cyclopentane, 0.33398 Mole 2,2-Dimethylbutane (Composition B) in the Liquid State at 298.16°K. from Calorimetric Data

Contribution	ΔS (e.u. mole^{-1})
0–15°K., Debye function, θ = 108 (5 degrees of freedom)	0.653 ± 0.02
15–83.200° (graphical)	13.453 ± .04
Second-order transition	4.014 ± .01
83.200–137.710°K. (graphical)	12.476 ± .00
Fusion (200.27/137.71)	1.454 ± .01
137.710–298.160°K. (graphical)	22.891 ± .02
Entropy of the liquid at 298.16°K.	54.94 ± 0.10

Table VII

The Entropy of the Mixture; 0.69327 Mole of Cyclopentane, 0.30673 Mole of 2,2-Dimethylbutane (Composition A) in the Liquid State at 298.16°K. from Calorimetric Data

Contribution	ΔS (e.u. mole^{-1})
0–15°K. Debye function, θ = 108 (5 degrees of freedom)	0.653 ± 0.02
15–83.150°K. (graphical)	13.380 ± .04
Second-order transition	4.297 ± .01
83.150–137.690°K. (graphical)	12.375 ± .00
Fusion (191.81/137.69)	1.393 ± .01
137.690–298.160°K. (graphical)	22.593 ± .02
Entropy of the liquid at 298.16°K.	54.69 ± 0.10

ments.—Three measurements of the heat of vaporization were made by a method previously described.[7] The temperatures of the calorimeter was followed during energy inputs by means of copper–constantan thermocouple S-1[11] which is fixed to the side of the calorimeter vessel. Pressure at which sample was vaporized was maintained constant by manipulation of a grooved stopcock between the calorimeter and the receiving bulbs. Results of the heat of vaporization

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(11) T. P. Zolki, Ph.D. Dissertation, The Pennsylvania State University, 1954.

TABLE VIII

VAPOR PRESSURES OF THE SOLUTION; 66.602 MOLE % CYCLOPENTANE (COMPOSITION B)

0°C. = 273.16°K., *g* for State College = 980.124

$T_{\text{obsd.}}$, °K.	$P_{\text{obsd.}}$, int. mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$,[a] int. mm.
265.01	76.69	0.01
269.52	95.07	.01
273.17	112.54	− .05
277.44	136.55	.05
282.74	172.11	.00
287.05	206.63	− .01
291.67	250.09	.04

[a] Calculated from equation 2.

measurements are given in Table IX for one total mole of components in composition B. The heat of vaporization to the real gas at 298.16°K. was calculated using heat capacities of gaseous cyclopentane[7] and 2,2-dimethylbutane[6] and the heat capacity of the liquid solution. The value calculated from equation 2 and thermodynamics is included for comparison.

TABLE IX

HEAT OF VAPORIZATION OF THE SOLUTION; 0.66602 MOLE OF CYCLOPENTANE, 0.33398 MOLE OF 2,2-DIMETHYLBUTANE (COMPOSITION B)

0°C. = 273.16°K., 1 cal. = 4.1833 int. joules.

Vaporized, mole	Mean temp. of vaporization, °K.	ΔH, real gas, T°K., cal. mole^{-1}	ΔH real gas, 298.16°K., cal. mole^{-1}
0.041131	295.007	6732	6698
.039103	295.393	6750	6720
.032628	296.468	6766	6748

Av. $\Delta H_{\text{vap}} = 6722 \pm 17$

Calcd. from eq. 2 and critical data (Berthelot corrn. = 155 cal.) = 6744.

Entropy of Solution: 0.66602 Mole of Cyclopentane, 0.33398 Mole of 2,2-Dimethylbutane in the Ideal Gas State at 298.16°K. from the Calorimetric Data (Composition B).— The calculation of the entropy of the solution of 0.66602 mole of cyclopentane, 0.33398 mole of 2,2-dimethylbutane in the ideal gas state at 298.16°K. is summarized in Table X. The value obtained is 75.87 ± 0.16 cal. deg.$^{-1}$ mole^{-1}.

TABLE X

ENTROPY OF COMPOSITION B IN THE IDEAL GAS STATE AT 298.16°K. AT 1 ATMOSPHERE

Contribution	ΔS (cal. deg.$^{-1}$ mole^{-1})
Entropy of the liquid at 298.16°K. (Table VI)	54.94 ± 0.10
Vaporization at 298.16°K. 6722/298.16	22.54 ± 0.06
Gas imperfection correction[a]	0.09
Correction to 1 atm.	−1.70
Entropy of ideal gas at 1 atm., 298.16°K. =	75.87 ± 0.16

[a] $\Delta S_{\text{ideal}} - \Delta S_{\text{real}} = 27RT_c^3P/32T^3P_c$ (calculated as a linear combination of component corrections).

Discussion

The entropy of the 66.602 mole % cyclopentane gaseous mixture can be calculated from the entropies of the components on the basis of additivity and ideal entropy of mixing at 298.16°K. The entropies of supercooled cyclopentane and 2,2-dimethylbutane vapors for the ideal gas state at 298.16°K. and 1 atmosphere are, respectively, 70.70 ± 0.07[7] and 85.72 ± 0.20[6] cal. deg.$^{-1}$ mole^{-1}. Thus for one mole of this mixture the entropy is 0.66602 (70.70 ± 0.07) + 0.33398 (85.72 ± 0.20) − (0.66602) R ln (0.66602) − 0.33398 R ln 0.33398 = 76.99 ± 0.10 cal. deg.$^{-1}$ mole^{-1}.

This value is higher than the measured value by 1.12 ± 0.26 cal. deg.$^{-1}$ mole^{-1}.

If there were ideal solution of the components in the solid state at the absolute zero, the entropy there would be that of the ideal entropy of mixing, namely, 1.27 cal. deg.$^{-1}$ mole^{-1}. In view of the fact that the two first-order transitions for each of the respective components have been replaced by a single second-order transition, such an explanation seems unlikely. More likely, the entropy at the absolute zero is due to disorder in the crystalline complex.

A more natural explanation is forthcoming when it is realized that the value 1.12 ± 0.26 is very close to (R ln 5)/3 or 1.07. It must be realized that 0.333 mole of 2,2-dimethylbutane together with 0.667 mole of cyclopentane is only one third of a mole of complex if this complex is regarded as a chemical species. Thus if five possible orientations of the complex are equally represented in each mole of complex at the absolute zero, the residual entropy would be 1.07 cal. deg.$^{-1}$ mole^{-1} based on one mole of solution. This value is so close to the experimental value as to make this explanation inviting. Actually there is a way of partially verifying it. This consists of examining the zero point entropy of a composition near that of the complex such as the 69.3 mole % cyclopentane solution.

It is not necessary to go into the vapor phase experimentally to compare the measured entropy of composition A with a value calculated from the components. One mole of composition A (0.69327 mole % cyclopentane) corresponds to 0.92019 mole of material as 0.30673 mole of complex and 0.07981 mole of excess cyclopentane. The heat of vaporization of complex is 6722 ± 17 cal. mole^{-1} (of components) at 298.16°K. while that of cyclopentane is 6982 ± 8 cal. mole^{-1}. Assuming additivity of the heats of vaporization of the complex and excess cyclopentane (6982 cal. mole^{-1}) the heat of vaporization of composition A is then 6743 ± 16 cal. mole^{-1}. It can be shown that calculation of the heat of vaporization of the complex (composition B) by assuming additivity gives a value differing from the measured value by only 2%. Thus the assumption of additivity of heats of vaporization of complex and cyclopentane to obtain the heat of vaporization of composition A should not introduce an error greater than 0.2%.

This value was used to calculate the heat of vaporization to the real gas at 298.16°K. and the equilibrium pressure. Since the boiling point of solutions with 55 to 90 mole per cent. cyclopentane at 1 atm. varied by only 0.08° the equilibrium pressure was taken as that of the 66.6 mole per cent. solution at 298.16°K. in calculating the entropy of vaporization to the real gas at 1 atm. The correction to the ideal gas state was taken as 0.09 cal. deg.$^{-1}$ mole^{-1}.

The entropy of vaporization of composition A at 298.16°K. to the ideal gas state at 1 atmosphere is then 21.00 ± 0.06 cal. deg.$^{-1}$ mole^{-1} and the entropy of composition A at these conditions is 75.69 ± 0.16 cal. deg.$^{-1}$ mole^{-1} (of components). The entropy calculated on the basis of additivity of entropies of the components of composition A and ideal entropy of mixing is

$$0.69327(70.70 \pm 0.07) + 0.30673(85.72 \pm 0.20) - 0.69327R \ln 0.69327 - R \ln 0.30673 = 76.53 \pm 0.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

This value is higher than the measured value for composition A by 0.84 ± 0.26 cal. deg.$^{-1}$ mole^{-1}.

If there were ideal solution of the components of composition A at the absolute zero, the residual entropy would be the ideal entropy of mixing, namely, 1.23 cal. deg.$^{-1}$ mole^{-1}. If it is assumed that the cyclopentane in excess of the 2:1 complex has separated from the solid solution as a new phase at the absolute zero, the residual entropy would be the ideal entropy of mixing of the components of the 2:1 solution, namely

$$(0.92019(1.27) = 1.17 \text{ cal. deg.}^{-1} \text{ mole}^{-1})$$

Neither of these values falls within the experimental accuracy of the residual entropy which has been found.

If the postulation of five possible orientations of the complex at the absolute zero is correct, and if cyclopentane in excess of the 2:1 complex has separated as a separate phase at the absolute zero, the residual entropy for composition A should be

$$(0.92019(R \ln 5)/3 = 0.98 \text{ cal. deg.}^{-1} \text{ mole}^{-1})$$

This value is in good agreement with the experimental value (0.84 ± 0.26 cal. deg.$^{-1}$ mole^{-1}).

It now must be shown that the cyclopentane in excess of the composition of the complex in composition A exists as a separate phase at the absolute zero. The entropy change associated with the second-order transition of composition B (complex) has been given as 4.01 ± 0.01 cal. deg.$^{-1}$ mole^{-1}. Consequently, for the complex in composition A, the corresponding contribution to the entropy change should be

$$(0.92019)(4.01 \pm 0.01) = 3.69 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

Since the rotational transitions of cyclopentane[7] were not observed in heat capacity measurements of composition A, it is quite obvious that the excess cyclopentane in this composition must be in solid solution in the complex at the temperatures corresponding to these transitions. It is apparent that this excess cyclopentane has begun rotation at the temperatures at which the complex passes through its transition due to a coöperative effect in the cyclopentane–complex solid solution and an additional contribution to the entropy change is to be expected.

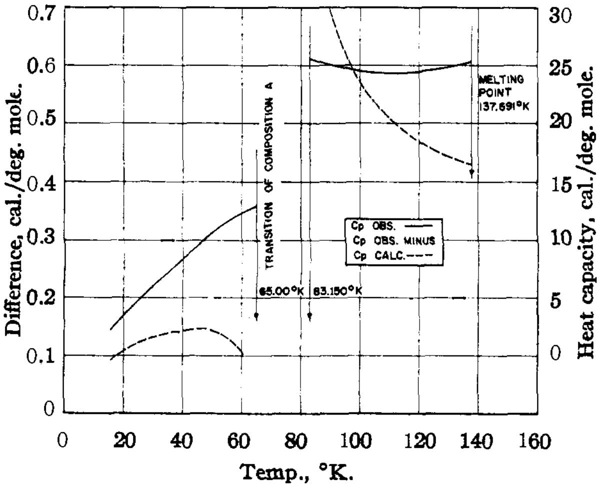

Fig. 2.—Observed heat capacity of composition A and difference from calculated values.

Rotation of 1 mole of cyclopentane results in an entropy increase[7] of 10.12 cal. deg.$^{-1}$ mole^{-1}. Rotation of the excess cyclopentane in composition A then corresponds to an entropy increase of

$$0.07981(10.12 \pm 0.01) = 0.80 \pm 0.00 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

If phase separation of the excess cyclopentane occurred during the second-order transition of composition A, then solution of the excess cyclopentane over this temperature region should result in an entropy increase corresponding to the ideal entropy of mixing of the excess cyclopentane in the complex, namely

$$0.38654\left(-\frac{0.30673}{0.38654}R \ln \frac{0.30673}{0.38654} - \frac{0.07981}{0.38654}R \ln \frac{0.07981}{0.38654}\right) = 0.39 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Thus if rotation of the complex and excess cyclopentane as well as reversible solution of the excess cyclopentane in the complex occurs in the temperature range of the second-order transition of composition A, the apparent entropy increase of the transition should be

$$(3.69 \pm 0.01) + (0.80 \pm 0.00) + 0.39 = 4.88 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

This value exceeds the measured entropy of the second-order transition of composition A by

$$4.88 \pm 0.01 - 4.30 \pm 0.01 = 0.58 \pm 0.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

implying that the entire entropy increase due to rotation of the excess cyclopentane and/or the entire entropy increase due to solution of the excess cyclopentane in the complex is not attained over the temperature range of the transition.

If heat capacities of composition A are calculated from heat capacities of complex (composition B) and cyclopentane[7] by assuming additivity, the values obtained are smaller than the observed values for composition A both below and above the transition up to the temperature of the first rotational transition of pure cyclopentane. A graph of the difference between the calculated and observed molal heat capacities over this range is shown in Fig. 2, along with the heat capacity curve for one mole of mixture.

It is not possible to calculate the differences above the first rotational transition of pure cyclopentane directly, but values up to the melting point of the complex can be obtained by extrapolating the heat capacities from below the first rotational transition or by extrapolation of the difference curve. The difference curves in this figure correspond to an entropy difference of 0.20 ± 0.02 cal. deg.$^{-1}$ mole^{-1} (of components) below the transition and 0.23 ± 0.02 cal. deg.$^{-1}$ mole^{-1} (of components) between transition and melting point, or a total of 0.43 ± 0.04 cal. deg.$^{-1}$ mole^{-1} (of components). If this value is added to the observed entropy of transition of composition A, a value of 4.73 ± 0.05 cal. deg.$^{-1}$ mole^{-1} (of components) is obtained. This differs from the sum of the entropy of transition of complex in composition A, of transition of excess cyclopentane in this composition and of solution of this excess cyclopentane in complex by only

$$4.88 \pm 0.01 - 4.73 \pm 0.05 = 0.15 \pm 0.06 \text{ cal. deg.}^{-1}\text{ mole}^{-1} \text{ (of components)}$$

This difference exceeds experimental accuracy; however it is felt that this discrepancy is probably due to the extrapolations involved to obtain entropies of transition in compositions A and B.

Thus, it appears that excess cyclopentane in composition A exists as a separate phase at the absolute zero and all disorder results from the five forms of complex randomly arranged in solid solution at this temperature. The occurrence of five isomers is certainly due to the non-planarity of the cyclopentane ring. Solution of excess cyclopentane in the complex begins as the temperature is increased and is almost completed at the rotational transition of the complex. The cyclopentane in solid solution is influenced by the complex to begin rotation at the rotational transition of the complex.

Note Added in Proof.—In calculating values of the entropies of the solutions from those of the components we have used the measured value of the entropy of gaseous cyclopentane at 298.16°K. and 1 atm.,[7] part of which was the entropy of vaporization calculated from a measured value of the heat. Kilpatrick, Pitzer and Spitzer[12] have pointed out that this value of the heat is inconsistent with the vapor pressure data, while a value calculated from the vapor pressure equation yields an entropy of the vapor which is more consistent with one calculated from reasonable spectroscopic and molecular data.

If the value of the entropy of ideally gaseous cyclopentane at 298.16°K. and 1 atm. recommended by Kilpatrick, Pitzer and Spitzer is used to calculate the entropy of the gaseous mixture the value obtained for solution B is 76.60 cal. deg.$^{-1}$ mole^{-1}, which is only 0.73 higher than the measured value. This difference is exactly (R ln 3)/3 (= 0.73). The value calculated for composition A is 0.44 cal. deg.$^{-1}$ mole^{-1} compared to (0.92 R ln 3)/3 (= 0.67).

It is possible that R ln 3 corresponds to three possible different orientations of the 2,2-dimethylbutane in the complex. It is of interest that a value of the entropy of the liquid of composition B calculated from the experimental values for the components at 298.16°K. using the ideal entropy mixing is 0.60 cal. deg.$^{-1}$ mole^{-1} higher than the experimental value. This is within experimental error of the difference found above (0.73). This might be considered as confirmation of the heat of vaporization calculated from the vapor pressures. It is hoped to make some new measurements in this laboratory to resolve this point.

The uncertainty in no way affects the arguments, based on the heat capacities concerning phase separation of the cyclopentane at low temperatures.

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[12] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, 69, 2483 (1947).

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The Silver Perchlorate–Benzene Complex, $C_6H_6 \cdot AgClO_4$, Crystal Structure and Charge Transfer Energy[1]

BY HAROLD G. SMITH AND R. E. RUNDLE

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The silver perchlorate–benzene complex consists of –Bz–Ag–Bz–Ag– chains and perchlorate ions. The two silver ions associated with each benzene lie above and below the ring over bonds one and four of the ring. The silver ion positions are asymmetric and disordered, with Ag–C distances of 2.50 and 2.63 Å. to the two carbons of the nearest bond. The benzene ring is distorted; the two C–C distances nearest the silver ions are 1.35 Å., the four others are 1.43 Å. Evidently polarization of the π-bonding system leads to an increase in electron density in bonds nearest silver ions, and this is far more important than charge-transfer bonding in determining electron density within the ring. An attempt has been made to calculate the charge-transfer bond energy, using crystal energies as a guide. Our result is that the $\mathrm{Ag}\ldots\begin{matrix}\mathrm{C}\\ |\\ \mathrm{C}\end{matrix}$ charge-transfer bond energy is ~15.7 kcal./mole, and our estimated errors are such as to suggest that this is an upper limit.

Introduction

Charge-transfer complexes, their stabilities, spectra and electronic structures have been of considerable theoretical and experimental interest.[2] Indeed, it has frequently been suggested that they play an important role as intermediates in reaction mechanisms.[3] Few such complexes have stabilities that permit direct observation of their structures, and of these, the most available is the silver perchlorate–benzene complex, $C_6H_6 \cdot AgClO_4$. The gross features of its structure have been given previously,[4] but an accurate refinement has revealed details about the benzene ring which appear to be important. In addition an accurate structure has permitted the calculation of the crystal lattice energy and an estimation of the energy of the charge-transfer bond which we believe is more reliable than those given previously.

Experimental Data

Single crystals of the silver perchlorate–benzene complex are obtained easily by dissolving silver perchlorate, either the anhydrous or the monohydrate, in liquid benzene and allowing the benzene to evaporate slowly. The crystals are usually flat plates or parallelopipeds and are stable under a vapor pressure of benzene but decompose rapidly when ex-

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[1] This paper is based in part on a thesis presented by Harold G. Smith to Iowa State College in partial fulfillment of the requirements for the Ph.D. degree, June, 1957.

[2] L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954), reviews both experimental work and theory. See additional references therein.

[3] P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); M. J. S. Dewar, *ibid.*, 777 (1946).

[4] R. E. Rundle and J. H. Goring, THIS JOURNAL, **72**, 5337 (1950).