[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND OF STANFORD UNIVERSITY]

CYCLOHEXANOL AND THE THIRD LAW OF THERMODYNAMICS[1]

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RECEIVED JANUARY 2, 1929 PUBLISHED MAY 6, 1929

All statements of the third law of thermodynamics with the exception of that of Eastman[3] agree that the entropies of two crystalline forms of the same substance may both be taken as zero at the absolute zero of temperature. The only test of this statement which has been made with sufficient accuracy to warrant consideration is for the two crystalline modifications of tin. Lange[4] has measured the specific heat of white tin down to 9.6°K. and of gray tin to 15.5°K. and Brönsted[5] has calorimetrically determined the heat of transition. The entropy of transition at 292°K. from Lange's data and the third law is 1.77 E. U. while Brönsted's measurement gives 1.83 E. U., a very good agreement. However, the gray tin which is transformed into the white on cooling goes back to the gray modification, thus making it necessary to use a sample of white tin in the specific heat measurements in a different physical state from that obtained by carrying the gray tin through the transition point. This probably causes only a very slight error. For a more complete discussion of the tin transition the reader is referred to that of Simon.[6]

The present paper presents data on two crystalline forms of cyclohexanol. The heat capacity curves for both forms were obtained down to about 13.5°K. and the heat of transition calorimetrically determined using the same sample of material and the same apparatus throughout. The apparatus and methods used have been described previously.[7]

Purification of Material.—The cyclohexanol was an Eastman Kodak Company product. It was dried with anhydrous sodium carbonate, decanted off and fractionally distilled twice. Further purification was obtained by fractional crystallization. The portion used for the measurements (about 50 cc. in volume) had a boiling range of 160.9–161.0° (760 mm.) and density $d_4^{22.2} = 0.9459$. It was kept in a sealed bottle until placed in the calorimeter.

The Measurements.—The specific heats in 15° calories per mole are given in Table I and shown graphically in Fig. 1.

When cyclohexanol is cooled slowly it undergoes a transformation at

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[1] The experimental work of this paper was done at the University of California.

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[3] Eastman, THIS JOURNAL, **46**, 43 (1924).

[4] Lange, *Z. physik. Chem.*, **110** (Nernstband), 343 (1924).

[5] Brönsted, *ibid.*, **88**, 479 (1914).

[6] Simon, "Handbuch der Physik," Julius Springer, Berlin, **1926**, Vol. X, p. 372.

[7] Kelley, THIS JOURNAL, **51**, 180 (1929).

Table I

Specific Heats of Cyclohexanol

1 mole = 100.1 g.

T, °K.	C_p, cal./mole
Low Temperature Form	
16.09	1.381
19.92	2.294
23.38	3.097
27.28	3.994
30.91	4.797
35.00	5.676
39.30	6.559
43.45	7.270
47.83	7.979
52.35	8.631
57.60	9.440
63.07	10.16
68.15	10.52
77.06	11.49
85.11	12.26
93.38	13.16
101.84	13.98
111.43	15.06
120.19	16.18
122.14	16.55
128.49	16.95
136.76	17.56
145.11	18.46
153.23	19.23
161.03	19.87
168.86	21.01
181.33	22.60
189.08	23.62
197.30	25.02
206.21	26.13
215.81	27.25
225.02	29.04
234.35	29.85
241.38	32.05
245.11	32.85
248.57	35.03
248.69	35.12
251.80	38.76
252.98	38.03
254.74	45.07
257.28	60.93
258.95	99.3
260.19	157
260.25	154
261.32	198
261.98	315
263.19	342
263.71	439
264.16	350
265.30	79.3
High Temperature Form	
15.25	1.919
18.75	2.838
22.11	3.701
25.69	4.503
29.07	5.281
33.00	6.066
37.32	6.946
41.45	7.589
45.70	8.258
50.09	8.887
59.70	10.25
69.91	11.46
75.40	12.17
85.20	13.28
93.42	14.25
101.31	15.12
108.64	16.11
109.63	16.21
118.03	17.42
119.15	17.50
126.81	18.55
135.07	19.92
142.68	22.21
145.56	23.70
148.21	27.73
149.22	27.94
150.45	28.39
153.02	28.66
155.56	28.78
158.99	28.76
212.80	32.98
217.31	33.28
231.02	34.50
235.50	35.26
244.13	36.34
252.03	37.31
260.41	38.55
264.84	39.39
267.95	39.98
271.96	40.70
280.01	41.90
Liquid	
298.15	49.96
298.68	49.90

about 263.5 °K. If cooled with sufficient rapidity the high temperature form is supercooled and may be taken down to the temperature of liquid hydrogen with no difficulty. The nature of the specific heat curves in the transition region may be seen better in Fig. 2.

On warming, the supercooled high temperature form exhibits regular specific heats up to about 135 °K. Here there is a very sharp rise similar to that encountered for glasses which are also supercooled forms of matter. This rise is over at 150 °K. At about 160 °K. the supercooled form on warming changes spontaneously into the low temperature form. This change always occurs at very nearly the same temperature, which is again similar to the behavior of glasses. Between 160 and 210 °K. no measurements could be made on the high temperature form for this reason.

The two measurements between 210 and 220°K. were made with the substance very slowly changing over into the low temperature form and for this reason these two results may be somewhat low. Above 230°K. the high temperature form had considerable apparent stability and no difficulty was found in making measurements from here up to the melting point. This was fortunate because it meant that results on this form could be obtained throughout the region in which the low temperature form was undergoing the transition to the high. It is interesting to note that in the case of white tin Lange found no such sharp rise as that occurring around 140° in the present work. However, he omitted two large temperature intervals, from 57 to 92°K. and from 101 to 286°K. It is in the latter interval that such a phenomenon might be expected.

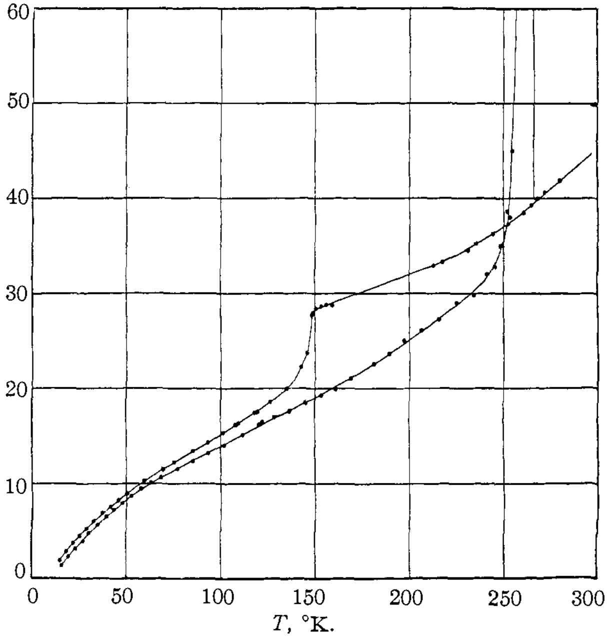

Fig. 1.—The specific heat of cyclohexanol in cal. per mole.

The low temperature form up to the transition region gave normal specific heats. The transition is apparently of the ammonium chloride type as is also the methyl alcohol transition.[7] It is not possible to say just how great an effect the small amounts of impurities present have on the nature of the specific heat curve in this region.

The Temperature and Heat of Transition.—The mean temperature of the transition was found to be 263.5°K. and the heat of transition was also measured, the results obtained being given in Table II. By heat of transition here is meant the heat absorbed per mole in passing through the transition region in excess of the energy $\int_{T_1}^{T_2} C_p \mathrm{d}T$, under the "normal" heat-capacity curves extrapolated to 263.5°K. This is admittedly somewhat arbitrary but can cause no appreciable error in the entropy calculations to follow.

Table II

Heat of Transition in Cal. per Mole

T, °K. (average)	1st result	2nd result	Mean
263.5	1963	1957	1960

The Temperature and Heat of Fusion.—Richards and Shipley[8] have measured the temperature of fusion of a very pure sample of cyclohexanol as 297.0°K. Considerable difficulty was found in obtaining the temperature of fusion of this substance in the calorimeter because of its very low heat of fusion. The best value obtained was 0.2 or 0.3 of one degree lower than that obtained by Richards and Shipley. However, their value is undoubtedly the better since the substance absorbs water very readily and consequently in filling the calorimeter a slight amount of moisture may have been introduced. Therefore the heats of fusion given in Table III have been corrected to 297.0°K.

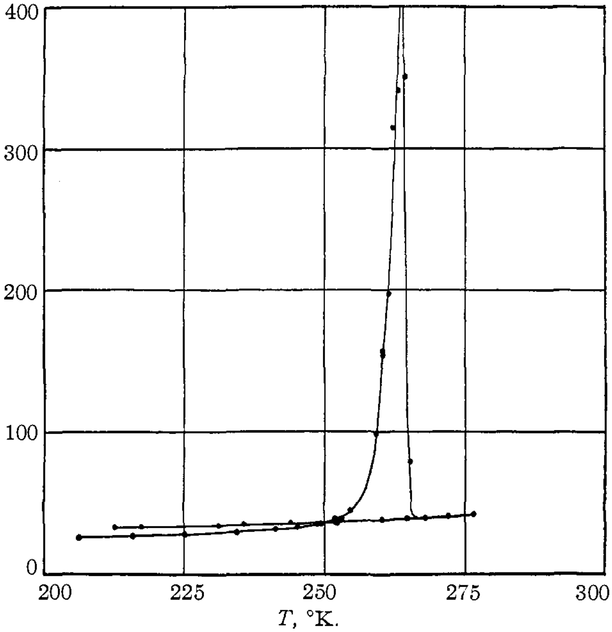

Fig. 2.—The specific heat of cyclohexanol in cal. per mole in the transition region.

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[8] Richards and Shipley, This Journal, **41**, 2002 (1919).

TABLE III

HEAT OF FUSION IN CAL. PER MOLE

T, °K.	1st result	2nd result	Mean
297.0	408	404	406

The heat of fusion was recently obtained by Cauquil[9] by dissolving the crystalline and liquid forms at the same temperature. The value so obtained is 427 cal. per mole which, considering the method used, agrees as well as could be expected with the present value.

Accuracy of Measurement.—The specific heat measurements, except for those in the transition region between the low and high temperature forms which are not used in the entropy calculations, are considered to be in error on the average by not more than 0.5%. A more detailed discussion of the accuracy of measurement given before[7] will also apply here. The heat of transition also is not considered to be in error by more than 0.5%. The heat of fusion may easily be in error by 1%.

Entropy Calculations.—The entropy changes were calculated in the usual manner. Extrapolation below 13.5°K. was made by means of Debye functions with $\Theta = 112$ for the low temperature form and $\Theta = 84$ for the high. The extrapolated values, 0.27 and 0.58 E. U., respectively, are small and cannot be greatly in error. This may be readily seen from a comparison of these results with limiting values obtained by other means and given in Table IV.

TABLE IV

VALUES OF $S_{13.5}$ (EXTRAPOLATED)

Low temperature form	0.25	0.27	0.38
Method	aT^3	Debye	aT^b
High temperature form	0.49	0.58	0.80

The T^3 law applied below 13.5°K. must certainly give results which are too low since neither form has a low enough specific heat at 13.5°K. for this law to apply. The T^3 law, however, should apply at lower temperatures theoretically and has been found to do so experimentally for one organic substance, glycerin.[10] Fitting the lower end of each curve by an equation, $C_p = aT^b$, and using this as a basis of extrapolation should give too high results since $b = 2.38$ for the low temperature form and 1.89 for the high in the neighborhood of 13.5°K.

In Table V are given the results of the entropy calculations. Under I are given the entropy changes in passing from 0°K. to 298.1°K. starting with the low temperature form, transforming to the high temperature form at 263.5°K. and to the liquid at 297.0°K. Under II are given the corresponding values starting at 0°K. with the high temperature form which is carried up to the melting point and changed to liquid.

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[9] Cauquil, *Compt. rend.*, **180**, 1207 (1925).

[10] Simon and Lange, *Z. Physik*, **38**, 227 (1926).

TABLE V

RESULTS OF ENTROPY CALCULATIONS

I			II		
(0–13.5) extrap. (Θ = 112)	0.27		Extrap. (Θ = 84)	0.58	
(13.5–263.5) crystals	33.55		Crystals	40.32	
(1960/263.5) transition	7.44		.....	...	
$S_{263.5}$	41.26	± 0.25		40.90	± 0.25
(263.5–297.0) crystals	5.02		Crystals	5.02	
(406/297.0) fusion	1.37		Fusion	1.37	
(297.0–298.1) liquid	0.17		Liquid	0.17	
$S_{298.1}$	47.8	± 0.3 E. U.		47.5	± 0.3 E. U.

Discussion

If the entropies of the two crystalline forms at 0 °K. are the same, then it follows that the entropy change corresponding to the warming of the substance from 0 °K. to any temperature above the transition is the same for both possible paths. In making the calculations for Table V it was convenient to obtain the total heat of transition and assign it to a "mean" temperature for the purpose of calculating the entropy of transition. Since this has been done it is now convenient to compare the entropies at this point, 263.5 °K., also. The values for the two paths are, respectively, 41.26 and 40.90 E. U., a difference of 0.36 E. U. Each of these values may be in error by ±0.25 E. U., so that this difference is within the upper limit of the experimental error and consequently in this case, as in the case of tin, the only conclusion which can be drawn is that both crystalline forms have the same entropy at 0 °K. in agreement with the third law of thermodynamics.

The Free Energy.—The free energy of formation from the elements may be calculated by means of the equation $\Delta F = \Delta H - T\Delta S$.

The heat of combustion of solid cyclohexanol at 291 °K. has been measured by Richards and Davis.[11] Their value when corrected to 15° calories gives 889,700 cal. per mole at constant pressure. From this value the heat of combustion of liquid cyclohexanol at 298.1 °K. may be calculated by means of the specific heats of the substances involved and the heat of fusion of cyclohexanol. It so happens that the effect due to differences in the specific heats almost exactly counterbalances the heat of fusion and we have, therefore, 889,700 cal. per mole for the heat of combustion of liquid cyclohexanol at 298.1 °K.

Making use of the values for the heats of combustion of graphitic carbon and of hydrogen previously adopted,[7] $\Delta H_{298.1}$ is found to be $-85{,}840$ cal. per mole.

Using 47.7 E. U. as $S_{298.1}$ for liquid cyclohexanol and the entropies of the elements,[7] $\Delta S_{298.1}$ is -162.2 E. U.

Therefore, $\Delta F_{298.1} = -37{,}500$ cal. per mole.

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[11] Richards and Davis, THIS JOURNAL, **42**, 1599 (1920).

Summary

1. The specific heats of two crystalline forms of cyclohexanol were measured down to about 13.5°K.
2. The "mean" temperature and heat of transition between the two crystalline modifications were obtained.
3. The heat of fusion of cyclohexanol was measured.
4. The entropy calculations show that both crystalline forms have the same entropy at 0°K. within the limits of experimental error.
5. The entropy and free energy of liquid cyclohexanol at 298.1°K. have been calculated.

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THE PREPARATION OF PHOSPHENYL CHLORIDE

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RECEIVED JANUARY 4, 1929 PUBLISHED MAY 6, 1929

Since derivatives of phosphenyl chloride have been desired from time to time during rare metal research, it was decided to investigate certain methods involved in the preparation of this substance with the hope of finding some suitable and convenient procedure.

The cheapest method appeared to be that of passing vapors of benzene and phosphorus trichloride repeatedly through a red-hot tube. The equipment required was very similar to that employed in the earlier method for the preparation of diphenyl. After giving this method a thorough trial it was discarded owing to the fact that such a long time was required to produce a small quantity of the product. It appeared to the workers that without doubt a considerable amount of the phosphenyl chloride was decomposed owing to the long heating as it passed through a considerable length of the red-hot quartz tube. It therefore seemed desirable to use an apparatus similar to that described in the preparation of diphenyl,[1] in which a glowing ribbon of nichrome was suspended in an atmosphere of benzene vapors. In this case the difficulty was to find a suitable ribbon or filament which would withstand the action of the vapors. The only material which resisted attack and fusion was a large carbon filament which was very carefully removed from a large and antiquated electric light bulb. Unfortunately in this case the filament kept gradually increasing in diameter due to the deposition of carbon, thereby requiring a gradual increase in current throughout the run. It was noticed, however, that much better yields were obtained than by the previous method.

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[1] Lowe and James, THIS JOURNAL, **45**, 2666 (1923).