

by combining two other series of measurements, can at best yield reasonable values of  $\Delta C_p^{0*}$  within the experimental concentration range, and cannot be expected to prove or disprove the requirements of theory below this range. Furthermore, the values of  $\Delta C_p^{0*}$  at the extremes of the temperature range are very sensitive to the form of the equation by which  $\log K^*$  is expressed as a function of  $T$ . We have used equation (23) for this purpose for reasons of convenience and precedent,<sup>24</sup> and because it more accurately represents the observed temperature variation of  $\log K^*$ , toward the limits of the range, than does equation (22).

Similar considerations led us to express the temperature variation of  $E^{0*}$  by equation (13) instead of by equation (16) with temperature dependent parameters. Equation (13) was more satisfactory on two counts. It gave a more accurate representation of the observed values of  $E^{0*}$ . Further, if  $E^{0*}$  is expressed by equation (16) at all temperatures (with the parameters smoothed against  $T$  by least squares) these new values of  $E^{0*}$  lead to values of  $\log K^*$  which cannot be represented by equation (22) as accurately as those based upon values of  $E^{0*}$  from equation (13). We therefore feel justified in expressing the temperature dependence of our primary quantities,  $E^{0*}$  and  $\log K^*$ , by the simplest equations, (13) and (23), which will represent them within

the experimental errors. This should lead to reasonable values of the derived quantities,  $\Delta H^{0*}$ ,  $\Delta S^{0*}$ , and  $\Delta C_p^{0*}$ , in the middle third of the temperature range and within the experimental concentration range.

### Summary

A method is described by which the ionization of a weak acid in salt solutions is determined by means of cells containing buffered solutions without liquid junctions. By a shift of standard state to conform with each salt concentration, the method is formally equivalent to that used in determining ionization constants in pure water, and in mixtures of water and non-aqueous solvents.

The necessary values of  $E^{0*}$  for the new standard states are given over a wide range of temperatures and salt concentrations.

The ionization constant,  $K^*$ , of boric acid is determined in sodium chloride solutions at seven concentrations between 0.02 and 3.0 molal, and at 5° intervals between 5 and 55°.

The derived thermodynamic quantities [ $\gamma_{\text{H}^+} \gamma_{\text{BO}_3} / \gamma_{\text{HBO}_3}$ ]<sub>0,M</sub>,  $\Delta H^{0*}$ ,  $\Delta C_p^{0*}$ , and  $\Delta S^{0*}$  are calculated, and their variations with temperature and salt concentration illustrated by plots and tables.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

## Thermal Data. XVII. The Heat Capacity, Entropy, and Free Energy of Formation of Cyclohexane. A New Method of Heat Transfer in Low Temperature Calorimetry

BY ROBERT A. RUEHRWEIN AND HUGH M. HUFFMAN<sup>1</sup>

We have measured the heat capacity of cyclohexane over the temperature range 13 to 300° K. The results of our measurements differ from those reported by Aston, Szasz and Fink<sup>2</sup> by an amount greater than the claimed experimental errors of both laboratories. We are presenting our results and a description of our apparatus and methods so as to have them on record and because they may be of use in tracing the source of the discrepancy.

We have also calculated the entropy of cyclo-

hexane and used this datum in conjunction with existing data to calculate the free energy of formation of cyclohexane.

**The Cyclohexane.**—The material used in this investigation was kindly furnished in a purified form by the Shell Development Company. An estimate of the liquid soluble-solid insoluble impurity was made by means of measurements of the temperature as a function of the fraction melted, and by observations on the premelting during the heat capacity measurements. The impurity was estimated by these means to be approximately 0.015 mole per cent.

**The Cryostat and Calorimeter.**—The cryostat is similar to that described by Blue and Hicks<sup>3</sup> except that a simpler

(1) Present address, Bureau of Mines, Bartlesville, Okla.

(2) Aston, Szasz and Fink, *This Journal*, **65**, 1135 (1913).

(3) Blue and Hicks, *ibid.*, **59**, 1962 (1937).

device is employed to transfer heat from the calorimeter during the cooling operation. Figure 1 shows a schematic drawing of the apparatus. In this figure (j) and (i) are chromium-plated copper reservoirs for liquid air and liquid hydrogen, respectively, and (d), (e) and (f) are chromium-plated, thin-walled copper radiation shields. The reservoirs are provided with thin-walled monel metal tubes (l), (m) and (n) which serve for filling, emptying and pumping as well as for supports. The whole assembly fits into a removable brass can (g) which is connected to the top at (k) by a joint which can be made vacuum tight by means of a rubber gasket and screws. This joint is always at room temperature and, consequently, is easy to make and maintain tight. The space enclosed by the can is evacuated by means of an oil diffusion pump backed by a Cenco Hyvac pump.

The calorimeter is surrounded by a light-weight, chromium-plated, copper adiabatic radiation shield consisting of three parts, top, tube and bottom. Each part of the adiabatic shield is provided with a closely wound non-inductive constantan heater which covers nearly all of the external surface. The no. 32 enamel and silk-covered copper lead wires are laid in a shallow helical groove, about 50 cm. in length, under the tube heater windings; good thermal contact and insulation for the heaters was assured by the application of electricians enamel and baking. All of the leads are continuous to the outside and are thermally anchored successively to the floating ring (h), the hydrogen reservoir and the liquid air reservoir. The floating ring and the three parts of the adiabatic shield can be heated independently, and their relative temperatures may be observed by means of interconnected copper-constantan difference thermocouples in conjunction with a high sensitivity Leeds and Northrup galvanometer. By this arrangement of heaters and thermocouples it is possible by suitable manual control to keep the ring, the shield and the calorimeter at the same temperature, within close limits, and at any desired temperature above that of the hydrogen reservoir.<sup>4</sup>

The calorimeter itself is of copper with a length of 67 mm., a diameter of 35 mm., an internal volume of 56.7 ml. and a mass of 44.8 g. Thin copper discs spaced along the reentrant thermometer well and making contact with the wall aid in the rapid attainment of thermal equilibrium. A small screw and nut serve to secure one junction of the difference thermocouples to the bottom of the calorimeter. Liquids are admitted through a small tube in the top of the calorimeter, the tube being soldered shut after the remaining free space is filled with helium.

**The Method of Heat Transfer.**—Heat transfer from the calorimeter and its radiation shield to the reservoirs of liquid air and liquid hydrogen is effected by a mechanical device or thermal switch rather than by the more cumbersome method employing conduction through helium gas and the subsequent evacuation of the helium. In the present cryostat the calorimeter is attached to a stout cord (not shown) passing through a hole in the shield and terminating at a vacuum windlass (o), the windlass being on the outside of the brass can and hence always

(4) This method of maintaining adiabatic conditions in low temperature calorimetry was first described by Southard and Brickwedde, *THIS JOURNAL*, **55**, 4378 (1933).

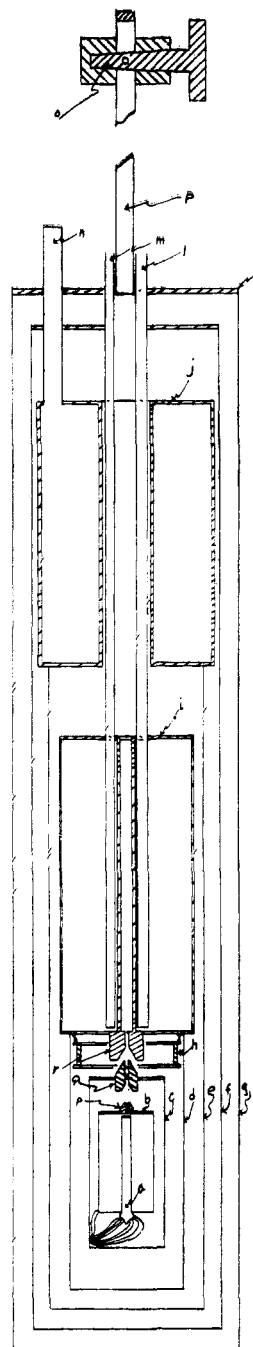


Fig. 1.—*The cryostat*: (a) combination resistance thermometer and heater, (b) calorimeter, (c) adiabatic radiation shield, (d) copper radiation shield in thermal contact with hydrogen reservoir, (e) copper radiation shield in contact with liquid air reservoir, (f) copper radiation shield at approximately room temperature, (g) outer brass vacuum can, (h) floating ring, (i) hydrogen reservoir, (j) liquid air reservoir, (k) vacuum tight joint, (l) monel metal filling tube, (m) monel metal emptying tube, (n) monel metal filling tube, (o) vacuum windlass, (p) monel metal tube to carry electrical lead, etc.

at room temperature. In operating the thermal switch the calorimeter and shield are drawn tightly into contact between accurately turned 60° conical fittings, shown at (p), (q) and (r). When the temperature has dropped to that of the reservoir, the shield and calorimeter are lowered to their normal, isolated positions, a knot in the cord just above the shield serving to hold the calorimeter isolated in about the center of the adiabatic shield.

The cooling operation is normally carried out in two steps. In the first the calorimeter and shield are cooled to 51–52° K., both reservoirs in this operation containing liquid air under partial vacuum. In the second operation the liquid air in the lower reservoir is emptied and replaced by liquid hydrogen which is subsequently frozen by pumping on it. The calorimeter and shield are again brought into contact with the hydrogen reservoir and held there until they have reached its temperature, this operation requiring from two to four hours.

In general the cooling operations require a longer time than is the case when helium gas is used, but the advantages of the present method are obviously many. For example a number of cooling and heating curves may be obtained in succession in the neighborhood of a transition region without having to break the vacuum in the apparatus.

**The Resistance Thermometers.**—A set of five strain-free platinum resistance thermometers were constructed according to the design published by Myers.<sup>5</sup> With one exception each thermometer contained a coil of annealed platinum wire and a coil of no. 40 constantan wire mounted on a mica cross, the former serving for temperature measurements and the latter as a heater. The thermometer-heater assemblies were enclosed in 65 × 7.6 mm. platinum tubes and the six platinum leads were brought out through glass heads sealed to the tubes. After repeated evacuation and annealing the thermometers were filled to 1/3 atm. with purified helium and then sealed. The thermometer well in the bottom of the calorimeter is such that a thermometer fits snugly into it, thermal contact being made by the use of Apiezon grease M.

The thermometers were compared at frequent temperature intervals from 12–320° K. with one, H25, calibrated at the Bureau of Standards over the international temperature scale range, –183° to 444.6°, and over the range 14–90° K. Carefully smoothed tables<sup>6</sup> of  $R/R_0$  against temperature were constructed for both the standard thermometer and the working thermometer-heaters; as a result of the method used in calibrating the thermometers and in constructing the smoothed tables, the temperatures defined by all of the thermometers are internally self consistent over the entire range from 12–320° K. According to Dr. Brickwedde<sup>7</sup> the scale of the standard thermometer used by the Bureau may be expected to deviate as much as 0.02° from the thermodynamic scale in the range 14–90° K. In view of the accuracy with which  $R/R_0$  may be measured, it is believed that both H25 and the working thermometer-heaters define the thermodynamic scale within 0.02 to 0.03° in the range 14–90° K. Above 90° K. the deviations may

be larger than this, since it is known that the international scale does not coincide with the thermodynamic scale within the accuracy of resistance or gas thermometer measurements. It will be evident from this discussion that our temperature scale consists of two parts, namely, the thermodynamic scale up to 90° K., and the international scale above 90° K.

Resistance measurements were made by comparing the drop in potential across the thermometer with that across a 100Ω or 10Ω Leeds and Northrup certified standard resistor in series with the thermometer. Below 36° K. a current of 4 ma. and the 10Ω resistor were used, above 36° K. the current was 1 ma. and the 100Ω standard was employed. The true values of the standards when used in resistance thermometry are not important, but a comparison with thermometer H25 at the ice point showed the standards to be within 0.01% of the values certified by the manufacturer.

All potential measurements were made with a White auto-calibrated double potentiometer and a sensitive galvanometer. An unsaturated Eppley cell served as the standard for potentials.

**The Heat Capacity of Cyclohexane.**—The calorimeter was operated adiabatically, the temperature of all parts of the shield being maintained within 0.01–0.02° of that of the calorimeter by one operator. The second operator made measurements of the temperatures and energy input. From two to four minutes were required for equilibrium after stopping the energy input, and the final temperature was taken as the initial temperature of the following heat capacity measurement. Since the calorimeter is operated adiabatically, no correction for heat interchange with the shield is necessary. Time was measured by means of an electric clock driven by power from Boulder Dam, the frequency of this source being maintained remarkably constant at the generating stations. The electric timer was occasionally checked against a calibrated stop watch. The agreement between the two timers was always 0.1 sec. or better. All resistors and cells were calibrated in terms of international units, and hence the energy input is calculated in international joules. Heat capacities and heat content changes presented here are expressed in terms of the conventional calorie which is equivalent to 4.1833 international joules.

A careful analysis was made of the errors involved in the heat capacity measurements. The calculated uncertainty above 25° K. amounts to 0.06%, and this has been arbitrarily increased to 0.1% in reporting the results. Below 25° the uncertainty is greater, 0.1 to 0.2%, due mainly to the decreasing sensitivity of the thermometer and the shorter temperature intervals covered in this range. Below 14° K. the errors may be 1% or greater.

The results of the heat capacity measurements are presented in Table I and are shown graphically in Fig. 2. Table II contains values of the heat capacity at rounded temperatures; these were taken from a large graph of the experimental

(5) Myers, *Bur. Standards J. Research*, **2**, 807 (1932).

(6) Hoge and Brickwedde, *ibid.*, **22**, 351 (1939).

(7) Brickwedde, private communication.

values. Included in this table are the values taken from Table II of Aston, Szasz and Fink<sup>2</sup> and also values calculated from the data of Parks, Huffman and Thomas.<sup>3</sup> Corrections for premelting have been made in arriving at the results in Table II. In the region 40–50° below the transition the attainment of equilibrium was slow, and for this reason the accuracy is not as high here as has been estimated for the range in which equilibrium is rapidly reached. In the upper temperature range, correction was made for vaporization of the liquid into the small free space of the calorimeter; this correction amounts at most to 0.02%.

TABLE I  
MOLAL HEAT CAPACITY OF CYCLOHEXANE  
Molecular weight = 84.156, 0° C. = 273.16° K.

$T_M$	$\Delta T$	$C_p$ , cal. mole <sup>-1</sup>	$T_M$	$\Delta T$	$C_p$ , cal. mole <sup>-1</sup>
12.96	0.920	0.579	148.91	8.738	18.746
14.56	2.251	0.842	150.93	6.001	18.895
16.49	1.570	1.205	156.84	5.820	19.557
17.72	1.697	1.466	157.47	8.376	19.661
18.08	1.615	1.556	162.58	5.652	20.228
19.70	1.616	1.932	165.68	8.043	20.599 <sup>a</sup>
21.23	5.297	2.324	168.15	5.493	20.912 <sup>a</sup>
21.54	2.069	2.394	173.56	7.724	21.609 <sup>a</sup>
23.81	2.455	2.980	173.57	5.335	21.655 <sup>a</sup>
26.35	2.639	3.640	180.40	5.938	22.675 <sup>a</sup>
26.74	5.728	3.739			
29.04	2.732	4.325			
			Crystals II		
31.69	4.179	4.972	190.24	4.579	25.917
32.01	3.213	5.050	195.80	6.533	26.095
35.38	3.510	5.817	203.58	9.027	26.412
39.72	5.176	6.715	212.41	8.632	26.865
41.97	4.106	7.123	221.81	10.167	27.377
44.83	5.042	7.619	231.87	9.954	28.018
50.11	5.519	8.451	241.71	9.735	28.724
55.35	4.949	9.186	251.34	9.516	29.478
57.24	1.318	9.435	260.74	9.291	30.286
58.96	2.121	9.675	267.73	3.879	30.915
62.27	4.497	10.093	269.92	9.067	31.152
67.03	5.018	10.641	271.20	3.071	31.271
72.31	5.546	11.213	274.07	2.061	31.607 <sup>b</sup>
77.68	5.200	11.784	276.53	2.256	32.021 <sup>b</sup>
82.74	4.918	12.337	278.54	1.761	43.541 <sup>b</sup>
87.54	4.688	12.843			
92.69	5.605	13.332			
			Liquid		
94.00	8.506	13.441	282.27	3.431	35.887
102.26	7.992	14.208	286.88	4.884	36.321
110.04	7.580	14.939	288.32	7.970	36.466
117.45	7.228	15.642	291.74	4.832	36.775
125.20	8.281	16.383	296.23	7.834	37.170
133.30	7.915	17.167	296.55	4.784	37.185
140.90	7.286	17.923	301.30	4.731	37.656

<sup>a</sup> These points lie above extrap. curve. <sup>b</sup> These points include premelting.

(8) Parks, Huffman and Thomas, THIS JOURNAL, 62, 1032 (1930).

TABLE II  
MOLAL HEAT CAPACITY OF CYCLOHEXANE AT ROUNDED TEMPERATURES

Molecular weight = 84.156, 0° C. = 273.16° K.

$T^\circ$ K.	$C_p$ , cal./degree		Deviation from		
	R. + H.	A., S. + F.	P., H. + T.	A., S. + F.	P., H. + T.
Crystals I					
13	0.58				
15	0.94	1.02		8.3	
20	2.00	2.17		8.5	
25	3.30	3.37		2.1	
30	4.56	4.50		-1.3	
35	5.74				
40	6.77	6.72		-0.7	
50	8.42	8.38		-0.5	
60	9.82	9.74		-0.8	
70	10.97	10.93		-0.4	
80	12.05	12.02		-0.3	
90	13.06	13.04	12.97	-0.2	-0.7
100	14.02	14.01	14.04	-0.1	0.1
110	14.95	14.95	15.00	-0.0	0.4
120	15.88	15.88	15.96	0.0	0.5
130	16.85	16.80	16.96	-0.3	0.7
140	17.84	17.73	17.84	-0.6	0.0
150	18.84	18.83	18.76	-0.1	-0.4
160	19.93	19.87	19.82	-0.3	-0.6
170	21.16	21.15	21.02	0.0	-0.7
180	22.62	22.50	22.48	-0.5	-0.6
Crystals II					
190	25.90	25.77	25.68	-0.5	-0.8
200	26.26	26.16	26.16	-0.4	-0.4
210	26.73	26.61	26.66	-0.4	-0.3
220	27.27	27.13	27.20	-0.5	-0.3
230	27.89	27.75	27.80	-0.5	-0.3
240	28.59	28.48	28.42	-0.5	-0.6
250	29.36	29.29	29.12	-0.2	-0.8
260	30.21	30.18	29.92	-0.1	-1.0
270	31.15	31.08	30.88	-0.2	-0.9
Liquid					
280	35.69	35.89	35.28	0.6	-1.1
290	36.61	36.97	36.16	1.0	-1.2
300	37.53				

**The Heat of Transition.**—Two measurements of the heat of transition were made, and the results are summarized in Table III. In making the calculations the marked rise in heat capacity just below the transition temperature was assumed to be due to pretransition, and the heat capacity curve was extrapolated linearly from 162.6° K. to the value  $C_p = 22.85$  cal./deg./mole at 186.1° K. The energy of pretransition so calculated amounted to only 7 cal./mole and will not introduce any significant error in the entropy.

The transition temperature,  $186.10 \pm 0.05^\circ$  K., was determined from observations in which equilibrium was approached from both sides and

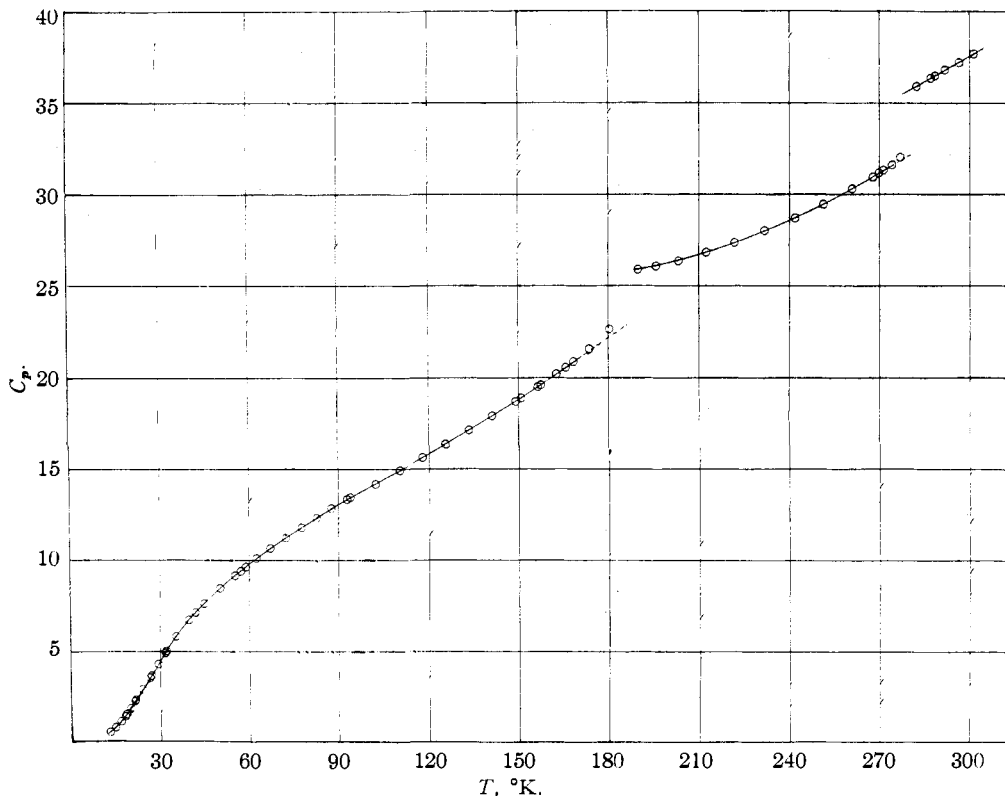


Fig. 2.—Molal heat capacity, cal./degrees.

with from 20 to 95% of the material in the high temperature form.

TABLE III

THE MOLAL HEAT OF TRANSITION OF CYCLOHEXANE AT 186.10° K.

Molecular weight = 84.156, 0° C. = 273.16° K., moles in calorimeter = 0.48837

Temp. interval	Energy input, cal.	$\int C_p dT$ , cal.	Pretransition, cal.	$\Delta H$ , cal./mole
170.508-196.182	1185.57	399.26	0.20	1610.47
176.234-193.562	1058.41	272.36	0.70	1611.17
Mean value of heat of transition				1610.8 $\pm$ 0.4

**The Heat of Fusion.**—The results of two measurements of the heat of fusion of cyclohexane are summarized in Table IV. In the calculations the observed heat capacities were corrected for premelting by a linear extrapolation of the heat

TABLE IV

THE MOLAL HEAT OF FUSION OF CYCLOHEXANE AT 279.82° K.

Molecular weight = 84.156, 0° C. = 273.16, moles in calorimeter = 0.48837.

Temp. interval	Energy input, cal.	$\int C_p dT$ , cal.	Premelt. ing. cal.	$\Delta H$ , cal./mole
274.454-284.340	519.70	207.16	0.05	640.06
273.401-284.438	542.54	230.24	0.02	639.52
Mean value of heat of fusion =				639.8 $\pm$ 0.3

capacity curve from 271.2° K. to the value  $C_p = 32.170$  cal./deg./mole at the melting point 279.82° K.

In arriving at the melting point of pure cyclohexane, the equilibrium temperatures obtained with different fractions of the material in the calorimeter melted were extrapolated to the temperature corresponding to the 100% melted. This temperature was corrected for the melting point depression caused by an impurity of 0.015 mole %. The melting point of pure cyclohexane is  $279.82 \pm 0.05^\circ$  K.

We have utilized the data obtained in this investigation to calculate the entropy of cyclohexane. The results of this calculation are summarized in Table V. This result is 0.11 entropy

TABLE V

THE MOLAL ENTROPY OF CYCLOHEXANE  
Molecular weight = 84.156, 0° C. = 273.16° K.  
Cal./degree

$S_{12}$ (Debye, 6° freedom, $\ominus 150$ )	0.201
$\Delta S_{(18.0-186.1^\circ \text{K.})}$ , graphical	23.887
$\Delta S_{(186.1)} = 1610.8/186.1$	8.655
$\Delta S_{(186.1-279.82)}$ , graphical	11.478
$\Delta S_{(279.82)} = 639.8/279.82$	2.286
$\Delta S_{(279.82-298.15)}$ , graphical	2.330
$S_{(298.15)}$ , liquid	48.84 $\pm$ 0.10

unit higher than that given by Aston, Szasz and Fink<sup>2</sup> and 0.36 entropy unit lower than that given by Parks, Huffman and Thomas.<sup>8</sup>

Moore, Renquist and Parks<sup>9</sup> and Spitzer and Huffman<sup>10</sup> have recently made careful determinations of the heat of combustion of cyclohexane. The mean of these two values which are in excellent agreement is  $\Delta H_R = -936.33$  kcal./mole at 298.16° K. This datum in conjunction with the entropy reported in this paper have been utilized

TABLE VI

THE MOLAL FREE ENERGY OF FORMATION OF LIQUID CYCLOHEXANE AT 298.16° K.

Heat of comb., $\Delta H^0$ , kcal.	$\Delta H^0_f$ , kcal.	$\Delta S$ , cal./degree	$\Delta F^0_f$ , kcal.
-936.33	-37.75	-146.71	5.99

(9) Moore, Renquist and Parks, *THIS JOURNAL*, **62**, 1505 (1940).

(10) Unpublished results.

to calculate the free energy of formation of liquid cyclohexane. The data are summarized in Table VI.

In conclusion we wish to thank the Shell Development Company for preparing the cyclohexane and for financial assistance which made possible this investigation.

### Summary

The heat capacity, heat of transition and heat of fusion of cyclohexane have been measured.

A description of the apparatus and experimental method, including a new method of heat transfer by mechanical contact, has been presented.

The molal entropy and free energy of liquid cyclohexane at 298.16° K. have been calculated,  $S = 48.84$  cal./degree,  $\Delta F^0_f = 5.99$  kcal.

BARTLESVILLE, OKLAHOMA RECEIVED MARCH 15, 1943

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

## Heats of Formation of MgO, MgCl<sub>2</sub>, MgCl<sub>2</sub>·H<sub>2</sub>O, MgCl<sub>2</sub>·2H<sub>2</sub>O, MgCl<sub>2</sub>·4H<sub>2</sub>O, and MgCl<sub>2</sub>·6H<sub>2</sub>O<sup>1</sup>

BY C. HOWARD SHOMATE<sup>2</sup> AND EUGENE H. HUFFMAN<sup>3</sup>

The determination of heats of formation of substances of technological importance is one of the programs of study of the Pacific Experiment Station of the Bureau of Mines. Previous papers<sup>4</sup> have dealt with the heats of formation of several manganese and calcium compounds.

The present paper reports heat-of-formation values of MgO, MgCl<sub>2</sub>, MgCl<sub>2</sub>·H<sub>2</sub>O, MgCl<sub>2</sub>·2H<sub>2</sub>O, MgCl<sub>2</sub>·4H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O. All of these substances had been studied previously, but the data are rather obsolete and could not be considered trustworthy for many purposes. To remedy this situation the present work was undertaken.

### Materials

The magnesium metal was supplied by the Bureau of Mines Laboratory at Pullman, Wash. It was made by carbon reduction of magnesium oxide, followed by vacuum sublimation. The total impurities were stated to be less than 0.01%, excepting surface oxidation. The material used in the measurements was taken from the interior of a

large ingot and was exposed only during the time required for weighing and sealing in glass bulbs.

Magnesium oxide was made by igniting magnesium hydroxide prepared from reagent-quality magnesium chloride and ammonium hydroxide. Care was taken in washing the hydroxide free of chlorides, and the ignition was carried out in a silica flask for one hundred hours during which time the temperature was raised gradually from 400 to 1000°. Analysis showed 60.36% Mg (calcd. 60.32%) and 99.90% MgO by titration.

The anhydrous magnesium chloride employed had been prepared previously by Kelley and Moore.<sup>5</sup> It was re-treated before use by heating in a silica flask at 600° in a stream of dry hydrogen chloride to remove any water that had been taken up during removal from Kelley and Moore's apparatus and subsequent storage. Analysis showed 74.27% Cl (calcd. 74.46%), 25.65% Mg (calcd. 25.54%), and 0.15% MgO.

Magnesium chloride monohydrate was prepared by heating equimolar quantities of anhydrous magnesium chloride and magnesium chloride dihydrate *in vacuo* at 135° for sixteen hours. Analysis gave 62.44% Cl (calcd. 62.62%), 21.57% Mg (calcd. 21.47%), and 0.14% MgO.

Magnesium chloride dihydrate was prepared from reagent quality magnesium chloride hexahydrate. The latter was heated in air at 103° until approximately 2 moles of water were removed. It was then heated in a stream of dry hydrogen chloride, the temperature being raised over a period of thirty hours from 170 to 220°. This treatment

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(4) (a) Southard, *Ind. Eng. Chem.*, **32**, 442 (1940); (b) Kelley, Southard, and Anderson, Bureau of Mines Technical Paper 625, 1941; (c) Southard and Shomate, *THIS JOURNAL*, **64**, 1770 (1942); (d) Shomate, *ibid.*, **65**, 785 (1943).

(5) Kelley and Moore, *THIS JOURNAL*, **65**, 1264 (1943).