

b. p. 125.6–126.9°, n_D^{20} 1.3940, 65.7% yield based on unrecovered butyl trichloroacetate.

Treatment of butyl trichloroacetate with acetic acid at 115° for nine hours in the presence of *p*-toluenesulfonic acid led to no products of acetolysis. Butyl trichloroacetate was recovered in 93% yield.

A solution of 56 g. of ethyl butyrate, 48 g. of fused potassium acetate and 5 cc. of acetic anhydride in 100 cc. of acetic acid–acetic anhydride was boiled for eight hours. No evidence of ethyl acetate was found. Ethyl butyrate was recovered, 119–120.5°, n_D^{20} 1.3923, 48.3 g., 86%.

Summary

The results of a qualitative study of the effect of structure of the alkyl group on the acetolysis of

esters are reported. In the acid catalyzed acetolysis of esters of benzoic acid, the *t*-butyl ester was found to be quite reactive, the *i*-propyl ester, less reactive, and the ethyl and methyl esters, inert under comparable conditions. In the base-catalyzed acetolysis, a typical aliphatic ester was found to be inert, while butyl trichloroacetate was reactive. These reactions lead to ester interchange by the exchange of the acid parts of the esters. The mechanisms of these reactions are discussed.

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The Heat Capacity of Potassium Dihydrogen Phosphate from 15 to 300°K. The Anomaly at the Curie Temperature

BY C. C. STEPHENSON AND J. G. HOOLEY¹

The heat capacity of KH_2PO_4 is of particular interest since this salt has unusual dielectric properties at low temperatures. Busch² found that KH_2PO_4 is similar to Rochelle salt in that it has an electric Curie point: below this temperature, the salt is spontaneously polarized along the *c*-axis. The electric properties of Rochelle salt, KH_2PO_4 and KH_2AsO_4 are very similar to the magnetic properties of ferromagnetic substances,³ and anomalies in the heat capacities of these substances are to be expected near the Curie points. The recent investigations of the heat capacity of Rochelle salt by Hicks and Hooley⁴ and by Wilson⁵ have shown that any anomalous increase in the heat capacity of this salt at the Curie points must be less than one per cent. of the total heat capacity. Professor Hans Mueller called our attention to the fact that KH_2PO_4 should have an easily detectable anomaly at the Curie point since this crystal has a much larger permanent polarization than Rochelle salt, and at his suggestion we have measured the heat capacity of this substance.

While these measurements were being made, a theory of the transition, derived from a consideration of the arrangement of the hydrogen bonds in the crystal, was proposed. The entropy change predicted from theory is in agreement with the experimental value reported in this paper. Confirmation of the theoretical entropy change has also been obtained from a later study of the transitions in KH_2AsO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$.

(1) Royal Society of Canada Fellow. Present address, University of British Columbia, Vancouver, Canada.

(2) G. Busch, *Helv. Phys. Acta*, **11**, 269 (1938).

(3) For a review of recent work, see H. Mueller, "Annals of the New York Academy of Sciences," XL, 321 (1940).

(4) J. F. G. Hicks and J. G. Hooley, *THIS JOURNAL*, **60**, 2994 (1938).

(5) A. J. C. Wilson, *Phys. Rev.*, **54**, 1103 (1938).

Material.—The salt was of c. p. reagent quality and contained less than 0.03% impurities⁶ other than water. The salt was dried over phosphorus pentoxide and in vacuum; the heat capacity measurements in the neighborhood of the ice point show the absence of water. The percentage loss of weight on ignition to KPO_3 was 13.29; theoretical, 13.24. The material used for the measurements consisted of small crystals approximately $1 \times 0.2 \times 0.2$ mm.

All measurements were made on a single calorimeter loading of 104.923 g. *in vacuo*, or 0.7710 mole. The molecular weight of KH_2PO_4 was taken as 136.09.

Method.—The apparatus and method of measurement have been described previously.⁷ It is of interest that the calorimeter is the same as that used by Hicks and Hooley⁴ for their measurements on Rochelle salt.

The temperatures were measured by means of a platinum–rhodium resistance thermometer–heater which had been calibrated previously against a helium gas thermometer.⁸ The ice-point resistance of this thermometer was measured during this investigation, and no appreciable departure from the original calibration value was found.

At the conclusion of these measurements and corresponding measurements on KH_2AsO_4 , the heat capacity of the empty calorimeter was re-determined. The new measurements are somewhat better than the previous ones due to improvements in the apparatus and are within the limits of accuracy of the older measurements.

The resistance thermometer and thermocouple readings were taken on a new Wenner potenti-

(6) Prof. S. G. Simpson of the Analytical Division of the Chemistry Department, M.I.T., kindly performed the quantitative analyses.

(7) J. F. G. Hicks, *THIS JOURNAL*, **60**, 1000 (1938).

(8) R. W. Blue and J. F. G. Hicks, *ibid.*, **59**, 1962 (1937).

TABLE I
HEAT CAPACITY OF POTASSIUM DIHYDROGEN PHOSPHATE
Molecular weight, 136.09; 0°C. = 273.19°K.

T , °K.	ΔT	C_p , cal. deg. ⁻¹ mole	Series	T , °K.	ΔT	C_p , cal. deg. ⁻¹ mole	Series	T , °K.	ΔT	C_p , cal. deg. ⁻¹ mole	Series
16.14	2.472	0.385	VIII	116.50	4.138	18.48	VI	135.95	4.712	16.84	VI
18.66	2.652	.626	VIII	116.51	2.333	18.42	II	139.73	5.452	17.13	III
22.50	2.337	1.065	VIII	117.43	1.704	19.20	I	146.54	5.299	17.39	III
25.28	2.452	1.438	VIII	118.48	1.428	20.42	II	147.56	5.686	17.74	VI
28.75	3.673	2.009	VIII	119.08	1.609	21.42	I	148.24	5.760	17.83	IV
32.58	3.260	2.720	VIII	119.44	1.507	21.95	VI	154.12	5.622	18.25	IV
35.97	3.354	3.400	VIII	119.85	1.336	23.20	II	159.94	5.489	18.69	IV
39.75	4.373	4.166	VIII	120.58	1.441	27.64	I	160.20	5.366	18.76	VI
44.00	4.872	5.049	VIII	120.64	0.815	25.83	VI	165.60	5.347	19.11	IV
48.58	4.464	5.932	VIII	120.89	.698	28.37	II	171.31	5.127	19.64	VI
53.24	4.934	6.82	VIII	121.39	.700	35.17	VI	171.45	5.646	19.52	IV
57.09	4.463	7.43	VII	121.40	.280	35.34	II	177.17	5.513	19.90	IV
60.66	2.678	8.05	VII	121.62	.148	42.80	II	182.87	5.392	20.31	IV
62.92	1.814	8.47	VII	121.76	.130	52.46	II	188.48	5.692	20.63	IV
64.28	0.797	8.69	VII	121.78	1.083	45.40	I	189.89	5.620	20.89	V
65.02	.626	8.82	VII	121.83	0.211	66.92	VI	194.65	5.615	21.05	IV
65.76	.769	8.98	VII	121.88	.100	75.79	II	195.66	5.500	21.29	V
66.65	.905	9.07	VII	121.96	.072	118.1	II	200.46	5.445	21.44	IV
68.09	1.932	9.24	VII	122.05	.233	57.74	VI	201.35	5.393	21.66	V
70.66	3.179	9.68	VII	122.07	.157	36.92	II	207.08	5.308	21.88	V
74.01	3.479	10.18	VII	122.25	.205	20.86	II	212.93	5.563	22.41	V
77.92	4.274	10.63	VII	122.39	.418	19.39	VI	219.08	5.463	22.90	V
83.57	4.036	11.60	I	122.39	.214	18.59	II	225.45	5.396	23.24	V
88.45	5.294	12.28	I	122.44	.439	17.53	III	231.27	5.266	23.69	V
92.52	4.967	12.69	VI	122.60	.218	17.30	II	237.20	5.604	24.01	V
93.59	4.963	12.99	I	122.81	.435	16.89	VI	243.83	5.498	24.41	V
97.36	4.681	13.45	VI	122.91	.444	16.73	II	250.23	6.115	24.83	V
102.18	4.944	14.15	VI	123.24	1.743	16.78	I	256.93	5.994	25.30	V
107.28	5.157	15.06	VI	123.33	0.995	16.46	III	263.33	5.886	25.73	V
109.29	5.109	15.63	I	123.43	.996	16.33	II	269.40	4.727	26.07	V
110.69	3.632	15.94	II	124.72	1.736	16.36	III	275.54	5.687	26.46	V
112.13	4.435	16.26	VI	125.03	1.743	16.37	I	281.53	4.694	26.77	V
113.29	2.819	16.80	I	125.64	4.971	16.30	VI	287.24	5.073	27.23	V
113.98	2.449	17.05	II	126.95	2.643	16.39	III	293.06	4.540	27.31	V
115.66	1.773	17.84	I	130.20	3.681	16.46	III	299.12	4.661	28.05	V
				134.52	4.809	16.76	III				

ometer having a range of 0.11 volt to one microvolt on the dials. This instrument was calibrated by the Bureau of Standards.

The calorie used in this work is defined equal to 4.1833 int. joules. The absolute temperature of the ice point is taken as 273.19°K.^{8a}

Heat Capacity Measurements.—The heat capacity measurements, made in eight series, are summarized in Table I, and plotted as a function of the temperature in Fig. 1. The average deviation of the points from a smooth curve is: from 15 to 30°K., 3.0%; from 30 to 200°K., 0.3%; and from 200 to 300°K., 0.2%. The very short runs near the transition, which are less accurate because of the small temperature intervals, are excluded from these averages.

(8a) The original calibrations of the resistance thermometers were based on an ice point of 273.19°K. which is higher than the commonly accepted value of 273.16°K. The original calibration is retained since the difference is negligible as far as the results of these measurements are concerned.

Table II presents values taken from the smooth curve through the observations. The values from 115 to 125°K. in Table II were obtained from the slope of a heat content versus temperature curve since the temperature interval was too large for many of the points in Table I to be considered as differential heat capacities in this region of rapid variation.

The rate of change of the temperature before and after supplying energy to the calorimeter at temperatures within a degree of the maximum in the heat capacity curve showed that complete thermal equilibrium was not attained within thirty minutes, while at other temperatures equilibrium was reached in five minutes. At least part of this slower rate of attainment of equilibrium may be accounted for by a change of conductivity of the sample. The temperature difference between the heater and the sample for a constant rate of energy input serves as a qualitative measure of the heat

conductivity of the sample. Near the transition temperature, this temperature difference showed

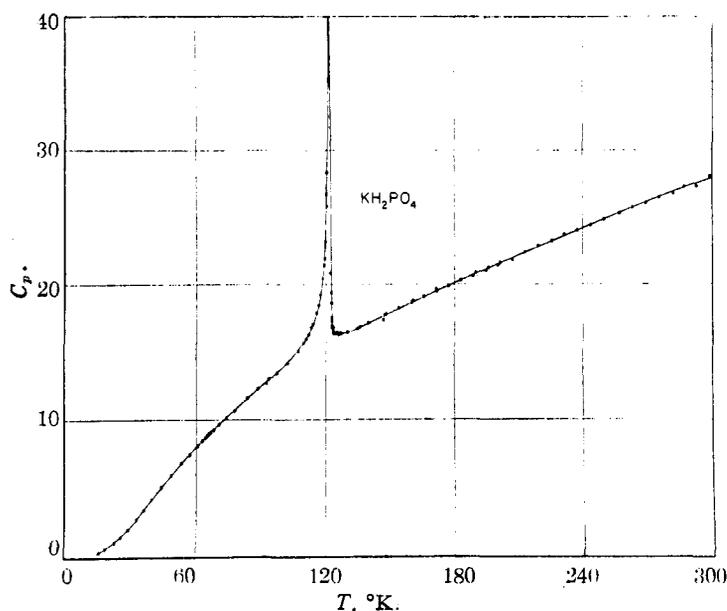


Fig. 1.

a marked increase, indicating that the thermal conductivity of the sample had decreased.

TABLE II

HEAT CAPACITY OF POTASSIUM DIHYDROGEN PHOSPHATE
Value from a smooth curve through the data.

$T, ^\circ\text{K.}$	$C_p, \text{ cal. deg.}^{-1} \text{ mole}^{-1}$	$T, ^\circ\text{K.}$	$C_p, \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
15	0.329	121	28.4
20	.767	121.97	Maximum
25	1.401	123	16.6
30	2.235	125	16.36
35	3.203	130	16.44
40	4.224	140	17.16
45	5.241	150	17.94
50	6.190	160	18.70
55	7.08	170	19.42
60	7.95	180	20.13
65	8.79	190	20.82
70	9.58	200	21.49
75	10.34	210	22.18
80	11.08	220	22.86
85	11.77	230	23.54
90	12.43	240	24.20
95	13.10	250	24.85
100	13.82	260	25.49
105	14.66	270	26.11
110	15.75	280	26.74
115	17.50	290	27.36
117	18.8	300	27.97
119	21.2		

Preliminary communications concerning the investigation of the heat capacity of potassium dihydrogen phosphate were given by W. Bantle and P. Scherrer⁹ and by J. Mendelssohn and K.

(9) W. Bantle and P. Scherrer, *Nature*, **143**, 980 (1939).

Mendelssohn¹⁰ at about the same time as the first report of this work.¹¹ An accurate comparison of the results of the three investigations is not yet possible because the data were presented only in a graphical form; however, the curve given by Bantle and Scherrer is much higher than that of either of the other investigations.

Transition Temperature.—The transition temperature, at which the heat capacity reaches a maximum, was studied by means of cooling curves because, within the limits of accuracy of the observations, there was no isothermal absorption of heat. Figure 2 shows one of these cooling curves with the rate of cooling plotted against the temperature.

The transition temperature, obtained from several cooling curves in this manner, is $121.97 \pm 0.05^\circ\text{K.}$ Although no warming curves were taken, the heat capacity measurements show that the maximum value of the heat capacity on warming is within a few hundredths of a degree of the temperature obtained on cooling. Any hysteresis, if it occurs at all, must be less than a tenth of a degree.

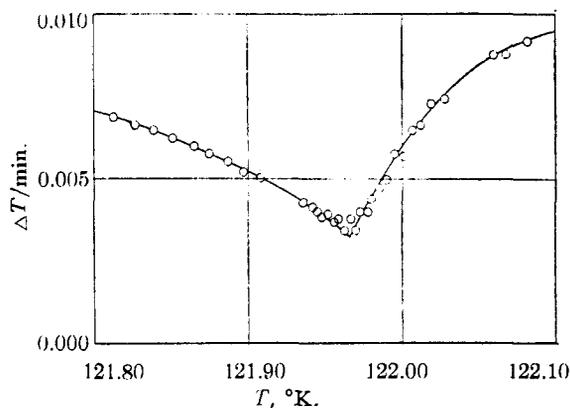


Fig. 2.

The maximum in the heat capacity curve given by Bantle and Scherrer⁹ occurs at about 113°K. , while Mendelssohn and Mendelssohn¹⁰ state that the transition occurs at 122°K. , in agreement with the temperature obtained in this work. Busch² finds that the spontaneous polarization occurs at 116°K. , but Lüdy,¹² in the same laboratory, gives 123°K. as the temperature at which the piezoelectric effect reaches a maximum. Measurements of Dr. J. F. Hutzenlaub in the Physics Department at M. I. T., using a thermocouple calibrated with respect to the temperature

(10) J. Mendelssohn and K. Mendelssohn, *ibid.*, **144**, 595 (1939).

(11) C. C. Stephenson and J. G. Hooley, *Phys. Rev.*, **56**, 121 (1939).

(12) W. Lüdy, *Helv. phys. acta*, **12**, 278 (1939).

scale of this research, show that the maximum dielectric constant occurs at the same temperature as the maximum in the heat capacity curve. The temperature measurements made in the Zürich laboratory are apparently inaccurate.

The transition temperature of KH_2PO_4 was also measured in a simple cooling-curve apparatus using a copper-constantan thermocouple which had been compared with a number of accurately measured transition temperatures. The temperature thus found was $122.01 \pm 0.10^\circ\text{K}$., in good agreement with the more accurate value of 121.97°K .. Three samples of the salt were used in the cooling-curve apparatus: one sample was of the same material used for the calorimetric measurements, another sample was very finely powdered, and the third sample consisted of fragments of large crystals which were originally about a centimeter in length. No difference was found in the transition temperature of these materials.

Heat and Entropy of the Transition.—The assignment of values for the entropy change and heat effect associated with the transition is made difficult by the fact that the transition is spread over a wide temperature range. In order to make this calculation, the heat content and entropy derived from an interpolated "normal" heat capacity curve are subtracted from the total entropy and heat content which may be obtained quite accurately from the heat capacity data.

The total amount of energy required to raise the temperature of one mole of KH_2PO_4 from 70 to 140°K ., temperatures well outside the region of anomalous heat capacity values, was obtained by integrating the heat capacity data of Series I, II, and VI. The values thus found are: for Series I, 1056.7 calories; Series II, 1055.9 calories; and Series VI, 1054.5 calories. In additional experiments, the energy required to raise the temperature from 114.726 to 123.243°K . was found to be 200.5 calories, and from 114.426 to 124.011°K ., 217.9 calories. These two measurements, combined with the heat capacity data, give 1056.0 and 1055.7 calories, respectively, for the change in heat content from 70 to 140°K .. These latter

figures are more accurate than those derived from the heat capacity data alone since the integration involves a smaller number of energy increments. The best value is taken as 1055.9 ± 0.5 calories.

The total entropy change, $\int C_p d \ln T$, was calculated in the usual manner except near the transition temperature where the heat capacities are less certain than the heat content. In this region, small increments of $\Delta H/T$, taken from a heat content versus temperature curve, give a better value for the entropy. The total entropy change from 70 to 140°K . is found to be 10.03 ± 0.01 cal. $\text{deg}^{-1} \text{mole}^{-1}$.

A number of equally reasonable heat capacity curves may be drawn to join the normal curve above the transition to the normal curve below the transition. Attempts to represent the normal curve above and below the transition by a single analytic function of a reasonably simple nature were unsuccessful, and finally two interpolated "normal" curves were drawn on a large scale plot of the data. One of these curves represented the highest plausible values and the other the lowest. The change in heat content for these two "normal" curves is 965.4 and 973.8 calories, and the corresponding entropy changes 9.26 and 9.34 cal. $\text{deg}^{-1} \text{mole}^{-1}$ between 70 and 140°K .. These values, subtracted from the experimentally observed values, give a heat of transition lying between the limits of 82 and 91 calories, and an entropy change between 0.69 and 0.77 cal. $\text{deg}^{-1} \text{mole}^{-1}$. Attention must be called to the fact that these figures are based on the assumption that a single curve may be drawn to represent the course of the "normal" heat capacity joining the high and low temperature curves; this assumption is open to question.

Entropy of KH_2PO_4 at 298.19°K .—The entropy was determined graphically from 15 to 298.19°K ., and combined with a Debye extrapolation to 0°K . of 0.109 entropy unit, to give 32.23 ± 0.1 cal. $\text{deg}^{-1} \text{mole}^{-1}$ at 298.19°K .. This is the correct entropy value to be used in thermodynamic calculations since the type of lack of equilibrium which occurs in ice does not exist in solid KH_2PO_4 at low temperatures.

The Nature of the Transition.—The crystal structure of potassium dihydrogen phosphate has been worked out in detail.¹³ In the crystal, hydrogen bonds are formed between the oxygen atoms of adjacent tetrahedral phosphate groups, each oxygen forming one such bond, as shown in Fig. 3. In so far as the hydrogen bonds are concerned, this arrangement is very similar to the arrangement of the hydrogen bonds in ice, as discussed by Pauling.¹⁴ If one assumes that only two hydrogens are associated with a phosphate tetrahedron, there will be a large number of orientations of the dipoles formed by the H_2PO_4^- groups, as in Fig. 3b. Figure 3a shows these groups arranged in a unique configuration of zero

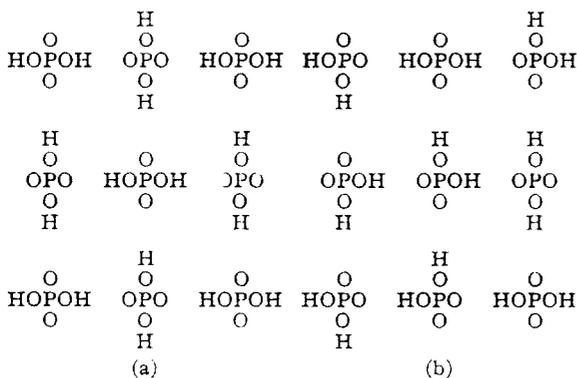


Fig. 3.—Oriented (a) and random (b) arrangement of the hydrogen bonds in KH_2PO_4 .

(13) J. West, *Z. Krist.*, **74**, 306 (1930).

(14) L. Pauling, *THIS JOURNAL*, **57**, 2680 (1935).

entropy. In this configuration, all of the dipoles are oriented parallel to the *c*-axis, in agreement with the spontaneous polarization of the crystal along this axis below the Curie point.

The calculation of the total increase in entropy associated with the increase in randomness has been made by Pauling for the ice crystal, and the same argument applies to the KH_2PO_4 crystal. The number of accessible configurations W for the crystal in its completely disordered arrangement is $(3/2)^N$; hence, the entropy change is $R \ln 3/2 = 0.806 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. In ice¹⁵ and heavy ice¹⁶ this amount of entropy persists even at extremely low temperatures because the allowed states are of nearly equal energy and there is no observable tendency for the crystal to assume a unique configuration of lower energy. However, the allowed states of the KH_2PO_4 crystal are not all equivalent; those states with dipoles oriented along the *c*-axis have a lower energy, and a transition to this arrangement therefore occurs.

The theory of the transition in potassium dihydrogen phosphate, taking into consideration the differences in energy of the allowed states, has been given by Onsager,¹⁷ and a more detailed treatment has been given by Slater.¹⁸ Their results predict a phase change of the first order at the Curie temperature, with an entropy change of $\frac{1}{2} R \ln 2 = 0.69 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, followed by a gradual increase in entropy over a wide range of temperature until at infinite temperatures the value $R \ln 3/2$ is reached.

The experimentally observed transition is, of course, of a higher order, and the above authors have suggested plausible modifications to the theory which would lead to such a transition. The experimental results suggest that the entropy value $R \ln 3/2$ is attained only a few degrees

(15) W. F. Giauque and J. W. Stout, *THIS JOURNAL*, **58**, 1144 (1936).

(16) E. A. Long and J. D. Kemp, *ibid.*, **58**, 1829 (1936).

(17) L. Onsager, talk presented at Conference on Dielectrics, New York Academy of Sciences, May, 1939, and private communications.

(18) J. C. Slater, *J. Chem. Phys.*, **9**, 16 (1941).

above the Curie point rather than the hundred or more degrees predicted by theory. Unfortunately, the uncertainty in the estimation of a "normal" heat capacity in the transition interval makes a comparison of theory and experiment difficult. Furthermore, the observed entropy change may include an entropy increase due to abnormal volume changes caused by interaction of the hydrogen bonds with the crystal lattice itself. The experimental data needed to calculate this effect are not available.

In spite of these difficulties, the experimental entropy value given in this paper, together with the corresponding study of KH_2AsO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$, supply good evidence that the hydrogen bonds in these crystals are responsible for the transition. We may infer, from the fact that there is no experimentally detectable entropy change at the Curie points in Rochelle salt, that large groups of molecules or perhaps chains of hydrogen bonds are involved in this transition.

We are indebted to Professors Hans Mueller and J. C. Slater for many helpful discussions of this problem, to Dr. A. C. Zettlemoyer for assistance with many of the calculations, and to Dr. R. W. Blue, who contributed to every phase of this work.

Summary

The heat capacity of crystalline KH_2PO_4 has been measured from 16 to 300°K. A maximum occurs in the heat capacity at $121.97 \pm 0.05^\circ\text{K}$. The heat of transition and entropy change associated with the anomalous portion of the heat capacity curve are $87 \pm 6 \text{ cal. per mole}$ and $0.74 \pm 0.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, respectively. This is in satisfactory agreement with the theoretical entropy change, $R \ln 3/2 = 0.81$, calculated from the assumption that the hydrogen bonds in these crystals are responsible for the transition.

The entropy of crystalline KH_2PO_4 at 298.19°K . is $32.23 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

CAMBRIDGE, MASS.

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