2%; in sodium, potassium and lead about 3%. Of course, to these must be added the errors of the coefficient of expansion values, the magnitude of which errors are in most cases unknown. No attempt was made to measure the coefficients of expansion of any of the liquids used, although there were some large discrepancies in the literature. When more reliable data for this factor are obtained, the calculated values of the specific heats will be rendered more accurate.

So far as these experiments show, the method used was found to be entirely feasible and reliable. As a test of the method, the use of liquid metals was the most severe that could be attempted, since their coefficients of expansion are relatively low and their heat conductivities are high. Using this method, a comparatively simple apparatus could be set up which would measure the specific heats of organic liquids, for example. In such a case, fine, bare thermocouples could be used and by proper calibrations the coefficients of expansion of the liquids and the pressure-temperature increments could be measured on the same sample in the same bulb. With such an apparatus the measurements of the specific heats of pure liquids would be reduced to a routine with a probable error of 1% or less.

Summary

An apparatus has been constructed to measure the specific heats of molten metals by a method suggested by Lewis.

Satisfactory data have been obtained for sodium, potassium and lead at temperatures above their melting points.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 196]

A FIXED POINT FOR THE CALIBRATION OF PRESSURE GAGES. THE VAPOR PRESSURE OF LIQUID CARBON DIOXIDE AT 0°[1]

BY OSCAR C. BRIDGEMAN[2]

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For a considerable period of years, piston gages of various types have been used for measuring pressures greater than a few atmospheres in place of the more cumbersome mercury column. The procedure used in calibrating the piston gage ordinarily consists either of a direct comparison with a mercury column or a determination of the diameters of the piston

[1] Professor F. G. Keyes suggested to the writer the advantage of utilizing the vapor pressure exerted by carbon dioxide at the ice point as a standard for the determination of piston gage constants. It is also a pleasure for the writer to express his indebtedness to Professor Keyes and the members of the Laboratory Staff for assistance and advice during the progress of this investigation.

[2] National Research Fellow in Chemistry.

and the cylinder into which it fits. In the latter case, the "constant" of the gage is assumed to be proportional to an "effective area" calculated from the average of the two diameters.

In this Laboratory, it has been the customary practice to compare the piston gages against a mercury column from time to time thus, referring all measurements directly to the international practical standard of pressure. While satisfactory in principle, this procedure requires considerable experience; moreover, it lacks convenience and simplicity of manipulation. It would be advantageous, therefore, to define a fixed point for the calibration of pressure gages which would eliminate, for the most part, the complications involved in the direct mercury column comparison.

The vapor pressure of liquid carbon dioxide at 0° was selected as a reference pressure for several reasons. A liquid-vapor system has one marked advantage in that temperature is the only independent variable; moreover, in utilizing the melting point of ice no uncertainties are introduced relative to the temperature scale. Further, a liquid-vapor phase equilibrium, suitably chosen, is easy to establish, reproduce and maintain over long periods of time. Carbon dioxide was chosen since it is comparatively easy to obtain in a pure state, and of those substances which are easily purified, it has the highest vapor pressure at 0°, approximately 34.4 atmospheres.

A number of different measurements have been recorded for the vapor pressure of carbon dioxide at 0°, of which the following is a summary: Amagat,[3] 34.3 atm., 26.07×10^3 mm.; Villard,[4] 34.25 atm., 26.03×10^3 mm.; Kuenen and Robson,[5] 34.34 atm., 26.10×10^3 mm.; Jenkin and Pye,[6] 34.6 atm., 26.30×10^3 mm.; Keyes and Kenney,[7] 34.28 atm., 26.05×10^3 mm.; Meyers and Van Dusen,[8] 34.38 atm., 26.13×10^3 mm. All of these values were obtained incidental to a general study of the vapor-pressure curve, and accordingly no special precautions seem to have been taken to obtain a particularly accurate value at 0°. The aim of the present work was to measure the vapor pressure of carbon dioxide at 0° with as high a precision as possible.

Experimental Procedure

The apparatus used in the measurement of the vapor pressure at 0° is shown schematically in Fig. 1. A is a pressure gage of the dead-weight piston type with mechanical oscillation, similar to that described by Keyes

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[3] Amagat, *Compt. rend.*, **114**, 1097 (1892).

[4] Villard, *Ann. chim. phys.*, [7] **10**, 387 (1897).

[5] Kuenen and Robson, *Phil. Mag.*, [6] **3**, 149 (1902).

[6] Jenkin and Pye, *Phil. Trans.*, **213A**, 67 (1914).

[7] Keyes and Kenney, *Am. Soc. Refrigerating Eng. J.*, **3**, 4 (1917). A correlation of the existing vapor-pressure data on carbon dioxide over the entire liquid range.

[8] Meyers and Van Dusen, *Refrigerating Eng.*, **17**, 180 (1926).

and Brownlee.[9] E is an injector to replace the oil lost by leakage past the piston, while at B there is shown a mercury-in-steel U-tube (5 mm. inside diameter), filled under a vacuum, and used to separate the oil system of the gage from the gaseous carbon dioxide as well as to detect equilibrium between the loaded gage balanced against the pressure exerted by the carbon dioxide. Through the steel stopcocks C and D, the U-tube could be connected either to the vacuum line or to the bomb G immersed in a mixture of finely shaved ice and distilled water, saturated with air and contained in a Dewar cylinder. Insulated steel needles of equal length were inserted to the same depth in the arms of the U-tube to detect the positions of the menisci. By means of a double-throw switch, either needle could be connected to a one-stage amplification system operating a sensitive relay, so that a small lamp was lighted when contact was broken, and vice versa.[9c,d] To compensate for temperature changes, the injector F was used to adjust the amount of mercury in the U-tube.

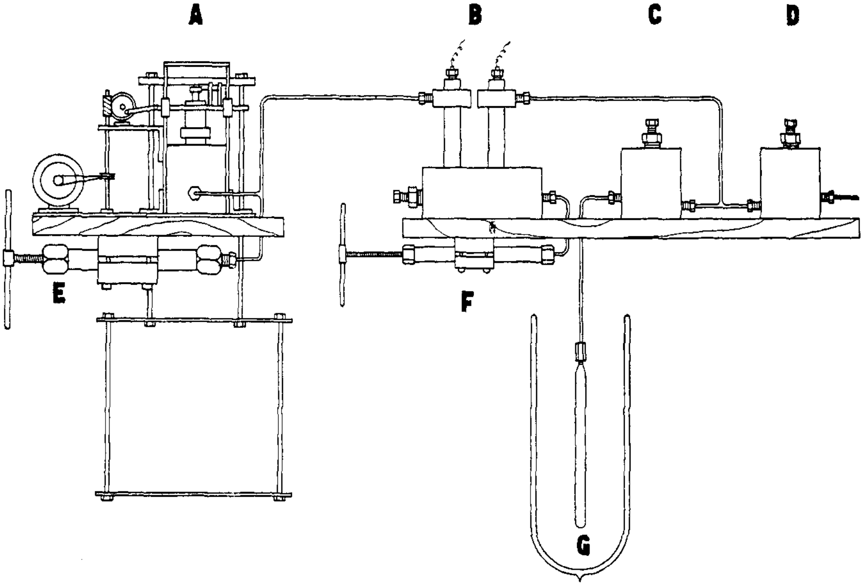

Fig. 1.

The pound weights used with the gages were checked at the State House in Boston, and those of a kilogram or under were compared with a standard set calibrated at the Bureau of Standards.

The carbon dioxide, prepared by heating sodium bicarbonate, was slowly passed through a tube of granular calcium chloride and then up

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[9] (a) Keyes and Brownlee, THIS JOURNAL, **40**, 25 (1918); (b) **41**, 589 (1919); (c) **45**, 2107 (1923); (d) **46**, 342 (1924). (e) For certain modifications, see Keyes and Dewey, *J. Opical Soc. Am.*, in press.

through two vertical tubes containing phosphorus pentoxide, a sample of 30 g. taking five to six hours for preparation. Previous to the generation of the carbon dioxide, the drying tubes were heated to a moderate temperature and evacuated for several days, after which they were twice swept out with carbon dioxide and pumped. In the purification of the carbon dioxide, five sublimations were performed, the last portions being discarded and the newly condensed snow being pumped in each case. Finally the sample of about 15 g. was sublimed over into the bomb G, which had previously been baked out under a vacuum for several days at 300–400°.

For a preliminary determination of the vapor pressure, all of the gages in the Laboratory (nine in number) were assembled and balanced against the carbon dioxide system. The bomb was immersed in a mixture of ice and water, the approximate weight was placed on the scale pan of the gage and the stopcock in the mercury U-block opened exactly one turn. The mercury was adjusted in the U-tube until it just touched both needles when the surfaces were level, and weights were taken off or added to the scale pan until equilibrium was obtained. In general, a weight equivalent to 1 part in 100,000 of the total weight on the pan was sufficient to make or break contact. To follow the constancy of temperature in the ice-bath, a platinum-resistance thermometer was used in conjunction with a thermostated bridge during most of the measurements.

In Table I are given the results of this preliminary determination of the vapor pressure. The constants of the gages at 30° in international millimeters of mercury per gram weight are given, together with the year of calibration. These constants were calculated to the temperature of the gage using the relation $C_t = C_{30}[1 - 2.2 \times 10^{-5}(t^\circ - 30^\circ)]$, based on a coefficient of expansion of steel of 1.1×10^{-5} per degree. The pressures given in Col. 4 were obtained by multiplication of the weight on the gage by the piston constant at the gage temperature, to which were added three corrections; (1) for hydrostatic pressure of the oil between the bottom of the piston and the top of the mercury surface in the U; (2) for the pressure exerted by the column of carbon dioxide vapor between the mercury and carbon dioxide liquid surfaces, which was constant for all of these measurements, being +3.78 mm. of mercury; (3) for the barometric pressure.

The two gages, 4 and 5, show considerable deviation[10] from the average value of all the gages, and if these are omitted, the others are in agreement within one part in 10,000, which shows a remarkable consistency in the pressure measurements in this Laboratory over a considerable period of years.

[10] Calculated from the general average of the vapor-pressure determinations, the constant for Gage 4 should be 1.01518. A recent calibration against the mercury column gives a value of 1.01512 at 30°, which is in good agreement with that predicted.

TABLE I

PRELIMINARY VALUE FOR VAPOR PRESSURE, USING PREVIOUSLY CALIBRATED PISTONS

Gage	Const. at 30°	Year of calibration	Vapor pressure, mm.
D9S	1.99492	1924	26141.4
D8S	1.99687	1924	26146.6
D8L	0.499376	1924	26143.2
D9L	.499401	1924	26148.2
1	.733897	1920	26140.6
2	4.13473	1911	26145.6
3	1.02497	1920	26141.1
4	1.01414	1923	26125.1
5	0.99924	1923	26165.1
		Total Av.	26144.1 ± 6.5
		Av. (excl. 4 and 5)	26143.8 ± 2.6

Vapor pressures in international mm. of Hg.
Piston constants in international mm. of Hg per gram weight.

Calibration of the Gages Used for the Final Measurements

After the preliminary vapor-pressure determinations, two of the gages, D9S and D8L, in addition to one not previously used, designated as Gage 6, were calibrated against the 9-meter steel mercury column described in detail by Keyes and Dewey.[9e] Glass riser tubes containing steel needles were used at the top and bottom, being arranged immediately above one another, and the tape, stretched under a load of 5 kg., was hung adjacent to them. The upper glass riser was open to the atmosphere while the lower one was joined to the pressure gage by means of a steel capillary filled with oil. Either needle could be connected to the electrical detection system described in conjunction with the carbon dioxide vapor-pressure apparatus, and a height of mercury was thus maintained between these fixed points. An injector at the bottom of the column was used to compensate for temperature changes. The mercury was purified in a nitric acid tower, distilled twice according to the method of Hulett,[11] and then forced into the column under a vacuum by means of a Cailletet pump.

The tape, under its usual load of 5 kg., was compared with a scale calibrated at the Bureau of Standards, the accuracy of reading being ±0.01 mm. Thermometers were hung beside the tape during the calibration and all corrections were referred to 25°.

The position of the tip of the needle in the lower riser was located on the tape by means of a cathetometer, while at the upper riser, the top of the needle, whose length was accurately known, was referred to the tape by means of a mechanic's square, a rule graduated in half millimeters being used to interpolate between the 5mm. divisions on the tape. Thermometers suspended every meter along the tape indicated its average

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[11] Hulett, *Phys. Rev.*, **21**, 388 (1905); **33**, 307 (1911).

Table II

Calibration of the Pressure Gages

Column temp., °C.	Height, int. mm.	Effective ht., int. mm.	Wt. on gage, g.	Gage temp., °C.	Constant at 30°	$\Delta \times 10^5$
		(*a*) Gage 6				
26.73	8666.78	8613.54	8495.03	36.6	1.01410	+5
26.73	8666.78	8613.54	8495.33	37.0	1.01407	+2
26.70	8666.83	8613.55	8494.43	30.4	1.01403	−2
26.70	8666.83	8613.55	8494.53	31.0	1.01403	−2
26.70	8666.83	8613.55	8494.53	31.6	1.01405	0
26.73	8666.78	8613.50	8495.13	34.2	1.01403	−2
26.73	8666.78	8613.50	8495.13	34.6	1.01403	−2
26.67	8666.87	8613.59	8495.18	34.8	1.01405	0
				Av.	1.01405 ± 0.00002	
		(*b*) Gage D9S				
25.50	8668.71	8619.85	4320.47	31.5	1.99519	+1
25.47	8668.75	8619.89	4320.69	33.0	1.99515	−3
25.47	8668.75	8619.89	4320.89	33.7	1.99509	−9
26.27	8667.56	8618.74	4319.59	29.2	1.99522	+4
26.23	8667.62	8618.80	4319.69	30.9	1.99527	+9
26.27	8667.56	8618.74	4319.97	32.9	1.99522	+4
26.03	8667.92	8619.08	4320.24	32.0	1.99513	−5
				Av.	1.99518 ± 0.00005	
		(*c*) Gage D8L				
26.10	8667.81	8618.98	17258.53	30.7	0.49941	−4
25.77	8668.30	8619.42	17258.54	30.9	.49944	−1
25.57	8668.28	8619.38	17258.55	30.9	.49944	−1
25.53	8668.66	8619.75	17258.05	30.2	.49946	+1
25.47	8668.75	8619.83	17257.85	30.2	.49947	+2
23.97	8680.14	8631.21	17279.35	25.8	.49946	+1
24.20	8679.80	8630.87	17278.15	25.6	.49948	+3
24.20	8679.80	8630.87	17278.15	25.8	.49948	+3
24.03	8680.06	8631.13	17281.75	26.8	.49940	−5
				Av.	0.49945 ± 0.00002	

Weight D9S, g.	Gage temp., °C.	Weight D8S, g.	Gage temp., °C.	Constant at 30°	$\Delta \times 10^5$
		(*d*) Gage D8S			
19195.13	20.9	19182.05	21.0	1.99659	−6
19195.63	20.9	19182.05	21.2	1.99665	0
19195.43	21.0	19182.05	21.5	1.99664	−1
19195.83	21.7	19182.05	22.0	1.99669	+4
19195.63	21.7	19182.05	22.0	1.99666	+1
			Av.	1.99665 ± 0.00002	

temperature, and from the temperature of the column jacket, the distance between the tips of the needles for a column temperature of 25° was found to be 8711.24 ± 0.06 mm. In the last four measurements with gage

D8L, a new lower riser was used and the column height at 25° was 8720.46 mm. for these.

In calibrating the gages, the approximate weight sufficient to balance the mercury column was placed on the scale pan and the stopcock at the bottom of the column was opened exactly one turn. The weights were adjusted until, at equilibrium, the mercury was just touching the tips of the needles in the upper and lower riser tubes. At each measurement, the temperatures of the column, the room and the gage were read. Table II *a*, *b* and *c* give the results obtained with these three gages. The figures in Col. 2 are the distances between the needle tips at the mean temperature of the column calculated from the fixed value at 25°, taking $(1/l)(\mathrm{d}l/\mathrm{d}t) = 1.1 \times 10^{-5}$ per degree for steel and transformed to standard conditions by the application of the following four corrections: (1) for the difference in the capillary depression of the mercury in the glass risers, which corresponded to —0.20 mm., the upper riser being 23 mm. inside diameter and the lower one 13 mm.; (2) for the difference in density of mercury at 0° and the mean column temperature; (3) for the difference between standard gravity, 980.665, and that in the laboratory, which is 980.397; (4) for the compressibility of the mercury, taking $\beta = —3.961$ at 25°, which leads to a constant value of +0.23 mm.

To calculate the effective pressure exerted by the mercury column against the bottom of the piston, two other corrections are necessary, namely, (5) for the difference in the air pressure at the top of the column and at the piston which is equal to 0.68 mm., and (6) for the hydrostatic pressure of the oil between the mercury surface in the lower riser and the bottom of the piston. This distance was 80.2 cm. with Gage 6 and 73.3 cm. with the other two. The density of the oil used was $d_t = 0.8913 + 0.0005625\ (30° - t°)$, which was determined experimentally during the course of this work. Col. 3 gives the effective height of mercury in international millimeters. Dividing these figures by the weight of the equilibrating system which includes the piston, the scale pan and supports and the corrected weights placed on the pan, there results the gage constant at $t°$ in international millimeters of mercury per gram weight. Correction of this constant to 30° was made by means of the relation previously given.

After the calibration against the mercury column, Gages D9S and D8S were compared directly with each other, using an intermediate mercury-in-steel U-tube. The data of this comparison are given in Table II *d* and the method of calculation is obvious. In addition to the correction for the gage temperatures, only one other was necessary, which arose from a difference in height of the two needles, so that the pressure on D8S was greater in every case by 1.0 mm.

The final values for the vapor pressure of carbon dioxide at 0° with the four gages, D8S, D9S, D8L and 6, are given in Table III, and the

TABLE III

FINAL VALUE FOR THE VAPOR PRESSURE OF CARBON DIOXIDE AT 0°

Date	Gage temp., °C.	Total wt., g.	Pressure, mm.	Bar. press., mm.	Vapor press., mm.
	Gage D9S.	Constant at 30° = 1.99518			
Apr. 3	28.9	12723.59	25386.5	759.6	26145.1
	29.4	12723.59	25386.2	759.7	26144.9
Apr. 4	28.0	12726.10	25392.1	753.6	26144.7
	30.6	12726.70	25391.7	753.8	26144.5
	31.0	12726.70	25391.6	754.1	26144.7
Nov. 9	29.3	12725.10	25389.3	755.8	26144.1[a]
				Av.	26144.7 ± 0.23
	Gage D8L.	Constant at 30° = 0.49945			
Apr. 5	27.3	50838.9	25393.0	755.1	26147.0
	28.3	50839.9	25392.9	754.9	26146.7
Nov. 8	28.2	50810.4	25378.2	769.5	26146.6[a]
	29.2	50810.0	25377.5	769.7	26146.1[a]
Nov. 9	26.5	50822.0	25385.0	761.7	26145.6[a]
	28.1	50832.8	25389.5	757.7	26146.1[a]
	28.1	50832.5	25389.3	757.7	26145.9[a]
				Av.	26146.3 ± 0.41
	Gage 6.	Constant at 30° = 1.01405			
Mar. 23	22.3	25042.18	25398.3	742.2	26144.4
	22.2	25042.18	25398.5	742.2	26144.6
	25.5	25043.68	25398.1	742.2	26144.2
	26.2	25043.18	25397.3	742.2	26143.4
	26.8	25043.18	25396.8	742.2	26142.9
	26.9	25043.18	25396.8	742.2	26142.9
Mar. 24	25.2	25048.19	25402.9	739.5	26146.3
	27.0	25048.69	25402.4	739.6	26145.9
	27.1	25047.69	25401.4	739.6	26144.9
				Av.	26144.4 ± 0.92
	Gage D8S.	Constant at 30° = 1.99665			
Mar. 28	25.0	12714.42	25389.0	755.3	26143.3
Mar. 29	23.0	12710.92	25383.2	760.9	26143.1
Apr. 1	24.6	12720.38	25401.2	743.5	26143.7
	27.0	12721.58	25402.2	743.5	26144.7
	28.6	12721.58	25401.3	743.5	26143.8
Apr. 3	24.0	12710.62	25382.1	762.9	26144.0
	28.1	12712.42	25383.3	761.5	26143.8
	29.0	12713.12	25384.2	760.9	26144.1
				Av.	26143.8 ± 0.34

Total av. of all measurements = 26144.7 ± 1.0 mm.

All pressures and corrections in international millimeters of mercury. Temperatures in degrees Centigrade. Piston constants in international millimeters of mercury per gram weight. G = 980.665.

[a] Measurements obtained with second sample of carbon dioxide.

method of computation is the same as that described in connection with Table I. The oil and carbon dioxide vapor height corrections for these measurements were as follows: D9S gage, —1.0 mm.; D8L gage, —1.1 mm.; 6 gage, +3.9 mm.; and D8S gage, —1.0 mm. A second sample of carbon dioxide was prepared as an additional check on the validity of the results, the values obtained with this sample being marked *a*. No noticeable difference can be detected between the results obtained with the two samples.

Discussion of Results

As indicated in Table III, the final value for the vapor pressure of carbon dioxide at 0° as obtained in this work is 26144.7 international millimeters of mercury (g = 980.665) which is the average of 30 independent measurements made with four different gages and which agree within ±1.0 mm. or 1 part in 26,000.

It is believed that the carbon dioxide was particularly pure in view of the care which was exercised in its preparation and purification, and two samples gave the same results within the experimental error. Further, an additional sublimation of the first sample during a series of measurements did not alter the value of the vapor pressure in any way. The establishing of the ice point is believed to have been satisfactory, and values obtained with different ice-baths were always the same, using any particular gage. Moreover, although distilled water ice was not used, tests were made of the purity of the ice employed by melting it, and the resultant water was found to be free from chlorides. To make certain that the heat leakage down the steel capillary into the ice-bath did not affect the temperature of the liquid carbon dioxide, a large block of copper was placed in good thermal contact with the steel tube just beneath the surface of the bath, and here again no difference in the value of the vapor pressure could be detected.

The assumption was made that the piston constants obtained at 12 atm. against the mercury column were unchanged at 34.4 atm., which would seem to be warranted in view of the results obtained by Keyes and Dewey[9e] who found that up to 600 atm. the constants of the gages used did not change within 1 part in 10,000. Further, a large number of comparisons have been made by the writer between pistons of varying sizes and with considerable differences in the width of the annular ring between the piston and the cylinder, and up to 500 atm. no changes in the ratios of these piston constants within 1 part in 20,000 have been detected.

Thus it would seem that as far as accuracy is concerned, the carbon dioxide liquid-vapor system at the ice point satisfies the requirements demanded of a suitable pressure device for the calibration of piston gages; moreover, the apparatus required is simple, inexpensive and particularly easy to manipulate.

Summary

1. The vapor pressure of carbon dioxide at the ice point was accurately measured to obtain a pressure system for the calibration of piston gages which would be less complicated than the mercury column. A description of the apparatus used in these measurements is given.

2. All of the gages in this Laboratory (nine in number) were balanced in turn against the vapor pressure of pure liquid carbon dioxide at 0°. On the basis of the constants of these gages, determined by comparison against a mercury column during the period from 1911 to 1924, a preliminary value of 26144 ± 2.6 mm. of mercury was obtained for the vapor pressure, omitting the measurements on one gage whose constant was obviously in error.

3. Three gages were calibrated with an improved, water-jacketed mercury column, yielding constants consistent to 1 part in 25,000, and a fourth one was compared directly with one of these three standard gages,

4. A number of new measurements of the vapor pressure were made with these standard gages and the preliminary values with these were recalculated, using the constants obtained by comparison with the improved mercury column. The value for the vapor pressure of liquid carbon dioxide at 0° thus deduced is 26144.7 ± 1.0 international millimeters of mercury, or 34.4009 ± 0.0013 atmospheres ($g = 980.665$).

5. It is suggested that the carbon dioxide liquid-vapor system at the ice point is suitable for adoption as a definite calibration point for pressure gages, since it satisfies the requirements as to accuracy, simplicity and ease of manipulation.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 135]

THE THERMAL DECOMPOSITION OF OZONE. I. THE HOMOGENEITY, ORDER, SPECIFIC RATE AND DEPENDENCE OF RATE ON TOTAL PRESSURE

BY OLIVER R. WULF[1] AND RICHARD C. TOLMAN

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1. Introduction

For several years the authors have been engaged in an investigation of the kinetics of the thermal decomposition of ozone. The justification for such an extended research upon this bothersome chemical change is three-fold. In the first place, there existed remarkable discrepancies in the results of the several researches previously carried out upon it, and these discrepancies were of sufficient significance to leave the kinetics of the decomposition entirely in doubt; second, it seemed desirable, from the point of view of developing the experimental technique of chemical

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[1] National Research Fellow in Chemistry.