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previously recorded when the light incident on the crystals contained all wave-lengths transmitted by quartz. When a Wollaston prism was placed between the crystal and the spectrograph, the lines were slightly sharper than before.

It has been known for a long time from Werner's work on complex salts and from transference experiments that the coordinated water molecules in the first shell about an ion in solution are probably fixed in number and position with respect to the central ion. Fig. 3, which shows spectra of a crystal and a solution of gadolinium chloride, gives further confirmation of this. The fact that in dilute solutions the multiplets are resolved into lines indicates that a field of definite symmetry is acting on the central ion. This means that the water molecules in the first shell about the central ion must be fixed in number and approximately in position, for if they were not and a condition of randomness existed, some atoms would have one type of splitting, other atoms another and the net result would be a blurred band, instead of discrete lines.

That the general order in solution is not as perfect as in solids is demonstrated by the fact

that the lines are from two to seven times as broad as the corresponding lines in the solid crystalline salts which were used in preparing the solutions. The field about the ion in dilute solution is almost certainly determined by the closest water molecules, which probably are situated at the corners of an octahedron. This octahedron for a given atom is distorted more or less depending on the position of the water molecules in the second shell, and that considerable variation in distortion is present can be seen from the great width of the lines. Most of the distortion is probably due to the lack of order in the outer shells of the water envelope but some of it is undoubtedly due to thermal motion. At present we have no way of separating these factors.

It is interesting to note that the solution spectrum resembles the monoclinic type of crystal spectrum more than it does the hexagonal. Furthermore, in solution the negative ion does not approach very close to the gadolinium ion, since we could detect no deviation from Beer's law even for saturated solutions of the very soluble gadolinium chloride.

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Carbon Dioxide. The Heat Capacity and Vapor Pressure of the Solid. The Heat of Sublimation. Thermodynamic and Spectroscopic Values of the Entropy

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An apparatus for low temperature calorimetric and vapor pressure measurements on condensed gases is described. The heat capacity of solid carbon dioxide has been measured from 15 to 195°K. The heat of vaporization at the sublimation point, 194.67°K, was found to be 6030 cal./mole. The vapor pressure has been measured and the observations are closely represented by the equation:

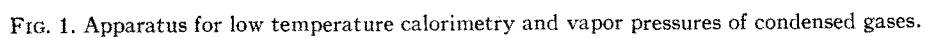
Solid carbon dioxide, 154–196°K; $\log_{10} P(\text{int. cm Hg}) = -(1354.210/T) + 8.69903 + 0.0015880T - 4.5107 \times 10^{-6}T^2$.

The entropy of carbon dioxide gas has been calculated from the calorimetric data and the third law of thermodynamics to be 51.11 cal./deg. per mole at 298.1°K. This value is in excellent agreement with the value 51.07 cal./deg. per mole obtained from band spectrum data.

BECAUSE of the importance of carbon dioxide, it seems desirable that its thermodynamic properties should be investigated as accurately as possible. The fact that its band spectrum has been measured and very satisfactorily interpreted by several investigators offers an unusually good opportunity to compare the entropy obtained from the third law of thermodynamics with that obtained with the

assistance of the spectroscopic data. The molecule is known to be of the linear symmetrical type. Thus there should be no possibility of encountering false equilibrium of the end for end random orientation type such as occurs in solid carbon monoxide, nitric oxide and nitrous oxide. Kelley¹ has shown that the available low

¹ Kelley, Bureau of Mines Bulletin, (a) **350**, 20 (1932); (b) **383**, 35 (1935).



DESCRIPTION OF FIG. 1. Apparatus for low temperature calorimetry and vapor pressures of condensed gases. 1. copper tubing; 2. cobalt glass seal; 3. soda glass tube; 4. De Khotinsky joint; 5. and 6. glass tubes; 7. glass line to vacuum system; 8. glass tubes containing heater leads and thermocouples; 9. German silver tube; 10. De Khotinsky joint; 11. valve handle; 12. vacuum jacketed transfer tube; 13. top of calorimeter tube heater; 14. tube for taking out thermocouple from bottom of container; 15. extra opening; 16. connection for rubber safety valve; 17. to vacuum pumps; 18. to low pressure hydrogen system; 19. hooks for raising apparatus; 20. tube for removing liquid in Dewar; 21. tube for introducing and precooling hydrogen gas; 22. monel cup for liquid air; 23. stainless steel disk; 24. ball-v type joint; 25. outlet tube; 26. valve in transfer tube; 27. end-of transfer tube; 28. steel supporting rings in monel case; 29. fluted tube; 30. silvered, Pyrex Dewar; 31. monel case; 32. asbestos plug in Dewar; 33. handle on outer kapok case; 34. ball-v type joint; 35. hooks in upper part of container; 36. lead blocks; 37. upper part of container; 38. suspension cords for protective cylinder; 39. suspension pins screwed into lower part of protective cylinder; 40. cobalt glass seal; 41. platinum tube; 42. calorimeter; 43. thermocouple well; platinum tube filled with Rose metal; 44. Woods metal; 45. lower part of container; 46. upper half of protective cylinder; 47. lower half of protective cylinder; 48. calorimeter heater terminals; 49. reinforcing rings in outer case; 50. removable plug in protective cylinder; 51. holes through protective cylinder; 52. balsa wood block; 53. outer kapok filled case; 54. high pressure manometer; 55. De Khotinsky joint; 56. tube containing copper foil; 57. valve to preparation line; 58. steel bomb; 59. and 60. McKay valves; 61. De Khotinsky joint; 62. tube to vacuum system; 63. manometer case; 64. manometer for vapor pressure measurements; 65. tube used for leveling purposes; 66. manometer tube containing fixed point; 67. standard meter bar; 68. mercury reservoir.

temperature calorimetric data for carbon dioxide lead to a third law entropy value which is about one entropy unit larger than the value known from spectroscopic data. There was no evident reason for this discrepancy other than inaccuracies in the available data.

The apparatus used in this investigation is similar to that employed in the large number of published and as yet unpublished researches on condensed gases which have been completed in this laboratory. The apparatus has not previously been adequately described and we will therefore include a full description in this paper.

Four calorimeters, which either have been or are to be referred to in the literature as Gold Calorimeters I,^{2a} II,² III and IV, have been built. Gold Calorimeter I was used in preliminary investigations and has been dismantled. Gold Calorimeter II was rebuilt³ in 1932. While the following description applies particularly to the

carbon dioxide experiments using Gold Calorimeter III, the other gold calorimeters differ only in minor particulars.

APPARATUS

The apparatus is shown in Fig. 1. The calorimeter, of laboratory designation Gold Calorimeter III, is represented at 42 in the diagram. It weighs 438 grams. The wall thickness is 0.1 cm. The height is 13.3 cm and the outside diameter 4.04 cm. 12 radial vanes, 0.2 cm thick and of length 12.5 cm, are welded on the inside wall of the calorimeter in order to facilitate the conduction of heat to the condensed gas. The carbon dioxide was introduced through a soda glass tube, 3, of inside diameter 0.2 cm, which is connected by means of a cobalt glass seal, 40, to a short platinum tube, 41, extending from the top of the calorimeter. The glass inlet tube is closely wound from the point, 13, to within 1 cm of the cobalt seal with a double silk covered B. and S. gauge number 30 constantan wire heater, which is used to aid in the removal of any gas condensed in the tube. The heater was painted with Bakelite varnish. Copper lead wires are taken off the heater at 10 cm intervals. The several leads from the tube heater could be used as thermocouples.

With the exception of 0.5 cm at each end, the outside of the calorimeter is roughened and covered with thin lens paper and is wound with number 40 double silk covered gold wire, which serves as a resistance thermometer heater. Both the lens paper and wire were painted with Bakelite varnish, and the calorimeter was baked at 120° for about 15 hours. 0.175 percent of silver was added to the gold to increase its resistance at the lower temperatures, since in this region pure gold is unsatisfactory as a heater. At each end, and about the middle of the thermometer, a copper lead wire of size B. and S. number 30 is attached. Each lead wire is joined to a thermometer terminal, 48, by one inch of B. and S. number 40 copper wire. The amount of stretching of the calorimeter when subjected to a pressure of 100 lbs. per square inch was calculated to determine if the resistance thermometer would be appreciably strained. The change in the diameter was only 0.0006 cm, which would not injure the thermometer.

² (a) Giauque and Wiebe, *J. Am. Chem. Soc.* **50**, 101 (1928); (b) Giauque and Johnston, *ibid.* **51**, 2300 (1929).

³ Blue and Giauque, *J. Am. Chem. Soc.* **57**, 991 (1935).

A copper-constantan thermocouple, of laboratory designation W-25, is attached to the calorimeter by inserting it in a platinum tube filled with Rose metal, 43. The platinum tube is welded to the bottom of the calorimeter. Another thermocouple of laboratory designation, W-28, is attached in the same way to the top. 63 cm of each thermocouple are below the top of a protective cylinder, 46. 50 cm are wrapped around the calorimeter. This serves to eliminate the possibility of thermal gradients near the junction.

The calorimeter is suspended by the glass tube, which is fastened to and brought into good thermal contact with the protective cylinder by means of Woods metal, 44. The protective cylinder is a massive block of metal which provides a constant temperature environment at any desired temperature. The upper half, 46, rests on the lower part, 47, by means of a ground, tapered copper joint, 1 cm in length and cut at an angle of 4° from the vertical. This type of connection assures good thermal contact at all temperatures. The lower part is suspended by the pins, 39, which are connected by means of stout cord, 38, to the hooks, 35, in the top of the container, 37. The upper part of the protective cylinder consists of 3700 g of lead and copper, the lower part, 2500 g of copper. Eight radial holes, 51, in the lower part of the protective cylinder, allow the space around the calorimeter to be evacuated. A plug, 50, in the bottom can be removed in order to center the calorimeter during the assembling of the apparatus. Both parts of the protective cylinder are wrapped with No. 30 B. and S. gauge double silk covered heater wire which is brought into good thermal contact by means of Bakelite lacquer. The heater is covered with a sheath of copper foil to reduce heat radiation between the protective cylinder and its surroundings. At room temperature, the resistance of the heater on the upper part of the cylinder is 216 ohms and the resistance of that on the lower part is 311 ohms. Two thermocouples, one on the upper part and one on the lower part, assure that the temperature of the protective cylinder is uniform.

The lower part of the container, 45, made from monel metal and stainless steel, is attached to the top of the container by means of a stainless

steel ball-v type joint, 34, which can be made vacuum tight. The temperatures of the top, 37, and bottom, 45, of the container are obtained from two thermocouples.

The container, 37, is supported by means of a German silver tube, 9, attached to the upper part of a large stainless steel and monel Dewar case, 23 and 31. Inside this tube are three glass tubes, 8, containing the heater and thermocouple wires, which are taken out through De Khotinsky cement between the two glass tubes, 5 and 6. Similarly, the glass calorimeter tube and the leads from the tube heater are taken out at 4.

Two lead blocks, 36, are on the top of the container to increase the heat capacity. The space above is filled with narrow strips of copper foil, which act as a baffle to prevent the spraying of liquid hydrogen.

The apparatus is suspended inside a highly evacuated, silvered, Pyrex Dewar, 30, which is supported by a balsa wood block, 52, inside the lower part of the large monel case, 31. The upper part of the case consists of a monel cup, 22, and a stainless steel disk, 23, to which are soldered the various metal tubes entering the apparatus. The upper and lower parts are connected by another stainless steel ball-v type joint, 24. The point, 32, represents three asbestos plugs between the walls of the Dewar, while the point, 28, indicates steel supporting rings inside the monel case.

Liquid air or liquid hydrogen is introduced through the vacuum-jacketed, German silver transfer tube, 12. A fluted tube, 29, prevents splashing of the liquid air or liquid hydrogen entering at 27. A valve, 26, operated at 11, allows the cooling liquid to be admitted when there is reduced pressure inside the monel case.

The vaporized air or hydrogen leaves the apparatus through tube 25, the ends of which are connected as follows: 18 leads to the low pressure storage tank for hydrogen gas; 17 is connected to a high capacity pumping line for cooling the apparatus under reduced pressure; 16 is either open to the atmosphere or is closed off by a rubber safety valve; 14 is the exit for the thermocouple from the bottom of the container; 15, being an extra outlet, is closed by a clamped rubber tube.

Any cooling liquid in the apparatus can be forced out from the bottom of the Dewar through tube 20. It is important to be able to do this; for example, when the apparatus is to be cooled to the temperatures of liquid hydrogen, it is pre-cooled with liquid air, which must be completely removed before the liquid hydrogen is introduced. Considerable economy in the use of liquid hydrogen can be obtained by cooling the apparatus to between 50 and 60°K by boiling liquid air under reduced pressure. Excess liquid air is then forced out through tube 20 by means of a small pressure of hydrogen gas. This hydrogen is pre-cooled by passing it through a coil of copper tubing, 21, immersed in liquid air in the monel cup, 22.

The whole apparatus is inside a large air-tight jacket, 53, which is filled with kapok insulator. The hooks, 19, were attached to a lifting device when the apparatus was raised during assembly.

The glass tube from the calorimeter is connected just above the apparatus by means of a second cobalt glass to platinum seal, 2, to a copper tube, 1, thereby decreasing the amount of glass in the line. This was desirable when the apparatus was used for carbon dioxide since, as mentioned above, the gas was condensed at a pressure of about seven atmospheres.

One end of a T joint in the copper line leads through the valve, 59, to a 485 cc steel bomb, 58, and to a U-shaped, high pressure, mercury manometer, 54, which is sealed off on one side. The manometer is 200 cm high and is made of capillary glass tubing of 0.2 cm bore and 0.4 cm wall. The capillary tubing is connected to a steel tube at 55 with De Khotinsky cement. Copper foil was placed in the tube at 56 to prevent mercury vapor from reaching the gold calorimeter. The valve, 57, leads to the preparation line.

The other end of the copper line leads through valve 60 and the De Khotinsky joint, 61, to the manometer, 64, which was used for the vapor pressure measurements. The manometer tubing is 1.6 cm i.d. The standard meter bar, 67, is suspended between the glass tubes, 66 and 65, the latter being used as a leveling tube. The complete manometer is mounted in a case kept at uniform temperature by a stream of air.

TEMPERATURE SCALE

Before the apparatus was assembled, thermocouple W-25 was compared with seven other thermocouples, including couple W-22, from 14 to 300°K in a comparison apparatus similar to that used by Giauque, Buffington and Schulze.⁴ Couple W-22 was then put in the gas thermometer apparatus described in the above reference. The thermometer bulb was filled with helium gas and the measurements were made from 15 to 300°K in a manner similar to that of Giauque, Buffington and Schulze. The data of Henning⁵ were used for correcting the helium scale to the thermodynamic scale. The temperature of the ice point on the thermodynamic scale was assumed to be 273.10°K, in conformity with the value given in the *International Critical Tables*.⁶ Some of the other thermocouples have since been compared with hydrogen and oxygen vapor pressures under the same conditions of their calibration in the gas thermometer, and with the melting point of mercury and the transition point of sodium sulfate under somewhat different conditions. In all cases the agreement is within the limit of accuracy claimed, namely, 0.05°.

PREPARATION OF CARBON DIOXIDE

The carbon dioxide was prepared from Merck's reagent quality sodium bicarbonate. The dry powder was heated to 200°C in a six-liter flask. All connections were made of glass, the preparation line being similar to that described by Meyers and Van Dusen.⁷ The carbon dioxide was passed through a water-cooled condenser and then through 5 tubes, 30 cm long, the first two containing C.P. calcium chloride, and the last three phosphorus pentoxide to remove the last traces of water. The whole system was evacuated to a pressure of 0.01 mm of mercury and flushed for one hour with carbon dioxide. The gas was condensed in liquid air and sublimed from one bulb to another several times. After each transfer, any foreign gas which may have

⁴ Giauque, Buffington and Schulze, *J. Am. Chem. Soc.* **49**, 2343 (1927).

⁵ Henning, *Zeits. f. ges. Kälte-Ind.* **37**, 169 (1930).

⁶ *International Critical Tables* (McGraw-Hill Book Co., New York, 1926), Vol. I.

⁷ Meyers and Van Dusen, *Nat. Bur. Stand. J. Research* **10**, 381 (1933).

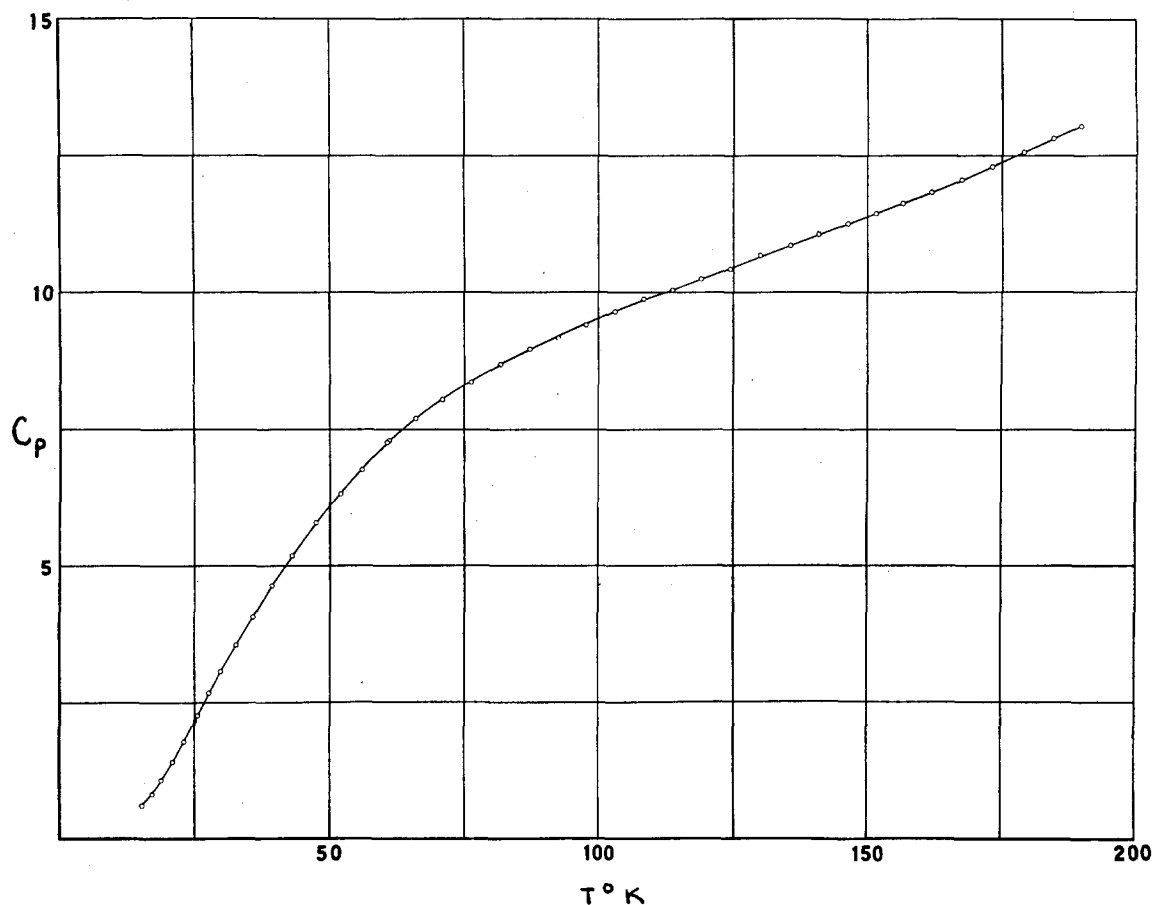


FIG. 2. Heat capacity of solid carbon dioxide in calories per degree per mole.

been previously occluded in the crystals was pumped out. The carbon dioxide was then sublimed into the bomb described previously.

By means of metal valves, the glass line could be shut off from the copper line. The carbon dioxide was allowed to melt in the bomb and the pressure was followed by reading the closed-

TABLE I. Vapor pressure of solid carbon dioxide ($0^\circ\text{C} = 273.10^\circ\text{K}$).

$T, ^\circ\text{K}$	P IN CM OBSERVED	P OBS. - P CALC.	T OBS. - T CALC.
154.196	1.132	-0.001	+0.006
158.403	1.940	-.002	+.008
162.597	3.221	-.010	+.025
166.704	5.186	-.002	+.003
170.691	8.039	+.004	-.004
174.688	12.220	+.013	-.010
178.569	17.994	+.002	-.001
182.333	25.785	-.007	+.003
187.356	40.718	-.040	+.010
192.663	64.336	-.028	+.005
194.982	77.962	-.001	+.000
195.831	83.530	+.002	-.000

end manometer. The liquid was frozen again and pumped to remove any gas which may have been previously occluded. The only probable impurity was a trace of air occluded in the sodium

TABLE II. Normal sublimation temperature of carbon dioxide ($0^\circ\text{C} = 273.10^\circ\text{K}$).

OBSERVER	$T, ^\circ\text{K}$
SIEMENS ¹⁰ (1913)	194.65
HENNING AND STOCK ⁹ (1921)	194.58
HEUSE AND OTTO ¹¹ (1931)	194.645
THIS RESEARCH	194.67

TABLE III. Comparison of temperatures from vapor pressure equations of other observers.

$T, ^\circ\text{K}$	$T_{\text{THIS RESEARCH}} - T_{\text{H. AND S.}}$	$T_{\text{THIS RESEARCH}} - T_{\text{SIEMENS}}$
165	+0.10	+0.03
175	+.12	+.11
185	+.09	+.14
190	+.09	+.10
195	+.09	+.02

bicarbonate, and this should have been removed by the above procedure.

The copper line was then opened to the calorimeter, which was at 227°K, 10° above the triple point. The protective cylinder was 5° above the triple point, with one atmosphere pressure of air between the calorimeter and the protective cylinder in order to reduce the excess of pressure inside the calorimeter and to conduct away the heat of condensation. The carbon dioxide in the steel bomb was allowed to warm until the gas was liquefying in the calorimeter at a steady state with the pressure about seven atmospheres. Under these conditions, 15 hours were required to fill the calorimeter.

VAPOR PRESSURE

The vapor pressure of the solid was measured by means of a Gaertner cathetometer, with a precision of 0.02 mm, used as a comparison instrument in connection with the standard meter mentioned above. The observations have been represented by the following equation: Solid carbon dioxide, 154 to 196°K;

$$\log_{10} P(\text{int. cm Hg}) = -(1354.210/T) + 8.69903 + 0.0015880T - 4.5107 \times 10^{-6}T^2. \quad (1)$$

The observed and calculated values are compared in Table I. The temperatures have been given to 0.001 degree because of the high relative accuracy. The absolute temperatures may be in error by several hundredths of a degree. The

pressures are corrected to International cm of mercury by means of data given in the International Critical Tables.⁶ The standard acceleration of gravity was taken as 980.665 cm/sec.². The gravitational acceleration, 979.973 cm/sec.², has been determined for this location.⁸ From Eq. (1) the temperature of the normal sublimation point on the thermodynamic temperature scale was found to be $194.67 \pm 0.05^\circ\text{K}$ ($0^\circ\text{C} = 273.10^\circ\text{K}$).

The previous vapor pressure measurements of carbon dioxide have been reviewed recently by Meyers and Van Dusen.⁷ The more recent values of the normal sublimation temperature are given in Table II. Table III is a comparison of the temperatures calculated from the vapor pressure equations of this research, of Henning and Stock,⁹ and of Siemens.¹⁰ The different values used for the ice point on the Kelvin scale have been considered in preparing Tables II and III. The best value in Table II is probably that of Heuse and Otto.¹¹

HEAT CAPACITIES

The heat capacities were measured by the method described in detail by Giauque, Wiebe

⁸ Sternewart, Landolt, Bornstein and Roth, *Physikalisch Chemische Tabellen* (Verlag Julius Springer, Berlin, 1923).

⁹ Henning and Stock, *Zeits. f. Physik* **4**, 226 (1921).

¹⁰ Siemens, *Ann. d. Physik* **42**, 871 (1913).

¹¹ Heuse and Otto, *Ann. d. Physik* **9**, 486 (1931); **14**, 181 (1932).

TABLE IV. Heat capacity of solid carbon dioxide (molecular weight, 44.00) ($0^\circ\text{C} = 273.10^\circ\text{K}$).

T, °K	APPROX. ΔT	C_p cal./deg./mole	T, °K	APPROX. ΔT	C_p cal./deg./mole
15.52	1.7	0.606	87.45	5.3	8.984
17.30	1.7	0.825	92.71	5.0	9.189
19.05	1.6	1.081	97.93	5.2	9.421
21.15	1.6	1.419	103.26	5.3	9.671
23.25	2.5	1.791	108.56	5.1	9.893
25.64	2.2	2.266	113.91	5.4	10.07
27.72	1.9	2.676	119.24	5.1	10.27
29.92	2.6	3.069	124.58	5.3	10.44
32.79	3.2	3.555	130.18	5.5	10.69
35.99	3.2	4.063	135.74	5.2	10.88
39.43	2.9	4.603	141.14	5.1	11.08
43.19	4.4	5.195	146.48	5.2	11.27
47.62	4.3	5.794	151.67	4.6	11.45
52.11	4.0	6.326	156.72	4.9	11.64
56.17	4.4	6.765	162.00	5.2	11.84
60.86	4.7	7.269	167.62	5.3	12.07
61.26	5.2	7.302	173.36	5.4	12.32
66.24	4.7	7.707	179.12	5.2	12.57
71.22	5.2	8.047	184.58	4.7	12.82
76.47	5.2	8.370	189.78	4.7	13.05
81.94	5.7	8.703			

TABLE V. *Heat capacity of solid carbon dioxide (molecular weight 44.00). Values taken from a smooth curve through observations.*

T, °K	C_p cal./deg./mole	DEVIATION E., E. AND H. —THIS RE- SEARCH, %	DEVIATION M. AND B. —THIS RE- SEARCH, %
15	0.540		
20	1.225	—3.0	
25	2.137	—3.7	
30	3.093	—2.0	
35	3.912	0.0	
40	4.690	2.7	
45	5.435	3.6	
50	6.095		
60	7.178		
70	7.972		
80	8.582	2.9	
90	9.105	3.2	
100	9.530	3.0	
110	9.915	4.1	
120	10.30	4.3	
130	10.67	4.1	
140	11.04	3.4	
150	11.39	2.8	
160	11.77	1.7	
170	12.17	0.3	1.6
180	12.61	—0.8	3.3
190	13.07	—1.5	5.8

and Johnston.² In calculating energy, 1.0004 absolute joules were taken equal to 1 International joule and 4.185 absolute joules were taken equal to 1 calorie (15°). The accuracy was ± 0.2 percent from 35 to 195°K, ± 1 percent at 20°K, and ± 3 percent at 15°K. 2.3 cm pressure of helium was admitted to the calorimeter at 59°K before the measurements were made, in order to assure heat conduction at low temperatures.

The amount of carbon dioxide, 3.618 moles, was determined by measuring the increase in weight of an absorption bulb containing 40 percent potassium hydroxide solution.

The measured heat capacities are shown in Fig. 2 and in Tables IV and V. Table V shows values picked from a smooth curve through the observations. They are compared with those of Eucken,¹² Eucken and Hauck,¹³ and Maas and Barnes.¹⁴

HEAT OF SUBLIMATION

During the measurement of the heat of sublimation, energy was introduced only by the

¹² Eucken, Verh. Deut. phys. Gesell. **18**, 4 (1916).

¹³ Eucken and Hauck, Zeits. f. physik. Chemie **134**, 161 (1928).

¹⁴ Maas and Barnes, Proc. Roy. Soc. London **A111**, 224 (1926).

lower half of the gold resistance thermometer-heater. Only a small portion of the total amount of carbon dioxide in the calorimeter was sublimed during the measurements. Thus the gas leaving the calorimeter was forced to pass along narrow channels between the upper portion of the solidified gas and the vanes or outer wall of the calorimeter. The above conditions insured that the amount of superheating of the gas did not decrease the accuracy of the measurements.

The method used in measuring heats of sublimation was similar to the method of measuring heats of vaporization used in this laboratory. The energy was started into the calorimeter, which was at the normal sublimation temperature, and a few seconds later a stopcock was opened which allowed the carbon dioxide to bubble through a mercury trap in the bottom of an absorption bulb containing 40 percent KOH solution. The bubbles were made to pass through a spiral tube as they moved upward in the solution. This tube increased the length of path and decreased the speed of the bubbles, thereby assuring complete absorption of the gas.

The thermocouple on the top of the calorimeter was compared with thermocouple W-25, on the bottom, before the measurements, and was read during the time of energy input to determine if the gas leaving the calorimeter was at the temperature of the solid carbon dioxide. Other experimenters have encountered difficulty in eliminating this superheating. Table VI shows the small temperature difference and also the correction applied to the heat of sublimation.

TABLE VI. *Corrections for superheating during measurements of heat of sublimation.*

MEASUREMENT NUMBER	TEMP. GAS— TEMP. SOLID	CORRECTION IN CAL./MOLE
1	0.02°	0.2
2	0.11°	0.9
3	0.20°	1.6

TABLE VII. *Heat of sublimation of carbon dioxide. Sublimation temp., 194.67°K. (0°C = 273.10°K.)*

NO. MOLES SUBLIMED	TIME OF ENERGY INPUT	ΔH AT 760 mm cal./mole
0.47154	200 MIN.	6028
0.23423	100 MIN.	6031
0.23466	100 MIN.	6032
		MEAN 6030 ± 5

TABLE VIII. Calculation of normal heat of sublimation from the data of Eucken and Donath.

	$T = 140^\circ\text{K}$ 6334	$T = 170^\circ\text{K}$ 6190 cal./mole
ΔH_T (SUBLIMATION) E. AND D.		
$\int_{P_{\text{sublimation}}}^{P=0} (\partial H/\partial P)_T dP$	0.1	3.2
(Berthelot gas at $T_{\text{sublimation}}$)		
$\int_{T_{\text{sub.}}}^{T=194.67^\circ\text{K}} (Cp_{\text{ideal gas}} - Cp_{\text{solid}}) dT$	-256.5	-127.9
$\int_{P=0}^{P=1} (\partial H/\partial P)_T dP$	-25.0	-25.0
(Berthelot gas at 194.67°K)		
DATA OF EUCKEN AND DONATH CALCULATED TO 194.67°K	6053	6040 cal./mole

TABLE IX. Heat of sublimation of carbon dioxide at 1 atmosphere. ($T = 194.67^\circ\text{K}$.)

ΔH (at 760 mm Hg) in cal./mole	OBSERVERS
6205	ANDREWS ¹⁶ (1925)
6024	MAAS AND BARNES ¹⁴ (1926)
6047	EUCKEN AND DONATH ¹⁵ (1926)
6029	FROM VAPOR PRESSURES
6030 \pm 5	CALORIMETRIC
	} THIS RESEARCH

The results are summarized in Table VII. Table IX contains a summary of recent measurements of the heat of sublimation. The value given for Eucken and Donath¹⁵ is based on their measurements at 140 and 170°K. Our calculation of the corresponding value at 194.67°K from their data is summarized in Table VIII. In the correction for gas imperfection the thermodynamic equation $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P$ has been combined with Berthelot's equation

$$PV = RT \left[1 + \frac{9PT_c}{128P_cT} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right],$$

$$T_c = 304.1^\circ\text{K},^6 \quad P_c = 72.8 \text{ atmos.}^6$$

From which

$$\int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_T dP = \frac{9}{128} \frac{RT_c}{P_c} \left(1 - 18 \frac{T_c^2}{T^2} \right) (P_2 - P_1).$$

The change of heat content of the ideal gas

¹⁵ Eucken and Donath, *Zeits. f. physik. Chemie* **124**, 181 (1926).

¹⁶ Andrews, *J. Am. Chem. Soc.* **47**, 1597 (1925).

TABLE X. Entropy of carbon dioxide from calorimetric data.

0-15°K, DEBYE EXTRAPOLATION ($h\nu/k$) = 140	0.190
15-194.67°K, GRAPHICAL	16.33
SUBLIMATION 6030/194.67	30.98
ENTROPY OF ACTUAL GAS AT NORMAL SUBLIMATION TEMPERATURE	47.50 \pm 0.10
CORRECTION FOR GAS IMPERFECTION	.09
ENTROPY OF IDEAL GAS AT 1 ATMOS. AND 194.67°K.	47.59 cal./deg. per mole

TABLE XI. Entropy of carbon dioxide from spectroscopic data.

	$T = 194.67^\circ\text{K}$	$T = 298.10^\circ\text{K}$
$S_{\text{trans.}} = 3/2 R \ln M + 5/2 R \ln T$ $- R \ln P - 2.300$	35.161	37.279
$S_{\text{rot.}} = R \ln IT - R \ln \sigma + 177.676$	12.215	13.062
$S_{\text{vib.}} = R \ln Q_{\text{vib.}} + RT \frac{d \ln Q_{\text{vib.}}}{dT}$	0.175	0.725
TOTAL ENTROPY IN cal./deg. per mole	47.55	51.07

TABLE XII. Comparison of experimental and spectroscopic values for the entropy of carbon dioxide.

$T, ^\circ\text{K}$	SPECTROSCOPIC	EXPERIMENTAL
194.67	47.55	47.59 cal./deg.
298.10	51.07	51.11

was obtained from spectroscopic constants to be given later.

The value of 6029 cal./mole for the heat of sublimation was obtained using vapor pressure Eq. (1) and Berthelot's equation. Although the agreement is excellent, the calculation using the vapor pressure data included a Berthelot gas imperfection correction of -127 cal./mole. Thus we can give this value no weight in comparison with the direct calorimetric observation.

THE ENTROPY FROM CALORIMETRIC DATA

A summary of the entropy calculation from the calorimetric data is given in Table X. A small correction for gas imperfection was made by combining Berthelot's equation of state with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, giving

$$S_{\text{ideal}} - S_{\text{actual}} = (27RT_c^3P)/(32T^3P_c) = 0.09 \text{ cal./deg. per mole.}$$

COMPARISON OF THE ENTROPY VALUES FROM CALORIMETRIC AND SPECTROSCOPIC DATA

The entropy of carbon dioxide gas was calculated from the available band spectrum data on this substance. Adel and Dennison¹⁷ have given a classified summary of the observations. They have also derived equations for calculating the possible vibrational levels of the molecule. The moment of inertia in the normal state was taken to be 70.1×10^{-40} g cm².

The entropy calculation has been given in detail in Table XI. The symmetry number σ is 2. The vibrational entropy was calculated by means of the state sum, $Q_{\text{vib.}} = \sum_p p_v e^{-\epsilon_v/kT}$, where p_v and ϵ_v are the *a priori* weight and energy of the

ν th state. The values of all natural constants used here are those given in the I.C.T.⁶

The entropy at 298.1°K has also been calculated by Badger and Woo¹⁸ and by Gordon and Barnes.¹⁹ These authors obtain the values 51.07 and 51.09 cal./deg. mole, respectively.

The calorimetric and spectroscopic values of the entropy have been compared in Table XII. The experimental value given at 298.1°K was obtained by using the spectroscopic data to calculate the entropy change of the gas between 194.67 and 298.1°K.

It is evident from Table XII that the entropy obtained from the third law of thermodynamics and the experimental data is in excellent agreement with that calculated from statistics and band spectrum data.

¹⁷ Adel and Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).

¹⁸ Badger and Woo, J. Am. Chem. Soc. **54**, 3523 (1932).

¹⁹ Gordon and Barnes, J. Chem. Phys. **1**, 308 (1933).

The Transfer of Energy in Molecular Systems¹

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A method of investigating problems of energy transfer, by means of potential energy surfaces, outlined in an earlier paper, has been extended to include a more general type of surface. The probability of energy transfer among atoms has been related with the rate of change of curvature of the equipotential lines. It has been shown that the relative reactivity of atoms depends on the degree of excitation of the system. An explanation has been suggested for the discrepancy existing between the data on the relative efficiencies of the inert gases as obtained from sound dispersion experiments and from reaction rate measurements.

I

IN a recent communication, hereafter called (I),² a technique was developed that seems to be applicable to the study of the transfer of energy. A complete calculation of the rate of combination of hydrogen atoms to form molecules was carried out by means of a potential energy surface. Since the problem is essentially one of energy transfer, the rate determining factor being the probability that some of the relative translational energy of two atoms will be removed

by a third body before the atoms separate, it was possible to make some qualitative deductions concerning the more general problem of energy transfer. These were given only briefly in (I), since it was only indirectly concerned with this problem. This paper elaborates on them and gives some further extensions of the method.

It has long been obvious that classical mechanics alone can help us but little in the problem of calculating theoretically the mechanism and probability of the transfer of energy among the degrees of freedom of a system. The transfer of energy is essentially a quantum phenomenon, and the characteristics of molecules considered as hard spheres, or even as ensembles of classical oscillators, give little information about the

¹ Presented at the group symposium on Quantum Mechanics and Chemical Kinetics at the Pittsburgh meeting of the A. C. S.

² Eyring, Gershinowitz and Sun, J. Chem. Phys. **3**, 786 (1935).