THE VAPOR PRESSURE OF CARBONIC ACID AT LOW TEMPERATURES.

By John Zeleny and Roy H. Smith.

1. Carbonic acid is remarkable for having a relatively high vapor pressure when in the solid state. At its melting point this pressure is greater than five atmospheres. The boiling or sublimation point, where the vapor pressure is equal to that of one atmosphere, is therefore considerably (over 20° C.) lower than the melting point.

The vapor pressures of carbonic acid, between 0° C. and the boiling point, have been measured by several observers but the results are not in good agreement.[1] For temperatures below the boiling point, we know of but one set of observations.[2]

The determinations described in this paper extend over the range from — 7° C. to the lowest temperature at which the pressure is appreciable.

2. The apparatus used for making the measurements is represented diagrammatically in Fig. 1.
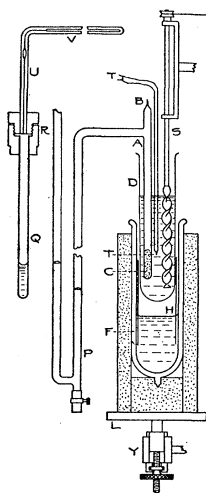
The solid carbonic acid, C, was contained in the glass tube, A, whose lower end was immersed in pentane in the glass tube, D. The temperatures were measured by the thermo-electric couple, T, one of whose junctions was placed near to the carbonic acid tube while the other was kept in ice.

Fig. 1.

The pentane was agitated vigorously by means of the stirrer, S, which was operated by a water motor, and under these conditions

[1] See M. Faraday, Phil. Trans., 1845, p. 155.　Kuenen and Robson, Phil. Mag. (6), 3, p. 149.

[2] Du Bois and Wills, Beibl. zu den Ann. der Physik, 24, p. 428.

it was found that the junction indicated the same temperature in all parts of the bath.

The pentane bath was brought to any desired temperature by means of the liquid air contained in the Dewar vessel, *F.* The stand, *L,* which carried this vessel was arranged so that it could be moved vertically by the slow-motion screw, *Y.* By watching the temperature as indicated by the deflection of a galvanometer and carefully moving this screw, the temperature of the pentane could be maintained at a constant value to $0°.1$ C. for considerable periods of time, which enabled all of the contents to assume a common temperature before a reading was taken. A metal cylinder, *H,* was fastened to the lower end of the tube, *D,* and dipped into the liquid air. This was a great aid in maintaining some of the temperatures as it made the changes produced by moving the liquid air vessel more gradual and uniform.

Two different arrangements of the apparatus were used, one for the low pressures and one for the high pressures.

3. For the low pressures, the tube, *A,* having a diameter of 1 cm., was connected by a glass tube to the open mercury manometer, *P.* Pressures up to three atmospheres could be measured by this manometer, the readings being taken with the aid of a simple cathetometer together with the reading of the barometer.

The apparatus was filled with pure carbonic acid in the following manner. A small glass tube was introduced into the tube, *A,* through the open end, *B,* and fastened to it by rubber tubing. Carbonic acid from a cylinder of commercial liquid carbonic acid was allowed to flow into *A* through this tube, and passed out through the gauge, *P,* from which nearly all of the mercury had been removed previously. After the air had been displaced the lower end of the tube, *A,* was introduced into a flask of liquid air. The carbonic acid coming from the jet froze at the bottom of the tube while the air mixed with it passed out. The tube, *A,* was lowered little by little until it was filled with solid carbonic acid for about two thirds of its total length. The tube was then partly raised from the liquid air and after the temperature had risen so that the pressure inside was greater than an atmosphere, the end, *B,* was hermetically sealed with a blow-pipe, the auxiliary glass tube having been withdrawn previously.

The solid carbonic acid was then allowed to vaporize from the top and to pass out through the gauge until a length of about 3 cm. only was left. The gas coming out of the open gauge was tested several times and found to contain only about one fortieth of 1 per cent. of impurities, although the original carbonic acid had 1.7 per cent. The tube, *A*, was now introduced into the cooled pentane bath and the taking of observations begun.

4. The tube, *Q*, was used for the higher pressures. This was 25 cm. long and had an outside diameter of 6 mm. and an inside one of 4.5 mm. It was joined to the closed air gauge, *V*, by means of the brass coupling, *R*, into which the two parts were sealed with cement. Apparatus made entirely of glass, with the gauge sealed in as a side joint, was first tried but in all except one case the whole exploded with considerable violence after the pressure had increased to about 60 atmospheres.

The tube, *Q*, was nearly filled with solid carbonic acid in the manner described in the previous section. The gauge, *V*, was then partly screwed on and its mercury thread was forced down to the open end of its tube. The vaporized carbonic acid escaped through the loose joint of the brass coupling and the apparatus was thus cleared of air. When all but a small portion of the solid carbonic acid had disappeared, the coupling was screwed tight against a leather washer by two powerful wrenches. The joint thus made was practically perfect as no leakage was ever detected after standing several days. The amount of carbonic acid left in the tube was such that liquid began to form in the tube when it was cooled a few degrees below 0° C.

The gauge, *V*, was filled with dry air, having a length of 69 cm. at atmospheric pressure. The tube was 1.2 mm. in diameter and was carefully calibrated. The liquid carbonic acid underwent so much supercooling that it usually froze so explosively as to shatter the mercury thread in the gauge. This difficulty was overcome by having a 15 cm. length of thermometer tubing, *U*, with an enlargement blown at its center, placed between the gauge proper and the brass coupling.

The readings of the gauge were corrected for inequality of the bore, for temperature, and for deviations from Boyle's law. The

last corrections were obtained by interpolation from Amagat's values.[1]

5. The thermo-electric couple used for measuring the temperatures was made of nickel and iron. These metals were chosen because their thermo-electric power changes less with temperature than for most metals so that the calibration of the couple does not necessitate the use of so many temperatures. The readings were taken with a d'Arsonval galvanometer, the deflections being brought to zero aperiodically after each reading so as to obtain the correct zero point.

The couple was calibrated by determining the deflections for six known temperatures.

The temperatures used, besides that of 0° C., were obtained as follows :

(*a*) A pentane bath, stirred vigorously, was maintained at a constant temperature whose value was read by a calibrated thermometer as — 29°.2 C.

(*b*) The temperature of a thick mixture of carbonic acid snow and ether was taken as — 78°.77 C.[2] for the barometric pressure 73.5 cm.

(*c*) The boiling point of ethylene, for the barometric pressure 74.0 cm. was taken as — 103°.9 C.[3]

(*d*) The freezing point of ethylene was used as — 169° C.[4]

(*e*) The temperature of liquid air was determined from its density.[5]

This was conveniently measured with sufficient accuracy by weighing a small mouthed, 600 c.c. Dewar flask filled with the liquid up to a fixed point for which the volume had been determined and reduced to the temperature of liquid air.

The galvanometer deflections obtained with the above temperatures were plotted on a large scale and the curve, drawn through the points, was then used for getting the temperature corresponding to any deflection.

The galvanometer had a large resistance of manganin wire in

[1] Compt. Rend., 1884, p. 1153.

[2] J. Zeleny and A. Zeleny, this volume.

[3] Travers, Study of Gases, p. 243. (Wroblewski, Witkowski, Ramsey and Travers.)

[4] K. Olzewski, Wied. Annalen (37), p. 337.

[5] Behn and Kiebitz, Annal. der Physik. (4), 12, p. 425.

series with it, in order to diminish the errors, due to changes of the room temperature, to a negligible quantity.

6. The final observations were made on several days and over a hundred readings were taken. The corrected results were then plotted all together on a large scale and those for the lower pressures were also plotted separately on a still larger scale. The results agreed well among themselves not only with either form of apparatus but also where the readings for the two forms overlapped.

The curves drawn through the plotted points were then used to find the vapor pressure corresponding to any temperature.

The results obtained in this way are given in columns II. and III. of the following tables.

TABLE I.

Vapor Pressures of Liquid Carbonic Acid.

Temperature. °C.	Vapor Pressure in Atmospheres.	Vapor Pressure in Meters of Mercury.	K. and R. Meters of Mercury.
− 7	27.80	21.13	
−10	25.83	19.63	19.8
−12	24.50	18.62	
−15	22.46	17.07	17.0
−18	20.65	15.69	
−20	19.52	14.83	14.7
−22	18.33	13.93	
−25	16.74	12.72	12.5
−28	15.10	11.48	
−30	14.21	10.80	10.6
−32	13.30	10.11	
−35	11.92	9.06	8.97
−38	10.67	8.11	
−40	9.88	7.51	7.46
−42	9.18	6.98	
−44	8.53	6.48	
−46	7.89	6.00	
−48	7.30	5.55	
−50	6.73	5.115	5.02
−52	6.18	4.70	
−54	5.66	4.31	
−56	5.19	3.945	
−56.4	5.11	3.911 Triple Point.	
−58	4.75	3.610 Supercooled.	
−60	4.35	3.306 "	3.27
−62	3.96	3.01 "	
−64	3.58	2.721 "	
−65.5	3.30	2.508 "	

TABLE II.

Vapor Pressures of Solid Carbonic Acid.

Temperature. °C.	Vapor Pressure in Atmospheres.	Vapor Pressure in Centimeters of Mercury.	K. and R. / D. and W.	Z. and Z.
− 56.4	5.11	391		
− 57	4.85	368.5		
− 58	4.51	343		
− 59	4.20	319		
− 60	3.92	298	302	
− 61	3.67	279		
− 62	3.43	260.5		
− 63	3.20	243		
− 64	2.98	226.5		
− 65	2.78	210	211	
− 66	2.59	195.5		
− 68	2.21	168		
− 70	1.88	144	143	
− 72	1.638	124.0		
− 74	1.395	106.0		
− 75	1.283	97.5	97	
			D. and W.	Z. and Z.
− 77	1.102	83.9	88.5	84.0
− 78.2	1.00	76		
− 80		65.7		66.6
− 82		55.8		57.0
− 84		47.3		48.4
− 85		43.5	51.0	44.6
− 86		40.0		41.2
− 88		34.0		35.0
− 90		28.8		29.2
− 92		24.1		24.4
− 94		20.2		20.4
− 96		17.0		16.8
− 98		14.1		13.9
−100		11.9		11.3
−102		9.9	11.0	9.2
−104		8.0		7.4
−106		6.4		6.0
−108		5.3		4.9
−110		4.3		4.0
−112		3.4	4.0	3.25
−114		2.7		2.7
−116		2.2		
−118		1.8		
−120		1.4		
−122		1.1		
−124		.8	.5	
−126		.6		
−128		.45		
−130		.25		
−132		.15		
−134		.1		

The values in the column marked *K.* and *R.* are those given by Kuenen and Robson.[1] Considering the different methods used in making the determinations the results are seen to be in fair agreement with the corresponding ones here obtained. The values under *D.* and *W.* are those obtained by du Bois and Wills[2] for the temperature of carbonic acid snow at different pressures. Their values are in general higher than those obtained by us. The value of the boiling point given by them is $-79°.2$ C., which is $1°$ lower than that given in our tables. By raising all of their temperatures $1°$, the two sets of results are brought into much better agreement.

In the last column of Table II., under *Z.* and *Z.*, are added the values recently obtained in this laboratory[3] for the temperatures of carbonic acid snow and its mixtures with ether and alcohol when these are maintained under different pressures. They differ but little from these determinations.

7. It was noticed that the amount of impurity in the low pressure apparatus increased somewhat during a set of observations. This was inferred from the value of the pressure for the temperature of liquid air, which at the start was practically zero, but which towards the end of a set of observations had increased to more than 0.1 cm. The supposed reason for this is that the solid carbonic acid contained a trace of absorbed air. When the pressure of the vapor was increased to two or three atmospheres some of the solid vaporized, freeing the absorbed air. On recooling the tube, the carbonic acid was condensed, but the air was nearly all left free in the tube. By repeated heating and cooling of the tube the amount of impurity was increased in this way. The value of the pressure for the temperature of liquid air was reduced to zero again by allowing the accumulated gas to bubble out through the manometer. In any case the value of the pressure obtained for the temperature of liquid air was subtracted from the other readings taken.

The triple point was determined in the following way. The frozen carbonic acid in the high pressure apparatus was warmed slowly and the pressure noted as it gradually increased. When

---

[1] Loc. cit.

[2] Loc. cit.

[3] J. Zeleny and A. Zeleny, loc. cit

the carbonic acid began to melt the pressure became constant and remained so for some time, so that its value could be determined with precision. It was found to be 5.11 atmospheres. The temperature of the triple point was determined from the temperature-pressure curve for the liquid carbonic acid, by finding the temperature corresponding to this pressure of 5.11 atmospheres. The value was found to be − 56°.4 C.

The corresponding values obtained by Kuenen and Robson are 5.10 atmospheres and − 56°.2 C. and those obtained by Villard and Jarry[1] are 5.1 atmospheres and − 56°.7 C.

By means of the formula for the latent heat of evaporation,

$$L = (v_v - v_l)T\frac{dp}{dT},$$

Kuenen and Robson[2] calculated the value of the latent heat at the boiling point to be 121 calories, by taking 355 as the specific volume of the vapor of carbonic acid at the boiling point and using for dp/dT, 5.5 cm. per 1° C., the value obtained by du Bois and Wills.[3] This result is much smaller than the experimental values obtained by Behn[4] (142.4 calories) and by Favre and Silbermann[5] (142.2 calories). The value of dp/dT obtained from our curves is 6.35 cm. per 1° C., and using this number the value of L becomes 140 calories. which is in very good agreement with the experimental results.

PHYSICAL LABORATORY,
   UNIVERSITY OF MINNESOTA,
     June 29, 1906.

[1] Compt. Rend., 120, p. 1413.
[2] Phil. Mag. (6), 3, p. 627.
[3] Loc. cit.
[4] Annal. der Physik, 1, p. 272.
[5] Ann. de Chim. et de Phys. (3), 37, p. 470.