

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

**THE PARTIAL MOLAL HEAT CAPACITY OF THE CONSTITUENTS  
AND THE SPECIFIC HEAT OF AQUEOUS SOLUTIONS OF  
SODIUM AND HYDROGEN CHLORIDES**

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In determining the change of the activity of a constituent or of an equilibrium constant with the temperature, when solutions are involved, the partial molal heat content and the partial molal heat capacity replace the molal heat content and the molal heat capacity in the ordinary equations. The partial molal heat capacity of a constituent of a solution is the differential rate of change in the total heat capacity of a solution per mole of the constituent added, the amount of the other constituents remaining constant. Experimentally, it is the increase in the total heat capacity of a very large amount of solution when one mole of the constituent is added.

No direct measurements of partial specific heats have been described in the literature, although some values have been roughly calculated from meager data in the case of a few solutions.<sup>1</sup> The present paper describes a direct method of obtaining the average partial molal heat capacity of the solute over a small concentration range, and indirectly that of the solvent, and the heat capacity of the solution.

We have used<sup>2</sup> a modification of the differential twin calorimeter as employed for the determination of the specific heats of solutions. As the history of the various differential methods has been recently discussed by Richards and Gucker<sup>3</sup> we shall omit a formal theoretical treatment. Our apparatus was that used by Randall and Bisson,<sup>2</sup> and we shall merely describe our additions to their apparatus.

**Modifications of the Apparatus of Randall and Bisson.**—The apparatus consisted essentially of three vacuum flasks (Figs. 1, 2 and 4 of the previous paper), each of about 1 liter capacity, and with nearly identical heat leaks, fastened in a frame in such a way that they could be lowered into a constant-temperature oil-bath. The flasks were covered with polished, silver-plated caps, through which passed the stirrers, thermels, etc. The upper part of the apparatus was surrounded by a constant-temperature air-bath.

Flasks 1 and 2 were the working flasks, and the difference in temperature was determined by means of a 50-junction copper-constantan thermel (thermo-couple), while Flask 3 was used as a reference, being at the temperature of the bath, except in the case of some of the measurements at the lowest temperatures, when it was filled with an

<sup>1</sup> See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, chaps. IV, VIII, IX and XXIII.

<sup>2</sup> The experimental method was indicated in a footnote in the paper by Randall and Bisson, *THIS JOURNAL*, **42**, 347 (1920). The experiments were completed in May, 1922.

<sup>3</sup> Richards and Gucker, *ibid.*, **47**, 1876 (1925).

ice-and-water mixture. A 20-junction thermel gave the difference between the temperature of Flasks 1 and 3, and a 12-junction thermel the difference between the temperature of Flask 3 and the bath.

The same amount of electrical energy is to be added to solutions in Flasks 1 and 2 which have approximately the same heat capacity. This was done by passing an electric current through resistances connected in series. Our heating coils consisted of about 2 ohms of No. 26 double, silk-covered (d.s.c.) Therlo wire wound on a thin mica sheet 2.5 cm. by 5.0 cm. The leads were No. 18 d.s.c. copper wire, silver-soldered to the Therlo wire. The resistances of the two coils were carefully adjusted to the same value, the leads given a heavy coat of Bakelite varnish, the coils a thin coat of Bakelite, and a thin plate of mica was placed on each side of the coil. The whole was placed in a case of thin copper foil which was mashed flat to insure good heat interchange between the coil and the case. After the case had been soldered, the coils were baked for 24 hours at 140°.

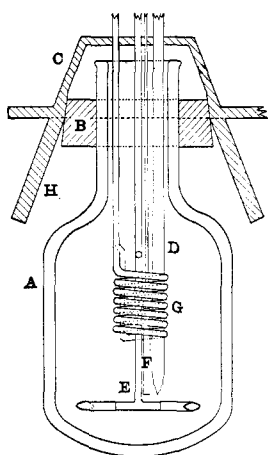


Fig. 1.—Calorimeter flask.  
Scale, 1 cm. = 5 cm.

The modified arrangement is shown in Fig. 1. A is one of the vacuum flasks, B is a rubber stopper, C is the heavy, silver-plated brass cap, D is the glass protecting tube of the thermel, E is the stirrer shaft, F is the heating resistance and G is the cooling coil. Heavy brass blocks H, soldered to the cap C, assisted in maintaining the cap at the bath temperature.

During the measurements at 25° the room temperature was kept at 24° ± 0.5°, and the air-bath was not separately regulated. The temperature of the oil-bath varied less than 0.01°. Coils, through which cold brine could be circulated, which were used in the experiments at the lower temperatures, were placed in the oil-bath and in the air-bath. At the lowest temperature the temperature of the circulating brine varied, and we experienced difficulty in obtaining satisfactory regulation. Independent regulators were used in both oil- and air-baths in the latter experiments. The results at the lower temperatures can only be considered as preliminary. Before continuing this work, however, it is our intention to rebuild the apparatus, using a submarine jacket and frame similar to that used by Randall and Vanselow.<sup>4</sup>

**Heat Capacity of the Flasks.**—We selected flasks whose heat capacities

<sup>4</sup> Randall and Vanselow, *THIS JOURNAL*, **46**, 2418 (1924).

and rates of heat leak were found to be approximately the same. The heat capacity of Flask 2, which was the only flask whose contents were changed during an experiment, enters in a secondary way into the calculations. The heat capacity of Flask 2, together with the thermel, stirrer and heating and cooling coils, was obtained by making a direct measurement of the heat capacity of the system when the flask contained a known amount of water, as has been described in the work of Randall and Bisson.<sup>2</sup> The mean of several determinations gave: Flask 2,  $C_p = 42.5 \pm 0.5$  cal. per degree.

The heat capacity of the flask depends somewhat upon the volume of liquid contained in the flask. In the foregoing determination the volume of water was about that used in the normal experiment. From the experience of Randall and Bisson, the change in heat capacity of Flask 2 when the volume of solution is changed slightly may be taken as 0.02 cal. per degree per cc.

**Experimental Results.**—If the amount of water, or solution, is correctly chosen so that the total heat capacities of Flasks 1 and 2 are identical, and the flasks are at the same temperature, then if a current is passed through the coils connected in series, the rise in temperature,  $\Delta t_1$  and  $\Delta t_2$ , will be the same in each flask,<sup>5</sup> and the temperature difference  $\Delta(\Delta t)$ , measured by the 50-junction thermel, will be zero. If now the flasks are cooled to the initial temperature, a weighed amount of salt added (small enough so that the concentration of the solution is not greatly changed), and the experiment repeated, the change in total heat capacity,  $\Delta C_p$ , is proportional to  $\Delta(\Delta t)/\Delta t_2$ , and  $\bar{C}_p$  is approximately  $\Delta C_p$  per mole of salt added. The method of calculation is illustrated by the condensed log of a typical experiment as given in Table I.

The experimental data for sodium chloride at 25° are given in Table II and those for hydrochloric acid in Table III. Col. 1 gives the number of the experiment, all numbers under the same letter being for the same series. During any series the solutions in Flasks 1 and 2 were not disturbed, except for the purpose of adding solute to Flask 2. Each series, however, was begun with a new solution, which was analyzed before the first run of the series and after the last run. In any series each solution is the initial solution for the one immediately following it. Col. 2 gives the weight of the solution in Flask 2, the third the concentration in moles per 1000 g. of water, and the fourth the number of moles of solute added

<sup>5</sup> The stirrers were driven by the chain at the same speed, and were adjusted so that after one hour the difference in temperature of the two flasks changed by a negligible amount. The heat leak was small and nearly identical, but since the rate of heating was the same and the thermal head the same in each case, no appreciable error is introduced. Slight inequalities in these quantities and in the resistances of the heating coils, and absolute calibration of the 20-junction thermel, are neutralized by the method of the experiments.

TABLE I  
 CONDENSED LOG OF A TYPICAL EXPERIMENT

Initial temperature, 24.5°. 1004 g. of water in Flask 2.

$C_{p\text{H}_2\text{O}} = 1004 \times C_p(\text{H}_2\text{O}) (0.9979) = 1001.89 \text{ cal./deg.}$

$\Delta t_1$ , temp. rise in Flask 1, = 0.977°.

$\Delta(\Delta t)$ , temp. rise of Flask 2 above Flask 1, = -0.00265°.

$\Delta t_2$ , temp. rise of Flask 2 per degree rise in Flask 1, =  $1 + \Delta(\Delta t)/\Delta t_1 = 0.99729^\circ$ .

Both flasks cooled to 24.5°; Flask 1 not changed, but 4.22 g. of NaCl = 4.22/58.46 moles =  $\Delta n_2 = 0.0722$  moles added to Flask 2.

$\Delta t_1'$ , temp. rise in Flask 1, = 0.960°.

$\Delta(\Delta t')$ , temp. rise of Flask 2 above Flask 1, = -0.00145°.

$\Delta t_2' = 0.99849^\circ$ .

$\Delta C_p = (\Delta t_2 - \Delta t_2')/\Delta t_2' [C_{p\text{H}_2\text{O}} + C_p(\text{Flask 2})] - \Delta t_2' \Delta C_p(\text{Flask 2})^a = [(0.99729 - 0.99849)/0.99849] [1001.89 + 42.5] - 0.03 = -1.28 \text{ cal./deg.}$

$\bar{C}_{p2} = \Delta C_p/\Delta n_2 = -17.7 \text{ cal./mole/deg. at approximately } 0.04M.$

NaCl in Flask 2 is  $0.0722/1004 = 0.719M$ .

Weight of solution in Flask 2 = 1008.22 g.

$C_{p\text{soln}} = C_{p\text{H}_2\text{O}} + \text{net } \Delta C_p = 1000.6 \text{ cal./deg.}$

Specific heat of solution (0.719M) = 0.9925 cal./deg.

<sup>a</sup> The increase of volume of the solution was about 1.3 cm.<sup>3</sup> or the increase in the heat capacity of Flask 2 was about 0.03 cal.

 TABLE II  
 $\bar{C}_{p2}$  IN DILUTE SODIUM CHLORIDE SOLUTIONS AT 25°

No.	Wt. of soln., g.	<i>m</i>	$\Delta n_2$	$\Delta t$	$\Delta(\Delta t)$	$\Delta t_2$	$\Delta C_p$	$\bar{C}_{p2}$	Sp. heat	Sp. heat Eq. 6
A 1	998	0.000	....	1.133	-0.00487	0.99570	....	....	0.9979	
2	1002.01	.069	0.0686	1.073	-0.00335	.99688	-1.25	-18.2	.9927	
3	1006.47	.145	.0745	1.007	-0.00227	.99775	-0.94	-12.6	.9873	
4	1010.02	.206	.0607	0.953	-0.00137	.99856	-0.87	-14.3	.9830	
5	1015.30	.297	.0903	.905	+0.00019	1.00021	-1.74	-19.3	.9762	
B 1	1003	.000	....	.998	-0.00360	0.99640	....	....	.9979	
2	1008.00	.085	.0855	.965	-0.00190	.99803	-1.73	-20.2	.9913	
3 <sup>a</sup>	1011.37	.143	.0577	.912	-0.00146	.99840	-0.41	-7.1	.9875	
4 <sup>a</sup>	1015.15	.207	.0647	.862	-0.00071	.99918	-0.83	-12.8	.9830	
5 <sup>a</sup>	1019.14	.275	.0683	.809	-0.00048	.99941	-0.28	-4.1	.9789	
C 1	1007	.000	....	.981	+0.00317	1.00323	....	....	.9979	
2	1010.97	.068	.0679	.967	+0.00398	1.00412	-0.95	-14.0	.9931	
3	1014.43	.126	.0592	.948	+0.00493	1.00520	-1.15	-19.4	.9885	
4	1021.15	.241	.1150	.928	+0.00623	1.00672	-1.62	-14.1	.9803	0.9804
D 1	1004	.000	....	.977	-0.00265	0.99729	....	....	.9979	
2	1008.22	.072	.0722	.960	-0.00145	.99849	-1.28	-17.7	.9925	
3	1011.99	.136	.0645	.939	-0.00045	.99952	-1.10	-17.0	.9876	
4	1016.83	.218	.0829	.923	+0.00071	1.00077	-1.33	-16.2	.9815	
5	1022.21	.310	.0920	.902	+0.00149	1.00165	-0.96	-10.9	.9755	.9757
E 1	1015	.310	....	2.033	+0.00427	1.00210	....	....	.9755	
2	1025.1	.484	.1727	2.000	+0.00727	1.00369	-1.70	-9.9	.9642	
3	1035.3	.659	.1744	1.970	+0.00900	1.00457	-0.96	-5.5	.9538	
4	1045.7	.837	.1778	1.944	+0.01083	1.00557	-1.08	-6.1	.9433	.9432
F 1	1030	.837	....	1.827	+0.00100	1.00055	....	....	.9433	
2	1039.8	1.005	.1676	1.804	+0.00270	1.00150	-1.02	-6.1	.9334	
3	1048.9	1.164	.1556	1.775	+0.00301	1.00175	-0.31	-2.0	.9250	
4	1057.7	1.315	.1505	1.743	+0.00305	1.00175	-0.06	-0.4	.9173	.9176
G 1	1050	1.320	....	1.795	-0.00324	0.99820	....	....	.9173	
2	1061.2	1.554	.1916	1.769	-0.00345	.99805	.08	0.4	.9077	
3	1073.8	1.774	.2154	1.737	-0.00408	.99765	.33	1.5	.8974	
4	1082.1	1.899	.1420	1.703	-0.00488	.99713	.48	3.4	.8909	.8911

<sup>a</sup> Owing to an observed irregularity during Run B3 these results may be in error.

to Flask 2 between successive runs. Cols. 5, 6 and 7 give, respectively, the rise in temperature in Flask 1 (20-junction thermel), the rise in temperature of Flask 2 above that of Flask 1 (50-junction thermel), and the rise in temperature in Flask 2 per degree rise in Flask 1. The temperature rise given is the mean of two closely agreeing experiments in nearly every case. Column 8 gives the change in heat capacity of the solution in Flask 2 caused by the addition of the  $\Delta n_2$  moles of salt to the solution measured on the row above, corrected for the change in heat capacity of Flask 2 due to the change in volume of the solution. The ninth gives the partial molal heat capacity of the solute at a concentration between that on the same row and that on the preceding row. The tenth gives the specific heat of the solution after each addition of solute.

In Table III, as in Table II, the value of  $\Delta n_2$  is for the number of moles of solute added to Flask 2, the amount of water added along with the hydrochloric acid being shown by the increased mass of the solution. The values of  $\Delta C_p$  in Table III are not the measured values, but these values minus the partial heat capacity of the water added along with the acid. That is, they are the changes in heat capacity which would have been caused by adding the hydrochloric acid alone.

TABLE III

$\bar{C}_{p2}$ IN DILUTE HYDROCHLORIC ACID SOLUTIONS AT 25°										
No.	Wt. of soln., g.	<i>m</i>	$\Delta n_2$	$\Delta t$	$\Delta(\Delta t)$	$\Delta t_2$	$\Delta C_p$	$\bar{C}_{p2}$	Sp. heat	Sp. heat, Eq. 6
A 1	990	0.000	....	1.936	+0.00258	1.00133	....	....	0.9979	
2	999.80	.082	0.0817	1.930	-.00473	0.99755	-3.07	-37.6	.9919	
3	1010.40	.170	.0887	1.895	-.01258	.99335	-3.19	-35.9	.9855	
4	1020.07	.248	.0801	1.858	-.01973	.98938	-2.77	-34.6	.9802	
B 1	990	.000	...	1.871	+ .00319	1.00171	....	....	.9979	
2	1000.0	.083	.0823	1.837	-.00434	0.99763	-2.97	-36.1	.9919	
3	1009.7	.166	.0806	1.805	-.01132	.99373	-2.92	-36.3	.9861	
4	1020.3	.247	.0878	1.766	-.01903	.98923	-2.86	-32.6	.9805	
C 1	990	.000	...	2.167	-.00609	.99719	....	....	.9979	
2	999.60	.080	.0801	2.130	-.01401	.99342	-2.94	-36.7	.9921	
3	1009.50	.162	.0826	2.074	-.02180	.98050	-2.99	-36.0	.9862	
4	1021.41	.259	.0992	1.995	-.03050	.98472	-3.47	-35.0	.9795	
D 1	995	.261	...	1.766	-.00297	.99832	....	....	.9799	
2	1005.26	.345	.0853	1.732	-.01003	.99421	-3.13	-36.7	.9733	
3	1016.28	.434	.0916	1.671	-.01788	.98930	-2.81	-31.8	.9674	0.9675
4	1026.55	.515	.0853	1.606	-.02330	.98550	-3.39	-39.7	.9614	.9622
E 1	995	.521	...	1.810	+ .00706	1.00390	....	....	.9610	
2	1004.94	.608	.0826	1.740	-.00041	0.99976	-2.97	-36.0	.9545	
3	1014.72	.682	.0812	1.660	-.00920	.99446	-1.71	-21.1	.9512	
4	1025.80	.766	.0925	1.589	-.01710	.98924	-2.68	-29.0	.9438	.9447
F 1	1000	.778	...	1.921	+ .01211	1.00583	....	....	.9432	
2	1010.75	.862	.0894	1.884	+ .00214	1.00114	-3.03	-33.9	.9375	
3	1021.35	.944	.0880	1.830	-.00815	0.99555	-2.00	-22.7	.9316	
4	1031.90	1.025	.0877	1.775	-.01745	.99017	-2.11	-24.1	.9215	.9308

The value of  $\bar{C}_{p2}$  given in Col. 9 is, in fact, the average of the  $\bar{C}_{p2}$  over the concentration range used. If the curve of partial molal heat capacity of the solute against the molality were linear, then it would be the value at the mean of the molalities. We have found, however, that  $\bar{C}_{p2}$  is approxi-

mately proportional to the square root of the molality, and we have therefore plotted in Fig. 2 the values given in Col. 9 of Tables II and III against the mean of the square root of the molality of the two solutions used in the calculation.

If we represent the partial molal heat capacity of the solute by the equation

$$\bar{c}_{p2} = \bar{c}_{p2}^{\circ} + Am^{0.5} \quad (1)$$

then by the partial molal equation<sup>6</sup>

$$55.51 d\bar{c}_{p1} + m d\bar{c}_{p2} = 0 \quad (2)$$

Differentiating Equation 1, substituting in Equation 2 and integrating, we find

$$\bar{c}_{p1} = \bar{c}_{p1}^{\circ} - 0.00601 Am^{1.5} \quad (3)$$

or, if the partial molal heat capacity of the solute varies as the square root of the molality, then the partial molal heat capacity of the solvent varies as the 1.5 power of the molality.

From the curves of Fig. 2 we find

$$\text{NaCl(aq.)}; \bar{c}_{p1} (298) = 17.98 - 0.1082 m^{1.5}; \bar{c}_{p2} (298) = -21 + 18 m^{0.5} \quad (4)$$

$$\text{HCl(aq.)}; \bar{c}_{p1} (298) = 17.98 - 0.0842 m^{1.5}; \bar{c}_{p2} (298) = -41 + 14 m^{0.5} \quad (5)$$

If  $n_1$  and  $n_2$  are the number of moles of the two constituents, then the total heat capacity of the solution is

$$C_p = n_1 \bar{c}_{p1} + n_2 \bar{c}_{p2} \quad (6)$$

Several values of the specific heat of the solution calculated from the

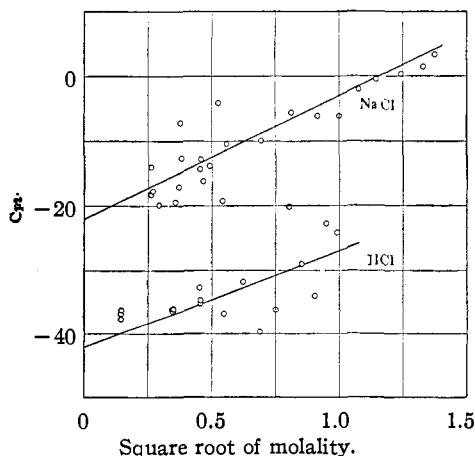


Fig. 2.—Partial molal heat capacity of the solute.

values of the constants in Equations 4 and 5 are given in the last columns of Tables II and III. The agreement of the observed and calculated values is not a criterion of the accuracy of the measurements but only of the average suitability of Equations 4 and 5.

The errors in the values of the measured specific heats are cumulative. The values for sodium chloride are more reliable than those for hydrochloric acid, as the uncertainty of the change of the heat capacity of the flask

with volume is smaller.

The values of the partial molal heat capacities and the specific heats at round concentrations are given in Table IV.

<sup>6</sup> Ref. 1, p. 43, Eq. 17.

TABLE IV  
PARTIAL MOLAL HEAT CAPACITIES AND SPECIFIC HEATS OF AQUEOUS SODIUM CHLORIDE  
AND HYDROCHLORIC ACID AT 25°

<i>m</i>	Sodium chloride			Hydrochloric acid		
	$\bar{c}_{p1}$	$\bar{c}_{p2}$	Sp. heat	$\bar{c}_{p1}$	$\bar{c}_{p2}$	Sp. heat
0.00	17.977	-21.0	0.9979	17.977	-41	0.9979
.05	17.976	-17.0	.9939	17.976	-37.8	.9939
.1	17.974	-15.4	.9904	17.974	-36.5	.9903
.2	17.967	-13.0	.9832	17.969	-34.6	.9830
.5	17.939	- 8.4	.9635	17.947	-31.0	.9631
1.0	17.869	- 3.0	.9342	17.893	-27.0	.932
1.5	17.78	1.0	.9085	....	....	...

Our value for the partial molal heat capacity of the solute in 0.1 *M* solution is larger than that obtained by Randall and Bisson<sup>2</sup> for sodium chloride, and smaller than that obtained by Lewis and Randall<sup>7</sup> for hydrochloric acid.

**The Temperature Coefficient of the Partial Molal Heat Capacity of Sodium Chloride.**—It was impossible to obtain measurements of high accuracy at temperatures much different from room temperature, where the temperature of the bath was difficult to maintain. Below room temperature it was also difficult to keep the air dry enough to prevent moisture from condensing on the apparatus and thus causing electrical leakage.

We will not give the details of the various experiments. The results for 0.1 *M* sodium chloride solution, which were most concordant but which must be regarded as only preliminary, are plotted in Fig. 3. Each of the circles is the mean of two determinations shown as dots in the figure. Excepting the point at 9°, which is probably too high, there seems to be a gradual algebraic increase in the value of  $\bar{c}_{p2}$  as the temperature increases. The partial molal heat capacity of the solute is negative, which may be considered an abnormal condition, and an algebraic increase in its value may be considered as a decrease in the abnormality of the solution. This is, in general, the prediction made by Lewis and Randall,<sup>8</sup> our results furnish, however, only a partial test of the principle, since the possible error of the points is large.

We shall not discuss further these experiments, as the apparatus has been reconstructed, and new experiments are in progress.

### Summary

1. The differential twin calorimeter has been used to determine directly the partial molal heat capacity of the solute.

<sup>7</sup> Lewis and Randall, *THIS JOURNAL*, **36**, 1969 (1914).

<sup>8</sup> Ref. 1, pp. 106-108.

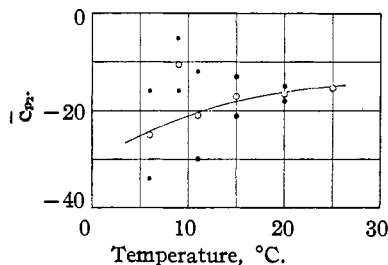


Fig. 3.—Partial molal heat capacity of sodium chloride in 0.1 *M* solution.

2. Measurements of the partial molal heat capacities of the constituents and the specific heats of aqueous sodium chloride at several temperatures, and of hydrochloric acid at 25°, are given.

3. The partial molal heat capacity of the solute is found to vary approximately as the square root of the molality in dilute solutions, and that of the solvent as the 1.5 power of the molality.

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## THE SUBLIMATION PRESSURES OF SUBSTITUTED QUINONES AND HYDROQUINONES

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At the request of Professor J. B. Conant, we undertook to find approximate values of the sublimation pressures of a series of substituted quinones and corresponding hydroquinones at 25°. The materials were those described by Conant and Fieser.<sup>1</sup> The measurements were made by the quartz fiber manometer previously described by one of us.<sup>2</sup> In some cases it was necessary to work at a higher temperature in order to obtain measurable pressures. This required that the gage and connecting tubing should be heated in order to prevent condensation. The gage was mounted in an oven and calibrated at different temperatures against a McLeod gage, using pure dry air. In accordance with theory, the reading of the quartz gage, for a given pressure and temperature in the McLeod gage, was found independent of the temperature of the quartz gage, except that the intrinsic damping constant, called *Z* in the previous articles referred to, increased slightly with rise in temperature. This increase was allowed for in the subsequent measurements.

The substances were placed in an appendix close to the quartz fiber gage and maintained at the desired temperature, while the gage and connections were kept somewhat hotter. Except while a reading was in progress, the system was continuously pumped with a diffusion pump, access of mercury vapor being prevented by the interposition of a carbon dioxide cold trap. During a reading, the gage was cut off from the pump and cold trap by a ground-glass valve operated by a solenoid. The valve was not lubricated, and undoubtedly leaked slightly, but this leakage was presumably negligible in comparison with the rate of evaporation from the surface of the substance. Two hours of pumping was generally sufficient to remove all traces of solvent from which the substances had been crystallized, and produce pressures that did not decrease on further pumping, and were therefore accepted as true sublimation pressures. In a few cases, however, it was necessary to volatilize the substance completely

<sup>1</sup> Conant and Fieser, *THIS JOURNAL*, **45**, 2194 (1923).

<sup>2</sup> Coolidge, *ibid.*, **45**, 1637 (1923); **46**, 680 (1924).