

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

## STUDIES IN VAPOR PRESSURE: V. A DYNAMIC METHOD FOR MEASURING VAPOR PRESSURES, WITH ITS APPLICATION TO BENZENE AND AMMONIUM CHLORIDE.

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For high vapor pressures, to the measurement of which a vessel closed with a rubber stopper is unsuitable, a modified form of the submerged bulblet apparatus<sup>1</sup> may be used. The new apparatus is less easily constructed, but, when made, has several advantages, for all purposes, over the simpler form. To avoid repetition, we mention only the few points in which the new apparatus differs from the old, and refer the reader for all further description and directions, and for a discussion of the theory and characteristics of the method, to the former papers. This instrument, to distinguish it from the static apparatus described in a preceding paper, will be called the "dynamic isoteniscope."

### THE EXPERIMENTAL METHOD.

**The Apparatus.**—The opening *C* (Fig. 1) is connected with the gage, the exit to the air, and the pressure (or vacuum) bottle and pump.<sup>2</sup> The bulb *B* (diameter 23 mm.) contains the liquid through which the stream of vapor is discharged. The bulblet *A* is made as a separate part and, after being charged with the solid or liquid substance under investigation, is fused on to the side tube at the dotted line. When cut apart carefully at this point, after use, the apparatus may be employed repeatedly. The bulb between *A* and *B* prevents access of the liquid in *B* to the bulb *A*. The total length from *B* to *C* is about 30 cm.

The method of manipulation is the same as that described in connection with the submerged-bulblet vapor pressure apparatus.<sup>3</sup>

**Necessary Corrections.**—When the apparatus is employed, the usual precautions and corrections in connection with the gage and thermometer are required. Two corrections are peculiar to this apparatus. One is that for immersed depth, measured in this instance from the surface of the liquid in *B* down to the opening of, or the point of ascension in, the capillary.<sup>4</sup> The second is that due to capillary ascension, which increases the pressure beyond that shown by the gage.<sup>5</sup> The amounts of both corrections may be measured together as follows: After the observations are completed, and the bulb *A* has been cut off, the opening

<sup>1</sup> Submerged bulblet papers: THIS JOURNAL, 32, 897 and 907.

<sup>2</sup> For general arrangement, see this series, No. III, Fig. 3.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> THIS JOURNAL, 32, 901.

<sup>5</sup> *Ibid.*, 32, 902.

*C* is connected with a wide tube standing in a beaker of water. The latter tube is raised, drawing its water content with it until the surface of the confining liquid in *B* falls to the point of ascension, or until bubbles issue from the capillary, as the case may require. The elevation of the water above the surface in the open beaker gives the value in water height of the capillary effect plus the submerged-depth effect. This is reduced to mercury height at  $0^{\circ}$ , and added to the gage pressure, as usual. The interior of the capillary must be wet with the substance just before the measurement is made. As we have seen, the amount of these corrections is small.

#### Characteristics of this Method.—

The valuable characteristics of the submerged-bulblet apparatus, which have already been described in full are, of course, retained in this dynamic isotenscope. This form of the apparatus possesses, however, several additional advantages: (1) It can be used for high pressures as well as low. (2) The test tube in the former apparatus contains a large volume of the confining liquid.

This acquires the temperature of the outside bath—and therefore transmits it to the bulb of the thermometer—rather slowly. Here the quantity of the confining liquid is much smaller. Then, too, the thermometer is hung directly in the bath liquid and a slight lag in the temperature of the confining liquid in the bulb *B*, if any existed, would have little or no effect upon the vapor pressure values obtained. This arrangement, therefore, permits the making of measurements of equal accuracy more rapidly. (3) The thermometer is not subjected to varying pressures, and the correction for the dilatation<sup>1</sup> of the bulb when the pressures are below 760 mm. is eliminated. Correction for compression of the bulb, due to the immersion in a liquid, may be made, but the magnitude of this correction is very small, averaging only  $0.02^{\circ}$  for 10 cm. immersion in water.

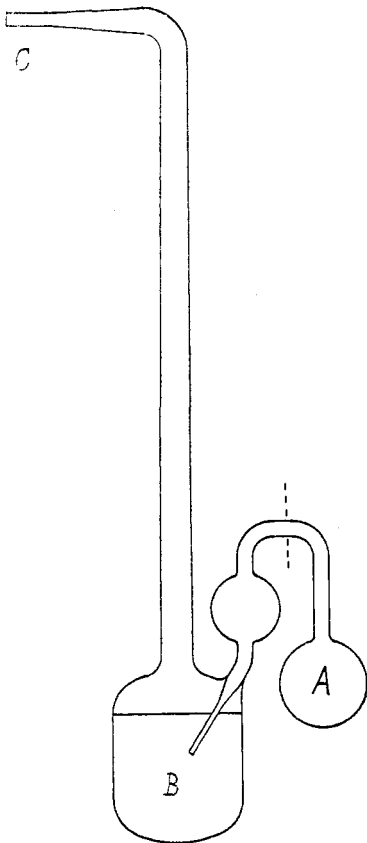


Fig. 1

<sup>1</sup> THIS JOURNAL, 32, 905.

When compared with the static apparatus, this dynamic apparatus will be seen to retain all the characteristics enumerated when that apparatus was described,<sup>1</sup> and to possess several additional advantages:

(1) There may be difficulty, with the static apparatus, in finding a suitable confining liquid. This difficulty cannot arise when the substance is a liquid, since the substance is employed in the U-tube to confine its own vapor. But when the substance is a solid, no liquid which has an appreciable vapor pressure of its own at the temperatures concerned, and none which interacts with the substance to give a gaseous product, and none in which the vapor of the substance is soluble, may be employed. Cases, such as those of the ammonium halides, phosphorus pentachloride, etc., therefore arise in which suitable confining fluids for certain ranges of temperature are hard to find. Thus, for ammonium chloride, fused silver chloride might be used, but would be available only above its melting point (450–460°). The present dynamic method is much more flexible, since possession of an appreciable vapor pressure by, or miscibility of the substance with, or chemical activity of the substance toward the confining liquid do not usually interfere with the operation of the apparatus, and would not, save in extreme cases, impair the accuracy of the results. The dynamic isoteniscope is therefore applicable to a wider range of cases.

(2) This dynamic method would find application when results by the static and the dynamic methods are to be compared. Such a case is mentioned, for example, by Smits and Scheffer,<sup>2</sup> who give reasons for anticipating that the values of the dissociation pressures of substances like aldehyde-ammonia might be widely different, according as the one or the other method was used.

This method has one disadvantage when compared with the static method, namely, that, in the latter, no corrections for submerged depth or for capillarity are required. The static method is therefore to be preferred, save where use of the dynamic one is indicated by considerations such as those mentioned in the preceding paragraphs.

**The Sample Determinations.**—As we have seen, water is at present the only substance suitable for testing the accuracy of a method of measuring vapor pressures. The determinations with this substance, using the simple form of the submerged bulblet, have already shown, however, that an apparatus operating on this principle is capable of yielding results of a high order of accuracy. The present form of the apparatus was applied, therefore, to the measurement of the vapor pressures of benzene and of ammonium chloride.

The bath, stirrer, barometer, gage, and platinum resistance ther-

<sup>1</sup> Studies in Vapor Pressure, III, Sec. 3, THIS JOURNAL, 32, 1419.

<sup>2</sup> Z. *physik. Chem.*, 65, 70 (1908)

meter, and the corrections involved in their use, were the same as those employed in the work with the static isoteniscope.<sup>1</sup> It is sufficient here to say that the temperatures are on the thermodynamic scale, assuming the boiling point of sulphur to be 445°, and that the error below 120° (benzene) was ascertained to be less than  $\pm 0.01^\circ$  and above 120° (ammonium chloride) less than  $\pm 0.1^\circ$ .

#### THE VAPOR PRESSURES OF BENZENE.

**Determinations by Previous Observers.**—The sample used by Regnault<sup>2</sup> melted at 4.45°, nearly a degree too low, and must have been impure. He employed the dynamic method above 24°. Ramsay and Young<sup>3</sup> removed thiophene and otherwise purified their sample, but do not give the melting point. They used their dynamic method<sup>4</sup> (up to 80°), in which the liquid trickled onto cotton surrounding the bulb of the thermometer. In this instance they state that correction was made for the dilatation of the bulb of the latter *in vacuo*. Young<sup>5</sup> continued the series above 80° by the barometer-static method<sup>6</sup> over mercury, using a part of the original material, and giving temperatures on the scale of the constant-volume air thermometer. Neubeck<sup>7</sup> used purified benzene boiling at 79.9° at 760 mm. The freezing point is not given. He boiled the substance in a flask under reduced pressure. His thermometer was compared with an air thermometer, but he did not correct for dilatation of the bulb *in vacuo*. The values given below are obtained by graphic interpolation from his data. Mangold<sup>8</sup> used benzene from benzoic acid. He gives the melting point 5.5°. He used Schmidt's<sup>9</sup> dynamic apparatus and did not correct for dilatation of the thermometer bulb *in vacuo*. Kahlbaum<sup>10</sup> purified his benzene, but gives no melting point. He determined the boiling points under reduced pressure, admitting air through a capillary, and did not correct for dilatation of the thermometer bulb. Woringer<sup>11</sup> gives no melting point of his purified benzene. He used the static method, over mercury, admitting the substance through a stopcock, but gives no facts in regard to exclusion of dissolved gases. The results found by these six observers are tabulated along with our own below.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Mem. Acad.*, 26, 416 (1862).

<sup>3</sup> *Phil. Mag.*, [5] 23, 61 (1887).

<sup>4</sup> Criticized, this series, No. III, Sec. 2, THIS JOURNAL, 32, 1418.

<sup>5</sup> *J. Chem. Soc.*, 55, 486 (1889).

<sup>6</sup> Criticized, this series, No. III, Secs. 1 and 2, THIS JOURNAL, 32, 1414 and 1416.

<sup>7</sup> *Z. physik. Chem.*, 1, 649 (1887).

<sup>8</sup> *Sitzungsber. Math.-Nat. Klasse, Kaiserl. Akad.*, 102 (IIa), 1071 (1893).

<sup>9</sup> *Z. physik. Chem.*, 7, 441.

<sup>10</sup> *Ibid.*, 26, 600 (1898).

<sup>11</sup> *Ibid.*, 34, 262 (1900).

**Purification of the Benzene.**—Kahlbaum's "thiophenfrei," crystallizable benzene was used. It was boiled under reflux with much sodium for three hours, at the end of which time no trace of hydrogen evolution could be detected. It was distilled, and the middle portion of the distillate, amounting to 1.46 liters, was used. This came over, after correction of the temperatures for changes in the barometric pressure, within  $0.01^\circ$ . A portion used for a freezing-point determination was boiled for fifteen minutes to remove dissolved gases. The freezing point was taken by two thermometers, the ice points of which had been ascertained immediately before, and they agreed in giving the value  $+5.40^\circ$ .

The physical properties of benzene have been carefully investigated by Lackowitz,<sup>1</sup> who found that they were greatly affected by dissolved air. He showed, for example, that the removal of dissolved air, not considered by previous observers, produced a marked lowering in the specific gravity. His freezing point was  $5.42 \pm 0.02^\circ$ . The lower freezing points of previous observers, namely, Regnault  $4.45^\circ$ , Jungfleisch  $3.00^\circ$ , W. Fischer  $5.3$ , and Schoop  $5.04$ , undoubtedly indicate insufficient purification. Linebarger<sup>2</sup> found  $5.4^\circ$  and Mangold  $5.5^\circ$ . Only Flink<sup>3</sup> claims to have reached  $6.06^\circ$ .

It appears, therefore, that our sample was probably as pure as that of Lackowitz. Even if we ignore the possibility, which he admits, that his freezing point may have been  $0.02^\circ$  too high, and assume that ours was lower than his by the same amount, the proportion of impurity which this represents would not noticeably affect the accuracy of the results. At the boiling point (about  $80^\circ$ ) it would give an elevation of only  $0.01^\circ$  and lower the vapor pressure by only  $0.2$  mm. This is the maximum effect reached by assuming that the whole of the supposed impurity was involatil, for our method provides for the removal of dissolved gases during the measurement.

**The Vapor Pressures of Benzene.**—Concentrated sulphuric acid was used as confining liquid in the bulb *B*. Since benzene vapor is soluble in this liquid, the reading was taken when the liquid had ascended the capillary to a fixed mark. Correction was made for submerged depth and for capillarity. The values obtained were as follows:

T.	63.16	66.55	71.09	74.79	80.30	90.48	95.67	100.42	105.97	111.54	119.93
P.	439.1	492.0	563.7	640.8	765.5	1031	1197	1364	1581	1820	2235

The observed pressures were plotted against the temperatures, a smooth curve was drawn through the resulting points, and the value of the pressure every  $5^\circ$  was read off. The results are given in the following table: For comparison, the corresponding values of Regnault (Rg), Ramsay

<sup>1</sup> *Berichte*, 21, 2210 (1888).

<sup>2</sup> *Am. Chem. J.*, 18, 437.

<sup>3</sup> *Beibl., Ann. Physik*, 8, 262.

and Young and Young (Y), Neubeck (N), Mangold (M), Kahlbaum (K), and Woringer (W) are given. The essential details of their methods have been discussed already.

t.	S & M.	Rg.	Y.	N.	M.	K.	W.
65°	463	463.4	...	465	468	...	...
70	551	547	548	550	554	546.5	559.5
75	650	643	...	645	653	...	...
80	757.5	752	755	760	764.5	750	773.5
85	879	...	...	...	...	...	...
90	1018	1015	1008	...	...	...	...
95	1180	...	...	...	...	...	...
100	1348	1340	1335	...	...	...	...
105	1542	...	...	...	...	...	...
110	1751	1744	1739	...	...	...	...
115	1983	....	...	...	...	...	...
120	2240	2235	2230	...	...	...	...

The boiling point, 80.12° at 760 mm., was also read from the curve. The values found by different observers are as follows:

Kopp (1847).....	80.40°	Ramsay and Young (1887)....	80.2°
Regnault (1863).....	80.36	Neubeck (1887).....	79.9
Brühl (1880).....	80.08	Louguinine.....	80.20
Flink (1884).....	80.37	Smith and Menzies (1910)....	80.12

#### THE VAPOR PRESSURES OF AMMONIUM CHLORIDE.

In order further to test the value of the dynamic isoteniscope method of measuring vapor pressures, we sought some substance difficult of study by the older methods. A non-fusing solid, the vapor of which attacked mercury, was required. That comparison might be possible, it was desirable also that the vapor pressures of the substance should have been previously determined by more than one observer and using methods professing some degree of accuracy. Ammonium chloride seemed to be the only such substance. Even with the present exceedingly adaptable method, this salt presented a problem of exceptional difficulty, and the results cannot claim the same degree of accuracy as do those with water and benzene. It will appear, however, that even in this case the limits of accuracy can be stated, and that the results are free from the undefined, and undoubtedly considerable sources of error with which the previous determinations may be charged.

**Previous Determinations.**—The vapor pressures of this salt have been determined by Horstmann,<sup>1</sup> by Ramsay and Young,<sup>2</sup> and by F. M. G. Johnson.<sup>3</sup> Horstmann's method was a dynamic one. He heated ammonium chloride in a combustion tube and noted the readings of a mer-

<sup>1</sup> *Ber.*, 2, 137 (1869).

<sup>2</sup> *Phil. Trans.*, 177, 71 (1886).

<sup>3</sup> *Z. physik. Chem.*, 61, 458 (1908); 65, 36 (1908).

cury thermometer immersed in the vapor, while the pressure of the air in the tube rose by stages from about 10 mm. to 760 mm.

Ramsay and Young made a large number of observations by several methods. One series from  $98^{\circ}$  to  $280^{\circ}$  was obtained statically over mercury in a barometer tube. Some permanent gas accumulated during the observations, and the value at the highest of these temperatures, for example, may be in doubt on this account alone about  $0.5^{\circ}$  (or 4.5 mm. = 3 per cent. of the whole). Observations from  $290^{\circ}$  to  $340^{\circ}$  were secured by enclosing a lump of the salt above a constriction in the closed limb of a U-tube. The bend was filled with mercury, and air pressures of known value could be applied to the vapor of the metal through the open limb. The U-tube was heated by the vapor of mercury boiling under various known pressures, and the corresponding temperatures were taken from Regnault's data, with an error, therefore, of  $1^{\circ}$  at  $340^{\circ}$ . Foreign gases and vapors were expelled by lowering the pressure, and allowing the vapor of the salt to escape past the mercury in the U-tube. At  $320^{\circ}$  and  $340^{\circ}$  the vapor pressure of the ammonium chloride did not give a constant value, but increased continuously. At  $320^{\circ}$  this increase was a linear function of the time, but the rate of increase per minute varied in different experiments from 0.2 mm. to 1 mm. per minute. The increase was under observation for as long as 390 minutes in one instance. With the help of time curves, the observations were corrected. This increase is attributed by the authors to the liberation of hydrogen by chemical action of the hydrogen chloride on the mercury. At  $340^{\circ}$  there was always a very rapid rise in pressure, amounting to from 32 to 67 mm., during the first twenty minutes, before the slower, uniform rise (of from 0.2 to 1 mm. per minute) set in. The authors suggest that the salt was cooled by the immediately preceding, rapid vaporization, and during the twenty minutes was regaining the temperature of the vapor bath. But this effect should have been almost as great at  $320^{\circ}$ , where no rapid rise was observed. In explaining both of these increases in pressure, the authors ignore entirely the effect of diffusion of the mercury vapor backwards to the surface of the salt. The result of this diffusion must be to increase the pressure and, if complete interdiffusion of the vapors had occurred, the limit would have been reached only when the total pressure equaled the sum of the vapor pressures of ammonium chloride and mercury. The evident fact is that when the confining liquid has a considerable vapor pressure of its own, and the interdiffusion of the vapors is possible during the observation, the resulting measurements of vapor pressure must always be of uncertain value. When we consider the fact that here the vapor pressure of the confining liquid, although less than that of the substance, was of the same order (at  $320^{\circ}$ , the pressures are 369 mm. and 445 mm., and at  $340^{\circ}$ , 548 mm. and 760 mm.,

respectively), it is surprising that the readings could be utilized at all.

The same observers made an independent series of measurements by their dynamic method, described in an earlier paper.<sup>1</sup> Here a block of the salt surrounded the thermometer bulb, and the distilling vessel containing the thermometer was heated by means of boiling mercury. The observations were made from 178.5° to 338.9°. The results, when plotted, were found to be somewhat scattered, and all on one side of the rather smooth curve that could be drawn through the points determined by the static method. The pressures at corresponding temperatures are all higher, being at 320° on an average about 56 mm. higher (estimated graphically), at 330° about 80 mm. higher, and at 333.5° about 100 mm. higher. The results by the static and dynamic methods, separately, as well as the values finally adopted, are given in a table at the close of this paper. A supplementary observation by a different dynamic method, in which the mass of the salt surrounding the thermometer bulb was placed in a combustion tube and heated with a Bunsen burner, gave a value at 338.35° of 762.1 mm. This confirmed the results by the static method rather than those by the dynamic, being less than 2° (equivalent to about 35 mm.) below the static temperature at the same pressure, while the dynamic temperature at the same pressure was 6° below static. Hence, the dynamic results were considered to be the less trustworthy, and in the curve which embodies the final results, much greater weight is given the static results. The final data are therefore essentially derived from a static method. The authors state that the difference of less than 2° above mentioned "may well be due to error of experiment." The results at the highest temperature are thus estimated to be subject to an error of at least  $\pm 2^\circ$ , or, according to their curve,  $\pm 35$  mm. Considering the extreme experimental difficulties involved in the method, this error cannot be considered excessive. The specific sources of error in these methods have already been discussed at length.<sup>2</sup>

F. M. G. Johnson employed the Ladenburg manometer, consisting of a flattened glass tube, wound in a spiral. The external pressure required to bring the attached mirror back to the zero position was measured. His method was therefore static, but he avoided the great difficulties connected with the common static methods in which mercury is used. Assuming that, as the author says, the spiral was capable easily of showing a pressure change of "the order of 1 mm." (although he does not state that this degree of sensitiveness was maintained at 335°), the chief errors to which his method was liable arise from four causes, namely, gases occluded in or absorbed by the solid substance, unequal distribu-

<sup>1</sup> *Phil. Trans.*, 175, 37 (1886); *J. Chem. Soc.*, 47, 42 (1885).

<sup>2</sup> This series, No. III, Secs. 1 and 2, *THIS JOURNAL*, 32, 1413-9.



tion of temperature in the air bath he used for heating, the untrustworthiness of mercury thermometers at such high temperatures, and the unfortunate method used for standardizing the thermometers. The efficiency of the whole arrangement was, indeed, tested by a determination of the vapor pressures of iodine, and the results were found to agree well with those of Ramsay and Young. But the test ranged from  $80.5^{\circ}$  to only  $178.5^{\circ}$ , while the experiments with ammonium chloride ran from  $211^{\circ}$  to  $335^{\circ}$ . The temperature errors would not assert themselves strongly until above  $200^{\circ}$ , so that this test cannot be accepted as a rigid demonstration of the adequacy of the precautions. Attention must therefore be drawn to the sources of error individually.

The apparatus and material were freed thoroughly from moisture by means of phosphorus pentoxide, and to effect this the former was pumped out repeatedly and left evacuated for a long period. The apparatus was heated during the process, for the purpose of assisting the desiccation and of driving out adhering air. But the parts containing the pentoxide and the salt could not be heated. The salt had previously been sublimed twice. It will be seen, however, that the complete expulsion of adhering gases was not insured. The quartz spiral gage used by Preuner and Schupp<sup>1</sup> is so constructed as to permit of boiling out before sealing, when vapor pressures are to be determined. But this process could not be applied when, as was the case with Johnson's apparatus, a bulb for the simultaneous determination of the vapor density was attached. It is a pity that the zero of the gage was not redetermined after the experiments, as this would not only have shown whether any permanent gas had been liberated, but would also have afforded a means of detecting other irregularities, such as a permanent distortion of the spiral.

Johnson's apparatus was heated in an unstirred air bath provided with a gas pressure regulator which kept the temperature constant  $\pm 1^{\circ}$ . As we have seen,<sup>2</sup> however, an air bath is by far the least satisfactory means of keeping the temperature uniform and constant. Aside from the inherent causes of defective thermal equilibrium, in this case a copper tube was inserted through the top of the bath, forming a separate compartment surrounding the pocket containing the solid ammonium chloride. The purpose of this was to keep the salt cooler than the bulb and spiral. The temperatures in the copper tube and in the rest of the bath differed by  $22^{\circ}$  at  $323^{\circ}$ . Now, if maintaining *one* temperature in an air bath is difficult, keeping *two* temperatures each constant and uniform is much more difficult. This feature of the apparatus, therefore, involves a source of considerable uncertainty.

The temperatures were ascertained with a nitrogen-filled, mercury

<sup>1</sup> *Z. physik. Chem.*, 68, 129.

<sup>2</sup> This series, No. III, Sec. I, *THIS JOURNAL*, 32, 1413.

thermometer. It is well known, however, that such a thermometer, when kept for a considerable time at a high temperature, suffers distillation of the mercury into the upper part of the bore,<sup>1</sup> and gives untrustworthy readings, with an error of about  $\pm 1^\circ$ . On account of the difficulty in making due correction, the error is greater when the thread is not completely immersed.

Finally Johnson standardized the thermometer by using the vapor pressure curve of mercury. The data used were those of Ramsay and Young.<sup>2</sup> Young,<sup>3</sup> however, has himself pointed out and corrected some of the most serious inaccuracies which have meantime come to light in these data. His corrections alter the temperature at  $340^\circ$  by  $1^\circ$ .

The present status of our knowledge of the vapor pressures of ammonium chloride may now be summed up. Horstmann makes no professions of exact thermometry and  $\pm 5^\circ$  at the highest temperature is a conservative estimate of the limits of error involved. The known error of Ramsay and Young's measurements is  $\pm 1^\circ$  at the lower temperatures and  $\pm 2^\circ$  at the highest. But the uncertainty of interpreting the progressive increase in the pressures at  $320^\circ$  and  $340^\circ$  introduces an additional possibility of error, the magnitude of which cannot be assessed. Johnson's measurements are affected by such considerable temperature errors, the most serious of which are of unknown magnitude, that his measurements can be regarded as approximate only. In considering all these determinations, it must be remembered that, at  $335^\circ$ , an error of  $\pm 1^\circ$  corresponds to an error of  $\pm 15$  mm. in pressure. It is therefore evident that the vapor pressures of ammonium chloride are in need of re-determination by a method which permits of the definite estimation of the limits of error involved.

**The Vapor Pressures of Ammonium Chloride.**—The bulb *A* (outside diameter 22 mm.) was filled completely with ammonium chloride. The latter, Kahlbaum's purest form of the salt, was finely pulverized and was purposely used without drying. Since the method itself involves a fractionation, special treatment to remove volatil impurities was unnecessary. Hydrochlorides of coal-tar bases were proved to be absent.

The bath was filled with the mixture of potassium and sodium nitrates, and, no other transparent, fusible substance of a suitable nature being available, the outer bulb *B* was charged with the same mixture. The ammonium chloride vapor, in passing through this liquid, caused a continuous production of nitrous oxide. The method was therefore seen

<sup>1</sup> Ostwald-Luther, *Physikochem. Mess*, [1902] 78. In such a thermometer we have frequently observed with a lens droplets of mercury and particles of a red substance (HgO?) accumulating above the thread.

<sup>2</sup> *J. Chem. Soc.*, 49, 37 (1886). We are indebted to the author for privately informing us of this fact.

<sup>3</sup> *J. Chem. Soc.*, 59, 629 (1891).

under the greatest disadvantage, since it was impossible to observe a complete cessation of the stream of vapor. The pressure taken was that at which the stream of gas reached a minimum volume.

Our temperature error of less than  $\pm 0.1^\circ$  corresponds at the lowest temperature to  $\pm 0.25$  mm. and at the highest to  $\pm 1.5$  mm. These are therefore the limits of error of the apparatus *per se*. The difficulty in observing the point of minimum gas evolution, however, introduces a special source of error peculiar to this substance. From a consideration of the degree of sharpness with which the observations could be made, we estimate this error at about  $\pm 5$  mm. in the individual readings. The consistency of our results, as shown by the way in which they lie upon a smooth pressure-temperature curve, confirms our belief that the errors are not greater than this.

The following results are corrected for immersed depth and for capillarity, and are given to the nearest millimeter:

Temperature.....	278.3	291.6	298.7	308.5	316.4	325.4	332.9
Pressure.....	131	199	240	322	406	518	633

For comparison, the data of Horstmann (two points, X), Ramsay and Young<sup>1</sup> (curve I), Johnson, undried substance<sup>2</sup> (curve II), and Smith and Menzies (curve III), are plotted in Fig. 2. It will be seen that the last curve lies between the other two.

The following table contains the data read from the various curves. As throwing some light on the relative trustworthiness of Ramsay and Young's static and dynamic methods, as applied to a substance like this, the observations obtained by each of these have been treated separately and the resulting pressure readings are given in two additional columns:

R & Y.						
t.	H.	Curve.	Observations.		J.	S & M.
			Static.	Dynamic.		
280	...	143	140.5	147	132	138
290	...	195.5	189	200	178	189
300	259.5	264.5	251	275	237	252
310	...	350	333.5	367	309	336
320	...	460.5	443.5	500	401	447
330	...	599.5	596	675	518	587
333.5	...	661	653	750	566	642
340	778.1	777	759.5	...	678	...

From this comparison it will be seen that Ramsay and Young's static results, when taken by themselves, agrees remarkably well with our dy-

<sup>1</sup> Reproduction of the author's own curve. Johnson ignores the curve, which embodies the authors' conclusions from all their observations, and uses for comparison only certain of the single observations, all taken from the static series.

<sup>2</sup> Dr. Johnson informs us that in his first paper (p. 462), the last temperature,  $335^\circ$ , should be  $345^\circ$ . In the curve on the opposite page, the  $211^\circ$  point is misplaced. In the second paper (p. 37), the  $\text{NH}_4\text{Cl}$  curve is incorrect.

dynamic results, the divergencies exceeding the estimated error of our measurements, namely  $\pm 5$  mm., only above  $320^\circ$ . The inferiority of their

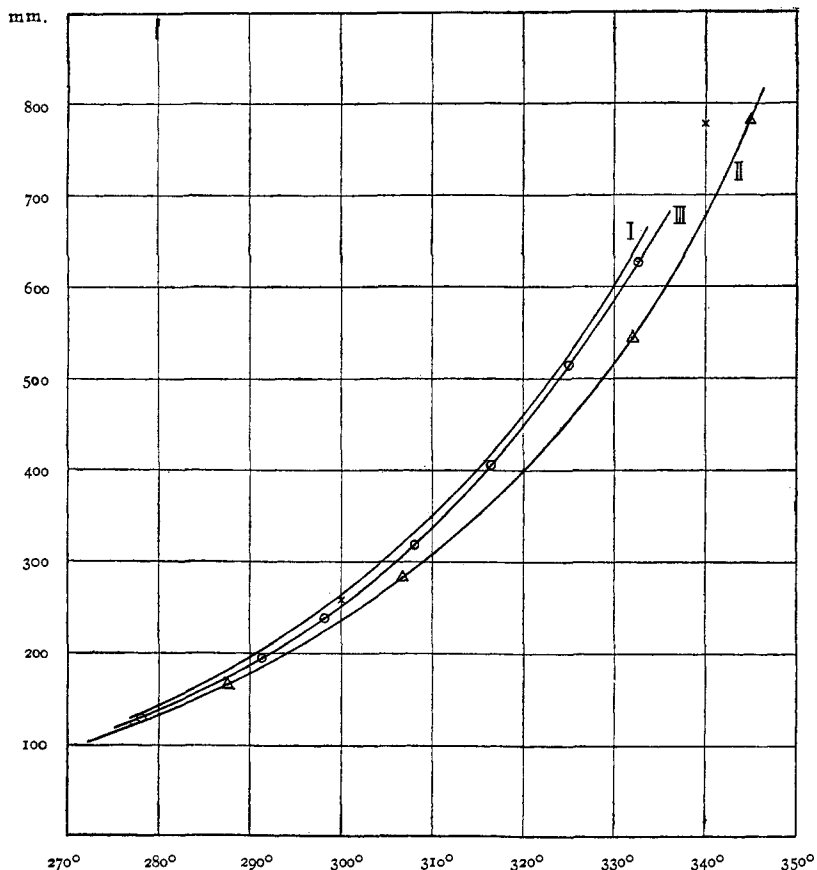


Fig. 2.

dynamic method, at least when applied to a substance like this, is apparent.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 61.]

### THE POTENTIAL OF THE SODIUM ELECTRODE.

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The electrode potentials of a number of important groups of metals have not been measured hitherto, because their action upon water is such as to preclude the possibility of obtaining equilibrium conditions. Among these groups, those comprising the alkali metals and the metals