VOL. XXXIII. JUNE, 1911. NO. 6.

THE JOURNAL

OF THE

American Chemical Society

THE VAPOR PRESSURES OF MERCURIC CHLORIDE, BROMIDE AND IODIDE.

BY F. M. G. JOHNSON.

Received March 10, 1911.

The measurement of the vapor pressures of mercuric chloride, bromide and iodide has already received the attention of a number of investigators. Faraday appears to have been the first to observe that these salts are volatil at comparatively low temperatures (later contradicted by Riegel[1]) but until a much later date no quantitative measurements were made. The chloride has been studied by Richter[2] and Carnelley,[3] while this salt and the bromide and iodide have been investigated by Arctowski[4] and Wiedemann, Stelzner and Niederschulte,[5] the iodide by Ditte.[6] Dynamic methods chiefly were employed, which at high temperatures are not likely to give reliable results; further, the figures given by these investigators show considerable disagreement in many instances.

The method employed in this work was similar to that used for determining the dissociation pressures of ammonium chloride, etc.[7] A few changes were made in the apparatus and are shown in Fig. 1.

The substance, of which the vapor pressure is to be determined, is placed in the tube at F which, having been evacuated with the mercury pump

[1] *Arch. Pharm.*, 2, 61, 294.

[2] *Ber.*, 19, 1057 (1886).

[3] Melting and Boiling Pt. Tables, (1887).

[4] *Z. anorg. Chem.*, 7, 167 (1894). *Ibid.*, 12, 260 (1903). } Abegg, Handbuch, 2, II, 622.

[5] *Verh. phys. Ges.*, 3, 159 (1905).

[6] *Compt. rend.*, 140, 1162.

[7] *Z. physik. Chem.*, 61, 457 (1908); 65, 36 (1908).

and sealed, is surrounded by the metal tube shown in the diagram to insure equalization of temperature.

To obtain the zero reading of the spiral at any temperature at zero pressure, air is blown through the tube *A* to cool the substance in *F*. The tube *A* may be removed and replaced by a plug of asbestos when a pressure reading is to be taken. *B* is a cylinder of asbestos closed at the bottom by a plug of asbestos wool. Readings of the spiral at zero pressure were taken before and after each vapor pressure reading. If they differed appreciably, the observations were repeated.

The interior of the hollow copper cylinder *E* was connected by means of the rubber tube *D* with a reservoir of nitrogen *C*. This had as its object the prevention of oxidation in the interior of the cylinder, which when air was used became considerable at high temperatures, with consequent inefficiency of the temperature regulation. The spiral used was sensitive to a pressure change of 1 mm. of mercury.

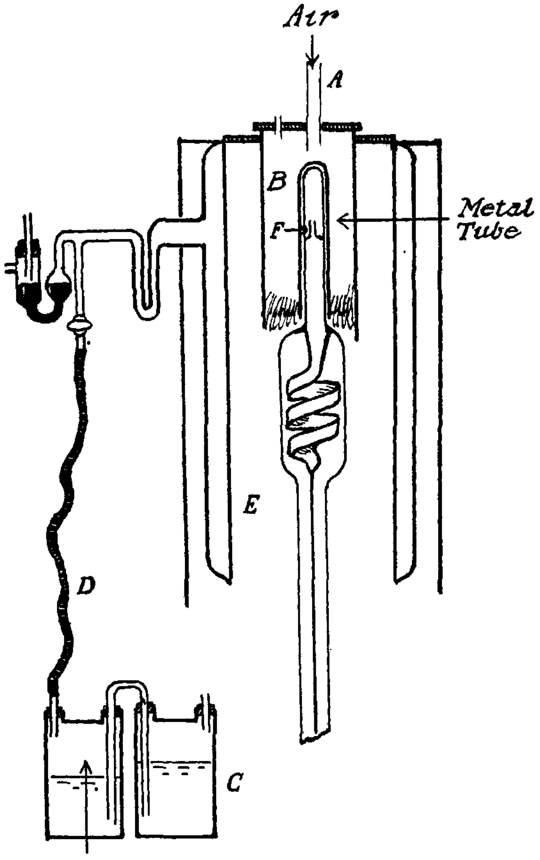

Fig. 1.

Mercuric Chloride.

The salt used was obtained from Harrington Bros. It was recrystallized several times from its aqueous solution and then sublimed. The following figures were obtained:

Temp.	Press. in mm. Hg.
152°	3
195	20
231	82
256	198
262	237
275	375
278	421
283	481
302	754

As may be seen from the diagram, Fig. 2, there is a decided break in the curve at 277° corresponding to the melting point as found recently by Jonker.[1] Carnelley[2] gives 287° as the temperature at the melting point. From the curve the boiling point under 760 mm. pressure is 302.5°. The values found by Hittorf, Carnelley, and Freyer and Freyer[2] vary between 302° and 307°.[2]

Mercuric Bromide.

The salt employed was prepared from mercury and bromine in aqueous solution. It was then recrystallized several times, dried and sublimed. The following results were obtained:

Temp.	Press. of mm. Hg.
162°	3
206	29
229	73
233	88
238	106
247	136
255	174
276	293
290	413
306	597
318.5	764

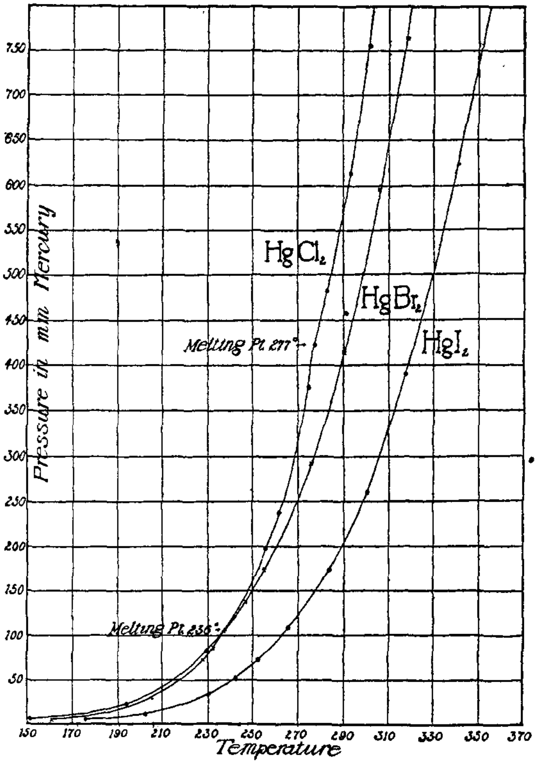

Fig. 2.

The curve obtained is shown in Fig. 2, in which the effect of the melting point is quite evident. The temperature at this point, 236°, agrees with

---

[1] *Chem. Weekblad*, 6, 1053 (1909).

[2] Landolt and Börnstein, Tabellen.

that found by Reinders.[1] Other values found previously by Oppenheim[2] and Carnelley[2] vary between 222° and 244°. The curve shows the boiling point under 760 mm. pressure to be 318°. Carnelley and Freyer and Freyer[2] found 319° and 325° respectively.

Mercuric Iodide.

The salt used was prepared from mercuric nitrate and potassium iodide in aqueous solution. It was recrystallized several times from a nitric acid solution, carefully washed, dried and sublimed. The following are the values found:

Temp.	Press. in mm. Hg.
177°	3
203	10
231	32
243.5	51
253	73
266	108
284.5	173
301	260
318	390
341	624

Fig. 2 shows the curve. It was impossible to observe any decided change in the curve at the melting point 254°, as observed by Reinders.[1] By extrapolation of the curve the boiling point under 760 mm. pressure is seen to be in the neighborhood of 351°. Carnelley[2] found 349°. Other values found previously by Hittorf[2] and Carnelley[2] vary between 339° and 359°.

The following table is perhaps of interest. The heats of vaporization between the pressures of 700 and 800 mm. have been calculated by means of the Clausius formula, $d \log p/dT = Q/RT^2$ assuming that no dissociation of the vapor occurs.

	M. p.	B. p.	Q in cal.	$Q/T_{1\ 750\ \text{mm.}}$	$T_{1\ 750\ \text{mm.}}/T_{2\ 450\ \text{mm.}}$
HgCl..............	277	302.5	14.630	25.44	1.040
HgBr..............	236	318	14.240	24.13	1.043
HgI................	254	351	15.840	25.47	1.042

The values for Q/T_1 (Trouton's rule) and T_1/T_2 (rule of Ramsay and Young) show good agreement.

Note (added April 24, 1911).—Since this work was completed a paper on "The Vapor Pressures and Molecular Volumes of the Mercuric Halides," by Prideaux,[3] has been published. The method for measuring the vapor pressures consisted in determining the boiling point under

---

[1] *Z. physik. Chem.*, **32**, 494 (1900).

[2] Landolt and Börnstein, Tabellen.

[3] *J. Chem. Soc.*, **97**, 2032.

definit pressures, hence values for the vapor pressures at temperatures below the melting points are not given.

McGill University,
Montreal.

[Contribution from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 67.]

THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE, HYDROCHLORIC ACID AND THEIR MIXTURES.

By William C. Bray and Franklin L. Hunt.

Received April 1, 1911.

Introduction.

The object of this investigation was to study, for two salts of widely different conductances, the validity of the present method of calculating the specific conductance of mixtures of salts with a common ion. It has been concluded, from a consideration of existing conductance data,[1] that the degree of ionization of each salt in such a mixture is the same as in a solution of the pure salt at the same total ion concentration. By means of this "ionization rule," and with the additional assumption that the conductances of the ions are constant, values have been calculated for the specific conductances of mixtures which agree well with those determined experimentally.

In any method of calculating the specific conductance L of a binary mixture, this quantity may be divided into two parts, L′ and L″, the *individual specific conductances* of the separate salts, when L = L′ + L″. Each of these may be calculated by means of a relation of the form:

$$1000\,L' = (C'\gamma')(\Lambda'_k + \Lambda'_a), \qquad (1)$$

where C′ is the concentration, γ' the degree of ionization, $(\Lambda'_k + \Lambda'_a)$ the sum of the equivalent conductances of the ions of one of the salts in the mixture. According to the above rule γ' has the same value as in a solution of the single salt at the same total ion concentration, and has hitherto been calculated by a method of approximation on the assumption that $\Lambda'_k + \Lambda'_a$ is constant and equal to Λ'_0 the conductance of the salt at zero concentration. This assumption is, of course, an uncertain one in any case, and especially when the transference number is known to change with the concentration. For this reason it must be admitted that the values of ion concentrations calculated by the above method may be considerably in error and it will be shown later that this may be the case even when the calculated and measured conductances agree perfectly.

If in the above formula stress is laid on the idea of equivalent conductance, instead of ion concentration $(C'\gamma')$, then we may write:

---

[1] For references see Sherrill, This Journal, 32, 74 (1910); Mackay, *Ibid.*, 33, 308 (1911).