25°. Col. 7 shows that the degree of dissociation of potassium iodide is greater at 0° than at 25°. Bray and MacKay found the same effect of temperature on comparing their results at 25° with those of Kohlrausch at 18°. The influence of temperature on the dissociation of KI_3, on the other hand, although slight, is in the opposite direction. The solubility of iodine in potassium iodide solutions is somewhat less at 0° than at 25° (Cols. 13 and 14).

The most interesting comparison is found in Cols. 16, 22 and 23, which show a much greater constancy at 0° than at 25°. It is evident that the results conform to the requirements of the mass law much better at 0° than at 25°.

There is a slight deviation in the results at 0° with the two strongest solutions in the same direction as at 25°, but the deviations are comparatively small. The deviation from the mass law at 25° is discussed in considerable detail by Bray and MacKay, who reach the conclusion that the "activity of the ions is not proportional to their concentration."

Summary.

1. The conductances at 0° of potassium iodide solutions and of the same solutions saturated with iodine between 0.1 and 0.001 *N* have been measured.
2. The solubility of iodine in each of the solutions and in pure water has been determined.
3. The degree of dissociation of potassium iodide at 0° and 25° have been corrected for the change of viscosity of the solution.
4. The mobilities of the iodide and triiodide ions were found to be 43.4 and 22.8, respectively, at 0°.
5. The hydrolysis constant of iodine in water at 0° was found to be 9×10^{-15}.
6. The increase of the mass-law constant of the reaction $I_2 + I^- \rightleftarrows I_3^-$ with the concentration of the solutions, which was found by Bray and MacKay at 25°, we now find at 0°.

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ON THE ASSOCIATION OF MERCURIC CHLORIDE IN WATER SOLUTION.

BY G. A. LINHART.

Received December 7, 1914.

It is a generally accepted fact that mercuric chloride in solution of a pure indifferent solvent does not associate.[1] The data thus far published are the results obtained from a study of the molecular weight of mercuric chloride in several organic solvents,[2] and seem to justify the above con-

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[1] Abegg's *Handbuch der Anorg. Chem.*, II, 2, 615.

[2] Castro, *Gazz. chim. ital.*, 28, II, 317; Salvadori, *Ibid.*, 26, I, 237.

clusion. The ebullioscopic data, however, relative to the molecular weight in water solution are wholly unsatisfactory, as no two sets of figures, not even of the same investigator, agree. Thus Beckmann[1] gives for the molecular weight of mercuric chloride 318 and 297, although the amounts of mercuric chloride used in each of these determinations differed only by about 2%. Again he gives 284 and 275 when the original amounts of mercuric chloride used differed only by about 0.4%. Finally he gives 342 as the molecular weight. The same is true of the work of Kahlenberg[2] and Landsberger[3] on the same subject. Another striking example of this unusual behavior of mercuric chloride in water solution are the results obtained by Hantzsch and Vagt,[4] and Morse[5] from distribution ratio measurements of mercuric chloride between water and toluene.

In view of these obvious discrepancies and of others more involved[6] the present work had been undertaken to discover, if possible, some general property of mercuric chloride in water solution, which would account for its peculiar behavior in the several cases cited above. It will be shown in this paper, both experimentally and theoretically, that the deviation in the molecular weight, as well as in the distribution ratio, is due to the presence in water solution of the double molecules of mercuric chloride to a considerable extent, and also that the degree of association varies with the concentration and temperature, and may be determined accurately by means of several physical-chemical methods.

From the work of Hantzsch and Vagt, as well as that of Morse, it is evident that the distribution ratio of mercuric chloride between water and toluene is not constant, but decreases with the dilution. As mercuric chloride exists in the form of simple molecules in organic non-aqueous indifferent solvents,[4] this is exactly what would be expected, since only the simple molecules can then enter the toluene layer. It follows that the lower the concentration of the total mercuric chloride in the water phase, the lower will be the number of double molecules, Hg_2Cl_4, and therefore the proportionately greater will be the number of simple molecules entering the toluene phase, thereby causing a gradual decrease in the distribution ratio of mercuric chloride between the water and toluene. That this is actually the case may be shown from a recalculation of the results of the authors mentioned above.[7] A small correction, however,

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[1] *Z. phys. Chem.*, 6, 460 (1890).

[2] *J. Phys. Chem.*, 5, 367 (1901).

[3] *Z. anorg. Chem.*, 17, 450 (1898).

[4] *Z. phys. Chem.*, 38, 735 (1901).

[5] *Ibid.*, 41, 709 (1902).

[6] Sand and Breest, *Z. phys. Chem.*, 59, 426 (1907); 60, 237 (1907); Sherrill, *Z. Elektrochem.*, 9, 549 (1903); *Z. phys. Chem.*, 43, 705 (1903); 47, 103 (1904).

[7] See these in discussion of results.

had to be applied in order to make their results fit the theory developed in this paper, because these investigators analyzed the water phase only. This means that a 0.3% error (which is within experimental error in the use of the sulfide method) in the water phase would correspond to about 4% error in the toluene phase. In recalculating their results, therefore, the corrections were applied to the actual amounts of mercuric chloride found in the water phase (and these corrections were in all cases well within experimental error) and the difference between these and the total mercuric chloride was taken as the amount of mercuric chloride in the toluene phase. It might be stated here that the method developed in this work and described below makes it possible not only to remove every trace of mercuric chloride from the benzene or toluene but also aids greatly in the subsequent precipitation as mercuric sulfide by hydrogen sulfide.

In a recent investigation[1] of the complex salts that mercuric chloride forms with sodium chloride and barium chloride, respectively, it was found that in a saturated solution of either of the above salts a comparatively small amount of mercuric chloride does not exist as such, but is completely in the form of complexes, such as $NaHgCl_3$, Na_2HgCl_4, and $BaHgCl_4$. Moreover, as these compounds have been found to be practically insoluble in benzene, the usefulness of this method of extracting the mercuric chloride from the benzene phase was at once apparent. Attention is also called to the fact that in order to establish the existence of the double molecules of mercuric chloride in water solution, the greatest possible degree of accuracy is required in carrying out the experiments, and the results obtained from the analyses of the benzene phase and not those of the water phase must be used in the calculation of the equilibrium constants of the simple and double molecules existing together in water solution. The amount of mercuric chloride in the water phase is found by difference.

Experimental Part.

Method of Procedure.—The desired amount of pure mercuric chloride was weighed out on a watch glass and washed into a calibrated 250 cc. flask by means of a funnel, sufficient water added to dissolve the mercuric chloride completely (which was hastened by frequent shaking) and the flask then placed in a thermostat. After the solution reached the temperature of the bath the flask was filled to the mark, was thoroughly shaken and then replaced in the thermostat. Of this solution 200 cc. were transferred by means of a calibrated pipet into a stout bottle of 500 cc. capacity provided with a ground glass topper. 200 cc. of thiophene-free benzene, which was also at the temperature of the thermostat, were then added after which the glass stopper was carefully inserted and the bottle rendered airtight by pouring paraffin upon the depression be-

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[1] The work on this subject will appear in a subsequent number of THIS JOURNAL.

tween the outer part of the stopper and the lip of the bottle. After the paraffin solidified and showed no air holes a piece of strong canvas strap, about two inches in width, was used in strapping the stopper to the neck of the bottle. (This precaution was found necessary, as the paraffin seal would sometimes soften and allow a perceptible amount of benzene to escape which could be noticed by its odor.) The bottles thus prepared were immersed up to the necks in a thermostat kept at constant temperature. Every two hours for about ten hours the bottles were thoroughly shaken and then allowed to remain over night in the thermostat. Each bottle was then in turn carefully removed, placed up to the neck in a glass vessel containing water of approximately the same temperature as that of the thermostat. (This precaution both in the filling and in the subsequent withdrawing of the solution was taken because of the uneven expansion of the two phases, since 200 cc. of water at room tem-

CURVES REPRESENTING SOLUBILITIES OF MERCURIC CHLORIDE IN WATER AND BENZENE, RESPECTIVELY.

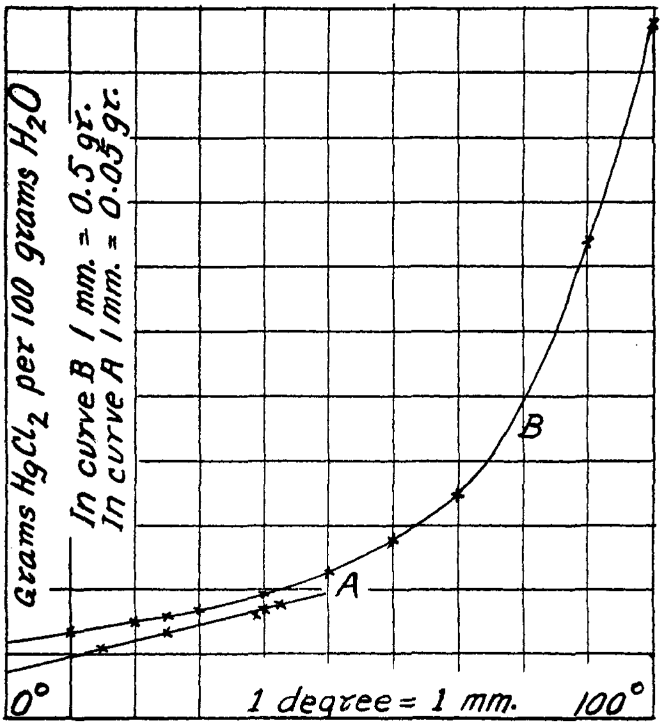

Fig. 1.

Curve A represents the solubility of mercuric chloride in benzene.
Curve B represents the solubility of mercuric chloride in water.

perature would expand to about 201 cc. at 40°, while 200 cc. of benzene would expand to about 204 cc. under like conditions.) After removing the strap and the paraffin seal the groove was carefully wiped with a piece of filter paper, and the stopper gently tapped and removed without disturbing the two layers.

CURVES REPRESENTING THE DISTRIBUTION RATIOS OF MERCURIC CHLORIDE BETWEEN WATER AND BENZENE AND BETWEEN WATER AND TOLUENE.

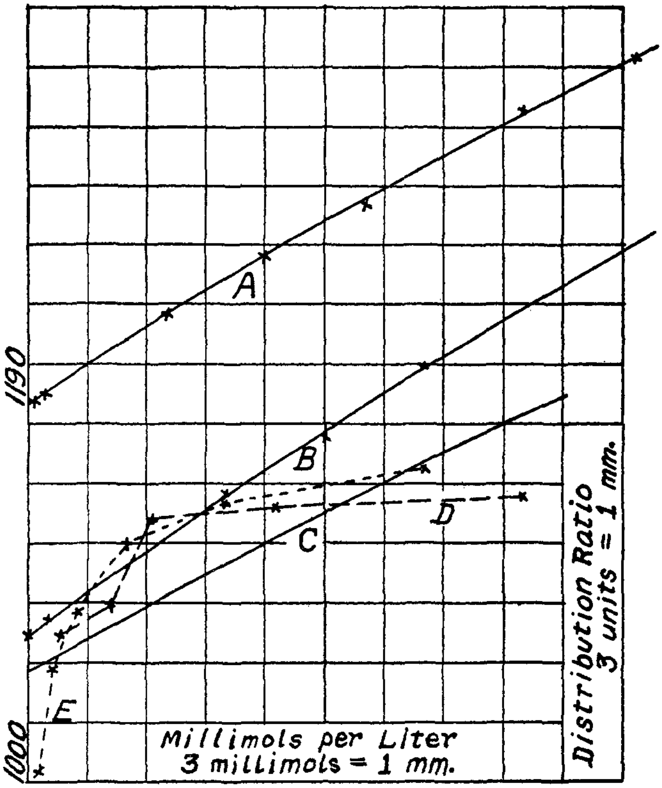

Fig. 2.

Curve A represents the slope of the distribution ratio at 25° of mercuric chloride between water and benzene.

Curve B represents the slope of the distribution ratio of mercuric chloride at 40° between water and benzene.

Curve C represents the slope of the calculated ratios of mercuric chloride between water and toluene at 25°.

Curve D represents the ratios given by Hantzsch and Vagt.

Curve E represents the ratios given by Morse.

Both of these curves (D and E) should coincide with C, which is the one theoretically calculated.

It has been found expedient in pipeting benzene not to apply suction, but to blow the benzene into the pipet which was provided with a two-hole rubber stopper exactly fitting the glass bottle. Before inserting the pipet for the purpose of withdrawing the solution, the rubber stopper was so adjusted that the end of the pipet reached within about $^1/_2$ inch of the lower layer, in order not to disturb it. Of the 200 cc. of the benzene layer about three-fourths were slowly and uninterruptedly blown into the pipet to some distance above the 150 cc. mark, the upper end of the pipet stopped with the finger, the pipet slowly removed with the rubber stopper on it, and after allowing the benzene to flow down to the mark it was run into a 500 cc. separatory funnel. (The pipet was, of course, thoroughly rinsed with pure benzene after each operation, allowed to drain and then dried by means of a current of air.) 100 cc. of a clear saturated sodium chloride solution were then added, and the funnel vigorously shaken and finally allowed to remain at rest until the boundary line between the two layers became sharp. The lower layer was then run out into a 500 cc. beaker and the treatment of the benzene repeated with another 100 cc. of the clear saturated sodium chloride solution. Two treatments were found sufficient in most cases to remove every trace of the mercuric chloride from the benzene. To these 200 cc. of the saturated sodium chloride solution in the beaker containing the mercuric chloride were added 150 cc. of hot distilled water and a few cubic centimeters of pure hydrochloric acid. A slow current of well washed hydrogen sulfide gas was then passed into the solution (care being taken to keep the beaker always covered, thereby excluding possible oxidation of the hydrogen sulfide to free sulfur) until the precipitate was completely settled and the supernatant liquid became perfectly clear. This supernatant liquid was then passed through an ignited and weighed perforated platinum crucible fitted with an asbestos mat, the precipitate washed several times by decantation with freshly prepared warm hydrogen sulfide water, the precipitate washed into the crucible and the washing continued until all traces of chlorides were removed. It is important to note that the precipitate in the crucible cakes and shrinks, due to the suction, and that the crevices thus formed allow the wash water to be sucked through without effectively washing the precipitate. It is therefore necessary to plaster over these crevices with the flattened end of a glass rod. Also if the proper precautions have been taken in the precipitation of the mercuric sulfide, as well as in the preparation of the hydrogen sulfide water, the washing of the precipitate need not be followed by carbon disulfide and must not be followed by pure water, which would cause the mercuric sulfide to go through the asbestos filter in the form of colloidal mercuric sulfide. The precipitate was then dried in an oven between 105° and 110° to constant weight, allowed to cool in a desiccator and finally weighed.

TABLE I.—EXPERIMENTAL RESULTS.

A.	Cw°.	$^3/_4B$.	Cb.	Cw.	R.	C_{HgCl_2}.	$C_{Hg_2Cl_4}$.	$(10)^4K$.
				25°				
...	...	...	21.000[1]	286.600[1]	13.65	249.900	18.350	2.94
13550.0	250.0	605.2	17.391	232.609	13.38	206.953	12.828	3.00
9214.0	170.0	425.4	12.224	157.776	12.91	145.478	6.149	2.91
6504.0	120.0	306.2	8.798	111.202	12.64	104.696	3.253	2.97
3794.0	70.0	182.5	5.244	64.756	12.35	62.404	1.176	3.02
433.6	8.0	21.5	0.6177	7.3823	11.95	7.3506	0.0159	2.94
216.8	4.0	10.8	0.310	3.690	11.90	....	...	..
108.4	2.0	5.4	0.155	1.845	11.90	....	...	..
			At extreme dilution		11.90 = R_∞			
				40°				
...	...	...	26.470[1]	346.000[1]	13.07	284.023	30.989	3.84
10840.0	200.0	532.6	15.296	184.704	12.08	164.126	10.289	3.83
8130.0	150.0	409.7	11.774	138.226	11.74	126.335	5.946	3.73
5420.0	100.0	279.8	8.041	91.959	11.44	86.280	2.840	3.82
2710.0	50.0	144.1	4.140	45.860	11.08	44.422	0.720	3.65
542.0	10.0	29.5	0.847	9.153	10.81	9.088	0.032	3.87
			At extreme dilution		10.73 = R_∞			

A denotes the number of milligrams of mercuric chloride per 200 cc. of water solution.

Cw° denotes the number of millimols of mercuric chloride per liter of water solution.

$^3/_4B$ denotes the milligrams of mercuric sulfide actually obtained from the analyses of $^3/_4 \times 200 = 150$ cm³. of the benzene phase.

Cb denotes the number of millimols of mercuric chloride per liter of the benzene phase.

$Cw^\circ - Cb = Cw$, denotes the number of millimols of mercuric chloride per liter of the water phase.

$$\frac{Cw}{Cb} = R \text{ denotes, the distribution ratio.}$$

$$C_{HgCl_2} = R_\infty Cb$$

$$C_{HgCl_2} = \frac{Cw - R_\infty Cb}{2}$$

$$(10)^4K = \frac{C_{Hg_2Cl_4}}{C^2_{HgCl_2}}$$

Discussion of the Results.

From the form of the equation,

$$HgCl_2 + HgCl_2 \rightleftarrows Hg.HgCl_4 \quad \text{or}$$

$$K = \frac{C_{Hg_2Cl_4}}{C^2_{HgCl_2}} = \frac{^1/_2(Cw - CbR_\infty)}{(CbR_\infty)^2},$$

by means of which the equilibrium constants were calculated, it is evident that a knowledge of the true distribution ratio of the simple molecules, $HgCl_2$, between the water and the benzene ($H_2O \longleftarrow HgCl_2 \longrightarrow C_6H_6$)

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[1] See calculations at the end of the article regarding these figures.

is very essential. This value may be found either by working with dilutions (4 and 2 millimols per liter, respectively) at which practically all the mercuric chloride is in the form of $HgCl_2$, when the resulting distribution ratios become concordant; or, by plotting the several ratios obtained from the experiments at more convenient concentrations, and extending the line connecting these points to the coördinate representing zero concentration. In the experiments at 25° the former, or experi-

CURVES REPRESENTING THE ELEVATION OF THE BOILING POINTS.

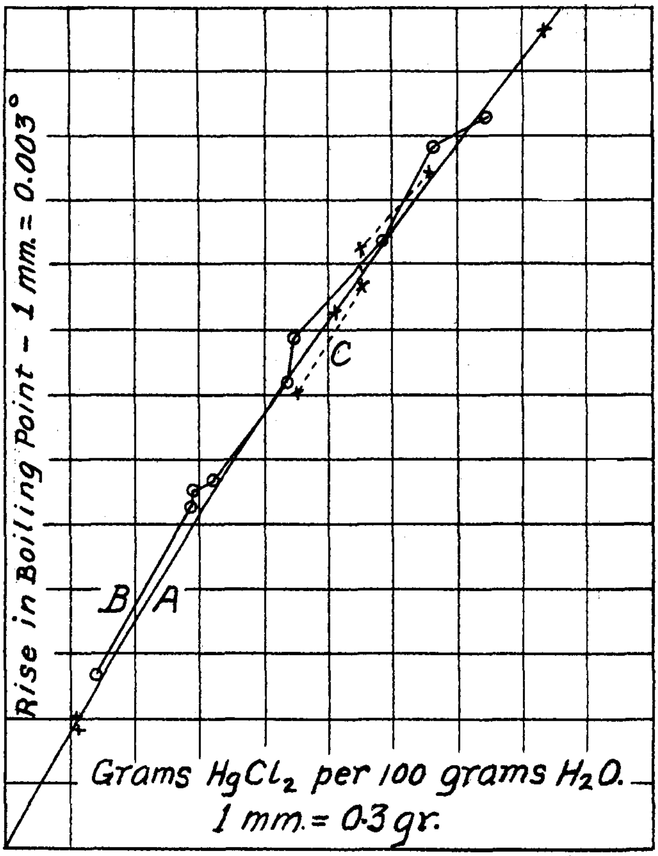

Fig. 3.

Curve A is obtained from the theoretically calculated values and practically coincides with the curve representing Kahlenberg's figures.

Curve B represents the values observed by Beckmann. It will be noticed that the 5th, 7th and 10th points lie close enough to the calculated line. These are the only ones that yield constants which are concordant with those of Kahlenberg, or those theoretically calculated.

Curve C represents the figures of Landsberger.

mental, method was used, while in the experiments at 40° the graphical method was applied.

It will be noted also that the distribution ratio is slightly lower at 40° than at 25°. This is due to the fact that the rate of solubility of mercuric chloride is proportionately greater in benzene than in water up to a certain temperature, as is shown by the relative positions of the curves representing the solubility of mercuric chloride in water and benzene, respectively. This decrease in the distribution ratio with rise in temperature is observed also in the results of similar experiments with toluene by Hantzsch and Vagt.[1]

Curves Representing the Association of Mercuric Chloride and the Equilibrium Constants between 0° and 100°.

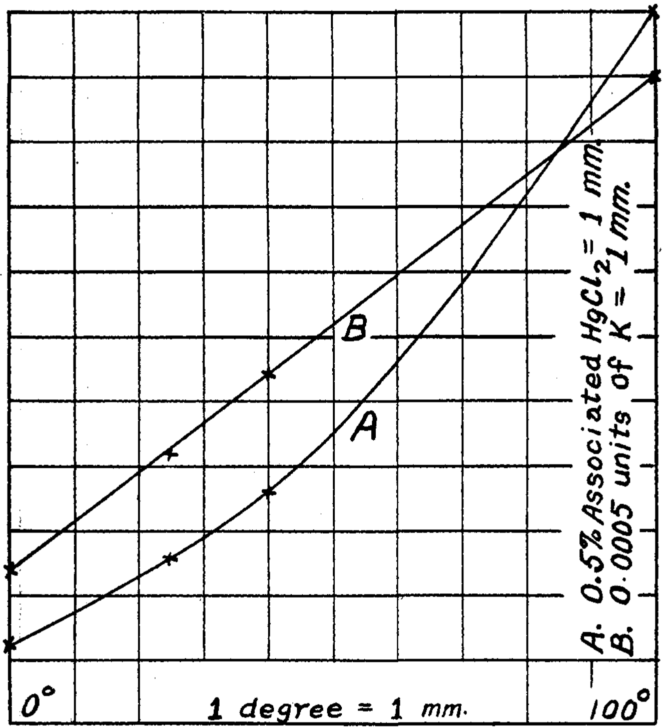

Fig. 4.

Finally, attention is called to the fact that K remains fairly constant from extreme dilution to saturation, which fact leads to the plausible conclusion that Hg_2Cl_4 is the only complex formed in pure water solution, for the given range of temperature, and possibly for any temperature between 0° and 100° as will be shown further on.

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[1] *Z. phys. Chem.*, 38, 716 (1901).

TABLE II.—WORK OF OTHER INVESTIGATORS ON $H_2O \longleftarrow HgCl_2 \longrightarrow C_7H_8$.

Calculated values.

$Cw°$.	Cw.	Ct.	R.	C_{HgCl_2}.	$C_{Hg_2Cl_4}$.	$(10)^4 K$.
250.0	230.544	19.456	11.85	205.261	12.642	3
125.0	114.782	10.218	11.23	107.800	3.491	3
62.5	57.248	5.252	10.90	55.409	0.919	3
31.2	28.540	2.660	10.73	28.063	0.238	3
15.6	14.2597	1.3403	10.64	14.140	0.060	3

At extreme dilution 10.55 = R_∞

Original data of Hantzsch and Vagt 25°.				
$Cw°$.	Cw.	Ct.	R.	Cw calc. — Cw found. Correction in %.
250.0	229.9	20.1	11.44	+0.28
125.0	114.9	10.1	11.38	—0.10
62.5	57.4	5.1	11.32	—0.26
31.2	28.6	2.6	10.88	—0.21
15.6	14.3	1.3	10.73	—0.28
				—0.11 Av.

Calculated values.

$Cw°$.	Cw.	Ct.	R.	C_{HgCl_2}.	$C_{Hg_2Cl_4}$.	$(10)^4 K$.
200.0	184.139	15.861	11.61	167.334	8.4025	3
100.0	91.737	8.263	11.10	87.175	2.2810	3
50.0	45.774	4.226	10.83	44.584	0.5950	3
25.0	22.862	2.138	10.69	22.556	0.1530	3
12.5	11.4245	1.0755	10.62	11.3465	0.0390	3
6.3	5.75626	0.54374	10.59	5.73646	0.0099	3

At extreme dilution 10.55 = R_∞

Original data of Morse 25°.				
$Cw°$.	Cw.	Ct.	R.	Cw calc. — Cw found. Correction in %.
200.0	184.10	15.90	11.58	+0.08
100.0	91.93	8.07	11.39	—0.18
50.0	45.90	4.10	11.20	—0.27
25.0	22.89	2.11	10.85	—0.12
12.5	11.42	1.08	10.57	+0.04
6.3	5.73	0.57	10.05	+0.45
				0.00 Av.

Discussion of the Results of Hantzsch and Vagt, and of Morse.

It is evident from the experiments at 25° of Table I that the equilibrium constant K is equal approximately to 0.0003. Substituting this value of K and such value for R that would bring the necessary corrections within experimental error, in the equation

$$K = \frac{C_{Hg_2Cl_4}}{C^2_{HgCl_2}} = \frac{1/2(Cw° - R_\infty Ct - Ct)}{(R_\infty Ct)^2}.$$

We have,

$$Ct = -\frac{R_\infty + 1}{4R^2_\infty K} \pm \sqrt{\frac{Cw°}{2KR^2_\infty} + \left(\frac{R_\infty + 1}{4R^2_\infty K}\right)^2}.$$

The significance of the letters is the same as that of those in Table I, except that in place of *Cb* we have *Ct*. *Cw* may then be found by subtracting *Ct* from *Cw*°. This procedure is legitimate, since these investigators analyzed the water phase only, although Morse claims to have analyzed the toluene phase also, by extracting the mercuric chloride from the toluene by means of water and subsequently evaporating the large volume of water solution of mercuric chloride, thus resulting to dryness. Realizing the unreliability of this method he has apparently not laid much stress upon the results thus obtained and has evidently made use of those found by the analysis of the water phase only, in the calculation of his results, which agree fairly well with those obtained by Hantzsch and Vagt.

TABLE III.

Kahlenberg's original data.			Cal. from original data.		
g.	*D.*	*M.*	*i.*	*a.*	*K.*
3.341	0.056	310.1	0.874	0.252	(0.135)
8.580	0.143	312.0	0.869	0.262	0.0567
15.463	0.248	324.2	0.836	0.328	0.0470
24.858	0.376	343.8	0.788	0.424	0.0514
					0.0517 = Av.

Calculated values.

						D calc.—*D* obs. Correction in degrees.
3.341	0.060	289.4	0.936	0.127	0.05	+0.004
8.580	0.144	308.8	0.877	0.245	0.05	+0.001
15.463	0.247	326.1	0.831	0.338	0.05	—0.001
24.858	0.377	343.0	0.790	0.420	0.05	+0.001
53.965[1]	...	...	...	0.550[1]	0.05	
						+0.001 = Av.

Landsberger's original data.			Cal. from original data.		
g.	*D.*	*M.*	*i.*	*a.*	*K.*
13.54	0.210	335	0.810	0.38	0.073
16.53	0.259	332	0.820	0.36	0.053
16.54	0.277*	311	0.870	0.26	0.030
19.70	0.312	329	0.850	0.30	0.042
					0.049 = Av.

Calculated values.

						D calc.—*D* obs. Correction in degrees.
13.54	0.218	322.6	0.840	0.32	0.05	+0.008
16.53	0.262	328.5	0.825	0.35	0.05	+0.003
16.54	0.262	328.5	0.825	0.35	0.05	—0.015
19.70	0.306	334.6	0.810	0.38	0.05	—0.006
						—0.0025 = Av.

* Landsberger's extreme error 0.018.

[1] See discussion of results below under (*b*).

Table III (*continued*).

Beckmann's original data.			Cal. from original data.		
g.	*D.*	*M.*	*i.*	*a.*	*K.*
4.35	0.080	283	0.957	0.085	(0.024)
8.68	0.159	284	0.954	0.091	(0.012)
8.72	0.165*	275	0.985	0.029	(0.004)
9.75	0.170	298	0.909	0.181	(0.027)
13.16	0.215	318	0.852	0.296	0.047
13.42	0.235*	297	0.912	0.176	(0.019)
17.60	0.281	326	0.831	0.338	0.045
19.93	0.325	319	0.849	0.301	(0.031)
22.22	0.338	342	0.792	0.416	0.056
					0.049 = Av.

* Beckmann's extreme 0.006 and 0.020.

Calculated values.

						D calc.—*D* obs. Correction in degrees.
4.35	0.077	293.6	0.923	0.154	0.05	—0.003
8.68	0.146	309.0	0.877	0.246	0.05	—0.013
8.72	0.147	309.4	0.876	0.247	0.05	—0.018
9.75	0.162	312.2	0.868	0.264	0.05	—0.008
13.16	0.213	320.7	0.845	0.310	0.05	—0.002
13.42	0.217	321.9	0.842	0.315	0.05	—0.018
17.60	0.277	330.5	0.820	0.360	0.05	—0.004
19.93	0.309	335.0	0.809	0.381	0.05	—0.016
22.22	0.341	338.8	0.800	0.400	0.05	+0.003
						—0.009 = Av.

Biltz's original data.		Calculated from original data.				
Mols $HgCl_2$ to 1000 g. H_2O.	*D.*	*g.*	*M.*	*i.*	*a.*	*K.*
0.01867	0.033	0.505957	283.64	0.9554	0.0891	(0.2122)
0.04512	0.083	1.222752	272.54	0.9944	0.0112	0.0094
0.06464	0.118	1.751744	274.64	0.9868	0.0264	0.0159
0.09230	0.168	2.501330	275.43	0.9839	0.0322	0.0137
						0.0130 = Av.

Calculated values.

D.	*g.*	*M.*	*i.*	*a.*	*K.*	*D* calc.—*D* obs. Correction in degrees.
0.034*43*	0.505957	271.82	0.9970	0.0060	0.012	+0.001*43*
0.082*88*	1.222752	272.94	0.9929	0.0143	0.012	—0.000*12*
0.118*39*	1.751744	273.74	0.9900	0.0200	0.012	+0.000*39*
0.168*34*	2.501330	274.88	0.9859	0.0283	0.012	+0.000*34*
...	5.73[1]	..	..	0.0607[1]	0.012	
						+0.00050 = Av.

Observed *D*.	**Calculated *D*.**
0.033	0.034*43*
0.083	0.082*88*
0.118	0.118*39*
0.168	0.168*34*

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[1] See discussion of results below under (*b*).

Further evidence of the existence of the double molecule of mercuric chloride in water solution is shown by the ebullioscopic measurements of Kahlenberg, Landsberger and Beckmann,[1] and by the cryoscopic measurements of Biltz.[2]

Discussion of the Results of Kahlenberg, Landsberger, Beckmann and Biltz.

The equilibrium constants were first calculated from the original data, and then by means of the average of these constants the *calculated values* were obtained from the following well-known relations:

$$(1)\ K = \frac{a}{g(1-a)^2} \quad \text{or} \quad a = \frac{2Kg+1}{2Kg} \pm \sqrt{-1+\left(\frac{2Kg+1}{2Kg}\right)^2}$$

$$(2)\ a = \frac{1-i}{1-n} \quad \text{or} \quad i = 1 - a(1-n)$$

$$(3)\ i = \frac{271}{M} \quad \text{or}\ M = \frac{271}{i}$$

$$(4)\ D = \frac{520g}{100M} \ \text{in the ebullioscopic measurements}$$

$$\text{and}\ \frac{1850g}{100M} \ \text{in the cryoscopic measurements,}$$

where g denotes the number of grams of mercuric chloride per 100 g. of water; D, the rise in the boiling point or lowering of the freezing point, as the case may be; M, the apparent molecular weight; i, the ratio of the true and apparent molecular weights; n, instead of denoting a whole number as in the case of substances which dissociate, equals $^1/_2$, because two molecules associate to form one; $100a$, the percentage of the mercuric chloride associated in the water solution; and K, the equilibrium constant of the equation:

$$HgCl_2 + HgCl_2 \rightleftarrows Hg.HgCl_4$$

$$\text{or,}\quad K = \frac{C_{Hg_2Cl_4}}{C^2_{HgCl_2}} = \frac{ag}{(g-ag)^2} = \frac{a}{g(1-a)^2}$$

It is interesting to compare (a) the equilibrium constants obtained for the several temperatures 0°, 25°, 40°, and 100°, and (b) the percentage association in saturated solution of mercuric chloride in pure water at the given temperatures. For this purpose it is essential that the data from which the several constants were obtained be expressed in the same units; that is, the data must be expressed in millimols of mercuric chloride per liter, as in the distribution ratio measurements, or in grams of mercuric chloride to 100 g. of water, as in the ebullioscopic and cryoscopic experiments. The latter unit was chosen.

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[1] *Loc. cit.*

[2] *Z. phys. Chem.*, 40, 199 (1902).

(*a*) From Table I we have at 25°, 286.6 millimols per liter corresponding to 7.9 g. of mercuric chloride per 100 g. of water; 18.35 millimols per liter of Hg_2Cl_4 corresponding to 1 g. of mercuric chloride per 100 g. of water. At 40° we have 346.0 millimols per liter of mercuric chloride corresponding to 9.62 g. of mercuric chloride per 100 g. of water, and 30.989 millimols per liter of Hg_2Cl_4 correspond to 1.7 g. of mercuric chloride per 100 g. of water.

Substituting these values in the equation:

$$K = \frac{ag}{(g - ag)^2}$$

and comparing the resulting constants with K for 100° and 0°, we have:

t	0°	25°	40°	100°
K	0.012	0.021	0.027	0.050

If these four values of K are plotted on millimeter paper against their respective temperatures, the line formed by connecting the points is practically a straight line.

(*b*) Since the equilibrium constant K for 100° is equal to 0.050 and since the number of grams of mercuric chloride dissolved by 100 g. of water at 100° is equal to 53.965, we can calculate the percentages of association from the relation

$$K = \frac{ag}{g(g - ag)^2}$$

or, $100a = 55.00\%$ of the mercuric chloride associated at 100°. In a similar manner the percentages of the association of the mercuric chloride in saturated water solution at 40°, 25°, and 0° were calculated and tabulated together with the equilibrium constants for the corresponding temperatures.

t	0°	25°	40°	100°
K	0.012	0.021	0.027	0.050
% association of mercuric chloride in saturated water solution	6.07	12.65	17.67	55.00

Summary and General Conclusions.

1. A method has been devised by means of which mercuric chloride may be removed from benzene quantitatively in a form very well adapted for the subsequent precipitation of the mercuric chloride by hydrogen sulfide.

2. By means of this method of analysis the proof of the existence of the double molecule of mercuric chloride in water solution was made possible by measuring the distribution ratio of mercuric chloride between water and benzene at 25° and at 40°, respectively.

3. The association of mercuric chloride in pure water is further established by the recalculated data of Morse, and Hantzsch and Vagt,

obtained from the measurements of the distribution ratio of mercuric chloride between water and toluene; of Biltz, obtained by cryoscopic measurements; and finally of Kahlenberg, Landsberger, and Beckmann, obtained by ebullioscopic measurements. Moreover, it is remarkable how closely the calculated values agree with those observed by the several investigators mentioned above. The differences between the calculated and the observed values are in every case well within experimental error, except in those of Beckmann; but even here the difference is lower than *his own experimental error* as is shown in the table.

4. From the fact that the equilibrium constants have been found to be fairly concordant from practically extreme dilution to saturation for a given temperature, it is reasonable to assume that Hg_2Cl_4 is the only complex in pure water at any temperature between 0° and 100°, and at any concentration.

5. It is interesting to note that the equilibrium constants from 0° to 100° all lie on practically a straight line, and also that the associated fraction of the mercuric chloride in the saturated water solutions between these temperatures, when plotted, lie on a perfectly smooth curve.

6. Finally it is hoped that by means of these equilibrium constants it may be possible to account for the many discrepancies and contradictory data given in the recent literature concerning the complex compound which mercuric salts form with other salts.

Method employed in this article of converting grams of mercuric chloride per 100 g. of water to millimols per liter of water solution and grams of mercuric chloride per 100 g. of benzene to millimols per liter of benzene solution and *vice versa*, by means of solubility and specific gravity data taken from the literature.

These figures were obtained from solubility data of mercuric chloride at 25° and 40° in water and benzene, respectively, by plotting on millimeter paper the number of grams of mercuric chloride per 100 g. of water against the temperatures, drawing a smooth curve along the points and reading off the figures (which are enclosed in parentheses in table) for any desired temperature accurately to three significant figures. The figures thus obtained were converted to millimols per liter of solution by means of specific gravity data as follows:

GIVEN.

$t°$.	Grams of $HgCl_2$ per 100 g. H_2O.[1]	Grams of $HgCl_2$ per 100 g. C_6H_6.[2]	Sp. gr. of a 4.72% $HgCl_2$ water sol.[3]	Sp. gr. of water.	Sp. gr. of C_6H_6.[4]
0.0	5.73	...	1.04070	0.99987	...
10.0	6.57	...	1.04033	0.99975	...
15.0	...	0.540	...	...	...
20.0	7.39	...	1.03856	0.99826	...
25.0	(7.90)	(0.652)	...	0.99712	0.87417

[1] Abegg's *Handbuch der Anorg. Chem.*, **2**, II, 614.

[2] 0.540 was taken from Laszczynski; and 0.800 and 0.870 were taken from Linebarger, both of which are given in Landolt-Börnstein Tabellen, p. 593.

[3] Abegg's *Handbuch der Anorg. Chem.*, **2**, II, 615.

[4] Beilstein, **2**, 16.

GIVEN (*continued*).

t°.	Grams of $HgCl_2$ per 100 g. H_2O.	Grams of $HgCl_2$ per 100 g. C_6H_6.	Sp. gr. of a 4.72% $HgCl_2$ water sol.	Sp. gr. of water.	Sp. gr. of C_6H_6.
30.0	8.43	...	1.03566	0.99577	...
38.8	...	0.800	...	...	...
40.0	9.62	(0.837)	...	0.99235	0.85829
40.5	...	0.870	...	...	...
50.0	11.34	...	...	...	...
60.0	13.86	...	...	...	...
70.0	17.29	...	...	...	...
80.0	24.30	...	...	...	...
90.0	37.05	...	...	...	...
100.00	53.96	...	...	...	...

FIND.

(*a*) The volume occupied by 1 g. of mercuric chloride, for example at 0°.

(*b*) Convert grams of mercuric chloride per 100 g. of water or benzene to millimols per liter of solution, at a given temperature.

(*a*)

From the table we have:

104.07 = the weight in grams of 100 cc. of solution, and (104.07), (0.0472) = 4.912 = weight in grams of $HgCl_2$ in 100 cc. of solution. 104.07 — 4.912 = 99.158 = weight in grams of water in 100 cc. of solution. $\frac{99.158}{0.99987} = 99.171$ = volume in cc. of water in 100 cc. of solution. 100.000 — 99.171 = 0.829 = volume in cc. of 4.912 g. of $HgCl_2$ in 100 cc. of solution. Hence, the volume occupied by 1 g. of mercuric chloride at 0° = $\frac{0.829}{4.912}$ = 0.169 cc. In a similar manner were found the volumes occupied by 1 g. of mercuric chloride at 10°, 20°, and 30°, and the results tabulated below:

t.	Volume occupied by 1 g. $HgCl_2$.	Difference for 10°.	Average difference for 10°.
0°	0.169	...	...
		0.005	
10°	0.174		
		0.004	0.005
20°	0.178		
		0.007	
30°	0.185		

For the volume occupied by 1 g. of mercuric chloride at 25°, we may take the average of the volumes at 20° and at 30°, and the volume occupied by 1 g. of mercuric chloride at 40° we may find by adding the average difference 0.005 to the volume at 30°. Hence at 25° 1 g. of mercuric chloride occupies approximately 0.18 cc. and at 40° 0.19 cc.

Example: Conversion of solution at 40° of 9.62 g. of mercuric chloride per 100 g. of water to millimols per liter of solution:

$\frac{100}{0.99235}$ = 100.771 cc. occupied by 100 g. of water

(9.62) (0.19) = 1.828 cc. occupied by 9.62 g. of mercuric chloride. Total volume occupied by 100 g. of water and 9.62 g. of mercuric chloride = 102.6 cc. Therefore, 102.6 : 1000 = 9.62 : x or, x = 93.7622 g. of mercuric chloride per liter of solution, and

$$\frac{93.7622}{0.271} = 346.0 \text{ millimols per liter of solution of mercuric chloride and water at } 40°.$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL.]

THE ELECTRON CONCEPTION OF VALENCE. VI. INORGANIC COMPOUNDS.

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In the previous papers of this series,[1] the view that two atoms when combining acquire opposite electric charges was developed and applied to various classes of compounds and reactions.

In this paper, the electron conception of valence will be applied more especially to compounds and reactions of inorganic chemistry. The natural method of studying the present problem is to take the classifications developed by Werner and to consider them from the point of view of the electron conception of valence. It is manifestly impossible in a paper such as this, to take up all the relations Werner has developed. Instead, only some of the more important will be chosen, and the application of the electronic view to these, considered.

In discussing the structures of inorganic compounds, it is useful to consider many of them as tautomeric. The conception of tautomerism has been most useful in organic chemistry, where a number of tautomeric forms of various substances have been isolated and their chemical and physical properties studied. Tautomeric formulas have also been proposed for certain inorganic substances. Recently, Bray and Branch,[2] as well as Lewis,[3] developed valence views from this standpoint in papers entitled "Valence and Tautomerism."

The application of the electron conception of valence to the phenomenon of tautomerism was outlined in previous papers. It was shown that the algebraic sum of the charges on each atom in a substance capable of existing in tautomeric forms remains the same in each of the forms, although the arrangement of the atoms may be different. This may be illustrated by the formulas for hydrocyanic acid, nitrous acid, and ethyl acetoacetate:

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[1] *School of Mines Quarterly*, 30, 179 (1909); THIS JOURNAL, 32, 1637 (1910); 33, 1140 (1911); 35, 1810 (1913); 36, 209 (1914); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 6, 212 (1912); *J. prakt. Chem.*, (*N. F.*), 88, 97 (1913); *Proc. Amer. Philosoph. Soc.*, 53, 25 (1914).

[2] THIS JOURNAL, 35, 1440 (1913).

[3] *Ibid.*, 35, 1449 (1913).