brane, the equilibrium of distribution of the electrolyte is disturbed, and part of the adsorbed electrolyte diffuses into the dispersion medium from which it can now dialyze. Heating accelerates the re-establishment of equilibrium and consequently hastens dialysis.

Furthermore, in general, adsorption decreases[1] considerably with rise in temperature. For a given total concentration of electrolyte in a colloidal solution at equilibrium there will be more of it in the dispersion medium if the solution is heated, and since diffusion through the membrane depends only on the concentration of the electrolyte in the dispersion medium, heating should be favorable to rapid dialysis.

By placing the solution to be dialyzed in the outside vessel (the beaker) and heating, the large increase in volume due to osmosis, which results in the usual procedure, is avoided. An equilibrium sets in between evaporation from the colloidal solution and osmosis of water into it through the membrane, and the volume remains practically constant. Or, if desired, the solution may be concentrated during dialysis.

The steady flow of distilled water inside the dialyzer helps dialysis by maintaining a maximum difference of concentration of diffusible substances on both sides of the membrane, and also by maintaining within the latter a lower temperature than outside, which introduces the Soret[2] phenomenon.

Our experience is that parchment paper membranes of about one liter capacity are far easier to prepare than collodion membranes of the same size. They stand rough usage, a temperature of over 90° for a long period, and cost very little.

PITTSBURGH, PA.

ON THE EQUILIBRIA OF MERCURIC CHLORIDE WITH OTHER CHLORIDES.

BY G. A. LINHART.

Received March 6, 1916.

In a recent paper[3] it is shown that the association of mercuric chloride in water solution depends both on the concentration and the temperature, and that the degree of association ranges, in saturated solutions, from 6% at 0° to 58% at 100°. It is, therefore, not surprising that in the absence of these data, previous investigators were not able to account for the abnormal behavior of mercuric chloride in water solution with reference to its molecular weight, distribution ratio, and solubility. Of particular interest are the attempts made by several investigators to establish the type or types of complex compounds which mercuric chloride

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[1] *Freundlich Kapillarchemie*, 169–173.

[2] Nernst, *Theoretische Chemie*, 7th ed., p. 801.

[3] THIS JOURNAL, 37, 258 (1915).

forms with other chlorides in solution. The results were, of course, entirely unsatisfactory as is evident from the polemics that followed.[1] It is the purpose of this paper to harmonize these opposing views, which resulted partly from the use of unreliable methods of analyses, but chiefly from not taking into account the formation of the double molecules of mercuric chloride in solution.

It has been shown fairly conclusively[2] that in a water solution of mercuric chloride there are two types of molecules, $HgCl_2$ and Hg_2Cl_4, which combine to form complex compounds with sodium chloride in water solution, and it only remains to establish, if possible, the type or types of these complexes.

Assuming *only* those complexes which have been isolated[3] from water solutions in definite crystalline forms and of definite chemical composition, then the reactions between the chloride ions of the sodium chloride and the two kinds of molecules of mercuric chloride may be represented by the equations

(*a*), $(HgCl_2) + (Cl)^- \rightleftharpoons (HgCl_3)^-$; (*b*), $(Hg_2Cl_4) + Cl)^- \rightleftharpoons (Hg_2Cl_5)^-$

when the mercuric chloride is in excess, and by

(*c*), $(HgCl_3)^- + (Cl)^- \rightleftharpoons (HgCl_4)^{--}$; (*d*), $(Hg_2Cl_5)^- + (Cl)^- \rightleftharpoons (Hg_2Cl_6)^{--}$; (*e*), $(Hg_2Cl_6)^{--} + (Cl)^- \rightleftharpoons (HgCl_3)^- + (HgCl_4)^{--}$

when the sodium chloride is in large excess.

It is evident that in any concentration of the reacting substances the total concentration of the sodium chloride and the mercuric chloride may be expressed by the sums

$$(HgCl_2) + (2Hg_2Cl_4) + \frac{(HgCl_3)^-}{\gamma} + \frac{(HgCl_4)^{--}}{\gamma^2} + \frac{(2Hg_2Cl_5)^-}{\gamma} + \frac{(2Hg_2Cl_6)^{--}}{\gamma^2} = \Sigma HgCl_2.$$

$$\frac{(HgCl_3)^-}{\gamma} + \frac{(2HgCl_4)^{--}}{\gamma^2} + \frac{(Hg_2Cl_5)^-}{\gamma} + \frac{(2Hg_2Cl_6)^{--}}{\gamma^2} + \frac{(Cl)^-}{\gamma} = \Sigma NaCl.$$

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

[2] THIS JOURNAL, **37**, 271 (1915).

[3] It is interesting to note that by saturating concentrated aqueous hydrochloric acid solutions with mercuric chloride and cooling to incipient crystallization Ditte obtained compounds of the following composition:

Substance.	60°.	30°.	15°.	5°.	—10°.
$HgCl_2$	86.58%	82.30%	78.97%	67.10%	57.60%
HCl	3.86	5.54	5.33	12.04	15.51
H_2O	9.56	12.16	15.70	20.86	26.88
	$HHg_3Cl_7.5H_2O$	$HHg_2Cl_5.4H_2O$	$HHg_2Cl_5.6H_2O$	$H_2Hg_2Cl_6.7H_2O$ $H_2HgCl_4.7H_2O$	$H_2HgCl_4.7H_2O$

The corresponding potassium salts, with the exception of the first, were first prepared by Bonsdorf (see Abegg's *Handbuch der anorg. Chem.*, II, 2).

It is here assumed that the compounds $NaHgCl_3$, $NaHg_2Cl_5$, and NaCl in the same (water) solution dissociate to the same extent. The degree of dissociation of the corresponding divalent ions will then be equal to[1] (γ^2), so that the dissociation factors in the equilibrium equations cancel out and we have

$$\frac{(HgCl_3)^-}{(HgCl_2)(Cl)^-} = K_1. \quad (3) \qquad \frac{(Hg_2Cl_5)^-}{(Hg_2Cl_4)(Cl)^-} = K_3. \quad (5)$$

$$\frac{(HgCl_4)^{--}}{(HgCl_3)^-(Cl)^-} = K_2. \quad (4) \qquad \frac{(Hg_2Cl_6)^{--}}{(Hg_2Cl_5)^-(Cl)^-} = K_4. \quad (6)$$

Expressing now these equations in terms of the known quantities $(HgCl_2)$, (Hg_2Cl_4), $\Sigma HgCl_2$, and $\Sigma NaCl$ and collecting common terms into N, M, N′ and M′ we finally obtain

$$-\frac{N}{2M} \pm \sqrt{\frac{\Sigma(HgCl_2) - (HgCl_2) - (2Hg_2Cl_4)}{M} + \left(\frac{N}{2M}\right)^2} = -\frac{N'}{2M'} \pm \sqrt{\frac{\Sigma(NaCl)}{M'} + \left(\frac{N'}{2M'}\right)^2}. \quad (7)$$

The concentrations of the $HgCl_2$ and 2 Hg_2Cl_4 are obtained from partition measurements as described in a previous paper.[2] By means of Equation 7, in which the only unknown quantities are the equilibrium constants (included in N, M, N′ and M′), we can test the accuracy of the extrapolated constants, which were derived as follows:

From a study of the velocity of the reaction[3] between mercuric chloride and sodium formate to form HgCl it was found that the specific reaction rate gradually decreased with increase in concentration of NaCl formed in the reaction, but that in very dilute solution, the velocity coefficients remained practically constant during the entire course of the reaction, because the amount of complex compounds formed under these conditions is extremely small. It may, therefore, be safely assumed, as a first approximation, that in the experiment with 0.03 molal mercuric chloride and 0.01 molal of sodium chloride, the chief sodium chloride complex in the solution is $NaHgCl_3$, as indicated in Equation *a*. Introducing the results of this experiment in Equation 3, it was found that

$$\frac{(HgCl_3)^-}{(HgCl_2)(Cl)^-} = K_1 = 9.8 \text{ at } 25°. \quad (8)$$

The amount of HgS obtained from the analysis of $^3/_4$ of the benzene phase or 150 cc., was 0.0745 g., corresponding to 0.002141 mol of mercuric chloride per liter of solution of benzene phase, and this was denoted by Cb. If now R_∞ denotes the true distribution ratio (11.9) of mercuric chloride between water and benzene then, CbR_∞ = the concentration of the

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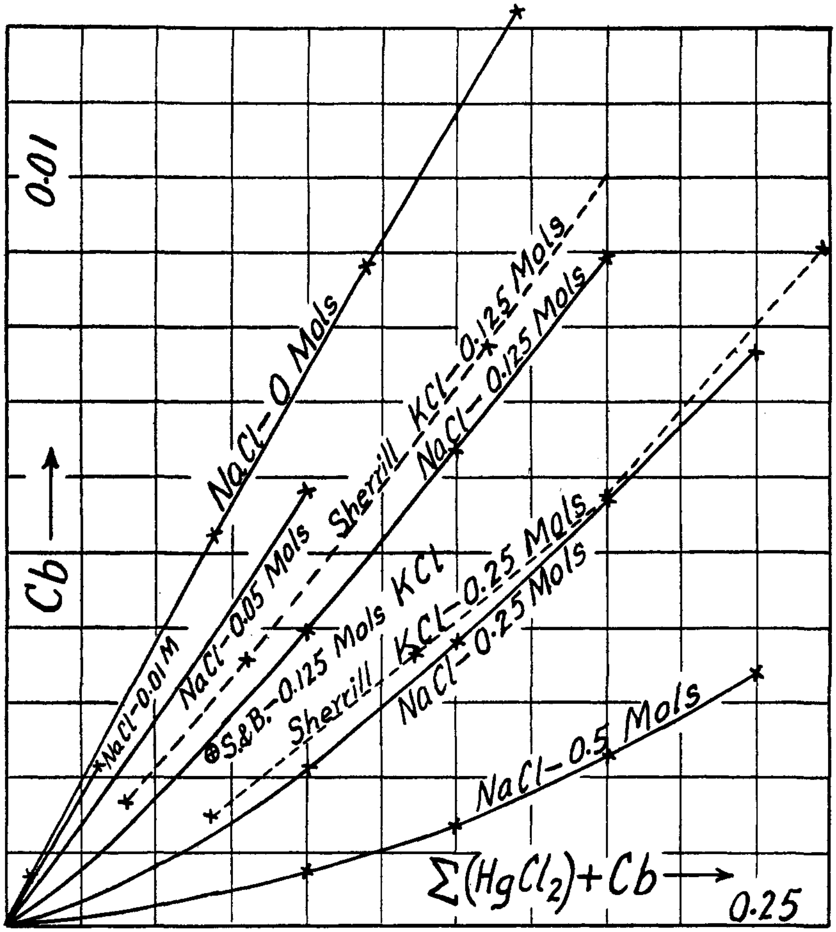
[1] Adams and Rosenstein, THIS JOURNAL, 36, 1464 (1914).

[2] *Loc. cit.*

[3] THIS JOURNAL, 37, 73 (1915).

Fig. 1.—25°.—Curves representing the amounts of mercuric chloride found in the benzene phase (Cb) plotted against the total mercuric chloride expressed in mols per liter of solution.



Curve for O.NaCl represents the results taken from a previous paper already cited. The curves (— — — —) represent results of Sherrill's investigation. The somewhat high results, especially for KCl = 0.125, Sherrill attributes to the fact that the benzene which he used was not quite thiophene free. This explanation is substantiated by the single result of Sand and Breest, indicated by a circle and followed by S. & B.

uncombined mercuric chloride in the water phase, and $2K(Cb)^2(R_\infty)^2$ = the amount of mercuric chloride in the form of double molecules, as is evident from the equation, taken from a previous paper already cited.

$$\frac{(Hg_2Cl_4)}{(HgCl_2)^2} = K = 0.3.$$

Now substituting the experimental results in Equation 8 we have

$$\frac{\Sigma(HgCl_2) - (Cb) - (CbR_\infty) - 2K(Cb)^2(R_\infty)^2}{(CbR_\infty)[\Sigma(NaCl) - (NaHgCl_3)]} = 9.8. \qquad (9)$$

(In the paper just cited (10)[4] $K = 3$, K being calculated on the basis of millimols instead of mols per liter of solution as in the above.)

In order to evaluate K_2, K_3 and K_4, the following experiments were performed:[1]

TABLE I.—25°.

Expt. No.	$\Sigma(NaCl)$.	$\Sigma(HgCl_2)$ + (Cb).	HgS from 150 cc. C_6H_6 (g.).	(Cb).	$\Sigma(HgCl_2)$.	R.
			Series I.			
(*a*)	0.000	0.100	..	0.007400	0.092600	12.51
(*b*)	(0.005)	(0.100)	..	(0.007210)	....	..
1	0.050	0.100	0.2003	0.005756	0.094244	13.01
2	0.125	0.100	0.1372	0.003943	0.096057	24.36
3	0.250	0.100	0.0748	0.002149	0.097851	45.52
4	0.500	0.100	0.0259	0.000744	0.099256	132.96
			Series II.			
1	0.125	0.15	0.2223	0.006388	0.143612	22.48
2	0.250	0.15	0.1316	0.003781	0.146219	38.67
3	0.500	0.15	0.0468	0.001345	0.148655	110.52
			Series III.			
1	0.125	0.20	0.3099	0.008905	0.191095	21.46
2	0.250	0.20	0.1974	0.005672	0.194328	34.26
3	0.500	0.20	0.0782	0.002247	0.197753	88.01
			Series IV.			
1	0.250	0.25	0.2668	0.007667	0.242333	31.61
2	0.500	0.25	0.1167	0.003353	0.246647	73.55

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[1] In order to determine the relative amounts of the several complex substances in the solution, the distribution ratios

$$(NaCl\ aqua) \longleftarrow HgCl_2 \longrightarrow C_6H_6,$$

were measured. This method was preferred because it is capable of yielding results of a very high degree of accuracy, if the method of analysis, given in a previous paper dealing with the distribution ratio of mercuric chloride between water and benzene, is strictly followed.

The reliability of this method of determining the mercuric chloride in the benzene phase is even more evident in this work than in the previous as a glance at the distribution ratios will show. Thus in Table I, Expt. 4, a 0.2% error in the water phase would correspond to a 21% error in the benzene phase, if the latter were determined by difference. It was therefore deemed desirable and sufficient to determine the amount of mercuric chloride in the benzene phase only, and to take the difference between the initial concentration and the amounts thus found as the quantity of mercuric chloride in the water phase. The experimental procedure was exactly the same in every detail as already described in a previous article (THIS JOURNAL, 37, 260 (1915)) except that the desired amount of pure sodium chloride was added to the contents of of the 250 cc. flask before it was filled to the mark with distilled water at the desired temperature.

In the above table $\Sigma(NaCl)$ denotes the total concentration of the sodium chloride in the water phase in mols per liter of solution.

$\Sigma(HgCl_2) + (Cb)$ denotes the total concentration of the mercuric chloride in the water phase and benzene phase.

HgS from 150 cc. C_6H_6 denotes the number of grams of mercuric sulfide obtained from the analysis of $^3/_4$ of the benzene phase, the total being 200 cc.

(Cb) denotes the number of mols of mercuric chloride in the benzene phase in mols per liter of solution.

$\Sigma(HgCl_2)$ denotes the total number of mols, both free and combined, of mercuric chloride in the water phase per liter of solution.

R denotes the distribution ratio of the system

$$(NaCl\ aqua) \longleftarrow HgCl_2 \longrightarrow C_6H_6.$$

Since, in Experiment 4, Series I, the amount of free mercuric chloride is very small, as is evident from the amount of mercuric chloride found in the benzene phase, then, according to Equations *a*, *c* and *e*, the only complex ions we need to consider here (as a first approximation) are $(HgCl_3)^-$ and $(HgCl_4)^{--}$. Substituting the results of this experiment into Equation 9 we have:

$$\frac{(HgCl_3)^-}{(HgCl_2)(Cl)^-} = \frac{\Sigma(HgCl_2) - (Cb) - (CbR_\infty) - 2K(Cb)^2(R_\infty)^2 - (Na_2HgCl_4)}{(CbR_\infty)[\Sigma(NaCl) - (NaHgCl_3) - (2Na_2HgCl_4)]} = 9.8$$

Whence $Na_2HgCl_4 = 0.06$, $NaHgCl_3 = 0.03$, $NaCl = 0.35$ and

$$\frac{(HgCl_4)^{--}}{(HgCl_3)^-(Cl)^-} = 5.7 = K_2 \text{ approximately.}$$

Similarly an approximate value for K_3 was obtained by plotting on a large scale Cb (millimols for 10 cm.) against $\Sigma NaCl$ (millimols per 1 cm.) of Series I. The extrapolated values (given in Table I in parentheses) were then substituted into Equation 9,

$$\frac{(HgCl_3)^-}{(HgCl_2)(Cl)^-} = \frac{\Sigma(HgCl_2) - (Cb) - (CbR_\infty) - 2K(Cb)^2(R_\infty)^2 - (2NaHg_2Cl_5)}{(CbR_\infty)[\Sigma(NaCl) - (NaHgCl_3) - (NaHg_2Cl_5)]} = 9.8,$$

where, according to Equations *a* and *b* we may, as a first approximation, neglect the quantities $Na_2Hg_2Cl_6$ and Na_2HgCl_4. We then obtain $NaHg_2Cl_5 = 0.000188$, $NaHgCl_3 = 0.002198$, $HgCl_2 = 0.0858$, $NaCl = 0.002614$ and $Hg_2Cl_4 = 0.002209$, and finally

$$\frac{(Hg_2Cl_5)^-}{(Hg_2Cl_4)(Cl)^-} = 33 = K_3 \text{ approximately.}$$

Finally K_4 was obtained by substituting the approximate values for the equilibrium constants and the experimental results of every experiment into the general Equation 7. The four equilibrium constants thus obtained were then readjusted in order to satisfy the summation Equations 1 and 2.[1] The final results are given in Table II, the headings being self-explanatory.

TABLE II.

	$(HgCl_2)$.	$\frac{(HgCl_3)^-}{\gamma}$.	$\frac{(HgCl_4)^{--}}{\gamma^2}$.	(Hg_2Cl_4).	$\frac{(Hg_2Cl_5)^-}{\gamma}$.	$\frac{(Hg_2Cl_6)^{--}}{\gamma^2}$.	$\frac{(Cl)^-}{\gamma}$.
Series I.							
1......	0.068496	0.017050	0.002120	0.001407	0.001250	0.000632	0.026196
2......	0.046915	0.030280	0.010098	0.000661	0.001621	0.002100	0.068703
3......	0.025578	0.036841	0.026626	0.000196	0.001086	0.003121	0.152579
4......	0.008856	0.031000	0.054200	0.000024	0.000328	0.002248	0.355776
Series II.							
1......	0.076017	0.039687	0.010326	0.001733	0.003475	0.003583	0.054020
2......	0.044995	0.051802	0.030104	0.000607	0.002721	0.006331	0.122607
3......	0.016066	0.048600	0.071917	0.000077	0.000872	0.005087	0.296520
Series III.							
1......	0.105970	0.046098	0.010137	0.003369	0.005800	0.005276	0.042276
2......	0.067497	0.063800	0.031003	0.001367	0.005047	0.009600	0.099947
3......	0.026741	0.066270	0.080912	0.000214	0.002019	0.009682	0.250523
Series IV.							
1......	0.091238	0.076166	0.030049	0.002497	0.007733	0.012210	0.081583
2......	0.039906	0.083257	0.084648	0.000478	0.003703	0.015237	0.213270

No. of expt.	$\frac{(HgCl_3)^-}{(HgCl_2)(Cl)^-}$.	$\frac{(HgCl_4)^{--}}{(HgCl_3)^-(Cl)^-}$.	$\frac{(Hg_2Cl_5)^-}{(Hg_2Cl_4)(Cl)^-}$.	$\frac{(Hg_2Cl_6)^{--}}{(Hg_2Cl_5)^-(Cl)^-}$.
Series I.				
1..............	9.5	4.7	34	19
2..............	9.4	4.8	36	19
3..............	9.4	4.7	36	19
4..............	9.8	4.9	38	19
Series II.				
1..............	9.7	4.8	37	20
2..............	9.4	4.8	37	19
3..............	10.2	5.0	38	20
Series III.				
1..............	10.3	5.2	40	21
2..............	9.5	4.9	37	19
3..............	9.9	4.8	38	19
Series IV.				
1..............	10.2	4.8	38	19
2..............	9.7	4.8	36	19
	Av. K_1 = 9.8	Av. K_2 = 4.9	Av. K_3 = 37	Av. K_4 = 19

[1] It does not seem justifiable to substitute the average values of the equilibrium constants thus obtained for $K_1 = 9.8$, $K_2 = 4.9$, $K_3 = 37$, $K_4 = 19$ in the general Equation 7 in order to obtain "calculated values" for Cb and compare them with the "Cb found," because the deviations of the equilibrium constants from the corresponding average, although small, may well be due to the assumptions made in reference to their degree of association, which is only approximately correct.

Conclusion.

(1) The complex compounds of mercuric chloride and sodium chloride which have been assumed to exist in water solution and whose presence have been confirmed sufficiently by experimental evidence, have all been prepared in solid crystalline form.

(2) No complex mercuric chloride of sodium, potassium or hydrogen has been shown to exist either in the solution or in solid form having a higher chloride content than is indicated by the type Na_2HgCl_4. It is especially interesting to note that from a saturated solution of mercuric chloride and hydrochloric acid at about —10° no compound richer in HCl than H_2HgCl_4 could be obtained by Ditte, although the solution was supersaturated with HCl gas. This is a conclusive test since the increase of the hydrochloric acid content in these compounds with the fall in temperature should be favorable, due to the fact that the solubility of hydrochloric acid increases with a decrease in temperature while the solubility of mercuric chloride decreases.

(3) The complex H_3HgCl_5 given in Abegg's Anorganische Chemie[1] by Ley is the result of a misunderstanding of the original data from which it was calculated, as is shown below.

16°.

Mols HCl. a.	Mols $HgCl_2$. c.	a/c.
1.57	1.52	1.0
2.09	2.83	1.0
4.03	4.34	1.0
6.44	5.11	1.3
9.51	5.06	1.7
16.00	6.37	2.0
22.00	6.90	3.3

From these figures Ley concluded that a compound containing the anion $(HgCl_2)_x(Cl)_{3x}$ must exist in solution. As a matter of fact on consulting the original data, it was found that Ditte claims to have added the

SOLUBILITY RESULTS OF DITTE.

16°.

	Ditte's original[1] data.	Calculated from original data.		
Grams HCl to 100 grams H_2O. a.	Grams $HgCl_2$ to 100 grams of solution a. b.	$\frac{(b-6.8)}{271}$. d.	$\frac{100\,a}{(a+100)\,36.5}$. c.	c/d.
0.0	6.8	0.000	0.000	—
5.6	46.8	0.148	0.145	1.0
10.1	73.7	0.247	0.252	1.0
13.8	87.8	0.299	0.332	1.1
21.6	127.4	0.447	0.488	1.1
31.0	141.9	0.499	0.649	1.3
50.0	148.0	0.521	0.912	1.8
68.0 sat.	154.0	0.548	1.110 sat.	2.0

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[1] II, 2, p. 642.

mercuric chloride to 100 g. of the hydrochloric acid solutions, as is shown in the table above, and not to the amounts of hydrochloric acid contained in 100 g. of pure water as interpreted by Ley.

BERKELEY, CALIFORNIA.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

A STUDY OF THE SILVER ARSENATE TEST FOR ARSENIC.

By L. J. CURTMAN AND P. DASCHAVSKY.

Received February 18, 1916.

The precipitation of arsenic in the form of an arsenate, by silver nitrate in a neutral solution is so striking that it recommends itself as an excellent confirmatory test. However, the results obtained by students in this laboratory have been so irregular that it was thought worth while to investigate this test for the purpose of ascertaining the conditions under which it could be relied upon to give constant results. It was also the object of the experiments recorded in this paper to determine whether this test is sufficiently sensitive to serve as a confirmatory test for amounts of arsenic from 1–5 mg.

Preparation of Standard Sodium Arsenate Solution.—41.6 g. $Na_2HAsO_4.7H_2O$ were dissolved in water and the volume made up to a liter. 20 cc. portions of this solution were run out from a buret and the arsenic determined gravimetrically by the method given by Treadwell.[1] The results of well-agreeing determinations gave the solution a value of 10 mg. of As per cc. By suitable dilution in volumetric flasks, solutions of lower concentrations were obtained.

Determination of the Sensitiveness of the Test.—By means of graduated pipets, definite amounts of the standard arsenate solution were introduced into a series of test tubes. 2 cc. of a silver nitrate solution of strength 50 mg. Ag per cc. were then added. After the addition of one drop of a 1% solution of phenolphthalein, the solutions were made alkaline with dilute NH_4OH and finally made just acid with 5% acetic acid. After standing for several minutes the tubes were examined and the results compared with a blank run under the same conditions. The following results were obtained:

TABLE I.

No.	As (mg.).	Result.	No.	As (mg.).	Result.
1	10.00	Heavy precipitate	5	0.10	Faint precipitate
2	5.00	Heavy precipitate	6–7	0.05	Faint precipitate on standing
3	1.00	Small precipitate	8–10	0.02	Brown coloration. Limit
4	0.50	Small precipitate	11–12	0.01	Negative

The above results show that the limit of the test (0.02 mg. in a volume of 3 cc.) represents a concentration of 1 part in 150,000. While this limit-

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[1] Treadwell, "Quantitative Analysis," translated by H. T. Hall (1904), p. 165.