Ammonium chloride vapor is 67–63% dissociated between 280° and 330°; and although the degree of dissociation is very nearly constant, it decreases slightly between these temperatures. Ammonium bromide vapor is about 39% dissociated at 320°, and above this temperature the percentage dissociation decreases linearly, until, at 388°, it is about 10%. Ammonium iodide vapor is associated, especially at lower temperatures, but the amount of association decreases, and the dissociation increases as the temperature rises. The assumption that the vapors of the ammonium halides are completely dissociated is therefore no longer tenable.

The dissociation constants of ammonium chloride and bromide are calculated. That of ammonium chloride vapor increases steadily with the temperature, whereas that of ammonium bromide vapor passes through a maximum near 320°, and then decreases.

The heat of dissociation of ammonium chloride vapor is computed by the van't Hoff equation, and is represented by the relation, $U = -12800-0.00967T^2$ gram calories (U is heat evolved). The mode of variation of the dissociation constant with the temperature indicates that the dissociation of ammonium bromide vapor above 320° is accompanied by the evolution of heat, but the actual value of the heat of dissociation can not be computed.

The latent heats of vaporization are calculated by the Clausius-Clapeyron equation. That of ammonium chloride is 32.9 kg. cal. between 280° and 330°, and is constant within 1%; that of ammonium bromide is 28.7 kg. cal. at 320°, and decreases to 24.1 at 388°; that of ammonium iodide increases from 18.0 kg. cal., at 300°, to 24.2 at 380°.

The partial pressures of the various components in the ammonium chloride and bromide vapors are computed.

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ON THE RATE OF REDUCTION OF MERCURIC CHLORIDE BY SODIUM FORMATE.

By G. A. Linhart.

Received November 12, 1914.

In a previous paper[1] an investigation of the rate of the reduction of mercuric chloride by phosphorous acid was described. The purpose of this article is to present the results of a similar study of the rate of reduction of mercuric chloride by sodium formate, with special reference to the influence of sodium chloride upon it, which has already been shown to have a great effect on the reduction by phosphorous acid.

Very recently, after the experimental work described below had been

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[1] Linhart, *Am. J. Sci.*, 35, 353–368 (1913).

completed, a preliminary communication on this same subject was published by Findlay and Davies.[1] These investigators conclude from a large number of experiments at various temperatures and concentrations that the reaction between sodium formate and mercuric chloride is one of the second order, because when their experimental results are substituted in an equation representing a reaction of the third order the reaction velocity coefficient gradually increases to about 40%, while if substituted in one representing a reaction of the second order, the velocity coefficient decreases only by about 17%. As these figures created some doubt, in the authors' own minds as to the mechanism of this reaction, they cited the similar reaction between mercuric chloride and phosphorous acid,[2] which has been shown to be of the second order, and state that a similar explanation to justify the assumption that the reaction between mercuric chloride and sodium formate is theoretically one of the second order, appears to be very doubtful. It will be evident from what follows, not only that the mechanism of the reaction between mercuric chloride and sodium formate may be interpreted in a similar manner to that of mercuric chloride and phosphorous acid, but that concordant velocity constants may be obtained if the experiments are performed under the proper conditions.

There are two opposing factors which tend to obscure the mechanism of the reaction between mercuric chloride and sodium formate. First, the association of the mercuric chloride in water solution;[3] and secondly, the formation of sodium chloride. The double molecules of mercuric chloride being present in considerable proportion at higher temperatures and gradually dissociating with the dilution would tend to accelerate the velocity of the reaction to some extent, as the simple molecules are found to be more reactive. On the other hand, the sodium chloride, increasing in concentration as the reaction proceeds, combines with the mercuric chloride, forming $NaHgCl_3$, and subsequently Na_2HgCl_4, which react with the sodium formate extremely slowly, as is shown in the table, Expt. 7. Since the second factor very much more than compensates the first, the velocity coefficient, K, will consequently decrease. In order to overcome these difficulties the reaction must be allowed to take place either at such dilutions that the mercuric chloride is practically all in the form of simple molecules, $HgCl_2$, so that the resulting sodium chloride can exert no appreciable influence; or, in a large excess of sodium chloride so that there could be no free $HgCl_2$ molecules, and the influence of the small amount of sodium chloride, formed in the course of the reaction, would

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[1] *J. Chem. Soc.*, 103, 1550–1554 (1913).

[2] See discussion of results.

[3] A paper on this subject is ready for publication See also Sand and Breest, *Z. physik. Chem.*, 59, 426; 60, 237; Jander, *Z. Electrochem.*, 8, 688.

be negligible as compared with the total amount initially present. There is another factor which tends to modify the course of the reaction, namely, the formation of hydrochloric acid, but this may easily be remedied either by the addition to the reaction mixture of a soluble salt of a weak acid, as was recommended in a previous paper,[1] or by the addition of a sufficient amount of finely divided barium carbonate.

Experimental.

Standardization of the Mercuric Chloride and Sodium Formate.—A weighed amount of mercuric chloride was dissolved in distilled water or in aqueous sodium chloride of known concentration. Of this solution 10 cc. were pipeted off, by means of a carefully calibrated pipet, and transferred into several glass test tubes, of about 40 cc. capacity, which had previously been constricted at about $1^1/_2''$ from the mouth to a size just large enough to admit the stem of the pipet and to allow the displaced air to escape. To this were added 10 cc. of a solution containing about twice the theoretical amount of sodium formate. The tubes were then sealed, allowed to cool, the contents well mixed, and the tubes submerged in a thermostat kept at 40°. When two consecutive analyses of the mercurous chloride in the tubes about twenty-four hours apart showed no increase in the amount of the mercurous chloride, the reduction was considered complete. Moreover, these results always agreed within 0.2–0.3%, with the theoretical amount of mercurous chloride calculated from the mercuric chloride originally present. In a similar manner the concentration of the sodium formate was determined by using an excess of mercuric chloride.

Reaction Velocity Measurements.—All experiments were carried out in sealed glass test tubes. As soon as two tubes were filled with 10 cc. of the standardized mercuric chloride containing the sodium chloride, and 10 cc. of the standardized sodium formate, containing the sodium acetate, they were sealed, allowed to cool, shaken and submerged in a thermostat kept at 40°, where they were held in position by means of coiled brass springs. The time, t, was counted from the moment the tube was submerged until it was removed from the thermostat and plunged into ice water to check the reaction. At definite intervals a tube was withdrawn; the capillary tip carefully broken off and three scratches made with a sharp triangular file in a horizontal plane, on each side of which was placed a folded piece of wet filter paper. The tube was then brought in a vertical position ot the point of a small blast lamp flame, care being taken not to allow the upper part of the tube to fly off, as it often contained some

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[1] Linhart, *New York Med. J.*, June 14, 1913. The addition of sodium acetate, sodium citrate, and sodium bicarbonate, in particular, causes the reaction between mercuric chloride and phosphorous acid to become instantaneous, while in the case of mercuric chloride and sodium formate the action is merely accelerated.

mercurous chloride. After the tube was thus cracked the upper part was lifted off and the contents filtered through an ignited and weighed perforated platinum crucible, fitted with an asbestos mat. The precipitate was washed first with warm water, then with a little dilute hydrochloric acid, and finally with warm water until the wash water was free of impurities. It was found advisable in filtering the mercurous chloride to use light suction at first to avoid clogging of the asbestos mat, which would vitiate the experiment because of the delay in stopping the reaction. After most of the moisture had been exhausted by the aspirator, the crucible was suspended in a drying oven maintained at a temperature between 105° and 110° for thirty minutes. The crucible was then allowed to cool in a desiccator and weighed.

Table I.

Experimental Results at 40° Showing the Retarding Influence of Sodium Chloride.

Expt. No.	Initial concen.	t in hours.	HgCl in grams.	x in mols.	K.
1	A = 0.01	3.1	0.0135	0.002866	1.80
	B = 0.061	4.6	0.0182	0.003864	1.79
	(NaAc = 0.5)	8.6	0.0282	0.005987	1.79
	(NaCl = 0.0)	18.8	0.0404	0.008578	1.78
		23.7	0.0431	0.009151	1.80
		...	0.0471	0.010000	...
2	A = 0.01	36.5	0.0135	0.002866	1.74
	B = 0.0061	83.0	0.0231	0.004904	1.75
	(NaAc = 0.5)	106.0	0.0262	0.005563	1.75
	(NaCl = 0.0)	205.0	0.0345	0.007325	1.77
		318.0	0.0388	0.008238	1.75
		560.0	0.0431	0.009149	1.75
		...	0.0471	0.010000	...
3	A = 0.1	1.9	0.0685	0.01454	1.43
	B = 0.061	5.7	0.1528	0.03244	1.32
	(NaAc = 0.5)	8.4	0.1930	0.04098	1.27
	(NaCl = 0.0)	18.1	0.2797	0.05938	1.17
		29.0	0.3340	0.07091	1.14
		44.8	0.3772	0.08008	1.10
		55.0	0.3946	0.08378	1.09
		76.5	0.4196	0.08909	1.07
		...	0.4710	0.10000	...
4	A = 0.1	2.3	0.0460	0.00977	0.773
	B = 0.061	11.7	0.1615	0.03429	0.709
	(NaAc = 0.5)	22.3	0.2330	0.04947	0.660
	(NaCl = 0.25)	42.0	0.3042	0.06459	0.614
		51.3	0.3278	0.06960	0.610
		60.0	0.3453	0.07331	0.608
		72.0	0.3634	0.07716	0.600
		96.5	0.3893	0.08263	0.584
		...	0.4710	0.10000	...

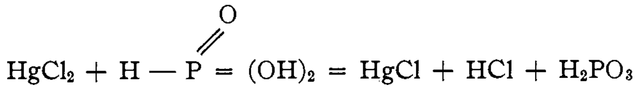
TABLE I (*continued*).

Expt. No.	Initial concen.	t in hours.	HgCl in grams.	x in mols.	K.
5............	A = 0.1	3.1	0.0386	0.00820	0.466
	B = 0.061	12.4	0.1192	0.02531	0.445
	(NaAc = 0.5)	22.9	0.1800	0.03822	0.418
	(NaCl = 0.5)	42.5	0.2535	0.05382	0.408
		63.8	0.2993	0.06355	0.389
		74.3	0.3168	0.06726	0.385
		86.4	0.3336	0.07083	0.380
		99.0	0.3475	0.07378	0.376
		119.4	0.3677	0.07807	0.376
		...	0.4710	0.10000	...
6............	A = 0.0985	12.5	0.0710	0.01507	0.229
	B = 0.0610	22.6	0.1146	0.02433	0.229
	(NaAc = 0.5)	47.2	0.1894	0.04021	0.225
	(NaCl = 1.0)	69.3	0.2342	0.04977	0.219
		108.6	0.2890	0.06136	0.215
		143.0	0.3220	0.06837	0.215
		...	0.4638	0.09850	...
7............	A = 0.0985	28.0	0.0726	0.01541	0.106
	B = 0.0610	53.3	0.1235	0.02622	0.107
	(NaAc = 0.5)	77.3	0.1600	0.03397	0.106
	(NaCl = 2.0)	102.4	0.1916	0.04068	0.105
		146.0	0.2355	0.05000	0.105
		197.4	0.2708	0.05749	0.103
		...	0.4638	0.09850	...

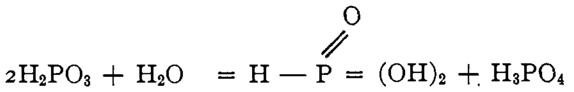
Discussion of the Results.

It is evident from Expts. 1, 2 and 7 that fairly concordant velocity constants may be obtained if the reaction proceeds under favorable conditions. It is also interesting to note that as the initial concentration of the sodium chloride is increased from 0.0 in Expt. 3 to twice normal in Expt. 7, the velocity coefficient gradually approaches constancy until in Expt. 6 the difference between the first and the last figures is only about 6%; also the total effect of the sodium chloride in the lowering of the magnitude of the velocity coefficient is seen to vary gradually from approximately 1.8 in Expt. 1 to 0.105 in Expt. 7. As far as the constants of Expts. 1, 2, 6 and 7 show, then, the reaction between mercuric chloride and sodium formate is evidently one of the second order, and it only remains to make the theory fit the figures.

The reaction between mercuric chloride and sodium formate may be represented in a similar manner to the one between mercuric chloride and phosphorous acid, thus:

(*a*) 

$$HgCl_2 + H - \overset{\overset{O}{/\!/}}{P} = (OH)_2 = HgCl + HCl + H_2PO_3$$

(b) 

$$2H_2PO_3 + H_2O = H - \overset{\overset{O}{/\!/}}{P} = (OH)_2 + H_3PO_4$$

where reaction (b) is assumed to be practically instantaneous. Similarly:

$$(c)\ HgCl_2 + H - COONa = HgCl + HCl + (-COONa)$$

In (a) we have a well-known compound formed, hypophosphoric acid, readily hydrated and incapable of reducing mercuric chloride except indirectly as indicated in (b). But no such compound as —COONa is known. However, two such radicals in their nascent state might unite to form one molecule of sodium oxalate. But it is well known that sodium oxalate does not have the property of reducing mercuric chloride under ordinary conditions. Moreover, no trace of oxalates could be detected at any stage of the reaction. The most plausible assumption, then, is that the secondary reaction is similar to (b); that is, two radicals at the instant of liberation combine with one molecule of water to form one molecule of sodium formate and one of sodium hydrogen carbonate which is at once decomposed by the hydrochloric acid generated at the same time. The reactions, although occurring simultaneously, may be represented by the following equations:

$$(d)\ HgCl_2 + H - COONa = HgCl + HCl + (-COONa)$$

$$(e)\ 2 - COONa + H_2O = HCOONa + NaHCO_3$$

$$(f)\ NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

Denoting the molal concentration of the mercuric chloride by A, that of the sodium formate by B, and by x the amount of the reacting substances decomposed, or the amount of mercurous chloride formed at time t, we have

$$\frac{dx}{dt} = K(A - X)(B - X + {}^1/_2X)^1$$

$$\frac{dx}{dt} = {}^1/_2K(A - X)(2B - X)$$

$$K = \frac{(2)(2.3)}{(2B - A)t} \log \frac{A(2B - X)}{2B(A - X)}$$

Summary and Conclusion.

1. It has been shown fairly conclusively, both experimentally and theoretically, that the reaction between mercuric chloride and sodium formate, like that between mercuric chloride and phosphorous acid, is one of the second order.

2. The retarding influence of the sodium chloride formed in the reaction is remarkable. Its effect, however, was reduced to a minimum by working, on the one hand, with dilute solutions of mercuric chloride, and, on the

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[1] Since for every two molecules decomposed one molecule is regenerated, see also *Am. J. Sci.*, **35**, 353–368 (1913).

other hand, by adding a large excess of sodium chloride initially to the reaction mixture, so that the amount of sodium chloride formed in the reaction was rendered negligible. Under these conditions concordant velocity constants were obtained as may be seen from Expts. 1, 2 and 7.

The experimental part of this work was begun at the Kent Chemical Laboratory of Yale University.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE EFFECT UPON THEIR SOLUTION TENSIONS OF DISSOLVING THE ALKALI AND ALKALI EARTH METALS IN MERCURY, AND THE CONSTITUTION OF SUCH SOLUTIONS.

BY GEORGE MCPHAIL SMITH.

Received November 2, 1914.

In a discussion of the constitution of liquid amalgams, C. H. Desch[1] makes the following statements: "In simple eutectiferous series, in which the freezing-point curve shows no indication of the formation of compounds, we may safely accept the conclusion arrived at by the three methods described above (*i. e.*, the cryoscopic, vapor-pressure, and electromotive-force methods), that the dissolved metals are monatomic. *In series in which compounds occur, it remains as yet an open question whether the same condition prevails, or whether compounds containing a single atom of the dissolved metal in each molecule, are also present.*[2] The only experimental method which gives any indication of a definite answer to this question is that of measuring the velocity of diffusion in liquid metals." He then proceeds to describe a portion of a paper by the writer[3] in which this method is developed by the latter by means of M. von Wogau's[4] experimental measurements of the rate of diffusion of various metals in mercury, and in which it is shown by this method that, in the case of the alkali and alkali earth amalgams, such compounds do actually exist in the mercurial solutions.[5]

In the above-mentioned paper,[3] however, another experimental method is also developed, which, although it is at least capable of furnishing confirmatory evidence of the same thing, was in that paper apparently not explained sufficiently in detail. It is with the purpose of furnishing a clearer exposition of the latter method that the present paper is written.

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[1] "Text-Books of Physical Chemistry," edited by Sir William Ramsay; "Metallography," by Cecil H. Desch, ed. 1910, p. 333f.

[2] The italics are the writer's.

[3] G. Mc. P. Smith, *Z. anorg. Chem.*, **58**, 381 (1908).

[4] Max von Wogau, *Ann. Physik*, **23**, 345 (1907).

[5] The diffusion method as applied to the study of the constitution of metallic solutions has subsequently been placed upon a firm theoretical basis (cf. G. Mc. P. Smith, THIS JOURNAL, **36**, 859 (1914)).