[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

SECONDARY KINETIC SALT EFFECT IN THE CASE OF HYDROXYL-ION CATALYSIS

BY J. N. BRÖNSTED AND CECIL V. KING

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Introduction

The term "secondary kinetic salt effect" is used to indicate a kinetic salt effect due to a change in concentration of the reacting molecules on account of a change in the inter-ionic forces.[1,2] Such effects are very commonly met in the study of kinetic reactions. For instance, the enhanced catalytic activity of acetic acid on addition of neutral salts originates, as surmised already by Arrhenius[3] in his investigation on sucrose inversion, from the displacement of the dissociation equilibrium of the acid. Such displacement also accounts for the effect of salts upon the decomposition of nitro-amide[1] and of diazo-acetic ester[2] by weak acids, and for several related phenomena. It is the purpose of the present paper to show the same influence of salts to exist in the case of hydroxyl-ion catalysis when this ion enters in a displaceable homogeneous equilibrium.

Now, it is quite remarkable that in the important work of Arrhenius,[4] where the theory of basic catalysis as an hydroxyl-ion effect was set forth, the experimental material from which the author drew his conclusions in reality does exhibit a secondary salt effect of the precise magnitude to be expected from the present point of view.

The experiments referred to consisted in measuring the speed of saponification of ethyl acetate by 0.025 *M* ammonium hydroxide solution in the presence of ammonium chloride ranging in concentration from 0.0025 to 0.050 *M*. The velocity was found to be roughly proportional to the hydroxyl-ion concentration calculated according to the classical principles. A closer examination, however, reveals a considerable positive salt effect, that is, the speed is proportionally too high in the solution containing much ammonium chloride. This is in agreement with the theory of the secondary kinetic salt effect.

The equilibrium in a basic NH_3—NH_4^+—mixture, $NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$, is determined by the equation, $(c_{NH_4^+}c_{OH^-}/c_{NH_3})(f_{NH_4^+}f_{OH^-}/f_{NH_3}) = K_a$, where c and f indicate concentration and activity coefficient, respectively, and K_a is the thermodynamic equilibrium constant.

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[1] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[2] Brönsted and Teeter, *J. Phys. Chem.*, **28**, 579 (1924).

[3] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899). Brönsted, *J. Chem. Soc.*, **119**, 579 (1921).

[4] Arrhenius, *Z. physik. Chem.*, **2**, 284 (1888).

Introducing the classical equilibrium constant, $(c_{NH_4^+}c_{OH^-}/c_{NH_3}) = K_c$, and putting $f_{NH_3} = 1$ and $f_{NH_4^+} = f_{OH^-} = f_1$, we obtain $f_1 = \sqrt{K_a/K_c}$.

Now, calculating c_{OH^-}, and from this again K_c, by means of the velocity measured, the change in f_1 obviously becomes computable, since K_a is a constant. The results of this calculation are given in Table I, where k indicates the velocity constant. The value of K_a has been so chosen that f_1 at the concentration 0.0025 becomes 0.95, since this value of f_1 is known from other sources of information to be approximately correct at this concentration.

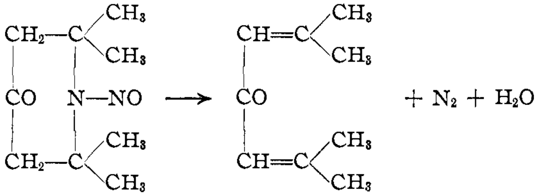
TABLE I

VELOCITY CONSTANT k AND ACTIVITY COEFFICIENT f_1 IN NH_3—NH_4^+—MIXTURES

c_{NH_4Cl}	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150
k	38.7	22.6	16.2	12.7	10.6	9.2
f_1,	0.95	0.91	0.88	0.86	0.85	0.83
c_{NH_4Cl}		0.0175	0.020	0.0225	0.0250	0.0500
k		8.1	7.3	6.7	6.2	3.3
f_1,		0.82	0.80	0.79	0.79	0.76

Constant values of f_1, thus calculated, would mean agreement with the classical views, that is, no salt effect. The change in f_1, actually found, proves that a considerable positive salt effect exists. In fact, the numerical values of f_1 given in the table agree well with existing measurements of activity coefficients of univalent ions.

In order to provide more evidence in favor of the theory of secondary salt effect we have taken up a study of the catalytic decomposition of nitroso-triacetone-amine, which in the presence of hydroxyl ions changes into phorone and nitrogen.



This reaction found by Heintz[5] has been thoroughly studied by F. Francis[6] and his co-workers, who showed that at small hydroxyl-ion concentration it is a simple unimolecular catalytic reaction. At higher hydroxyl-ion concentration the course of the reaction is more complicated. Since our purpose is only the application of the theory of secondary salt effect upon the simple catalytic process, we have made no effort to elucidate those complications.

The process offers an advantage for the experimental work in the fact

[5] Heintz, *Ann.*, **187**, 250 (1877).

[6] Francis and Cliddens, *J. Chem. Soc.*, **101**, 2358 (1912). Francis and Geake, *ibid.*, **103**, 1722 (1913). Francis, Geake and Roche, *ibid.*, **107**, 1651 (1915).

that it is accompanied by an evolution of gas and so can be followed by a simple manometric arrangement.

Calculation of Secondary Salt Effect

Catalytic reactions in which the hydroxyl ion is the active catalyst may be influenced differently by salt addition, according to the type of equilibrium in which the hydroxyl ion enters.

Taking as an example a piperidine-piperidinium ion buffer, the equilibrium $C_5H_{11}N + H_2O \rightleftarrows C_5H_{12}N^+ + OH^-$ existing here is obviously shifted from the left to the right by the addition of salt. The equilibrium constant in dilute solution is given by $(c_{C_5H_{12}N^+}c_{OH^-}/c_{C_5H_{11}N})(f_{C_5H_{12}N^+}f_{OH^-}/f_{C_5H_{11}N}) = K_a$. Putting $f_{C_5H_{12}N^+} = f_{OH^-} = f_1$ and $f_{C_5H_{11}N} = 1$, the hydroxyl-ion concentration is $c_{OH} = K_a(c_{C_5H_{11}N}/c_{C_5H_{12}N^+})(1/f_1^2)$.

Increasing salt concentration, therefore, increases the hydroxyl-ion concentration and thus, also, the reaction velocity. That is, we have to expect in this case a positive salt effect. In dilute solution the effect is approximately computable from the change in f_1 with salt concentration.

On the other hand, considering the following phosphate buffers, $PO_4^{---} + H_2O \rightleftarrows HPO_4^{--} + OH^-$, application of the mass-action law furnishes the expression, $(c_{HPO_4^{--}}c_{OH^-}/c_{PO_4^{---}})(f_{HPO_4^{--}}f_{OH^-}/f_{PO_4^{---}}) = K_a$, or $c_{OH^-} = K_a(c_{PO_4^{---}}/c_{HPO_4^{--}})(f_3/f_1f_2)$, f_1, f_2 and f_3 referring to uni-, bi- and trivalent ions, respectively. As the fraction f_3/f_1f_2 decreases by increasing concentration of salt, we have to expect in this case a negative salt effect.

These results can easily be generalized. When writing the equilibrium in question, $A \rightleftarrows B$, the hydroxyl ion, or generally the catalyzing molecule, belonging to the system B, a positive salt effect will usually have to be expected if $\Sigma z_B^2 > \Sigma z_A^2$ and a negative salt effect if $\Sigma z_A^2 > \Sigma z_B^2$. Σz_A^2 and Σz_B^2 here mean the sum of the squares of the electric charges of the molecules belonging to System A and System B, respectively.[7]

The question has to be answered here, whether we are allowed to assume the velocity of the catalytic reaction proportional to the concentration of the reacting molecule M and the hydroxyl-ion concentration. According to the recent theory of reaction velocity[8] a reaction between an ion and a neutral molecule is characterized by a linear salt effect, in dilute solution usually very small compared with the secondary effect here dealt with. In other words, the velocity "constant" k in the kinetic equation

$$h = k\, c_M c_{OH^-} \tag{1}$$

can be considered a constant at small concentrations, but at higher concentrations varies with the salt concentration according to a linear expression

$$k = k_0 + \alpha c \tag{2}$$

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[7] This result is obtainable from the theory of velocity of ionic reaction[8] in combination with the Debye-Hückel theory of electrolytes, *Physik. Z.*, **24**, 185 (1923).[8]

[8] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

where α is a constant and c the equivalent salt concentration of the solution. In order to be able to calculate the hydroxyl-ion concentration in any experiment from the rate of decomposition of the nitroso-triacetone-amine, the values of k_0 and α, therefore, have to be known. This, of course, is possible from velocity measurements with solutions of a strong base such as sodium hydroxide with addition of various amounts of neutral salt.

The present investigation covers measurements of the nitroso-triacetone-amine in sodium hydroxide, piperidine and phosphate buffer solutions with addition of various amounts of neutral salt.

Description and Use of Apparatus

The apparatus used for the study of the decomposition of nitroso-triacetone-amine was designed to measure quite generally the velocity of a reaction in which a gas is evolved by a measure of the increase in pressure above the solution as the reaction proceeds.

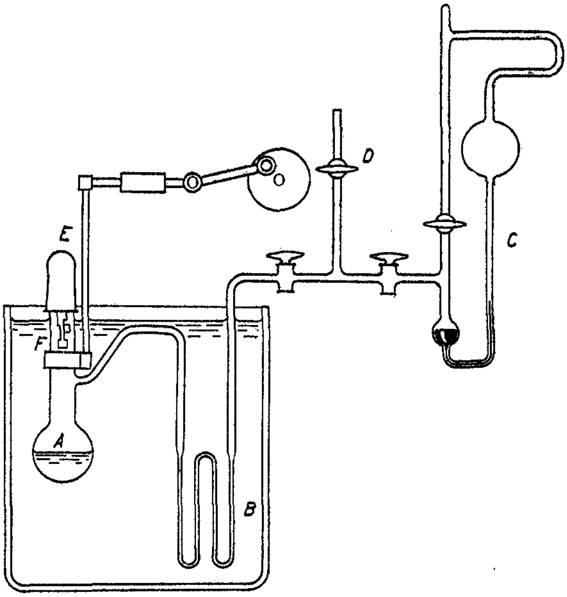

Fig. 1.

The reaction vessel is the 200cc. flask A (Fig. 1), which is fitted with the ground, slip-on stopper E. It is connected with the manometer through the side arm and the capillary at B. The elasticity of this capillary allows the reaction flask to be mechanically shaken, thus rapidly establishing equilibrium between gas above and in the solution. The flask is immersed in a thermostat as shown. The stopper and all stopcocks are lubricated with a good stopcock grease.

The manipulation of the apparatus is as follows. The space above the mercury in C is evacuated through D to a low pressure (0.1 mm. or less) with the reaction flask closed off; then the manometer is closed and the reaction flask containing the solution and capillaries evacuated (with the flask in motion to assist in freeing the solution from dissolved air). After a few minutes' evacuation D is closed, the reaction flask and manometer are connected, and thereafter pressure readings are taken at suitable intervals.

F is an arrangement to hold a small platinum pail, which may be released at any desired time by a magnet. In these relatively slow experiments where the reaction was known to be unimolecular, and an arbitrary time could be used as a zero point, the nitroso-triacetone-amine was dissolved in the solution before its introduction into the reaction flask, and the device used in only a few experiments of dropping in solid barium hydroxide after a sufficient number of pressure readings had been taken and, thus, by making the solution more alkaline, hastening the attainment of the final pressure. In other experiments where the reaction is more rapid, or for other reasons the starting point ought to be known, this device was used to start the reaction by dropping in one of the reactive substances after the apparatus had been evacuated.

In all of these experiments the temperature of the thermostat was maintained at 15° ±0.01° by an electrically-controlled regulation.

Experimental Results and Discussion

Sodium Hydroxide Solutions.—These measurements were carried out in order to determine k_0 and α of Equation 2.

A solution of 0.24 g. of nitroso-triacetone-amine in warm water free from carbon dioxide in a 200cc. volumetric flask was cooled, the air above the solution replaced by air free from carbon dioxide, enough 0.1012 N sodium hydroxide solution run in to make the whole 0.01 N, and the flask filled to the mark with water free from carbon dioxide. Half of this solution was poured into a 100cc. volumetric flask containing the desired amount of solid sodium chloride and filled with air free from carbon dioxide, and the two solutions were at once poured into the reaction flasks of duplicate pieces of apparatus, the air in these reaction flasks having been previously replaced by air free from carbon dioxide. In this way each solution containing sodium chloride was directly comparable with one containing the same concentration of sodium hydroxide but no sodium chloride, and the several experiments with no sodium chloride showed that experiments could be duplicated satisfactorily.

Piperidine Solutions.—A sample of commercial piperidine was distilled thrice and the portion boiling between 205.5° and 206.5° finally collected. A portion of this was weighed and dissolved in enough water to make a 0.3 M solution; titrations of samples of this with 0.1 N hydrochloric acid showed 99.5% of the calculated alkalinity. For each experiment, 50 cc. of this solution and 10 cc. of 0.1 N hydrochloric acid were added to a solution of 0.12 g. of nitroso-triacetone-amine, and the whole was diluted to 100 cc.

Phosphate Solutions.—2.969 g. of pure disodium phosphate, $Na_2HPO_4.2H_2O$, was weighed into a 500cc. volumetric flask ($^1/_{80}$ mole per liter) and dissolved, enough 0.1 N sodium hydroxide solution added to make 0.025 equivalent per liter and the whole diluted to 500 cc. For each experiment, 40 cc. of this was added to the solution of 0.12 g. of nitroso-triacetone-amine and diluted to 100 cc.

Table II

Decomposition of Nitroso-triacetone-amine at 15° in 0.01 M Sodium Hydroxide

c_{NaCl}	0	0	0	0	0.03	0.05	0.1	0.15	0.20
c	0.01	0.01	0.01	0.01	.04	.06	.11	.16	.21
		0.190							
$k' \times 10^2$	0.189	.190	.191	.191	.188	.186	.176	.168	.165

In Table II are given the results for 0.01 M sodium hydroxide solution with various concentrations of sodium chloride; c is the total salt concentration and k' is the monomolecular constant of the experiment, using decadic logarithms and measuring the time in minutes.

The values are plotted in Fig. 2, which shows a linear negative salt effect amounting to about 7% in 0.1 N salt solution. The data can be satisfied by the equation,

$$k = 0.192 - 0.13\ c \tag{3}$$

where $k(=100\ k')$ is the decadic-logarithmic velocity constant of Equation 1.

Direct comparison with the measurements of Francis cannot be made since the temperatures of experiment are different[9] and the temperature coefficient is not known with sufficient accuracy. A salt effect in experiments with various concentrations of strong base is not clearly observable in the experiments stated by Francis. Addition of much neutral salt, however, caused a decided decrease in velocity in agreement with the results of Table II. That these show a considerably higher salt effect than indicated by the data of Francis may be due to the much smaller concentrations and the lower temperature of our experiments.

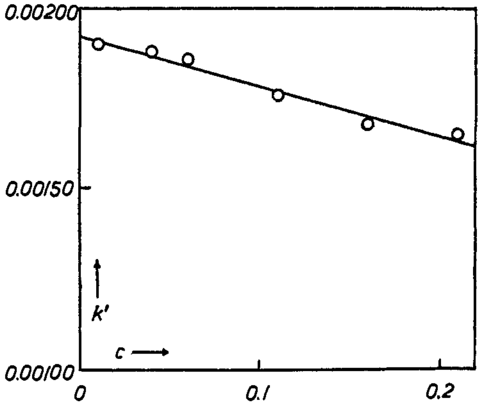

Fig. 2.

TABLE III

DECOMPOSITION OF NITROSO-TRIACETONE-AMINE AT 15° IN PIPERIDINE SOLUTIONS

Stoichiometric concentrations: $c_{\text{Pip.}} = 0.15\ M$, $c_{\text{HCl}} = 0.01\ M$

c_{NaCl}	c	k'	k	c_{OH^-}	$c_{\text{Pip}\cdot\text{H}^+}$	$c_{\text{Pip.}}$	K_c
0	0.0205	0.001985	0.190	0.0105	0.0205	0.1295	0.00166
.02	.0411	.00207	.187	.0111	.0211	.1289	.00182
.05	.0719	.00217	.183	.0119	.0219	.1281	.00203
.08	.1025	.00223	.179	.0125	.0225	.1275	.00221
.15	.1736	.00232	.170	.0136	.0236	.1264	.00254
.20	.2244	.00234	.163	.0144	.0244	.1256	.00280

In Table III are given the results for the piperidine buffer solution with sodium chloride up to 0.2 N. The hydroxyl-ion concentration (Col. 5) is obtained by dividing the observed velocity constant k' (Col. 3) by the

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[9] The temperature of 15° for our experiments was chosen because the apparatus used is applicable only at temperatures below room temperature.

velocity constant k of Equation 3 for approximately the same total salt concentration as calculated from Equation 3 and given in Col. 4. From this and the stoichiometric concentrations, the values in Cols. 6 and 7 can be obtained, by means of $c_{\text{Pip.H}^+} = 0.01 + c_{\text{OH}^-}$, $c_{\text{Pip.}} = 0.14 - c_{\text{OH}^-}$ and so $K_c = c_{\text{Pip.H}^+}.c_{\text{OH}^-}/c_{\text{Pip.}}$ (Col. 8), calculated. The exact total salt concentration (Col. 2) is the sum of c_{NaCl} and $c_{\text{Pip.H}^+}$.

Table IV

Decomposition of Nitroso-triacetone-amine at 15° in Phosphate Solutions

Stoichiometric concentrations: $C_{\text{PO}_4^{---}} = 0.01\ M$, $c_{\text{HPO}_4^{--}} = 0.00333\ M$

c_{NaCl}	c	k'	k	c_{OH^-}	$c_{\text{PO}_4^{---}}$	$c_{\text{HPO}_4^{--}}$	K_c
0	0.0367	0.000854	0.1875	0.00455	0.00545	0.00788	0.00658
.02	.0567	.000774	.185	.00418	.00582	.00751	.00539
.05	.0867	.000718	.181	.00397	.00603	.00730	.00481
.10	.1367	.000621	.1745	.00356	.00643	.00689	.00381
.15	.1867	.000556	.168	.00331	.00669	.00664	.00329
.20	.2367	.000497	.164	.00303	.00697	.00636	.00276

In Table IV are the results for the phosphate buffer solution with sodium chloride up to 0.2 N. From the materials used to make up the solutions, it is seen that the stoichiometric concentrations were $c_{\text{PO}_4^{---}} = 0.01\ M$ and $c_{\text{HPO}_4^{--}} = 0.00333\ M$. The total equivalent salt concentration (Col. 2) is, then, $c_{\text{Na}^+} = (3 \times 0.01) + (2 \times 0.00333) + c_{\text{NaCl}}$. The hydroxyl-ion concentration is obtained as before, the phosphate ions by means of $c_{\text{PO}_4^{---}} = 0.01 - c_{\text{OH}^-}$ and $c_{\text{HPO}_4^{--}} = 0.00333 + c_{\text{OH}^-}$. The equilibrium constant K_c is $K_c = c_{\text{HPO}_4^{--}}\,c_{\text{OH}^-}/c_{\text{PO}_4^{---}}$.

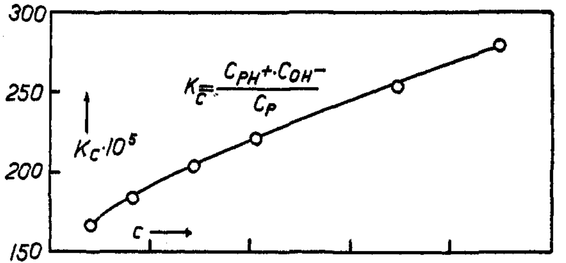

Fig. 3.

As shown by the k' values in Tables III and IV, the piperidine buffer is characterized by a considerable positive salt effect, while in the case of the phosphate buffer a strong negative salt effect is present. As already pointed out in the theoretical part, these results are both in agreement with the theory.

The best survey of the salt effect is obtained by considering the change in K_c caused by the salt addition and computed from the velocity measurements. These values are given in the last column of the tables and plotted in Figs. 3 and 4.

For the piperidine equilibrium we have $K_c = K_a/f_2$ and for the phosphate equilibrium $K_c = K_a f_3/f_1 f_2$, K_a in both cases being the thermodynamic constant for the reaction considered. The change in K_c with salt concentration as represented by the two curves actually does exhibit approximate agreement with the change in the two activity factors the values of which are known at least with a rough approximation from solubility measurements and other sources of information.

The considerable changes with salt concentration shown by the equilibrium constants K_c illustrate clearly the inadequacy in stating the strength of acids and bases by means of the usual mass action "constants" unless simultaneously the region of salt concentration for which the "constant" applies is also stated.

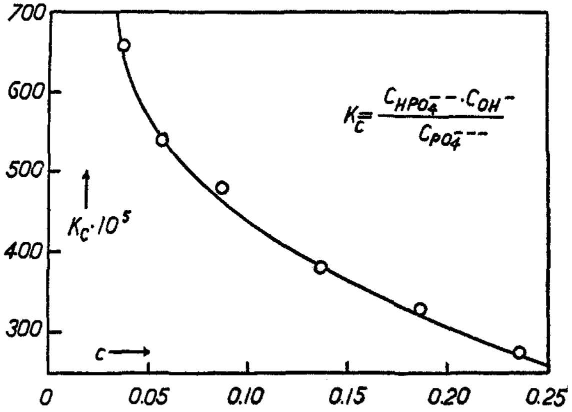

Fig. 4.

The authors wish to thank the American Scandinavian Foundation for the grant of a fellowship to the junior author which made this investigation possible. They also are indebted to Professor F. Francis of the University of Bristol for having kindly placed at their disposal the amount of nitroso-triacetone-amine necessary for this investigation.

Summary

1. The velocity data found by Arrhenius in 1888 in the saponification of ethyl acetate by ammonia-ammonium buffers show a considerable secondary salt effect.

2. An apparatus is described to determine the speed of reactions accompanied by the evolution of a gas. With this apparatus measurements were carried out to determine the decomposition of nitroso-triacetone-amine catalyzed by hydroxyl ions under various conditions.

3. When catalyzed by a strong base this reaction shows a negative primary salt effect.

4. The same reaction measured in a piperidine-piperidinium ion and a phosphate buffer shows a considerable secondary salt effect, positive in the first and negative in the second case. These effects are in agreement with the theory of kinetic salt effect.

5. The reaction studied exemplifies the inadequacy of stating an ion-equilibrium constant without reference to the specific region of salt concentration to which it applies.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE EPPLEY LABORATORY]

SATURATED STANDARD CELLS WITH SMALL TEMPERATURE COEFFICIENTS

BY WARREN C. VOSBURGH

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Two kinds of Weston cells are used as standards of electromotive force, the unsaturated cell and the normal cell. The unsaturated cell has the advantage of a negligible temperature coefficient,[1] but its electromotive force is not constant over long periods of time,[2] and from a practical standpoint it is not as reproducible as the normal cell. The normal cell has the advantage of reproducibility and constancy and the disadvantage of an appreciable temperature coefficient. It has been found possible to alter the normal cell in such a way as to reduce its temperature coefficient considerably. This can be done by using for the amalgam electrode an amalgam containing tin or lead as well as cadmium.

The systems cadmium-tin-mercury and cadmium-lead-mercury have been investigated by Kremann, Prammer and Helly.[3] They found that the addition of tin or lead to a two-phase cadmium amalgam gave an amalgam that showed a constant potential difference against a solution containing cadmium ion for quantities of the added metal between 10 and 75 atomic per cent. of the whole.

Preparation of Materials

Cadmium Sulfate.—The cadmium sulfate was twice recrystallized by slow evaporation of a saturated solution at room temperature.

Mercurous Sulfate.—Mercurous sulfate 11 was used. This was a coarse-grained, electrolytic preparation which had been used in previous work.[4]

Mercury.—The mercury was passed through a column of mercurous nitrate solution in a finely divided state and then redistilled in a current of air.

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[1] Vosburgh and Eppley, THIS JOURNAL, **45**, 2268 (1923).

[2] Vosburgh, *J. Optical Soc. Am.*, **11**, 59 (1925).

[3] Kremann, Prammer and Helly, *Z. anorg. allgem. Chem.*, **127**, 295 (1923).

[4] Vosburgh, THIS JOURNAL, **47**, 1256 (1925).