in normal sodium sulfate, in Tables I, II and III. It seems, therefore, that the original supposition that metals with low solution tensions passivify at a lower current density than those with high solution tensions is in general correct for this character of material. but the statement cannot be made more definite at this time.

Summary.

1. Samples of iron of very different composition and structure can be made passive when the anode is an electric circuit. The transition density from active to passive is not related in any simple way to the composition and structure of the samples. The nature and concentration of the electrolyte are factors in bringing about passivity in samples of the character of these just as for the pure metal.

2. We believe that the phenomenon is not an instantaneous change from active to passive, but a gradual adjustment toward a new condition of equilibrium, since in the majority of the experiments less iron goes into solution as the current density necessary for passivifying is approached. No statement can be made relative to the solubility of passive iron of this character, since the samples behaved normally, *i. e.*, when the circuit was broken the anode became active.

3. The current density required for passivifying increases with the electrode potential. In general, metals with low solution tension passivify at a lower current density than those with high solution tension.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE.]

DETERMINATION OF THE SOLUBILITY OF SILVER NITRITE AND ITS DEGREE OF DISSOCIATION IN A SATURATED SOLUTION.

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The pure silver nitrite used in the following measurements was prepared as follows: To a solution of silver nitrate, a solution containing a 25% excess of potassium nitrite was added, the precipitated silver nitrite allowed to settle, the supernatant liquid then decanted off and the crystals washed several times with cold water. These crystals were then recrystallized twice from hot, distilled water, and finally dried between filter paper. In order to ascertain the purity of these crystals of silver nitrite, which were pale, lemon yellow in color, their silver content was estimated by analysis with standard ammonium thiocyanate solution, ferric alum being used as an indicator. The results obtained were as follows: (I), 70.05% Ag; (II), 70.08% Ag; (III), 70.07% Ag. The close agreement between these values and the theoretical (70.10% Ag) is indicative of the high degree of purity of the silver nitrite used in the following measurements. Owing to the rapid action of light on silver nitrite, it was kept in brown bottles which were completely covered with black paper. That silver nitrite when so kept undergoes but slight decomposition is shown by the fact that a sample of the salt, at the end of two months, was found to contain 70.01% Ag, and a three-year-old sample, 69.04% Ag.

The solutions of pure potassium nitrite, employed in some of the experiments, were prepared by adding solutions of pure potassium chloride to hot solutions containing a slight excess of pure silver nitrite, the precipitated silver chloride being removed by filtration.

Measurements of the conductivity of silver nitrite were carried out at 25 ± 0.01°, the temperature being maintained by means of an electrically heated and regulated thermostat. The resistances were measured by means of a drum form of Wheatstone bridge, the wire of which was accurate to 0.01%. The coils of the resistance box were accurate to 0.02%. The electrolytic cell was 3 cm. in diameter and 10 cm. high. The cell constant was determined with a standard solution of potassium chloride. The water employed in the preparation of the silver nitrite solutions was prepared by the method of Jones and Mackay,[1] and had a specific conductivity of $1.3-1.6 \times 10^{-6}$. The conductivity at 25° of silver nitrite at a number of different concentrations is given in Table I.

TABLE I.—CONDUCTIVITY OF SILVER NITRITE.

Dilution. ϕ.	Equiv. cond. Λ.	$\Lambda_\phi/\Lambda_\infty$.
37.13	78.25	0.63
50.14	84.45	0.68
74.26	95.90	0.77
100.28	102.53	0.82
148.52	109.9	0.88
200.56	115.0	0.93
297	122.0	..
401	125.1	..
594	129.8	..

For Λ_∞, the value 124.2 has been used. This value has been calculated from the electrolytic mobility of the cathion,[2] $l_{Ag} = 62.5$, and that of the anion,[3] $l_{NO_2} = 61.7$, at 25°. From the rapidity with which the equivalent conductivity increases with dilution, exceeding the limiting value, Λ_∞, at a dilution of 400, it is probable that hydrolysis of silver nitrite occurs.

In order to determine the solubility of silver nitrite, a large excess of the salt was placed in each of two bottles of 300 cc. capacity, which were three-fourths filled with "conductivity" water and closed with tight-fitting, glass stoppers. These bottles were agitated in a large thermostat,

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[1] H. C. Jones, and E. Mackay, *Am. Chem. J.*, **19**, 283 (1897).

[2] Ostwald-Luther, *Phys. Chem. Messungen*, p. 481, 3rd edition.

[3] F. Vogel, *Z. anorg. Chem.*, **35**, 403 (1903).

the temperature of which was kept constant within 0.02°, for at least fourteen hours at temperatures below 40°, and for several hours at higher temperatures. At the end of the period of agitation the bottles were removed from the stirring device and kept in the thermostat for two or three hours longer, in order to allow the finely divided silver nitrite to settle. About 25 cc. of each solution were then withdrawn through a small tube filled with glass wool into a pipet, and placed in Erlenmeyer flasks fitted with glass stoppers. At the higher temperatures, the pipet was surrounded with a hot water jacket, so as to prevent the silver nitrite from crystallizing out from the solution. The weights of the solutions removed were determined. and the weight of silver nitrite contained therein ascertained by analysis with ammonium thiocyanate. From the results obtained the solubility of silver nitrite in water, *i. e.*, the weight of silver nitrite in 100 g. of solution, was calculated. The change in the solubility of silver nitrite with temperature is given in Table II. The values in this table represent the means of at least two determinations which seldom differed by more than a few tenths of 1%.

TABLE II.—CHANGE IN SOLUBILITY.

Temperature. C°.	Solubility. G. per 100 grams of solution.	Solubility. Mols per 1000 cc. of solution.
1	0.1589	0.01031
15	0.2752	0.01788
25	0.4135	0.02693
35	0.6016	0.03903
51	1.0240	0.06654
60	1.3625	0.08855

The influence of the presence of a second electrolyte containing a mutual ion upon the solubility of another is governed by these laws: (1) In a saturated solution of a partially dissociated electrolyte, the concentration of the undissociated portion remains constant even when another dissociated substance is added. (2) The product of the active mass of the ions of the electrolyte remains constant even when another electrolyte having a mutual ion is added. These laws may be expressed mathematically as follows:

$$m_0 (1 - \alpha_0) = m (1 - \alpha);$$

$$(m_0 \alpha_0)^2 = m\alpha (m\alpha + x\alpha_1),$$

where m_0 and m represent the solubility of the first electrolyte before and after the addition of the second, α_0 and α the degree of dissociation of the first electrolyte before and after the addition of the second, α_1 the degree of dissociation and x the concentration of the second electrolyte in the mixture. In the foregoing equations, m_0, m and x are expressed in mols per liter. If, therefore, to a saturated solution of an electrolyte there is added a second electrolyte, having either an anion or cathion in common with the first, it is evident from the foregoing that the equilibrium, existing between the undissociated molecules and the ions of the first electrolyte, will be displaced in such a way that a decrease in the solubility of the first electrolyte results; and, moreover, equimolar additions of the mutual anion or cathion should bring about the same decrease in the solubility. In order to determine whether this conclusion holds for silver nitrite, measurements of its solubility in the presence of silver nitrate and in the presence of potassium nitrite have been carried out at 25°. The results of these measurements are recorded in Table III.

Table III.—Effect of Added Salts on Solubility.

Conc. of $AgNO_3$ or KNO_3 in mols per liter.	Solubility of silver nitrite in the presence of				
	Silver nitrate.			Potassium nitrite.	
	G. per 100 grams of sol.	Mols per 1000 cc. of soln.		G. per 100 grams of sol.	Mols per 1000 cc. sol.
		Obs.	Calc.		
0.0000	0.4135	0.0269	..	0.4135	0.0269
0.00258	0.3991	0.0260	0.0259	0.3974	0.0259
0.00588	0.3735	0.0244	0.0247	0.3820	0.0249
0.01177	0.3432	0.0224	0.0227	0.3560	0.0232
0.02355	0.2943	0.0192	0.0187	0.3119	0.0203
0.04710	0.2498	0.0164	0.0139	0.2765	0.0181

As is to be expected, the results in the preceding table show that the addition of silver or nitrite ions brings about a decrease in the solubility of silver nitrite, and that the greater the concentration of these added ions, the greater the decrease in the solubility of the salt. It will be observed, however, that although at the smaller concentrations equimolar additions bring about approximately the same decrease in the solubility of silver nitrite, as the concentration of the addition increases, the difference between the decrease in solubility brought about by each of the two ions becomes more and more marked, reaching 10.4% when the concentration of the added salt is 0.0471 mol per liter.

By means of the preceding equations, it should be possible to calculate the solubility of silver nitrite in the presence of an electrolyte having a common ion. On solving the second of these equations for m, we obtain

$$m = -\frac{x\alpha_1}{2\alpha} + \sqrt{m_0^{\,2}\left(\frac{\alpha_0}{\alpha}\right)^2 + \frac{x^2}{4}\left(\frac{\alpha_1}{\alpha}\right)^2}.$$

Since Nernst has shown[1] that in a mixture of two binary electrolytes of like strength (*e. g.*, salts of K, Na, NH_4, Ag, etc.), which have a common ion and concentrations c_1 and c_2, respectively, the degree of dissociation is equal to and of the same value as that which would correspond to each alone for the concentration $(c_1 + c_2)$, accordingly, in the above equation, $\alpha = \alpha_1$, and

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[1] W. Nernst, *Z. physik. Chem.*, **4**, 380 (1889).

$$m = -\frac{x}{2} + \sqrt{m_0^2\left(\frac{\alpha_0}{\alpha}\right)^2 + \frac{x^2}{4}}.$$

This equation has been used to calculate the solubility of silver nitrite in the presence of the different concentrations of silver nitrate given in Table III, by employing for α_0 (the degree of dissociation of silver nitrite in a saturated solution), the value calculated from the conductivity data in Table I, *i. e.*, $\Lambda_{37.13}/\Lambda_\infty = 0.63$, and for α, values obtained by graphic interpolation of Kohlrausch's[1] values for the conductivity of silver nitrate, after converting them from 18° to 25°. As the values so calculated for the solubility of silver nitrite are very much smaller than those determined by experiment, it is probable that the value for α_0 calculated from conductivity data is much too low. The degree of dissociation of silver nitrite in a saturated solution has also been calculated by means of the equation expressing the constancy of the undissociated molecules,

$$\alpha_0 = \frac{m_0 - m + m\alpha}{m_0}.$$

The data employed for the calculation of α_0 and the values obtained are given in Table IV.

TABLE IV.—$m_0 = 0.0269$.

$m = c_1$.	c_2.	$c_1 + c_2$.	$\alpha = \alpha_1$.	α_0.
0.0260	0.00258	0.0286	0.89	0.894
0.0244	0.00588	0.0303	0.88	0.892
0.0224	0.01177	0.0342	0.87	0.892
0.0192	0.02355	0.0428	0.86	0.899
0.0164	0.04710	0.0635	0.85	0.909
			Mean,	0.90

In the above table, Col. 1 gives the solubility of silver nitrite in the presence of a concentration, c_2, of silver nitrate. Col. 4 gives the degree of dissociation of silver nitrate corresponding to a concentration, $(c_1 + c_2)$. These values have been obtained from Kohlrausch's conductivity data for silver nitrate. The last column of the table records the values calculated for the degree of dissociation of silver nitrite in a saturated solution at 25°.

The mean value given above for α_0 has been used to calculate the solubility of silver nitrite in the presence of silver nitrate. The values obtained are recorded in Col. 4 of Table III, where it will be observed that these values agree fairly well with those determined by experiment. The large deviations between the calculated and experimental values of the solubility of silver nitrite, when the degree of dissociation α_0 is obtained from conductivity measurements, together with the constancy of the values for α_0 obtained from solubility data, indicate that it is very probable that the degree of dissociation of silver nitrite in saturated solu-

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[1] Kohlrausch, F., *Wied. Ann.*, **26**, 161 (1885).

tion is considerably higher than the value calculated from conductivity data. Using $\alpha_0 = 0.90$, the solubility product of silver nitrite at 25° is $L = 5.86 \times 10^{-4}$.

Summary.

1. Measurements have been made of the conductivity of aqueous solutions of silver nitrite at 25°. The results obtained indicate that hydrolysis of the salt takes place.

2. The solubility of silver nitrite has been determined at a number of temperatures between 1 and 60°.

3. The decrease produced in the solubility of silver nitrite by the addition of silver or nitrite ions has been measured at 25°. It has been found that equimolar quantities of these ions bring about approximately the same decrease in the solubility.

4. Calculations of the solubility of silver nitrite, in the presence of different quantities of silver nitrate, indicate that the degree of dissociation of silver nitrite in a saturated solution is considerably greater than is indicated by conductivity measurements.

5. From the data obtained in the solubility measurements, a mean value of 0.90 has been calculated for the degree of dissociation of silver nitrite in a saturated solution at 25°. Using this value, the solubility product of silver nitrite is 5.86×10^{-4} at 25°.

SWARTHMORE, PA.

THE DERIVATIVES OF PERCERIC OXIDE.

[FIRST PAPER.[1]]

BY C. C. MELOCHE.

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The preparation and analysis of a derivative of perceric oxide was first described by Cleve,[2] who found that perceric hydroxide corresponded to the oxide CeO_3. In the same year Lecoq de Boisbaudran[3] published a note confirming the conclusions of the former investigator. However, the work of von Knorre[4] does not entirely substantiate the conclusions of Cleve, and Mengel[5] agrees with von Knorre in his position. Pissarjewski[6] has also contributed to the study of perceric hydroxide.

Methods for the preparation of a perceric potassium carbonate solution were first described by Job.[7] He showed that the oxidation could be

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[1] This paper is the abstract of part of a thesis submitted to the Graduate Faculty of the University of Wisconsin for the Degree of Doctor of Philosophy.

[2] *Bull. soc. chim.*, [2] **43**, 53 (1885); *Jahrb. Fortsch. Chem.*, **1885**, 491.

[3] *Compt. rend.*, **100**, 605 (1885); *Chem. News*, **51**, 148 (1885); *Jahrb. Fortsch. Chem.*, **1885**, 493.

[4] *Z. angew. Chem.*, **1897**, 723.

[5] *Z. anorg. Chem.*, **19**, 71 (1899).

[6] *J. Russ. Phys. Chem. Ges.*, **32**, 609 (1900); *Centr.*, [1] **1901**, 86.

[7] *Compt. rend.*, **128**, 178, 1098 (1899); *Ann. chim. phys.*, [7] **20**, 246, 253, 261 (1900).