[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

FERROUS NITROSO COMPOUNDS

BY H. I. SCHLESINGER AND H. B. VAN VALKENBURGH[1,2]

RECEIVED SEPTEMBER 1, 1928 PUBLISHED MAY 6, 1929

When nitric oxide is passed into solutions of ferrous sulfate, the compound $FeSO_4 \cdot NO$ is formed. The work of Manchot,[3] of Kohlschütter,[4] and more recently of Schlesinger and Salathe,[5] has shown that there are two substances, one brown and one red, which have this composition. Schlesinger and Salathe have demonstrated that the brown compound exists in solutions containing up to about 55% acid, and that the red compound exists in solutions of acid concentration greater than 65%.[6] Between these limits the two compounds are apparently in equilibrium with each other.

Manchot has proved that the aqueous or dilute sulfuric acid solutions contain a complex ion of nitric oxide and ferrous iron by demonstrating that this ion travels to the cathode. About the compound existing in concentrated acid solutions, several views have been expressed. Manchot believes that the nitric oxide in the compound is attached to the ferrous sulfate molecule as a whole. Raschig[7] holds that it is a derivative of the hypothetical nitrosi-sulfonic acid, H_2SNO_5, and makes use of this hypothesis in demonstrating his theory of the lead chamber process. Kohlschütter, finally, is of the opinion that the effect of the sulfuric acid is due in part to auto-complex formation and in part to the dehydrating action of the acid. The latter view receives decisive support from the investigation herein reported.

Kohlschütter has already shown that ferrous chloride in alcoholic solutions reacts with nitric oxide, and that the compound formed in the presence of water is brown, like the ferrous sulfate complex, while in the alcoholic solutions a green color is obtained, and that the two have dif-

---

[1] This material is taken from a thesis to be presented by H. B. Van Valkenburgh to the Ogden Graduate School of Science in partial fulfilment of the requirements of the degree of Doctor of Philosophy. The work was completed in the summer of 1926.

[2] The work herein reported is part of a more comprehensive line of investigation undertaken with the assistance of a grant from the Bache fund of the National Academy of Sciences.

[3] Manchot, *Ann.*, **350**, 368 (1906); **372**, 153 (1910); *Ber.*, **47**, 1601 (1914); *Z. anorg. allgem. Chem.*, **140**, 22 (1924).

[4] Kohlschütter, *Ber.*, **37**, 3044 (1904); **40**, 873 (1907); **44**, 1423 (1911).

[5] Schlesinger and Salathe, THIS JOURNAL, **45**, 1871 (1923).

[6] Manchot and Linckh, *Ber.*, **59**, 406 (1926), apparently without knowledge of the earlier work of Schlesinger and Salathe, published data concerning the absorption spectra of various metal–nitroso compounds in different solvents and obtained results in close agreement with those found in this Laboratory. The question of the range of concentration in which the transition occurs was not studied by them.

[7] Raschig, *Z. angew. Chem.*, **18**, 1281 (1905); *J. Soc. Chem. Ind.*, **30**, 166 (1911).

ferent absorption spectra. The spectra obtained visually by Kohlschütter are not accurate enough to be of use in deciding definitely whether they are of the same character as those of solutions of the ferrous sulfate–nitric oxide complex, or to determine at what concentration the transition from one compound to the other occurs. Photographs taken by us answer these questions more satisfactorily.

In Fig. 1 are shown the absorption spectra of the compound $FeCl_2 \cdot NO$ when dissolved in water, in water alcohol mixtures and in absolute alcohol. An absorption band extending approximately from oscillation frequencies 1920 to 2320 is shown in 30, 70 and 90% alcohol. In the aqueous solution the band is somewhat narrower, but its right-hand margin and the region of maximum transmission are the same as for the alcohol–water mixtures. The slight difference observed may be accounted for by the fact that in solutions containing water the concentration of the complex is lower than in alcoholic solutions because its stability decreases as the concentration of alcohol decreases. Consequently at a given nitric oxide pressure (atmospheric in our experiments) less of the ferrous chloride is converted into the complex than in the solutions containing more alcohol. This fact also explains the greater depth of the band in alcoholic solutions. When absolute alcohol is used the band is definitely different from all of the others, showing with respect to them a displacement toward the red of both margins and of the region of maximum transmission.

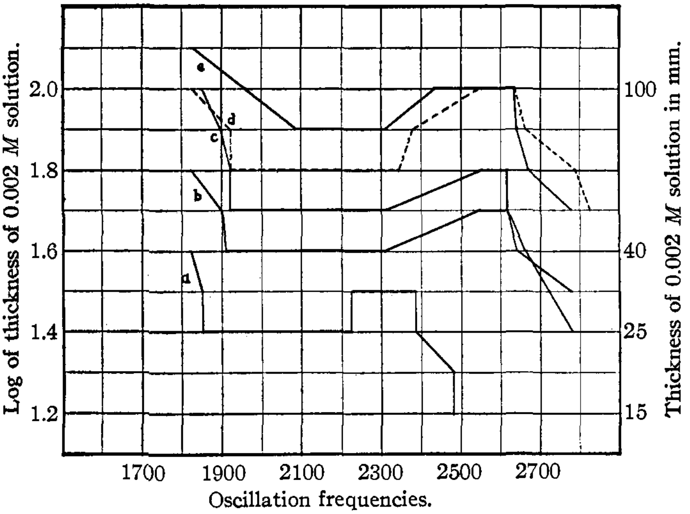

Fig. 1.—0.002 *M* $FeCl_2 \cdot NO$ in alcohol of following concentrations: a = absolute, b = 90%, c = 70%, d = 30%, e = water solution.

Comparison of these spectra with those obtained by Schlesinger and Salathe[5] reveals several significant facts. As shown in Fig. 2, the spectra of the dilute alcoholic solutions of the complex $FeCl_2 \cdot NO$ are practically identical, so far as location of the band is concerned, with those of the less strongly acid solutions of the compound $FeSO_4 \cdot NO$. The slight differences which exist are unquestionably due in part to the difficulty of obtaining exact measurements of solutions so subject to contamination with actinic substances as are those under investigation, and in part to difference in the stability of the two solutions. The second point to be considered is

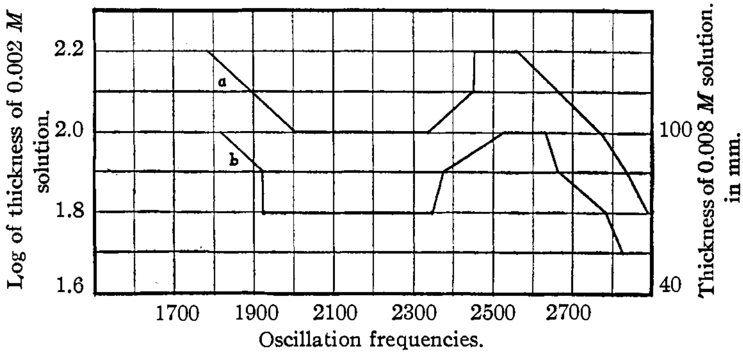

Fig. 2.—a = 0.0125 *M* $FeSO_4 \cdot NO$ in 45% H_2SO_4, after Schlesinger and Salathe; b = 0.002 *M* $FeCl_2 \cdot NO$ in 30% C_2H_5OH.

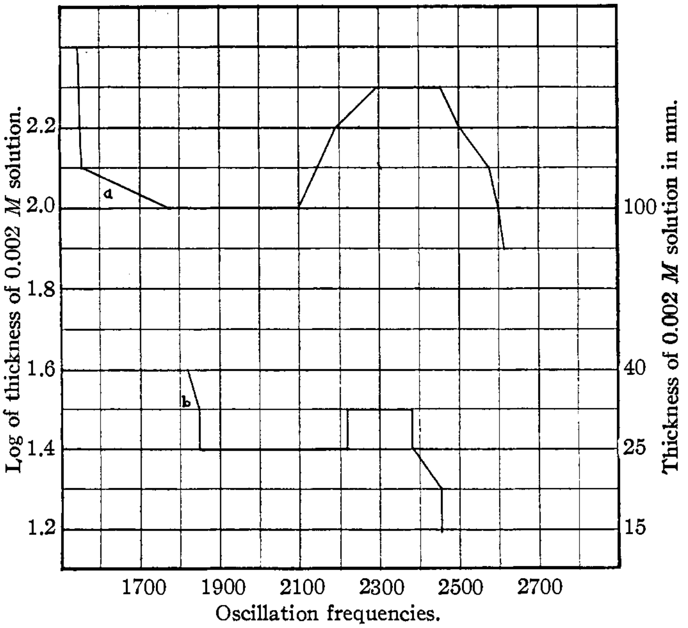

Fig. 3.—a = 0.0125 *M* $FeSO_4 \cdot NO$ in 93.1% H_2SO_4, after Schlesinger and Salathe; b = 0.002 *M* $FeCl_2 \cdot NO$ in absolute alcohol.

that both in the alcoholic solutions of $FeCl_2 \cdot NO$ and in the acid solution of $FeSO_4 \cdot NO$, decrease in the amount of water causes a similar shift in the absorption spectrum. It is true that the band in the concentrated sulfuric acid is not identical with that in absolute alcohol (See Fig. 3), a fact which will be discussed more fully below; but the spectra and their changes are sufficiently similar to point to the conclusion that the sulfate ion is not concerned in the reaction. They seem therefore to contradict the view of Raschig[7] that a salt of nitrosi-sulfonic acid is involved.

On account of the slight but definite differences between the spectra of $FeCl_2 \cdot NO$ in absolute alcohol and of $FeSO_4 \cdot NO$ in concentrated sulfuric acid, the results just described do not settle the problem definitely; hence we undertook a study of the behavior of the compound $FeHPO_4 \cdot NO$, the preparation of which has been described by Manchot.[8] In aqueous solutions it has the brown color characteristic of aqueous and slightly acid solutions of $FeSO_4 \cdot NO$. If phosphoric acid is added, the color changes and finally becomes cherry-red as the phosphoric acid becomes very concentrated. To show that this phenomenon is analogous to that with the sulfate, it is necessary to demonstrate that the change in color is not accompanied by a change in the ratio of ferrous salt to nitric oxide. For this purpose the procedure of Manchot was used; that is, as shown in Table I, the amount of nitric oxide absorbed per gram molecule of ferrous phosphate was determined, due allowance being made for the solubility of the gas in the concentrated acid used as solvent.

TABLE I

THE SOLUBILITY OF NITRIC OXIDE IN CONCENTRATED PHOSPHORIC ACID SOLUTIONS OF FERROUS PHOSPHATE

Acid, g.	Fe, g.	Concn. of Fe, mole	Temp., °C.	Press., mm.	NO absorbed by soln., cc.	NO absorbed at S. T. P. by $FeHPO_4$ per g. atom of Fe	
						Cc.	Liters
25.880	0.0034	0.004	26	625	7.4	1.18	19.6
20.880	.0027	.004	24	632	6.0	1.05	21.7
22.245	.0029	.004	25	626	6.6	1.20	23.1
23.521	.0030	.004	23	628	6.6	1.06	19.7
23.438	.0061	.008	23	628	8.8	2.75	25.2
21.549	.0056	.008	20	630	7.8	2.38	23.6
22.667	.0059	.008	20	632	8.4	2.67	25.3
25.820	.0067	.008	20	632	9.0	2.50	20.8
22.703	.0118	.016	20	626	10.8	4.44	21.0
						Av.	22.2

The data in the sixth column of the table represent the total volume of nitric oxide absorbed by the solution at the temperature and pressure indicated. The data in Col. 7 give the volume of nitric oxide, referred to standard conditions, absorbed by the ferrous phosphate alone; allowance

---

[8] Manchot, *Ber.*, **47**, 1601 (1914).

is made for the solubility of the gas in the acid on the assumption that this solubility is the same in the solution as it is in the pure solvent. The solubility of nitric oxide in concentrated phosphoric acid, referred to standard conditions, was found to be 16.9 cc. per 100 g. of acid.

The fact that 22.2 liters of nitric oxide, referred to standard conditions, are absorbed, on the average, per gram atom of iron shows that the formula of the red compound, like that of the brown one, is $FeHPO_4 \cdot NO$, except for the possibility of hydration, which will be discussed below. The variation in the data of Col. 8 is due to experimental error, as shown by the fact that it is entirely unrelated to changes in concentration of the solutions. The experimental difficulty is a secondary reaction of the nitric oxide with the ferrous salt, for if nitric oxide is passed through the solution for some time, the color entirely disappears as a result of oxidation of ferrous to ferric salt. It is, therefore, difficult to be sure that the solution is neither unsaturated nor treated with an excess of the gas.

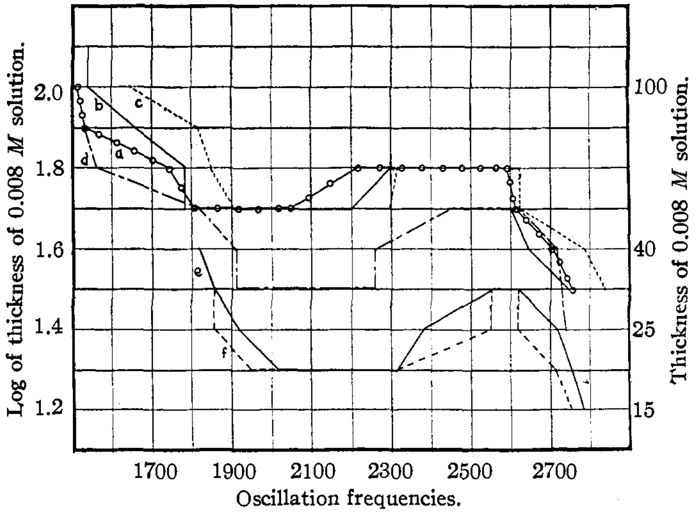

Fig. 4.—0.008 *M* $FeHPO_4 \cdot NO$ in H_3PO_4 of following concentrations: a = 90%, b = 85%, c = 70%, d = 60%, e = 20%, f = 10%.

The absorption spectra of ferrous phosphate saturated with nitric oxide in solutions containing various amounts of phosphoric acid are shown in Fig. 4. The absorption band in solutions of 88 to 90% acid is almost identical in position with that of $FeSO_4 \cdot NO$ in solutions of sulfuric acid stronger than 65%. As the phosphoric acid becomes more dilute the absorption band widens and shifts toward the violet end of the spectrum, as is the case when the concentration of sulfuric acid in solutions of $FeSO_4 \cdot NO$ is decreased. In aqueous and dilute acid solutions the absorption spectra of the ferrous sulfate complex are again almost identical with those of the ferrous phosphate complex. For comparison Fig. 5 is reproduced from the work of Schlesinger and Salathe.

A study of the composition of the solvent in which the transition from one type of compound to the other occurs reveals a very significant relationship between the beginning and the completion of the shift of the absorption band and the aqueous tension of the solvent. The data for the latter could not all be found for the temperature at which our work was done. Consequently, the comparison for phosphoric and sulfuric acids is made at 0°, while the comparison of the sulfuric acid with the alcoholic solutions is made at 25°. There seems to be no reason to believe that the conclusions reached are, in any important way, affected by the discrepancy. In sulfuric acid the shift begins in 55% solution which has an aqueous tension at 0° of 1.04 mm., and is complete in 65% acid in which the aqueous tension is 0.36 mm. To have these same aqueous tensions phosphoric acid solutions must be, respectively, 68 and 88%, and it is exactly in this range that the transition occurs for the ferrous phosphate–nitric oxide complex. The solutions of sulfuric acid just mentioned have at 25° aqueous tensions of 6.5 mm. and 2.75 mm., respectively. These aqueous tensions are reproduced by 94 and 97% solutions of alcohol. Our observations show that the transition of the complex $FeCl_2 \cdot NO$ begins when the concentration of the alcohol is above 90% and is complete in absolute alcohol.[9]

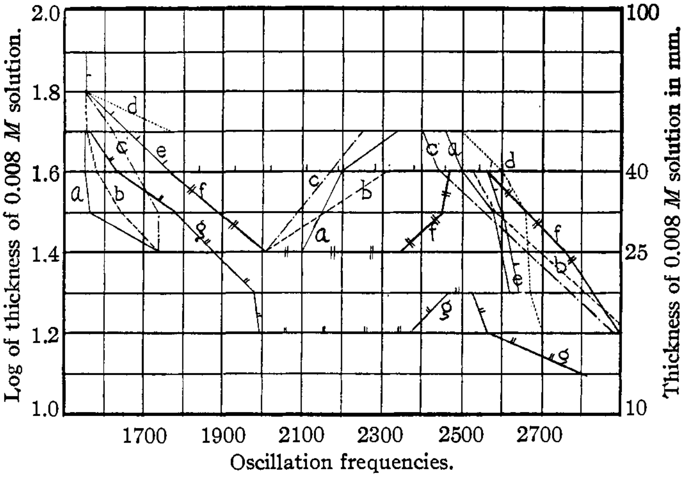

Fig. 5.—0.0125 M $FeSO_4 \cdot NO$ in H_2SO_4 of following concentrations: (taken from the work of Schlesinger and Salathe) a = 93.1%, b = 82.3%, c = 71.5%, d = 65.0%, e = 59.4%, f = 45.0%, g = 0%.

---

[9] The data for the aqueous tensions of the acid solutions are taken from Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5th ed., p. 1395, and those for the alcoholic solutions from Foote and Scholes, This Journal, 33, 1309 (1911).

The foregoing offers strong support for the conclusion that the transition in the three pairs of compounds having, respectively, the empirical formulas $FeSO_4{\cdot}NO$, $FeHPO_4{\cdot}NO$ and $FeCl_2{\cdot}NO$, is in no way related to the nature of the negative ion but is determined by the activity of the water in the solution. The influence of the water is best explained by the assumption that in dilute aqueous solutions the positive ion in each case is $[Fe{\cdot}NO{\cdot}(H_2O)_x]^{++}$ and that the action of sulfuric acid, of phosphoric acid and of alcohol consists in removing all or part of the water in the complex ion. It is of interest to note that when Manchot attempted to prepare the solid brown compound $FeNOSO_4$ by precipitation with alcohol, he obtained a crystalline product containing ferrous sulfate and a much larger amount of water than that due to hydration of the ferrous sulfate present. Manchot also prepared the solid complex of nitric oxide and ferrous phosphate but the analytical data given by him refer only to the ratio NO:Fe and cannot be used to determine whether the salt is hydrated. On the other hand, Manchot and Linckh[10] found that the solid brown complex of ferrous selenate and nitric oxide, when precipitated from solutions containing water, alcohol and acetone, has the formula $FeSeO_4{\cdot}NO{\cdot}4H_2O$. These facts confirm the idea that in aqueous solutions hydrated complex ions are present; they cannot, however, be accepted as guides to judge of the formula of the complex.

That this is not the only factor involved in the alcoholic solutions of the ferrous chloride–nitric oxide complex is shown by the fact that the absorption spectrum of this substance in absolute alcohol is not quite identical with that of the solutions of complexes with the phosphate and the sulfate in the concentrated acids. According to Kohlschütter the nitric oxide in alcoholic solutions of $FeCl_2$ is at least in part attached to a negative ion which also contains iron. He has therefore assumed that ferrous chloride is associated into $FeFeCl_4$ in these solutions, and that the nitric oxide reacts with the ion $FeCl_4$.[11] Our work does not bear on this phase of the problem. It does, however, emphasize the fact that dehydration of the aquo ion precedes formation of the chloro ion. This agrees with what is known to happen in the formation of the $CuCl_4$-ion from the hydrated cupric ion. The great similarity in the absorption spectra of $FeSO_4{\cdot}NO$ in concentrated sulfuric acid and of $FeHPO_4{\cdot}NO$ in concentrated phosphoric acid seems to indicate that the dehydrating action is the only function of the acids in these cases and that no complex ion containing iron, nitric oxide and the simple negative ion is formed. This

---

[10] Manchot and Linckh, *Z. anorg. allgem. Chem.*, **140**, 37 (1924).

[11] Our results explain why, in transference experiments, nitric oxide in alcoholic ferrous chloride solution is transported both to the anode and to the cathode. Since the transition from one type of compound to the other is not complete except in nearly 100% alcohol, the presence of water from the layer of diluted alcohol used causes a partial formation of the hydrated complex ion.

conclusion is supported by the fact that Kohlschütter observed no transport of nitric oxide toward the anode in concentrated sulfuric acid solutions of $FeSO_4 \cdot NO$.[12]

An investigation was made to determine whether similar phenomena could be observed with other salts. Accordingly, the spectra of the following solutions were photographed before and after saturation with nitric oxide: nickel, cobalt and cadmium sulfates in water and sulfuric acid; cadmium chloride in water and in hydrochloric acid; nickel and cobalt chlorides in absolute alcohol. Cadmium chloride was studied because of its great tendency to form complexes, and cobalt and nickel sulfates because of the reports in the literature[13] that they dissolve appreciable quantities of nitric oxide. The spectrograms, however, failed to reveal even traces of complex ions in the solutions.

Experimental

It is not necessary to discuss in detail the experimental procedures because, in general, the methods and apparatus described by Schlesinger and Salathe were employed. The data obtained with the quartz spectrograph were in some instances supplemented by visual observations in the spectral region, for which the quartz instrument has small dispersion. Ferrous chloride was prepared by passing dry hydrogen chloride over hot iron wire in the absence of oxygen and was purified by sublimation. The product dissolves more slowly in concentrated than in dilute and very slowly in absolute alcohol, but no difficulty was encountered in finally obtaining solutions of the desired concentration. For the preparation of ferrous phosphate the method of Evans[14] was first tried but the analysis showed that only 79% of the iron in the product was in the ferrous condition, and the method was abandoned in favor of that of Debray.[15] Phosphoric acid of the desired concentration was obtained either by diluting the 85% acid with water or by heating it for several hours at 110–115° to obtain the stronger solutions. Weighed amounts of pure iron wire were then dissolved in the acid while a stream of oxygen-free hydrogen was passing through the solution. Thus were obtained solutions of ferrous salt free from ferric compounds and of the desired concentration. The solutions were then forced into the Baly tubes by a stream of hydrogen. The precautions mentioned by Schlesinger and Salathe for preventing access of oxygen to the tubes during the observations were taken.

Summary

Absorption spectra of the complexes formed by ferrous phosphate with nitric oxide in solutions of phosphoric acid of various concentrations, and by ferrous chloride with nitric oxide in alcohol solutions of various concentrations, have been photographed and found to be almost identical with those of the ferrous sulfate–nitric oxide complex in sulfuric acid.

---

[12] Too great stress, however, must not be placed on the transference experiments in concentrated sulfuric acid. In these solutions the conductance of the solvent is so high that only a small fraction of the current is carried by the solute, which is present in relatively small amounts.

[13] Hüfner, *Z. physik. Chem.*, **59**, 416 (1907); Usher, *ibid.*, **62**, 622 (1908).

[14] Evans, *Pharm. J.*, [4] **4**, 141 (1897).

[15] Debray, *Ann. chim.*, [3] **61**, 437 (1861).

The shift of the absorption band toward the violet end of the spectrum, which occurs with increasing dilution of sulfuric acid solutions of ferrous sulfate saturated with nitric oxide, also occurs on diluting phosphoric acid solutions of ferrous phosphate, and alcohol solutions of ferrous chloride saturated with nitric oxide. This shift of the absorption band indicates a transition of one compound into another. The transition of the three pairs of compounds having, respectively, the empirical formulas $FeSO_4 \cdot NO$, $FeHPO_4 \cdot NO$, $FeCl_2 \cdot NO$ is probably determined in each case by the activity of the water in the solutions, that is, the transition occurs when the aqueous tensions of the solutions reach the same numerical value. This condition obtains when the concentrations of the three solvents H_2SO_4, H_3PO_4 and C_2H_5OH are, respectively, about 65, 88 and 97%.

The function of the concentrated acids and alcohol is probably largely that of dehydrating the complex ion which exists in dilute solutions.

CHICAGO, ILLINOIS

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

TEMPERATURE–CONDUCTANCE CURVES OF SOLID SALTS. II. HALIDES OF POTASSIUM AND THALLIUM

BY T. E. PHIPPS AND E. G. PARTRIDGE[1]

RECEIVED SEPTEMBER 6, 1928 PUBLISHED MAY 6, 1929

In a recent investigation[2] of temperature–conductance curves of the solid halides of sodium, the data in most cases showed two distinct slopes when plotted to the axes log k (logarithm of specific conductance) against $1/T$ (reciprocal of the absolute temperature). In the discussion of these data it was assumed that the conductance of the solid is proportional only to the number of ions in its lattice which have an energy greater than a certain threshold value and, further, that the mobility of these ions is nearly independent of the temperature. With these assumptions it was shown that the slope of the log k–$1/T$ curve may measure the threshold energy (designated as heat of liberation) which the conducting ion or ions must acquire in order to participate in the conduction process. To explain the existence at higher temperatures of a second slope, which was within experimental error double the slope at lower temperatures it was assumed[3] that at higher temperatures both ions take part in the conduction

---

[1] This paper is an abstract of a thesis submitted by E. G. Partridge in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Phipps, Lansing and Cooke, THIS JOURNAL, **48**, 112 (1926).

[3] A subsequent investigation by Phipps and Leslie [*ibid.*, **50**, 2412 (1928)] of transference numbers in solid sodium chloride at high temperatures gives definite evidence that both ions conduct at high temperatures.