completely accidental, particularly when results for the two molecules are compared. At the same time the moderately good agreement can be taken as an indication that the method of estimating coefficients in wave functions from electronegativities may be useful in crude intensity calculations.

The authors express appreciation to Mr. J. A. Pople for some helpful suggestions in regard to the computation of some of the integrals, and especially to the referee of this paper, who made many helpful suggestions during the course of revision.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Further Studies of Nitrosyl Chloride as an Ionizing Solvent

BY ANTON B. BURG AND DONALD E. MCKENZIE[1]

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The ionization constant of $NOFeCl_4$ in liquid NOCl was determined from conductance data by the Shedlovsky method: $K_{ion} = 0.00373$ and $\Lambda_0 = 401.2$, at −10°. Its solubility is 93 g. $FeCl_3$ per 100 g. NOCl at 0°, and it forms the solid solvate $NOFeCl_4 \cdot NOCl$ (dissoc. pressure 224 mm. at 0°). The highly conducting $NOAlCl_4$ has a solubility of 61.2 g. $AlCl_3$ per 100 g. of NOCl at −25°, 68.6 g./100 at 0°, or 93 g./100 at 18°, and forms solid $NOAlCl_4 \cdot NOCl$ (dissoc. pressure 180 mm. at 0°). On the other hand, the nearly insoluble $NOBF_4$ and $(NO)_2SnCl_6$ are not recognizably solvated. Nitrosyl salts react with the slightly soluble $(CH_3)_4NCl$ in the sense of the acid–base neutralization $NO^+ + Cl^- \rightarrow NOCl$, as demonstrated by a conductometric titration of $NOFeCl_4$ by $(CH_3)_4NCl$ and by the partial neutralization equilibria of $NOBF_4$, $NOClO_4$ and $(NO)_2S_2O_7$, each with $(CH_3)_4NCl$. The idea that NO^+ represents acid, and Cl^- base, is further justified by the electrolysis of $NOFeCl_4$ in NOCl, forming NO at the cathode and Cl_2 at the anode. The transference ratio of NO^+ to $FeCl_4^-$ is about 7:1, suggesting a solvo-chain mechanism of transporting NO^+. In relation to this work, the vapor tensions of very pure NOCl were redetermined, with results near to the average of the most acceptable literature values. The dielectric constant was measured as 19.7 at −10°, 21.4 at -19.5° and 22.5 at −27°—a trend indicating a mild association, negatively correlated with temperature.

It was indicated earlier that certain nitrosyl salts of complex anions are very soluble strong electrolytes in liquid nitrosyl chloride, while others are relatively insoluble or poorly conducting.[2] The study now has been extended to establish a more definitely quantitative understanding of NOCl as an ionizing solvent, and to develop the increased variety of chemical knowledge implied by solvation, the phenomena accompanying electrolysis, and reactions of the neutralization type.

Experiments, Results and Interpretations

I. Properties of Nitrosyl Chloride

Purification.—Nitrosyl chloride, prepared by the action of hydrogen chloride upon nitrosyl acid sulfate,[3] was purified first by a rough fractional condensation and then by a helix-packed fractionating column, attached to the high-vacuum apparatus and operating with a reflux temperature of −42° (boiling propane), in a fairly dark room. In the final refractionation, one-third of the product was rejected as first and last fractions, which still showed vapor tension agreement. The samples were preserved in sealed tubes at −78°, in a dark cupboard to minimize photodecomposition, and usually were repurified between experiments.

Vapor Tensions.—The vapor tensions of several different samples of purified nitrosyl chloride were measured over the range −48 to −6°, in a black painted apparatus employing a quartz Jackson-type gage[4] as a null-instrument. The ammonia and sulfur dioxide vapor tension thermometers,[5] and a standardized mercury thermometer graduated to 0.1°, were used in their appropriate ranges. The results, presented in Table I, determine the equation $\log_{10} p_{mm.} = -(1373.82/T) + 1.75 \log_{10} T - 0.0036716T + 4.74582$, from which the check values were calculated (average deviation 0.05 mm.). This implies the normal boiling point to be −5.38°, or near the average of previous determinations.[6-9] Taking the critical pressure as 92 atm.,[10] the heat of vaporization is calculated as 5953 cal./mole. at the boiling point, and the Trouton constant is 22.23 cal./deg. mole.

TABLE I

VAPOR TENSIONS OF PURE NITROSYL CHLORIDE

t, °C.	−47.59	−46.39	−44.37	−41.97	−31.77	−29.38
$p_{mm.}$ (obsd.)	88.11	94.97	107.29	123.36	217.79	246.82
$p_{mm.}$ (calcd.)	88.19	94.90	107.18	123.47	217.77	246.90
t	−25.63	−22.27	−17.52	−15.03	−9.23	−7.79
p (obsd.)	299.05	353.10	443.13	497.28	644.34	685.85
p (calcd.)	299.03	353.14	443.11	497.27	644.37	685.85

The Dielectric Constant.—The only previous value of the dielectric constant of nitrosyl chloride, 18.2 at 12°, was obtained by extrapolation from solutions of NOCl in CCl_4.[11] Direct determinations now have been made at three lower temperatures, using an 18-ml. cell in which the pure liquid covered two parallel platinum plates 6 cm. in diameter, rigidly held 1 mm. apart. Capacitances were measured by a Schering bridge circuit (Capacitance Bridge Type 716-C, General Radio Co.), employing a Hewlett-Packard Model 200A variable oscillator as a source. The detector circuit consisted of a one-stage amplifier and oscilloscope, connected to the bridge in the manner recommended by Jones, Mysels and Juda.[12] The cell and connecting wires were surrounded by grounded shields. The temperature of the bath (trichloroethylene contained in an unsilvered dewar vessel sur-

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[1] This paper represents a dissertation presented by Donald E. McKenzie to the Graduate Faculty of the University of Southern California, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1950. The support of a considerable part of this work through a research fellowship granted by the Standard Oil Company of California is gratefully acknowledged. The present address of Dr. McKenzie is Canadian National Research Council, Chalk River, Ontario, Canada.

[2] A. B. Burg and G. W. Campbell, Jr., THIS JOURNAL, **70**, 1964 (1948).

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[7] M. Trautz and W. Gerwig, *Z. anorg. allgem. Chem.*, **134**, 409 (1924).

[8] M. E. Briner and C. Pylkoff, *J. chim. phys.*, **10**, 660 (1912).

[9] J. R. Partington and A. L. Whynes, *J. Phys. and Colloid Chem.*, **53**, 500 (1949).

[10] M. E. Briner and C. Pylkoff, *J. chim. phys.*, **10**, 640 (1912).

[11] J. A. A. Ketelaar, *Rec. trav. chim.*, **62**, 289 (1943).

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rounded by a slush of Dry Ice in ether) was held constant to 0.02° by a knife-heater and a Fenwall (Cat. No. 17510) thermoregulator with an electronic relay.

The cell-constant (7.35) was determined at 0°, using pure chloroform and carbon tetrachloride as standardizing liquids. For measurements on nitrosyl chloride, it was necessary to employ a variable resistor external to the bridge, in order to balance the relatively low resistance (9,000 ohms) of the cell system[13]; this substitution increased the probable error in the dielectric constant to 0.7 unit. A polarization effect, observable as an apparent change of capacitance with frequency, was overcome by extrapolations to infinite frequency.[14] The data at three frequencies and three temperatures, and the final results, are given in Table II. The observed increase of dielectric constant with decreasing temperature is less marked than that found for most protic solvents having hydrogen bond association.

Table II

Dielectric Constants of Liquid NOCl

t, °C.	Cell Capacitance ($\mu\mu$f.) 6 Kc.	10 Kc.	30 Kc.	∞	Dielectric constant
−10.0	147.4	145.9	144.8	144.6	19.7
−19.5	159.4	158.4	157.6	157.5	21.4
−27.0	166.6	165.8	165.3	165.2	22.5

II. Properties of Nitrosyl Compounds

Solvation and Solubility of $NOFeCl_4$ and $NOAlCl_4$.—As mentioned in the earlier note,[2] the nitrosyl salts which are highly soluble in liquid NOCl probably are well solvated in solution. As an indication of this effect, the vacuum stable compounds $NOFeCl_4$ and $NOAlCl_4$ were formed in the high-vacuum apparatus (from resublimed Fe_2Cl_6 and Al_2Cl_6, transferred only in the dry-box), and their NOCl pressure–composition isotherms were determined at 0° by means of the Jackson gage system. The data, presented in Tables III and IV, clearly demonstrate the existence of $NOFeCl_4 \cdot NOCl$ and $NOAlCl_4 \cdot NOCl$. The roughness of the data is due to the slowness of approach to equilibrium.

Table III

Equilibrium pressures of system NOCl–$FeCl_3$ at 0°

Mole ratio NOCl/$FeCl_3$	*p*(mm.)
2.827	528
2.695	462
2.412	448
2.185	447
2.090	442
2.030	438
1.805	226
1.716	230
1.622	222
1.498	224
1.308	223
1.020	221

Table IV

Equilibrium pressures of system NOCl–$AlCl_3$ at 0°

Mole ratio NOCl/$AlCl_3$	*p*(mm.)
3.202	588
3.018	490
2.827	444
2.760	429
2.611	441
2.398	435
2.135	425
2.014	426
1.850	178
1.411	181
1.292	182
1.113	176
1.036	171

For the iron salt, the saturated solution plateau (average pressure 444 mm.) ends at 2.67 NOCl per $FeCl_3$, implying that the solubility corresponds to 93 g. of $FeCl_3$ per 100 g. of NOCl at 0°. For the aluminum salt the saturated solution (average pressure 434 mm.) contains 2.93 NOCl per $AlCl_3$; solubility 68.6 g. of $AlCl_3$ per 100 g. of NOCl at 0°. A similar determination at −25° gave 61.2 g. of $AlCl_3$ per 100 g. of NOCl, and at 18°, 93.0 g. per 100. At 18° the solvate $NOAlCl_4 \cdot NOCl$ is not found; the solid phase in equilibrium with the solution is $NOAlCl_4$.

Magnetism of the Iron Chloride Solution.—The magnetic susceptibility of a half-molar solution of ferric chloride in liquid NOCl was measured by S. S. Dharmatti and W. K. Wilmarth (this Laboratory) and found to correspond to five unpaired electrons per atom of iron. This result (6.3 Bohr magnetons) argues against formulating the solute as $NO^+FeNOCl_5^-$, in which the anion would be a nitrosyl–iron complex. Further details of this work will be published separately.

Other Nitrosyl Compounds.—The compound $SnCl_4 \cdot 2NOCl$,[15] previously indicated to be insoluble and non-conducting in liquid NOCl,[2] now was shown also to be non-solvated. Nitrosyl fluoborate[16] also showed no solvation by NOCl at temperatures down to −78°. Its slight solubility, conductance and acid behavior are considered in section V. Cuprous chloride formed the known compound $CuCl \cdot NOCl$,[17] without further solvation or apparent solubility in liquid NOCl. Under normal illumination in the vacuum system at room temperature, this material changed color from purple to gray, forming NO and $CuCl_2$. A fresh sample appeared to be diamagnetic, with a rapidly increasing paramagnetism ascribed to decomposition.[18] The diamagnetism would correspond either to the nitrosyl salt $NO^+ \, CuCl_2^-$ or to the nitrosyl complex $(CuNO)Cl_2$. The latter might be favored, since the addition of NO to $CuCl_2$ gave a product which apparently was the same substance.[19]

Trimethylamine oxide reacted with NOCl at −78° to form a white solid, $(CH_3)_3NO \cdot NOCl$, which was stable up to 10° but decomposed at room temperature to form a yellow vapor and an orange-red oil. Trimethylphosphine oxide, $(CH_3)_3PO$, formed no addition compound with NOCl at temperatures down to −40°, and was not attacked at room temperature.

III. The Conductances of Solutions of $NOFeCl_4$ in NOCl

Methods.—The resistance measurements were made by the Kohlrausch method, using the conventional bridge circuit with a slide-wire scale graduated to 2000 divisions (Leeds and Northrup No. 4258). The oscillator and detector circuits, and also the thermostat, were as described for the dielectric measurements. The two cells employed for dilute solutions were as shown in Fig. 1; the 10- or 18-mm. square bright platinum electrodes were fixed 10 mm. apart. The third cell, shown in Fig. 2, was used for more concentrated solutions; the 4-sq. cm. electrodes were set 8 cm. apart. Each cell was fitted with a magnetically-operated plunger for thorough mixing of the solution. The cell constants for the first two cells were determined as 0.3438 and 0.1485 cm.$^{-1}$, respectively, by comparison with the data of Jones and Bradshaw for very dilute KCl solutions at 0°,[20] avoiding polarization effects by extrapolation to infinite frequency.[21] The constant for the third cell was

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(13) *Cf.* General Radio Co. Form 455-C, p. 10, Fig. 4.

(14) J. L. Oncley, This Journal, **60**, 1119 (1938).

(15) W. J. van Heteren, *Z. anorg. Chem.*, **22**, 278 (1900).

(16) Prepared according to G. Balz and E. Mailander, *Z. anorg. allgem. Chem.*, **217**, 161 (1934), and purified by sublimation *in vacuo.*

(17) H. Gall and H. Mengdehl, *Ber.*, **60B**, 86 (1927).

(18) According to results obtained at this University by Dr. S. S. Dharmatti.

(19) W. Manchot, *Ann.*, **375**, 313 (1910).

(20) G. Jones and B. C. Bradshaw, This Journal, **55**, 1780 (1933).

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determined in the same manner, as 36.70 cm.$^{-1}$, in terms of the data for more concentrated KCl solutions.[20]

Preliminary experiments showed that the platinum electrodes were attacked by the nitrosyl chloride solutions if a trace of moisture was present, but that this effect was avoided if the cell was previously dried by heating *in vacuo*. The ferric chloride was transferred in a dry atmosphere, using a weighing bottle with a greased ground-on cap, and the well-purified nitrosyl chloride was distilled into the cell from the high-vacuum apparatus, up to the volume-calibrated mark (> 20 ml.) to which the cell had been filled in the determination of its constant. Nitrosyl chloride from two separate preparations was used for duplicate measurements.

The resistance of each solution was measured at two or more frequencies and if the results varied, an extrapolation to infinite frequency was used to correct for polarization. In no case was the actual cell resistance less than 100 ohms.

Results

The equivalent conductance values at −10°, for twenty-two different concentrations of $NOFeCl_4$ in NOCl, are given in Table V. The results for concentrations below 0.0101 molar were used for determining the limiting equivalent conductance Λ_0 and the ionization constant K. The method was as suggested by Shedlovsky[22,23]: the equation

TABLE V

CONDUCTANCES OF $NOFeCl_4$ IN NOCl AT −10°

Concn., mole/l.	Λ	Concn., moles/l.	Λ
0.000328	358.7	0.0211	185.5
.000481	347.3	.0356	177.4
.000704	332.3	.0511	172.4
.00133	307.8	.0880	167.9
.00153	299.7	.160	162.8
.00219	280.2	.291	171.3
.00465	248.4	.499	179.3
.00613	235.8	.742	184.2
.01010	216.7	1.000	187.9
.01430	198.8	1.13	188.3
.01680	193.9	1.49	183.5

$$\frac{1}{s(z)} = \frac{1}{\Lambda_0} + \frac{c\Lambda f^2 s(z)}{k\Lambda_0^2}$$

was evaluated by finding the value of Λ_0 which gave the best straight line when $1/\Lambda s(z)$ was plotted against $c\Lambda f^2 s(z)$, giving an intercept agreeing with the postulated Λ_0 and a slope from which K could be computed. This procedure was equivalent to the solution of the simultaneous equations

$$K = c\gamma f^2/(1 - \gamma),\ -\log f^2 = \beta\sqrt{c\gamma},\ \text{and}$$
$$\Lambda = \gamma(\Lambda_0 - \alpha\Lambda\sqrt{c\gamma}/\Lambda_0)$$

where β is the Debye–Hückel coefficient and α is the Onsager coefficient, the equation for which involved the value 0.00523 for the viscosity of NOCl, extrapolated from the data of Briner and Pylkoff.[24] The method thus yielded values of the degree of dissociation, γ, as shown in Table VI; also $\Lambda_0 = 401.2$ and $K_{ion} = 3.73 \times 10^{-3}$, at −10°.

TABLE VI

THE DISSOCIATION OF $NOFeCl_4$ IN NOCl AT −10°

Concn., mmoles/l.	0.328	0.481	0.704	1.53	2.19	4.65	6.13
Fr. dissoc. (γ)	.937	.916	.885	0.820	0.792	0.717	0.693

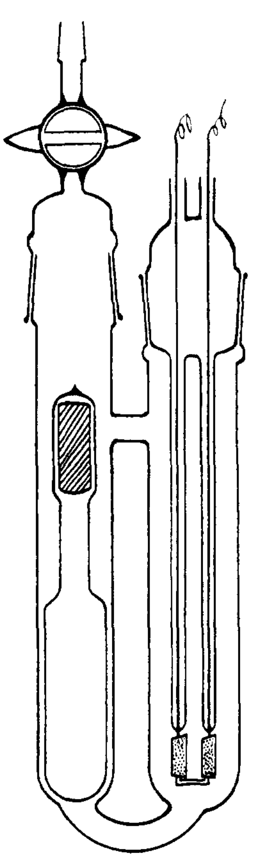

Fig. 1.—Low-conductance cell (shortened vertically).

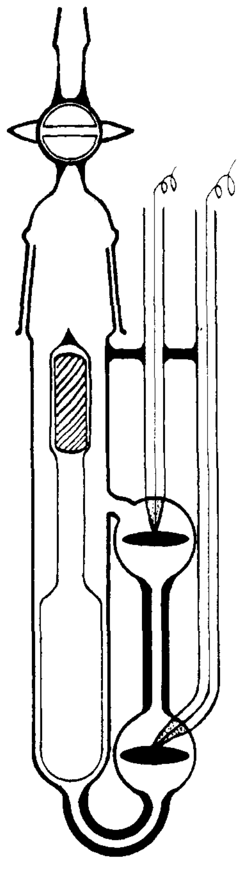

Fig. 2.—High-conductance cell (upper part shortened).

These results depend upon the assumption that the Debye–Hückel–Onsager theory is applicable to this system. Actually, the equation $\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma})$ can be represented by a plot of $(\Lambda - \gamma\Lambda_0)/\alpha$ against $\sqrt{c\gamma}$, and the points approach the limiting value asymptotically from above, as demanded by the Onsager version of the theory of strong electrolytes.

The equivalent conductance values pass through a minimum at 0.16 mm., suggesting that the Kraus–Fuoss theory of polyionic association[25] might become applicable at the higher concentrations. However, no quantitative check of this idea could be obtained, because the necessary approximations proved too crude, relative to the small degree of polyassociation indicated by the data.

The very high value of Λ_0 can be understood in terms of the high mobility of the NO^+ ion, as described in the next section.

IV. Electrolysis Experiments

Electrode Gases.—The electrolytic cell used for $NOFeCl_4$ solutions is shown in Fig. 3a. The central stopcock permitted separate delivery of the gases from the electrodes to the vacuum system, for isolation by fractional condensation. The large bulb served to prevent the NO from forcing the solution below the cathode. The room was darkened to prevent any possible photolysis of the solvent.

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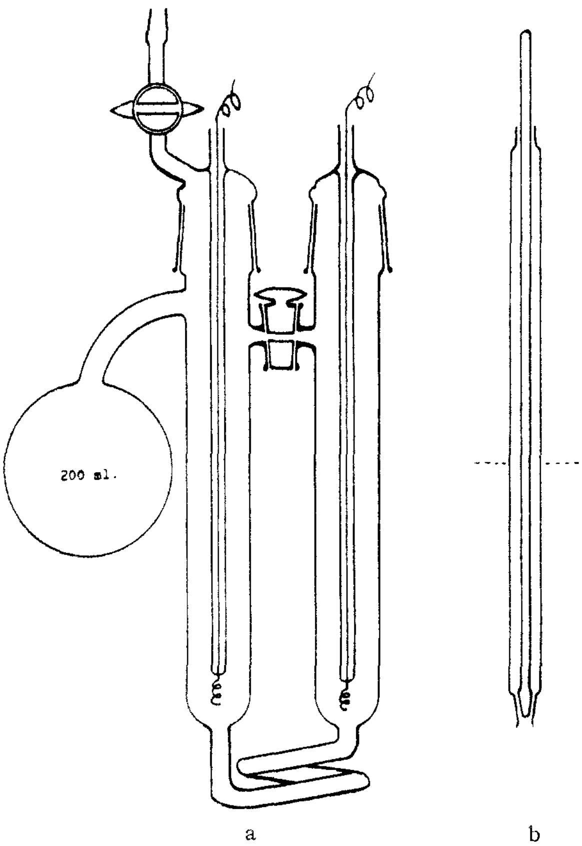

Fig. 3.—(a) Electrolysis apparatus; (b) sampling pipet.

One solution, containing 0.04 mg. of $FeCl_3$ per ml., was electrolyzed 3 hours at 8 milliamp., yielding 6 cc. of NO and 3.5 cc. of Cl_2 (gases at S.C.; calcd. 19.5 and 9.7). Another solution, containing 80 mg. of $FeCl_3$ per ml., was electrolyzed 30 minutes at 80 milliamp., yielding 8 cc. of NO and 3.5 cc. of Cl_2 (calcd. from current, 25 and 12.5). Since the recovery of each gas was less than 30%, the appearance of the 2:1 ratio of NO to Cl_2 may be fortuitous, although the absence of any electroplating leaves no explanation of the over-all electrode processes except the electrolysis of nitrosyl chloride

$$2NOCl \longrightarrow 2NO + Cl_2$$

Ionic Transference.—For the iron-transference study, the ground joints holding the platinum electrodes were replaced by rubber stoppers carrying not only platinum electrodes, but also the special inner-joint sampling tubes indicated in Fig. 3b. The ground-glass stoppers at the lower ends of these tubes were held down during the electrolysis, then lifted to admit the samples up to the calibrated marks, and then kept closed while the tubes were quickly removed and dipped under water. Thus the iron contents of samples of known volume were made available for analysis by 8-hydroxyquinoline. During the electrolysis the electrode chambers were open to the air, through drying tubes, to avoid any surging of the solution. Diffusion between the two arms was minimized by placing glass beads within the spiral connecting tube.

In this way a solution containing 80.0 mg. of $FeCl_3$ per ml. was electrolyzed for 90 minutes at a current of 60 milliamp. The result was a concentration of 85.9 mg./ml. in the anode chamber and 74.4 mg./ml. in the cathode chamber. The average value, 80.15, was near enough to the original 80.0 to show that no iron had been deposited, or precipitated in any form.

It was estimated that each electrode chamber contained effectively 11 ml. of the solution, adequately stirred by the gas evolution; hence 0.40 mg. atom of iron was transported by 0.0034 faraday. Thus a tentative value of the transport number of the $FeCl_4^-$ ion is 0.12, implying the value 0.88 for the nitrosyl ion. Should this preliminary evidence of high mobility of nitrosyl be confirmed, it could be explained only by a solvo-chain mechanism, analogous to the cause of the high mobilities of H^+ and OH^- in water.

V. Acid-Base Reactions

Neutralization of $NOFeCl_4$ by $(CH_3)_4NCl$.—The expected neutralization type reaction $NO^+ + Cl^-$ had not been realized in the earlier work,[2] for lack of a chloride salt which would be soluble in liquid nitrosyl chloride and sufficiently resistant to oxidation. In the present study, however, tetramethylammonium chloride (analysis: 32.30% Cl; calcd. 32.35) was found suitable, for its saturated solution in NOCl at $-10°$ (approximately 2 g. per liter) was stable and had a specific conductance of 0.00332 ohm^{-1}, comparable to a 0.017 *m* solution of $NOFeCl_4$. The reaction $NOFeCl_4 + (CH_3)_4NCl \rightarrow (CH_3)_4NFeCl_4 + NOCl$ was indicated by an experiment in which 0.5596 g. of $NOFeCl_4$ (2.45 meq.) and 0.9985 g. of $(CH_3)_4NCl$ (9.11 meq.) were mixed in 30 ml. of liquid NOCl and left for 3 hours at $-10°$. After complete evaporation of the solvent *in vacuo* the total chloride in the residual solid was determined as 16.55 meq. (originally 18.91), implying that 2.36 meq. of Cl^- had been converted to NOCl by an equivalent amount of NO^+.

Conductometric Titration of $NOFeCl_4$ by $(CH_3)_4NCl$.—As a further evidence of this neutralization, a process equivalent to titration was managed by adding (in the dry-box) a series of weighed portions of dry $(CH_3)_4NCl$ to a conductance cell initially containing pure $NOFeCl_4$. Before each addition of the chloride, a standard portion of pure NOCl was distilled in from the vacuum system, and, after thorough mixing, the resistance was measured at $-10°$, with the usual correction for polarization; then the solvent was evaporated off to permit the introduction of the next portion of the chloride. The data of such an experiment are presented in Table VII, and shown graphically in Fig. 4.

The increase of resistance is attributed to the replacement of the very mobile NO^+ ion by the far more sluggish $(CH_3)_4N^+$ ion; beyond the stoichiometric point, of course, the addition of $(CH_3)_4NCl$ can only lower the resistance, until the solution becomes saturated.

Partial Neutralizations.—The "nitrosyl acid" $NOBF_4$[16] proved to be appreciably soluble in liquid NOCl, for the specific conductance of the saturated solution at $-10°$ (taken as the constant value obtained after long stirring) was 65.6×10^{-6} ohm^{-1}, exactly 100 times that of the solvent. The neutralization reaction $NOBF_4 + (CH_3)_4NCl \rightleftarrows$

TABLE VII

CONDUCTOMETRIC TITRATION OF 61.0 MG. OF $NOFeCl_4$ BY $(CH_3)_4NCl$ AT −10°

$(CH_3)_4NCl$, mg.	0	17.8	24.8	32.6	37.5	41.8	46.3	51.2	56.6	62.0	68.5	80.7	91.1	106.6
Mole ratio $R_4NCl/NOFeCl_4$	0	0.432	0.602	0.790	0.910	1.014	1.123	1.242	1.373	1.505	1.662	1.958	2.211	2.586
Cell resistance, ohms	102.1	136.8	176.2	220.0	260.7	313.0	332.8	327.3	313.7	300.0	283.2	262.2	251.2	238.1

$(CH_3)_4NBF_4$ + NOCl thus was feasible, and could be demonstrated by the decrease of non-volatile chloride after equilibration of a mixture of solid $NOBF_4$ and $(CH_3)_4NCl$ with NOCl at −10°. However, the reaction was far from complete, probably because the low solubility of the acid favored the reverse, or solvolysis, reaction.

The same behavior was observed for $NOClO_4$, a sample of which was prepared by known methods[26] and treated with nitrosyl chloride to remove perchloric acid by the new reaction $NOCl + HClO_4 \rightarrow NOClO_4 + HCl$. Analysis by nitron gave 77.2% ClO_4^-; calcd., 76.8. The saturated solution of $NOClO_4$ at −10° had a specific conductance of 68.7×10^{-6} ohm^{-1}. Furthermore, dinitrosyl pyrosulfate, $(NO)_2S_2O_7$[27] (purified by heating *in vacuo* at 100°; $SO_4^=$ analysis 81.2%—calcd. 81.4%), had a specific conductance of 252×10^{-6} ohm^{-1} (saturated at −10°), and also showed partial neutralization.

TABLE VIII

SATURATED SOLUTION EQUILIBRIA OF THREE NITROSYL ACIDS WITH $(CH_3)_4NCl$ AT −10°

Acid	Wt. of acid, mg.	Wt. of R_4NCl, mg.	Sp. cond., ohm^{-1} × 10^6	Wt. of R_4NCl in residue, mg.	Acid neutralized, %
......	None	403.3	3321	403.3	...
$NOBF_4$	58.0	57.7	1803	39.7	33
$NOClO_4$	133.9	74.0	1193	33.4	36
$(NO)_2S_2O_7$	466.5	403.3	1334	320.1	37[a]

[a] Assuming one stage of ionization.

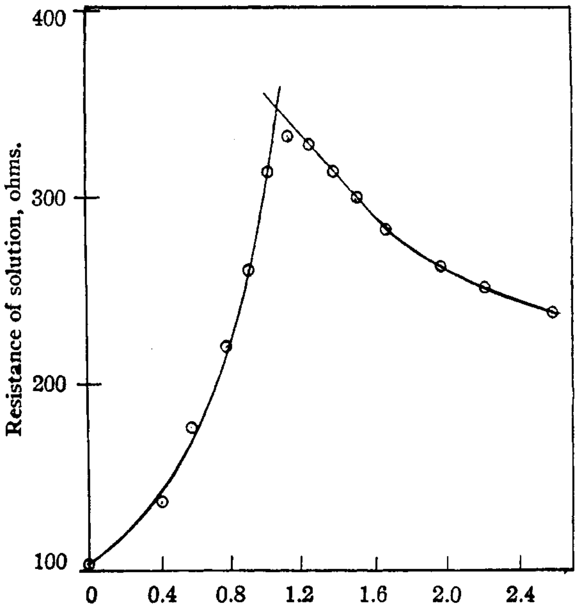

Fig. 4.—Conductometric titration of $NOFeCl_4$ by $(CH_3)_4NCl$.

The conductance and analytical data relevant to the partial neutralizations of $NOBF_4$, $NOClO_4$ and $(NO)_2S_2O_7$ are presented in Table VIII. Each system was brought to equilibrium (as shown by the approach to constant conductance) by long stirring at −10°, in a cell of the type shown in Fig. 1. After the conductance measurements, the solvent was evaporated and the residual chloride determined by the Fajans method.

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