

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

A LOW TEMPERATURE ELECTROLYTE

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The authors' attention was called by W. A. Noyes to the fact that a mixture of nitric oxide and hydrogen chloride condenses at liquid-air temperatures to a solid of an intense purple color which, upon warming, dissociates into the original constituents. This fact, first noticed by Briner,¹ is of considerable interest because nitric oxide appears to be the only certain exception to the generalization of G. N. Lewis² that molecules containing an odd number of electrons are colored. The prediction was at once made that if the compound (assuming it to be such) could be liquefied without the color disappearing, it would show a very considerable electrical conductivity. On account of the great interest in the electronic structure of nitric oxide and the nitrogen compounds in general, it seemed worth while to verify this prediction and determine as well the exact nature of the complex formed with the hope of obtaining some additional information about the "odd" electron.

As hydrogen chloride solidifies at 160° K. while nitric oxide boils at 120° K. it was evident that temperatures and pressures would have to be carefully controlled in order to obtain a liquid phase.

Experimental Part

The hydrogen chloride was generated as needed by dropping conc. sulfuric acid on a mixture of conc. hydrochloric acid and sodium chloride. The gas was dried by bubbling it through sulfuric acid. The nitric oxide was made by dropping conc. sulfuric acid into a solution of sodium nitrite, the gas being collected over water in a gas holder. The gas was bubbled through sodium hydroxide solution to remove nitrogen peroxide and through conc. sulfuric acid to dry it before use.

Apparatus.—The apparatus, including the stopcocks, was made of Pyrex glass. It is shown diagrammatically in Fig. 1, A and B are condensation bulbs, C a 500cc. flask for measuring gas volumes, D the conductivity cell, E a closed-end manometer filled with mercury and reading with fair accuracy from a vacuum to 20 atmospheres; F is a charcoal bulb. The cell D was vacuum-jacketed with an outlet to the vacuum space so that the vacuum could be varied. Around the lower end of the inner tube was a copper sheath and upon this was wound a heating coil. When this was surrounded by a bath of liquid air the temperature could be controlled at will by varying the heating current and the vacuum. Because the copper sheath equalized the temperature over the surface of the tube, and the heating coil lay between the tube and the surrounding bath of liquid air, there could be very little tendency toward the establishment of a temperature gradient in the contents of the cell. Since the change in pressure as read by the manometer proved to be a sensitive indicator of changes in temperature, it was possible to keep the temperature of the cell from varying by more than 0.5° over long periods of time by hand regulation of the heating current. This arrangement provided

¹ Briner, *Compt. rend.*, **148**, 1518 (1909).

² Lewis, *THIS JOURNAL*, **38**, 784 (1916).

a very satisfactory thermostat free from the complications of inflammable liquid baths, and one which could be constructed on a fairly large scale and operated with any desired degree of constancy.

Two platinum wire electrodes and a copper-constantan thermocouple enclosed in a glass tube were introduced into the cell, reaching to the bottom so that a small quantity of substance could be used. The top of the cell was sealed with de Khotinsky cement. The cell served for the determination of both melting points and conductivities. As only the order of magnitude of the conductivity was desired, a simple set-up of voltmeter

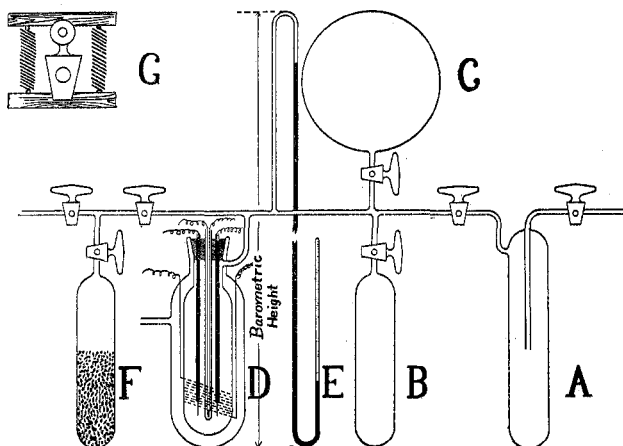


Fig. 1.

and millimeter was used. The cell was calibrated with 0.01 *N* potassium chloride solution. A specific conductivity of 10^{-6} mhos was easily detectable with the apparatus, while pure liquid hydrogen chloride and pure liquid nitric oxide caused no deflection of the needle whatever.

As pressures of 15 to 20 atmospheres were sometimes used, it was necessary to hold the stopcocks in place. A spring shackle (G, Fig. 1) that was entirely satisfactory was made from 2 pieces of wood and 2 brass springs. When the pressure became too high the stopcock lifted and relieved it like a safety valve. For vacuum work it is more satisfactory than the complicated vacuum-chambered stopcock.

Procedure.—On account of the corrosive nature of the gases the apparatus was exhausted as far as possible with a water pump and the remaining gas taken out by cooling the charcoal bulb with liquid air. One of the constituents was then introduced and condensed in bulb A. When a considerable excess had been condensed the inlet cock was closed, the bulb A allowed to warm very slowly, and the first fractions volatilizing were drawn off by means of the charcoal bulb. The measuring bulb was then filled to any desired pressure, Bulb A closed off, and the contents of the measuring bulb condensed down into Bulb B. The residue in Bulb A was discarded and the second constituent introduced in a similar manner.

It may be remarked that purification by fractional distillation is highly satisfactory at low temperatures provided it is carefully carried out. The substance to be purified should be condensed at the bottom of the bulb

and should be liquefied before any fractions are drawn off, for if any condensate collects and remains on the sides of the bulb, the temperature there will probably rise enough to volatilize impurities. If these precautions are observed, almost any substance volatile at low temperatures can be purified by fractionation alone, for a few degrees makes a great difference in the vapor pressure.

Having introduced the 2 pure constituents into the apparatus, it was an easy matter to distil them into the cell D in any definite proportions. The temperature there could be varied at will. As the pressure rose it could be released if desired by partially opening the stopcock leading to the 500cc. bulb.

Results.—Assuming the formation of a simple molecular compound between hydrogen chloride and nitric oxide, a melting-point diagram showing 2 eutectics and a maximum at the composition corresponding to the compound was to be expected. An attempt was made to determine the actual melting-point curve by the usual method of taking time-temperature curves while the temperature was slowly raised or lowered. The conductivity was read at the same time and furnished a check on the solidification point, as it was only the liquid that showed any conductivity. The fusion points of the pure substances were readily obtainable and their conductivities were nil. When a very small amount of either constituent was added to the other, a slightly colored solution was obtained which showed a slight lowering of the freezing point and a slight conductivity. When an attempt was made, however, to work with compositions nearly equimolecular, it was found that the gases tended to condense separately as pure solid phases with the surface between the phases brilliantly colored. On warming, the nitric oxide evaporated, leaving the hydrogen chloride as a pure white solid. By raising the pressure to 15 or 20 atmospheres, the nitric oxide could be prevented from evaporating until the hydrogen chloride had melted to a considerable extent at least, and the homogenous liquid phase was obtained which was, however, without color or conductivity. This indicated that the complex dissociated completely above a temperature of about 130° K. and that it would be futile to try to determine the composition by the maximum of the melting-point curve.

It was found, however, that compositions of about 1 mole of hydrogen chloride to 3 moles of nitric oxide, when condensed in as intimate contact as possible, melted to form a liquid of a dense purple color resembling that of Concord grape juice which showed a very considerable conductivity. Curiously enough, it was much easier to produce the liquid by condensing the gases over a layer of petroleum ether. The effect seemed to be purely mechanical.³ The petroleum ether prevented the solids from

³ The petroleum ether dissolved very little of the hydrogen chloride at this temperature and showed negligible conductivity.

adhering to the walls of the tube and as it was liquid just above the melting point of the nitric oxide, the liquid nitric oxide and solid hydrogen chloride, being heavier, sank through the layer of petroleum ether and came into intimate contact in the bottom of the tube where they formed an opaque purple layer which showed a specific conductivity as high as 10^{-3} mhos, about that of 0.01 *N* potassium chloride. The maximum specific conductivity is believed to be higher because it was very difficult to liquefy the layer completely without losing the nitric oxide by evaporation, and the conductivity readings were obtained on a mixture of solid and liquid. The range of temperature over which this colored phase exists is small, being roughly between 120 K. and 130 K. The pressure ranges from 1 to 2 atmospheres.

As hydrogen chloride has a negligible vapor pressure at the boiling point of nitric oxide, it appeared possible to determine the composition of the complex by finding the isothermal *p-v* curve for nitric oxide in the presence of a known amount of hydrogen chloride. This was attempted, but the surprising fact developed that the partial pressure of nitric oxide from the purple solid is not appreciably less than from pure liquid nitric oxide at the same temperature. Evidently, the complex is of so unstable a nature that a definite determination of its composition is out of the question.

An attempt was made to determine the composition which gave the deepest color when the 2 gases were condensed in a thin film with liquid air. Apparently, equimolecular proportions gave the most intense color but the results were by no means conclusive.

Discussion

A great deal of time was spent in trying to determine the exact composition of the compound because of the great interest in molecules containing an odd number of electrons from the standpoint of the Lewis theory of valence. While the experimental evidence was not conclusive, it seems highly probable that a simple molecular complex is formed. How unstable this must be is apparent from the fact that the partial pressure of liquid nitric oxide is not appreciably lowered by the presence of an excess of solid hydrogen chloride. Thus, if a salt hydrate shows practically the same vapor pressure as pure water at the same temperature, we should have a very unstable hydrate indeed. This may be contrasted with the partial pressure of hydrogen chloride in the presence of excess of ammonia.

It is very probable that the compound contains one molecule of each constituent. We should not expect a complex containing 2 molecules of nitric oxide to be colored, as it no longer contains an odd number of electrons. That there should be 2 molecules of hydrogen chloride in the complex is also unlikely if the following considerations are correct. Hydrogen chloride ionizes only in the presence of so-called basic substances such as

ammonia or water. Actually, by a basic substance we mean one which has a pair of electrons exposed so that the hydrogen ion may associate with them. In the case of ammonia where the exposed pair of electrons is loosely held by the nitrogen, the hydrogen is attached very firmly and we have the polar ammonium chloride with a high melting point. The electrons on the oxygen molecule in water are not so available to the hydrogen ion and the complex of hydrogen chloride with water has a much lower melting point. The substances which show conductivity in liquid hydrogen chloride are those in which the exposed electrons are held so firmly that there is no great tendency to form a polar compound. An example is ether, which forms an "oxonium" complex, $\left[\begin{array}{c} \text{R} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{H} \right]^+ \text{Cl}^-$.

In nitric oxide there occurs some peculiarly stable arrangement of an odd number of electrons. The hydrogen ion must exert enough attraction on some of these electrons to disturb the whole arrangement and the odd electrons become apparent. Presumably, the hydrogen associates itself with 2 electrons although it might be associated with only 1, the "odd" one. Whether these electrons are on the oxygen or nitrogen is likewise uncertain. The complex formed is undoubtedly $[\text{NOH}]^+ \text{Cl}^-$. It seems likely that a complex of the formula, $\text{NO} \cdot 2\text{HCl}$, would be even more unstable than the equimolecular combination.

The behavior of the conductivity is that usually found in solvents of low dielectric constant. The substances which exhibit greatest conductivity in liquid hydrogen chloride are, as we have said above, those not in themselves polar or basic, but which have pairs of electrons exposed and held loosely enough to attract the hydrogen ion slightly but not strongly enough to crystallize in a true polar lattice at the low temperature of the solution. The maximum specific conductivity is obtained when the composition of the solution is somewhere within the region where complex formation takes place to a considerable extent, since then we have a condition of a somewhat polar substance in a liquid condition like that of a fused salt.⁴ The conductivity falls to low values for compositions where either constituent is present in great excess. The specific conductivity of 10^{-3} mhos obtained is believed to be the greatest conductivity likely to be obtained in solution at temperatures below 130°K . On account of the low

⁴ Maass and McIntosh [THIS JOURNAL, 35, 53 (1913)] have concluded that a solution of the composition of the molecular complex will show a minimum conductivity, citing this conclusion as a general rule for everything except *fused salts*. If the analogy to fused salts, as suggested above, is correct, this conclusion would not necessarily follow but the composition of *maximum* conductivity would depend upon accidental factors such as the relative viscosity of the constituents. The extent of dissociation of the molecular complexes into the original constituents where more than one complex is formed, and the amount of solvation of the ions would tend to complicate the conductivity relations. See Latimer and Rodebush, THIS JOURNAL, 42, 1423 (1920).

mobilities at low temperatures, as much ionization is indicated by this conductivity as would be shown by a much higher conductivity at high temperatures.

Summary

Nitric oxide and hydrogen chloride form a molecular complex, probably $[\text{NOH}]^+\text{Cl}^-$, which exhibits the properties of an "odd" molecule.

The solution has a maximum specific conductivity greater than 10^{-3} mhos between 120° and 130° K.

An apparatus which is convenient for working with gases at low temperature, and a low temperature thermostat are described.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A STUDY OF THE LUMINOUS DISCHARGE IN IODINE. A DETERMINATION OF THE IONIZATION POTENTIAL OF IODINE

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In a previous article,¹ Gibson and Noyes studied the effect of certain gases and vapors on the emission spectra of metals. Measurements of the sparking potential were also made and it was found that those gases which obliterated the spectra of metals also possessed high sparking potentials. The theory was advanced that heavy negative ions were formed due to the combination of the electronegative gases with electrons and that these ions could not be accelerated sufficiently with the potentials used to produce ionization by collision. In another article,² the same authors presented a more quantitative study of the potential necessary to produce luminosity in a gas by measuring the glow potential at low pressures with a heated cathode. It was shown that this potential was a function of the ionization potential of the gas, but both gases studied (hydrogen and mercury) had no appreciable effect on the spectra of metals.

In this article it is desired to present results obtained in studying the glow discharge in one of the typical electronegative gases which have a marked obliterating effect on the spectra of metals. Part I gives a brief theoretical discussion based on the theory presented in the previous article. Part II gives the experimental procedure, while Part III gives the experimental results. Part IV gives a brief discussion of the results together with the most probable value of the ionization potential of iodine as determined in the experiments described.

¹ Gibson and Noyes, *THIS JOURNAL*, **43**, 1255 (1921).

² Gibson and Noyes, *ibid.*, **44**, 2091 (1922).