These data are plotted in Fig. 2. The invariant point lies at a concentration in solution of 0.38% Li_2SO_4 and 25.03% LiCl, and the solution is saturated with respect to $Li_2SO_4 \cdot H_2O$ and LiCl. The tie-lines show clearly that the stable solid phase is the monohydrate throughout the concentration range investigated; it is possible that the dihydrate, if it exists, is dehydrated to monohydrate by less than 3.16% LiCl.

Summary

1. For the system Li_2SO_4–H_2O, the following data have been elucidated: (a) The transition point of the change: $Li_2SO_4 \cdot H_2O \rightleftarrows Li_2SO_4 + H_2O$, which is shown to lie at 232.8° and a pressure of 26.7 atm. Three independent methods were used, *viz.*, the dilatometric, the method of vapor pressure and the thermometric. (b) The solubility between 110 and 214°. (c) The ice-line.

2. The existence of a higher hydrate of lithium sulfate, possibly $Li_2SO_4 \cdot 2H_2O$, is considered to be doubtful. The technique involved was (a) dilatometric, and (b) a study of the equilibrium diagram of the system Li_2SO_4–LiCl–H_2O, at −12.25°. The existence of the dihydrate cannot, however, be considered as entirely disproved.

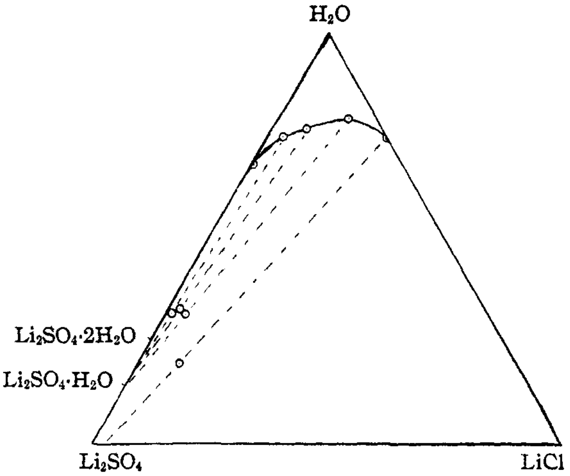

Fig. 2.—The system Li_2SO_4-LiCl-H_2O at −12.25°.

WINNIPEG, CANADA RECEIVED MAY 29, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

Cyanates and Thiocyanates of Germanium, Phosphorus, Sulfur and Chromium

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The preparation and properties of cyanates or thiocyanates, or both derived from boron bromide, silicon tetrachloride, phosphorus, arsenic and antimony trichlorides and phosphoryl chloride have recently been investigated[1,2] in this Laboratory. The successful preparation of silicon tetra-(iso)cyanate suggested that germanium tetrachloride also would react completely with silver isocyanate. The formation of phosphoryl isocyanate,[2] though in low yields, gave promise that thiophosphoryl (iso)cyanate might be obtained, though in even lower yields and smaller thermal stability. In addition, sulfur monochloride, thionyl chloride, sulfuryl chloride and chromyl chloride provided an interesting range of possibilities as yet but little explored.[3]

Germanium Isocyanate.—The preparation involved 18.9 g. of germanium tetrachloride, 60 g. of powdered silver (iso)cyanate, and 100 ml. of pure benzene. Upon gradual addition of the chloride there was considerable rise in temperature. Two hours' reflux and shaking were sufficient for essential completion of the reaction. Upon filtration and careful washing of the silver salt with hot benzene, a very pale yellow solution was obtained. Upon removal of benzene at atmospheric pressure nearly 10 ml. of a pale yellow liquid remained. Colorless germanium isocyanate was obtained by distillation at 128° and 62 mm. both uncorrected; the first 6 ml. was collected and used for all physical measurements. Subsequently, this sample was found to distil entirely between 203.7 and 204.2° (corrected to 760 mm.), using a thermometer calibrated with a middle fraction of benzoyl chloride. No change in boiling point, melting point or refractive index was observed in successive fractions. It has been shown[4] that the boiling point of the isocyanate of a non-metal exceeds that of the corresponding chloride by 31°, on the average, for each isocyanate group. As germanium chloride boils at 83°, germanium isocyanate ought to boil at 207°, in good agreement with the observed boiling point 204°.

Analysis of redistilled material followed. A weighed sample in a weighed crucible with cover was carefully hydrolyzed by slow addition of water. Time was allowed for complete hydrolysis; a trace of nitric acid was added and the mixture stirred with a tiny glass rod. Careful evaporation and ignition gave germanium dioxide. Results from tenth-gram samples of germanium isocyanate were as follows: %Ge 29.6, 30.4, av. 30.0; calculated value 30.17%. The molecular weights were obtained by means of the Dumas method: found 247 and 248; calculated 240.7.

Germanium isocyanate is a colorless liquid which showed no tendency to pass into a more stable solid phase. When it was treated with water, there was a strong effervescence, typical of cyanates, but the hydrolysis appeared somewhat less rapid than that of silicon isocyanate. Upon cooling, the liquid became very viscous, and solidified only at −65°. It melted quite sharply at −8° ± 0.5°. The density was found to be 1.760 by delivery from a calibrated 1-ml. pipet at 30° and also by use of a micropycnometer at 25°. Refractive index, read on an Abbe refractometer with thermostated prism, was 1.4858 at 20°. The boiling point (760 mm.) is 204° ± 0.4°. Boiling points at four other pressures were measured by a dynamic method in an all-glass system with a calibrated thermometer. The equation for vapor pressure is $\log p = 8.6578 - 2757/T$ so that $\lambda = 12{,}600$ cal. and $\lambda/T_b = 26.4$ cal./deg./mole.

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(1) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

(2) Anderson, *ibid.*, **64**, 1757 (1942).

(3) Dixon, *J. Chem. Soc.*, **79**, 541 (1901).

(4) Ref. 2, p. 1759.

Upon evaporation of the last four ml. of the original benzene solution, a solid residue, about 1% of the whole, remained. Upon treatment with water, a vigorous evolution of gas was observed, indicating a cyanate. The possibility was entertained that this residue was germanium cyanate $Ge(OCN)_4$. It is hoped to do more work on this substance when more of it is available.

Thiophosphoryl isocyanate $PS(NCO)_3$, was very slowly formed from thiophosphoryl chloride and silver isocyanate. After thirty hours of refluxing in xylene, there was much unchanged silver isocyanate, and only a small amount of product was recovered. Since phosphorous isocyanate, $P(NCO)_3$, is easily prepared, its reaction with sulfur in a sealed tube was next considered. The desired product was obtained, though in poor yields. Methods of recovery included direct distillation from the Carius tube under diminished pressure, also the soaking of the fragments in benzene for several weeks at room temperature. The chief product was believed to be a non-volatile solid thiophosphoryl cyanate, $PS(OCN)_3$, holding the desired product as well as unchanged phosphorous isocyanate in cavities. Expressed in equations, $P(NCO)_3 + S \rightarrow PS(NCO)_3 \rightarrow PS(OCN)_3$. The object was to stop heating the tube before the velocity of the second reaction exceeded that of the first.

6 hours at 130°, no reaction
12 hours at 140°, 24% yield
20 hours at 140°, 11% yield
30 hours at 150°, 6% yield
30 hours at 170°, $PS(OCN)_3$ only?

The desired product was purified by repeated distillation under diminished pressure. In the final operation about 1.5 ml. came over with slightly rising boiling point, and then about 3.5 ml. without further change. Phosphorus, determined as ammonium phosphomolybdate, was 16.7 and 16.7%; calculated for $PS(NCO)_3$, 16.40%. Molecular weight by the Dumas method 190 and 197, calculated 189.1.

Thiophosphoryl isocyanate at 25° is a colorless viscous liquid which is very rapidly hydrolyzed when added to water. At 0° it crystallizes in long needles melting at 8.8°. In measuring the boiling point under atmospheric pressure haste was necessary because of conversion into a solid phase. The corrected reading on a thermometer calibrated under similar conditions in boiling naphthalene was 215°. The boiling points under 30 mm. and 60 mm. were 135 and 150°, respectively. Therefore, $\log p = 10.032 - 3492/T$, $\lambda = 16{,}000$ cal. (very roughly) and $\lambda/(215 + 273) = 33$ (very roughly). The index of refraction using an Abbe refractometer with daylight was 1.5116 and the density, by delivery from a calibrated 1-ml. pipet, was 1.538.

Evidence was forthcoming to show that the volatile liquid was $PS(NCO)_3$ rather than the isomer $PO(NCO)_2SCN$. A freshly hydrolyzed sample treated with nitric acid gives a strong white opalescence indicating sulfur as sulfide rather than as thiocyanate which could be expected to form sulfate upon oxidation. Another sample treated with silver nitrate yielded a black precipitate, evidently silver sulfide. It is true that some thiocyanate could be detected in the hydrolyzed solution, but this was believed to be due to a reaction such as $HNCO + H_2S = HSCN + H_2O$, and in fact an acidified mixture of potassium cyanate and sodium sulfide gave a red coloration upon adding ferric nitrate. Further evidence is afforded by the boiling point. It has been shown[4] that the boiling point of the isocyanate of a tervalent non-metal exceeds that of the corresponding chloride, on the average, by 93°. Thiophosphoryl chloride boils at 125°, so that thiophosphoryl isocyanate should boil at 218°, in good agreement with 215°, the observed value. But if one starts with phosphoryl chloride (boiling point 107°) and adds two thirds of 93° for two cyanate groups, also one third of 193° for one thiocyanate group, a boiling point of 233° is predicted for $PO(NCO)_2SCN$ which is 18° too high.

Finally it is of interest to compare the rates of formation of non-volatile isomers from three isocyanates.

$As(NCO)_3 \longrightarrow As(OCN)_3$ rapidly[2] at 230°
$PS(NCO)_3 \longrightarrow PS(OCN)_3$ somewhat less rapidly at 215°
$PO(NCO)_3 \longrightarrow PO(OCN)_3$ very much more slowly[2] at 156°

It would appear that the rates are largely determined by temperature.

Sulfur mono(iso)cyanate exists, apparently as a monomer, in benzene solution, but the insoluble solid isolated was more likely a polymeric form. For this and analogous solids we use the term cyanate, and its formula, in a generic sense without implications as to structure. Ten milliliters of redistilled sulfur monochloride was boiled for thirty minutes in 25 ml. of benzene with 28 g. of silver (iso)-cyanate. The evaporated filtrate deposited several grams of a pale yellow solid nearly insoluble in benzene which was filtered, washed with benzene and dried. Weighed portions, oxidized by nitric acid and liquid bromine, were precipitated as barium sulfate. Calculated for $S_2(OCN)_2$: 43.3% of sulfur. Found: S, 41.9 and 42.0. This solid decomposed slowly in water, also in alcohol, with evolution of gas. Heated in a small soft glass test-tube it turned red, gave off much sulfur, melted, and disappeared completely before red heat was attained.

Thionyl Cyanate.—Benzene solutions, prepared and filtered as usual, deposited a brownish-yellow solid, but since this solid, as well as the dissolved material, proved to be unstable in air, further investigation was postponed.

Sulfuryl cyanate was not obtained at all from sulfuryl chloride and silver isocyanate either in the customary benzene solution or by reaction in a sealed tube at 100°. Further experiments, under different conditions, are being considered.

Sulfur mono(iso)thiocyanate was obtained first as a monomer in solution, then as an insoluble polymer, by boiling for half an hour 10 ml. of redistilled sulfur monochloride in 100 ml. of benzene with 50 g. of dry silver thiocyanate. Considerable red solid separated out upon the silver salts. The filtrate was at first clear, but upon partial evaporation several grams more of the red solid was deposited. Preliminary analysis of such material indicated that it occluded considerable sulfur. Therefore, the final preparation was repeatedly extracted by grinding it in a mortar with a mixture of "reagent" carbon disulfide and benzene until an evaporated extract yielded a negligible amount of sulfur. The product was scarlet when wet, orange-red when dry. For this and analogous solids we use the term thiocyanate, and its formula, in a generic sense, without implications as to structure. Upon heating in a small soft glass test-tube sulfur appeared at a relatively high temperature. Melting did not occur, but as red heat was approached the residue became quite small and very dark in color, possibly carbon.

Weighed portions of the best sample, oxidized by nitric acid and liquid bromine, were precipitated as barium sulfate. Calculated for $S_2(SCN)_2$: 71.1% of sulfur. Found: S, 72.9 and 73.7. Making allowances for the obstinacy with which sulfur was retained, the analyses would seem to confirm the postulated formula.

Thionyl thiocyanate was first prepared (as a relatively insoluble polymer) by McMurtry[5] through reaction between thionyl chloride and mercuric thiocyanate in benzene at room temperature. After several days he isolated an amorphous orange solid, and analyzed it for sulfur, nitrogen and carbon. His figures corresponded very closely to the composition $SO(SCN)_2$. The solid resisted hot water, hydrochloric acid and ammonia. We obtained a product of the same appearance as McMurtry's from thionyl chloride and silver thiocyanate in benzene boiled for three minutes only and kept hot, after filtration, for ten minutes more. This was the most rapid reaction of the kind observed in our studies on cyanates and thiocyanates. It appeared superfluous to check McMurtry's analysis. Some chemical properties of the product are discussed below.

Sulfuryl thiocyanate was doubtless prepared by Dixon[3] as described below, but the formula was not established

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(5) McMurtry, *J. Chem. Soc.*, **55**, 48 (1889).

by analysis. We found that it was rapidly formed from 7 ml. of sulfuryl chloride and 50 g. of silver thiocyanate in boiling benzene. In the first experiment the filtrate was evaporated to dryness in a flask, and the solid was doubtless impure. The final preparation was filtered after ten minutes, when considerable product had already precipitated on the silver salts. While the first third of the benzene was being distilled off from the filtrate, about 2 g. of an orange-red solid precipitated out. This was filtered, washed with pure benzene under suction, dried at 30° overnight and freed from traces of solvent by evacuation on an oil pump. Portions of about 0.2 g. each were completely oxidized by pure concentrated nitric acid with small additions of potassium chlorate. Weighed as barium sulfate the sulfur content was found to be 51.9 and 51.85%. Sulfur calculated for $SO_2(SCN)_2$ is 53.3%.

Dixon[3] treated a number of non-metallic chlorides and oxychlorides including thionyl and sulfuryl chlorides with mercuric thiocyanate in various solvents over long periods at room temperature. Few details are given, and no analyses. Much stress is laid upon the products obtained by boiling with aqueous sodium hydroxide followed by acidification. His solutions gave black precipitates with lead or mercuric salts, and varying amounts of thiocyanic acid were detected with ferric chloride. He assigned the formula $[R(NCS)_2]_n$, "polymeric thiocarbimides," to compounds in this series.

The solids formulated by us as $S_2(SCN)_2$, $SO(SCN)_2$ and $SO_2(SCN)_2$, doubtless all polymeric, were orange or orange-red. Such differences in color as appeared might be attributable to varying grain size. They were entirely stable in air, and were oxidized slowly by boiling nitric acid. The solubility in benzene was inconsiderable. All were dissolved (or disintegrated) by boiling aqueous sodium or potassium hydroxide. Upon acidification a gelatinous precipitate, lighter in color than the original substance, appeared. After filtration ferric chloride gave in each case a deep red color. Dixon[3] obtained none from thionyl thiocyanate. No sulfate was found in solution starting with the sulfuryl compound. A faint odor of hydrogen sulfide was always noted, but the precipitate thrown down by very dilute mercuric chloride was light colored, possibly a mixture such as $HgCl_2 \cdot 2HgS + Hg(SCN)_2$ except with the sulfur monothiocyanate. This precipitate was black. When each solid was heated in a small soft glass test-tube, sulfur condensed upon the cooler surface. No fusion occurred, and a solid residue persisted even at red heat, black from sulfur monothiocyanate, light brown from the other two compounds, possibly a cyanogen derivative. Quantitative analysis, thus far, was the only means of distinguishing the individual compounds.

Chromyl isocyanate proved to be stable in solution only. In a typical experiment 50 g. of silver isocyanate and 6 ml. of purified chromyl chloride (from potassium dichromate, stannic chloride and sulfuric acid) were refluxed in 70 ml. of carbon tetrachloride for half an hour. The filtered solution was a deeper red than that of chromyl chloride. Upon shaking with water, gas was evolved, an indication of cyanate. Chloride was present in traces only. There was no evidence that the oxidation level of chromium had been lowered. It was repeatedly shown that the solution could be evaporated under diminished pressure at room temperature without explosion. The product obtained, however, was a brown solid, the color and behavior of which corresponded to the so-called chromium dioxide obtained by precipitating chromates with chromic salts. At the end of the evaporation under atmospheric pressure, a flash of light and a weak explosion were observed. A plausible equation for the decomposition is $CrO_2(NCO)_2 \rightarrow CrO_2 + 2CO + N_2$.

Chromyl (iso)thiocyanate may exist for a short time in solution. In carbon tetrachloride, phosphoryl thiocyanate, $PO(SCN)_3$, and chromyl chloride yielded a turbid solution which later turned dark purple. In view of the strong tendency of phosphoryl derivatives to form addition compounds, silicon thiocyanate was next employed. A brownish solid separated out, and the reaction was progressively accelerated by the heat evolved. Several feeble explosions were heard. Upon treatment with water a green chromic solution resulted. Thiocyanate, a much stronger reductant than cyanate, was evidently oxidized by sexivalent chromium in dilute carbon tetrachloride solution even at room temperature.

The following experiments on chromyl bromide and iodide were made to compare their stabilities with those of chromyl isocyanate and isothiocyanate under similar conditions.

Chromyl Bromide.—Fry[6] obtained permanganate-red colorations in carbon tetrachloride, stable for several minutes, and they were believed by him to be due to chromyl bromide. He tried four reactions: chromic anhydride or chromyl chloride with anhydrous hydrobromic acid, chromic anhydride with acetyl bromide plus glacial acetic acid, chromyl chloride with acetyl bromide. We obtained similar colorations by three metatheses in carbon tetrachloride, treating dilute chromyl chloride with boron tribromide, silicon tetrabromide and stannic bromide. The results were always the same: with chromyl chloride at 2000 p. p. m. a dark color; at 100 p. p. m. a color somewhat redder than dilute permanganate; at 20 p. p. m. a dilute permanganate color. Excess of boron tribromide produced the characteristic color of bromine in carbon tetrachloride, with immediate formation of a precipitate. Mercury promptly decolorized this solution, and the peroxide–ether test for chromate in an aqueous extract was negative. An approximate equation for the decomposition is $CrO_2Br_2 = CrO_2 + Br_2$.

Chromyl iodide is generally regarded as unstable. Fry[6] treated chromic anhydride with acetyl iodide in carbon tetrachloride and obtained iodine only. Our observations lead to a similar conclusion. When chromyl chloride, 2000 p. p. m., was treated with stannic iodide a good iodine-violet color and a definite precipitate resulted. A chromyl chloride solution at 200 p. p. m. similarly treated showed only a slight darkening of color. The equation $2CrO_2Cl_2 + SnI_4 = 2CrO_2 + 2I_2 + SnCl_4$ might express the outcome.

At present, interest is centered upon mixed derivatives of the inorganic chlorides. Of these, two liquids apparently $SiCl_3SCN$ boiling at about 129°, and $POCl_2SCN$ boiling at about 173°, have already been isolated. Further work upon the remaining members of this series, and upon analogous compounds, is in progress.

Summary

Germanium isocyanate, $Ge(NCO)_4$ (b. p. 204°), has been prepared by action of silver isocyanate on germanium tetrachloride in boiling benzene.

Thiophosphoryl isocyanate, $PS(NCO)_3$ (b. p. 215°) has been prepared from phosphorus tri(iso)cyanate and sulfur in a sealed tube at 140°.

Sulfur monocyanate, $[S_2(OCN)_2]_x$, was obtained from silver isocyanate and sulfur monochloride in benzene as a stable pale yellow solid. A brownish yellow solid unstable in air, presumably thionyl cyanate $[SO(OCN)_2]_x$ was observed but not further investigated. The above names and formulas are not intended to carry implications regarding structure.

Sulfur monothiocyanate, $[S_2(SCN)_2]_x$, was obtained as a red solid and compared with thionyl thiocyanate, $[SO(SCN)_2]_x$ (previously investigated by McMurtry), also with sulfuryl thiocyanate, $[SO_2(SCN)_2]_x$ (probably observed by Dixon). Physical and chemical properties of these three compounds appear to be almost identical. The above names and formulas are

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(6) Fry, This Journal, **33**, 697 (1911).

not intended to carry implications regarding structure.

Chromyl isocyanate, $CrO_2(NCO)_2$, appeared to be quite stable as a deep red solution in carbon tetrachloride. Upon evaporation to dryness under atmospheric pressure an explosion occurred. Chromyl thiocyanate, $CrO_2(SCN)_2$, seemed to be present for a few minutes as a dark purple solution in cold carbon tetrachloride which shortly decomposed in the cold, and explosively at higher temperatures.

CAMBRIDGE, MASS. RECEIVED MAY 11, 1943

[CONTRIBUTION FROM THE DIVISION OF SOIL AND FERTILIZER INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, SOILS, AND AGRICULTURAL ENGINEERING OF THE U. S. DEPARTMENT OF AGRICULTURE]

Equilibrium Measurements by Infrared Absorption for the Formation of Nitric Acid from Oxygen, Water Vapor and Nitrogen Dioxide

BY ERNEST J. JONES

Several workers[1] have studied the reaction

$$3NO_2(g) + H_2O(g) = 2HNO_3(g) + NO(g) \quad (1)$$

while others[2] have studied the reaction

$$NO(g) + {}^1/_2O_2(g) = NO_2(g) \quad (2)$$

These two equations combine to give the equation of the reaction

$$2NO_2(g) + {}^1/_2O_2(g) + H_2O(g) = 2HNO_3(g) \quad (3)$$

In line with the interest of this Laboratory in problems concerning the chemistry of nitrogen it was felt that a direct determination of the equilibrium constant of reaction (3) would be helpful.

During the course of some absorption studies on nitrogen oxides in the infrared it was noted that nitric acid in the vapor phase possessed a characteristic absorption, due presumably to the first overtone of the O·H vibration, in a region (1.4 μ) which was sufficiently clear from the interfering absorption of nitrogen dioxide, water vapor and nitric oxide to permit measurement. This suggested that the direct study of the equilibrium could be made using the infrared absorption of nitric acid as a measure of its concentration, while the concentrations of nitrogen dioxide and water could be calculated from a knowledge of the initial concentration of nitric acid.

The experimental work reported here was terminated due to the dismantling of the apparatus preparatory to moving the laboratory to Beltsville, Maryland. During the period of preparing this material for publication a paper by Forsythe and Giauque[3] on the thermodynamic study of nitric acid appeared. These authors give in addition to their own experimental results a complete review of the work on the thermodynamics of nitric acid and some of the reactions leading to its formation. One of these is reaction (3) the direct determination of the equilibrium constant of which is the purpose of the present paper.

Apparatus and Method

The large infrared recording spectrograph which has previously been described by Brackett and Liddel[4] was used in making the measurements. An electric oven equipped with double windows housed the absorption cells and this assembly was mounted on an optical bench in front of the slit of the spectrograph. Measurement and control of the cell temperature (to within 1°) was made outside the spectrograph room to avoid interference with the automatic operation of the spectrograph itself. Pyrex glass tubing 5 cm. in diameter and 50 cm. in length with ground and polished windows fused to each end constituted the cells. These cells were sealed by means of side tubes to an all-glass vacuum system.

Construction of a working curve that would allow one to determine the concentration of nitric acid in the vapor phase as a function of its infrared absorption in the 1.4μ region was the first step in the work. To do this a number of cells were filled with known amounts of nitric acid vapor. Nitric acid was prepared by pumping excess nitrogen dioxide off fuming nitric acid at room temperature until the liquid was colorless, the time required being about thirty minutes. The liquid was then immediately frozen under continued pumping and after a short time introduced into the evacuated cell (10^{-3} mm.) by allowing the solid nitric acid to warm up by adjusting the position of the cooling bath surrounding it until the vapor pressure had attained the desired value as determined roughly by a "nujol" manometer. Temperatures of the liquid nitric acid never exceeded 30°. At this point the tube containing the nitric acid was closed and the cell and three sampling bulbs which had been connected in parallel through a manifold were each sealed off. Titration of the contents of each bulb gave values, the average of which was taken as the concentration of the nitric acid vapor for the cell. The nitric acid vapor remained colorless, a sensitive test for the absence of nitrogen dioxide, throughout the period of measurement.

The spectral absorption of each cell was then measured throughout the 1.4μ region by recording the galvanometer trace on a photographic plate. By reading the height of this trace above an arbitrary base line at regular intervals along the frequency scale the area under the absorption peak could be determined.[5] Each area so obtained was plotted against the corresponding concentration and

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[1] Burdick and Freed, THIS JOURNAL, **43**, 526 (1921); Chambers and Sherwood, **59**, 316 (1937); Abel, Schmid and Stein, *Z. Elektrochem.*, **36**, 692 (1930).

[2] Giauque and Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

[3] Forsythe and Giauque, THIS JOURNAL, **64**, 48 (1942).

[4] Brackett and Liddell, *Smithsonian Miscel. Collections*, **85**, No. 5 (1931).

[5] An approximate calculation of the absorption coefficient yields a value of

$$k = 150 \frac{\text{liters}}{\text{mole cm.}^2}$$

which is close to the values of other OH containing molecules for the same type of vibration; *cf.* Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).