

Summary

The reaction between propylene and oxygen at high propylene and low oxygen concentrations has been studied in a recirculation apparatus between 500 and 600°. In addition to oxidation of propylene, pyrolysis of propylene takes place.

The oxidation products were acetaldehyde, formaldehyde, formic acid, carbon oxides and water.

The primary products of the pyrolysis were higher mono-olefins, butylenes, amylenes and hexylenes. Secondary products of pyrolysis are olefins, paraffins and hydrogen.

The temperature at which pyrolysis of propylene is appreciable is lowered greatly by the presence of small amounts of oxygen, and the rate of pyrolysis is markedly increased.

A mechanism of the oxidation and pyrolysis of propylene based on the activation of the carbon double bond has been outlined.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 307]

THE GAS PHASE EQUILIBRIUM BETWEEN METHYL NITRITE, HYDROGEN CHLORIDE, METHYL ALCOHOL, AND NITROSYL CHLORIDE. THE ABSORPTION SPECTRUM OF NITROSYL CHLORIDE

BY J. A. LEERMAKERS AND H. C. RAMSPERGER

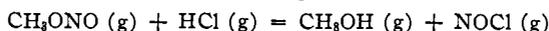
RECEIVED DECEMBER 16, 1931

PUBLISHED MAY 7, 1932

Free energy values of organic substances will probably most often be obtained from heats of combustion and specific heat data by use of the third law of thermodynamics. They may, of course, be obtained with considerable accuracy from equilibrium data, but often a good equilibrium free from side reactions cannot be obtained with organic compounds. It is still more unusual to establish a gas phase equilibrium at room temperature. In the course of an investigation by the junior author to locate a gas phase reaction suitable for reaction rate research it was found that an equilibrium was very rapidly established between the gases listed in the title at room temperature. This was shown by the immediate partial disappearance of the color of nitrosyl chloride gas when added to an excess of methyl alcohol gas, and the appearance of the same color when hydrogen chloride gas was added to methyl nitrite gas. The thermodynamic data for the three gases, methyl alcohol, nitrosyl chloride and hydrogen chloride are quite accurately known so that from equilibrium measurements at two temperatures we are able to calculate the free energy of formation, the heat of formation and entropy of methyl nitrite.

Experimental Method

The equilibrium concentrations were obtained by quantitative measurements of the absorption of light in the spectral region 4000 to 5000 Å., where the absorption of nitrosyl chloride is quite strong. Of the other substances only methyl nitrite absorbs light in this region and then only faintly between 4000 and 4200 Å. From our determination of the absorption of pure nitrosyl chloride and methyl nitrite, the absorption of an equilibrium mixture of the four substances and the initial pressures of two of them it is possible to calculate an equilibrium constant for the reaction



Preparation and Purification of the Compounds.—Nitrosyl chloride was prepared by passing hydrogen chloride into nitrosyl sulfuric acid obtained from sulfur dioxide and fuming nitric acid.¹ The nitrosyl chloride was repeatedly distilled and collected at -20° to remove traces of hydrogen chloride and finally fractionally distilled through a column surrounded by a bath at -25° . The middle fraction boiling at $-6.0 \pm 0.2^\circ$ was used. This was distilled at a low temperature on a high vacuum line into a number of small tubes each drawn down to a capillary and maintained at -78° . When sufficient nitrosyl chloride had collected in a small tube, the supply was also cooled to -78° stopping the distillation and the tube was sealed off.

Methyl nitrite was prepared by dropping sulfuric acid into a stirred and gently heated mixture of sodium nitrite and methyl alcohol. The evolved gas was passed through fused calcium chloride and collected at -78° . The liquid was fractionally distilled through a column surrounded by ether cooled by solid carbon dioxide to about -30° and was collected at -78° . It boiled at a constant temperature of -17.0° and the middle portion was used. It was found necessary to eliminate traces of nitrogen dioxide since the strong characteristic absorption bands of this substance interfered with the measurements. A supply of pure methyl nitrite was obtained by allowing the gas to pass through a long tube containing soda lime into a one-liter storage flask sealed onto the vacuum system and previously evacuated. No bands of nitrogen dioxide were then found in the sample even when a pressure of the gas as high as 40 cm. was in the absorption tube.

The methyl alcohol used was Baker's Analyzed absolute methyl alcohol. This was further dried by refluxing over aluminum amalgam and was then fractionally distilled. It was placed in a small receiver equipped with a stopcock, sealed to the vacuum system, and enough of the vapor pumped off to displace all of the air.

Hydrogen chloride was obtained by dropping c. p. hydrochloric acid on concentrated c. p. sulfuric acid. The hydrogen chloride gas was passed through wash bottles containing concentrated c. p. sulfuric acid, then through a tube filled with c. p. anhydrous calcium chloride, and was collected in a half-liter flask equipped with a stopcock and a tube sealed to the bottom. When gas sufficient to displace the air had passed through the flask the stopcock was closed and the entrance tube sealed off. The flask was sealed to the vacuum system and the hydrogen chloride was frozen down by means of liquid air into the tube at the bottom. Any air left in the flask was then pumped off, the stopcock was closed, and the solid hydrogen chloride allowed to evaporate into the flask. It was used without further treatment.

The Absorption Curve of Nitrosyl Chloride and Methyl Nitrite.—A Pyrex absorption cell 4 cm. in diameter and 40.0 cm. long with plane parallel windows was filled with ni-

¹ Scott and Johnson, *J. Phys. Chem.*, **33**, 1975 (1929).

trostyl chloride or methyl nitrite gas as shown in Fig. 1. The absorption cell A was evacuated with a mercury diffusion pump through G. It was filled with nitrosyl chloride by breaking the capillary end of the tube B containing liquid nitrosyl chloride with the magnetic hammer C, or filled with methyl nitrite from the supply D.

The pressure was measured by a "clicker" system. The pressure on the "clicker"² sealed in the bottom of the bulb F was controlled by the variable leaks J or by vacuum through H and was measured by a McLeod gage having a compression of about eight-fold so as to read accurately pressures of several cm.

The absorption cell was then immediately sealed off just above the side tube. Capillary tubing was used to prevent too much reaction of nitrosyl chloride with the grease of the stopcock before sealing off.

Figure 2 shows the apparatus for photographing the absorption spectrum. Light from the 40-watt mazda lamp B operating under constant voltage passes through the diaphragm C which is covered with a ground glass, then through the partition D, the shutter E, the diaphragm F, the absorption cell H containing the absorbing substance, the diaphragm F', and finally into the slit of the spectrograph N. The cell is attached to the galvanized iron thermostat by the large rubber tubes at G and G' which slip over the brass tubes soldered into the ends of the thermostat. The cell has a side tube J (not shown in Fig. 1) used for freezing out the contents of the cell with liquid air. K is a heater and stirrer, L the mercury thermo-regulator and M is a thermometer which was calibrated against a Bureau of Standards thermometer.

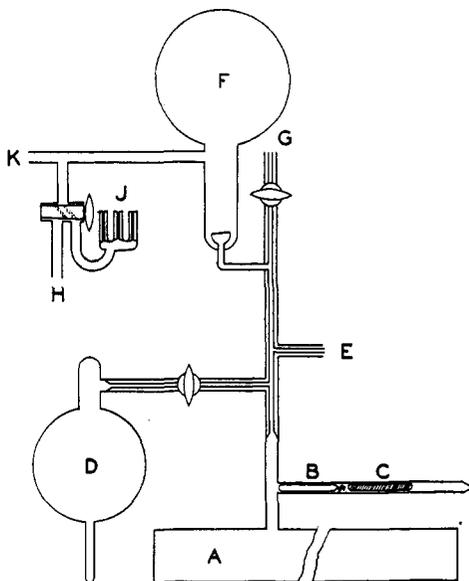


Fig. 1.

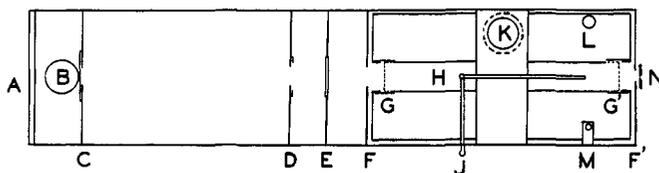


Fig. 2.

A series of spectra are photographed with the absorbing medium in the cell, the cell contents are frozen out, and then a series of photographs are taken on the same plate in between the first exposures. These latter exposures are given the same exposure time but are uniformly reduced in intensity for all wave lengths by placing screens of known absorption in the light path at D. The blackening of the photographic plate on two adjacent spectra is the same for those wave lengths for which the particular screen and the gas in the cell have the same absorption. Positions of equal intensity were deter-

² Smith and Taylor, THIS JOURNAL, 46, 1393 (1924).

mined by a method similar to that used by Ramsperger and Porter.⁸ The photometer system for this purpose is shown in Fig. 3. The photographic lens D projects an image of the plate in the holder C on the screen L with a magnification of about eight times. A high light intensity is obtained by the 500-watt projection lamp A and the condensing lenses B. A slit in the screen 2 cm. long and 2 mm. wide allows the light from a very narrow region of the spectrum to fall onto a cesium photoelectric cell E. F is a 45-volt battery, G a 10-megohm resistance, H a Leeds and Northrup high-sensitivity galvanometer with critical damping resistance J. With a scale at two meters, deflections of 6 to 20 cm. were obtained. The plate in the holder C could be moved either vertically or horizontally so as to bring the image of the spectra on the slit at any wave length. Points of equal deflection could be located with an accuracy of 2 to 5 Å. An iron arc spectrum served as a wave length reference. We wish to thank Professors Dickinson and Beckman of this Laboratory for the use of the screens which were constructed and calibrated by them. They determined the transmission of the screens by use of a thermopile and a constant light source.

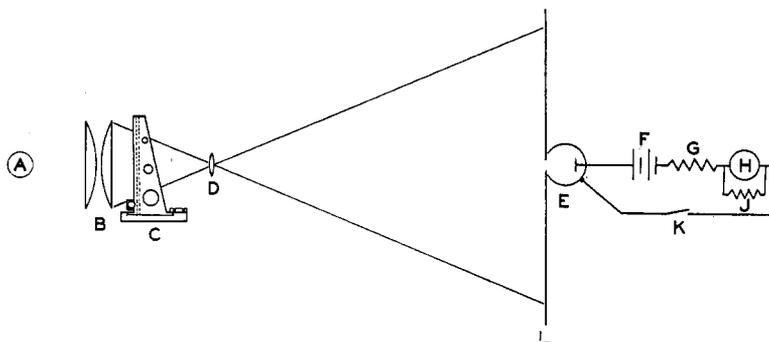


Fig. 3.

Table I gives the data obtained for the absorption of nitrosyl chloride and methyl nitrite at temperatures of 25 and 50°. The pressures are calculated to 25°. The absorption coefficients at the wave lengths listed are then calculated by assuming that Beer's law is obeyed over the range of pressure investigated. The relation used was $I_t/I_0 = 10^{-\epsilon cd}$ where I_t/I_0 is the fraction of light transmitted, c is the concentration expressed in cm. of mercury pressure at 25°, d is the length of the absorption cell (40.0 cm.) and ϵ is the absorption coefficient. Values of ϵ are plotted against the wave length in Fig. 4.

The small circles on the dotted line portion of the curve at 25° were estimated from the difference in galvanometer deflections from the nearest points of equal intensity on one of the plates. This region of the curve was not used in determinations of the equilibrium concentrations of nitrosyl chloride. The coincidence of several points at different pressures indicates that Beer's law is obeyed fairly well in the range studied.

The Partial Pressure of Nitrosyl Chloride at Equilibrium.—When nitrosyl chloride of concentration c and of absorption coefficient ϵ_1 is present

⁸ Ramsperger and Porter, THIS JOURNAL, 48, 1267 (1926).

TABLE I
POINTS OF EQUAL INTENSITIES (ÅNGSTRÖM UNITS) ON PHOTOGRAPHS TAKEN THROUGH SCREENS AND THROUGH NITROSYL CHLORIDE AND METHYL NITRITE AT VARIOUS TEMPERATURES AND PRESSURES

| Screen no. | Light transmitted by screen | 3.86 cm. | | NOCl 11.02 cm. | | 8.44 cm. | | CH ₂ ONO 41.84 cm. | |
|------------|-----------------------------|-------------------|------|----------------|------|----------|------|-------------------------------|------|
| | | 25° | 50° | 25° | 50° | 25° | 50° | 25° | 50° |
| 2 | 0.459 | 4960 | 4940 | | | | | 4108 | 4115 |
| | | 4530 | 4543 | | | | | | |
| | | 4520 | | | | | | | |
| 3 | .2395 | 4170 | 4190 | | | | | 4065 | 4080 |
| | | 4168 ^a | | | | | | | |
| 4 | .1032 | 4005 | 4010 | 4960 | 4945 | 4862 | 4855 | 4037 | 4045 |
| | | 4007 ^a | | 4550 | | 4255 | 4642 | | |
| | | | | 4505 | | 4653 | 4432 | | |
| 5 | .0553 | | | 4850 | 4847 | 4186 | 4208 | 4018 | 4025 |
| | | | | 4650 | 4647 | | | | |
| | | | | 4263 | 4406 | | | | |
| | | | | | 4340 | | | | |
| | | | | | 4295 | | | | |

^a Duplicate plate to check accuracy.

in the same cell with methyl nitrite of concentration c_2 and absorption coefficient ϵ_2 the Beer's law expression becomes $I_1/I_0 = 10^{-(\epsilon_1 c_1 + \epsilon_2 c_2)d}$. If

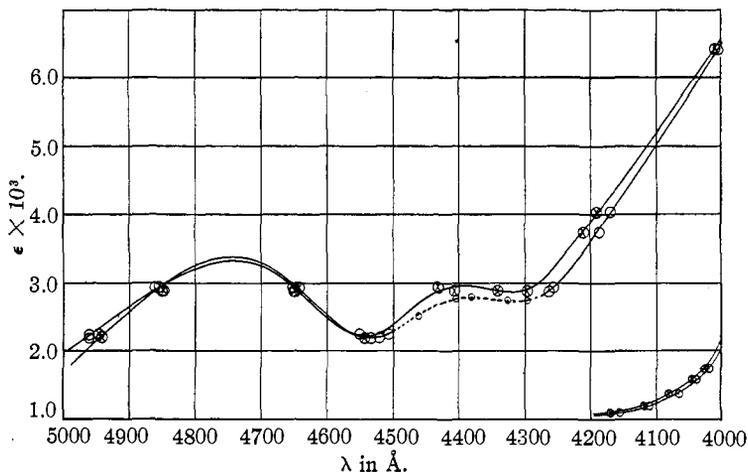


Fig. 4.—Absorption coefficients of nitrosyl chloride and of methyl nitrite plotted against wave lengths. The two upper curves are for nitrosyl chloride; those in the lower right-hand corner are for methyl nitrite. The open circles are for 25°, the circles enclosing crosses are for 50°.

the initial concentration of nitrosyl chloride is a and its equilibrium concentration after adding methyl alcohol is x , the expression becomes $I_1/I_0 = 10^{-\{\epsilon_1 x + \epsilon_2(a-x)\}d}$.

The same expression results if, in starting with methyl nitrite and hydro-

gen chloride, a is the initial concentration of methyl nitrite. The equilibrium concentration x can then be calculated from values of ϵ_1 and ϵ_2 obtained from the absorption curve for the wave length at which I_i/I_0 is measured.

The cell was filled with the two initial substances and their pressures were determined as described before and shown in Fig. 1. Methyl alcohol or hydrogen chloride was attached at E. Capillary tubing was used as indicated so that when the cell was sealed off just above the side tube no appreciable error was made in the partial pressures of gases admitted even though perfect mixing in the tubing had not taken place. The procedure in making the exposures and finding the points of equal intensity was similar to that for determining the absorption curves for the pure gases. Table II gives the complete data of two experiments. Table III gives a summary of all of the experiments.

TABLE II
SAMPLE EXPERIMENTS

| Exposure | Absorbing medium | Points of equal intensity, Å. | Pressure NOCl |
|--|-------------------|-------------------------------|---------------|
| Expt. 4b. CH_3ONO , 4.03 cm.; HCl, 7.45 cm.; T , 50° | | | |
| 1 | Cell and contents | 4235 | 2.43 |
| 2 | Screen No. 2 | 4230 | 2.39 |
| 3 | Cell and contents | | |
| 4 | Iron arc source | | |
| 5 | Cell and contents | 4043 | 2.47 |
| 6 | Screen No. 3 | 4037 | 2.44 |
| 7 | Cell and contents | | |
| | | | Average 2.43 |
| Expt. 5a. CH_3ONO , 5.90 cm.; HCl, 3.07 cm.; T , 25° | | | |
| 1 | Cell and contents | | |
| 2 | Screen No. 2 | 4125 | 1.69 |
| 3 | Cell and contents | 4123 | 1.69 |
| 4 | Iron arc source | | |
| 5 | Cell and contents | | |
| 6 | Screen No. 3 | 4000 | 1.72 |
| 7 | Cell and contents | 4003 | 1.73 |
| | | | Average 1.71 |

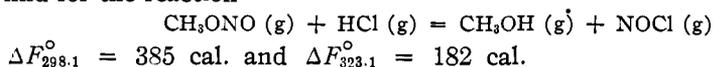
TABLE III
SUMMARY OF EXPERIMENTS

| Expt. no. | Initial pressures, cm. | | | | Pressure of NOCl at equilibrium | | K_{298} | K_{323} |
|-----------|-------------------------|------|-------|------------------------|---------------------------------|-----------------|-----------|-----------|
| | CH_3ONO | HCl | NOCl | CH_3OH | 25° | 50° | | |
| 4 | 4.03 | 7.45 | | | 2.26 ± 0.04 | 2.43 ± 0.02 | 0.556 | 0.735 |
| 5 | 5.90 | 3.07 | | | $1.71 \pm .01$ | $1.88 \pm .02$ | .513 | .739 |
| 6 | | | 4.58 | 2.87 | $2.47 \pm .02$ | | .422 | |
| 7 | | | 4.56 | 4.14 | $2.04 \pm .03$ | $2.26 \pm .03$ | .520 | .785 |
| 8 | | | 12.70 | 3.44 | $9.64 \pm .10$ | $9.78 \pm .09$ | .391 | .596 |
| 12 | | | 6.02 | 4.06 | | $3.44 \pm .10$ | | .764 |
| 13 | | | 4.75 | 4.19 | $2.14 \pm .01$ | $2.26 \pm .06$ | .497 | .620 |
| 14 | | | 4.20 | 3.76 | | $2.07 \pm .03$ | | .744 |

Experiments 1 and 2 are not included because they were preliminary experiments made before the apparatus was in its final form. In Expts. 3, 9, 10 and 11 the total pressure in the cell was sufficiently high so that there was some evidence of condensation in each case. The equilibrium pressures of nitrosyl chloride are generally the average of four points. The average deviation from the average is shown by the \pm sign in columns 6 and 7. Equilibrium constants have been calculated by assuming the fugacities of the gases equal to their pressures. Experiments 6 and 8 deviate rather badly from the others listed. In these cases the concentration of methyl alcohol at equilibrium is very low, in fact so low that the estimated experimental error in the measurement of the nitrosyl chloride pressure will produce a very large error in the equilibrium constant. These experiments have not been used in obtaining an average equilibrium constant. Experiment 13 at 50° gives a constant which differs widely from the remaining constants at this temperature. No explanation is known for this discrepancy. The probable error of the average constant at 50° , if this value is excluded, is about equal to the probable error introduced by the probable errors in the measured pressures of nitrosyl chloride, while if this value be included the probable error of the average equilibrium constant is increased three-fold. We feel therefore that this value should likewise be excluded in obtaining an average equilibrium constant. When these values are excluded the average value of $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$.

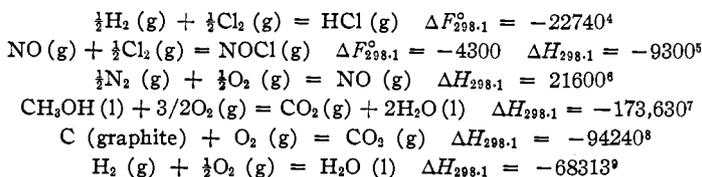
Evidence of a True Equilibrium.—We may present the following evidence that a true equilibrium free from side reactions has been obtained. The data of Table III show that the equilibrium constant is independent of the direction from which the equilibrium is established. It is independent of moderate variations in the partial pressure of the starting materials. No light-absorbing gas other than nitrosyl chloride or methyl nitrite (such as nitrogen dioxide) is likely to be present in appreciable amounts since the calculated concentration of nitrosyl chloride was the same at several wave lengths and any other absorbing gas would not likely have a characteristic absorption curve so very much like nitrosyl chloride. An experiment was carried out in which definite amounts of hydrogen chloride and methyl nitrite were mixed and the calculated pressure was obtained showing that no change in pressure occurred during the reaction. The equilibrium pressure of nitrosyl chloride as determined by its light absorption was found not to be changed on standing in the dark for an hour or on being illuminated for two hours.

Thermodynamic Calculations.—From the equilibrium constants we find for the reaction



Assuming ΔC_p zero over the range of temperature investigated $\Delta H_{298.1} = 2805$ cal. Then $\Delta S_{298.1}^\circ = 8.12$. The error in ΔF is quite small. The probable error of ΔH may be estimated roughly at 300 to 400 cal. and of ΔS about 1.0 entropy unit.

To calculate $\Delta F_{298.1}^\circ$, $\Delta H_{298.1}$ and $\Delta S_{298.1}^\circ$ for the reaction of formation of methyl nitrite from the elements and the entropy of methyl nitrite it will be necessary to make some choice of the available thermodynamic data of the other three substances occurring in the equilibrium. We have chosen the following data



Vapor pressure of $\text{CH}_3\text{OH}(\text{l})$ at $298.1^\circ = 122.2$ mm.¹⁰



The following values of the molal entropy at $T = 298.1^\circ$ and one atmosphere have been used for third law calculations

| | |
|---|--|
| $\text{H}_2(\text{g}) = 31.23$ | Giauque, THIS JOURNAL, 52, 4825 (1930) |
| $\text{C}(\text{graphite}) = 1.3$ | Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 464 |
| $\text{N}_2(\text{g}) = 45.78$ | Giauque, private communication |
| $\text{O}_2(\text{g}) = 49.03$ | Giauque and Johnson, THIS JOURNAL, 51, 2300 (1929) |
| $\text{Cl}_2(\text{g}) = 53.3$ | McMorris and Yost, <i>ibid.</i> , 53, 2625 (1931), footnote 2631 |
| $\text{NO}(\text{g}) = 50.43$ | Johnson and Giauque, <i>ibid.</i> , 51, 3194 (1929) |
| $\text{HCl}(\text{g}) = 44.64$ | Giauque and Wiebe, <i>ibid.</i> , 50, 101 (1928) |
| $\text{CH}_3\text{OH}(\text{l}) = 30.3$ | Kelley, <i>ibid.</i> , 51, 180 (1929) |

The resulting data for the free energy, heat and entropy of formation at 298.1° and one atmosphere and the entropy of the four substances occurring in the equilibrium are listed in Table IV.

⁴ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1930, Vol. VII, p. 233.

⁵ Dixon, *Z. physik. Chem.*, Bodenstein Festband, p. 679, July 15 (1931).

⁶ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 560.

⁷ Rossini, *Proc. Nat. Acad. Sci.*, 17, 343 (1931).

⁸ Roth and Naeser, *Z. Electrochem.*, 31, 461 (1925).

⁹ Rossini, *Bur. Standards J. Research*, 6, 1 (1931).

¹⁰ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. 3, p. 216.

¹¹ Fiock, Ginning and Holton, *Bur. Standards J. Research*, 6, 881 (1931).

TABLE IV
CONSTANTS AND DATA FOR COMPOUNDS

| | HCl (g) | NOCl (g) | CH ₃ OH (g) | CH ₃ ONO (g) |
|----------------------------|---------|----------|------------------------|-------------------------|
| $\Delta F_{298.1}^{\circ}$ | -22,740 | 16,400 | -38,870 | -100 |
| $\Delta H_{298.1}^{\circ}$ | -22,030 | 12,300 | -48,290 | -16,750 |
| $\Delta S_{298.1}^{\circ}$ | 2.38 | -13.8 | -31.6 | -55.9 |
| $S_{298.1}^{\circ}$ | 44.64 | 60.3 | 56.7 | 64.2 |

Summary

Quantitative measurements of the light absorption of nitrosyl chloride and methyl nitrite have been made. Measurements of the light absorption due to nitrosyl chloride present in the gas phase equilibrium $\text{CH}_3\text{ONO (g)} + \text{HCl (g)} = \text{CH}_3\text{OH (g)} + \text{NOCl (g)}$ have been made and equilibrium constants calculated for the temperatures of 25 and 50° for both the forward and reverse reactions. The equilibrium is instantly established, is independent of the direction from which it is established and is free from side reactions. The equilibrium constants are $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$. From these values and from thermodynamic data in the literature for hydrogen chloride, nitrosyl chloride and methyl alcohol we have calculated the free energy, the heat and the entropy of formation and the entropy of methyl nitrite.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

REACTION OF GASES WITH INCANDESCENT TANTALUM

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RECEIVED DECEMBER 19, 1931

PUBLISHED MAY 7, 1932

It has been known for many years that tantalum, when heated, absorbs actively such gases as nitrogen and hydrogen, but early experimentation was confined to the comparatively low temperatures obtainable in furnaces, and the pressures were the comparatively large ones measurable with a manometer.¹ With modern methods of vacuum technique, it is possible to study reactions at very low pressures and at temperatures up to the melting point of the material under observation. Tantalum offers a particularly interesting subject for such a study.

The following work was done with tantalum filaments mounted in bulbs on an exhaust system. The system contained a reservoir of the particular gas in use and suitable mercury traps for shutting off known volumes. Pressures were read with McLeod gages.

¹ Von Bolton, *Z. Electrochem.*, **11**, 45 (1905); Sieverts and Bergner, *Ber.*, **44**, 2394 (1911); Balke, *Chem. Met. Eng.*, **27**, 1271 (1922); Borelius, *Metallwirtschaft*, **8**, 105-108 (1929)