

all of the adsorbed hydrogen is released upon treatment with ammonium salts in liquid ammonia. By experiments of which the following is typical, we have also confirmed indirectly their statement that as much as 100 cc. of hydrogen/g. nickel may be adsorbed. Thus, in a case similar to Expt. 10, analyses showed a total nickel content of 86.68% and 10.10% nitrogen. If it is assumed that all of the nitrogen is present as nickel(II) amide 2-ammoniate, that this compound will decompose thermally as described earlier in this paper, and that hydrogen is present in the quantity specified by Burgess and Eastes, then a 0.2858-g. sample heated above 358° should evolve 38.7 cc. of ammonia, 21.8 cc. of hydrogen, and 1.9 cc. of nitrogen. The volumes of these gases found experimentally were 37.2, 20.9 and 2.7, respectively.

Summary

1. The action of potassium amide in liquid ammonia at -33.5° upon cationic nickel salts yields nickel(II) amide 2-ammoniate.

2. Thermal decomposition of nickel(II) amide 2-ammoniate at 10⁻³ mm. produces successively: nickel(II) amide (at 42.3°), nickel(II) nitride (at 119.3°), nickel(I) nitride (at 362°), and elemental nickel and nitrogen (at 585°).

3. The reduction of nickel(II) bromide and iodide by solutions of potassium in liquid ammonia at -33.5° yields, respectively, pyrophoric and non-pyrophoric nickel together with some nickel (II) amide 2-ammoniate. Conditions required to minimize formation of the latter are described.

4. Preliminary experiments on the catalytic activity of nickel from the reduction of nickel salts in ammonia in the hydrogenation of propene-1-ol-3 are described.

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A Measurement of the Diffusion Coefficient of Hydrogen Peroxide Vapor into Air

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I. Introduction

The measurement of hydrogen peroxide vapor diffusion is complicated, in common with the measurement of other physical properties, by the unavoidable decomposition of peroxide in contact with any known surface. Among the methods available for the measurement of gaseous diffusion, the only one which appears applicable to peroxide measurements is a method first developed by Stefan¹ in which diffusion takes place unidirectionally at constant rate from a source of saturated vapor to a point of low vapor concentration.

An apparatus has been developed for the application of this method to peroxide diffusion and measurements made of the diffusion rate of peroxide vapor into air.

II. Method

The method used is a basically simple one originally developed by Stefan¹ applicable where one of the diffusing components is a liquid at ordinary temperatures. Diffusion takes place through a stagnant gas in a glass tube; liquid at the bottom of the tube provides vapor of a fixed known concentration, while at the top of the tube zero concentration of vapor is effected by conducting a stream of the second gas across the end of the tube. The rate of diffusion is determined from the observed loss of liquid with time. One thus has a

concentration gradient. Under these conditions the fundamental differential expression for diffusion becomes

$$\Gamma = -Dn/n_2 \partial n_1 / \partial x \quad (1)$$

Gamma is the diffusion rate, g. moles per sq. cm. per second, D the diffusion coefficient, and n_1 the concentration of the diffusing gas, in gram moles per cc. Integrating between limits x from 0 to L , n_1 from n_{10} to 0, we find

$$\Gamma = Dn/L \ln (1 - n_{10}/n) \quad (2)$$

where x is measured from the liquid surface above which the concentration of the diffusing gas is n_{10} ; n_2 is the concentration of stagnant gas; and n is the total concentration.

In the case of peroxide diffusion the situation is complicated by the simultaneous diffusion of the oxygen evolved by the slowly decomposing liquid peroxide. For this case of diffusion of two gases through a third stagnant gas, the following differential equations apply

$$-\partial n_1 / \partial x = \Gamma_1 n_2 / D_{12} - \Gamma_2 n_1 / D_{12} + \Gamma_1 n_3 / D_{13} \quad (3)$$

$$-\partial n_2 / \partial x = \Gamma_2 n_1 / D_{12} - \Gamma_1 n_2 / D_{12} + \Gamma_2 n_3 / D_{13} \quad (4)$$

where subscripts 1 and 2 refer to the first and second diffusing gases, and n to the total concentration.

A solution of these equations in the form of two simultaneous equations has been obtained.²

$$\Gamma_1 / D_{13} + \Gamma_2 / D_{23} = n / L \ln n / n_{30} \quad (5)$$

$$\Gamma_1 + \Gamma_2 = D_{12} n / L \ln \frac{n(1/D_{13} - 1/D_{23})}{n(1/D_{13} - 1/D_{23}) + n_{20}(\Gamma_1 + \Gamma_2) / \Gamma_2(1/D_{12} - 1/D_{13}) - n_{10}(\Gamma_1 + \Gamma_2) / (\Gamma_1(1/D_{12} - 1/D_{13}))} \quad (6)$$

case of steady unidirectional diffusion of one gas through a second stagnant gas, under a fixed con-

For small concentrations of the diffusing substances the results are but little different from

(1) Stefan, *Sitz. Akad. Wiss. Wien., Abt. II*, **62**, 388 (1870); *Ann. Physik*, **41**, 723 (1890).

(2) Sherwood, "Absorption and Extraction," McGraw-Hill Book Co., New York, N. Y., 1937.

TABLE I
 PEROXIDE-AIR DIFFUSION, 60°

Run	Tube no.	Air flow rate, cc./min.	Weight % peroxide in liquid	Rate of decomposition, wt. % per hour	Initial rate of change of liquid volume cu. mm./hr.	Calcd. rate change of vol. due to decomposition cu. mm./hr.	Diffusion rate of change of liquid volume cu. mm./hr.	Diffusion rate g./sq. cm. sec.	Diffusion coefficient 60° sq. cm./sec.
1	2	1200	99.0 to 98.4	0.011	6.94	1.68	5.26	3.24×10^{-7}	0.191
2	2	1000	99.4 to 98.6	.0066	6.19	1.02	5.18	3.18	.189
3	2	1050	99.0 to 96.8	.030	9.68	4.59	5.09	3.13	.183

Tube No. 1 17.43 cm. length 6.12 sq. cm. cross sectional area
 2 17.62 cm. length 6.32 sq. cm. cross sectional area
 3 17.47 cm. length 2.095 sq. cm. cross sectional area

Density of peroxide, 60°: 1.40 gm./cc., extrapolated from data of Maass and Hatcher.⁵

Vapor pressure of peroxide, 60°: 17.8 mm., data of Maass and Hibert.⁷

those obtained by a simple calculation of each diffusion, neglecting the other.

III. Experimental Procedure

Three diffusion tubes were used, each approximately 17 cm. in length (liquid surface to end) and with cross-sectional areas of 6 and 2 sq. cm. The rate of loss of liquid was measured by displacement of the liquid back to a fixed zero level with a glass rod of uniform diameter. A sharply defined zero point was provided by the contact of a glass pointer with the liquid surface. The displacement rod was contained in a secondary tube connected to the main tube as shown in the sketch (Fig. 1). The rod, 0.524 cm. in diameter (area 0.2160 sq. cm.) was adjusted by means of a screw thread, millimeter pitch with 30 turns. A knob provided adjustment to $\frac{1}{100}$ turn. This gave a total available range of volume displacement of about 0.7 cc. The volume of liquid contained in the larger diffusion apparatus at minimum displacement was 30.4 cc.

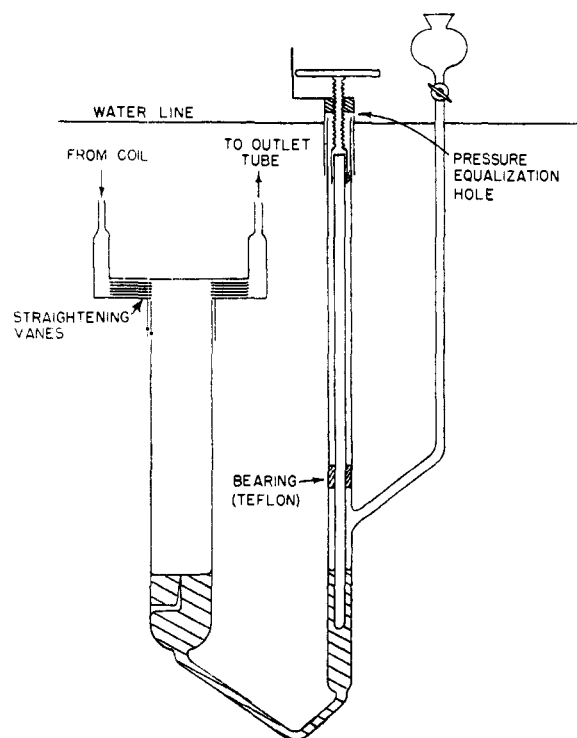


Fig. 1.—Diffusion apparatus.

The entire apparatus was placed in a water thermostat with temperature control to $\pm 0.1^\circ$. To eliminate vibration, the stirring motor of the bath was independently mounted on the stone floor. A brass box containing several plates designed to act as straightening vanes directed the flow of the second gas stream across the end of the diffusion tube. The same box was used with both large and narrow tubes. The gas stream was brought to bath temperature by conducting it through a long copper coil placed in the bath. The air was drawn through a calcium chloride tower; the hydrogen was forced through the apparatus. The pressure drop was negligible in each case, the diffusion apparatus itself providing a sensitive water manometer. The rate of flow was measured by a dry gas meter.

The apparatus differs to a considerable extent from the usual device for diffusion rate measurement by this method. Stefan,¹ Winkelmann,³ and all succeeding investigators have used diffusion tubes of very small diameter, from 1 to 6 mm., with ratios of length to diameter varying from 10 to 100. The rates of diffusion were determined by measuring the rate of fall of the liquid level in the diffusion tube; this rate is independent of the diameter of the tube. The use of small tubes has the advantage of giving a large surface to volume ratio, acting to damp out thermal or other currents which might interfere with diffusion. Measuring the diffusion rate by measuring the change in liquid level has the disadvantage of involving changing length of the diffusion path. The length of the diffusion path is essentially constant in the present apparatus.

In a given experimental run the loss of liquid with time was followed continuously, usually over a 0.5–0.6 cc. volume range. For peroxide determinations liquid peroxide of above 99% weight concentration was prepared by the evaporative concentration, to about one-tenth volume, of distilled 95% peroxide available from the project still. This concentration was followed by a distillation of the concentrate.⁴ The peroxide sample was analyzed before and after each diffusion measurement to fix the decomposition rate, using the analytical procedure of Huckaba and Keyes.⁵ Because of the low vapor pressure of peroxide, a temperature of at least 60° was required to make diffusion measurements practical. At this temperature considerable difficulty was experienced with peroxide decomposition. The most thorough chemical cleaning (fuming sulfuric acid) of a glass surface does not remove completely catalytic activity which the surface may possess, activity probably due to material adsorbed in the microscopic pores of the glass surface or fused into the surface during glass blowing operations.

(3) Winkelmann, *Ann. Physik*, **36**, 93 (1889).

(4) No difficulty was experienced in this evaporation to dryness of concentrated peroxide, using a bath temperature of 60°.

(5) Huckaba and Keyes, *THIS JOURNAL*, **70**, 1840 (1948).

(6) Maass and Hatcher, *ibid.*, **42**, 2548 (1920).

(7) Maass and Hibert, *ibid.*, **46**, 2693 (1924).

A hydrofluoric acid etching of the glass surface was found initially effective in reducing the decomposition rate. It was in this manner that the lowest decomposition rate, 0.0066% per hour at 60°, was obtained. The repeated application of this treatment appeared, however, to result in a gradual pitting of portions of the glass surface, with consequent disadvantage, and subsequent rates of decomposition were higher.

In order to have some comparison between the diffusion coefficients to be obtained with this apparatus and other available data, a number of measurements were made of a system for which data were available, the diffusion of water vapor into hydrogen. (Water-air diffusion cannot be measured by the present method because of the unfavorable density gradient existing in this case.) The water-hydrogen measurements were also used to determine the effect of variation of gas flow rate and of variation of tube diameter.

The gas flow rate must be sufficient to effect a negligible vapor concentration at the top of the diffusion tube. The hydrogen flow rate was varied from 1000 to 3000 cc./min. A flow rate of 2000 cc./min. or greater was found to be satisfactory. This corresponds to a linear gas velocity across the end of the tube of 11 cm./sec., the same box to direct the gas stream being used with both the large and small diffusion tubes. For peroxide-air measurements, where the diffusion coefficient is much lower,⁸ a flow rate of 1000 cc./min. was used.

The water vapor-hydrogen diffusion data obtained with the three tubes at various temperatures are presented in Table II. The data for the large tubes lie 1.5 to 3.5% below the narrow tube data, and the data of Winkelmann.³ The data of Guglielmo⁹ lie above the results here obtained.

TABLE II
WATER-HYDROGEN DIFFUSION

Tube	Hydrogen flow rate, cc./min.	Diffusion rate g./sq. cm. sec.	Diffusion coefficient sq. cm./sec.
2	2200	1.55×10^{-6}	0.882
	2150	1.53	.870
30° 2	2050	1.57	.897
	2150	1.56	.890
1	2050	6.40×10^{-6}	0.988
	2100	6.47	.999
55° 1	2100	6.45	.996
	3300	6.34	.979
(1	1050	6.00	...) ^a
	3	2200	6.63×10^{-6}
55° 3	2050	6.51	1.007
	3	2050	6.63
3	1900	8.78×10^{-6}	1.065
	3	2000	8.80
60° 3	2050	8.80	1.067
	3	3000	8.75
(3	1100	8.60	...) ^a

^a Insufficient gas rate.

IV. Interpretation of Experimental Results

In peroxide diffusion measurements there is, in addition to liquid loss due to evaporation and diffusion, a change in liquid volume due to decomposition. For the bulk of the liquid, neglecting the portion diffusing, the total number of moles remains constant as decomposition proceeds.

(8) The ratio of (average) vapor concentration in the (exit) gas stream to vapor concentration at the liquid surface is independent of the vapor pressure, depending only on the diffusion coefficient, the flow rate, and the tube dimensions.

(9) Guglielmo, *Atti accad. del scienze di Torino*, **17**, 54 (1881).

$$V\rho W/34M = \text{constant} \quad (7)$$

$$V_2 = V_1\rho_1 W_1/M_1 \times M_2/\rho_2 W_2 \quad (8)$$

where V and ρ refer to the liquid volume and density, W to the weight composition of peroxide, M the molal composition of peroxide, and the numerals 1 and 2 to time scale positions.

The change in concentration is known, the densities of various concentrations of peroxide at 60° are not known; however, only relative values are needed, hence the known 18° data⁵ may properly be used. For a liquid volume of 30 cc. the change in volume per per cent. by weight decomposition is

100 to 99%	0.156 cc.
99 to 98	.153
98 to 97	.151

The peroxide was analyzed at the beginning and end of each determination. A linear decomposition rate was assumed. This assumption appears justifiable for pure unstabilized peroxide. The diffusion liquid loss with time may then be determined, and correspondingly Γ , the diffusion rate in g. moles/sq. cm. sec.¹⁰ The peroxide concentration is decreasing with time and the total vapor pressure increasing; however, the diffusion rate is found to be constant to the accuracy of measurement for liquid concentrations down to 98 weight per cent., increasing slowly beyond that point. The highest initial concentration used was 99.4 weight per cent. liquid; the results were extrapolated back to 100% peroxide.

In the peroxide-air diffusion measurements (treating air as a separate gas) there are two substances, peroxide vapor and oxygen, diffusing through a layer of air in which there is no net motion (stagnant). The rate of peroxide diffusion is, however, known from our observation. The rate of oxygen diffusion is also known from the measured rate of decomposition and oxygen evolution. The oxygen-air diffusion coefficient has been measured¹¹; the peroxide-oxygen coefficient is not known, but various assumptions may be made as to its value and the effect calculated using equations (5) and (6).

Calculation shows that for the rates of oxygen evolution involved, the effect of oxygen diffusion on the diffusion of peroxide is small or negligible. For the maximum rate of oxygen evolution the difference between exact calculation considering oxygen diffusion and a calculation which neglects oxygen diffusion is 2%, when $D_{H_2O_2-O_2}$ is taken as $0.9 D_{H_2O_2-air}$. Also in this most unfavorable case, effect of a variation of the value of $D_{H_2O_2-O_2}$ from $0.8 D_{H_2O_2-air}$ to $1.0 D_{H_2O_2-air}$ is 1.6%. The reason for this small interference of the two diffusing gases is the low concentration of both compared to the total concentration. The peroxide

(10) The slight correction for barometric variation was applied to Γ , which for normal barometric changes in pressure varies as D varies; i. e., inversely with the pressure.

(11) "International Critical Tables," **5**, 62 (1929), data of von Obermayer.

pressure at the liquid surface is 17.8 mm.; the calculated oxygen concentrations at this point necessary to effect the known rates of oxygen transfer correspond to partial pressures of 2.6 to 11.8 mm.

V. Conclusions

The diffusion coefficients of peroxide into various permanent gases may be measured to an accuracy of $\pm 2\%$ by the method and apparatus described in this report. Peroxide decomposition does not interfere with diffusion measurement, for rates of decomposition which are not excessively high.

(An important diffusion coefficient, that of

peroxide vapor into its decomposition products, is not however measurable by this method.)

VI. Summary

The diffusion coefficient of peroxide vapor into air has been measured at a temperature of 60° . A value of 0.188 ± 0.004 sq. cm./sec. was obtained. The method and apparatus used are applicable to the measurement of peroxide vapor diffusion rates into other permanent gases. An estimate of the coefficient, using the Edwin R. Gilliland formula¹² gives the number 0.1982.

(12) E. R. Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

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Organosilicon Polymers. IV. Infrared Studies on Cyclic Disubstituted Siloxanes¹

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Numerous reports⁴ have appeared on cyclic disubstituted siloxanes, and it has been observed that the cyclic forms are often the prevalent structures obtained from the hydrolysis of R_2SiCl_2 type compounds in organic solutions. Most frequently the cyclics so obtained are the trimer and tetramer polymers. When the R group is relatively small, separation of the trimer and tetramer polymers is reasonably satisfactory by fractional distillation. In order to be certain of the molecular size, it has been necessary in the past to rely on molecular weight determinations. Difficulties in these determinations have been expressed by certain workers.^{4e, 4g}

The purpose of this paper is to show how infrared absorption spectra may be used to distinguish between cyclic trimer and tetramer siloxane forms, and also to point out the characteristic bands for methyl, ethyl, and phenyl groups attached to silicon. The spectra of the cyclics used in this study are given in Figs. 1 and 2. Besides the dimethyl and diphenyl cyclic forms which are well known, this paper will present the spectra of the diethyl and new ethyl phenyl compounds. Included also are the two isomers of the methyl phenyl cyclic trimers recently described by Lewis,⁵ and in addition, a new crystalline isomer of the cyclic tetramers in the same system.

Experimental

Source of Materials.—The dimethyl cyclic trimer and tetramer samples were identical with those used in the

(1) Presented in part at the Chicago Meeting of the American Chemical Society, April, 1948.

(2) The Dow Chemical Company.

(3) Dow Corning Corporation.

(4) (a) Kipping, *J. Chem. Soc.*, **101**, 2125 (1912); (b) Kipping and Robinson, *ibid.*, **105**, 484 (1914); (c) Hyde and DeLong, *This Journal*, **68**, 1194 (1941); (d) Burkhard, Decker and Harker, *ibid.*, **67**, 2174 (1945); (e) Hyde, Frevel, Nutting, Petrie and Purcell, *ibid.*, **69**, 488 (1947); (f) Patnode and Wilcock, *ibid.*, **68**, 358 (1946); (g) Hunter, Hyde, Warrick and Fletcher, *ibid.*, **68**, 667 (1946).

(5) Lewis, *ibid.*, **70**, 1115 (1948).

previous paper⁶ and are described well in other reports.^{4f, 4h}

The diphenyl cyclosiloxane trimer and tetramer were prepared according to procedures well described in other articles.^{4a, 4b, 4c, 4d, 4e}

Hexaethylcyclotrisiloxane-Octaethylcyclotetrasiloxane.—Diethyl siloxanes have been reported^{7, 4c} in rather general terms, but accurate physical properties of the cyclic trimer and tetramer forms have not been given. Hydrolysis of the $(C_2H_5)_2SiCl_2$ was carried out as follows: To a mixture of 478 g. of $(C_2H_5)_2SiCl_2$ in 700 cc. of diethyl ether was added 478 g. of ice. After all of the ice had melted, the mixture was refluxed for one hour with the hydrochloric acid solution so formed. The aqueous layer was separated and the ether solution washed with an equal volume of water. The solution was then refluxed for one hour with a 5% sodium hydroxide solution which served to remove any lingering chloride groups as well as to condense hydroxyl groups. Concentration of the siloxane by removal of the ether gave a clear white fluid which contained 62% of volatile cyclic polymers. Hydrolysis of dichlorodiethylsilane with ice using no ether gave 27% volatiles. In a third run, dropping the dichlorodiethylsilane into boiling water yielded only 22% of volatile $[(C_2H_5)_2SiO]_x$ polymers.

Fractional distillation of the accumulated volatiles gave 60–70% of cyclic trimer and 10–20% of cyclic tetramer. Redistillation of $[(C_2H_5)_2SiO]_x$ through a glass helices packed column (20 plates) yielded the pure trimer with the following properties: b. p. 156.7° (50 mm.), m. p. 9.9° , d^{20}_4 0.9549, n^{20}_D 1.4308, visc.²⁵ 3.6 centistokes. *Anal.* Calcd. for $(C_2H_5)_2SiO$: Si, 27.45; C, 47.06. Found: Si, 27.5; C, 46.95.

A much lower yield of higher boiling cyclic tetramer was found to have the following properties: visc.²⁵ 11.2 centistokes, b. p. 127° (1 mm.), f. p. -64° , d^{20}_4 0.964, n^{20}_D 1.4336.

2,4,6-Trimethyltriphenylcyclotrisiloxane (α and β Isomers); 2,4,6,8-Tetramethyltetraphenylcyclotetrasiloxane (α Isomer).—These two geometric isomers have recently been reported by Lewis,⁵ but he did not describe the crystalline tetramer form which we have found in the same preparation. Five hundred grams of pure dichloromethylphenylsilane (b. p. 204° (760 mm.), d^{20}_4 1.1578, n^{20}_D 1.5190) was diluted with three volumes of ether and cooled in an ice-bath. To this solution was slowly added 370 cc. of water per mole of dichloromethylphenylsilane. The ether solution was then washed free of chloride with dis-

(6) Wright and Hunter, *ibid.*, **69**, 808 (1947).

(7) (a) Martin and Kipping, *J. Chem. Soc.*, **95**, 302 (1909); (b) Alfrey, Honn and Mark, *J. Polymer Sci.*, **1**, 102 (1946).