trance of hydrogen into the lattice structure of nickel by an exothermic reaction process or to "sorption of hydrogen into the interfaces between the crystallites." The exothermic nature of the process distinguishes it from the endothermic solubility already considered.

Our data with Nickel–Kieselguhr du Pont which we have obtained with a single sample both unsintered and subsequently sintered do not accord with Beeck's observations. At −126.5° the difference between the values on the isobars for increasing and decreasing temperatures amounts to 4.9 cc. with the unsintered material and to 8.35 cc. with the sintered material. On each of these surfaces the van der Waals adsorption at this temperature cannot exceed 1.5 cc. If one subtracts this value from the values received from the descending isobars, the amount of hydrogen chemisorbed, *plus* that taken up into the interior or interfaces (on Beeck's postulate), amounts to 17.8 cc. for the unsintered and 9.75 cc. for the sintered sample. By neither method of calculation do we obtain the identity of divergence between the two isobars that Beeck and his co-workers observe. The differences which we observe are straightforwardly interpretable on the basis of surface areas with different activation energies. The data for rates of chemisorption at single temperatures support this view. The kinetic data for the hydrogen–deuterium exchange are additional confirmation. Indeed, all our experiments with these metal catalysts are parallel to those previously recorded with oxide catalysts, the only difference being the temperature range in which the phenomena, desorption–readsorption, or measurable rates of adsorption are observed. With our nickel catalysts the principal temperature range is −126.5 to −78°. With zinc oxide it is in the range +110° upward. The Beeck interpretation could not be generalized for all our observations since that would require that hydrogen (and indeed other gases such as carbon monoxide and nitrogen) enter oxide or metal lattices or interfaces.

Acknowledgment.—One of us (H. S.) wishes to express his appreciation to the Government of Egypt for a fellowship which enabled him to carry out these investigations in fulfillment of the thesis requirements for the Ph.D. degree at Princeton University during 1947 and 1948.

Summary

1. The heterogeneity of the surfaces of six different nickel catalyst preparations has been confirmed, using the technique devised by Taylor and Liang and hydrogen as the adsorbate.

2. The adsorptions at −195° have been analyzed to determine the relative amounts of van der Waals adsorption and chemisorption of hydrogen and to show that different preparations adsorb different relative amounts of the two types.

3. The velocity of the hydrogen–deuterium exchange reaction on nickel–chromia and nickel–thoria has been studied to support these findings. There are marked differences in rates with activation energies of 0.45 and 2 kcal., respectively.

4. Our data do not support an interpretation based either on solubility of hydrogen in the lattice or an exothermic entry of hydrogen into the nickel lattice at temperatures between −195 and −78°.

PRINCETON, NEW JERSEY RECEIVED APRIL 12, 1949

[CONTRIBUTION FROM THE ATLANTIC REFINING COMPANY]

Nitrous Oxide as a Constituent of the Atmosphere

BY R. L. SLOBOD AND M. E. KROGH

The presence of nitrous oxide in soil gas samples has previously been established by the mass spectrometer as shown by R. A. Brown, *et al.*[1] Consideration of these findings by the present authors suggested nitrous oxide as a possible constituent of the atmosphere which, although previously suspected,[2,3] had not been isolated and confirmed, in part at least, because of the difficult analytical problem presented by this relatively inert gas. Because of the unequivocal nature of its findings, the mass spectrometer was chosen in this case to establish the presence of nitrous oxide in the atmosphere. A nitrous oxide concentrate obtained by fractional condensation of atmospheric samples improves the precision of the mass spectrometer analyses, making possible quantitative determinations.

Results.—Ten samples of air from six locations including five in Texas (two in Dallas, two in East Texas, and one in Irving) and one in Wyoming have been analyzed using the methods and apparatus described below. The significant data on each run including location, amount of gas sampled, amount of condensed gas after purification in high vacuum system, amount of nitrous oxide, per cent. of nitrous oxide in original sample, and finally, the deviation of each value from the mean are given in Table I. An appreciable variation in nitrous oxide content was observed, the extremes being 0.000025% and 0.000067%.

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(1) Brown, *et al.*, *Anal. Chem.*, **20**, 396–401 (1948).

(2) Adel, *Astrophys. J.*, **90**, 627 (1939); **93**, 509 (1941); *Science*, **103**, 280 (1946).

(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, 1931, p. 12.

The average deviation from the mean, however, is only 0.000009%. Consequently, the nitrous oxide content of the atmosphere is concluded to be 0.00005 ± 0.00001% by volume.

Table I

Nitrous Oxide in Atmospheric Air

Sample location	Amount of air sample, cc. mm.	Purified condensable gas, cc. mm.	Amount of nitrous oxide, cc. mm.	N_2O, %	Dev. from av.
Dallas, Texas (1)	4.5×10^6	2.05	1.66	0.000037	0.000010
Dallas, Texas (1)	4.5×10^6	1.35	1.14	.000025	.000022
Dallas, Texas (1)	4.5×10^6	2.68	2.07	.000046	.000001
Dallas, Texas (2)	4.5×10^6	3.60	2.46	.000055	.000008
Dallas, Texas (2)	4.5×10^6	2.27	1.76	.000039	.000008
Dallas, Texas (2)	4.5×10^6	2.98	2.32	.000051	.000004
Irving, Texas	4.5×10^6	2.8	1.95	.000043	.000004
East Texas	4.5×10^6	3.51	2.63	.000058	.000011
East Texas	4.5×10^6	3.75	3.01	.000067	.000020
Lusk, Wyoming	4.5×10^6	2.44	2.05	.000045	.000002
			Av.	.000047	.000009

Apparatus and Methods.—The concentrate of the condensable gases of the atmosphere which is introduced into the mass spectrometer for the quantitative determination of nitrous oxide is prepared in the apparatus shown in Fig. 1. Air enters the system at A. The rate of flow observed with flowmeter B is maintained at approximately six liters (N. T. P.) per hour. The system is maintained at a reduced pressure of approximately one-half atmosphere by adjusting stopcocks N and L while evacuating the system at M. Water vapor and carbon dioxide are largely removed in chambers C and D by passage of the air over calcium chloride and ascarite. The air is then passed through trap G which is cooled with liquid nitrogen in Dewar flask H to approximately −195°. At this temperature the nitrous oxide is condensed and removed from the air stream. By virtue of the reduced pressure in the system, the partial pressure of the oxygen is maintained below the vapor pressure of pure oxygen for this temperature. Consequently, no appreciable amount of oxygen collects in the cold trap. The same conclusion obviously applies to the nitrogen and the fixed gases. To further purify the sample, the condensed nitrous oxide is exposed to the vacuum pump by closing stopcock F and opening stopcocks I and L. This operation tends to enrich the nitrous oxide at the expense of any more volatile constituents (oxygen, nitrogen, etc.) which may be present. The gas from trap G is then admitted to a high vacuum system of the type described by Prescott and Morrison.[4] In this all-glass vacuum system using mercury cut-offs in place of greased stopcocks and using carefully baked out solid reagents, the sample is further purified by the removal of practically all residual water vapor and acidic gases. The residual gas volume (mainly nitrous oxide) is measured in a small pipet in cc. mm. units, and the gas is then transferred to a small Pyrex tube (3 mm. o. d. × 10 cm. long). This transfer is accomplished by maintaining the sample tube at liquid nitrogen temperature while the nitrous oxide is circulated through the system until the entire gas sample is condensed in the small tube. The sample is then sealed off in the glass tube. In this way the sample is transferred to the mass spectrometer where the analysis of the gas is accomplished.

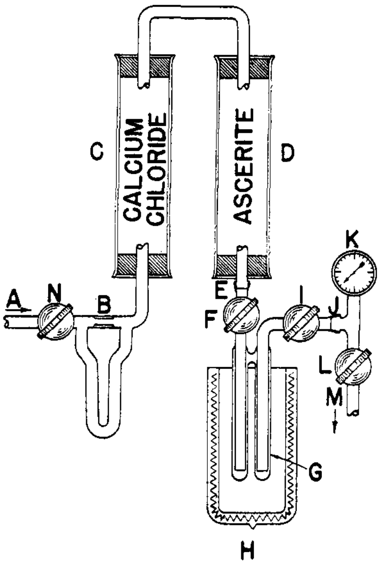

Fig. 1.—Apparatus for separating nitrous oxide from atmospheric air.

Discussion.—The concentration of the more rare constituents in the atmosphere on a volume basis is described by the values[5,6,7] given in Table II. On the basis of the work reported above, nitrous oxide present to the extent of 0.00005 ± 0.00001% by volume has been added to the list.

Table II

Concentration of More Rare Constituents in the Atmosphere

Constituent	Per cent. by volume in dry air
Hydrogen	0.01
Neon	.00123–0.0018
Helium	.0004–0.0005
Krypton	.00005–0.0001
Nitrous oxide	.00005
Xenon	.000006–0.000008

It is not surprising to find nitrous oxide present in the atmosphere in small concentrations since the physical and chemical properties indicate this compound to have sufficient stability. Thus nitrous oxide, a colorless nearly odorless gas melting at −102.4° and boiling at −89.5°, is very stable at ordinary temperatures. This gas is an oxidizing agent, but it will not react even with hydrogen except at elevated temperatures or in the presence of a catalyst such as platinum sponge. In addition, this gas shows no reaction with nitrogen, oxygen or the other known constituents of the atmosphere, and apparently is not utilized by living matter. In view of the above data, which indicate an abundance of nitrous oxide at low concentrations, an investigation of the place of nitrous oxide in the life cycle may be in order.

The value 0.00005% by volume for the nitrous oxide content of the atmosphere is based on the

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[4] C. H. Prescott, Jr., and James Morrison, *Ind. Eng. Chem., Anal. Ed.*, **11**, 230–238 (1939).

[5] "Handbook of Chemistry and Physics," Hodgman and Holmes, Editors, 24th Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1940, p. 2516.

[6] "Encyclopedia Britannica," Vol. 2, p. 640 (14th ed.); Humphrey's Scientific Monthly, 1927.

[7] "International Critical Tables," Vol. I, p. 393.

analysis of ten samples of air. These samples came from widely separated points (Wyoming and Texas) and include samples taken in winter as well as summer. The possible effect of urban areas is also considered since approximately half of the air samples were taken in cities while the other half represent farm and essentially uninhabited areas. While no blanks were run, all steps in the field procedure were examined to exclude conditions which might introduce nitrous oxide. For example, the motor and pump used to evacuate the system were mounted downwind from the sampling point wherever possible. The relatively uniform analytical findings obtained under widely varying conditions offer some confirmatory evidence for the reliability of the results.

Separating the nitrous oxide from air by freezing at liquid nitrogen temperature is a fundamentally sound procedure since the vapor pressure for nitrous oxide is truly negligible at this low temperature. The equation for the vapor pressure of nitrous oxide in mm. is given by the equation[8] $\log_{10} p = -1232.2/T + 9.579$ when T is the absolute temperature. This equation was derived from data over the temperature range from −144 to −90°. Extrapolating this equation to −195° (+78.1° K.), the calculated vapor pressure of nitrous oxide is given as 6×10^{-7} mm. The above equation may not apply exactly over the wide temperature range used, but any small error would be insignificant in view of the extremely low calculated vapor pressure. Consequently, it is concluded that at equilibrium nitrous oxide can be quantitatively removed from air. Since the determination of nitrous oxide in the atmosphere was incidental in that the data were obtained in the course of another study, the effect of the rate of air flow through the trap on the fraction of nitrous oxide condensed has not been experimentally verified. It is reasonable, however, to assume complete condensation since at the low flow rate used the air requires approximately thirty seconds to pass through the cold trap. This time should be ample, particularly since complete thermal equilibrium is not required in view of the extremely low vapor pressure of the nitrous oxide. The possibility, however, of losing nitrous oxide as a solid suspension passing through the traps has not been evaluated. Since a possible loss of nitrous oxide has not been rigorously excluded, the experimental value of 0.00005% may be regarded as a lower limit.

The above data indicate that the concentration of nitrous oxide in the atmosphere is approximately only one-tenth that of helium. Since the extremely small concentration of helium is generally detected by spectrographic means, a method ideally suited for detecting a constituent at extreme dilution, the present work on nitrous oxide demonstrates the power of the mass spectrometer as an analytical tool when used in conjunction with relatively standard procedures for concentrating the element being analyzed prior to measurement in the mass spectrometer.

The presence of hydrocarbons in the atmosphere has been suggested by a number of investigators.[9] In this connection it is interesting to note that in practically all air samples analyzed small amounts of hydrocarbons, approximately 10 to 20% of the amount of nitrous oxide present, were observed.

The analytical results of the mass spectrometer have been carefully examined with particular emphasis on the validity of the nitrous oxide identification. While materials such as carbon dioxide and propane may interfere somewhat in the quantitative analysis for nitrous oxide using the mass spectrometer, this possibility has been carefully considered and evaluated. The quantitative determinations of nitrous oxide are, therefore, believed to be reliable.

While the earlier work[1] in which nitrous oxide was postulated to be present in the atmosphere was perhaps only semi-quantitative in nature, a comparison of the nitrous oxide content estimated on the basis of absorption data with the value obtained by direct analysis on nitrous oxide concentrates from the atmosphere shows a remarkable agreement. Thus, from the absorption data the amount of nitrous oxide was estimated to be the equivalent of a layer of gas *several* millimeters thick under atmospheric pressure. It is extremely interesting to note that a layer four millimeters thick corresponds to exactly the concentration of 0.00005% reported in this paper. More recent work[10] also based on absorption data from solar spectra gives a nitrous oxide content of the atmosphere slightly in excess of this value.

In view of the striking agreement obtained for the nitrous oxide content in the atmosphere by two such vastly different methods, considerable confidence may be placed on the value. In addition, since the nitrous oxide was actually isolated from air sampled at the earth's surface, it is obvious that the nitrous oxide is not present merely as a thin layer high in the atmosphere, but must be distributed throughout the entire system.

Summary

Nitrous oxide has been found to be a constituent of the atmosphere present to the extent of 0.00005 ± 0.00001% by volume. The nitrous oxide was separated from the air by condensation under reduced pressure at approximately −195°. The gas was purified in a high vacuum system, and was qualitatively and quantitatively determined using the mass spectrometer.

DALLAS, TEXAS RECEIVED JULY 18, 1949

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[8] G. A. Burrell and I. W. Robertson, THIS JOURNAL, **37**, 2691 (1915).

[9] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longman-Green & Co., New York, N. Y., Vol. VIII, pp. 10–11.

[10] Shaw, Sutherland and Wormell, *Phys. Rev.*, **74**, 978 (1948).