On the Relative Abundances of the Nitrogen and Oxygen Isotopes

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The absorption spectra of samples of nitric oxide were investigated for the purpose of obtaining the relative abundance of the nitrogen and oxygen isotopes. Nitrogen from four different sources was investigated: air nitrogen, obtained from the Haber and Birkeland-Eyde processes; nitrogen from Pennsylvania coal and from Chili saltpeter. One sample of oxygen was obtained from a Pre-Cambrian magnetite. A method has been described for converting the nitrogen and oxygen from these different sources into nitric oxide. A method of photographic photometry has been applied to the spectra obtained. The procedure for obtaining the relative abundance of the isotopes is discussed together with the possible sources of error. The average of 32 measurements gives for the ratio of $N^{15}O^{16}/N^{14}O^{18}$ the result $0.549 \pm 0.007 : 1$. This gives the value 346:1 for the ratio N^{14}/N^{15}. The isotopic composition of the four samples of nitrogen and two samples of oxygen is constant within approximately 10 percent.

THE relative abundances of isotopes that are present only in small amounts such as those of carbon, nitrogen, oxygen and hydrogen are of great importance for several reasons. Because of the fact that oxygen is chosen as the standard for atomic weight determinations, the relative abundance of its isotopes is required as precisely as possible in order to convert from the chemical scale to the mass spectrograph scale. Recent discussions[1] as to other possible standards for atomic weights, also point out that it is very important to discover whether rare isotopes such as those of oxygen are constant in abundance with respect to samples of oxygen from different sources. Although the constancy of the more common isotopes is fairly well established both for terrestrial elements and for some from meteoric sources, no experiments of this sort have been made for the rarer isotopes mentioned above.[2]

Moreover, spectroscopic determinations of King and Birge[3] on the relative abundance of C^{13} indicate an apparent dependence of this quantity on the method of excitation of the spectra. Three typical sources such as arc, furnace and *N*-type stars, the effective temperatures of which probably decrease in this order, show that the abundance of C^{13} relative to C^{12} increases in the same order.

The detection of rare isotopes in molecular emission spectra seems to be particularly difficult. King and Birge failed to find C^{13} and $C^{13}N^{14}$ in arc spec-

[1] R. T. Birge and D. H. Menzel, Phys. Rev. **37**, 1669 (1931); R. Mecke, Phys. Zeits. **33**, 49 (1932); S. Meyer, Phys. Zeits. **33**, 301 (1932).

[2] Charles A. Bradley, Jr. and Harold C. Urey have investigated the relative abundance of the H^1 and H^2 isotopes in hydrogen samples from different sources and find that any variation in relative abundances is not large. Phys. Rev. **40**, 889 (1932).

[3] A. S. King and R. T. Birge, Astrophys. J. **72**, 251 (1930).

tra. Watson and Parker[4] were not able to observe the oxygen isotopes in the BeO emission spectra and Estey[5] failed to find any indication of the O^{17}, O^{18} or C^{13} atoms in the fourth positive emission bands of CO. Almy and Rahrer[6] failed to find bands due to $O^{18}H$ in the OH spectrum. On account of these as yet unexplained difficulties, it seems that the most reliable determination of the relative abundance can be made from absorption spectra.

The discovery of an isotope of nitrogen of mass 15 and the determination of its abundance relative to N^{14} is due to Naudé[7] who investigated the γ bands of nitric oxide. He redetermined the abundance of O^{16} relative to O^{18}, obtaining $1075 \pm 110:1$. He then determined the ratio of the nitrogen isotopes from the relative intensities of the $N^{15}O^{16}\,{}^{O}P_{12}$ and the $N^{14}O^{18}\,{}^{P}Q_{12}+P_2$ branches of the $(v', v'') = (1, 0)$ band, which he states have nearly the same intensities. Our own investigation shows that this is not the case (see Fig. 1). The results of Naudé are also open to objection because even if these heads were of the same intensity, the $N^{14}O^{18}\,{}^{P}Q_{12}+P_2$ branch is superimposed on the $N^{15}O^{16}\,{}^{O}P_{12}$ branch, so that it is difficult or impossible to determine what part of the absorption is due to each molecule. The determination of Naudé has also been criticized by Mecke and Childs.[8] Using the values of Mecke and Childs for the relative abundance of O^{16}/O^{18}, Naudé's result for N^{14}/N^{15} becomes 409 ± 20 percent. Birge and Menzel have calculated from atomic weight considerations that this figure should be 320.

Because of these considerations, we have thought it worth while to redetermine the relative abundance of the nitrogen isotopes by the methods of photographic photometry. Moreover, we have worked with samples of nitrogen and oxygen from different sources as follows: Nitrogen: (1) from the air by the Haber process; (2) from the air by the Birkeland-Eyde process; (3) from Chili salt-peter; (4) from Pennsylvania coal. Oxygen: (5) from Pre-Cambrian magnetite.

The various samples of nitrogen were selected with the objects (1) of search for any variation of relative abundances of nitrogen isotopes in natural nitrogen samples, and (2) of finding whether any variation might be produced by the electric arc used in the Birkeland-Eyde process. The latter possibility seemed worth testing because of the general failure to observe these rare isotopes in emission spectra. The oxygen sample comes from the Pre-Cambrian magnetite of New York State and has not been a part of the atmosphere of the earth since the time the crust of the earth formed according to the best judgment of geologists.

Preparation of Nitric Oxide

Because of the variety of samples used, the method of preparation of the NO was different in each case. The Haber process nitrogen[9] was in the form

[4] W. W. Watson and A. E. Parker, Phys. Rev. **37,** 167 (1931).
[5] R. S. Estey, Phys. Rev. **35,** 309 (1930).
[6] G. M. Almy and G. D. Rahrer, Phys. Rev. **38,** 1816 (1931).
[7] S. M. Naudé, Phys. Rev. **34,** 1498 (1929); **35,** 130; **36,** 333 (1930).
[8] R. Mecke and W. H. J. Childs, Zeits. f. Physik **68,** 376 (1931).
[9] Kindly furnished by The Grasselli Chemical Company.

of 60 percent nitric acid and presented little difficulty. The gas generating apparatus was part of an all-glass system that also contained the absorption cell which was mounted directly in front of the slit of the spectrograph. This apparatus was first thoroughly swept out with nitrogen. The nitric acid was then allowed to drop into a solution of ferrous sulfate and concentrated sulfuric acid. By gently heating this mixture, the NO gas was evolved and after passing through several traps containing a solid CO_2-alcohol mixture was collected in a trap immersed in liquid air. After all the gas had been collected, this last container was closed from the generator by means of a stopcock and both it and the absorption cell were evacuated. Nitric oxide was admitted into the absorption cell by partially removing the liquid air and allowing it to distill slowly until the desired pressure as read on a manometer attached, was reached. Gas pressures ranging from 1 to 10 cm were used, the most convenient pressure being about 4 cm.

Sample 2 was in the form of "nitrate of lime."[10] This was dissolved in hot water, and Na_2CO_3 solution was then added to convert the calcium nitrate to sodium nitrate. The insoluble material was filtered off and the concentrated solution of sodium nitrate was added to the $FeSO_4$–H_2SO_4 mixture in the same way as described above.

Sample 3 was simply dissolved in H_2O, filtered and then added to the $FeSO_4$–H_2SO_4 mixture.

Sample 4 caused more difficulty as it was furnished to us in the form of ammonium sulfate.[11] Ammonia was liberated by adding NaOH solution. Oxygen was bubbled through this solution and then over an electrically heated platinum spiral where it was converted into oxides of nitrogen. The gases, NO and NO_2, were collected in a trap immersed in liquid air. These gases were then passed into the H_2SO_4–$FeSO_4$ solution by means of a stream of nitrogen and the NO gas collected as before in a liquid air trap.

The method for sample 5 was similar to that for sample 4. The magnetite[12] was first broken into small pieces and the oxygen was removed in the form of H_2O by passing hydrogen over the mineral at about 450°C. The H_2O was collected in a trap placed in a solid CO_2-alcohol mixture. After the addition of about 10 percent of H_2SO_4 it was electrolyzed in a small cell. The gases evolved were collected by displacement of oil from two chambers that had a volume ratio of 2:1 so that the hydrogen and oxygen gases were kept at the same pressure. After the electrolysis was finished, the oxygen was mixed with

[10] We wish to thank the Department of Chemistry of the College of the City of New York for supplying us with the sample of Birkeland-Eyde nitrogen.

[11] The ammonium sulfate was made from coal from the Pittsburgh seam mined in Washington County, Pennsylvania. The coal comes from two mines Vesta No. 4 and No. 5. These two mines are very close to one another but differ slightly in chemical analysis. It was kindly sent to us by Mr. M. W. St. John of the Jones and Laughlin Steel Corporation, Pittsburgh, Penna., whom we would like to thank in this place.

[12] The magnetite was a sample of Pre-Cambrian origin from Fort Henry, New York and came from the collection of the Geology Department of this University through the kindness of Professor Charles P. Berkey.

nitrogen and ammonia and the mixture was passed over the platinum spiral. From this point on the procedure was the same as for sample 4.[13]

Experimental Method

The absorption cell was 50 cm long and 4 cm in diameter and was fitted with two crystal-quartz windows stuck on with deKhotinsky cement.

A hydrogen discharge tube* was used as a continuous source of ultraviolet light. This tube carried about 2 amperes at 2500 volts and was constant in intensity within about 1 percent during an exposure. This was determined by means of a Moll surface thermopile placed at the back window of the tube. The deflections of a galvanometer connected to the thermopile were read continually during the time that was required to put the density marks on the plates. Two crystal-quartz lenses were used, one between the discharge tube and the absorption cell which gave a parallel beam of light through the cell and the second lens brought this light to a focus on the slit of the spectrograph. With this arrangement of lenses, a good exposure of the (1, 0) band could be obtained in one minute while the (2, 0) band at 2051A could be photographed in about five minutes. The Hilger E1 quartz spectrograph was used.

Various kinds of photographic plates were used. At first we sensitized Eastman 33 plates with vaseline or oil dissolved in petroleum ether. We then obtained an ultraviolet sensitizing solution from the Eastman Kodak Company and used this on Eastman 33 plates. These proved quite satisfactory and most of the results in this paper were obtained with them. More recently, we have secured Eastman U.V. spectroscopic plates.[13a] These have been even more convenient than the ones that we sensitized ourselves.

Calibration of Plates

We used two methods of putting density marks on our plates. At first we used a quartz wedge[14] with five steps of sputtered platinum and one clear step. It was calibrated directly on the spectrograph by means of the hydrogen tube and the method of variation of the width of the slit. Because of the irregularities on the surface of the sputtered steps and the uncertainties of the calibration of the wedge for a wave-length so far in the ultraviolet, we thought it desirable to use some other method of obtaining density marks.

We therefore made a set of neutral wire screens.[15] These screens were prepared as described by Harrison and were arranged so that they were kept in motion during use by means of a motor. Screens of this sort must be covered with CuO in order to give them a black surface. The usual method of oxidiz-

* This tube will be described in another place.

[13] We wish to thank Miss Pilar de Madariaga and Mr. S. H. Manian for their aid in working out the method and the preparation of the gas from sample 5.

[13a] C. E. K. Mees, J. Opt. Soc. Am. **21**, 753 (1931).

[14] The method of making these wedges has been investigated by Professor H. W. Webb of the Physics Department of this University. The wedge that we used was very kindly prepared for us by Professor Webb with our assistance.

[15] G. R. Harrison, J.O.S.A. and R.S.I. **18**, 492 (1929).

ing the surface by heating is not very satisfactory since the coat of CuO so formed is not adherent. We have found that the following method gives a good dull surface that is very permanent. The screens were first cleaned by dipping into a so-called mat solution which is used for producing a dull surface on articles that are to be electroplated. They were washed quickly and dipped into a boiling solution containing 1 percent potassium persulfate and 5 percent sodium hydroxide.* After the surface was black enough, they were washed and dried.

We had four screens, combinations of which would give 10 density marks. They were calibrated by means of the thermopile mentioned above and also by means of a photoelectric cell with a large tungsten lamp running on a constant source of alternating current. The results from the two methods of calibration are given in Table I.

TABLE I. *Transmission of screens.*

Screen	Photoelectric cell	Thermopile	Average
1	73.4	74.5	74.0
2	45.5	45.7	45.6
1+2	34.5	34.6	34.6
3	32.5	32.1	32.3
1+3	24.2	24.3	24.2
4	17.8	17.5	17.6
2+3	16.6	16.9	16.8
1+4	14.6	14.8	14.7
2+4	8.6	8.1	8.4
3+4	6.5	5.9	6.2

A Moll recording microphotometer was used to determine the density of the calibration marks on the plates and of the two isotopic band heads. Since the transmission of the wedge or screens was known, a curve of log i *vs.* d could be plotted by means of the relation

$$\log_{10} O = d = \log F_0/F \tag{1}$$

where O is the opacity, d is the density and F_0 and F are intensities of light transmitted by the unexposed and exposed parts of the plate respectively. Moreover

$$d = \log g_0/g \tag{2}$$

where g_0 and g are the throws of the galvanometer for an unexposed part of the plate and for one of the density marks, put on through a screen whose transmission was known.

The intensity of the isotopic bands could be determined by means of Beer's law

$$\log i_x - \log I = - kcx \tag{3}$$

where i_x and I are the intensities of the light transmitted by a layer of gas of thickness x and the incident radiation respectively; k is the molecular absorption coefficient and c is the molecular concentration.

* See: Electro-Deposition of Metals, 9th Edition, Langbein-Brannt, p. 278, 629, New York: Henry Carey Baird and Co., 1924.

The situation in the actual case is somewhat more involved because of the fact that bands are sometimes superimposed and that other absorbing molecules may be present, such as NO_2, for example. Then Eq. (3) must be replaced by

$$\log (i/I) = - (k_1 c + k_2) x \tag{4}$$

where k_1 is the molecular absorption coefficient and k_2 is the absorption coefficient due to other molecules which may be present. We assume that k_1 is the same for the same branches of the different isotopic molecules. But we cannot determine the value of I, since we do not have any point on the plate, where we are certain that there is no absorption due to extraneous molecules or superimposed bands. To avoid this difficulty we extrapolate the microphotometer curves as shown by the broken lines of Fig. 1. This gives an estimate of $\log i/I$, if k_1 were zero. Then we have

$$\log (i/I) - \log (i_0/I) = - (k_1 c + k_2) x + k_2 x = - k_1 c x \tag{5}$$

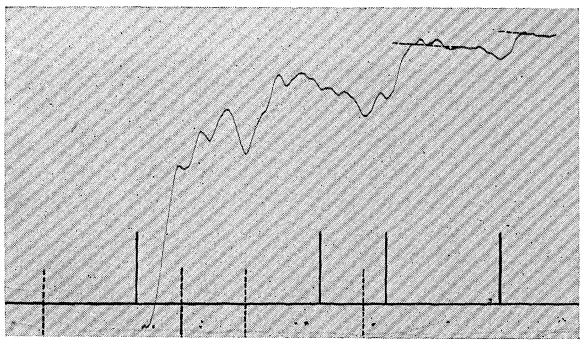


Fig. 1. A typical microphotometer curve of the (1, 0) γ-band of nitric oxide. The heads due to the different isotopic molecules are indicated. The full lines are the ${}^0P_{12}$ heads and the broken lines are the $({}^PQ_{12}+P_{12})$ heads.

where i_0 is the intensity (extrapolated) of the light which would have been transmitted if the band were not present. This equation reduces to

$$\log (i/i_0) = - k_1 c x \tag{6}$$

which is identical in form with Eq. (3).

Since k_1 and x are the same for the isotopic molecules

$$\log (i'/i'_0) - \log (i''/i_0'') = c'/c'' \tag{7}$$

where the primes refer to the quantities for the first and second molecules respectively.

These quantities are related to throws of the galvanometer by the relation

$$d = \log g_0 - \log g = f(\log i) \tag{8}$$

where g_0 is again the throw at a clear part of the plate and g is now the galvanometer throw at a band head or the estimated throw if the band were not present. In all cases our densities fell on the straight line portion of the d *vs.* $\log i$ curve and for this region

$$d = \gamma \log i + a. \tag{9}$$

A typical calibration curve is shown in Fig. 2. By using Eq. (9), we have

$$\gamma \log (i'/i_0') = d' - d_0' \tag{10a}$$

and

$$\gamma \log (i''/i_0'') = d'' - d_0'' \tag{10b}$$

where d and d_0 refer respectively to the density at the band head and the extrapolated density and the primes and double primes refer to the light and heavy isotopic molecules, respectively. These four points are indicated for a typical case on Fig. 2.

Taking the ratio, we secure the ratio of concentrations

$$\frac{\log i'/i_0'}{\log i''/i_0''} = \frac{d' - d_0'}{d'' - d_0''} = c'/c''. \tag{11}$$

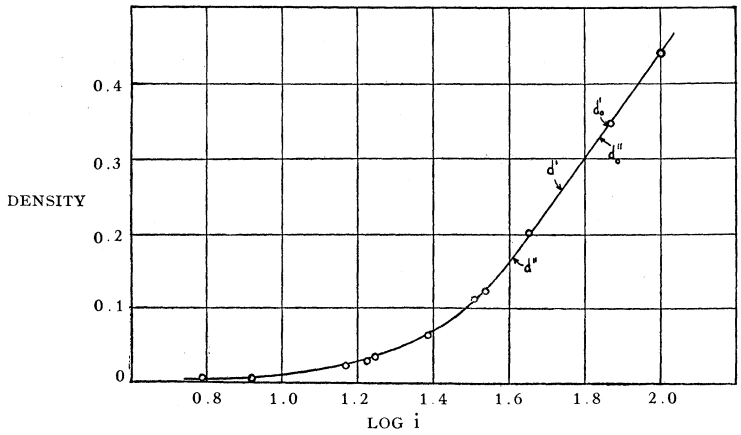


Fig. 2. A typical log i *vs.* density curve. The points indicated with arrows are those obtained from the microphotometer curves of the spectra and used for determining the ratio.

In this way we have compared the relative intensities of the ${}^{O}P_{12}$ branches of $N^{14}O^{18}$ and $N^{15}O^{16}$. Although the $N^{15}O^{16}$ ${}^{O}P_{12}$ branch is superimposed on the $N^{14}O^{18}$ ${}^{O}P_{12}$ branch, they are well separated by the spectrograph and it is therefore possible to estimate the contribution of each molecule to the absorption. A typical microphotometer curve is shown in Fig. 1, where the eight band heads due to the two branches and the four molecules are in-

TABLE II.

Source of sample	Number of microphotometer curves	Ratio $N^{15}O^{16}/N^{14}O^{18}$
Haber process	17(a)	0.54 ± 0.05
Coal	9(a)	0.56 ± 0.08
Birkeland-Eyde	4(b)	0.52 ± 0.08
Chili salt-peter	4(b)	0.56 ± 0.09
Haber	8(b)	0.58 ± 0.06
Pre-Cambrian	6(a)	0.54 ± 0.06

(a) Plates calibrated by means of screens.
(b) Plates calibrated by means of wedge.

dicated. The results from the four samples of nitrogen and the sample of oxygen are given in Table II.

Source of Error

The error given which is the root mean square represents only the error, if no systematic error is present. The possible errors are:

(1) The lines at the head of these bands may not give a true continuous absorption so that Beer's law may not hold. We have used gas pressures up to 10 cm of NO hoping that the lines would be somewhat broadened in this way. We have also added N_2 up to one atmosphere total pressure for the same purpose but in neither case was there any essential difference in the appearance of the microphotometer curves.

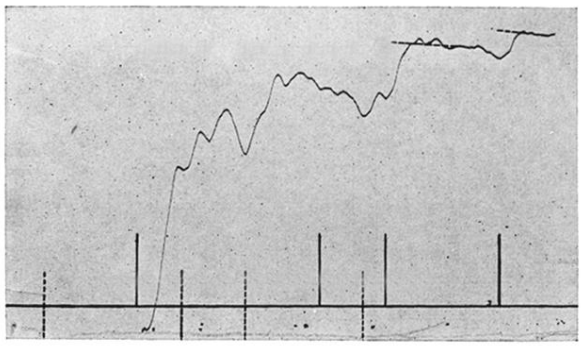
(2) It is not certain that there are no superimposed bands of $N^{14}O^{16}$. We had thought to eliminate this difficulty by working with the (2, 0) band but unfortunately a Si emission line from our hydrogen tube falls almost on top of the $N^{14}O^{18}$ $^OP_{12}$ band head. Moreover, the $^OP_{12}$ and $^PQ_{12}+P_2$ branches overlap here so we cannot allow for the continuous background.

Our most reliable determinations are those marked *a* in Table II since we have more confidence in the results from plates that were calibrated with the wire screens. The average from these thirty-two microphotometer curves is 0.549 ± 0.007 for the ratio of $N^{15}O^{16}:N^{14}O^{18}$. Because of the difficulties mentioned above, this result may be in error by more than the probable error quoted. But it seems certain that the possible source of error mentioned under 2 would be the same from sample to sample. Therefore, a change in the relative abundance of the isotopes of oxygen or nitrogen would have been detected. We feel safe in concluding that the isotopic composition of nitrogen and oxygen in the samples investigated is constant within approximately ± 10 percent.

Using Mecke and Child's[8] value for the ratio of $O^{16}:O^{18}=630:1$, we get for the ratio of N^{14} to N^{15}, the value 346:1 in satisfactory agreement with the ratio of 320:1 required by Birge and Menzel. This means that Aston's value for the atomic weight of N^{14} on the basis of $O^{16}=16.0000$ is consistent with the chemical value.

We wish to thank the Physics Department of this University and Professor H. W. Webb in particular for the use of the quartz spectrograph used in this investigation. We are also indebted to the Chemistry Department of New York University and to Mr. R. L. Garman in particular for the microphotometer curves.

Note added in proof. Herzberg (Zeits. f. physik. Chem. **B9,** 43 (1930)) has determined 800:1 for the ratio of N^{14} to N^{15} from the relative exposure times for the second positive nitrogen bands obtained in emission in an electrodeless discharge. This result differs from ours in the same direction as that of other workers for emission spectra compared with absorption spectra. Until this peculiarity is explained, relative abundances of isotopes obtained from absorption measurements seem more certain in view of the fact that the results in absorption make the values of Aston more consistent with the chemical results.



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