

THE CHEMISTRY OF THE ISOTOPES OF OXYGEN¹

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CONTENTS

I. Introduction.....	263
II. The isotopes of oxygen.....	264
III. Methods of measuring the abundance of the isotopes.....	265
A. Water-density methods.....	265
B. Mass spectrometric methods.....	266
IV. Methods of separating the isotopes of oxygen.....	273
A. Distillation of water.....	273
B. Thermal diffusion method.....	273
C. Chemical exchange method.....	273
V. Chemical applications of the isotopes of oxygen.....	274
A. Analysis of organic compounds for oxygen by the isotope-dilution method.....	274
B. Exchange of oxygen isotopes in inorganic salt solutions.....	275
C. Exchange of oxygen isotopes between oxygen gas and solid oxides.....	277
D. Use of oxygen isotopes in studying the mechanism of inorganic reactions.....	278
E. Exchange of oxygen isotopes between organic compounds and water.....	285
F. Use of oxygen isotopes in studying the mechanism of organic reactions.....	285
G. Studies of equilibrium isotopic exchange reactions involving oxygen.....	290
VI. Variations in nature of the natural abundance of the oxygen isotopes.....	292
A. Variations in the natural waters and ices of the world.....	292
B. Atmospheric and photosynthetic oxygen.....	293
C. Oxygen in carbonate rocks and the use of ratios of oxygen isotopes in estimating the temperatures of prehistoric oceans.....	294
D. Oxygen in silicate rocks and iron oxide ores.....	296
VII. The atomic weight of oxygen.....	296
VIII. References.....	297

I. INTRODUCTION

Oxygen is perhaps the most important element among the known ninety-eight species, as it is the most abundant in the earth's crust, it forms compounds with all the other elements except the inert gases, it supports life, and finally, the mass of its atoms serves as the standard on which the atomic weights of all other elements are based.

In 1929 oxygen was discovered by Giauque and Johnston (34) to consist of three isotopes of atomic weights 16, 17, and 18. This discovery, whose far-reaching consequences are described below, was made by them when analyzing atmospheric absorption bands due to the 1.6- μ electronic transition in the oxygen molecule.

¹ This review is an amplified translation of a lecture entitled "La Química de los Isótopos de Oxígeno," which was delivered by the author at the Fifth South American Congress of Chemistry, Lima, Perú, May 8, 1951. He is greatly indebted to Dr. Angel Maldonado, President of the Congress, for the invitation to be one of the participants in the Congress.

The demonstration of the existence of isotopes, the invention of methods of measuring their masses and abundances, and the discovery of means by which isotopes can be separated constitute one of the major fields of scientific discovery of the first half of the twentieth century. This review article will be limited to a discussion of the isotopes of oxygen, which previously were reviewed by Reitz (89) in 1939.

II. THE ISOTOPES OF OXYGEN

The element oxygen consists of a mixture of three stable isotopes of atomic weights 16, 17, and 18, whose abundances are approximately 99.8, 0.04, and 0.2 per cent, respectively. In addition, three unstable and radioactive isotopes are known of weights 14, 15, and 19. In table 1 are collected data for the abun-

TABLE 1*
The isotopes of oxygen

ISOTOPE	PERCENTAGE IN AIR	NUCLEAR REACTIONS FOR THEIR PREPARATION	HALF-LIFE	RADIATION EMITTED	ATOMIC WEIGHT	
					Physical scale	Chemical scale
	<i>per cent</i>		<i>seconds</i>			
O ¹⁴	0	N ¹⁴ (<i>p,n</i>)O ¹⁴	76.5	β ⁺ , γ	14.0130	
O ¹⁵	0	N ¹⁴ (<i>d,n</i>)O ¹⁵	118	β ⁺	15.0078	
O ¹⁶	99.7587				16.0000	15.99555
O ¹⁷	0.0374				17.00450	16.99977
O ¹⁸	0.2039				18.0049	17.99980
O ¹⁹	0	F ¹⁹ (<i>n,p</i>)O ¹⁹ O ¹⁸ (<i>n,γ</i>)O ¹⁹	29.5	β ⁻ , γ	19.0087	

* The percentages of the isotopes in air are those determined mass spectrometrically by Nier (82). The nuclear reactions and half-lives were taken mostly from the review by Seaborg and Perlman (97); the value for the half-life of O¹⁴ came from the paper of Sherr, Muether, and White (100), and that of O¹⁸ from Pérez-Méndez and Brown (85). The masses of the stable isotopes are the usually accepted values (31), while the masses of the unstable isotopes were calculated from the Einstein relation as described in the text.

dance and masses of the stable isotopes, and the masses, methods of preparation, half-lives, and products of radioactive disintegration of the unstable isotopes. It is interesting to note that the atomic weights of the unstable isotopes are accurately known, as they were obtained from the energy relations in the nuclear reactions by means of the Einstein relation

$$\Delta E = c^2 \cdot \Delta m \quad (1)$$

The calculation of the mass of the O¹⁴ isotope may be illustrated as follows:

$$\begin{aligned} \text{O}^{14} &\rightarrow \beta^+ + \gamma + \text{N}^{14} + \beta^- \\ \text{Energies (m.e.v.)} &= 1.8 + 2.3 \\ \text{Masses: O}^{14} \text{ mass} &= 0.00055 + 14.00751 + 0.00055 + \frac{4.1}{931} \\ &= 14.0130 \end{aligned}$$

Because of their rather short half-lives, the radioactive isotopes of oxygen have little importance in the study of reaction mechanisms or in other chemical applications and will therefore not be discussed further here.

III. METHODS OF MEASURING THE ABUNDANCE OF THE OXYGEN ISOTOPES

A. Water-density methods

In his comprehensive and authoritative book entitled *Physical Properties and Analysis of Heavy Water* Kirshenbaum (55) presents a complete discussion of

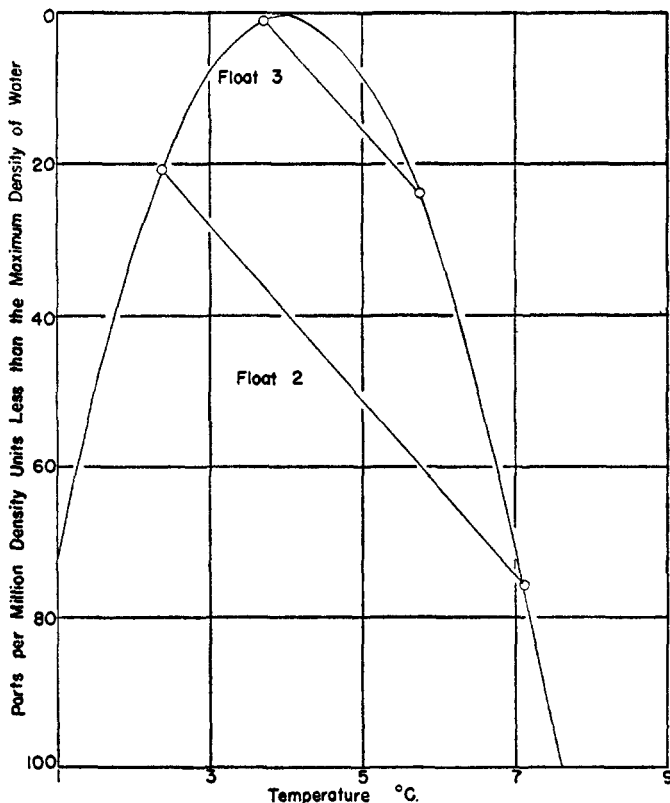


FIG. 1. Plot of the density of water from 1° to 8°C. Circles represent the temperatures at which Pyrex floats 2 and 3 had the same density as pure water. The slope of the straight lines is equal to the volume coefficient of expansion of the glass float.

water-density and mass spectrometric methods for the measurement of the abundance of the oxygen and hydrogen isotopes; hence this review will include only the description of recent refinements not contained in Kirshenbaum's treatise.

When Pyrex floats are used to measure relative water densities by the method of the totally submerged float, the volume thermal coefficient of expansion of the float must be known. This is particularly true when working near the temperature of the maximum density of water, as at some definite temperature

near 4°C. the float and the water will have identical coefficients of expansion. As the changes in density for a small change in temperature are much less near 4° than at room temperature, it is obvious that near the temperature of the maximum density of water, relative densities can be measured more accurately for the same accuracy of temperature measurement than at room temperature. Figure 1 is a plot of the density of water from 1° to 8°C. The points on the curve represent the temperatures at which each of two Pyrex floats have identically the same density as that of the water, to $\pm 0.1 \gamma$ (γ represents differences in density in parts per million); thus at two temperatures, one above and one below the temperature of maximum density, these floats have the same density as water. The measurements of figure 1 (24) were made using air-saturated water; the calculations were corrected to the density of water containing no air, using data of Marek (67) given by Kirshenbaum (56). As

$$\frac{1}{\rho} \left(\frac{d\rho}{dT} \right)_p = \frac{1}{V} \left(\frac{dV}{dT} \right)_p = \alpha \quad (2)$$

where ρ is the density, V the volume, and α the volume thermal coefficient of expansion, and as ρ is approximately equal to unity near 4°C., it is easily demonstrated that the slope of the tie-lines of figure 1 is equal to α . Data obtained by Dole and Brown (24) on two different unaged floats yielded identical results ($11.6 \pm \times 10^{-6}$) for α . This result is considerably higher than the value, 9.6×10^{-6} , given in the handbooks for borosilicate glass (60) and demonstrates the necessity of measuring the coefficient of expansion of the floats. The difference may be due to the presence of air within the float, which tends to expand on rise of temperature, thus increasing the internal pressure and causing an increased expansion of the float. Such an effect could be tested by preparing evacuated floats. The error of using 9.6×10^{-6} instead of the measured value, 11.6×10^{-6} , amounts to 2 p.p.m. for every degree rise in temperature between 5° and 6°C. This represents an error of about 16 per cent in the determination of γ .

B. Mass spectrometric methods

New developments in mass spectrometry have been recently reviewed by Stewart (101). It is customary to measure the relative abundance of the isotopes of oxygen in the form of either carbon dioxide or oxygen gas. Mass spectrometers which permit the simultaneous collection of ions of two different masses, as invented by Nier (81), are universally used.²

McKinney, McCrea, Epstein, Allen, and Urey (64) have described an adaptation of the Nier-type instrument for the specific purpose of measuring very accurately small differences in isotope ratios. They make use of a magnetically operated valve system which enables either the standard gas or the unknown sample to enter the ion source. As the valve arrangement is on the high-vacuum side of their capillary leaks, the switch-over from one sample to the other within

² Excellent commercial models, constructed by the Consolidated Engineering Corporation of Pasadena, California, are available.

the mass spectrometer occurs in about 20 sec. By also using a continuous recorder they are able to compare quickly and accurately the response of the instrument to the two samples before the various electrical circuits have had time to drift appreciably and before any changes in pressure or electron emission could influence the magnitude of the currents of the two ions being collected. Figure 2 illustrates an adaptation by Dole, Zaukelies, and Rudd (29) of the double-inlet system to the Consolidated-Nier mass spectrometer. This system was so arranged that either the original capillary-leak input manifold of the

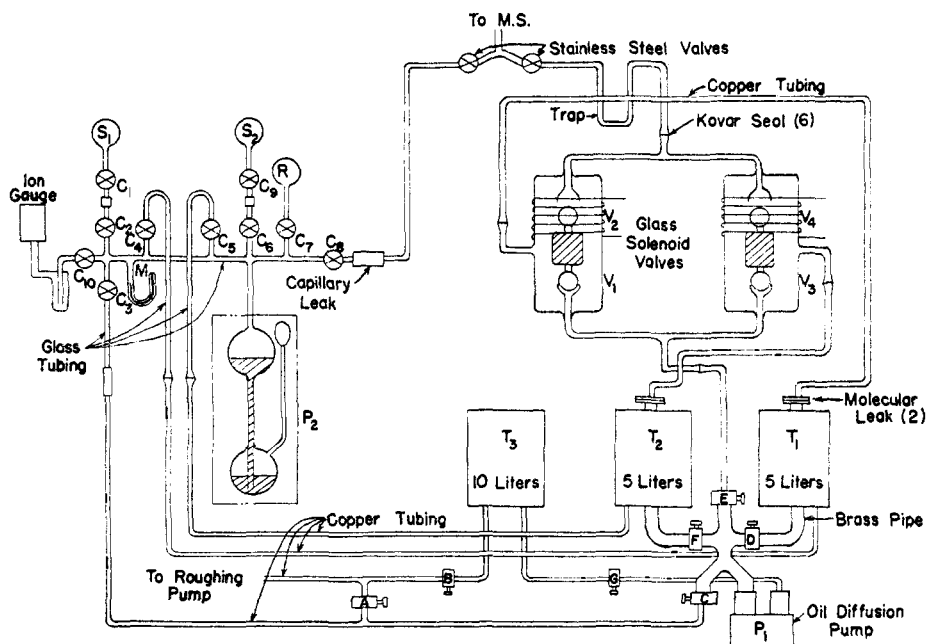


FIG. 2. Complete inlet system. S's represent sample bulbs; C's represent stopcocks; P₂ is the Toepler pump for controlling the gas pressure in the input system; R is the 25-ml. reservoir for measuring out a sample of gas to be expanded into one of the large brass tanks, T₁ or T₂.

Consolidated instrument could be used or the double-pinhole-leak solenoid-valve system.

Halsted and Nier (44) have made a study of isotope discrimination in mass spectrometers due to viscous (capillary) leak systems as compared to molecular (pinhole) leaks. Figure 3 is a plot of a similar set of data obtained by Dole and Rudd (27), using the apparatus illustrated in figure 2. From these results one can conclude that capillary-leak systems are satisfactory if the gas pressure in the manifold is higher than about 10 mm. In any case the apparatus must be calibrated with known gas samples. With molecular leak systems the difficulty due to a decrease in voltage ratios with decrease in manifold pressure is avoided; yet there are several disadvantages to pinhole leaks. The amount of gas required to fill the 5-l. storage tanks shown in figure 2 at a pressure of about 0.1 mm.

(25 ml. at 20 mm. pressure) is an order of magnitude greater than that required for the capillary-leak system. Inasmuch as the flow through the pinholes is

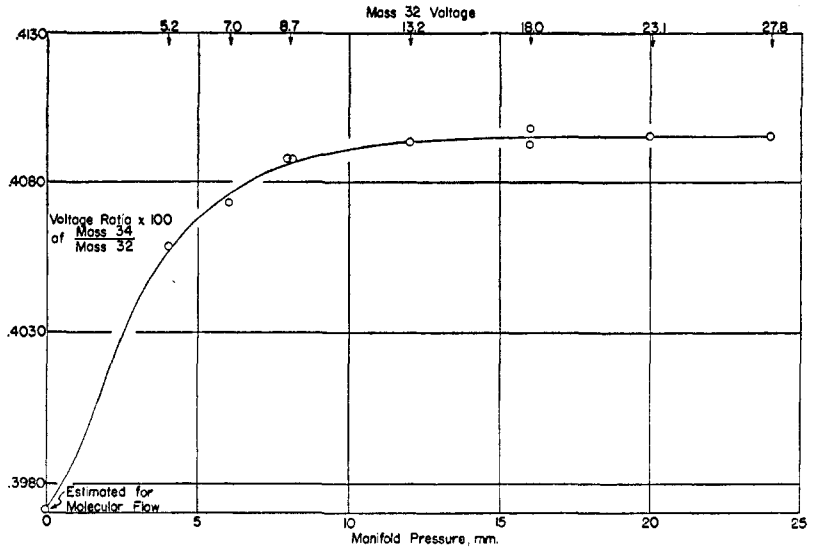


FIG. 3. Plot of the measured voltage ratios due to mass 34 as compared to mass 32 in the mass spectrometer as a function of the input pressure of gas before the capillary leak.

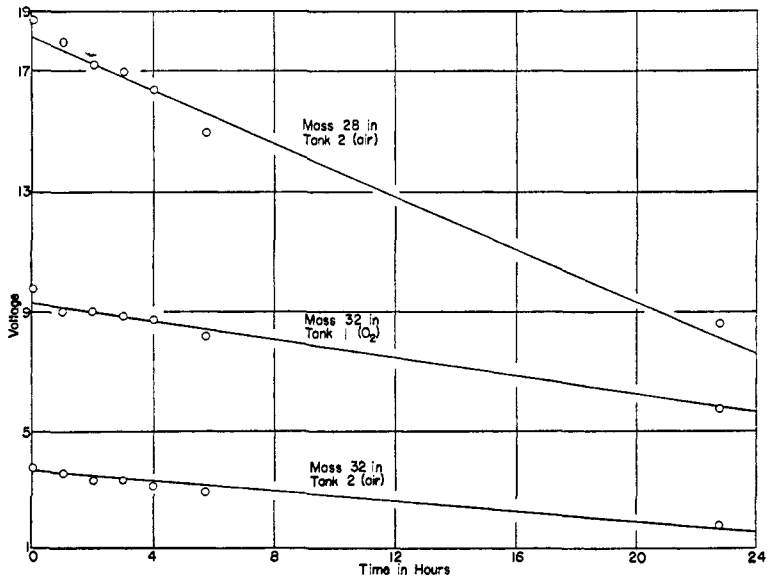


FIG. 4. Voltage produced by ion beams on collector No. 1

molecular, the lighter components will stream out of the reservoir at a rate greater than that of the heavier molecules in inverse proportion to the square root of the masses. Figure 4 illustrates this effect for pure oxygen (middle curve)

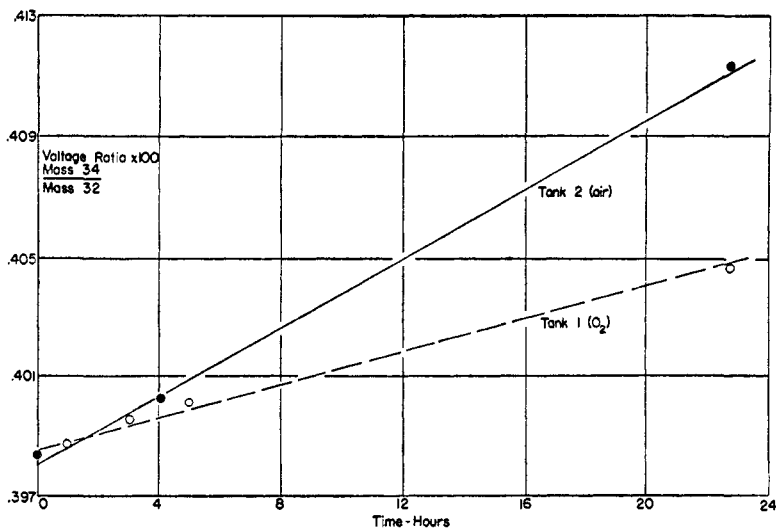


FIG. 5. Variation of measured voltage ratio due to masses 34 and 32 in the mass spectrometer as a function of time.

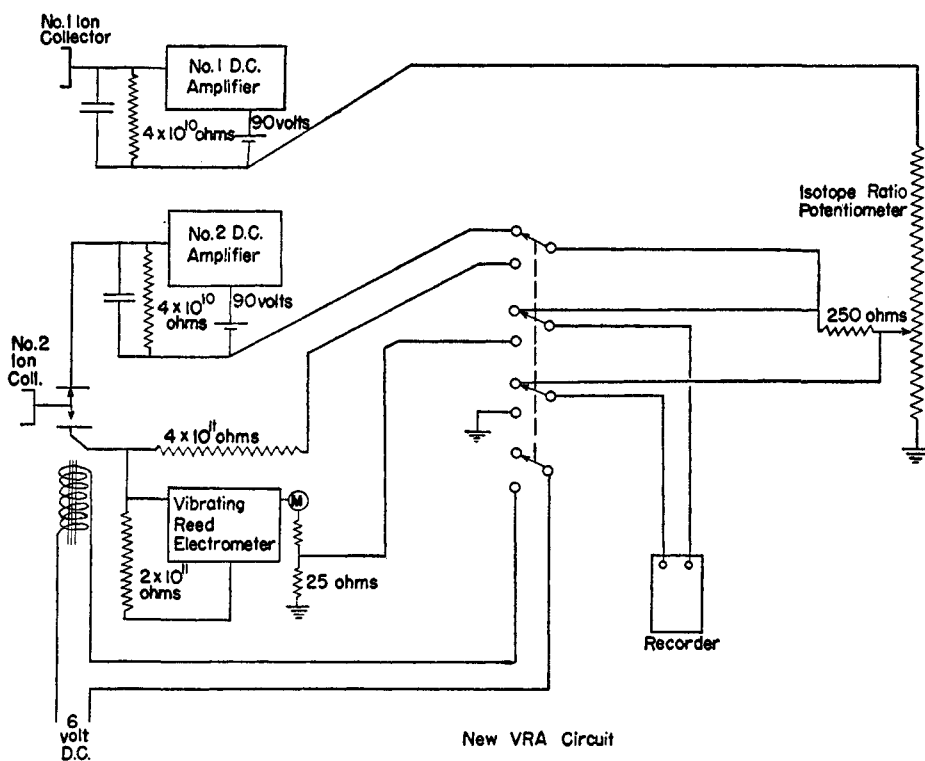


FIG. 6. Schematic diagram of switching system which enables either a vibrating reed electrometer or a d.c. amplifier to be used in measuring isotope ratios.

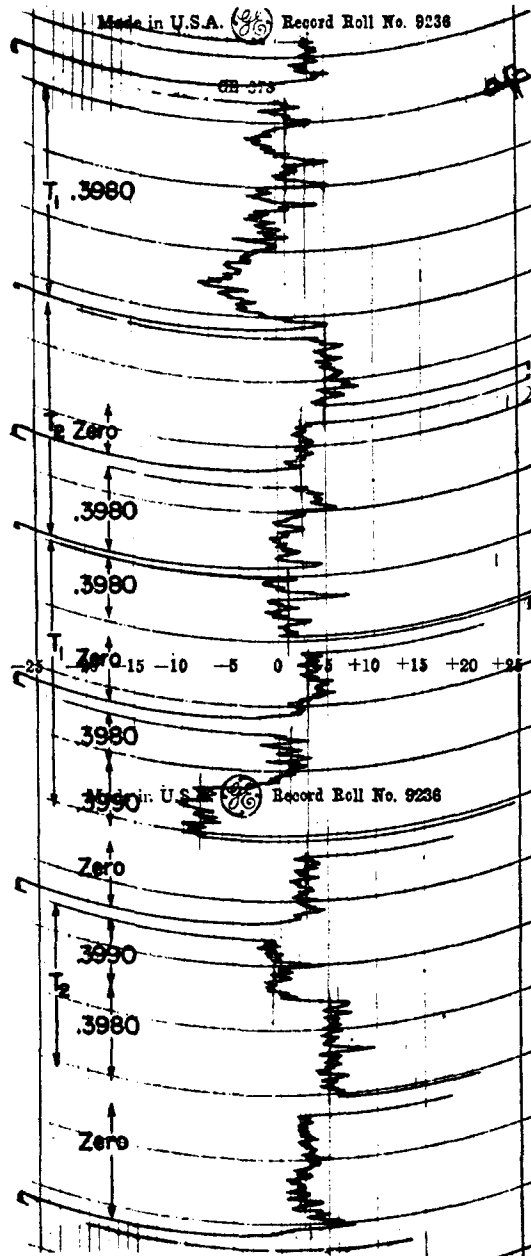


FIG. 7. General Electric recording potentiometer trace of galvanometer fluctuations in the measurement of isotope ratios. The distance between the horizontal arcs represents 1 min. T_1 and T_2 with associated arrows represent the time during which air from tank 1 (standard) or tank 2 (sample) was being admitted to the mass spectrometer. Zero indicates the zero of the galvanometer with the ion beam turned off. The numbers represent the readings on the isotope ratio dial.

TABLE 2

Data illustrating the reproducibility of measurements of isotope ratios

CARBON DIOXIDE (64)			OXYGEN (64)			65 PER CENT OXYGEN (27)		
Sample No.	Ratio*	Date	Sample No.	Ratio	Date	Sample No.	Ratio	Date
1.....	0.99947	December 13, 1949	1.....	1.01711	December 7, 1949	11.....	0.9868	April 4, 1951
	0.99941	January 4, 1950		1.01677	December 8, 1949		0.9865	May 4, 1951
2.....	0.99702	December 20, 1949	2.....	1.00023	February 10, 1950			
	0.99701	January 3, 1950		0.99990	February 13, 1950			
	0.99700	January 3, 1950						
3.....	0.99613	December 12, 1949	3.....	1.00000	February 10, 1950	41.....	0.9978	April 13, 1951
	0.99617	January 3, 1950		1.00000	February 11, 1950	43.....	0.9976	April 18, 1951
				0.99980	February 13, 1950	44.....	0.9980	April 20, 1951
4.....	0.99770	December 13, 1949	4.....	1.00044	February 10, 1950			
	0.99744	January 4, 1950		0.99998	February 11, 1950			
				0.99986	February 13, 1950			
5.....	0.99782	December 22, 1949						
	0.99778	January 4, 1950						

* The ratio is that of the O¹⁸ content of the sample to that of the standard.

and for air. The rate of flow of gas will depend on the area of the opening of the pinhole leak, and this will be different for the leaks on the two tanks, as it is virtually impossible to construct two leaks identical in hole area. In figure 5 measurements of the voltage ratio of mass 34 to that of 32 are plotted as a function of time in the case of pure oxygen (taken as the standard) in tank 1 and air in tank 2. In practice this difficulty is overcome by extrapolating the data back to zero time; at the end of half an hour from the moment of admitting the gases to the tanks, the correction is one part in 4000 in the isotope ratio in this particular case.

A number of workers, including Urey and his school (64) and the author (29), have installed vibrating reed electrometers³ as the amplifier to amplify the voltages produced by the currents due to the ions of the heavier mass of the isotope pair. Figure 6 illustrates our adaptation of this improvement to the Consolidated-Nier mass spectrometer. A magnetically operated switch, supported on solid polyethylene blocks for electrical insulation, serves to switch the input on the

TABLE 3

Percentage of O¹⁸ in a commercial source of oxygen as measured by the Consolidated-Nier mass spectrometer

DATE	O ¹⁸
	<i>per cent</i>
January 4, 1951	0.2031
January 13, 1951	0.2035
January 29, 1951	0.2042
February 1, 1951	0.2043
Average of many measurements	0.2031
True value	0.2043 ₅

No. 2 collector (the current due to the ion of heavier mass) either to the electronic amplifier supplied with the Consolidated mass spectrometer or to the vibrating reed amplifier.

In figure 7 a typical record is given from which an estimate of the sensitivity of this relative method of determining isotope ratios can be gleaned.

Data obtained by McKinney, McCrea, Epstein, Allen, and Urey (64) on the isotopic composition of oxygen in carbon dioxide are shown in table 2, along with data obtained by Dole and Rudd (27) on a mixture containing 65 per cent oxygen and 35 per cent nitrogen and on air.

It should be noted that the less the percentage of oxygen, for example, in the gas to be studied, the less accurate are the measurements of the ratio of the oxygen isotopes; hence isotope measurements should be made on the pure gas whenever possible.

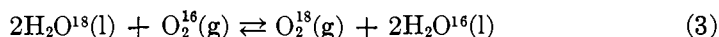
If the Consolidated-Nier mass spectrometer is used to measure absolute abundances of O¹⁸ in pure oxygen, for example, data similar to those quoted in table 3 will be obtained (27).

³ Built by the Applied Physics Corporation of Pasadena, California.

The true value of table 3 is based on Nier's absolute abundance determination of the percentage of O^{18} in the oxygen of air (82)—namely, 0.2039—coupled with many accurate determinations of the difference between the per cent of O^{18} in the oxygen of air and in the oxygen of table 3.

IV. METHODS OF SEPARATING THE ISOTOPES OF OXYGEN

It will be recalled that the heavy hydrogen isotope, deuterium, can be obtained by the electrolysis of water, the deuterium concentrating in the residue of undecomposed water. This method of concentrating the isotope of oxygen is not satisfactory, because of a very small fractionation factor, 1.008 (22, 52, 98), compared to values of 6 or higher obtained in the fractionation of the hydrogen isotopes. Such a small fractionation factor is possibly due to the fact that the oxygen isotopic exchange equilibrium



acts in the direction of concentrating the heavy isotope of oxygen in the gas phase, just the opposite of the tendency of electrolysis to concentrate it in the liquid phase. Successful methods of fractionating the isotopes of oxygen include the fractional distillation of water, the use of the thermal diffusion column of Clusius and Dickel (16), and the chemical exchange method of Urey and co-workers (107, 109).

A. Distillation of water

Thode, Smith, and Walkling (103) succeeded in obtaining 150 ml. of water enriched 6.5 times normal in O^{18} and 2.7 times normal in O^{17} by the distillation of water in three fractionating columns 8 m. high, the distillation being continued for 120 days.

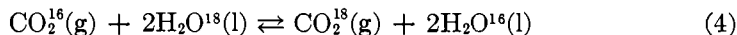
B. Thermal diffusion method

Clusius, Dickel, and Becker (17) prepared almost pure O^{18} by treating oxygen gas in six diffusion columns each about 14 m. high. They used a hot platinum wire to maintain isotopic equilibrium between the molecular species, $O^{16}O^{16}$, $O^{16}O^{18}$, and $O^{18}O^{18}$. After a two-stage operation the product of the process amounted to 250 ml. of 99.0 per cent $O^{18}O^{18}$ with only 1 per cent of $O^{17}O^{18}$.

Other workers reporting successful enrichment of O^{18} and O^{17} by the thermal diffusion method include Whalley, Winter, and Briscoe (118), Welles (115), and Lauder (61).

C. Chemical exchange method

Boyd and White (12) have recently made a chemical engineering study of the concentration of O^{18} by chemical exchange employing the reaction:



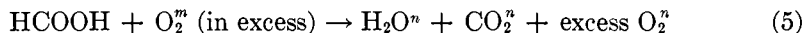
They used a 70-ft. column packed with aluminum and stainless-steel helices, and fed carbon dioxide in at the bottom and ammonia at the top. The addition

of the ammonia accelerated the rate of exchange because of the increased solubility of the carbon dioxide in the ammonium hydroxide solution. At the top of the column the carbon dioxide was reduced to methane and water and the water returned to the column as reflux. Excess water in the column was bled off at the bottom of the column and discarded, as this water was depleted in O^{18} . The experimentally determined fractionation factors amounted to 1.014 at 122°C. and 1.028 at 50°C., while the highest enrichment of O^{18} at the top of the column was 3.4 times normal after 100 hr. of operation.

V. CHEMICAL APPLICATIONS OF THE ISOTOPES OF OXYGEN

A. Analysis of organic compounds for oxygen by the isotope-dilution method

One of the most difficult problems of organic quantitative analysis is the determination of oxygen in acids, ketones, and other oxygen-containing compounds. Usually the percentage of oxygen is calculated indirectly after the percentages of all the other elements have been determined directly. By means of the isotopes of oxygen it is possible to determine oxygen directly according to the isotope-dilution method recently described by von Grosse, Hindin, and Kirshenbaum (38). In brief, the method consists of the following operations: The substance to be analyzed is weighed and introduced into a platinum boat, the boat is inserted into a platinum combustion tube, and the compound is oxidized at a temperature of 800°C. in the presence of a measured excess of oxygen enriched in O^{18} . The heavy isotope of oxygen distributes itself practically at random between the carbon dioxide, water, and excess oxygen present at the end of the combustion according to the following reaction (taking formic acid as an example):



In equation 5 m represents the difference in percentage of O^{18} between the oxygen added and the oxygen in the formic acid, while n represents the difference in percentage of O^{18} between the oxygen of the products and the oxygen of the sample. The percentage of oxygen is calculated from the equation

$$\text{Per cent of oxygen} = 100 \frac{b(m - n)}{a \cdot n} \quad (6)$$

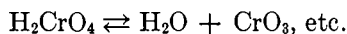
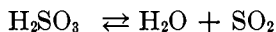
where a is the weight of the sample taken for analysis and b is the weight of the heavy oxygen gas used, calculated from the measurement of its volume and using 16.0000 as the atomic weight of oxygen in this calculation. Equation 6 is exact.

After the combustion the products of the reaction are pumped through a dry-ice trap to remove water vapor quickly before any exchange between carbon dioxide and water can occur, and then through a liquid-air trap to freeze out the carbon dioxide and to separate it from excess oxygen. Measurements of the ratio of the oxygen isotopes are then carried out on the carbon dioxide. Table 4 contains a representative set of data obtained in the analysis of a sample of formic acid.

B. Exchange of oxygen isotopes in inorganic salt solutions

For many years isotopes have been used for the study of exchange processes of atoms of the same element between different compounds. Table 5 presents observations on the possibility of exchange of oxygen isotopes between the salt in question and the water in which the salt is dissolved. Hall and Alexander (39) give the details of the necessary technique, which in their case involved the determination of the density of water enriched in O¹⁸ before and after having dissolved in it a known weight of salt.

According to Mills (70), the interchange of oxygen between the compounds listed in table 5 and water occurs through reversible anhydride formation such as:



Oxygen isotopes have been used in the study of the composition of ions and of hydrated ions by measuring the exchange or the rate of exchange of the O¹⁸

TABLE 4

Set of data illustrating the direct analysis of formic acid for its oxygen content by the isotope-dilution method

<i>a</i> = 38.2 mg. HCOOH	
<i>b</i> = 14.0 ml. of oxygen enriched in O ¹⁸ at 0°C. and 760 mm., or	
<i>b</i> = 20.0 mg., calculated taking 16.0000 as the atomic weight of oxygen	
<i>m</i> = 1.00 per cent	
<i>n</i> = 0.425 per cent	
Oxygen obtained = 70.8 per cent	}
Oxygen calculated for HCOOH = 69.5 per cent	
	difference = 1.3 per cent

in the solvent water with the O¹⁸ of the hydrated water. Thus, Crandall (19) demonstrated that the uranyl ion is UO₂⁺⁺ and not U(OH)₄⁺⁺ by his observation that in the compound UO₂Cl₂·*x*H₂O only *x* oxygen atoms of the *x*H₂O exchange with the oxygen atoms of the solvent. (This conclusion is based on the assumption that all four OH⁻ ions in U(OH)₄⁺⁺ would be equivalent.) Hunt and Taube (49) found that the hydrated chromic ion, Cr(H₂O)₆⁺⁺⁺, holds back initially six molecules of water from exchanging with the solvent when dissolved in water. The bound water molecules then exchange slowly, with a half-life for complete exchange equal to 40 hr. In contrast to Cr⁺⁺⁺, the following ions exchanged their hydrated water molecules rapidly with the solvent: H⁺, Al⁺⁺⁺, Ga⁺⁺⁺, Fe⁺⁺⁺ (at high acidities), and Th⁺⁺⁺⁺, while at low acidities there appeared to be a slight initial hold-back of water molecules by Fe⁺⁺⁺ (possibly in the form of a hydrated colloid). Plane and Taube (86) extended these observations to include a study of the influence of anions on the rate of exchange. Apparently the half-time of exchange of Cr(H₂O)₆⁺⁺⁺ is fixed by the concentration of perchlorate ion or by the sum of the concentrations of nitrate and perchlorate ions when nitrate ion is present. The chloride ion has a marked effect in catalyzing

TABLE 5

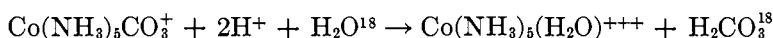
Studies on the exchange of oxygen isotopes in solutions of inorganic salts during 5 or more hr. in water at 95°C.

100 PER CENT EXCHANGE	NO EXCHANGE
CrO ₂ (39, 70)	KNO ₂ (39)
Na ₂ Cr ₂ O ₇ (15, 39, 70)	NaNO ₂ (39, 86, 92, 121)
Na ₂ CrO ₄ (39)	NaNO ₃ + NaOH (39)
NaOH (39)	NaNO ₃ + HCl (39)
Na ₂ CrO ₄ + NaOH (slow) (15, 39, 70)	Mg(ClO ₄) ₂ (39)
	Mg(ClO ₄) ₂ + HCl (39)
K ₂ MoO ₄ (39)	Ba(ClO ₄) ₂ + NaOH (39)
K ₂ MoO ₄ + NaOH (rapid) (39)	NaClO ₃ (39, 104)
Na ₂ WO ₄ (39)	KClO ₃ (121)
Na ₂ WO ₄ (rapid) (39)	KClO ₃ + NaOH (121)
NaBO ₂ (39)	NaClO ₄ (121)
K ₂ CO ₃ (slow) (39, 104)	NaClO ₄ + NaOH (121)
KH ₂ AsO ₄ (39, 104)	NaClO ₄ + HCl (121)
KH ₂ AsO ₄ + NaOH (rapid) (39)	Na ₂ SeO ₄ (39)
KAsO ₂ (39)	Na ₂ SeO ₄ + NaOH (39)
KAsO ₂ + NaOH (rapid) (39)	K ₂ SO ₃ + NaOH (39)
NaMnO ₄ (39, 70)	Na ₂ S ₂ O ₃ + NaOH (39, 70)
NaMnO ₄ + NaOH (39)	Na ₂ SO ₄ (39, 104, 121)
NaBrO ₃ (slow) (39)	Na ₂ SO ₄ + NaOH (39, 51, 121)
NaBrO ₃ + NaOH (rapid) (39)	Na ₂ O ₂ (3, 26)
NaIO ₃ (slow) (39)	H ₂ O ₂ (3, 120)
NaIO ₃ + NaOH (rapid) (39)	Na ₂ HPO ₄ (121)
Na ₂ SeO ₃ (39)	KH ₂ PO ₄ (121; see, however, 104)
Na ₂ SeO ₃ + NaOH (39)	Na ₂ HPO ₄ + NaOH (121)
Na ₂ SeO ₄ + HCl (slow) (39)	KHSO ₄ (121)
K ₂ SO ₃ (39, 70)	H ₂ SO ₄ 6 M or below, 25°C. (42)
Na ₂ SO ₃ + NaOH: 25°C. (42); 170°C. (66)	Na ₂ CO ₃ + NaOH, 25°C. (71)
Na ₂ S ₂ O ₃ (39, 70)	
Na ₂ SO ₄ + HCl (slow) (39, 104)	
NaClO ₃ + NaOH (slight) (39, 121)	
NaClO ₃ + HCl (extensive) (104, 121)	
NaClO ₂ + acid (slow), 25°C. (42)	
H ₂ SO ₄ (concentrated) (42, 51, 121)	
KHSO ₄ (70, 104)	
H ₃ BO ₃ (121)	
Na ₂ B ₄ O ₇ (121)	
KNO ₃ + H ₂ SO ₄ (121)	
Na ₂ CO ₃ ; (70); at 25°C. (slow) (104)	
Gases exchange: CO ₂ (71); SO ₂ (42)	
Gases do not exchange: N ₂ O (121); possibly some slight exchange (33)	

the exchange, but the explanation of the anion effect is not certain at the present time. Hunt and Taube (49) observed that the chromic ion tends to bind H₂O¹⁸ slightly in preference to H₂O¹⁶; this is in line with the conclusion given below that the heavier isotope always tends to accumulate in the heavier molecule.

$\text{Cr}(\text{H}_2\text{O})_z^{++}$ exchanges its water rapidly, so that the chloride-ion effect may be due to the promotion of the reaction $\text{Cr}^{+++} \rightarrow \text{Cr}^{++}$. Similarly the other anions may promote the reaction $\text{Cr}(\text{III}) \rightarrow \text{Cr}(\text{IV})$ and $\text{Cr}(\text{V})$; $\text{Cr}(\text{IV})$ and $\text{Cr}(\text{V})$ would then exchange their hydrated water molecules rapidly with the solvent. Friedman, Taube, and Hunt (32) studied the exchange of water between the solvent and hydrated cobaltic and cobaltous ions and concluded that these exchanges occur rapidly in the case of the cobaltic ion, probably because of a rapid electronic reaction between Co^{++} and Co^{+++} .

Hunt, Rutenberg, and Taube (50) showed that in all probability the carbonatopentaaminocobaltic ion in water has the structure $\text{Co}(\text{NH}_3)_5(\text{OCO}_2)^+$, because on hydrolysis in an acid solution of O^{18} -enriched water the following reaction occurs:



Nakata (79) investigated the exchange of O^{18} between sulfur dioxide and sulfur trioxide in liquid sulfur trioxide and found a rapid exchange at room temperature.

C. Exchange of oxygen isotopes between oxygen gas and solid oxides

Recently a number of interesting experiments studying the exchange of oxygen isotopes between oxygen gas and the surface of solid oxides such as aluminum oxide and titanium dioxide have been carried out by Winter and coworkers (117, 119). These experiments demonstrate that, in general, exchange can be produced if the temperature is raised sufficiently high, that the velocity of exchange is independent of the gas pressure, that the atoms in the surface readily exchange, and that the initial rapid exchange is followed by a slow exchange, whose rate is determined by the slow diffusion of oxygen from the interior of the solid to the surface. Figure 8 illustrates the decrease in the abundance of O^{18} in the gaseous phase during the time that oxygen enriched in O^{18} was in contact with aluminum oxide at 590°C . If the data are extrapolated to zero time, the exchange due to the slow diffusion can be eliminated and that due only to the surface exchange can be calculated. From a knowledge of this amount and of the area occupied by the oxygen atoms in the exposed surface of the unit cell of aluminum oxide, the area of the powdered aluminum oxide can be estimated. Good agreement was obtained between the surface area determined in this way and that measured by the nitrogen-adsorption method in the case of aluminum oxide, but when titanium dioxide and thorium dioxide were used, the areas determined by the oxygen-exchange method were greater than those determined by nitrogen adsorption by an order of magnitude (117).

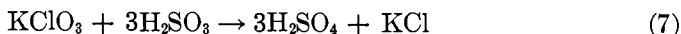
Data obtained by a number of workers for the exchange of oxygen isotopes between solid oxides and the gaseous phase are given in table 6.

It should be noted that the experimental evidence for exchange may be a function of the time of contact between gas and solid. For example, with a contact time of $1\frac{1}{2}$ min. Morita and Titani (78) could find little exchange between oxygen and copper oxide even at 900°C ., but Allen and Lauder (1) discovered

that 8 per cent of the oxygen atoms in their copper oxide had exchanged with oxygen gas during a 4-hr. contact of the oxide with the streaming oxygen at 400°C. The extent of the exchange rose continually with temperature above 400°C.

D. Use of oxygen isotopes in studying the mechanism of inorganic reactions

Taube and his students (41, 42, 43) have recently been making extensive use of the isotopes of oxygen in studying the mechanism of inorganic oxidation reactions. For example, Halperin and Taube (41) demonstrated in the reaction



that the oxygen of potassium chlorate adds directly to the sulfurous acid instead of coming from the solvent water. This conclusion was made possible by virtue

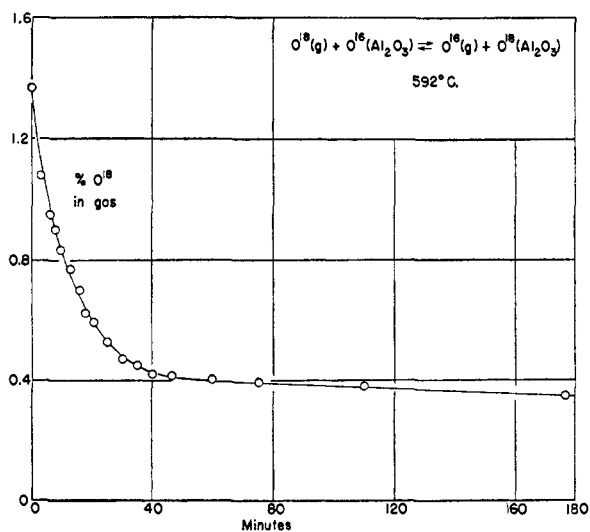
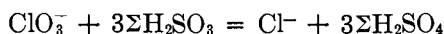


FIG. 8. Decrease in percentage of O¹⁸ content of enriched oxygen gas when exposed to aluminum oxide having a normal O¹⁸ content at 592°C.

of the fact that neither potassium chlorate, potassium sulfate, nor potassium bisulfate exchanged oxygen atoms with water under the conditions of their experiment. Instead of finding three atoms of oxygen per potassium chlorate molecule transferred to the reducing agent, the number varied from 1.9 to 2.9, possibly owing to exchange of oxygen with solvent when in the hypochlorite stage of reduction. A later, more detailed study of the oxidation of sulfites by halogenates carried out by Halperin and Taube (42) revealed that in the reaction



in the presence of 2 *M* hydrochloric acid, 2.51 atoms of oxygen transferred from one chlorate ion to sulfite. (The symbol Σ means all the sulfur in sulfurous acid, whether as HSO_3^- , as SO_3^{2-} , or as H_2SO_3 .) As the acidity decreased, less of the

TABLE 6

Conditions for the exchange of oxygen isotopes between solid oxides and the gaseous phase

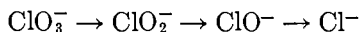
GAS	SOLID	TEMPERATURE REQUIRED TO INITIATE THE EXCHANGE	REFERENCE
		°C.	
O ₂	Al ₂ O ₃	360-600	(117)
O ₂	ThO ₂	360-600	(117)
O ₂	TiO ₂	360-600	(117)
O ₂	CuO	360-600	(1)
O ₂	ZnO	360-600	(48)
O ₂	NiO	600	(1)
O ₂	MgO	360	(48)
O ₂	Mn ₂ O ₃	300	(73)
O ₂	MnO ₂	200	(54)
O ₂	CoO	800	(1)
O ₂	Co ₃ O ₄	550	(1)
O ₂	Quartz	800	(13)
H ₂ O	Al ₂ O ₃	20	(117)
H ₂ O	ThO ₂	120	(117)
H ₂ O	TiO ₂	120	(117)
CO ₂	CuO	430	(106)
CO ₂	MnO ₂	70	(54)

Catalytic exchange of O¹⁸ between gases indicated

O ₂ + H ₂ O	Platinum wire	500	(77)
O ₂ + H ₂ O	Platinized asbestos	300	(77)
O ₂ + H ₂ O	Asbestos	800	(54)
O ₂ + CO ₂	Platinized asbestos	300	(77)
O ₂ + H ₂ O	MnO ₂	300	(77)
O ₂ + H ₂ O	CuO	650	(78)
O ₂ + H ₂ O	NaOH	360	(84)
O ₂ + H ₂ O	KOH	290	(84)
CO ₂ + O ₂	CuO	580	(106)
CO + O ₂	CuO	120	(106)
CO + CO ₂	Quartz	900	(13)
CO + O ₂ + H ₂ O	MnO ₂	90	(111)
O ₂ + H ₂ O	Cr ₂ O ₃ 10% + Al ₂ O ₃ 90%	350	(54)
O ₂ + H ₂ O	α-Fe ₂ O ₃	350	(74)
O ₂ + H ₂ O	γ-Fe ₂ O ₃	350	(74)
O ₂ + H ₂ O	2Fe ₂ O ₃ ·Bi ₂ O ₃	350	(74)
O ₂ + H ₂ O	Bi ₂ O ₃	450	(74)
O ₂ + H ₂ O	SiO ₂	680	(54)
O ₂ + SO ₂	Sponge platinum	No exchange	(80)
O ₂ + SO ₃	Sponge platinum	400	(80)
H ₂ O + O ₂	Fe ₂ O ₃	800	(54)
CO + O ₂	MnO ₂	200	(54)

oxygen in the sulfuric acid came from the chlorate ion, until at pH 5 the number of oxygen atoms transferred was 1.8 ± 0.1 . Theoretically one could expect 3 atoms transferred per molecule of chlorate. In 0.1 M hydrochloric acid the num-

ber of oxygen atoms transferred to the sulfate per molecule of oxidizing agent was 2.29 for ClO_3^- , 1.50 for ClO_2 , 1.55 for ClO_2^- , 0.36 for Cl_2O , and 2.20 for BrO_3^- at 25°C. Halperin and Taube interpret their data on the basis of a step-wise reduction of the oxidizing agent



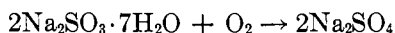
with the defection from complete transfer of the oxygen taking place in the hypochlorite stage. (The O^{18} content of the sulfate formed was found by precipitating the sulfate as barium sulfate, converting the oxygen in the barium sulfate to carbon dioxide with carbon, and analyzing the carbon dioxide in the mass spectrometer.)

In the fourth paper of their series Halperin and Taube (43) give data for the transfer of oxygen atoms from hydrogen peroxide, oxygen, manganese dioxide, and potassium permanganate to sulfite during oxidation of the latter and from hydrogen peroxide to thiosulfate. In the case of the hydrogen peroxide-sulfite reaction at pH 5 and higher acidities, the two atoms of oxygen in the hydrogen peroxide are transferred to sulfite without exchange with the solvent, although the latter needs only one oxygen atom per molecule to be converted to sulfate. To explain this interesting fact, Halperin and Taube postulate the existence of

O

the intermediate peroxysulfurous acid, $\text{HOSO}^{18}\text{O}^{18}\text{H}$, which reverts to sulfuric acid by an intramolecular rearrangement. When unlabelled oxygen gas oxidized labelled sulfite, 2.2 atoms of the oxygen per sulfite molecule were found in the barium sulfate. The slight excess over 2 is probably the result of isotopic fractionation during reaction. Manganese dioxide delivers the theoretically possible one oxygen atom to each sulfite molecule during oxidation of the latter, but potassium permanganate at pH 6 delivers practically no oxygen, the oxidation presumably being entirely electronic.

Winter and Briscoe (120) found in the reaction

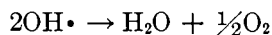
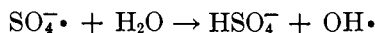
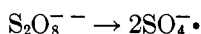


carried out in water enriched in O^{18} that the heavy-oxygen water was diluted with ordinary water only to the extent of the water of crystallization of the sodium sulfite, that in 72 hr. at room temperature there was no exchange of the oxygen atoms of sulfite with the oxygen of water, and that all the oxygen used in the oxidation of sulfite to sulfate came from the oxidizing agent and none from the water.

Rutenberg, Halperin, and Taube (96) found that in the hydrolysis of the compounds $(\text{KSO}_3)_2\text{NOH}$ and $(\text{KSO}_3)_3\text{N} \cdot 2\text{H}_2\text{O}$, formed as intermediates during the oxidation of sulfite by nitrite, no exchange of oxygen between sulfite bound in the complexes and the solvent occurred. This observation strengthens the postulate that the complexes are formed by internal nitrogen-sulfur bonds. The oxygen of the sulfate which resulted from the oxidation of sulfite was derived from the water.

Kolthoff and Miller (59) used water enriched in O^{18} to determine the source

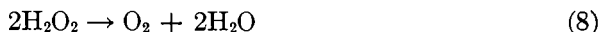
of the liberated oxygen in the thermal decomposition of the peroxy sulfate ion in aqueous medium. In the case of the uncatalyzed decomposition all the liberated oxygen came from the solvent water in accordance with the proposed mechanism:



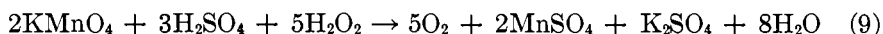
In strong acid solution, 0.5 *M* perchloric acid at 50°C., none of the liberated oxygen came from water, leading Kolthoff and Miller to suggest the following mechanism:



Dole, Muchow, Rudd, and Comte (26) investigated the isotopic composition of oxygen liberated catalytically from solutions of sodium peroxide in water. They found in the case of 100 per cent decomposition according to the reaction



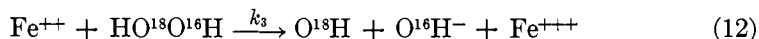
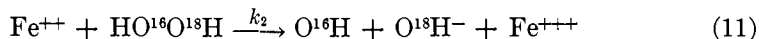
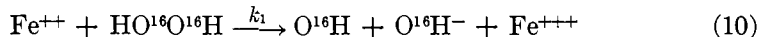
that the percentage of the heavy isotope of oxygen was 1.035 times greater in the oxygen produced than in the water of equation 8 when manganese dioxide, platinum, and colloidal gold were used as catalysts, and 1.048 greater in the case of ferric oxide, that there was no exchange of the oxygen of hydrogen peroxide between hydrogen peroxide and water even during decomposition, and that in the case of catalase as the catalyst no fractionation of the oxygen isotopes occurred. Some of these results confirm earlier observations of Winter and Briscoe (120). When the peroxide was completely oxidized by manganese dioxide or potassium permanganate according to the reaction



all the liberated oxygen came from the peroxide and none from the permanganate. Baertschi (3) has recently come to the same conclusion.

In addition to the use of isotopes to determine the path of some of the oxygen atoms in the reactions given as examples above, it is possible to gain additional insight into the mechanism of the reactions by studying rate effects. In figure 9 the percentage of O^{18} in the oxygen liberated from a buffered solution of catalase and sodium peroxide is plotted as a function of the fraction of the peroxide decomposed (26). The O^{18} per cent is at first greater than that in the original peroxide, 0.2041, but decreases to a value below 0.2041 and then slowly rises to this value at 100 per cent decomposition. The percentage of O^{18} extrapolated to zero time, or to zero amount of peroxide decomposed, seems to approach the initial value of the O^{18} percentage of the oxygen liberated when manganese dioxide is used as the catalyst. It is possible to explain the greater O^{18} abundance

in the oxygen of reaction 8 as compared to the percentage of O^{18} in the water by assuming that the molecule $HO^{16}O^{16}H$ reacts more rapidly than $HO^{16}O^{18}H$ in the initial stage of the decomposition. Dole, Rudd, Muchow, and Comte (26) have developed the kinetic equations applicable to the initial reactions



assuming that all following reactions proceed rapidly without any isotope fractionation. Letting

$$\epsilon = \frac{k_1}{k_2 + k_3} = \frac{k_1}{2k_2} \quad (13)$$

it can be shown that

$$\epsilon = \beta \quad (14)$$

where β is given by the equation containing measurable quantities:

$$\beta = \frac{y_\infty}{2x_0 - y_\infty} \quad (15)$$

In equation 15, x_0 represents the atom fraction of O^{18} in the original sodium peroxide and y_∞ represents the atom fraction of O^{18} in the liberated oxygen after complete catalytic decomposition.

Bigeleisen (8) has shown how the theory of absolute reaction rates can be applied to the calculation of expected isotope fractionations as the result of rate processes; his equation is

$$\epsilon = \frac{k_1}{2k_2} = \left\{ \frac{m_2^\ddagger}{m_1^\ddagger} \right\}^{1/2} \left\{ 1 + \sum_i^{3n-6} G(u_i) \Delta u_i - \sum_i^{3n'-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right\} \quad (16)$$

where

$$\Delta u_i = \frac{hc}{kT} (\omega_{1i} - \omega_{2i})$$

$$u_i = \frac{hc\omega}{kT}$$

$$G(u) = \frac{1}{2} - \frac{1}{u} - \frac{1}{e^u - 1}$$

and the symbol ‡ refers to the activated complex. In equation 16 m^\ddagger is "the effective mass of the complex along the coördinate of decomposition."

To apply equation 16 to the interpretation of the data the fundamental vibration frequencies of the molecules participating in the reaction must be known as well as the frequencies of the activated complex. The latter are generally assumed to be small and negligible; at least this assumption gives the maximum calculated value of ϵ . Dole and coworkers (26) calculated five of the six frequen-

cies of the $\text{HO}^{18}\text{O}^{18}\text{H}$ molecule, using equations of Morino and Mizushima (72) and force constants of Bailey and Gordon (5), and found 1.078 as a maximum value of ϵ . The mechanism adopted by them (26) does not explain the initial increase of O^{18} in the evolved oxygen as compared to the original hydrogen peroxide; at least this is true unless an *ad hoc* hypothesis is made concerning the nature of the activated complex. The unusual results obtained with catalase as the catalyst, shown in figure 9, must be the result of a change in mechanism as the reaction proceeds.

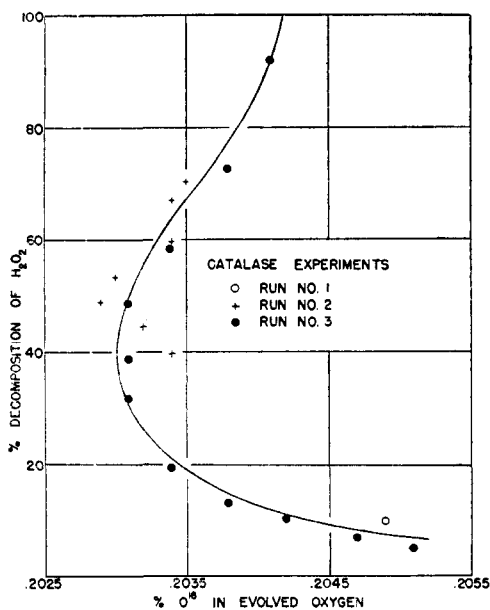


FIG. 9

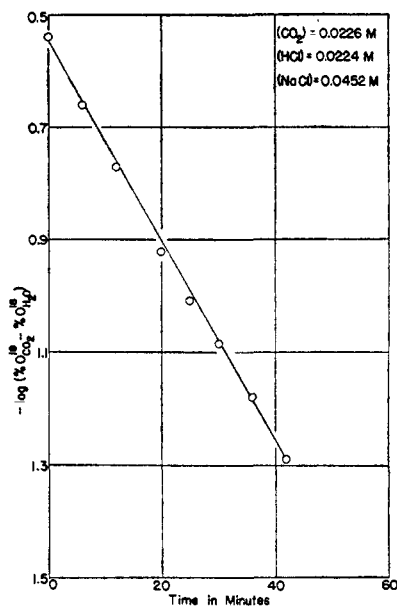
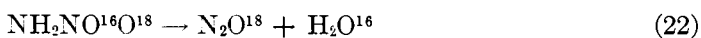
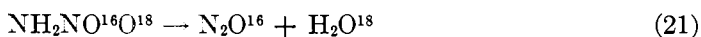
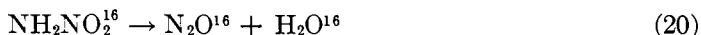
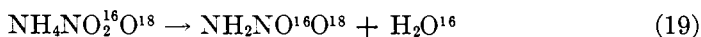
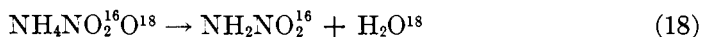
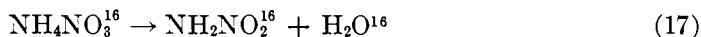


FIG. 10

FIG. 9. Per cent of O^{18} in oxygen evolved from sodium peroxide
 FIG. 10. Rate of exchange of O^{18} between enriched carbon dioxide and normal water at 0°C .

Friedman and Bigeleisen (33) investigated the effects of oxygen (and nitrogen) isotopes in the thermal decomposition of ammonium nitrate. They found satisfactory agreement between observed and calculated effects of oxygen isotopes on the basis of the following assumptions: (a) that the decomposition proceeds according to the equations,



(b) that the nitramide of each isotopic species or similar intermediate of reactions 17 to 19 is present in a steady-state concentration; (c) that the contribution of reactions 19 and 22 to the overall isotope effect can be neglected and that terms involving the concentration of $\text{NH}_4\text{NO}_2^{16}\text{O}^{18}$ can be occasionally neglected in comparison to terms involving the concentration of $\text{NH}_4\text{NO}_3^{16}$. Their equations deduced from the above kinetics are

$$\frac{\left[\frac{(\text{N}_2\text{O}^{18})}{(\text{N}_2\text{O}^{16})}\right]_{t=\infty}}{\left[\frac{(\text{H}_2\text{O}^{18})}{(\text{H}_2\text{O}^{16})}\right]_{t=\infty}} = \frac{2\left(\frac{k_{19}}{k_{18} + k_{19}}\right)\left(\frac{k_{22}}{k_{21} + k_{22}}\right)}{\left(\frac{k_{18}}{k_{18} + k_{19}}\right) + \left(\frac{k_{19}}{k_{18} + k_{19}}\right)\left(\frac{k_{21}}{k_{21} + k_{22}}\right)} \quad (23)$$

and

$$\frac{\left[\frac{(\text{N}_2\text{O}^{18})}{(\text{N}_2\text{O}^{16})}\right]_{t=a}}{\left[\frac{(\text{N}_2\text{O}^{18})}{(\text{N}_2\text{O}^{16})}\right]_{t=\infty}} = \frac{k_{18} + k_{19}}{k_{17}} \quad (24)$$

where the k 's represent the reaction rate constants of the above reactions and the parentheses indicate isotope abundances. In equation 24, $t = a$ represents the time for 1 per cent decomposition. Equation 24 states that there is no change in the O^{18} percentage of the liberated nitrous oxide during the course of the reaction, in agreement with observation.

Mills and Urey (71) in 1939 carried out an interesting kinetic study of isotope exchange between carbon dioxide, bicarbonate ion, carbonate ion, and water. First of all, they pointed out that the time required to establish isotopic equilibrium is many times greater than that to establish the chemical equilibrium itself; for example, only 1 sec. is required to attain the half-equilibrium concentration of carbonic acid when carbon dioxide is dissolved in water, while 1000 sec. are required for the half-time of oxygen exchange. This is due to the fact that the hydration reaction must occur many times to establish isotopic equilibrium if the isotopic compositions of the oxygen in the original water and in the carbon dioxide are different. Mills and Urey rapidly dissolved O^{18} -enriched carbon dioxide in water and then at various time intervals withdrew 10-ml. portions of the solution, pumped off the carbon dioxide, dried it, and analyzed it for its O^{18} content in a mass spectrometer. The total time necessary to take a sample for analysis was 10 sec. Results of a typical experiment are shown in figure 10, where the data demonstrate that, in common with all isotopic exchange reactions, the rate of exchange is of the first order with respect to the difference in the fraction of O^{18} in the carbon dioxide and in the water.

For the pH range in which only the hydration reaction determines the rate of exchange (below pH 8) the rate equation reduces to

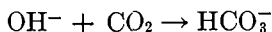
$$-\frac{d\alpha}{dt} = k_1 \frac{[\text{H}_2\text{O}]}{3} (\alpha - \beta) \quad (25)$$

where α and β are the atom fractions of O^{18} in the carbon dioxide and water, respectively. Equation 25 was derived on the simplifying assumption that all the different isotopic species of carbon dioxide react with water at the same rate.

Mills and Urey found that at 0°C. the rate constant for isotopic exchange was equal to the rate constant for the hydration of carbon dioxide. At pH values higher than 8, the rate of isotope exchange becomes much slower; this fact is interpreted by Mills and Urey to signify that the exchange of oxygen between bicarbonate and water proceeds through the series of reactions:



At certain pH values the rate of exchange becomes much greater than would be calculated on the basis of the hydration reaction, leading to the postulate that the significant reaction is



Wang (114) has made use of O^{18} as a tracer in studying the self-diffusion of water molecules in liquid water.

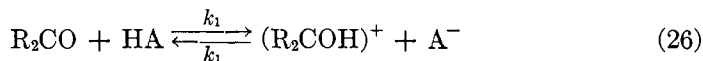
E. Exchange of oxygen isotopes between organic compounds in water

In general it can be stated that alcohols, esters, and frequently acids cannot exchange their oxygen atoms with the oxygen of water, but such exchange is possible in the case of aldehydes and ketones. The velocity of interchange is increased by acid or basic catalysis, especially in the case of benzaldehyde. The oxygen of carboxyl groups undergoes exchange only in the presence of strong acids, while the oxygen of peptide bonds, amides, and urea does not. Amino acids can exchange their oxygen atoms with water only in acid solution. These observations and others are summarized in table 7.

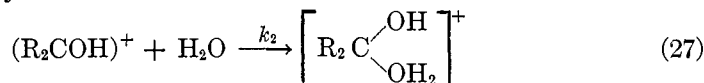
F. Use of oxygen isotopes in studying the mechanism of organic reactions

The heavy isotope of oxygen has had considerable use as a tracer in working out the mechanism of organic reactions. With it, for example, one can answer such questions as the following: Does the oxygen of the water molecule combine with the acid or the alcohol in the hydrolysis of esters? Table 8 contains a list of organic reactions studied by means of O^{18} .

Cohn and Urey (18) investigated the kinetics of the exchange of O^{18} between acetone and water. They found that the exchange was catalyzed by hydrogen and hydroxyl ions and by the salicylic acid molecule, but not by salicylate ions. In accordance with the scheme of general acid catalysis the first step of the reaction is believed to be



The second step may be either



or

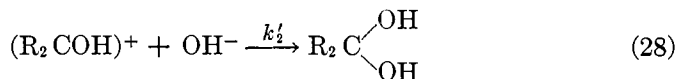


TABLE 7
Exchange of oxygen isotopes between organic compounds and water

COMPOUND	TEMPER- ATURE	TIME	EXCHANGE	REFERENCES
	°C.	hours	per cent	
CH ₃ OH	100	7	0	(18)
CH ₃ OH + acid or base	25	24	0	(91)
(CH ₃) ₃ COH + acid	95	2	0	(99)
C ₆ H ₅ OH	25	44	0	(18, 57)
C ₆ H ₅ ONa	170	20	0	(66)
Glycerol	100	6	0	(18)
Trianisylcarbinol	95	43	0	(99)
Trianisylcarbinol + 0.1% H ₂ SO ₄	95	24	100	(99)
Sucrose	55	100	0	(35)
Glucose	100	3	1 atom exchanges	(57)
Glucose → fructose	25	18 days	2 atoms exchange	(35)
Cellulose	18		0	(65)
Cellulose + NaOH	18	80	Slow exchange	(65)
Cellulose xanthate	18		0	(65)
Cellulose trialcoholate	18		0	(65)
CH ₃ CHO	25	24	100	(18, 45)
C ₆ H ₅ CHO	25	100	100	(57, 99)
C ₆ H ₅ CHO	25	1	31	(99)
C ₆ H ₅ CHO + 0.1% H ₂ SO ₄	25	1	100	(99)
C ₆ H ₅ CHO + 0.1% KOH	25	1	100	(99)
(CH ₃) ₂ CO	25	24	0	(18)
(CH ₃) ₂ CO	100	24	Partial exchange	(18)
Butyric acid	100	24	0	(18)
Maleic acid	100	45	100	(57)
Fumaric acid	25	44	0	(18)
Fumaric acid	100	45	2 atoms exchange	(57)
Phthalic acid	25	44	0	(57)
Terephthalic acid	100	20	0	(57)
Succinic acid	25	44	0	(18)
Succinic acid	130	5	100	(57)
Citric acid	25	24	0	(99)
Citric acid	75	24	91	(99)
Citric acid + 8% H ₂ SO ₄	25	24	41	(99)
Benzoic acid	130	5	1 atom exchanges	(57)
Benzoic acid	100	4	100	(91)
Acetic acid + 0.1 N HCl	25	40 days	100	(91)
CH ₂ ClCOOH	25	24	Partial exchange	(18)
CCl ₂ COOH	25	42	100	(18)
Cyanuric acid	100	40	0	(68)
Amyl acetate	25	44	0	(18)
Sodium acetate	100	48	0	(91, 99)
Acetanilide	20	15 days	0	(69)
Acetanilide + PCl ₅	20	15 days	Slight exchange	(69)
Urea	25	54	0	(18)
Benzamide	100	23	0	(68)
Benzanilide	20	15 days	0	(69)
Glycine (neutral)	100	72	0	(68)

TABLE 7—*Concluded*

COMPOUND	TEMPER- ATURE	TIME	EXCHANGE	REFERENCES
	°C.	hours	per cent	
Glycine (pH 2).....	100	24	100	(68)
Leucine.....	100	41	0	(68)
Diketopiperazine.....	100	48	0	(68)
Albumin.....	25	40	0	(68)
Tyrosine.....	100	40	0	(68)
Pepsin (pH 4).....			13	(68)
Nitrobenzene + acid or base.....	25	24	0	(91)
Alloxan hydrate.....	25	16	48	(99)
C ₁₀ H ₇ ONa.....	170	20	0	(66)
C ₆ H ₄ (CO) ₂ C ₆ H ₂ (ONa) ₂	170	20	0	(66)

The acetone hydrate formed in reaction 28 may revert to acetone and water by reaction with the acid HA to give the positive ion R₂C(OH)(OH₂)⁺, from which water could then be liberated and the ion R₂COH⁺ returned to acetone by the reverse of reaction 26.

If the second step is reaction 27, the complex with water reverts to acetone by reacting with a base to form the acetone hydrate as in reaction 28, and then follows all its reactions in reverse. As the differences in the rates of exchange were different from the rates of enolization (in contrast to hydrogen-deuterium exchange, which proceeds through the enolic form), it is evident that O¹⁸ exchange does not involve the enolic form.

The kinetics of the exchange of oxygen between benzoic acid and water has been studied both experimentally (93) and theoretically (94) by Roberts and Urey. If α is the atom fraction of O¹⁸ in carbon dioxide, they showed that if the three molecular species CO₂¹⁶, CO¹⁶O¹⁸, and CO₂¹⁸ are in statistical equilibrium, i.e., if

$$\frac{[\text{CO}^{16}\text{O}^{18}]^2}{[\text{CO}_2^{16}][\text{CO}_2^{18}]} = 4 \quad (29)$$

then

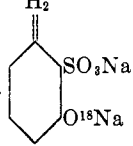
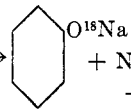
$$\alpha = \frac{\sqrt{(\text{CO}_2^{18})}}{\sqrt{(\text{CO}_2^{18})} + \sqrt{(\text{CO}_2^{16})}}$$

$$1 - \alpha = \frac{\sqrt{(\text{CO}_2^{16})}}{\sqrt{(\text{CO}_2^{18})} + \sqrt{(\text{CO}_2^{16})}}$$

and

$$2\alpha(1 - \alpha) = \frac{(\text{CO}^{16}\text{O}^{18})}{\{\sqrt{(\text{CO}_2^{18})} + \sqrt{(\text{CO}_2^{16})}\}^2}$$

TABLE 8
Organic reactions which have been studied using O¹⁸ as tracer element

NO.	REACTION	REFERENCES
1.....	$\text{C}_6\text{H}_5\text{COH} + \text{CH}_3\text{O}^{18}\text{H} \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5\text{CO}^{18}\text{CH}_3$ <div style="display: flex; justify-content: space-around; width: 100%;"> <div style="text-align: center;">\parallel O</div> <div style="text-align: center;">\parallel O</div> </div>	(20, 92)
2.....	$\text{C}_2\text{H}_5\text{O}^{18}\text{H} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{CO}^{18}\text{C}_2\text{H}_5 + \text{CH}_3\text{COOH}$ <div style="display: flex; justify-content: center; width: 100%;"> \parallel O </div>	(14)
3.....	$\text{C}_2\text{H}_5\text{OH} + \text{NaO}^{18}\text{H} + \text{CS}_2 \rightarrow \text{C}_2\text{H}_5\text{OCSNa} + \text{H}_2\text{O}^{18}$ <div style="display: flex; justify-content: center; width: 100%;"> \parallel S </div>	(14)
4.....	$\text{CH}_3\text{COOC}_8\text{H}_{11} + \text{H}_2\text{O}^{18} \rightarrow \text{C}_8\text{H}_{11}\text{OH} + \text{CH}_3\text{COO}^{18}\text{H}$	(20, 87)
5.....	$\text{C}_2\text{H}_5\text{O}^{18}\text{H} + (\text{C}_2\text{H}_5)_2\text{SO}_4 + \text{NaOH} \rightarrow \text{C}_2\text{H}_5\text{O}^{18}\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{NaSO}_4 + 2\text{H}_2\text{O}$	(62)
6.....	$(\text{C}_2\text{H}_5)_2\text{SO}_4 + \text{H}_2\text{O}^{18} \rightarrow \text{HO}^{18}(\text{C}_2\text{H}_5\text{O})\text{SO}_2 + \text{C}_2\text{H}_5\text{OH}$	(11)
7.....	$(\text{CH}_3)_3\text{PO}_4 + \text{H}_2\text{O}^{18} \text{ (basic)} \rightarrow (\text{CH}_3\text{O})_2(\text{O}^{18}\text{H})\text{PO} + \text{CH}_3\text{OH}$	(11)
8.....	$(\text{CH}_3)_3\text{PO}_4 + \text{H}_2\text{O}^{18} \text{ (acid or neutral)} \rightarrow (\text{CH}_3\text{O})_2(\text{OH})(\text{PO}) + \text{CH}_3\text{O}^{18}\text{H}$	(11)
9.....	$(\text{C}_2\text{H}_5)_2\text{C}=\text{NOH} \cdot \text{HCl} + \text{H}_2\text{O}^{18} \rightarrow \text{C}_2\text{H}_5\text{CO}^{18}\text{NHC}_2\text{H}_5 + \text{H}_2\text{O} + \text{HCl}$	(14)
10.....	$\text{C}_6\text{H}_5\text{SO}_3\text{H} + 3\text{NaO}^{18}\text{H} \rightarrow \text{C}_6\text{H}_5\text{O}^{18}\text{Na} + \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$	(14)
11.....	$\text{CH}_3\text{CHCH}_2\text{C}=\text{O} + \text{H}_2\text{O}^{18} \text{ (basic or strongly acid)} \rightarrow$ <div style="display: flex; justify-content: space-around; width: 100%; margin-top: 10px;"> <div style="text-align: center;"> $\underbrace{\hspace{2em}}_{\text{O}}$ </div> <div style="text-align: center;"> $\text{CH}_3\text{CHOHCH}_2\text{COO}^{18}\text{H}$ </div> </div>	(83)
12.....	$\text{CH}_3\text{CHCH}_2\text{C}=\text{O} + \text{H}_2\text{O}^{18} \text{ (pH 1-6)} \rightarrow \text{CH}_3\text{CHO}^{18}\text{HCH}_2\text{COOH}$ <div style="display: flex; justify-content: center; width: 100%; margin-top: 10px;"> $\underbrace{\hspace{2em}}_{\text{O}}$ </div>	(83)
13.....	$(\text{CH}_3\text{CO})\text{H}_2\text{PO}_4 + \text{H}_2\text{O}^{18} \text{ (acid)} \rightarrow \text{H}_3\text{PO}_3\text{O}^{18} + \text{CH}_3\text{COOH}$	(7)
14.....	$(\text{CH}_3\text{CO})\text{H}_2\text{PO}_4 + \text{H}_2\text{O}^{18} \text{ (basic)} \rightarrow \text{H}_3\text{PO}_4 + \text{CH}_3\text{COO}^{18}\text{H}$	(7)
15.....	$\text{C}_6\text{H}_5\text{SO}_3\text{Na} + \text{NaO}^{18}\text{H} \rightarrow$ <div style="display: flex; align-items: center; justify-content: center; margin-top: 10px;"> <div style="text-align: center;">  </div> <div style="margin: 0 10px;"> $\xrightarrow{\text{NaO}^{18}\text{H}}$ </div> <div style="text-align: center;">  </div> <div style="margin-left: 20px;"> $+ \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}^{18}$ </div> </div>	(66)
16.....	$\text{C}_6\text{H}_{10}\text{O}_5 \text{ (cellulose)} + \text{NaO}^{18}\text{H} \rightarrow \text{C}_6\text{H}_{10}\text{O}_5 \cdot \text{NaO}^{18}\text{H}$	(66)

Furthermore, if r is the measured ratio of mass 44 in the mass spectrometer to mass 46 (corrected for the mass of $C^{13}O^{16}O^{17}$), then in terms of α

$$r = \frac{(1 - \alpha)^2}{2\alpha(1 - \alpha)}$$

or

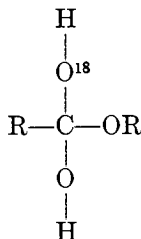
$$\alpha = \frac{1}{2r + 1} \quad (30)$$

Equation 30 enabled the atom fraction of O^{18} in the carbon dioxide liberated from the benzoic acid to be calculated from the measured r . Roberts and Urey found that the exchange reaction was of the first order with respect to the hydrogen-ion concentration and to the difference in atom fraction of O^{18} in the reactants, but independent of the concentration of benzoic acid and free of salt effects. Letting β be the atom fraction of O^{18} in the water, assuming that the O^{18} atoms were statistically distributed among the three species of benzoic acid (corresponding to the three species of carbon dioxide given above), and assuming that all three species of benzoic acid reacted without any specific difference due to the O^{16} or O^{18} atoms, Roberts and Urey were able to demonstrate that the rate of change of the O^{18} fraction in the benzoic acid was given by the equation

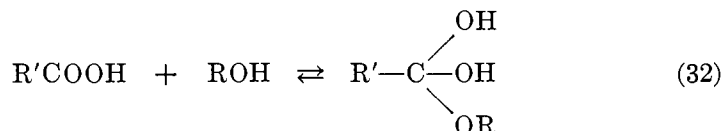
$$\frac{d\alpha}{dt} = k[H_2O][\beta - \alpha] \quad (31)$$

in agreement with observations.

Bender (6) has studied the rate of exchange of O^{18} as compared to the rate of hydrolysis when O^{18} -labelled esters of benzoic acid were partially hydrolyzed with unlabelled water. The fact that the O^{18} content of the residue of unhydrolyzed labelled ester decreased during the course of the hydrolysis indicated that an intermediate of symmetrical structure



was formed during the hydrolysis. The ratio of the rate of hydrolysis and rate of exchange of O^{18} in either acid or base was fairly close to unity, a result which suggests that the mechanism of the acid and basic hydrolysis involved a similar intermediate. Roberts and Urey (94), however, expressed doubt that such a complex could form in the esterification reaction, as an equilibrium of the type

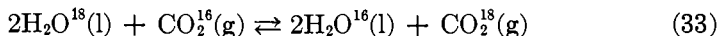


would give rise to a rapid uncatalyzed exchange. Roberts and Urey (94) used the data on oxygen exchange to eliminate a number of possible mechanisms which had previously been proposed for the esterification reaction.

Morita (75) burned methanol in O^{18} -enriched oxygen and found that the heavy oxygen and the normal oxygen originally present in the methanol were uniformly distributed in the products of combustion (carbon dioxide and water).

G. Studies of equilibrium isotopic exchange reactions involving oxygen

In many if not all reactions involving the exchange of O^{18} , such as



the isotopes of oxygen are not distributed among all molecular species at random, which would result in unity for the equilibrium constant of reaction 33, but the heavier isotope tends to become concentrated in the heavier molecule. Calculations of the equilibrium constant of isotopic exchange reactions like reaction 33 were first extensively carried out by Urey and Greiff (109) in 1935. Because of the differences in isotopic masses, the fundamental frequencies of vibration of the molecule H_2O^{18} will be smaller than the frequencies of vibration of H_2O^{16} . In simple diatomic molecules such as O_2 the frequencies of the various isotopic species—namely, $O^{16}O^{16}$, $O^{16}O^{18}$, and $O^{18}O^{18}$ —stand to one another in the inverse ratio of the square root of the reduced mass, μ , where

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

It is assumed that the vibrations of the O_2 molecule follow the equation for simple harmonic motion. In more complicated molecules it is necessary to know the force constants for the different vibrations and to have equations relating the frequencies to the force constants and reduced masses. Or, in certain favorable cases, the Teller-Redlich rule (46) for the calculation of frequencies of one molecule from its isotopic analog may be invoked. It is beyond the scope of this review to give the details of these calculations; the reader is referred to the extensive work and tabulation of Urey (107).

Bigeleisen and Mayer (10) have reduced the calculation of isotopic exchange equilibrium constants to rather simple expressions for cases where the rotational partition function of classical theory is applicable, i.e., for all molecules except H_2 , HD , and D_2 . In agreement with an earlier conclusion of Waldmann (113), Bigeleisen and Mayer demonstrate that the separation of isotopes in chemical reactions at equilibrium is a quantum effect; in other words, if classical vibrational partition functions were valid, there would be no separation. Bigeleisen and Mayer neglect interaction of rotation and vibration and anharmonicity of the vibrations (equivalent to assuming linear harmonic motion). Their equation is

$$\ln f = \sum_i G_i(u_i) \Delta u_i + \ln \frac{s}{s'} \quad (34)$$

where $G_i(u_i)$ and Δu_i have already been defined in equation 16, s and s' are the symmetry numbers of the two isotopic species such as $\text{CO}^{16}\text{O}^{16}$ ($s' = 2$) and $\text{CO}^{16}\text{O}^{18}$ ($s = 1$), and f is the ratio of the partition function of the heavier to the lighter molecule, multiplied by the products of the inverse mass ratios to the three-halves power with the exponent also multiplied by the number (n) of isotopic atoms undergoing exchange, i.e., $(m/m')^{3/2 \cdot n}$. For reaction 33 the equation relating K and f would be

$$K = \frac{f_{\text{CO}_2}}{f_{\text{H}_2\text{O}}^2} \quad (35)$$

Bigeleisen and Mayer have tabulated values of $G(u)$ in terms of u . About the same time, Urey (107) published his tabulation of partition function ratios of many isotopic species, including those for oxygen, water, sulfur dioxide, sulfate ion, carbon dioxide, carbonate ion, and chlorine dioxide. Table 9 contains some equilibrium constants for various simple reactions calculated for 0°C .

TABLE 9
Some isotopic exchange equilibrium constants and fractionation factors at 0°C .

NO.	REACTION	K	α	REFERENCE
1.....	$2\text{H}_2\text{O}^{18}(\text{g}) + \text{O}_2^{16}(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}^{16}(\text{g}) + \text{O}_2^{18}(\text{g})$	1.032	1.017	(107)
2.....	$2\text{H}_2\text{O}^{18}(\text{l}) + \text{O}_2^{16}(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}^{16}(\text{l}) + \text{O}_2^{18}(\text{g})$	1.010	1.006	(107)
3.....	$2\text{H}_2\text{O}^{18}(\text{l}) + \text{CO}_2^{16}(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}^{16}(\text{l}) + \text{CO}_2^{18}(\text{g})$	1.089	1.044	(107)
4.....	$\text{CaCO}_3^{16}(\text{s}) + 3\text{H}_2\text{O}^{18}(\text{l}) \rightleftharpoons \text{CaCO}_3^{18}(\text{s}) + 3\text{H}_2\text{O}^{16}(\text{l})$	1.077	1.025	(63)

The fractionation factors, α , of reactions 1, 2, and 3 of table 9 were calculated by taking the square root of the equilibrium constants, while that of reaction 4 was calculated by taking the cube root of K . This procedure involves the assumption of random distribution of isotopes among any one molecular type; in other words, that for the species CaCO_3^{16} , $\text{CaCO}^{18}\text{O}_2^{16}$, $\text{CaCO}_2^{18}\text{O}^{16}$, and CaCO_3^{18} the following equation holds,

$$\frac{(\text{CaCO}_2^{16}\text{O}^{18})(\text{CaCO}^{16}\text{O}_2^{18})}{(\text{CaCO}_3^{16})(\text{CaCO}_3^{18})} = 9 \quad (36)$$

where 9 is the symmetry number of CaCO_3^{16} , 3, multiplied by the symmetry number of CaCO_3^{18} , also 3.

Experimental confirmation of the results of the statistical-mechanical calculations has been satisfactory; for example, McCrea (63) calculated a variation of -2.75×10^{-5} per cent O^{18} per degree Centigrade in calcium carbonate precipitated at 31.5°C . Figure 11 illustrates the experimentally observed changes in percentage of O^{18} from the standard as a function of temperature in samples of calcium carbonate precipitated from water; the slope of the line is -2.94×10^{-5}

per cent O^{18}/O^{16} , a number that is considered in good agreement with the above.

Some of the scientific and technical consequences of the not wholly random distribution of the oxygen isotopes have already been mentioned, such as the use of chemical exchange reactions for the large-scale fractionation of the isotopes. The separation of isotopes as the result of rate processes in numerous chemical reactions is an analogous effect. Slight separations of the isotopes would be expected to occur in nature, so that the distribution and abundance

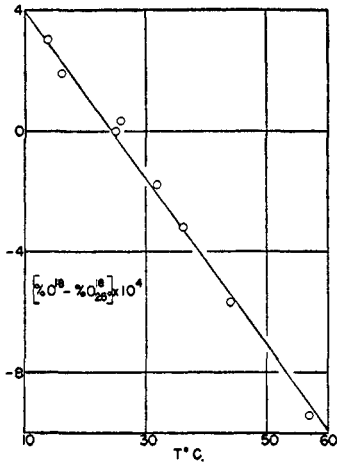


FIG. 11

FIG. 11. Variation in the percentage of O^{18} in the oxygen of calcium carbonate precipitated at the temperature in question.

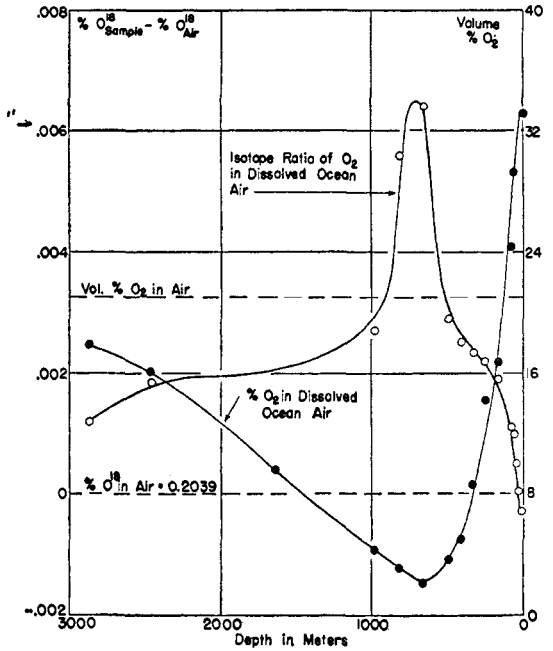


FIG. 12

FIG. 12. Variation in the percentage of O^{18} in the oxygen of air dissolved in Pacific Ocean water as a function of depth.

of the oxygen isotopes would be expected to vary slightly from one source to another. This is equivalent to slight variations in the atomic weight of oxygen. Both of these phenomena will now be described.

VI. VARIATIONS IN NATURE OF THE NATURAL ABUNDANCE OF THE OXYGEN ISOTOPES

A. Variations in the natural waters and ices of the world

Kirshenbaum (55) has recently reviewed variations in the isotopic abundance of deuterium and O^{18} in the waters of the world. In making sensitive measurements of the relative densities of the waters concerned, the density measurements do not serve to distinguish between variations in the O^{18} or deuterium contents. Such separate studies can be done directly with a mass spectrometer

or indirectly by measuring both the density and the refractive index of the waters concerned, as described in the review by Kirshenbaum (55). Conclusions regarding variations in the isotopic compositions of the waters of the world may be summarized as follows:

1. In the distillation of water both deuterium and O^{18} will tend to concentrate in the residue; hence fresh water, formed presumably by the evaporation and condensation of ocean waters, should contain a slightly smaller percentage of deuterium and O^{18} than does ocean water. The conclusion by Kirshenbaum after studying many results is that fresh water contains 0.0002 mole per cent less deuterium (equivalent to 0.22 γ in density difference) and 0.0014 mole per cent less O^{18} (equivalent to 1.6 γ in density difference).

2. As the freezing of water results in ice having a greater O^{18} content and a smaller deuterium content than the original water, according to the data of the Soviet workers Teis and Florensky (quoted by Kirshenbaum (55)), one would expect the water from arctic oceans near large ice masses to exhibit alterations in the O^{18} and deuterium content. Such alterations were discovered, again by Soviet scientists; for example, increases in density as high as +4.3 γ , due to increase in the O^{18} content, were observed. Depending on the source, the deuterium content showed increases as high as +2.4 γ and decreases as low as -1.7 γ .

3. Kirshenbaum concludes that more work needs to be done, particularly on samples of water whose isotopic composition has been studied with the mass spectrometer and whose density has also been measured. Such investigations should also be paralleled by laboratory studies of alterations in isotopic composition due to exchanges promoted by ultraviolet light, electric discharge, etc. A small beginning along the line of this last suggestion has been made by Roake and Dole (90).

B. Atmospheric and photosynthetic oxygen

Shortly after Urey and Greiff (109) published their theoretical predictions regarding the equilibrium constants of isotopic exchange reactions, the author (21, 22, 102) discovered that the O^{18} content of atmospheric oxygen was greater by about 0.005 mole percentage units (6.6 γ) than the oxygen of water.⁴ Morita and Titani (76) independently made the same observation. This difference, sometimes called the Dole Effect (53), was in the direction predicted by Urey and Greiff but somewhat greater than the calculated separation. Using more recent values for the equilibrium constant of the water-oxygen isotopic exchange equilibrium, the author calculated (23) that of the difference, 0.005 per cent of O^{18} , only 0.001 per cent or one-fifth of the total could be explained by the equilibrium exchange if the equilibrium is established between atmospheric oxygen and fresh water. If the equilibrium involves atmospheric oxygen and ocean water, then 0.002 per cent, or two-fifths of the difference, is accounted for.

⁴ Part of this increase in the density of water made from atmospheric oxygen as compared to Lake Michigan water may be due to an increase in the percentage of O^{17} . The author has assumed that about one-tenth of the increase is due to the presence of O^{17} in calculating the result, 0.005 per cent.

Kamen and Barker (53) have reviewed the problem of the isotopic composition of atmospheric oxygen.

Roake and Dole (90) suggested that the enhanced O^{18} content of the atmosphere may be the result of the isotopic exchange equilibrium established between carbon dioxide and water (reaction 3 of table 9), followed by an irreversible and random exchange of oxygen atoms between carbon dioxide and oxygen. The latter exchange could presumably be brought about by the action of the intense ultraviolet light of the stratosphere. Dole and Roake found that oxygen atoms would exchange between carbon dioxide and oxygen but not between water and oxygen as mixtures of these gases streamed through an electric discharge at low pressures.

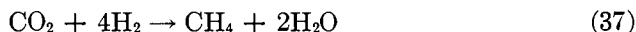
Another possibility, although a rather far-fetched one, is that oxygen, enhanced in O^{18} in deep ocean water to an extent of +0.006 mole per cent of O^{18} , greater than the required value of +0.005, as discovered by Rakestraw, Rudd, and Dole (88), somehow or other is returned to the atmosphere. Figure 12 illustrates the variation of the percentage of O^{18} in air dissolved in the Pacific Ocean as a function of depth.

As atmospheric oxygen presumably arises mostly if not entirely from the photosynthesis reaction, it becomes of great interest to examine the isotopic composition of oxygen liberated on photosynthesis in controlled laboratory experiments. This has been done by Ruben, Randall, Kamen, and Hyde (95), Vinogradov and Teis (112), Holt and French (47), and Dole and Jenks (25), with the general conclusion that the liberated oxygen has almost the isotopic composition of the water entering into the photosynthesis reaction. Dole and Jenks concluded that the isotopic composition of the oxygen corresponded to the value calculated by Urey (107) for isotopic exchange equilibrium between oxygen and water. These results demonstrate first, that there is some process or processes occurring in nature which enhance the O^{18} content of atmospheric oxygen beyond the equilibrium value, and second, that there is no mechanism in nature by which the isotopic exchange equilibrium can be reestablished between free oxygen and water.

C. Oxygen in carbonate rocks and the use of ratios of oxygen isotopes in estimating the temperatures of prehistoric oceans

Because of the significant fractionation of the oxygen isotopes between carbon dioxide and water, a similar fractionation would be expected between water and carbonate rocks. The calculations of McCrea (63), whose results are illustrated in figure 11, have already been mentioned.

Dole and Slobod (28) investigated carbonates in 1939. They recovered carbon dioxide from the carbonates both by treatment with hydrochloric acid and by heating crushed samples of the rocks in a furnace. The carbon dioxide was then reduced according to the reaction



and the density of the resulting water was measured. Nearly deuterium-free

hydrogen was used, as exploratory experiments demonstrated a fractionation of the hydrogen isotopes in reaction 37. Their results are summarized in table 10, where γ is the increase in density of the sample water (in parts per million) over that of purified Lake Michigan water.

No variation between the various samples greater than 1 γ could be detected, leading Dole and Slobod to conclude that there had been no significant change in the isotopic composition of the oxygen of carbonates over many millions of years. This last statement is based on the assumption that the oxygen of the rocks investigated was identically the original oxygen at the time of precipitation of the rocks.

McCrea (63) has published the results of an extensive study of the isotopic chemistry of the carbonates and the use of the data in establishing a paleotemperature scale. McCrea also found, in agreement with the data of table 10, that the O^{18} content of carbon dioxide liberated by acid from carbonates was slightly greater than the O^{18} content of carbon dioxide liberated by pyrolysis.

TABLE 10
Variations in the isotopic composition of oxygen from carbonate rocks

NO.	ROCK	ESTIMATED AGE	METHOD OF EVOLUTION OF CARBON DIOXIDE	γ
		<i>years</i>		
1.....	Grenville marble	1.2×10^6	HCl	9.2
2.....	Grenville marble	0.5×10^6	Pyrolysis	7.9
3.....	Niagara dolomite	0.5×10^6	HCl	9.1
4.....	Pennsylvania limestone	0.5×10^6	HCl	9.8
5.....	Clam shells	1	HCl	10.0

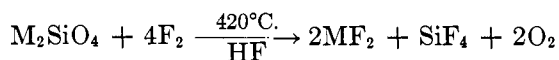
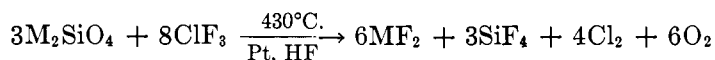
He found that the acid treatment (95 per cent phosphoric acid was used) gave carbon dioxide of much more reproducible O^{18} content than the thermal method. For example, he detected a difference of about 0.0005 unit in the percentage of O^{18} in carbon dioxide liberated thermally from powdered rock and rock particles about 0.1 g. each in weight. The powdered sample gave the higher abundance of O^{18} . McCrea's chief interest was in the variation in the O^{18} content of the carbonate as a function of the temperature of the aqueous solution at the time of precipitation of the carbonate in order to establish a "paleotemperature" scale. He did not determine the absolute value of the O^{18} percentage in carbonates. Urey (108) conceived the possibility of estimating the temperature of prehistoric oceans through a measurement of the isotopic composition of the oxygen in the rocks, followed by a comparison with a calibrated curve such as that illustrated in figure 11. Urey, Lowenstam, Epstein, and McKinney (110) have discussed their measurements and their geological significance, while Epstein, Buchsbaum, Lowenstam, and Urey (30) have emphasized the necessity of knowing the O^{18} percentage in the water from which the carbonates were precipitated. It is shown that, when this last factor is taken into account, good agreement is obtained from different specimens. Urey and coworkers hope to develop a phosphate

temperature scale which, if it yields a different equation relating O^{18} percentage and temperature, will make possible the elimination of the uncertainties regarding the O^{18} percentage of the water phase.

Baertschi (2) has studied the relative abundance of O^{18} and C^{13} in a number of carbonate rocks of geological interest.

D. Oxygen in silicate rocks and iron oxide ores

Baertschi and Silverman (4) have investigated the abundance of O^{18} in the oxygen of silicate rocks. They liberated the oxygen by two methods, one using chlorine trifluoride with hydrogen fluoride and platinum as catalyst and the other using fluoride with hydrogen fluoride:



The second method was shown to give more reproducible values. Unfortunately they published their data only in terms of differences between the O^{18} per cent of the sample and that of a standard source of oxygen; since the O^{18} percentage of the latter was not specified, no conclusions regarding the source of the oxygen in the silicates can be gained.

Dole and Slobod (28) reduced iron oxide ores with nearly deuterium-free hydrogen and measured the density of the resulting water. After isotopic correction for the hydrogen, the density of the water was the same as that of purified Lake Michigan water; thus, it was demonstrated that the oxygen of the iron oxide ores came from water and not from atmospheric oxygen.

Hall and Hochanadel (40) similarly found that the oxygen of cuprite (Cu_2O) has the same isotopic composition as the oxygen of water.

VII. THE ATOMIC WEIGHT OF OXYGEN

We have seen that the proportion of O^{18} in the element oxygen increases a little as one goes from pure fresh water, to ocean water, to atmospheric oxygen, and to the oxygen of carbonate rocks. This signifies, of course, that slight variations exist in the atomic weight of oxygen between these various substances. If we suppose that the atomic weight of oxygen of Atlantic Ocean Water is 16.00000 exactly, then the atomic weight of oxygen in the above-mentioned compounds will have the values given in table 11.

Evidently the atomic weight of oxygen is not precisely 16.00000 and has no precise significance unless the source of the oxygen is specified.

Because of the variation of the O^{18} percentage in the oxygen of different waters, it is recommended that the oxygen of the atmosphere be taken as the standard of reference. Dole and Rudd (27) have studied samples of air from many parts of both North and South America and have found no observed differences in O^{18} percentage greater than 0.00015 percentage unit. This corresponds approximately to 0.15 γ in water density or to about one part in ten million in the atomic

weight of oxygen. For this reason the author believes that atmospheric oxygen would be the best standard of reference in atomic weight determinations if the weight of oxygen continues to be the basis of the atomic weight scale. Ultimately, refinements in measurements of isotopic abundance will undoubtedly make possible the discovery of variations in the O^{18} percentage of atmospheric oxygen from different localities, so that even this standard of oxygen for the atomic weight scale will prove to be unsatisfactory. The soundest plan for a change in the chemical standard of atomic weights would be to choose the weight of an element such as fluorine or sodium, which has only one stable isotope, as the standard, or of the pure isotope protium, but to define the weight so that at-

TABLE 11
The atomic weight of oxygen in oxygen from various sources

SOURCE	ATOMIC WEIGHT
Atlantic Ocean water	16.00000
Lake Michigan water	15.99998
Air	16.00012
Carbonate rocks	16.00015
Carbon dioxide (at 0°C. in the presence of water)..	16.00019

mospheric oxygen is as close to 16.00000 as possible. This was the recommendation made by the author in 1936 (22).

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