The Relative Atomic Weight of Oxygen in Water and in Air A Discussion of the Atmospheric Distribution of the Oxygen Isotopes and of the Chemical Standard of Atomic Weights

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the theory necessary for treating such cases will be given in a subsequent paper.

CONCLUSION

It has been shown that the rotational energy levels of a semirigid asymmetric polyatomic molecule are given by the Wang equation for the rigid rotator with three "effective moments of inertia" if no accidental degeneracy occurs, and if centrifugal stretching terms are small enough to neglect. If these conditions are not fulfilled, the Wang equation may not apply.

In conclusion, we should like to thank Professor J. H. Van Vleck for several important suggestions.

The Relative Atomic Weight of Oxygen in Water and in Air

A Discussion of the Atmospheric Distribution of the Oxygen Isotopes and of the Chemical Standard of Atomic Weights

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(Received February 11, 1936)

A difference in the density of water made from atmospheric oxygen plus tank hydrogen and aqueous oxygen plus tank hydrogen is interpreted as indicating that the atomic weight of oxygen in the air is 0.000108 atomic weight units heavier than the oxygen of Lake Michigan water. This observation finds experimental confirmation in the work of several other investigators and can be applied in certain cases to the reinterpretation of already existing data, clarifying several anomalous and inexplicable effects. The difference in atomic weights can be accounted for quantitatively by assuming that an isotopic exchange equilibrium of the type discussed by Urey and Greiff occurs at a temperature of $-50°C$ in the lower regions of the stratosphere. The distribution of oxygen isotopes in the atmosphere is calculated by means of the usual hypsometric equation, but the separation due to gravity is not sufficient to explain quantitatively the excess atomic weight of atmospheric oxygen. The chemical and physical standards of atomic weights are discussed and the proposal is made that a single standard based on the mass of a pure isotope such as protium be adopted.

THE original discovery of isotopes gave rise to a considerable number of researches designed to test the constancy of chemical atomic weights of elements from a variety of natural sources, but no variation in the weights was observed, leading Aston,[1] for example, to conclude "that the evolution of the elements must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and, since we know of no natural process of separation, has remained constant ever since." However, shortly after the discovery of deuterium, slight differences in the density of water from many sources were observed;[2] these differences were smaller than the experimental errors involved in previous atomic weight determinations, which explains why they had not been noted hitherto, but to the present time, however, no one has determined whether these differences in density are caused by variations in the isotopic composition of hydrogen or oxygen, the differences being usually attributed to variations in the abundance of deuterium.

Since the atomic weight of oxygen is the basis for the chemical atomic weight scale, it is especially interesting and important to know whether the isotopic ratios of oxygen in different compounds are the same. Manian, Urey and Bleakney[3] in a careful research investigated the relative abundance of the oxygen isotopes in

[1] F. W. Aston, *Mass-Spectra and Isotopes* (Edward Arnold and Company, London, 1933), p. 188.
[2] For a review see H. C. Urey and G. K. Teal, Rev. Mod. Phys. **7**, 34 (1935).

[3] S. H. Manian, H. C. Urey and W. Bleakney, J. Am. Chem. Soc. **56**, 2601 (1934). This paper contains references to earlier work. See also W. Bleakney and J. A. Hipple Jr., Phys. Rev. **47**, 800 (1935).

stone meteorites and found no variations, but their mass-spectrograph method was not as sensitive as the density of water method and could not demonstrate differences of the order of a few p.p.m. Smythe[4] also using the mass-spectrograph method determined the ratio $[O^{16}]/[O^{18}]$ in oxygen evolved from lead dioxide. Since his ratio was somewhat lower than that calculated from band spectra data, he postulated that there might have been a separation of the isotopes of oxygen in the formation of the lead dioxide, but Taylor and Gould[5] found no difference in the ratio of $[O^{16}]/[O^{18}]$ between the first and last fraction of oxygen evolved from lead dioxide. Urey and Greiff[6] calculated theoretically that in many chemical reactions isotopic exchanges could occur at equilibrium which could give rise to a slight variation in the atomic weights of the elements involved, and they stated that their calculations showed that the accuracy with which chemical atomic weights could be determined was limited by these isotopic exchanges. Weber, Wahl and Urey[7] proved experimentally that the bringing of carbon dioxide into equilibrium with water resulted in a concentration of O^{18} in the carbon dioxide to just the extent calculated by Urey and Greiff. They did not investigate, however, any natural compounds to see if these isotopic exchanges took place in nature. Furthermore, the author has shown[8] that it is possible to carry out certain chemical reactions involving water and carbon dioxide without any measurable isotopic exchange taking place.

In the investigation of benzene for its deuterium content and of Nevada hot springs water for its deuterium content, data were obtained by the author which made possible a calculation of the relative atomic weight of oxygen in Lake Michigan water and in air. It was found that water made from atmospheric oxygen plus tank hydrogen was 4.6 p.p.m. heavier than water made from aqueous oxygen plus tank hydrogen. This conclusion has

already been communicated[9] in a brief note, but the value of 4.6 p.p.m. given there is uncertain because of the following facts: First, Linde oxygen was used instead of atmospheric oxygen, which made necessary the introduction of a correction factor; second, the hydrogen used was not from the same tank in each case and although the two hydrogens were compared, it is felt that this introduces the possibility of another experimental error; third, the necessary electrolyses were carried out a month or so apart instead of consecutively, thereby possibly allowing a change in the electrode surface which would alter the fractionation factor; and finally the density measurements were made weeks apart with a possible although not likely change in the method in the interim. It was concluded that a much more reliable value for the difference in the atomic weights of oxygen from the two sources could be obtained by carrying out a research with the sole purpose in view of measuring this difference.

EXPERIMENTAL

Two series of experiments were carried out using a slightly different electrolytic technique in the two cases. In both series oxygen of the air was converted into water by burning air with excess tank hydrogen over a copper catalyst. Excess hydrogen was used in order to eliminate any possible separation of the oxygen isotopes. Since the hydrogen of this water was different in atomic weight from the hydrogen of normal water, it was necessary to separate the oxygen in these two waters from their hydrogen by electrolysis and to convert both oxygens again to water by using hydrogen from the same tank. In this way the density of water made from tank hydrogen plus oxygen originally from the air could be compared with the density of water made from the same tank hydrogen plus oxygen originally from Lake Michigan water in order to compare the atomic weight of oxygen from the two sources. Two electrolysis cells were constructed so that they could be operated until a residue of about 40 cc remained in each cell. The electrodes were made of nickel and the electrolyte was 4 percent sodium hydroxide.

[4] W. R. Smythe, Phys. Rev. **45**, 299 (1934).

[5] H. S. Taylor and A. J. Gould, J. Am. Chem. Soc. **56**, 1823 (1934).

[6] H. C. Urey and Lotti J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

[7] L. A. Weber, M. H. Wahl and H. C. Urey, J. Chem. Phys. **3**, 129 (1935).

[8] M. Dole, J. Am. Chem. Soc. in press.

[9] M. Dole, J. Am. Chem. Soc. **57**, 2731 (1935).

The hydrogen from the electrolysis was rejected while the oxygen passed first over a hot copper oxide tube to remove traces of hydrogen, then through a soda-lime drying tower, and finally over hot copper where it was converted to water with tank hydrogen. The hydrogen was passed through roughly in an equivalent amount. A separation of the isotopes of oxygen or of hydrogen may have occurred at this point although experiments described elsewhere indicated that any such separation is negligible.[8] If the same separation occurred in all the experiments, no error in the final result would be admitted.

Methods of purifying the water and of measuring the density have already been described.[8]

Data for the electrolyses and densities are given in Table I. Volumes of water are expressed in cc, temperatures in degrees C, and densities in p.p.m. The first horizontal column under series I gives the total water added to the electrolysis cell in the normal water and air water experiments, the second horizontal column the number of cc of water collected in two fractions by combining the cell oxygen with tank hydrogen in the

normal water and air water experiments, the third horizontal column the volume of cell residue in the two electrolyses, the fourth horizontal column the water lost in the electrolysis process. Density measurements were made on the first and second fraction of the water obtained in the electrolysis of the normal and air waters, respectively; these results are given in terms of temperature differences between the temperature of floating equilibrium of the totally immersed float for ordinary water and the water under investigation in the horizontal column entitled "temperature of floating equilibrium." The horizontal column labeled "temperature difference between corresponding air and normal water" gives first, the difference between the temperature of floating equilibrium of the first electrolytic fraction of air water and the first electrolytic fraction of normal water, and second, the corresponding difference between the second fraction of the two waters. It should be noted that although the densities of the first and second fractions of each water are different, as is to be expected, nevertheless the difference between the first fraction in each case and the difference between the second fraction in each case are equal. The data for series II have similar meanings although here two separate electrolyses were carried out instead of taking two fractions of water during one electrolysis in each case.

In the first series all the normal water was electrolyzed and then all the air water. In the second series the two electrolyses of the normal water alternated with the two of air water. The results of the two series agree within the accuracy of the temperature measurements, the accepted difference in density between water made from oxygen of the air and water made from aqueous oxygen being 6.0 ± 0.6 p.p.m. The reliability of the data can be tested by calculating the fractionation factor for the oxygen isotopes, α_0. Before electrolysis the air water was 3.9 p.p.m. less dense than normal and after electrolysis it was 5.9 p.p.m., less dense than normal, the difference -2.0 p.p.m. being due to the electrolytic fractionation of the oxygen isotopes since the hydrogen was tank hydrogen in the two waters. A change in density of 2 p.p.m. in the water on electrolysis is equivalent to a value of α_0 equal to 1.009 in close agreement with

TABLE I. *Electrolysis and density data.*

| | SERIES I | | | |
| | NORMAL WATER | | AIR WATER | |
	I	II	I	II
Water added to cell		1150		1200
Water collected	405		347	450	470
Cell residue		120		150
Water lost in process		278		130
Temperature of floating equilibrium	(−0.054) −0.051	−0.047 −0.046	−0.026 −0.025	−0.020 −0.020
Temperature difference between corresponding air and normal water	(0.028) 0.026	0.027 0.026		
Av. Density difference	0.026 6.0			

| | SERIES II | | | |
| | NORMAL WATER | | AIR WATER | |
	I	II	I	II
Water added to cell	600	610	600	590
Water collected	450	465	450	440
Cell residue	60	66	70	68
Water lost in process	90	79	80	82
Temperature of floating equilibrium	−0.049 −0.049	−0.050 −0.049	−0.024 −0.022	−0.025 −0.022
Temperature difference between corresponding air and normal water	0.025 0.027	0.025 0.027		
Av. Density difference	0.026 6.0	0.026		

the value 1.008 given by Johnston[10] and the value 1.0088 given by Selwood, Taylor, Hipple and Bleakney.[11]

A difference of density of 6.0±0.6 p.p.m. due to oxygen in the water is equivalent to a difference in the atomic weight of oxygen in air and in water of 0.000108±0.00001 atomic weight units, the oxygen in the air being the heavier.[12]

EXPERIMENTAL CONFIRMATION IN WORK OF OTHER INVESTIGATORS, AND APPLICATIONS

The above conclusion that the atomic weight of oxygen from air is slightly greater than that from water is confirmed qualitatively by data already published by a number of other investigators. Hall and Johnston[13] burned oxygen from normal water with tank hydrogen and air with the same hydrogen. The latter water was denser than the former by about 4 p.p.m. in qualitative agreement with our finding of 6 p.p.m. However, they burned the oxygen in large excess of hydrogen and the hydrogen in a large excess of air, so that not too much reliance on their figure of 4 p.p.m. can be given. Greene and Voskuyl[14] burned tank hydrogen with air obtaining water heavier than normal. It is difficult to see why this water is heavier than normal unless it is caused by the oxygen of the air being denser than normal. Washburn, Smith and Smith[15] burned commercial electrolytic hydrogen which they state should be lighter than normal with air obtaining water of normal density. If the hydrogen is lighter than normal, then the oxygen of the air must be heavier than that of normal water.

Many investigators (including the author) have burned organic compounds with oxygen from the air, interpreting the excess density of

TABLE II. *Recalculation of the data of Washburn, Smith and Smith*. Changes in density (in p.p.m.) on electrolysis.

NUMBER OF LITERS COLLECTED	RECOMBINED GASES	CELL O WITH "NORMAL" H (W.S. and S.)	CELL H WITH "NORMAL" O (W.S. and S.)	CELL O WITH NORMAL H CORRECTED	CELL H WITH NORMAL O CORRECTED
1	−20.5	−13 2	−7.8	−7.2	−13.8
10	−17.1	−11.0	−6.2	−5.0	−12.2
20	−14.8	−10.5	−5.6	−4.5	−11.6
30	−14.1	−8.0	−5.5	−2.0	−11.5
50	−10.8	−6.3	−3.6	−0.3	−9.6
75	−7.3	−5.0	−2.0	+1.0	−8.0
105	−5.0	−3.0	− .1	+3.0	−6.1
124	−3.1	−2.0	+ .1	+4.0	−5.9
150	−1.5	−1.1	+ .2	+4.9	−5.8

the resulting water as demonstrating an excess concentration of deuterium in the organic compound. Such data will now have to be reinterpreted.*

Washburn, Smith and Smith[16] have presented some interesting data concerning the electrolytic separation of the isotopes of both oxygen and hydrogen. They first tested the atomic weight of their commercial (electrolytic) hydrogen by burning it with air obtaining water of normal density. They concluded that their hydrogen was normal, but as stated above, their hydrogen must have been lighter than normal since the oxygen of the air is heavier than normal. (By "normal" is meant the same as in normal water.) A correction of about +6 p.p.m. (assuming that their water is the same in density as Lake Michigan water) should be applied to their data labeled "Cell O with normal H" and a correction of −6.0 p.p.m. should be applied to their data labeled "Cell H with normal O." Such corrections completely alter the nature of their results as can be seen from Table II where their original data are tabulated along with the new corrected data. The greater decrease in density of the different waters in the first stages of electrolysis is now seen to be due to the hydrogen fractionation instead of as formerly to the oxygen fractionation.[17] This is a much more

[10] H. L. Johnston, J. Am. Chem. Soc. **57**, 484 (1935).

[11] P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr. and Walker Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).

[12] Dr. E. R. Smith has kindly pointed out to us that the difference in the isotopic composition of the air oxygen and water oxygen might not be the same after electrolysis as before because of a greater absolute electrolytic separation in the case of the air oxygen. On calculation, however, this error was shown to be only 0.1 p.p.m. because of the low value of the fractionation factor for oxygen and therefore negligible.

[13] W. H. Hall and H. L. Johnston, J. Am. Chem. Soc. **57**, 1515 (1935).

[14] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1649 (1934).

[15] E. W. Washburn, E. R. Smith and F. A. Smith, Bur. Standards J. Research **13**, 599 (1934).

* This has been done by the author, J. Am. Chem. Soc., in press.

[16] E. W. Washburn, E. R. Smith and F. A. Smith, Bur. Standards J. Research **13**, 599 (1934); E. R. Smith and M. Wojciechowski, ibid. **15**, 187 (1935).

[17] The author, M. Dole, J. Am. Chem. Soc., **57**, 2731 (1935) incorrectly stated that Washburn, Smith and Smith concluded that the oxygen isotopes fractionate more rapidly than those of hydrogen on electrolysis. They had concluded that the initial change of density of the water on electrolysis was due more to the oxygen than to the hydrogen, not that $\alpha O > \alpha H$.

reasonable conclusion. However, a most surprising observation is made when one examines the density of the cell-O-with-normal-hydrogen-water in the later stages of electrolysis. *The atomic weight of the oxygen now coming off is greater than that of the water being added!* It is difficult to explain this if we assume the correctness of the experimental measurements. It appears as if the surface condition of the electrodes must have changed during the electrolysis so that instead of the electrolytic fractionation being favored in the electrode reaction, it is the equilibrium reaction of Urey and Greiff that is being favored.*

Selwood, Taylor, Hipple and Bleakney[18] have calculated the fractionation factor for the oxygen isotopes from Washburn, Smith and Smith's data to be 1.062 for the first stage of electrolysis. This figure is known to be too high, but a calculation based on the corrected data of Table II yields the factor 1.03 which is more reasonable although still not in complete agreement with the factor given by Selwood, Taylor, Hipple and Bleakney. A recalculation of the oxygen fractionation factor from the data of Greene and Voskuyl[19] gives α_0 equal to 1.013, a value close to that of Selwood and co-workers and to that of Johnston (1.01).[20]

THEORETICAL

There are numerous postulates that one can make explaining the observed difference between the atomic weights of oxygen in air and in water. Smythe[21] suggests that "most of the oxygen on the earth has been used in oxidizing the earth's crust and only a small fraction of one percent remains in the air. It is possible that some concentration, probably of the O^{16}, has taken place in this process so that the ratio $[O^{16}]/[O^{18}]$ for air is above average." A more reasonable explanation is that the O^{16} reacted more rapidly with the metals and with hydrogen than did O^{18} so that it is the O^{18} that is concentrated in the air. Un-

fortunately this hypothesis cannot be tested quantitatively not only because of the lack of adequate theory, but also because there is no reason to suppose that the atomic weight of atmospheric oxygen would remain constant since the time that the atmosphere was first formed. It is more plausible to believe that there are processes going on at the present time which can account for a natural difference in the isotopic ratios. These processes may be divided into two groups, first, those occurring on the earth's surface and those occurring in the upper regions of the earth's atmosphere.

Urey and Greiff[6] calculated from spectroscopic and vapor pressure data the O^{18} enrichment factor for the equilibrium

$$2H_2O^{18}(l)+O_2{}^{16}\rightleftarrows 2H_2O^{16}(l)+O_2{}^{18} \qquad (1)$$
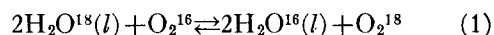
to be 1.006 at 25°C and 1.010 at 0°C. If the assumption is made that oxygen can be brought into equilibrium with water,[22] by some process occurring on the earth's surface such as contact catalysis or the catalyzing action of plant or animal life bringing the oxygen into equilibrium with carbon dioxide and hence with water, then we should expect from equilibrium (1) that the oxygen of the air would be richer in O^{18} than the oxygen of ocean water to the extent of 1.3 p.p.m. in terms of water density at 25° and 2.2 p.p.m. at 0°C. Since we find 4.4 p.p.m.,[23] it is evident that any such equilibrium as (1) occurring at normal temperatures fails to account quantitatively for the observed effect.

Professor Urey[24] has suggested that perhaps the oxygen is brought into equilibrium with water through the action of solar ultraviolet radiation in the upper regions of the atmosphere. Assuming that such an effect is most pronounced in the stratosphere, or isothermal portion of the atmosphere, at a height of 20 kilometers where the ultraviolet radiation produces the greatest

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* The positive values show that the oxygen coming off is heavier than the oxygen being added, not that it is heavier than the oxygen in the electrolyte.

[18] P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr. and W. Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).

[19] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1649 (1934).

[20] H. L. Johnston, J. Am. Chem. Soc. **57**, 484 (1935).

[21] W. R. Smythe, Phys. Rev. **45**, 299 (1934).

[22] There is, roughly, 10^3 times more oxygen in the water on the earth's surface than in the whole atmosphere, as can be calculated from the data given by Longwell, Knopf and Flint, *A Textbook of Geology* (John Wiley and Sons, Inc., N. Y., 1932) and by Humphreys, *Physics of the Air* (McGraw-Hill Book Co., New York, 1929), p. 76, hence we can assume that the isotopic ratio in water remains constant as the above equilibrium is set up.

[23] Correcting our value of 6.0 p.p.m. for the difference in density of ocean water and fresh water due to a difference in the isotopic composition of oxygen yields 4.4 p.p.m., *vide infra.*

[24] Private communication.

density of ozone,[25] it is possible to calculate the fractionation factor since the temperature for this part of the stratosphere is known to be $-50°C$ or $223°A$.[26] The fractionation fraction, α', for the equilibrium

$$2H_2O^{18} + O_2^{16} \rightleftarrows O_2^{18} + 2H_2O^{16} \qquad (2)$$
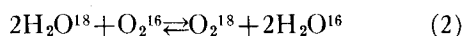
is given by the equation

$$(\alpha')^2 = K = f_{O_2^{18}} \cdot f^2_{H_2O^{16}} / f_{O_2^{16}} \cdot f^2_{H_2O^{18}}, \qquad (3)$$

where

$$f_{O_2^{18}}/f_{O_2^{16}} = 1.3424 \exp (129.78/2T) \qquad (4)$$

and

$$f_{H_2O^{18}}/f_{H_2O^{16}} = 1.1813 \exp (20.698/T) \qquad (5)$$

on inserting the numerical constants as given by Urey and Greiff, and omitting terms negligible at $273°A$ and below. Urey and Greiff state that their equation is valid at ordinary temperatures and above, but it should be also nearly valid at $223°A$ inasmuch as the water and oxygen molecules must still retain vibrational and rotational energies at this temperature. At $223°A$ α' is 1.034, but this value must be divided by 1.014 to obtain the fractionation factor for equilibrium (1); we are assuming, therefore, that the water which enters into equilibrium (2) in the stratosphere eventually diffuses to the earth's surface and gets into equilibrium with the water of the ocean. The calculated over-all fractionation factor for the equilibrium

$2H_2O^{18}$(ocean) $+O_2^{16}$(stratosphere)

$\rightleftarrows 2H_2O^{16}$(ocean) $+O_2^{18}$(stratosphere) (6)
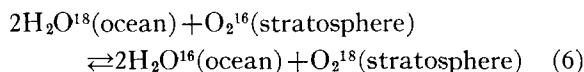
is, therefore, 1.020 or 4.4 p.p.m. in terms of water density. To this a correction of -0.2 p.p.m. should be applied to account for the fact that the equilibrium constant of the equilibrium

$$O_2^{16} + O_2^{18} \rightleftarrows 2O^{16}O^{18} \qquad (7)$$
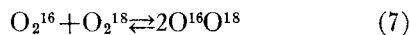
is equal to 3.988 instead of 4.000 at $223°A$;[27] the final value being 4.2 p.p.m. in terms of water density.

But in the experimental work presented above the atomic weight of oxygen of the air was compared with the atomic weight of oxygen in Lake Michigan water and not that of the ocean; a correction must be applied, therefore, to allow for the difference in the atomic weight of oxygen in Lake Michigan water and ocean water. Gilfillan[28] found on an average 2.3 p.p.m. excess density of Atlantic Ocean water over Cambridge, Mass. tap water, Greene and Voskuyl[29] found 1.8 p.p.m. and Wirth, Thompson and Utterback[30] found 1.47 p.p.m. for the average density difference between several samples of Pacific Ocean water and water of the Cedar River, State of Washington. Lake Michigan water has the same density as Cambridge, Mass., tap water,[31] but a comparison of Lake Michigan water with the State of Washington water has not yet been carried out to the author's knowledge. Assuming that they are identical, and averaging the three density differences given above, the figure 1.9 p.p.m. results for the density difference between purified ocean and fresh water. Of this difference we shall assume that 1.6 p.p.m.[28] is due to the difference in isotopic composition of the oxygen. We should add, therefore, approximately 1.6 p.p.m. to the value of 4.2 p.p.m., obtaining 5.8 p.p.m. as the calculated density difference between water composed of atmospheric oxygen and the oxygen of Lake Michigan water. This value agrees with the observed data given above within the experimental error, and indicates that the Urey and Greiff isotopic exchange equilibrium can account quantitatively for the effect providing the equilibrium is brought about at a sufficiently cold temperature. However, there may be isotopic exchanges occurring at warmer temperatures on the earth's surface which would tend to lower the value of 5.8 p.p.m. calculated for $-50°C$, so we should expect the observed value to be somewhat less than 5.8 p.p.m. This calculation indicates, therefore, that isotopic exchanges occur to a greater extent in the lower regions of the stratosphere than they do on the earth's surface.

In the isothermal portion of the atmosphere, the stratosphere, there are no winds or tempera-

[25] Private communication from Dr. O. R. Wulf. See also R. W. Ladenburg, J. Opt. Soc. Am. 25, 259 (1935).
[26] R. W. Ladenburg, J. Opt. Soc. Am. 25, 259 (1935).
[27] In calculating the equilibrium constant of (7) $\bar{\omega}O^{16}O^{18}$ was taken as 1540.6, $I_{O^{18}O^{16}}/I_{O_2^{16}}$ as 1.0598 and $I_{O_2^{18}}/I_{O^{16}O^{18}}$ as 1.0616.

[28] E. S. Gilfillan, Jr., J. Am. Chem. Soc. 56, 406 (1934).
[29] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. 56, 1649 (1934).
[30] H. E. Wirth with T. G. Thompson and C. L. Utterback, J. Am. Chem. Soc. 57, 400 (1935).
[31] Private communication from Dr. C. H. Greene.

TABLE III. *Calculated partial pressures in millimeters of Hg, of the isotopes of molecular oxygen and water in the stratosphere.*

Altitude (km)	$p_{O_2^{16}}$	$p_{O^{16}O^{18}}$	$p_{O^{18}O^{18}}$	$p_{H_2O^{16}}$	$p_{H_2O^{18}}$	α_{O_2}	α_{H_2O}
11	35.039	.14016	1.4×10^{-4}	1.677×10^{-2}	3.226×10^{-5}	1.000	1.000
20	7.3780	.02675	2.4×10^{-5}	6.981×10^{-3}	1.218×10^{-5}	1.103	1.102
30	1.3066	4.248×10^{-3}	3.5×10^{-6}	2.637×10^{-3}	4.130×10^{-6}	1.230	1.228
50	.040981	1.071×10^{-4}	7.0×10^{-8}	3.761×10^{-4}	4.745×10^{-7}	1.531	1.524
70	1.285×10^{-3}	2.701×10^{-6}	1.4×10^{-9}	5.365×10^{-5}	5.451×10^{-8}	1.903	1.892
90	4.031×10^{-5}	6.811×10^{-8}	2.9×10^{-11}	7.653×10^{-6}	6.263×10^{-9}	2.368	2.347
110	1.264×10^{-6}	1.717×10^{-9}	5.9×10^{-13}	1.092×10^{-6}	7.195×10^{-10}	2.944	2.918

ture gradients of any moment, so it is believed that the gases of the atmosphere distribute themselves in the earth's gravitational field in accordance with the well-known hypsometric equation which is

$$\log p = \log p_0 - \frac{0.014837}{T} \cdot \frac{M}{Ma}(h - h_0), \quad (8)$$

where Ma is the molecular weight of dry air, 28.97, M the molecular weight of the gas whose partial pressure is p at height h and p_0 at height h_0, the heights being expressed in units of meters, and T is the average absolute temperature of the stratosphere, $-55°C$ according to Humphreys.[32] The partial pressures of several isotopic species have been calculated by means of Eq. (8) from the beginning of the stratosphere, (11 kilometers) to a height of 110 kilometers. The results are given in Table III where the last two columns show the extent to which the relative concentration of O^{18} atoms changes with height for both oxygen and water, α_{O_2} being the atom fraction of O^{18} in molecular oxygen at 11 kilometers divided by the same quantity at the other altitudes (the concentration of $O^{18}O^{18}$ being taken into consideration) and α_{H_2O} the atom fraction of O^{18} in the water vapor present at 11 kilometers divided by the same quantity at other altitudes. The atom fraction of O^{18} is not, of course, the same for molecular oxygen and water at 11 kilometers. The data of Table III indicate that at 20 kilometers where we have assumed the Urey and Greiff isotopic exchanges to come to equilibrium, the relative concentrations of O^{18} in oxygen and water are substantially the same

as they are in the troposphere so that we do not need to correct our calculations based on Urey and Greiff's theory for any gravitational fractionation of the oxygen isotopes.

If the hypsometric Eq. (8) is valid, the data of Table III also indicate that there is a considerable variation in the concentration of O^{18} in the atmosphere with increasing altitude, and one is led to wonder if the relatively greater settling of molecules containing O^{18} in the atmosphere is responsible for the increased atomic weight of oxygen in the air as compared to that of oxygen in water. If the isotopic composition of oxygen was constant throughout the atmosphere and the earth when the atmosphere and the earth's crust were first formed, and later became altered in the atmosphere due to gravitational settling, we should expect just such a variation in the atomic weight of oxygen as we have reported above. Taking 0.002 as the atom fraction of O^{18} in the oxygen of the troposphere, and using other data and equations given by Humphreys[32] it is possible to calculate that in the entire atmosphere there are approximately 361.6×10^{17} moles of $O^{16}O^{16}$, 1.431×10^{17} moles of $O^{18}O^{16}$ and 0.0014×10^{17} moles of $O^{18}O^{18}$ which means that the atom fraction of O^{18} in oxygen for the entire atmosphere is 0.001979. The fractionation factor due to gravity is therefore 0.002000/0.001979 or 1.011 which is equivalent to 2.4 p.p.m. in terms of density of water. Adding 1.6 p.p.m. for the difference in density between the ocean water and fresh water due to the oxygen isotopic variation, we obtain 4.0 p.p.m. density difference instead of 6.0 p.p.m. as experimentally observed. It appears, therefore, that the explanation based on the Urey and Greiff isotopic exchange theory is more plausible that the gravitational theory as it predicts values in better quantitative agreement with actual fact although the gravitational theory could be improved by assuming a slight

[32] W. J. Humphreys, *Physics of the Air*, Chapter V (McGraw-Hill Book Company, Inc., New York, 1929). There does not seem to be at present enough quantitative information to include atomic oxygen in Table III although it apparently exists to a very great extent in the upper regions of the stratosphere, see O. R. Wulf, J. Opt. Soc. Am. **25**, 231 (1935).

difference in the atomic weight of oxygen between air and water when the atmosphere was first formed.

The hypsometric Eq. (8) gives partial pressures for the different molecular isotopes of oxygen which satisfy equilibrium (7) at every height.

THE STANDARD OF CHEMICAL AND PHYSICAL ATOMIC WEIGHTS

The "Fifth Report of the Committee on Atomic Weights of the International Union of Chemistry"[33] gives the atomic weight of oxygen as 16.0000. This is, of course, by definition, but we now have to ask ourselves, is this the atomic weight of oxygen in air or in water? If we take the atomic weight of oxygen in Lake Michigan water to be exactly 16.000000, then the atomic weight of oxygen in air is 16.000108. Measurements[34] of the density of water from Nevada hot springs indicate that if the atomic weight of oxygen in Nevada hot springs water is exactly 16.000000, then the atomic weight of oxygen in Lake Michigan water is 16.000034 and the atomic weight of oxygen in air is 16.000142. Clearly oxygen is not a suitable substance on which to base the standard of chemical atomic weights if we wish to express the atomic weight of oxygen or of other substances to six or more figures. The physicists have long since abandoned the element oxygen as the standard of reference in mass-spectrographic work, taking instead the isotope of oxygen of mass sixteen. This standard, however, is not a good one for chemists, inasmuch as there is no easy method suitable for the isolation of isotopically pure O^{16} isotope. It seems also to be losing favor with the physicists; for example, Bethe[35] states "The question of changing to the scale He = 4.0000 might be reconsidered at this moment when all atomic weights have to be changed anyhow." Helium would be a bad choice from the chemist's point of view, on account of its chemical inertness.

Because of the possibility of isotopic separation and exchange in chemical reactions or physical processes, the logical substance on which to base the atomic weight scale should be a pure isotope, preferably the isotope of hydrogen of mass one or the element sodium which at the present time seems to be isotopically pure. Protium can be obtained easily in pure isotopic form in large quantities, it is chemically active and appears to be "elementary" matter when nuclear disintegration experiments are considered. The mass of protium, however, should be set at a value which would keep the element oxygen as near sixteen as possible so that there would be no need of changing our present atomic weights except in the fourth or fifth figure. Unfortunately at the present time there appears considerable uncertainty in the ratio of the O^{16} and H^1 masses so that[36] the time does not appear to be quite yet ripe for changing the standard of atomic weights from oxygen to another element. It is to be hoped, however, that the chemists will soon give up their chemical scale to adopt one based on a pure isotope and that the physicists will change their isotopic scale to bring it into accord with the chemical atomic weights, thereby rectifying the confusing situation of two atomic mass scales, an isotopic scale and a chemical element scale.

ACKNOWLEDGMENTS

Note added to proof: The January number of Bull. Chem. Soc. Japan, p. 36, Volume 11, contains a preliminary announcement by N. Morita and T. Titani of some work which is closely similar to our work described above which we first announced in the December number of J. Am. Chem. Soc. Morita and Titani's results, which are not given in detail, confirm ours within 2 p.p.m., but their experimental procedure is open to criticism since they did not put their air-oxygen water through the same process of electrolysis, etc., as their water-oxygen water.

[33] J. Am. Chem. Soc. **57**, 787 (1935).
[34] M. Dole, Science, in press.
[35] H. Bethe, Phys. Rev. **47**, 633 (1935).

[36] See, for example, H. Bethe, Phys. Rev. **47**, 633 (1935); and Oliphant, Kempton and Rutherford, Proc. Roy. Soc. **A150**, 252 (1935).