

Bain, G. K. Rollefson, Drs. H. A. Spoehr, J. H. C. Smith, D. C. DeVault, W. Z. Hassid and H. Gaffron for many helpful ideas and discussions. We are indebted to Professor E. O. Lawrence and the members of the Radiation Laboratory for their interest and coöperation. Thanks are also due to the Rockefeller Foundation for support to the Radiation Laboratory.

### Summary

1. The molecular weight of the first detectable products formed in the light and dark by *Chlorella pyrenoidosa* has been found to be approximately 1000.
2. A tentative theory on the mechanism of photosynthesis is presented.

BERKELEY, CALIF.

RECEIVED AUGUST 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Oxygen Exchange between Anions and Water

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If a water-free oxy-salt such as potassium dichromate is dissolved in a known amount of water of known abnormal density due to excess O<sup>18</sup>, and the salt and water later completely separated, a decrease in the density of the water may occur. From the weights of salt and water it is possible to calculate the density change that corresponds to complete random distribution of the heavy water-oxygen between water and salt, and hence to determine the extent to which such complete exchange of oxygen has occurred.<sup>1a</sup> Complete information on the rate and extent of exchange with various salts under different conditions should give valuable indications of the relative firmness of binding of oxygen atoms to the various other atoms in the anions, and of the exchange mechanisms.

In this paper are reported determinations of the extent of oxygen exchange between water and twenty-two inorganic oxygen compounds completely dissolved in it. The times of contact with the water varied from one to one hundred hours, and the runs were carried out at temperatures from 95–100°. Pyrex glass flasks were used to hold the reaction mixtures, and in many cases the effect of added alkali and acid on the extent of reaction was investigated. Sixteen of the compounds studied had not been previously examined from the point of view of exchange.

During the progress of the work several similar

(1) This work was supported in part by grants from the Wisconsin Alumni Research Foundation. Presented in part before the Division of Physical and Inorganic Chemistry at the Baltimore meeting of the American Chemical Society, April 6, 1939.

(1a) The assumption is made throughout this paper that the equilibrium constants of the exchange reactions are not significantly different from their "probability" values (1, 4, etc.). This assumption is justified in most cases by the limited precision of the data. Further experimental studies of this point are planned.

researches were published<sup>2-5</sup> and since its completion, a further paper<sup>6a</sup> has appeared.

More detailed studies of some of these equilibria have been published by Urey and his collaborators.<sup>7</sup>

Compared to some of the other investigators in this field we had available larger quantities of water, but its excess density was less. We were therefore constrained to attempt extremely precise density measurements (to 0.02  $\gamma d$ ),<sup>8</sup> but could use relatively large samples (40 ml.).

In order to be suitable for investigation by this method a salt must be (a) obtainable in a definite and easily reproducible state of purity, particularly as regards water content (most of our salts were anhydrous), and (b) sufficiently soluble so that the ratio of the total oxygen in the salt to that in the water may be made to approach unity. These considerations considerably limited our choice of compounds.

### Experimental

**Heavy Oxygen Water.**—This was supplied through the generosity of Professor Harold C. Urey, whose kindness is gratefully acknowledged, and was found after normalization of its hydrogen content, to have an excess density due to oxygen of 21.7  $\gamma d$ . The normalization was carried out by electrolyzing the water and combining the oxygen with tank hydrogen. Since it could not be assumed that the tank hydrogen had the same composition as that of normal

(2) Datta, Day and Ingold, *J. Chem. Soc.*, 1968 (1937).

(3) Blumenthal and Herbert, *Trans. Faraday Soc.*, **33**, 849 (1937).

(4) Titani, Morita and Goto, *Bull. Chem. Soc. Japan*, **13**, 329 (1938).

(5) Titani and Goto, *ibid.*, **13**, 667–668 (1938); **14**, 77–85 (1939)

(6) Winter, Carlton and Briscoe, *J. Chem. Soc.*, 131–137 (1940).

(6a) See also Mills, *THIS JOURNAL*, **62**, 2833 (1940).

(7) For references see Mills and Urey, *ibid.*, **62**, 1019–1026 (1940).

(8) By " $\gamma d$ " is meant a difference in density of one part per million.

water, it was necessary to determine the concentration of heavy oxygen by an analytical method. Two independent methods were used in order to minimize as far as possible any error in this determination.

**I. Air Equilibration.**—The first method made use of the apparatus described by Jones and Hall.<sup>9</sup> Air and water vapor were passed together over a heated platinum filament. The water was condensed from the gas mixture and recycled with more air. At temperatures above 1800° K.<sup>9</sup> the distribution of oxygen atoms may be considered random within experimental error, and the O<sup>18</sup>/O<sup>16</sup> ratio of the water vapor therefore approached that of atmospheric oxygen. Simultaneous equilibrations were made with normal water and with heavy water. The density of the normal water increased, and that of the heavy water decreased, both samples approaching the same O<sup>18</sup>/O<sup>16</sup> ratio as that of atmospheric oxygen.

The results of these equilibrations are given in Table I and are plotted in Fig. 1.

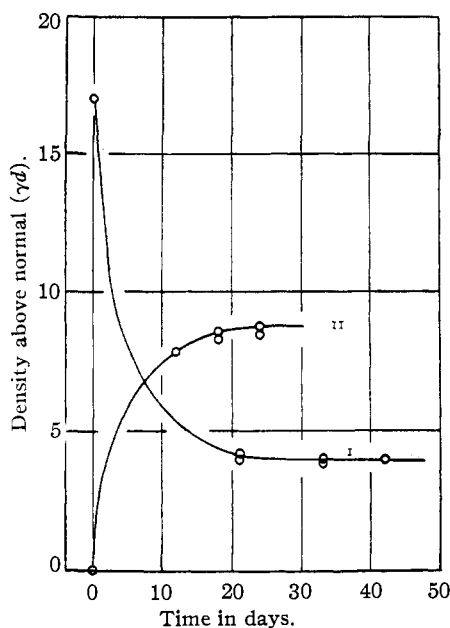


Fig. 1.—Density change of water on treatment with air: I, heavy oxygen water; II, normal water.

Taking +8.6  $\gamma d$  and +3.9  $\gamma d$  as the final values for the densities of the equilibrated normal and heavy water, respectively, the original abnormality of the heavy water due to oxygen alone is  $17.0 + (8.6 - 3.9) = 21.7 \gamma d$ .

**II. Carbon Dioxide Equilibration.**—In the second method of analysis, the heavy oxygen content of the heavy water was decreased to that of normal water by equilibration with carbon dioxide. Urey and his co-workers<sup>10</sup> have shown that the exchange of oxygen atoms will take place, and

(9) Jones and Hall, *THIS JOURNAL*, **59**, 259-261 (1937).

(10) Webster, Wahl and Urey, *J. Chem. Phys.*, **3**, 129 (1935).

TABLE I

Sample no.	Time in days	Density above normal ( $\gamma d$ )
Normal water	0	0.00
No. 1	12	7.82
	18	8.55
	24	8.59
Normal water		
No. 2	0	0.00
	12	7.82
	18	8.28
	24	8.42
Heavy water		
No. 1	0	17.0
	21	4.13
	33	3.97
	42	3.98
Heavy water		
No. 2	0	17.0
	21	3.92
	33	3.83

that at equilibrium the carbon dioxide has a higher O<sup>18</sup> content than the water. Roughton<sup>11</sup> and later Urey<sup>12</sup> have shown that carbonic anhydrase is an efficient catalyst in the promotion of reactions involving carbon dioxide, carbonate ion and bicarbonate ion. This enzyme was used in these equilibrations.

The carbon dioxide used was a commercial product. It was first thoroughly scrubbed with a large amount of normal water which was frequently renewed and to which a small amount of the enzyme had been added. The gas was then dried and passed through a series of two scrubbing towers of the type described by Kraus and Parker.<sup>13</sup> Freezing trains were inserted after each of the two columns so that the water vapor in the gas stream might be removed and returned to the equilibrator. Normal water was placed in the first tower as a check on the efficiency of the normalizing train, and heavy oxygen water was placed in the second tower. Carbon dioxide was passed at the rate of approximately 100 ml. per minute. Samples of water were withdrawn periodically and their densities determined.

The results of these equilibrations are given in Table II and in Fig. 2 where the density changes are plotted against the time in days.

Taking the value of -4.8  $\gamma d$  as the limit to which the density of the heavy water is lowered by equilibration with carbon dioxide, the abnormality due to the displaced oxygen isotope ratio becomes  $17.0 + 4.8 = 21.8 \gamma d$ . This value agrees well with the value 21.7  $\gamma d$  which was obtained in the previous experiment.

(11) Roughton, British Patent 403,096 (Dec. 1, 1933).

(12) Urey, Aten and Keston, *J. Chem. Phys.*, **4**, 622 (1936).

(13) Kraus and Parker, *THIS JOURNAL*, **44**, 2429 (1922).

TABLE II

Sample no.	Time in days	Density above normal
Normal water	0	0.00
	34	.03
	58	.08
Heavy water	0	17.0
	20	1.78
	34	- 1.88
	43	- 3.57
	51	- 4.97
	58	- 4.56

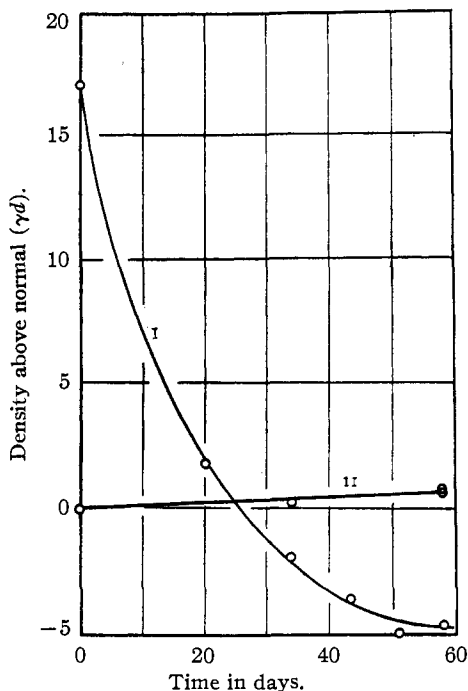


Fig. 2.—Density change of water on treatment with carbon dioxide: I, heavy oxygen water; II, normal water.

**Purification of Water.**—All samples, whether of normal or heavy water, were treated exactly alike and were distilled once from alkaline permanganate, once from phosphoric acid, and once without addition, through a quartz condenser into the densitometer cell. Discarded head and tail fractions were very small and were held rigidly constant. In order to determine the extent of fractionation resulting from this procedure several successive three-stage distillations were carried out on the same samples. The results are shown in Table III and Fig. 3.

TABLE III

Number of purifications	Number of samples	Normal water Density change	Heavy oxygen water Number of samples	Density change
1	5	0.00	4	0.00
2	3	.45	3	.69
3	2	.77	2	.99
4	1	1.05	1	1.58
5			1	2.40

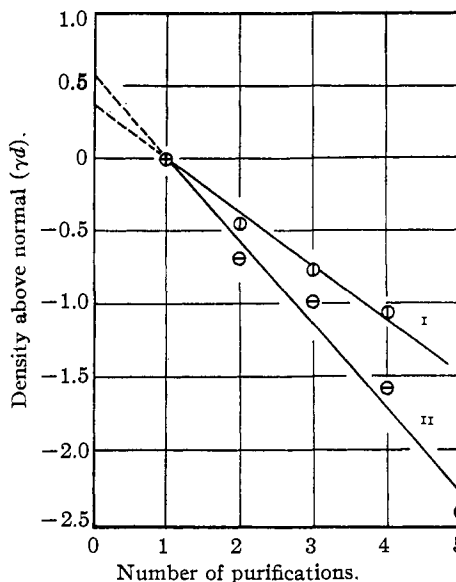


Fig. 3.—Density change of water on repeated distillation: I, normal water; II, heavy oxygen water.

In this table and figure each "sample" was of 40 ml. volume and each "purification" consisted of the *three* successive distillations referred to above. The average density decrease *per distillation* was then for the normal water  $1.05/9 = 0.12 \gamma d$  and for the heavy water  $2.40/12 = 0.20 \gamma d$ . Since all the results are comparative, these small density decreases cancel out in the actual procedure.

**Apparatus.**—The density measurements were made with a magnetically controlled submerged quartz swimmer. The apparatus was similar in principle to that described by Lamb and Lee<sup>14</sup> and essentially that described by Hall and Jones.<sup>15</sup> The quartz swimmer had a volume of 9.038 ml. and approximately 20 ml. of water was required to cover it completely. It showed no measurable thermal hysteresis. A second solenoid of copper wire was wound on the brass base of the cell, so that the larger current needed to pull the swimmer down from the top of the water need not be taken from the same battery that supplied the small and very constant current used to prevent the float from rising. It was found at first that there was some interaction of the fields of the two solenoids. When the switch in the auxiliary circuit was opened the swimmer was given a momentary upward impulse, and this behavior led to erratic results. This difficulty was overcome by first decreasing the current in the auxiliary circuit to a very small value before breaking the circuit completely. This was accomplished by placing a 5000 ohm resistance in series with the auxiliary circuit. A switch opened and closed a shunt across this resistance. The current was first passed through this high resistance, and then the circuit broken. Breaking this very small current produced no noticeable effect on the swimmer.

(14) Lamb and Lee, *THIS JOURNAL*, **35**, 1666 (1913).  
 (15) Hall and Jones, *ibid.*, **58**, 1915-1919 (1936).

The instrument was found to be very sensitive to external magnetic effects. The presence of iron-ware in the immediate vicinity of the densitometer caused the swimmer to be drawn to the side of the cell. For this reason, brass and copper were used almost exclusively in the construction of the instrument. Care was taken at all times to see that no ferromagnetic materials were moved about in the vicinity although iron objects at a distance of several feet had no effect if they remained in the same relative position.

The tip of the swimmer was observed through openings in the brass tube of the cell holder. A mirror at the back and a light above the instrument provided the necessary illumination. A good quality telescope of short focal length, giving a fifty-fold magnification was used.

In order to obtain the desired precision, it was necessary either to control the temperature to approximately  $0.003^\circ$  at ordinary temperatures or to operate at the temperature of the maximum density of water where small temperature variations have very little effect on the density. The latter course was adopted as the more practical.

Because of secondary factors, the optimum operating temperature is not exactly the temperature of maximum density of water, but approximately  $4.07\text{--}4.09^\circ$ . This is due in part to the thermal expansion of the quartz float, and in part to the change of resistance of the copper solenoid with temperature. The voltage-temperature relationship has been determined experimentally both at  $4^\circ$  and at  $25^\circ$ , and is shown in Fig. 4. The voltage differences have been converted to the equivalent density differences. These curves clearly illustrate the marked advantage of working at the lower temperature.<sup>15a</sup>

It was also found necessary to correct the observed

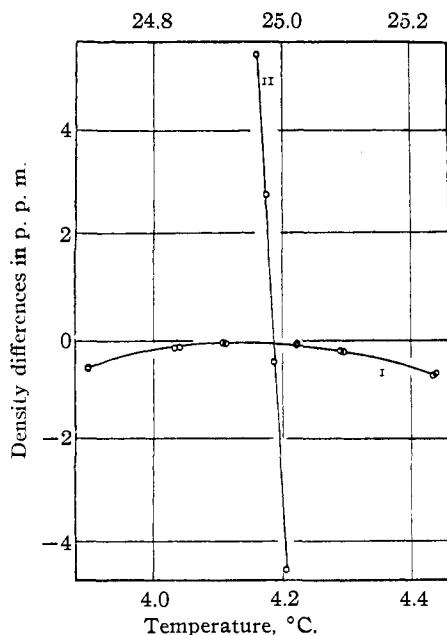


Fig. 4.—Effect of temperature on apparent density of water: I,  $4^\circ$ ; II,  $25^\circ$ .

(15a) This advantage was also emphasized by Greene and Voskuyl, *THIS JOURNAL*, 61, 1342 (1939).

density to allow for fluctuations in atmospheric pressure. The pressure effect on the observed density was linear and amounted to  $0.393 \gamma d/cm.$  Hg over a much wider range than was ever encountered.

**Calibration.**—Small weighed platinum rings were added to or removed from the upper tip of the swimmer. Four of these rings, weighed to micrograms, were used and as the average of six different weight combinations it was found that one millivolt change in the voltage drop across the standard resistance corresponded to a difference of  $0.702 = 0.002 \gamma d$  in the over-all density of the swimmer.

**Measurement.**—The cell containing the purified sample was placed in the thermostat and the voltage adjusted to a value a few millivolts higher than the equilibrium voltage, so that the float was held permanently at the bottom of the cell. It was found that thirty minutes was ample time to allow for the attainment of thermal equilibrium, and that the density remained constant within  $0.1 \gamma d$  for periods of at least twelve hours. At the end of thirty minutes, the voltage was gradually decreased until the swimmer began to rise. At this point it was drawn back down by passing a small current through the auxiliary circuit. The voltage across the measuring circuit was then increased by a small amount. The current through the auxiliary circuit was then decreased to a very small value by shunting in the high resistance, and then broken entirely. The voltage across the measuring circuit was slowly increased in this manner in progressively decreasing increments until the float remained permanently at the bottom of the cell. The float rose so slowly near the balance point that it was quite difficult to detect the very slow motion. By observing the float at the moment when the switch was closed in the auxiliary circuit, it was very easy to detect the small, more rapid movement as the float was drawn back to the bottom, which movement indicated that the float had risen somewhat and that the voltage was still too low.

A type K potentiometer was used to measure the voltage across a standard resistance in series with the "holding" coil, and repeated readings on the same sample agreed to within 0.03 mv. or to within  $0.02 \gamma d$ . Different samples of the same water carried through the entire procedure have an average deviation of  $0.1 \gamma d$ .

The readings for the standard water were quite constant from day to day, but samples of reference water were always run before and after each series of measurements. It was possible to make each determination in approximately two hours. This included the time required for the third and final distillation, as well as for the actual reading itself.

**Equilibrations.**—Where possible, reagent quality materials were used and were not subjected to further purification. In those cases where the material was available only in a state of questionable purity, the salts were recrystallized from purified reference water. Before use the salts were thoroughly dried by heating under vacuum and condensing the water in a trap immersed in liquid air. With this procedure, even such powerful desiccants as magnesium perchlorate could be dehydrated readily.

Forty grams of water was used for each determination and enough of the thoroughly dried salt was added to give a solution which at  $95^\circ$  was somewhat less than saturated. The equilibrations were carried out in Pyrex flasks closed

with well-fitting rubber stoppers. The reaction mixture was placed in a water-bath at 95–100°, shaken until the salt was completely dissolved, and allowed to stand. At the end of the desired time, the flask was removed and thoroughly chilled in a freezing mixture. The stopper was removed and the flask attached to the distillation apparatus. While the reaction mixture was still cold the system was evacuated to a pressure of 3–4 mm. and closed off by means of a stopcock. The receiver was then cooled in liquid air and the water removed from the salt as rapidly as possible. Most of the water came off at a relatively low temperature, and the remainder was removed by heating the reaction flask in an oil-bath. The temperature was gradually increased to 150° and maintained at this point for a few hours. In some cases, especially with magnesium perchlorate, a temperature of 250° was required to secure complete dehydration. It was essential that the water be removed completely in order to avoid diluting the succeeding sample, and also to avoid errors due to fractional distillations of the water. There was considerable spattering, but by using a flask with indentations in the neck, or one with a bent neck, mechanical carryover was prevented. The receiver and condensate were always weighed after the distillation in order to check the completeness of removal of the water. In almost every case the recovery was above 99%.

It was necessary, of course, to determine the oxygen isotope ratio of the salt itself. This was done by first equilibrating the salt with normal water. If the water did not change in density, it indicated either that the salt had the same isotopic ratio as the water, or else that there had been no exchange. If there was an appreciable change in density, it was an easy matter to make a small correction for the original deviation from the normal ratio. The dried residue from this first equilibration was then dissolved in heavy water. If there was an exchange of oxygen between the salt and the water, the density of the heavy water would decrease, and the salt would be left with a higher content of heavy oxygen than before. This salt was then treated a second time with normal water, and the density of this water would increase if there was any exchange. In this manner, it was possible to get two results with the expenditure of only one sample of the heavy oxygen water.

Although this procedure gives information on the relative reactivities of the oxyanions, it does not lend itself to a precise determination of reaction rates. The time required to remove the water from the reaction mixture is a matter of several hours, and this leads to some difficulty in definitely establishing the time of the reaction. This uncertainty, however, is not large, for the greater portion of the water is removed at a relatively low temperature where in most cases the rate of exchange is comparatively low.

### Results and Discussion

In the tabulation of results (Table V) the calculated density change is for complete random distribution of the O<sup>18</sup> between salt and water. The observed extent of the exchange expressed in per cent. is given in the last column. Figures above 100 obviously represent experimental error which is presumably present to an approximately

equal extent in the values below 100. Inspection will show that in the majority of cases either the exchange was complete or did not occur at all under the chosen conditions, so that in spite of the narrow working range (maximum calculated change 11  $\gamma d$  or less) the results are definite and unambiguous. Where the notation "+NaOH" or "+HCl" is used, the solution was 0.2 *N* in base or acid.

**Runs 1–8.**—Exchange was complete with CrO<sub>3</sub> and its salts in five hours time, at 95–100°. In the case of sodium chromate shorter times of contact (one to two hours) failed to produce complete reaction. An extremely rough extrapolation suggests that the half reaction time may be about five minutes or less, which may be compared to the value of four and one-half hours at 20° as found by Winter, Carlton and Briscoe<sup>6</sup> for potassium chromate.

**Runs 9–10** confirm the finding of these authors that added alkali strongly inhibits the exchange in chromate solutions. At 100° they found that after twenty-five hours the reaction is complete in 2 *N* alkali solution while we found that substantial completion (94%) was reached in three hours with 0.2 *N* alkali.

**Runs 11–13** show that K<sub>2</sub>MoO<sub>4</sub> exchanges completely even in one hour and even in the presence of alkali.

**Runs 14–16** indicate the same thing for Na<sub>2</sub>WO<sub>4</sub> although here the experimental error seems very large; due in part at least to the very unfavorable solubility conditions and the narrow margin (3  $\gamma d$ ) within which the work was carried out.

**Run 17** shows complete and rapid exchange for NaBO<sub>2</sub> in harmony with similar findings of the London authors for H<sub>3</sub>BO<sub>3</sub> and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O.

**Runs 18–21** show that exchange is definitely slow in potassium carbonate solutions under the conditions of our work. The half reaction time appears to be about four to five hours but the data are not conclusive. Mills and Urey<sup>7</sup> found a reaction time of twenty-eight hours at 25°.

**Run 22.**—Potassium nitrite shows no measurable exchange. The solution of the salt was slightly alkaline due to hydrolysis and to the presence of a trace of admixed potassium hydroxide.

**Runs 23–25.**—These runs are in only partial agreement with the work of the other investigators. Thus Titani and Goto<sup>6</sup> found no exchange with potassium nitrate at any temperature up to 180°, and with sodium nitrate we find none under

our conditions. We find that alkali has no accelerating effects. In the presence of acid, on the other hand, while we find no effect in the presence of excess nitric acid, and the Japanese work in the presence of potassium acid sulfate was inconclusive, the English authors, who used added sulfuric acid, found an exchange to the extent of 112% of the calculated value! Whether this interchange is really catalyzed by the presence of sulfuric acid seems to us still somewhat doubtful in view of the rather large experimental error and the well-known difficulty of freeing water completely from dissolved oxides of nitrogen.

TABLE IV  
RESULTS OF EXCHANGE REACTIONS

Run	Compound	Time in hours	Density Observed	change Calcu- lated	% of calcd. exchange
1	CrO <sub>3</sub>	5	11.97	11.62	103
2	CrO <sub>3</sub>	5	11.32	11.89	96
3	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5	10.65	10.85	98
4	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5	10.90	10.85	100
5	Na <sub>2</sub> CrO <sub>4</sub>	1	3.48	3.95	88
6	Na <sub>2</sub> CrO <sub>4</sub>	2	5.53	5.80	95
7	Na <sub>2</sub> CrO <sub>4</sub>	5	7.02	7.23	97
8	Na <sub>2</sub> CrO <sub>4</sub>	5	7.10	7.28	98
9	Na <sub>2</sub> CrO <sub>4</sub> + NaOH	1	1.93	3.89	49
10	Na <sub>2</sub> Cr <sub>2</sub> O <sub>4</sub> + NaOH	3	5.54	5.86	94
11	K <sub>2</sub> MoO <sub>4</sub>	25	4.80	4.67	103
12	K <sub>2</sub> MoO <sub>4</sub> + NaOH	13	3.33	3.25	102
13	K <sub>2</sub> MoO <sub>4</sub> + NaOH	1	2.93	2.85	103
14	Na <sub>2</sub> WO <sub>4</sub>	6	3.85	3.60	107
15	Na <sub>2</sub> WO <sub>4</sub> + NaOH	3	2.87	3.10	92
16	Na <sub>2</sub> WO <sub>4</sub> + NaOH	1	2.85	2.38	119
17	NaBO <sub>3</sub>	4	4.41	4.25	104
18	K <sub>2</sub> CO <sub>3</sub>	4	1.50	7.10	21
19	K <sub>2</sub> CO <sub>3</sub>	4	3.70	7.10	52
20	K <sub>2</sub> CO <sub>3</sub>	22	6.00	6.02	99
21	K <sub>2</sub> CO <sub>3</sub>	24	7.22	7.10	102
22	KNO <sub>3</sub>	10	0.18	10.10	2
23	NaNO <sub>3</sub>	5	0.15	10.57	1
24	NaNO <sub>3</sub> + NaOH	12	0.00	8.90	0
25	NaNO <sub>3</sub> + HNO <sub>3</sub>	12	0.25	8.56	3
26	KH <sub>2</sub> AsO <sub>4</sub>	14	4.04	4.36	93
27	KH <sub>2</sub> AsO <sub>4</sub>	14	2.96	3.14	94
28	KH <sub>2</sub> AsO <sub>4</sub> + NaOH	8	3.75	3.66	102
29	KH <sub>2</sub> AsO <sub>4</sub> + NaOH	1	2.74	2.93	93
30	KAsO <sub>2</sub>	12	4.38	4.46	98
31	KAsO <sub>2</sub>	9	6.20	5.97	104
32	KAsO <sub>2</sub> + NaOH	4	4.87	4.58	106
33	KAsO <sub>2</sub> + NaOH	1	3.48	3.67	95
34	NaMnO <sub>4</sub>	4	3.67	5.22	70
35	NaMnO <sub>4</sub>	4	1.62	2.79	58
36	NaMnO <sub>4</sub>	8	3.12	5.43	57
37	NaMnO <sub>4</sub>	8	2.51	2.34	107
38	NaMnO <sub>4</sub> + NaOH	4	5.30	5.05	105
39	NaMnO <sub>4</sub> + NaOH	4	3.01	4.05	74

40	Mg(ClO <sub>4</sub> ) <sub>2</sub>	4	0.04	6.66	1
41	Mg(ClO <sub>4</sub> ) <sub>2</sub> + HCl	12	.11	3.98	3
42	Ba(ClO <sub>4</sub> ) <sub>2</sub> + NaOH	24	.00	5.04	0
43	NaClO <sub>3</sub>	5	.05	12.68	0
44	NaClO <sub>3</sub> + NaOH	23	.70	10.25	7
45	NaBrO <sub>3</sub>	9	.65	4.70	14
46	NaBrO <sub>3</sub>	48	2.85	4.70	61
47	NaBrO <sub>3</sub> + NaOH	9	1.15	4.81	24
48	NaIO <sub>3</sub>	24	0.94	1.73	54
49	NaIO <sub>3</sub>	48	1.88	2.00	94
50	NaIO <sub>3</sub> + NaOH	9	1.35	1.70	79
51	NaIO <sub>3</sub> + NaOH	12	1.85	1.73	107
52	Na <sub>2</sub> SeO <sub>3</sub>	5	6.95	7.25	96
53	Na <sub>2</sub> SeO <sub>3</sub>	5	4.90	4.63	106
54	Na <sub>2</sub> SeO <sub>3</sub> + NaOH	3	3.50	3.66	96
55	Na <sub>2</sub> SeO <sub>3</sub> + NaOH	1	3.08	2.80	110
56	Na <sub>2</sub> SeO <sub>4</sub>	5	0.20	4.70	4
57	Na <sub>2</sub> SeO <sub>4</sub>	24	.20	4.70	4
58	Na <sub>2</sub> SeO <sub>4</sub> + NaOH	12	.16	3.23	4
59	Na <sub>2</sub> SeO <sub>4</sub> + HCl	12	.98	3.35	29
60	K <sub>2</sub> SO <sub>3</sub>	9	2.75	2.46	112
61	K <sub>2</sub> SO <sub>3</sub>	8	2.48	2.44	102
62	K <sub>2</sub> SO <sub>3</sub> + NaOH	5	0.00	2.12	0
63	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	6	4.85	4.82	101
64	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5	4.09	3.78	108
65	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + NaOH	3	0.00	4.05	0
66	Na <sub>2</sub> SO <sub>4</sub>	14	.10	2.57	4
67	Na <sub>2</sub> SO <sub>4</sub>	46	.11	2.54	4
68	Na <sub>2</sub> SO <sub>4</sub> + NaOH	15	.00	2.57	0
69	Na <sub>2</sub> SO <sub>4</sub> + NaOH	18	.13	2.74	4
70	Na <sub>2</sub> SO <sub>4</sub> + HCl	12	.58	2.58	23

Runs 26-29 agree with Titani and Goto<sup>5</sup> in showing essentially complete exchange with KH<sub>2</sub>AsO<sub>4</sub>. The addition of alkali (Runs 28 and 29) seemed to have a slight favorable effect on the exchange but this may be due to experimental error.

Runs 30-33.—Arsenite, not studied by others, shows complete exchange not affected by alkali.

Runs 34-39 with sodium permanganate are inconclusive due to the inadequate stability of the salt. That exchange is extensive, even in the presence of alkali, is clear.

Runs 40-42 with magnesium perchlorate and barium perchlorate show no exchange and none was found by Winter, *et al.*, using sodium perchlorate. Our results show no catalysis by either hydrochloric acid or sodium hydroxide.

Runs 43-44.—Titani and Goto found no reaction with NaClO<sub>3</sub>, and neither do we. Winter, Carlton and Biscoe, using KClO<sub>3</sub>, find a slight exchange in the presence of alkali, as do we, and an extensive exchange in the presence of sulfuric acid, as do Titani and Goto in the presence of hydrochloric acid.

**Runs 45-47.**—Sodium bromate shows a slow exchange. This seems to be somewhat promoted by alkali.

**Runs 48-51** show essentially similar effects in the case of sodium iodate.

**Runs 52-59.**—These results are among the most striking we obtained.

**Selenite** exchanges completely and rapidly, even in the presence of excess alkali. **Selenate** does not exchange at all in neutral or alkaline solution, but shows an appreciable exchange in the presence of added acid.

**Runs 60-65.**—These runs also present a striking result. Sulfite and thiosulfate exchange completely when present alone, and the exchange is completely inhibited by alkali.

**Runs 66-70.**—We find no appreciable interchange between sulfate and water, and no important catalysis by alkali. The first conclusion confirms the work of all the other investigators. Our second conclusion, that added alkali does *not* appreciably promote the exchange is in direct contradiction to the work of Datta, Day and Ingold,<sup>2</sup> but in agreement with Winter, Carlton and Briscoe.

The conclusion from run 70, that hydrochloric acid strongly catalyzes the sulfate exchange, agrees with the work of Titani and Goto, but Winter, Carlton and Briscoe, who used sulfuric acid, do not observe any such catalysis.

**Discussion.**—Apparently the only anions so far examined which have completely resisted exchange in the absence of added alkali or acid are nitrite, nitrate, phosphate (?), sulfate (?), selenate, perchlorate and chlorate. These anions contain central atoms of high charge and small size, are among the most weakly basic of anions, and may be supposed to contain especially firmly bound oxygen. However, other anions of these same central atoms exchange completely under similar conditions, namely, sulfite, thiosulfate, and selenite. These are in each case less weakly basic anions. A second group of elements, lying close to this first set in the periodic table, form anions that show partial, or measurably slow exchange. These are carbonate, bromate, and iodate. Two substances from the "A" sub-groups, chromate and permanganate, behave similarly to these. Elements farther from the upper right-hand corner of the table, and the other A sub-group elements stibide, exchange readily and completely. These are borate, metasilicate, arsenate, metarsenite, molybdate and tungstate.

It was predicted but **not demonstrated** by

other workers that a series of oxyanions with the same central atom would show increasing readiness to exchange as the number of oxygen atoms in the anion diminished. In confirmation of this view our work demonstrates that sulfate and selenate are much more stable than the corresponding sulfite and selenite, and while chlorate has been found to show some exchange (due to decomposition) on heating with acid, we found no effect of either acid or alkali on perchlorate.

**Acid Catalysis.**—The effect of added acid, in promoting exchanges, emphasized by Titani and Goto and Winter, Carlton and Briscoe was also unmistakable in our results, however, certain apparent disagreements still persist. Titani and Goto found that  $\text{KH}_2\text{PO}_4$  exchanged completely in 100 hours at  $100^\circ$ , while Winter, Carlton and Briscoe found essentially no exchange in forty-one hours at the same temperature. Similarly Titani and Goto found that while potassium sulfate alone showed practically no exchange ( $< 10\%$ ) in twenty hours at  $100^\circ$ , potassium acid sulfate showed 94% exchange under similar conditions. When the two salts were mixed, about 23% exchange occurred. Winter, Carlton and Briscoe found no exchange with sodium sulfate alone, none with potassium sulfate, and none when sodium sulfate and sulfuric acid were used together, *except that the added acid appeared to exchange completely*. We found no exchange with sodium sulfate, but a 23% exchange in twelve hours when 0.2 *N* hydrochloric acid was present. The added hydrochloric acid in this experiment was equivalent to only 3.6% of the sodium sulfate present so that unless the chloride ion itself has a specific catalytic effect, it is hard to harmonize this finding with that of the English workers, while it seems on the whole to substantiate the Japanese results. In a further experiment, Titani and Goto heated potassium sulfate with hydrochloric acid for varying times to  $180^\circ$ , and found, as would be expected from our results, a considerable exchange (70%).

In the case of nitrate, as previously mentioned, the English workers found that sulfuric acid not only completely exchanged its own oxygen but also caused complete exchange of the nitrate oxygen, while we found no effect of added *nitric acid*. No general explanation of these results now seems possible and further work on the effect of various acids on these exchanges is clearly needed.

**Catalysis by Alkali.**—Datta, Day and Ingold's report of the alkaline catalysis of sulfate ex-

change led us to repeat their work and to study the effect of added alkali on many exchanges. Like Winter, Carlton and Briscoe we were completely unable to confirm the effect in the case of sulfate, and are of the opinion that the observations were in error, or were due to exchange with silicate in the glass. We have some slight evidence of catalysis by alkali in the case of chlorate, bromate, iodate and arsenate, but the effects are so slight and the working range in the case of iodate so small (less than  $2 \gamma d$ ) that we cannot feel certain that the apparent effects are not due to silicate in the glass, or other experimental error. On the other hand, in the case of nitrate (run 24) perchlorate (run 42) selenate (run 58) and sulfate (runs 68, 69) we found no trace of such an effect of the glass container and a total absence of effect of the added alkali.

Finally, in line with Winter, Carlton and Briscoe's experience, we found that alkali somewhat retarded the exchange of chromate, and we have further found that the presence of 0.2 *N* sodium hydroxide completely inhibits the otherwise complete exchange of sulfite and thiosulfate.

### Summary

1. Extensive density measurements by the method of the magnetically controlled swimmer have been carried out with a routine precision of 0.02  $\gamma d$  and an over-all reproducibility (including the purification of samples) of 0.1  $\gamma d$ .

2. Attention is called to the advantage in comparing the densities of waters or dilute aqueous solutions, of working near the temperature of maximum density of the samples.

3. Oxygen exchange between anions and water enriched in  $O^{18}$  was studied at 95–100° in the case of 21 inorganic salts and  $CrO_3$ .

4. Resistance to exchange was found to increase toward the upper right-hand corner of the periodic table and with the number of oxygen atoms attached to a given central atom.

5. Many of the exchanges appear to be promoted by excess acid and retarded by excess base.

6. Most of the salts studied exchange completely under the conditions used, several show no exchange at all, and only a few show partial exchange.

MADISON, WISCONSIN

RECEIVED JULY 8, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Measurement of the Excess Weight of Air Oxygen by Exchange with Inorganic Salts<sup>1</sup>

BY ORVAL R. ALEXANDER AND NORRIS F. HALL

Since its discovery<sup>2</sup> the excess atomic weight of air oxygen (Dole effect) has been measured by numerous authors with fairly consistent results.<sup>3</sup> There has been critical discussion of the various methods used by the different authors but the chief uncertainties seem to be (1) the still imperfectly known degree to which different natural waters differ in density, (2) the possibility that samples even of the "same" water, such as "Lake Michigan," "Atlantic Ocean," or "Lake Mendota" used by different investigators or by the same investigators at different times are significantly different in density, and (3) the possibility of different degrees of isotopic fractionation during the purification of the various samples, particularly as the same purification process produces a slightly

different effect on waters of different composition.<sup>4,5,6</sup>

The present paper does not resolve these difficulties, which would require an extensive coöperative program between different laboratories, but merely presents an additional independent method of disclosing and measuring the Dole effect.

The finding that many inorganic salts exchange their oxygen rapidly and completely with water in which they are dissolved, suggested that the Dole effect could be measured by this method. Sodium dichromate appeared to be the most suitable salt.<sup>6</sup>

**Procedure.**—Reference water was prepared from Lake Mendota water by refluxing with permanganate and alkali for twelve hours, and finally distilled with the rejection of a 3% head and a 2% tail fraction. Samples of this were then purified in the regular way.<sup>6</sup> Several samples of air-oxygen water were prepared as follows. Air was washed

(1) This work was supported in part by grants from the Wisconsin Alumni Research Foundation.

(2) (a) Dole, *THIS JOURNAL*, **57**, 2731 (1935); (b) *J. Chem. Phys.*, **4**, 268 (1936); (c) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36, 414 (1936).

(3) For literature references see Swartout and Dole, *THIS JOURNAL*, **61**, 2025–2029 (1939).

(4) Greene and Voskuyl, *ibid.*, **61**, 1342 (1939).

(5) Dole and Slobod, *ibid.*, **62**, 471–479 (1940).

(6) Hall and Alexander, *ibid.*, **62**, 3455 (1940).