24. *The Interchange of Heavy Oxygen between Water and Inorganic Oxy-anions.*

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Using heavy-oxygen water, having an excess density due to ^{18}O of 150—200γd, the interchange of oxygen between water and several oxy-acid radicals has been investigated. The interchange has been followed by means of flotation-temperature determinations with a silica float on the micro-scale, using 2—4 c.c. of water. With alkaline solutions, the reacting system was hermetically sealed in a pure silver tube.

With perchlorate, sulphate, and phosphate, no measurable interchange occurs in 2 days at 100° whether in neutral, acid, or alkaline solution. It seems probable that the supposed interchange with sulphate and phosphate in alkaline solution at 100° recorded by previous workers was actually interchange with silicate produced by alkali attack upon the glass container. With chlorate, interchange is complete in acid solution (with decomposition) but does not occur in neutral or alkaline solution. Nitrate also exchanges completely (with decomposition) in acid solution. No oxygen interchange occurs between nitrous oxide and water in 14 days at 20°.

With sodium metasilicate, boric acid, and borax, oxygen interchange is complete in a very short time at 100°, with dichromate and with chromate in neutral or alkaline solution it is complete in 1 day at 100°, but in a neutral solution of chromate at 20° the interchange proceeds at a measurable rate, the time of half change being about 4½ hours. In presence of caustic alkali at 20°, however, there is no measurable interchange in 240 hours. This retardation by alkali is consistent with the view that oxygen interchange in this case occurs solely through the known reaction, $Cr_2O_7'' + H_2O \rightleftarrows 2HCrO_4'$.

It is provisionally concluded that oxygen interchange with oxy-acid anions occurs only where these are known to interact reversibly with water, as is the case with silicate, borate, and chromate ions, or are otherwise chemically changed as with chlorate and nitrate in acid solution.

It is generally recognised that the use of water enriched in heavy oxygen, ^{18}O, affords a convenient means of investigating any interchange of oxygen which may occur between water and dissolved oxy-acids and their salts. As a result of earlier work in these laboratories, we had at our disposal a quantity of such water and therefore began a series of experiments of this kind.

At that time the only publications on the subject were those of Datta, Day, and Ingold (J., 1937, 1968), Blumenthal and Herbert (*Trans. Faraday Soc.*, 1937, **33**, 849), and Titani, Morita, and Goto (*Bull. Chem. Soc. Japan*, 1938, **13**, 329), dealing mainly with interchange in solutions of sulphates and phosphates. By their observations on oxygen interchange in sulphate solutions, Datta, Day, and Ingold were led to postulate a mechanism involving proton addition followed by loss of hydroxyl ion. A similar mechanism was suggested by Blumenthal and Herbert to account for their observations on the interchange of tripotassium orthophosphate in solution.

This hypothesis being accepted, it seemed probable that the series of anions ClO_4', ClO_3', ClO_2', and ClO' would show increasing readiness to undergo interchange in aqueous solution as the number of oxygen atoms decreased. This point was therefore investigated by sealing known amounts of appropriate reagents in tubes of Pyrex glass and heating them at 100° for various periods. Parallel experiments proved that at room temperature no interchange occurred over long periods. Actually, only sodium perchlorate and potassium chlorate were thus investigated, because it was found that very little interchange occurred at 100° in alkaline solution, and indications were obtained that what interchange was observed might be associated with the attack of the alkali upon the glass container. Substantial interchange with chlorate ion occurred in acid solution, but this could be explained by the obvious decomposition which was observed under these conditions (see below).

Since it was suspected (and subsequently confirmed) that the small apparent interchanges observed could be accounted for quantitatively by interchange of oxygen with soluble silicate formed from the glass container, it was evidently unsatisfactory to carry the experiments further in glass. Therefore a convenient silver container was designed, in which the reagents could be hermetically sealed and heated for any desired period. On using this device, it was found that in alkaline solution no appreciable interchange of oxygen between sulphate ions and water occurred in two days at 100°. As the experimental error was of the order of $\pm$ 1·5γd and the density difference calculated for complete interchange of oxygen (using the quantities of reagents given in expts. 16—24) was about 35γd, it was concluded that in 48 hours at 100° the interchange cannot exceed 8—10%.

To test this point still further, two portions of the same 1·06N-solution of sodium hydroxide in water, having an excess density due to ^{18}O of + 210γd, were heated in sealed silver tubes at 100° for 456 hours with the addition, in one case, of 1·633 g. of anhydrous sodium sulphate. Subsequent comparison showed that the densities of the samples of water distilled from the residues were identical within $\pm$ 0·5γd, whereas complete interchange with the sulphate ion should have produced a difference of 40γd. It is clear, therefore, that even in this long period of heating the apparent interchange did not exceed about 1% of the calculated value.

The suspicion that the small differences in density observed in expts. 4—7, 13, 14, and 17—20 and the slightly larger differences observed by Datta, Day, and Ingold were due to silicate interchange led naturally to a direct examination of the interchange with pure sodium metasilicate. The results given below show clearly that with this salt interchange proceeds rapidly to completion.

In view of these facts, and having regard to the rather unsatisfactory nature of the data on which Blumenthal and Herbert had based their conclusion that oxygen interchange between water and the orthophosphate radical was complete in 3 hours at room temperature, this interchange was also re-examined. The difficulty of securing a solution of the pure salt in water of known ^{18}O concentration was overcome by using pure disodium hydrogen phosphate together with an equivalent of pure sodium hydroxide, and calculating the correction for the water formed by the interaction of these two compounds. In this way it was found, as with the sulphate, that no appreciable interchange occurs in 2 days at 100°. This work on the interchange of phosphate ions in aqueous solution opens up interesting possibilities in the biological field, as the treatment to which the salts were subjected was probably much more severe than any met with in Nature. In a similar manner the interchange with potassium dihydrogen phosphate was examined, but the observations of Titani and Goto (*Bull. Chem. Soc. Japan*, 1939, **14**, 77) were not confirmed.

It is of interest to note that, although no interchange is now observed with N-alkaline or N-acid solutions of sodium sulphate, or with solutions of potassium hydrogen sulphate under the conditions used, one experiment (No. 9) appears to indicate that dilute aqueous solutions of sulphuric acid show complete interchange. This point evidently merits further investigation and this is being undertaken.

In contrast with the foregoing cases where we can find no evidence of interchange it is interesting to review those where extensive interchange has been observed. (i) *Sodium metasilicate.* Here partial hydrolysis occurs, giving sodium hydroxide and metasilicic acid, and the latter takes up a molecule of water to give the ortho-acid :

$$\begin{aligned}&(1)\ Na_2SiO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2SiO_3\\&(2)\ H_2SiO_3 + H_2O \rightleftharpoons H_4SiO_4\end{aligned}$$

Although there is no reason to suppose that interchange of oxygen occurs in reaction (1), it is probable that in reaction (2) the four oxygen atoms of the orthosilicate ion are equally liable to be split off as water in the reverse reaction, so that equilibrium is rapidly attained.

(ii) *Hydrated borax* ($Na_2B_4O_7,10H_2O$). The dilution effect of the water of crystallisation can be precisely calculated if the pure reagent is used. In solution the salt undergoes hydrolysis followed by reversible hydration and dehydration of the boric acid :

$$\begin{aligned}&(3)\ Na_2B_4O_7 + 2H_2O \rightleftharpoons 2NaOH + H_2B_4O_7\\&(4)\ (a)\ H_2B_4O_7 + 5H_2O \rightleftharpoons 4H_3BO_3\\&\ (b)\ H_3BO_3 \rightleftharpoons H_2O + HBO_2\end{aligned}$$

Here, therefore, as with sodium silicate, simple well-known chemical changes suffice to explain the observed rapid interchange of heavy oxygen.

(iii) *Boric acid* (H_3BO_3). A similar rapid and complete interchange is observed and can be similarly explained.

(iv) *Potassium chromate and potassium dichromate.* These salts may be considered together and present the most interesting system so far examined. Various workers (see, *e.g.*, references by Friend, "A Textbook of Inorganic Chemistry," Vol. VII, Part III, pp. 44, 45) have shown that in an aqueous solution of these salts the following reversible equilibria occur :

$$\begin{aligned}&(5)\ K_2Cr_2O_7 \rightleftharpoons Cr_2O_7'' + 2K^{\bullet}\\&(6)\ K_2CrO_4 + H_2O \rightleftharpoons 2K^{\bullet} + OH' + HCrO_4'\end{aligned}$$

followed by

$$(7)\ Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$$

In conformity with what has been said of cases (i), (ii), and (iii) above, it seems probable that any interchange which occurs will take place through reaction (7) ; and this applies equally to solutions of either salt. It has been found possible to measure the rate of interchange of potassium chromate with enriched water at 20°, the time of half-change being approximately $4\frac{1}{2}$ hours. Though the experimental error is relatively large, since complete interchange in this case gives a density change of only $-18\gamma d$, the general significance of the results seems clear.

On the above hypothesis, addition of hydroxyl ions to a solution of potassium chromate should substantially diminish the equilibrium concentration of $HCrO_4'$ in reaction (6) and therefore minimise exchange *via* reaction (7). In accordance with this view it was found that a solution of potassium chromate in approximately N-sodium hydroxide in enriched water had suffered no interchange (other than that due to the sodium hydroxide itself) after 240 hours, at 20°. In the same solution at 100° the interchange is complete in 25 hours.

It should be noted that Blumenthal and Herbert (*loc. cit.*) and Datta, Day, and Ingold (*loc. cit.*) considered the possibility of a similar mechanism when discussing the theoretical aspects of phosphate interchange. The interchange which was observed when potassium chlorate was heated with N-sulphuric acid in enriched water may be accounted for in a similar manner. It was observed that appreciable decomposition of the salt occurred—a strong smell of oxides of chlorine being apparent when the reaction tube was opened—and it may be assumed that interchange occurred because the oxides were involved in a continuous cycle of reactions of the following type:

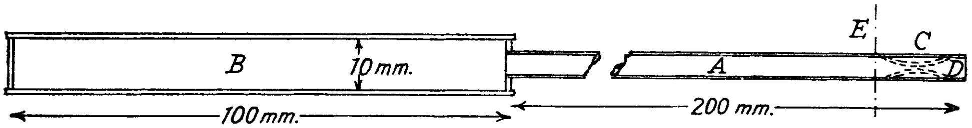
$$2\mathrm{ClO_2}\ \text{(gas)} \rightleftharpoons 2\mathrm{ClO_2}\ \text{(in solution)} + \mathrm{H_2O} \rightleftharpoons \mathrm{HClO_2} + \mathrm{HClO_3} \rightleftharpoons \underset{\text{(in solution)}}{\mathrm{KClO_3}}$$

The interchange observed when potassium nitrate was similarly treated may be explained in the same way. This effect has been observed by Titani and Goto (*loc. cit.*), who employed a solution of potassium hydrogen sulphate as the acid medium. The inter-exchange of oxygen between a gas and water in which it dissolves to form an acid has been investigated by Cohn and Urey (*J. Amer. Chem. Soc.*, 1938, **60**, 679) for the system carbon dioxide–water. We have found that nitrous oxide, which is appreciably soluble in water, suffers no detectable interchange with enriched water after being kept in contact with it at 20° for 14 days, and we connect this observation with the fact that no reaction between nitrous oxide and water is known to occur.

EXPERIMENTAL.

Water densities were determined with an experimental error of ± 1·5γd by the silica float method described in earlier papers (Briscoe and others, J., 1934, 1207, 1948). The sample of water was distilled off in a vacuum from the salt under examination, and then purified by distillation in a vacuum from potassium permanganate and sodium peroxide followed by a further distillation from phosphoric oxide, previous work having shown that no detectable interchange occurred with the small quantities of these reagents required for efficient purification. As little as 1·5 ml. of water sufficed for a determination. Before the interchange experiments, the water was purified by distillation at atmospheric pressure from the reagents mentioned above. The Pyrex reaction vessels were cleaned before use with chromic–sulphuric acid mixture, thoroughly rinsed out with distilled water, and dried. All salts employed (except hydrates) were dried for at least 24 hours in an air oven at 170°.

FIG. 1.



The silver tubes used for the later experiments with alkaline solutions were of the form shown in Fig. 1 and of about 10 ml. capacity, having the joints soldered with hard silver solder (m. p. 820°). After the experimental solution had been introduced, they were sealed by squeezing the narrow tube *A* flat at *C*, and then melting a small quantity of soft silver solder (m. p. 450°) in the cup *D*, while the body *B* and part of the narrow tube were kept cool by immersion in water. To recover the solution at the end of the experiment, the narrow tube was cut cleanly at *E* with a sharp penknife and could then be used again. Actually, two silver tubes served for all the experiments made, and proved a convenient and effective device.

Experiments 1—24.—The results obtained for potassium chlorate, sodium perchlorate, and sodium sulphate are given in Table I. Cols. 1—5 are self-explanatory and give the conditions employed for each pair of comparative experiments; a Pyrex-glass tube was used in all cases except those marked otherwise. Col. 6 gives the difference in density between the water used for the interchange and that recovered from the reaction tube, and Col. 7 gives the calculated value for this density difference, complete interchange being assumed. In experiment No. 4, for example, the figure given in col. 7 includes the effect both of the potassium chlorate and of the sodium hydroxide. Cols. 8 and 9 give, respectively, for each pair of experiments, the observed difference attributable to oxygen interchange with the dissolved salt and the calculated difference for complete interchange.

Expts. nos. 5, 7, 18, and 20 show the small but definite discrepancies between observed and calculated values when a solution of sodium hydroxide is heated in glass tubes, which we attribute to silicate interchange.

Expt. no. 24 is of special value as it involves no calculated corrections. It was performed by cooling the sodium sulphate and enriched water to − 78° in a 50-ml. Pyrex conical flask, and then adding the metallic sodium, which had previously been purified by distillation in a vacuum. After the neck had been plugged with asbestos wool to exclude atmospheric moisture, the flask was allowed to warm gradually to room temperature, and finally, after being warmed to dissolve the sodium sulphate, the solution was transferred to the silver tube, sealed up, and kept for 2 days at 100°. No change whatever in the density of the water could be detected.

TABLE I.

Expt. No. 1.	Wt. of salt, g. 2.	Liquid used.* 3.	Vol. of liquid, ml. 4.	Conditions of reaction. 5.		Change in water density expressed as $\Delta\gamma d$.			
				Hrs.	Temp.	Obs. 6.	Calc. 7.	Differences. Obs. 8.	Calc. 9.
(a) *Potassium chlorate.*									
1	0·500	Water	4·0	289	20°	0	− 6	—	—
2	1·600	Water	3·0	22·5	100	− 3	−26	—	—
3	2·200	Water	4·0	22·5	100	0	−26	—	—
4	1·300	1·175N-NaOH	2·0	66	20	− 5	−34	0	−31
5	nil	1·175N-NaOH	2·0	63	20	− 5	− 3		
6	1·550	1·06N-NaOH	3·0	43	100	−11	−29	− 3	−26
7	nil	1·06N-NaOH	3·0	46·25	100	− 8	− 3		
8	1·550	1·028N-H_2SO_4	3·0	37·5	100	−35	−33	−29	−27
9	nil	1·028N-H_2SO_4	3·0	37·5	100	− 6	− 6		
(b) *Sodium perchlorate.*									
10	0·500	Water	4·0	193	20	0	− 4	—	—
11	4·000	Water	4·0	22·5	100	− 2	−34	—	—
12	4·000	Water	4·0	98·3	100	+ 1	−34	—	—
13	1·500	1·175N-NaOH	2·0	64·5	20	− 7	−28	− 2	−25
5	nil	1·175N-NaOH	2·0	63	20	− 5	− 3		
14	4·000	1·06N-NaOH	3·0	43	100	−10	−48	− 2	−45
7	nil	1·06N-NaOH	3·0	46·25	100	− 8	− 3		
15	3·000	1·028N-H_2SO_4	3·0	37·5	100	− 9	−38	− 3	−32
9	nil	1·028N-H_2SO_4	3·0	37·5	100	− 6	− 6		
(c) *Sodium sulphate.*									
16	1·300	1·028N-H_2SO_4	3·0	37·5	100	− 5	−28	+ 1	−22
9	nil	1·028N-H_2SO_4	3·0	37·5	100	− 6	− 6		
17	1·300	0·998N-NaOH	3·0	29·25	100	− 8	−39	− 1	−35
18	nil	0·998N-NaOH	3·0	29·25	100	− 7	− 4		
19†	1·300	0·988N-NaOH	3·0	29·25	100	−11	−39	− 4	−35
20†	nil	0·988N-NaOH	3·0	29·25	100	− 8	− 4		
21‡	1·300	0·988N-NaOH	3·0	44·6	100	− 2	−39	+ 2	−35
22‡	1·300	0·998N-NaOH	3·0	44·6	100	− 1	−39		
23‡	nil	0·998N-NaOH	3·0	44·6	100	− 3	− 4		
24‡	2·160	Water + 0·122 g. metallic Na	5·0	46·5	100	0	−34	—	—

* The " liquid used " (col. 3) was always water enriched in heavy oxygen or, in the parallel experiments, the solution indicated made with the same water.

† Hard-glass tubes were used in these experiments.

‡ Silver tubes were used in these experiments.

In expts. 1—7 and 10—14 inclusive the water used had $\Delta\gamma d = + 130$ due to ^{18}O and $\Delta\gamma d = + 115$ due to deuterium : a total enrichment of $\Delta\gamma d = + 245$. In expts. 8, 9, 15, and 16, the corresponding figures were + 125 and + 106, making a total of $+ 231\gamma d$, and the water employed in expts. 17—24 inclusive had the values + 200 and $+ 180\gamma d$, making a total of $+ 380\gamma d$.

In several cases a single experiment with plain water (*e.g.*, expt. 9) served as the blank for two or three experiments with dissolved salt (*e.g.*, expts. 8, 15, and 16).

Experiment 42.—This experiment is described here because it afforded a crucial test of the conclusion drawn from Expt. 24. Sodium hydroxide (0·335 g.) was dissolved in 8 ml. of enriched water having a total excess density of $+ 395\gamma d$ of which that due to ^{18}O was $+ 210\gamma d$, and this solution was equally distributed between two silver tubes, 1·633 g. of anhydrous sodium sulphate being added also to one of them. The tubes were hermetically sealed and then heated to 100° for 19 days (456 hours).

The two samples of purified water subsequently recovered from the tubes were subjected to flotation-temperature determinations having a greater precision ($\pm$ $0{\cdot}5\gamma d$) than in the other experiments. The excess density found in both cases was the same, *viz.*, + 391*γd*, the calculated decrease caused by the added sodium hydroxide being − 4*γd* as observed. The calculated decrease of density for complete oxygen interchange with the sulphate present is − 40*γd*.

Experiments 24*a*—38.—The results of a further series of miscellaneous experiments are recorded in Table II, where the data have the same significance as in Table I. Expts. 24*a*, 25, and 26 afford no evidence of interchange with orthophosphates, the density decrease observed in expt. 26 being almost precisely that due to dilution by water produced from the reagents.

TABLE II.

Expt. No. 1.	Salt used. 1*a*.	Wt. of salt, g. 2.	Liquid used.* 3.	Vol. of liquid, ml. 4.	Conditions of reaction.‡ 5. Hrs.	Temp.	Change in water density expressed as Δ*γd*. Obs. 6.	Calc. 7.	Differences. Obs. 8.	Calc. 9.
24(*a*)	Na_2HPO_4	1·500	H_2O	3·0	23	100°	0	−32	—	—
25	KH_2PO_4	1·000	,,	3·0	41	100	− 2	−20	—	—
26§	Na_2HPO_4 NaOH	2·000 0·671	,,	4·0	46·5	100	−26†	−45	—	—
27§	H_3BO_3	1·200	,,	4·0	46·5	100	−32	−33	—	—
28	H_3BO_3	1·200	,,	4·0	1 min. at 100° and distilled at once		−34	−33	—	—
29	$Na_2B_4O_7,10H_2O$	1·500	,,	3·0	,,	,,	−91	−91	—	—
30	$KHSO_4$	1·574	,,	3·0	23	100	0	−29	—	—
31§	K_2CrO_4	1·000	,,	3·0	22	100	−22	−24	—	—
32§	$K_2Cr_2O_7$	1·000	,,	3·0	22	100	−22	−22	—	—
33	K_2CrO_4	1·000	,,	3·0	3·75	100	−24	−24	—	—
34§	K_2CrO_4 NaOH	1·330 0·320	,,	4·0	25	100	−34	−33	—	—
35§	K_2CrO_4 NaOH	1·000 0·24	,,	3·0	25	100	−30	−33	—	—
36	K_2CrO_4 NaOH	4·000 0·456	,,	12·0	Various times at 20°; 3 ml. of liquid withdrawn at a time:					
					(a) 1 hour		− 4	−29	—	—
					(b) 3 hours		− 4	−29	—	—
					(c) 24 ,,		− 4	−29	—	—
					(d) 240 ,,		− 3	−29	—	—
37	K_2CrO_4	4·000	,,	12·0	Various times at 20°; 3 ml. of liquid withdrawn at a time:					
					(a) ½ hour		− 4	−17	—	—
					(b) 2 hours		− 6	−17	—	—
					(c) 5·5 ,,		− 9	−17	—	—
					(d) 24·0 ,,		−14	−17	—	—
38	KNO_3	1·500	1·028N-H_2SO_4	3·0	24	100°	−35	−32	−29	−26
39	—	nil	1·028N-H_2SO_4	3·0	37·5	100	− 6	− 6		

* The density of the water used was as follows:

Experiments No.	Excess density, *γd*, due to Deuterium.	^{18}O.	Experiments No.	Excess density, *γd*, due to Deuterium.	^{18}O.
24, 27, 28	0	+157	36	+180	+210
25, 30	0	+135	37	+165	+150
26, 29, 31, 32, 33, 34, 35	+180	+200	38	+106	+125

† In expt. no. 26, the water liberated by the reaction, $Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$ is calculated to cause a decrease in density of the total water = − 24*γd*, in good agreement with the observed figure of 26*γd*.

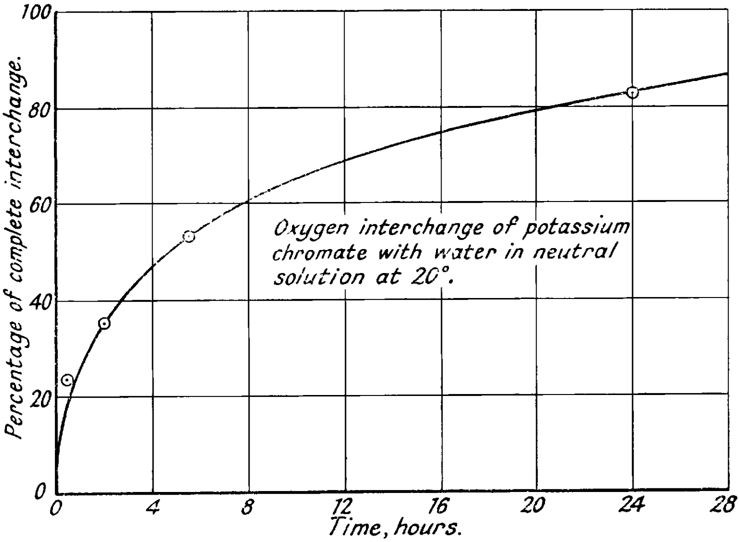
‡ A Pyrex-glass tube was used except in those experiments marked §, in which a silver tube was used.

Expts. 27, 28, and 29 show that the exchange of oxygen with boric acid and borax is complete, not only in the usual 2 days' heating at 100°, but even in the shortest time necessary for merely heating the solution to 100° and distilling off the solvent. In expt. no. 29 the diluting effect of the water of crystallisation is to reduce the total density of the water used from 380*γd* to 308*γd*, while for complete interchange of all seven oxygen atoms in the salt the density should be reduced further to 289*γd*—a total decrease of 91*γd*, as observed.

In expts. nos. 34, 35, and 36 the figures in col. 7 include values of − 8, − 8, and − 4γd respectively, which represent the effect of the sodium hydroxide alone on the water density. It is clear from these and the three preceding experiments that for potassium dichromate and chromate, with or without added alkali, oxygen exchange is complete in one day at 100°. On the other hand, the results of expt. 37 plotted in Fig. 2 show clearly the progress of the slow exchange with the chromate in neutral solution at 20°, while expt. 36 proves that addition of caustic alkali greatly retards the exchange under the same conditions.

Experiment 39.—This was designed to seek evidence of interchange with nitrous oxide. The gas was obtained from a cylinder and condensed in a trap at − 120°. It was then subjected to fractionation in a vacuum in a normal vacuum fractionating apparatus, and slightly over 3 l. of the pure gas at 76 cm. Hg were condensed in a receiver connected to an evacuated reservoir of approximately 3 l. capacity. Then 3 ml. of enriched water were distilled on to the solid nitrous oxide at − 120° and the system was sealed off and left for 14 days at room temperature. The system was then reconnected to the vacuum line by means of a Stock vacuum seal breaker, and the gas was pumped off through a trap at − 80° in which the water collected. The water was purified in the usual manner and its density determined.

FIG. 2.



Density of water used + 380γd (200γd due to ^{18}O)
,, ,, recovered + 381γd

The calculated decrease for interchange of the nitrous oxide is approximately 90γd.

Experiment 40.—Some " Pure Crystalline " (Hopkin & Williams) sodium metasilicate was dried for 48 hours at 170° in an air-oven and powdered in an agate mortar. 4 G. of the powder were boiled with 9 ml. of enriched water, and the solution divided into two parts: (*a*) was heated for 46·5 hours at 100° in a silver tube; (*b*) was cooled at once and the water distilled off in a vacuum. In both cases the change in water density observed was − 30γd; the water used had an enrichment of + 380γd (+ 200γd due to ^{18}O). The change in density calculated for complete oxygen interchange is −33γd.

Experiment 41.—The calculated equivalent amounts of " AnalaR " sodium carbonate (anhydrous) and pure powdered quartz were fused together in a tared platinum crucible over a blast Meker flame, cooled, and reweighed : the decrease in weight due to carbon dioxide lost agreed well with the calculated value.

A weighed amount of this synthetic sodium metasilicate was treated as in 40(*b*) above, 1·527 g. of sodium metasilicate and 3·5 ml. of enriched water being used. The density of the water used was the same as in expt. 40 : the observed change in density was − 34γd, whilst that calculated for complete oxygen interchange is − 32γd.

From the work here recorded we conclude that, if oxygen interchange occurs at all with the sulphate or the phosphate radical in neutral or alkaline solution, it is so slow that its detection is difficult. Examination of other cases suggests that, in general, where oxygen interchange occurs with oxy-anions it may be attributed to known reactions involving the reversible addition of a water molecule to the anion. It is satisfactory that for oxy-anions such as the phosphate and sulphate ions, which need not on ordinary chemical grounds be assumed to react with water, it is no longer necessary to postulate a special mechanism to explain oxygen interchange.

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