132. *Some Further Observations on the Interchange of Heavy Oxygen between Water and Certain Inorganic Oxy-anions.*

By E. R. S. Winter and H. V. A. Briscoe.

Using heavy-oxygen water having an excess density due to ^{18}O of 150—210γd, the study of the interchange of oxygen between water and oxyacid radicals has been extended, with particular reference to the interchange of the sulphate and bisulphate ion. This work arose from observations previously published (Winter, Carlton, and Briscoe, J., 1940, 131) wherein some puzzling aspects of such interchanges were revealed. Two of the observations recorded in the above paper require amendment, since it has now been found that potassium hydrogen sulphate and potassium dihydrogen orthophosphate do interchange, though slowly, at 100°. The interchange of potassium hydrogen sulphate has been examined for concentrations ranging from 1·226 to 6·13M at 100°, and in 3·85 and 6·13M-solutions at 108°. The interchange of the sodium salt has been studied at 100° in 6·13 and 3·85M-solutions. In certain cases the effect of the addition of other salts and of free acid has also been examined. The results of all the experiments now reported are given in Tables I and II, and the more important of them are plotted in Fig. 1. It is established that the rate of interchange in bisulphate solutions increases with concentration, and with temperature; that the nature of the cation exerts a marked influence on the rate of interchange, which is substantially greater with the sodium than with the potassium salt; and that the addition of other (inert) salts or of free acid to the system also increases the rate of interchange. It is also apparent that the rate of interchange for potassium dihydrogen orthophosphate is substantially lower than that for potassium hydrogen sulphate.

Analysis of the results shows that no simple mechanism will satisfactorily explain the experimental figures, and it is concluded that the most probable explanation is that interchange occurs through anhydride formation. This statement is shown also to apply to the interchange with potassium dihydrogen orthophosphate at 100° and with potassium chromate at 20°.

Various theories have been proposed to account for the interchange of oxygen between water and inorganic compounds. Datta, Day, and Ingold (J., 1937, 1968) put forward three possibilities : (1) Dehydration followed by hydration; this seems to be the mechanism whereby silicates, borates, and possibly chromates suffer interchange (Winter, Carlton, and Briscoe, *loc. cit.*). (2) Hydration followed by dehydration; this has been realised by Mills and Urey (*J. Amer. Chem. Soc.*, 1940, **62**, 1019) in the system carbon dioxide–water, and it also most probably plays a part in the interchange of borates (Winter, Carlton, and Briscoe, *loc. cit.*). (3) Temporary covalency increase; this was the mechanism put forward for the interchange observed in alkaline solutions of sodium sulphate, and was also used by Blumenthal and Herbert (*Trans. Faraday Soc.*, 1937, **33**, 849) to explain the interchange they observed in solutions of tripotassium orthophosphate. Titani and Goto (*Bull. Chem. Soc. Japan*, 1939, **14**, 77) examined the interchange of various salts in acid and neutral solutions

Table I.

Heavy oxygen interchange in solutions of acid salts of oxy-acids.

[All experiments were at 100° except where otherwise indicated, and the original heaviness of water due to ^{18}O (γd) is 210 except where annotated.]

Expt. No.	Molarity.	Time (hrs.).	Inter-change, %.	$\Delta\gamma d_t$.	$\Delta\gamma d_\infty$.	Expt. No.	Molarity.	Time (hrs.).	Inter-change, %.	$\Delta\gamma d_t$.	$\Delta\gamma d_\infty$.
					$KHSO_4$.						
1	6·13	22	47·0	−30	−64	15	2·45	72	35·5	−11	−31
2	,,	45	65·6	−42	,,	16	,,	115	45·1	−14	,,
3	,,	90	86·0	−55	,,	17	,,	194	55·0	−17	,,
4	,,	120	92·2	−59	,,	18	1·226	43	11·8	− 2	−17
5	4·53	14	32·7	−17	−52	19	,,	93	29·4	− 5	,,
6	,,	22	42·3	−22	,,	20	,,	144	35·3	− 6	,,
7	,,	50	60·0	−31	,,	21	,,	186	47·1	− 8	,,
8	,,	136	73·0	−38	,,	22 *	6·13	5	40·0	−23	−58
9	3·85	10	19·6	− 9	−46	23 *	,,	13	72·4	−42	,,
10	,,	20	34·8	−16	,,	24 *	,,	20	88·0	−51	,,
11	,,	45	52·2	−24	,,	25 *	3·85	5	31·7	−13	−41
12	,,	100	60·1	−28	,,	26 *	,,	13	58·5	−24	,,
13	,,	160	63·0	−29	,,	27 *	,,	30	75·6	−31	,,
14	2·45	42	29·0	− 9	−31	28 †	6·13	5	100·0	−59	−58
					$NaHSO_4$.						
29 ‡	6·13	10	41·4	−24	−58	32	3·85	20	41·3	−19	−46
30 ‡	,,	23	62·0	−36	,,	33	,,	45	60·1	−28	,,
31 ‡	,,	46	80·0	−47	,,	34	,,	96	74·0	−34	,,
						35	,,	190	84·8	−39	,,
					KH_2PO_4.						
36 §	2·78	70	29·0	− 9	−31	38 §	2·78	167	45·0	−14	−31
37 §	,,	100	35·5	−11	,,						

* Temperature = 108° and γd = 186.
† ,, 132° and γd = 186.
‡ γd = 186.
§ γd = 156.

TABLE II.

Miscellaneous experiments, mainly on interchange in solutions of mixtures.

[Temp. = 100° except in No. 40, where temp. = 0°. 3 Ml. of water used in each expt.]

Expt. No.	Substance.	Wt. used (g.).	Molarity.	Time, hrs.	Interchange, %.	γd_0.	$\Delta\gamma d_t$.	$\Delta\gamma d_\infty$.
39	H_2SO_4	0·49	1·67	169	100	210	−24	−23
40	,,	,,	,,	<0·5	,,	,,	−23	−23
41	Na_2SO_4	1·4	3·29	151	48·5	,,	−16	−33
	H_2SO_4	0·45	1·53	,,	100 *	,,	−21 *	−21 *
42	$NaClO_4$	1·0	2·73	210	14·3	,,	− 4	−28
	H_2SO_4	0·56	1·71	,,	100 *	,,	−23 *	−23 *
43	$NaHSO_4$	1·388	3·85	157	100	,,	−46	−46
	$NaClO_4$	1·0	2·73	,,	13·3 †	,,	− 4 †	−30 †
44	$NaHSO_4$	1·388	3·85	100	87·0	,,	−40	−46
	$NaClO_4$	1·0	2·73	,,	13·3 †	,,	− 4 †	−30 †
45	$KHSO_4$	1·574	3·85	21	45·6 ‡	,,	−21 ‡	−46 ‡
	KCl	0·25	1·12	,,	—	,,	—	—
46	$KHSO_4$	1·00	2·45	72	57·1 ‡	186	−16 ‡	−28
	KCl	0·25	1·12	,,	—	,,	—	—
47	$KHSO_4$	1·00	2·45	70	63·0	,,	−17 ‡	−27
	HCl (conc.)	0·3	1·11	,,	—	,,	—	—
48	$Na_4P_2O_7$	1·5	1·88	41	0	210	0	−40
49	$Na_4P_2O_7$	1·5	1·88	41	2·5 §	,,	− 1 §	−40
	NaOH	0·10	0·83	,,	100	,,	− 3	− 3
50	$Na_4P_2O_7$	1·5	1·88	64	15·0	,,	− 6	−40
	H_2SO_4	0·04	0·13	,,	100 *	,,	− 2 *	− 2 *

* Interchange of the H_2SO_4 assumed here to be 100%, by reason of experiments 39 and 40.

† A value of −4 for $\Delta\gamma d_t$ is here assumed for the interchange of $NaClO_4$, by reason of experiment 42. The balance of the observed decrease in water density is assumed due to interchange of $NaHSO_4$.

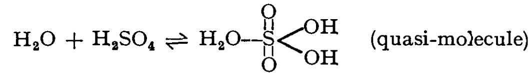
‡ These results have been corrected for the amount of NaOH added during the purification of the water.

§ This experiment was performed in a silver tube. The interchange of the NaOH was assumed to be 100% (Winter, Carlton, and Briscoe, *loc. cit.*).

and at temperatures up to 180°. They suggested that interchange could be accounted for by the formation of either a " quasi-molecule " or an anhydride; *e.g.*, for the bisulphate ion the mechanism would be

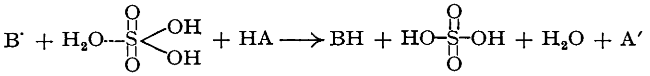
either

$$H_2OH^{\cdot} + HSO'_4 \rightleftharpoons H_2O + H_2SO_4$$



$$H_2O + H_2SO_4 \rightleftharpoons H_2O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\!\!<\!\begin{smallmatrix}OH\\OH\end{smallmatrix}$$

(quasi-molecule)



$$B^{\cdot} + H_2O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\!\!<\!\begin{smallmatrix}OH\\OH\end{smallmatrix} + HA \longrightarrow BH + HO{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}{-}OH + H_2O + A'$$

(where B˙ and A′ are Brönsted base and acid respectively)

or

$$H_2OH^{\cdot} + HSO'_4 \rightleftharpoons H_2O + H_2SO_4$$
$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

It should be noted that the latter mechanism is really the same as mechanism (1), above.

From a study of the interchange of potassium hydrogen sulphate, sodium chromate, chromic anhydride, potassium sulphite, and other salts, Mills (*J. Amer. Chem. Soc.*, 1940, **62**, 2833) concluded that salts suffer interchange through anhydride formation or some other reaction. From a theoretical consideration of the mechanism put forward to account for the interchange of potassium chromate (Winter, Carlton, and Briscoe, *loc. cit.*), Mills concluded that this mechanism (involving the formation of the dichromate ion Cr_2O_7'') did not account for the observed rapid interchange, and assumed that this interchange occurs *via* anhydride formation.

The whole problem is complex, and its difficulty is accentuated by the fact that these interchange experiments are necessarily performed in concentrated solutions, about the constitution of which little is known. Some attempt at a mathematical formulation may be made as follows.

Neglect for the moment any consideration of the precise mechanism whereby interchange occurs, and consider the four equations below as representing the net result during the interchange of bisulphates (in the following discussion **O** represents a heavy, and O a normal oxygen atom) :

$$\left.\begin{aligned}
&\mathrm{SOOOOH'} + \mathrm{H\mathbf{O}H} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S\mathbf{O}OOOH'} + \mathrm{HOH}\\
&\mathrm{S\mathbf{O}OOOH'} + \mathrm{H\mathbf{O}H} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S\mathbf{OO}OOH'} + \mathbf{HOH}\\
&\mathrm{S\mathbf{OO}OOH'} + \mathrm{H\mathbf{O}H} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S\mathbf{OOO}OH'} + \mathrm{HOH}\\
&\mathrm{S\mathbf{OOO}OH'} \quad \mathrm{H\mathbf{O}H} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S\mathbf{OOOO}H'} + \mathrm{HOH}
\end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (1) \, .$$

Hence

$$\begin{aligned} \mathrm{d[H\mathbf{O}H]/d}t = {} & k_1[\mathrm{H\mathbf{O}H}]_t\,\{[\mathrm{SOOOOH'}]_t + \tfrac{3}{4}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{2}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{OOO}OH'}]_t\} \\ & - k_{-1}[\mathrm{HOH}]_t\,\{[\mathrm{S\mathbf{OOOO}H'}]_t + \tfrac{3}{4}[\mathrm{S\mathbf{OOO}OH'}]_t + \tfrac{1}{2}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{O}OOOH'}]_t\} \end{aligned} \quad . \quad . \quad . \quad (2)$$

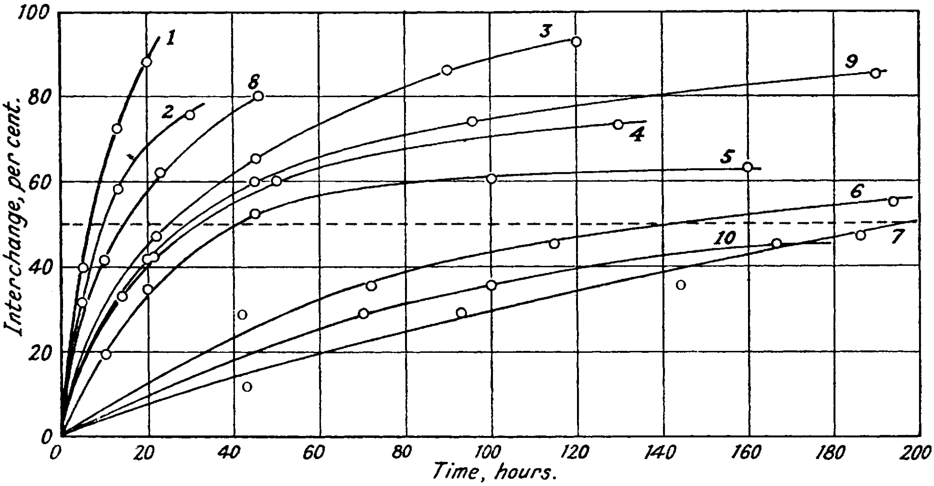
Then if a_t and ε_t be the atom fractions of **O** in the water and the bisulphate respectively at the same time

$$\left.\begin{aligned} a_t &= [\mathrm{H\mathbf{O}H}]_t/[\mathrm{H_2O}], \quad 1 - a_t = [\mathrm{HOH}]_t/[\mathrm{H_2O}] \\ \varepsilon_t &= \{[\mathrm{S\mathbf{OOOO}H'}]_t + \tfrac{3}{4}[\mathrm{S\mathbf{OOO}OH'}]_t + \tfrac{1}{2}[\mathrm{S\mathbf{OO}OOH'}]_t + \tfrac{1}{4}[\mathrm{S\mathbf{O}OOOH'}]_t\}/[\mathrm{HSO_4'}] \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

with a similar expression for $1 - \varepsilon_t$. ($[\mathrm{H_2O}]$ and $[\mathrm{HSO_4'}]$ here represent the total amount of water and of bisulphate radical respectively present in the system.)

FIG. 1.

Rates of interchange.



1. $\mathrm{KHSO_4}$, 6·13M, 108°.
2. $\mathrm{KHSO_4}$, 3·85M, 108°.
3. $\mathrm{KHSO_4}$, 6·13M, 100°.
4. $\mathrm{KHSO_4}$, 4·53M, 100°.
5. $\mathrm{KHSO_4}$, 3·85M, 100°.
6. $\mathrm{KHSO_4}$, 2·45M, 100°.
7. $\mathrm{KHSO_4}$, 1·226M, 100°.
8. $\mathrm{NaHSO_4}$, 6·13M, 100°.
9. $\mathrm{NaHSO_4}$, 3·85M, 100°.
10. $\mathrm{KH_2PO_4}$, 2·78M, 100°.

Assuming that $k_1 = k_{-1}$, as will be approximately true, it follows from (2) and (3) that

$$-\,\mathrm{d}a_t/\mathrm{d}t = k_1[\mathrm{HSO_4'}](a_t - \varepsilon_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now at equilibrium,

$$a_\infty\{[\mathrm{H_2O}] + [\mathrm{HSO_4'}]\} = a_t[\mathrm{H_2O}] + \varepsilon_t[\mathrm{HSO_4'}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

hence

$$-\,\mathrm{d}a_t/\mathrm{d}t = k_1(c_1 + c_2)(a_t - a_\infty) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$c_1 = [\mathrm{H_2O}] \text{ and } c_2 = [\mathrm{HSO_4'}]$$

Integrating, we have

$$-\log_e(a_t - a_\infty) = k_1(c_1 + c_2)t + A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The value of A is found from the limiting conditions : $t = 0$, $a_t = a_0$; so that finally we may write

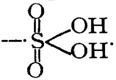
$$\log_{10}(a_0 - a_\infty)/(a_t - a_\infty) = k(c_1 + c_2)t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Equation (8) has been applied to the experimental data and the results are given in Table III.

In all cases k has been calculated with t in hours and the concentrations c_2 and c_1 (= 55·56) in g.-mols./l. These results are presented in Fig. 2, the values of k for the interchange of potassium chromate being multiplied by 10^{-3} to bring them to a convenient magnitude.

On examining the results of the bisulphate interchange, it is seen that this approach does not give a constant value for k, neither is k, as so calculated, independent of the concentration of bisulphate. It is possible to show that the stoicheiometric concentration of bisulphate may not be the only concentration term necessary.

Titani and Goto (*loc. cit.*) have suggested that the interchange may occur through the formation of sulphuric acid from bisulphate ions, followed by interchange through the medium of a " quasi " molecule



$\mathrm{H_2O{-}S(=O)_2{<}^{OH}_{OH}}$.

In view of the observed rapid interchange of sulphuric acid, and of the non-interchange of sodium sulphate in neutral or alkaline solution, this suggestion would appear quite reasonable. We have then

$$\mathrm{H^{\cdot} + HSO_4' \rightleftharpoons H_2SO_4}$$

TABLE III.

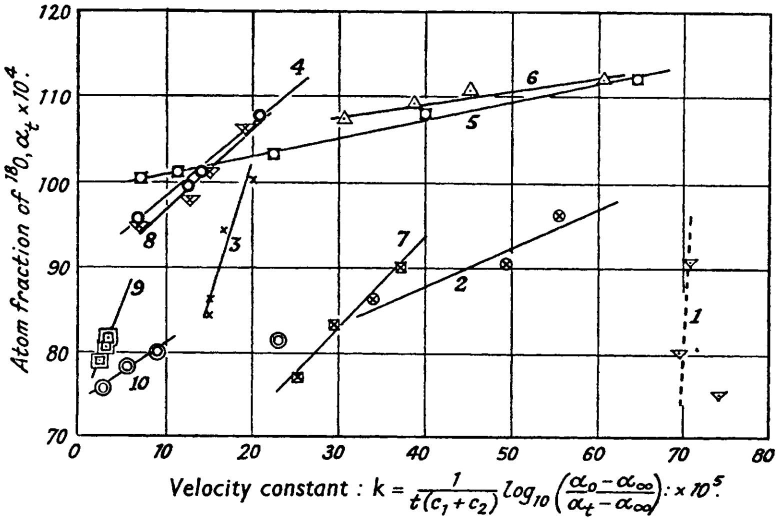
c_2.	t (hrs.).	Interch., %.	a_t.	a_∞.	$k \times 10^4$.	c_2.	t (hrs.).	Interch., %.	a_t.	a_∞.	$k \times 10^4$.
Interchange of $KHSO_4$ *at* 100° (a_0 = 0·01167).											
6·13	22	47·0	0·01000	0·00811	2·02	3·85	100	60·1	0·01011	0·00911	1·18
,,	45	65·6	0·00933	,,	1·67	,,	160	63·0	0·01006	,,	0·76
,,	90	86·0	0·00861	,,	1·52	2·45	42	29·0	0·01117	0·00994	6·08
,,	120	92·2	0·00839	,,	1·54	,,	72	35·5	0·01106	,,	4·52
4·53	14	32·7	0·0107	0·00878	2·11	,,	115	45·1	0·01089	,,	3·90
,,	22	42·3	0·0101	,,	1·45	,,	194	55·0	0·01072	,,	3·07
,,	50	60·0	0·00995	,,	1·31	1·226	43	11·8	0·01156	0·01073	0·221
,,	136	73·0	0·00956	,,	0·70	,,	93	29·4	0·01142	,,	0·254
3·85	10	19·6	0·01117	0·00911	6·48	,,	144	35·3	0·01134	,,	0·230
,,	20	34·8	0·01078	,,	4·02	,,	186	47·1	0·01123	,,	0·260
,,	45	52·2	0·01033	,,	2·29						
Interchange of $KHSO_4$ *at* 108° (a_0 = 0·01033).											
6·13	5	40·0	0·00906	0·00711	7·07	3·85	5	31·7	0·00961	0·00806	5·58
,,	13	72·4	0·00800	,,	6·97	,,	13	58·5	0·00900	,,	4·96
,,	20	88·0	0·00750	,,	7·43	,,	30	75·6	0·00861	,,	3·45
Interchange of $NaHSO_4$ *at* 100° (a_0 = 0·01033 for c_2 = 6·13; a_0 = 0·01167 for c_2 = 3·85).											
6·13	10	41·4	0·00900	0·00711	3·76	3·85	20	41·3	0·01061	0·00911	1·95
,,	23	62·0	0·00833	,,	2·97	,,	45	60·1	0·01011	,,	1·53
,,	46	80·0	0·00772	,,	2·54	,,	96	74·0	0·00977	,,	1·03
						,,	190	84·8	0·00950	,,	0·70
Interchange of KH_2PO_4 *at* 100° (a_0 = 0·00867).											
2·78	70	29·0	0·00817	0·00694	0·363	2·78	167	45·0	0·00789	0·00694	0·267
,,	100	35·5	0·00806	,,	0·324						
Interchange of K_2CrO_4 *at* 20° (a_0 = 0·00833).*											
1·66	0·5	23·5	0·00811	0·00739	23·3 †	1·66	5·5	52·9	0·00783	0·00739	5·95 †
,,	2·0	35·3	0·00800	,,	9·45 †	,,	24·0	82·4	0·00756	,,	3·14 †

* These results are taken from the previous communication (Winter, Carlton, and Briscoe, *loc. cit.*).

† This value of $k = \log_{10} (a_0 - a_\infty)/(a_t - a_\infty)$.

FIG. 2.

Variation of velocity of interchange (k) *with residual concentration of* $H_2{}^{18}O(a_t)$.



1. $KHSO_4$, 6·13M, 108°.
2. $KHSO_4$, 3·85M, 108°.
3. $KHSO_4$, 6·13M, 100°.
4. $KHSO_4$, 4·53M, 100°.
5. $KHSO_4$, 3·85M, 100°.
6. $KHSO_4$, 2·45M, 100°.
7. $NaHSO_4$, 6·13M, 100°.
8. $NaHSO_4$, 3·85M, 100°.
9. KH_2PO_4, 2·78M, 100°.
10. K_2CrO_4, 1·66M, 20°.

If x is the concentration of $H^\cdot$, $c_2 - x$ that of HSO_4', and ϕ that of H_2SO_4, we have $\phi = (x)(c_2 - x)/K_{H_2SO_4}$, where x is a function of c_2, being approximately determined by the dissociation of HSO_4' into $H^\cdot$ and SO_4''. It would appear reasonable to assume that the rate-determining step in the interchange would here be the formation and destruction of the " quasi-molecule " $H_2O \ldots H_2SO_4$, in which case the simple relationship given in equation (8) should become :

$$\log_{10}(a_0 - a_\infty)/(a_t - a_\infty) = k_0 t(x)(c_2 - x)(c_1 + c_2)/(c_2) \quad \ldots \ldots \quad (9)$$

where

$$k_0 = k/K_{H_2SO_4}$$

This may well give a truer picture of the underlying relationships than equation (8), but does not account in any way for the fact that k is not constant over the range of observations at any one concentration. It appears that k varies regularly in the main with the residual heaviness of the water, a_t; why this should be so is obscure, but the dependence is clearly shown in Fig. 2, where a_t is plotted against k. It is seen that within the limits of experimental error, with the exception of the interchange of 6·13M-potassium hydrogen sulphate at 108° (and of 1·226M-potassium hydrogen sulphate at 100°, which is not shown in Fig. 2) the points all lie on straight lines.

Equation (8) has been applied to the observations of the interchange of potassium dihydrogen orthophosphate at 100° and potassium chromate at 20°, with similar results. The apparent large deviation of the first point in the chromate observations is within the limits of error of the density determination ($\pm 1{\cdot}5\gamma d$) and of the time of interchange (approximately ±10 mins.). The inclusion in this discussion of the observations on potassium chromate interchange seems legitimate, for if the interchange occurs through the reaction $Cr_2O_7'' + H_2O = 2HCrO_4'$, the mathematical investigation leads to an equation of the same form as (9) above (Mills, *loc. cit.*), and it seems reasonable to suppose that the course of the phosphate interchange will closely resemble that of the bisulphate.

It has been suggested by Mills (*loc. cit.*) and by Titani and Goto (*loc. cit.*) that interchange in concentrated solutions may occur through anhydride formation. This conception is difficult to prove directly, as it is not easy to estimate the amount (if any) of anhydride present in any given solution of, say, potassium hydrogen sulphate or potassium chromate. The following mathematical investigation is possible, based on the method used by Mills and Urey (*loc. cit.*) for the system CO_2–H_2O–H_2CO_3–Na_2CO_3. The case of bisulphate interchange will be discussed, the anhydride in this case being assumed to be SO_3. The equilibria possible are :

$$\left.\begin{aligned} \mathrm{SOOO + HOH} &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HHSOOOO} \rightleftharpoons \mathrm{H^{\bullet} + SOOOOH'} \\ \mathrm{SOOO + H\mathbf{O}H} &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HHS\mathbf{O}OOO} \rightleftharpoons \mathrm{H + S\mathbf{O}OOOH'} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

and so on, the equations being analogous to those of (1) above.

Let α_t, β_t, and ε_t represent respectively the atom fraction of **O** at the time t in the water, the anhydride, and the sulphuric acid. Then from (10) we may obtain similar expressions to (2) above for $d\alpha_t/dt$, $d\beta_t/dt$, and $d\varepsilon_t/dt$. From these we arrive finally at the following equations :

$$d\alpha/dt = p(\epsilon - \alpha),\ d\beta/dt = q(\beta - \epsilon),\ d\epsilon/dt = r(4\epsilon - 3\beta - \alpha)/4 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

where

$$p = k_1[SO_3],\ q = k_1[H_2O],\ r = k_1[H_2O][SO_3]/[H_2SO_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

Here also the quantities in square brackets represent the total concentration of anhydride, water, and sulphuric acid present in the reacting system. The solution of equations (11) will be of the form

$$\left.\begin{aligned} \alpha &= a_1e^{-\lambda_1 t} + a_2e^{-\lambda_2 t} \\ \beta &= b_1e^{-\lambda_1 t} + b_2e^{-\lambda_2 t} \\ \epsilon &= c_1e^{-\lambda_1 t} + c_2e^{-\lambda_2 t} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

where

$$\lambda_{1,\,2} = \tfrac{1}{2}(p - q - r \pm \sqrt{p^2 + q^2 + r^2 + 2pq + pr + qr}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

The boundary conditions are $t = 0$, $\beta = \varepsilon = 0$, $\alpha = \alpha_0$; $t = \infty$, $\alpha = \beta = \varepsilon = \alpha_\infty$.

It will be shown that the mechanism examined above is most likely to be the correct one, but owing to the fact that values of $[SO_3]$ and $[H_2SO_4]$ in solutions of bisulphates of the concentration used in these experiments do not appear to have been determined, it is not possible directly to justify this conclusion, although it is difficult to imagine any other mechanism than the two examined above whereby interchange could occur.

Equation (11) is similar to equation (4) obtained during the simpler analysis, since, because the reaction $H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$ is rapid, ε_t will be a measure of the heaviness of the bisulphate. We have shown in Table III that the simple relationship obtained in (4) does not hold, and the analysis of the interchange which would occur if formation of the anhydride SO_3 is an essential part of the mechanism shows clearly that this will be the case, as equation (4) does not sufficiently define the relationship of ε_t to α_t.

It is possible that the interchange of potassium dihydrogen orthophosphate, and, in view of the calculations of Mills (*loc. cit.*), that of potassium chromate also, may occur through the formation of anhydride. This view is to some extent strengthened by the fact that for these salts also, equation (4) does not represent the state of affairs during interchange (Table III).

It is evident that the observed large retarding action of sodium hydroxide when added to solutions of potassium chromate may very well be accounted for by this new mechanism, since such an addition would largely suppress the formation of anhydride. It may be that the slower mechanism which occurs in such alkaline solutions (observed at 100°; Winter, Carlton, and Briscoe, *loc. cit.*) involves the ionic mechanism originally proposed. If these interchanges are to be explained on the basis of anhydride formation, the amount of anhydride present in these solutions, except in the case of potassium chromate, must be very small, as the interchange of bisulphates and orthophosphates is relatively slow. The far smaller concentration of anhydride which would appear to be present in the last two cases may be correlated with the greater avidity for water of sulphuric and phosphoric acids.

Some support is given to the anhydride-interchange concept by the following consideration. From equation (13) we have

$$\log_e a_t = -t\{\lambda_1 \log_e a_1 + \lambda_2 \log_e a_2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

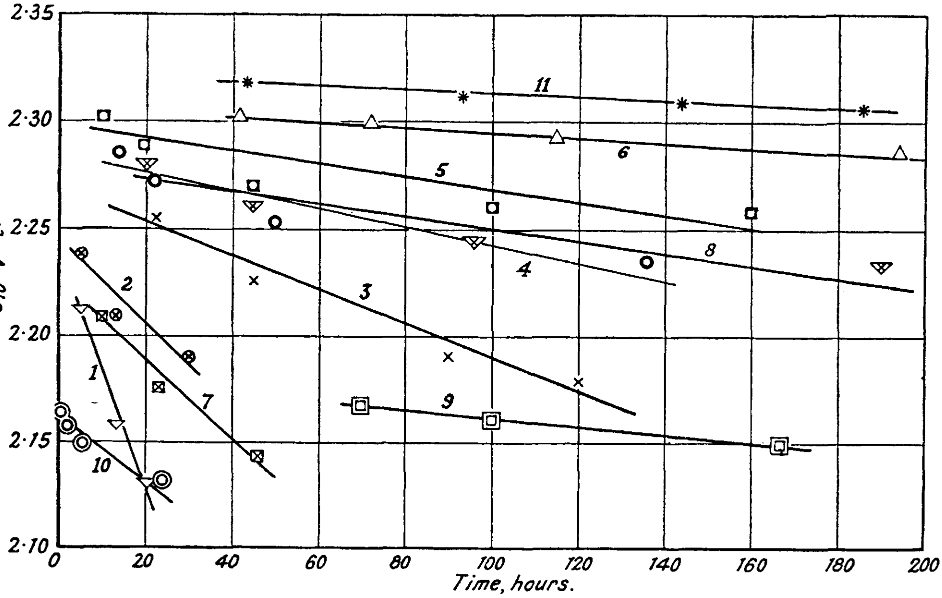
so that if $\log_e a_t$ be plotted against t a straight line should result, the slope of which will be

$$-\{\lambda_1 \log_e a_1 + \lambda_2 \log_e a_2\}.$$

In Fig. 3, $\log_{10} (\gamma d_t)$ has been plotted against t, the values of γd_t being obtained from Table I by subtracting $\Delta\gamma d_t$ from γd_0, and it is seen that the points for each concentration do lie approximately on straight lines, although the agreement in the case of 4·53 and 3·85M-potassium hydrogen sulphate at 100° is not very good, the points here forming a concave curve. The deviations from this generalisation are, however, in most cases within the limits of experimental error. It is obvious from equation (5) that the slope of the lines will not be the same since both λ_1 and λ_2, and a_1 and a_2 are functions of p, q, and r, which themselves are functions of the concentration of the solution It is noteworthy also that, not only do the bisulphate–water systems appear to interchange through this mechanism, but also potassium chromate–water and potassium dihydrogen orthophosphate–water. It is necessary to bear in mind the possibility in all these cases of the reversible formation of traces of condensed acids (such as $H_2S_2O_7$, $H_4P_2O_7$, and $H_2Cr_2O_7$) and their salts. Salts of these acids are known, and such reversible reactions, occurring only to a very small extent, might conceivably account for the observations. In this connection, however, the results of experiments 48, 49, and 50 dealing with pyrophosphate interchange are of interest; here it is shown that in neutral, alkaline, or weakly acid solutions of sodium pyrophosphate no large interchange occurs after up to 64 hours' heating at 100°. It therefore seems unlikely that any such reaction as $2HPO_4'' \rightleftharpoons H_2O + P_2O_7''''$ occurs in solutions of potassium dihydrogen orthophosphate (see also Blumenthal and Herbert, *loc. cit.*).

FIG. 3.

Variation of $\log_{10}$ (*residual concentration of* $H_2{}^{18}O$) *with time of interchange.*



1. $KHSO_4$, 6·13M, 108°.
2. $KHSO_4$, 3·85M, 108°.
3. $KHSO_4$, 6·13M, 100°.
4. $KHSO_4$, 4·53M, 100°.
5. $KHSO_4$, 3·85M, 100°.
6. $KHSO_4$, 2·45M, 100°.
7. $NaHSO_4$, 6·13M, 100°.
8. $NaHSO_4$, 3·85M, 100°.
9. KH_2PO_4, 2·78M, 100°.
10. K_2CrO_4, 1·66M, 20°.
11. $KHSO_4$, 1·226M, 100°.

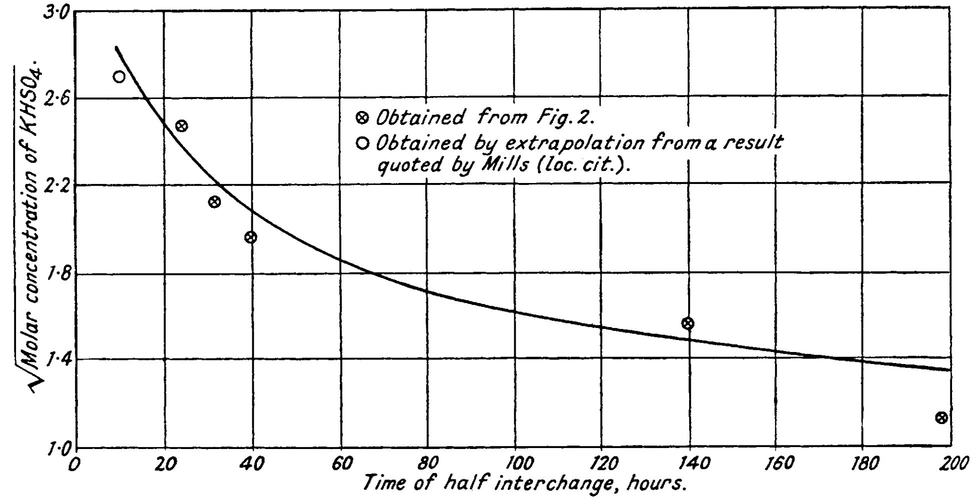
The greater rate of interchange of sodium hydrogen sulphate solutions than of solutions of the potassium salt of the same molarity (see Fig. 1) is difficult to account for with certainty, but is probably attributable to the greater degree of hydration of the sodium ion. This would increase the effective concentration of the bisulphate ion, and so increase the tendency to anhydride formation, giving a more rapid rate of interchange. If this be the true explanation, it throws an interesting light upon the structure of concentrated aqueous solutions : since no appreciable falling off is apparent in the rate of interchange, which proceeds smoothly to approach 100%, it would appear that the forces attracting water molecules to the sodium ions are so much stronger than in the case of the potassium ions as to cause an appreciable increase in $[SO_3]$, but yet are in neither case so strong as to " bind " the water completely and so prevent it from suffering interchange. It may be necessary to exclude from the above generalisation the interchange of 3·85M-potassium hydrogen sulphate at 100°, which does show a falling off in the rate of interchange after interchange has reached 50% (see Fig. 1).

This may be a solution of such a concentration that the two tendencies outlined above are nearly balanced, so that some of the water is more or less completely " bound " to the potassium ions, and so suffers slower interchange than the remainder. In solutions more concentrated than this, the interionic forces may be sufficiently large to ensure a regular exchange of molecules between the cation- and the anion-water, while in less concentrated solutions (where the reaction was not followed above 50% interchange) the fraction of the total water which is bound to the cation may well be so small as to have no detectable effect on the reaction rate until more than 50% interchange has occurred. This theory would mean that in the more dilute solutions the cation water is in fact very rigidly bound, as the number of collisions which would occur between a molecule of cation water and molecules of non-cation water during, say, 100 hrs. at 100° is enormous. It may be noted that Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, **35**, 1380) explained the decrease in heat capacity accompanying the ionisation of an acid by assuming that certain rotational degrees of freedom of the solvent molecules around the ions were " frozen out."

The effect of the addition of potassium chloride, hydrochloric acid, sulphuric acid, and sodium perchlorate to solutions of bisulphate is in all cases to increase the rate of interchange above that of the pure bisulphate solution. The acids most probably act by virtue of their hydrogen ions, which would cause an increase in the concentration of undissociated sulphuric acid, and so of the anhydride. The salts would increase the effective concentration of the bisulphate by attracting water of hydration to their constituent ions. On this basis, however, it is not easy to explain the rapid interchange of relatively dilute solutions of sulphuric acid (Expts. Nos. 39 and 40, Table II). In view of the notable avidity of sulphuric acid for water, it is possible that some fundamental change takes place at the moment of mixing, which ensures rapid interchange. In this connection it is of interest that Lichty (*J. Amer. Chem. Soc.*, 1908, **30**, 1834) has shown that pure sulphuric acid dissociates to some extent into water and sulphur trioxide.

FIG. 4.

Effect of concentration upon the time of half interchange for potassium hydrogen sulphate in $H_2{}^{18}O$.



It is noteworthy that acid solutions of sodium perchlorate interchange very slowly at 100°; in this case the interchange can only occur through the free acid, or through an anhydride, since here no condensed acids are known.

Fig. 4 provides independent conformation of the observations of bisulphate interchange quoted in this paper. The square root of the molarity of solutions of potassium hydrogen sulphate has been plotted against the time of half interchange (obtained from Fig. 1). Mills (*loc. cit.*) records a result for interchange of potassium hydrogen sulphate; this result was marked on a replica of Fig. 1, and a curve of the same form as those obtained by us was drawn to pass through this point. The time of half interchange read off from this curve fits into Fig. 4 quite well.

Experimental.—The experimental details are essentially the same as in the previous work (Winter, Carlton, and Briscoe, *loc. cit.*). In expts. 45, 46, and 47 it was assumed that all the hydrochloric acid (liberated from potassium hydrogen sulphate and potassium chloride or present originally as such in the reaction tube) was distilled over with the water during the first distillation. A calculated slight excess of solid sodium hydroxide was added to this distillate, and the distillation repeated. This second distillate was then purified as usual. A correction for the (light) water liberated from the alkali was applied when calculating the results.

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