and

$$b \equiv -z_1 z_2 e^2 / a D k T \tag{4}$$

If only ion-pairs between a and p < q are detected, rather than all Bjerrum-Fuoss ion-pairs, the limits of integration in equation (1) should be from a to prather than from a to q. Equation (1) now becomes

$$K' = (4\pi N/1000) \left[ \int_{a}^{q} r^{2} dr e^{-z_{1} z_{2} e^{2}/Dr kT} - \int_{p}^{q} r^{2} dr e^{-z_{1} z_{2} e^{2}/Dr kT} \right]$$
(1')

which is transformed to

$$K' = -(4\pi N/1000)(z_1 z_2 e^2/DkT)^3 Q(b') \qquad (2')$$

$$Q(b') = Q(b) - Q(b''),$$
 (5)

and

$$b'' = -z_1 z_2 e^2 / p D k T \tag{6}$$

Using Equations 3 and 4, b' and the corresponding apparent distance of closest approach a', may be found.

As an illustration, the error caused by not detecting long range ion-pairs was computed at 25° for aqueous solutions (D 78.54).<sup>3</sup> The distance of approach was taken to be 5 Å., a typical value for systems involving one complex ion, and the maximum separation of measurable ion-pairs to be 8 Å., which allows for two molecules of water between the ions. Values of Q(b) were taken from Harned and Owen.<sup>4</sup> The results are tabulated below. Similar results may be found with other assumed values of q, p, T, and D.

ion-pairs becomes less. However even with the highly associated 4-2 electrolytes, distant ionpairs easily increase the equilibrium constant 15 or 20%.

Unfortunately, at present we have no really satisfactory direct method for estimating distant ionpairs, and consequently no adequate experimental method for checking any proposed theory of ionpair formation. Although the indirect methods of conductivity measurements or ionic activity measurements detect the effect of distant ion-pairs. the extent of association which is computed depends on the validity of the theoretical or empirical equation used to compute the conductivity, or ionic activity, of the solution in the absence of ion-pairing. Without a "natural" generally accepted definition of an ion-pair (as distinguished from the diffuse ionic atmosphere about an ion, or from an essentially covalent bond between two oppositely charged ions) the ion-pairs in a system must remain defined by the method used to study them.

# ISOTOPIC OXYGEN IN THE STUDY OF THE SOLID REACTION OF SILVER SULFATE AND CALCIUM OXIDE

### By Ellington M. Magee<sup>1</sup>

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Recent experiments on the kinetics of the solidsolid reaction

	· E	EFFECT OF NOT DETECTING DISTANT ION-PAIRS			
Electrolyte type	2-1	3-1	2-2 or 4-1	3-2	4-2
a, Å.	5	5	5	5	5
p, Å.	8	8	8	8	8
q, Å.	7.1	10.7	14.3	21.4	28.5
K	9.9	<b>44.5</b>	166	$1.47 imes10^{3}$	1.32  imes 10
K'	12.4	21.7	84	$0.97 imes10^{3}$	$1.11 \times 10^{-1}$
a', Å.	3.49	6.84	5.98	5.77	5.14

These calculations clearly show that the observed equilibrium constant for an electrostatic ion-pair will be decreased significantly if the experimental method used does not detect distant ion-pairs. Conversely, as the calculations for a 2–1 electrolyte show, the observed equilibrium constant will be increased significantly if the experimental method detects fortuitous ion-pairs which are separated by a greater distance than the maximum distance for ion-pairing considered by the theory. (Because qis 3.57 Å., which is less than the assumed a in these calculations, 1-1 electrolytes were not considered. As they show little or no electrostatic ion-pairing in water, any observed equilibrium constant is almost certainly the result of "chemical" bonding or fortuitous ion-pairs.) Somewhat unexpectedly, as the charges on the associating ions increase, and the maximum interionic distance for a Bjerrum-Fuoss ion-pair increases, the importance of distant **N**4 N4

 $Ag_2SO_4 + CaO \longrightarrow 2Ag + \frac{1}{2}O_2 + CaSO_4$ 

at temperatures around 500°<sup>2</sup> indicate that the limiting factor in the rate of the reaction is the diffusion of the silver ion. It diffuses rapidly over the surfaces of the particles and then slowly into the interior of the calcium oxide particles. The present experiment using isotopic oxygen was carried out to determine by a different technique whether or not the diffusion of oxygen is a limiting factor.

Calcium oxide containing excess oxygen-18 was prepared by shaking pure CaO with water containing 1.5 mole % of oxygen-18. The O<sup>18</sup>-water was obtained from the Stuart Oxygen Company of San Francisco, California. The Ca- $(OH)_2$  was then heated for several hours to give CaO with excess O<sup>18</sup>.

Stoichiometric amounts of dry Ag<sub>2</sub>SO<sub>4</sub> and the enriched CaO were mixed by grinding in a mortar and screening through a 200 mesh screen onto a 325 mesh screen. The part of the mixture on the 325 mesh screen was stored in a desiccator over NaOH.

A Vycor tube, 20 mm. in diameter and about 4 inches long had a ground-glass joint attached at one end and was sealed

<sup>(3)</sup> G. Åkerlöf, Values given in H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1950, p. 118, Table (5-1-3).

<sup>(4)</sup> Ref. 3, p. 123 Table (5-2-3).

<sup>(1)</sup> Humble Oil and Refining Company, Baytown, Texas.

<sup>(2)</sup> W. P. Riemen and F. Daniels, THIS JOURNAL, 61, 802 (1957).

The reaction tube was then heated at  $500^{\circ}$  for 45 minutes. Previous rate studies indicated that the reaction was 25% complete at this time. The reaction tube was then removed from the furnace and chilled quickly. It was attached to the vacuum system by means of one of the side arms and the system was evacuated. The break-seal was broken and the oxygen which had been liberated by the reaction was collected in a sample bulb by means of a Toepler pump.

The reaction tube was again evacuated, sealed off and placed in the furnace. After eight hours, at which time 40% of the material had reacted, the bulb was again chilled and evacuated. The oxygen sample was collected as before.

and evacuated. The oxygen sample was collected as before. The 34 to 32 m/e ratios for the two oxygen samples were determined with a Consolidated-Nier ratio-type mass spectrometer. Values of the 34/32 ratio obtained were 0.004589 and 0.004574 for the first and second samples of oxygen, respectively. These values are the same within the accuracy of the instrument.

If the diffusion of oxygen were the rate-determining step in the reaction, the O<sup>16</sup> would have diffused faster than the O<sup>18</sup>, equivalent to the square root of 16/18,<sup>8</sup> and it should have reacted faster than the O<sup>18</sup>. The second sample of oxygen coming from a later part of the reaction should have been depleted in O<sup>16</sup> and enriched in O<sup>18</sup>.

Mason<sup>4</sup> has published a graph of the fraction, X, of material reacted in a solid-solid reaction vs. kt obtained from the equation

$$1 - X = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 kt}$$
(1)

where  $k = \pi^2 D/a^2$ . *D* is the diffusivity and *a* is the particle size. Mason's graph may be approximated up to X = 0.25 by

$$X = A_1 kt \tag{2}$$

and it may be approximated from X = 0.25 to X = 0.40 by

$$X = A_2 kt + B \tag{3}$$

Assuming  $D_{16} = (18/16)^{1/2} D_{18}$ , then

$$k_{18}t = (16/18)^{1/2}k_{16}t \tag{4}$$

The value of  $k_{16}t$  is found from Mason's curve using the total fraction of material reacted ( $X_{0.25}$  and  $X_{0.40}$ ) and  $k_{18}t$  is calculated using equation 4. Equations 2 and 3 then give the value of  $X_{18}$  at  $X_{16} =$ 0.25 and 0.40. Using these relationships, it is found that if the ratio  $O_{18}/O_{16}$  were 0.004589 for the first sample, it should be 0.004920 for the second.

This difference could have been determined easily with the mass spectrometer used. Since no such enrichment was obtained, it is concluded that the diffusion of oxygen in the solids is not the ratedetermining process, and the hypothesis that the rate-determining step is the diffusion of the silver ion<sup>2</sup> is thus strengthened.

This method of determining whether or not the diffusion of oxygen is rate determining may find applications in the study of the kinetics of other reactions.

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## A COMPLEX ION FORMED FROM BIS-MUTH AND IODIDE IONS<sup>1</sup>

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In solutions strongly acidic with sulfuric acid and relatively concentrated in iodide ion, a small amount of bismuth produces a yellow-colored complex ion with an absorption maximum at 4600 Å. This complex ion has a large molar extinction coefficient (9200 at 4600 Å.) and has been used for many years to estimate small amounts of bismuth colorimetrically.<sup>2</sup> The characteristic absorption band at 4600 Å. is shown in Fig. 1.



Fig. 1.—Each solution was 1.0 m in H<sub>2</sub>SO<sub>4</sub>, 0.050 m in KI and 0.001 m in Na<sub>2</sub>SO<sub>3</sub>:  $\Box$ , 0.0 m bismuth;  $\triangle$ , 5 × 10<sup>-6</sup> m bismuth;  $\bigcirc$ , 20 × 10<sup>-6</sup> m bismuth.

The present investigation had its inception in an attempt to establish the formula and instability constant of this complex ion using the method of continuous variations.<sup>8,4</sup> It immediately developed, however, that such a study could not be made because, when solutions approximately 0.1 m in Bi<sup>+++</sup> and I<sup>-</sup> were mixed in 1.0 m H<sub>2</sub>SO<sub>4</sub>, a black precipitate was formed which presumably was BiI<sub>3</sub>.

On using more dilute solutions it was found that

(1) Taken in part from research performed by L. J. F. and W. S. H. while they were undergraduates at the University of Oregon.

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 161.
(3) Job, Ann. Chim., [10] 9, 113 (1928).

(4) W. C. Vosburgh and G. R. Cooper, J. Am. Chem. Soc., 63, 437 (1941).

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<sup>(3)</sup> This is only approximately correct and ignores several vibrational frequencies of the reacting atom and the activated complex which tend to cancel. See J. Bigeleisen, *ibid.*, **56**, 823 (1952).

<sup>(4)</sup> H. F. Mason, ibid., 61, 796 (1957).