would lead to separation factors of 13.5 in place of the observed values of 3.1 and 3.3.

From the overvoltage data presented in this paper, separation factors of 3.0 to 3.2 are computed (Fig. 3). As has been pointed out, computed separation factors are based on the relative amounts of pure H_2 and D_2 evolved at fixed overpotentials. The good agreement between these computed values and the experimental values for cases where H_2 and HD were evolved, indicates that the separation factor is independent of the molecular form in which the hydrogen and deuterium atoms are evolved.

These findings are incompatible with theories of hydrogen overvoltage which postulate as the slow step of the discharge process the combination of two or more entities on the electrode. These overvoltage and separation data can be interpreted only in terms of theories which postulate that only one particle is involved in the discharge process.

Summary

Measurements of deuterium overvoltage on mercury cathodes at current densities from 10^{-6} to over 10^{-3} amp./sq. cm. and at temperatures from 4 to 70° are reported in this paper. These have been compared with previously reported measurements of hydrogen overvoltage made under similar conditions.[1] From these data, electrolytic separation factors for hydrogen and deuterium have been computed which agree very well with experimental separation data. These overvoltage and separation data appear to preclude the possibility that the slow step of the hydrogen discharge process, at mercury cathodes, involves more than one ion or atom.

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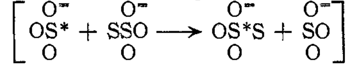
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Kinetics of the Exchange of Sulfur between Thiosulfate and Sulfite[1]

BY DONALD P. AMES[2] AND JOHN E. WILLARD

Voge[3] has reported a measurable rate at 100° for the exchange of sulfur between thiosulfate and sulfite. We have investigated the kinetics of this reaction  $\left[O\underset{O}{\overset{O^{=}}{S}}{}^{*} + S\underset{O}{\overset{O^{=}}{S}}O \longrightarrow O\underset{O}{\overset{O^{=}}{S}}{}^{*}S + \underset{O}{\overset{O^{=}}{S}}O \right]$ because it appears to be sufficiently simple so that its study offers opportunity of obtaining useful information regarding reactions between ions of similar charge.

Experimental

Radioactive Sulfur.—Elemental sulfur containing S^{35} produced by neutron bombardment[4] was heated at 100° for 10 hours[5] to convert amorphous sulfur ($S\mu$) into the soluble $S\lambda$ form. It was then dissolved in toluene, the solution was centrifuged, and sulfur was crystallized from the supernatant. Absorption curves taken on the radiations from this material agreed with those in the literature.[6]

Radioactive Sulfite.—Radioactive sulfur dioxide was prepared by burning 10-mg. samples of radioactive sulfur by careful heating in a stream of oxygen. With the excess oxygen serving as carrier, the sulfur dioxide produced was bubbled through toluene to remove any unreacted sulfur and then absorbed in a solution of sodium hydroxide (*ca.* 3*M* Merck reagent grade). The caustic scrubber consisted of a conical centrifuge tube with a two-hole stopper fitted with an inlet tube and a 6 mm. i.d., two-foot long, Vigreux column, the lower end of which extended to the bottom of the cone which contained 3 ml. of the caustic solution. The incoming gas stream forced the solution to rise in the Vigreux column and wet its surfaces.

The alkaline sulfite solutions were shown to be stable to air oxidation by periodic titrations with iodine which showed no significant change in sulfite concentration over periods of two weeks or more.

Radioactive Thiosulfate.—Radioactive thiosulfate was made by exchange of radiosulfite in aqueous solution with thiosulfate at elevated temperatures under the conditions reported in detail as the main subject of this paper. It was also made by treating elemental sulfur with sulfite in alkaline solutions.[7] Excess sulfur was removed by extraction with toluene and the thiosulfate and remaining sulfite were separated either by precipitation of the latter as strontium sulfite[8] or of the former as triethylenediaminenickel thiosulfate.[9] Depending on whether radiosulfur or radiosulfite is used in this synthesis, the thiosulfate can be tagged on either the outer or inner sulfur atom, whereas in the former synthesis it is tagged on the central sulfur atom.

Separation of the Two Sulfur Atoms of Thiosulfate.—When it was desired to determine the specific activity of the outer or inner sulfur atoms of a given sample of thiosulfate, a portion of the solution (or of the triethylenediaminenickel thiosulfate) from which sulfite and free sulfur had been removed, was frozen in a 25-ml. flask with the aid of liquid air and a few ml. of concd. hydrochloric acid was added. The flask containing the frozen reactants was then attached by a ground-glass joint to a gas absorption train, and was thermostated at 90° for 15 min. Under these conditions[10] the thiosulfate is decomposed quantitatively to sulfur dioxide and sulfur. With the aid of a stream of nitrogen the sulfur dioxide was carried into a Vigreux column absorption trap (described above) where it was absorbed by a solution of sodium hydroxide and oxidized by addition of sodium peroxide. Barium sulfate was then precipitated with excess barium chloride and prepared for counting.

The elemental sulfur produced by the acidification of the thiosulfate solution was extracted from its aqueous suspension with toluene. The toluene extract was evaporated to dryness and the sulfur residue was oxidized to sulfate by heating for four hours at 90° with fuming nitric acid. The nitric acid was decomposed by evaporation in the presence of hydrochloric acid, and barium chloride was added to precipitate barium sulfate for counting. This barium sulfate represented the outer sulfur of the thiosulfate whereas the barium sulfate produced from the sulfur dioxide fraction represented the central sulfur. In order to avoid the necessity for quantitative recovery in the chemical preparation of samples for counting, the specific activity of each barium

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[1] Presented, in part, before the Division of Physical and Inorganic Chemistry at the Sept., 1949, Meeting of the American Chemical Society at Atlantic City, N. J.

[2] Los Alamos Scientific Laboratory, Los Alamos, N. M.

[3] Voge, THIS JOURNAL, **61**, 1032 (1939).

[4] U. S. Atomic Energy Commission Isotopes Catalogue, Aug. 11, 1949, Item No. 75, procured from the Oak Ridge National Laboratory.

[5] Cooley, Yost and McMillan, THIS JOURNAL, **61**, 2970 (1939).

[6] See for example: (a) Solomon, Gould and Anfinsen, *Phys. Rev.*, **72**, 1097 (1947); (b) Yaffe and Justus, *Can. J. Research*, **26B**, 734 (1948).

[7] Watson and Rajagopalan, *J. Indian Inst. Sci.*, **8A**, 275 (1925).

[8] (a) Ephraim, "Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1947, p. 551; (b) Autenrieth and Windaus, *Z. anal. Chem.*, **37**, 290 (1898).

[9] Spacu and Spacu, *ibid.*, **89**, 192 (1932).

[10] (a) Bassett and Durrant, *J. Chem. Soc.*, 1416 (1927); (b) Friend, "Textbook of Inorganic Chemistry," Charles Griffin Co., London, 1931, Vol. VII, Part II, p. 30.

sulfate sample was determined by weighing it as well as counting it.

Chemical Assay of Thiosulfate and Sulfite Solutions.—Determination of the concentration of both thiosulfate and sulfite in the same solution was achieved by a modification of a procedure given by Kurtenacker and Wollak.[11] The sum of the concentrations of sulfite and thiosulfate was determined by titration with a standardized potassium iodide-iodine solution, and thiosulfate alone was determined in a second aliquot of the solution by a similar titration after addition of formaldehyde to complex the sulfite. The iodine solutions used in this work were standardized prior to, and following, each series of analyses by titration against standard arsenite solution and independently by titration against thiosulfate solutions which had in turn been standardized by titration of iodine liberated from solutions of iodide and acid by weighed amounts of iodate. Experiments designed to test the efficacy of analytical methods showed that: (1) the addition of formaldehyde to an aliquot of standard thiosulfate did not change its titer value by more than 1%; (2) an acetic acid-sulfite solution such as used in these analyses required less than 0.04 ml. of 0.01 *N* iodine solution to give the blue color of the starch-iodine end-point, if formaldehyde was present to complex the sulfite; (3) titrations of sulfite in the presence of acetic acid under the conditions of these analyses were reproducible within 1%, thus showing that no significant loss of sulfur dioxide occurred by volatilization.

Sample Preparation and Counting Techniques.—Since the radiation from S^{35} has a self absorption half thickness of only *ca.* 7 mg./sq. cm. particular care was necessary to obtain reproducibly spread weighable samples for counting, so that self absorption corrections could be applied. The barium sulfate fractions containing the S^{35} were transferred as slurries in 0.01 *N* HCl to a demountable centrifugation device containing the counting plate. This unit consisted of a Pyrex chimney 1.7 cm. i.d. and 10 cm. long with a ground flange on the bottom which rested on a 26 mm. 18-8 stainless steel plate with a circular 2 sq. cm. die-stamped indentation. In order to hold the plate and chimney together the plate was seated on a washer in a brass cap which was threaded on the inside, and a threaded brass sleeve which just fitted over the barrel of the chimney was screwed into the cap. A rubber washer was used above the glass flange. A thin layer of rubber cement (diluted with petroleum ether) was painted on the flange before assembly. After addition of the slurried sample, the unit was placed in a holder of the No. 215 head of an International Clinical Centrifuge and centrifuged for 3-5 minutes at top speed to produce a uniformly spread and rather adherent layer of the precipitate on the bottom of the 2 sq. cm. area of the indentation in the stainless steel plate. By tilting the unit at a 45° angle it was possible to remove all but a few drops of the supernatant with the aid of a transfer pipet. The unit was then carefully disassembled and the plate containing the sample dried under an infrared lamp and then flamed to remove adhering rubber cement.[12] After cooling, the plate, which had been weighed to 0.2 mg. before use, was weighed again and counted with a mica window Geiger tube. The stainless steel plates were not attacked by the exposures to 0.01 *N* HCl and in no case was there a change of more than 0.2 mg. when test plates were reweighed after successive ignitions. This unit for preparing barium sulfate samples for counting is similar in some respects to one devised independently and described recently by Larson, Maas, Robinson and Gordon,[13] in which a Lusteroid plate is used to receive the sample.

The dependence of the specific counting rate on the sample thickness was experimentally determined by counting plates containing different weights of barium sulfate of the same specific activity. Extrapolation of a plot of the logarithm of the apparent specific activity (c./min./mg. $BaSO_4$) against the sample thickness (mg./sq. cm.) to the condition of zero thickness gave a value for n_0, the apparent[14] specific activity under this condition. A graph of log n_0/n (where n was the measured apparent specific activity at any thickness in question) against thickness (mg./sq. cm.) gave a straight line which was used for convenience in obtaining the correction factor to apply to the observed counting rates of subsequent samples of different thickness in order to convert them to standard (n_0) values.[15] Values of n_0 so obtained have the same ratio to each other as true specific activities would have and so may be used as criteria of the extent of exchange. The over-all accuracy of the weighing procedure and self absorption corrections is suggested by comparing the n_0 values obtained for samples of the same specific activity but different weights. For example, in one such test a sample of barium sulfate weighing 16.3 mg. gave a counting rate of 2177 c./m. while another of 4.7 mg. gave 1100 c./m. and the corresponding n_0 values were 2162 and 2179 c./m./mg. S. In many such tests there were very few cases in which the deviation of the specific activity of a single sample from the average for the pair was greater than 1.5%.

The Geiger tube used in most of this work was monitored frequently with a UX_2 (in equilibrium with U) standard and all counts observed were within the limits expected due to statistical fluctuations. The response of the counter was a linear function of the activity of the sample within about 2% up to the highest counting rate used (3000 c./m.). The majority of the radioactive samples was counted for a sufficient length of time to give a statistical accuracy of ±1.6% at the 0.9 reliability level. Because samples to be intercompared were counted within a few hours of one another, a short period compared to the 87.1 day half-life of S^{35}, no decay corrections were applied.

Procedure Used in Exchange Experiments.—Aliquots of 4.00 *M* sodium chloride solution or 2.00 *M* sodium sulfate solution, inactive sodium thiosulfate solution (all Mallinckrodt Analytical Reagent), inactive sodium sulfite (Mallinckrodt Photo-Purified Grade) solution, and of the stock solution of radiosulfite tracer, calculated to give the desired concentrations and ionic strength, were added to a 25-ml. volumetric flask. The *p*H was adjusted by the addition of an aliquot of either 1 *N* HCl, 1 *N* H_2SO_4 or 1 *N* NaOH. Then the solution was diluted to the mark on the volumetric flask with redistilled water and was transferred to a 25-ml. round bottom flask which served as the reaction vessel. At this point a 4-ml. sample was removed. This and subsequent samples from the reaction mixture were stored on ice to await determination of the *p*H and titer or radioassay values. Control determinations showed that no exchange occurred under these conditions even if samples were kept as long as two days.

The reaction flask was next attached by means of an ungreased ground glass joint to a vertical water cooled condenser open to the air at the top, and was immersed in a thermostated oil-bath at the temperature desired for the experiment. From the time of immersion until the end of the experiment "Prepurified" nitrogen was allowed to bubble slowly through the solution in order to preclude air oxidation of the sulfite.

The time at which the reaction flask was immersed in the thermostated bath was taken as zero time for the reaction. Because the solution required about six min. to reach the temperature of the bath and the method used in analyzing the data did not require information about the reaction during this time interval, the first sample for radioassay was taken at 10 minutes. Samples were removed by inserting a long transfer pipet through the condenser into the solution. Except for the *p*H samples they were immediately discharged from the pipet into water at 0° to stop the reaction. The titer and *p*H values were determined on samples taken at the end of each experiment for comparison with values obtained at the start. The maximum changes observed were 0.4 *p*H unit; 3% increase in titer presumably due to evaporation losses; and a 3% decrease in sulfite at the lowest *p*H, presumably due to sulfur dioxide evolution.

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(11) Kurtenacker and Wollak, *Z. anorg. allgem. Chem.*, **161**, 201 (1927).

(12) S. Goldhaber of our laboratory has found that if a lucite chimney with a circular groove in the flange is used in place of the glass chimney a rubber "O" ring (manufactured by Linear, Inc., State Road and Levick St., Philadelphia 35, Pa.) may be used instead of rubber cement to make the seal. This may be an advantage if it is desired to work with precipitates which would decompose on strong heating.

(13) Larson, Maas, Robinson and Gordon, *Anal. Chem.*, **21**, 1206 (1949).

(14) All measurements were made with samples of more than 2 mg./cm.^{2} in order to avoid the maximum in the curve at lower thicknesses, which results from self-scattering effects.

(15) Broda, Grummett, Gueron, Kowarski and Wilkinson, *Proc. Phys. Soc.*, **60**, 460 (1948).

A platinum reaction vessel used in early experiments was abandoned because it was found to catalyze the disproportionation of sulfite to sulfur and sulfate.[16] A Teflon reaction vessel was also tried but because of its poor thermal conductivity and the consequent difficulty of maintaining the desired temperature of the reaction mixture, it was abandoned in favor of Pyrex.

Reaction temperatures were measured with a mercury thermometer standardized against a Bureau of Standards platinum resistance thermometer. The *p*H measurements were made with a Beckman model G *p*H meter. A Type E lithium glass electrode was used for measurements above *p*H 8. Buffer solutions of *p*H 10 and 7 were used to standardize the instrument.

In all experiments on the exchange of sulfite with thiosulfate the radiosulfur was initially present as sulfite and the rate of the exchange was followed by determining the rate of appearance of radioactivity in the central sulfur atom of the thiosulfate. To separate a fraction representing this atom from the samples taken for analysis, the sulfite was first removed as strontium sulfite by addition of an excess of strontium chloride followed by addition of about 10 mg. of inactive sulfite and removal of the second strontium sulfite precipitate so formed. This second precipitation removed a small amount of active sulfite which remained from the first precipitation as the result of the slight solubility of strontium sulfite. The weight of this soluble sulfite was negligible compared to that evolved from the thiosulfate but at the start of the exchange the relative activity was significant. In experiments where the *p*H of the reaction solution was less than 9, sodium hydroxide was added before strontium sulfite precipitation to decrease the solubility. After removal of the sulfite, the supernatant was treated, as described above, to separate the sulfur atoms of the thiosulfate. Since it had been established that the outer sulfur does not exchange with the central atom, the outer sulfur fraction was not prepared for counting.

Ionic Strength.—The rate experiments reported here were carried out at concentrations of thiosulfate in the range from 0.2 to 0.02 *M* and of sulfite in the range from 0.2 to 0.02 *M*. In order to avoid differences in ionic strength sodium chloride was added in sufficient amount to give an ionic strength of 2 (for example see Table II) except where otherwise noted. Chloride rather than sulfate was used to adjust the ionic strength in the majority of the experiments because of the separation difficulties introduced by the fact that all of the latter must be precipitated with the sulfite in the analytical procedure.

In nearly all cases the major contribution to the ionic strength was from the added salt rather than the reactants. Ionic strengths were all calculated on the basis of molar concentrations and the concentration values used for this purpose and for determining the rate law were all based on the concentration of the solutions at room temperature, the change in concentration due to expansion with change in temperature being negligible for this purpose.

Non-equivalence of Sulfur Atoms of Thiosulfate

Andersen[17] has shown that when an excess of silver nitrate is added to thiosulfate, prepared by the action of an alkaline solution of inactive sulfite on radiosulfur, the silver sulfide formed by the reaction

$$2Ag^+ + S_2O_3^= + H_2O \longrightarrow Ag_2S + H_2SO_4$$

contains all of the radioactive sulfur. This result indicates that the two sulfur atoms of thiosulfate are not chemically equivalent and that they do not exchange as a result of this sequence of chemical steps. Andersen also decomposed thiosulfate, prepared in the same way, by the addition of hydrochloric acid and observed that both the sulfur and sulfur dioxide produced contained activity. The apparent exchange was attributed to some step in the mechanism of the decomposition of the thiosulfuric acid. Voge[3] has interpreted his observations on the exchange of sulfite with thiosulfate to indicate that only one of the sulfur atoms of the latter undergoes exchange. Utilizing the stable S^{34} isotope as tracer, Williams[18] observed no exchange between the sulfur atoms in aqueous thiosulfate heated for two days at 90°, and then decomposed by addition of acid.

In the work of the present paper we have conducted three types of experiments which have extended the previous evidence on the conditions under which the sulfur atoms of thiosulfate fail to exchange. (1) Radioactive thiosulfate solutions prepared by treating radiosulfur with inactive sulfite in alkaline solution for 2.5 hours at 85°, extracting excess sulfur with toluene, and precipitating excess sulfite with strontium chloride were heated in sealed Pyrex tubes for various times and at temperatures indicated in Table I. After heating, the thiosulfate was decomposed with hydrochloric acid and the specific activities of the fractions representing the central and outer sulfur atoms were determined separately by counting as barium sulfate. The results shown in Table I seem to indicate that no exchange occurred even after 5.5 hours heating at 125°.

TABLE I

EVIDENCE FOR NON-EXCHANGE OF SULFUR ATOMS IN THIOSULFATE WHEN HEATED AND DECOMPOSED WITH ACID

Time of heating, hours	Temp., °C.	Spec. act. of outer S fraction, counts min.$^{-1}$ (mg. S)$^{-1}$	Spec. act. of central S fraction, counts min.$^{-1}$ (mg. S)$^{-1}$
3	100	650	29
4	100	775	40
5.5	125	726	30

(2) Triethylenediaminenickel thiosulfate ($\text{Ni en}_3\text{S}_2\text{O}_3$) was precipitated from a solution of thiosulfate prepared as described above, except that the strontium sulfite precipitation was omitted. The complex salt was recrystallized from hot water and samples were then decomposed with hydrochloric acid. The specific activities of the fractions representing the two different sulfur atoms were determined. In two experiments 477 and 564 c./m. were found in the "outer" sulfur fractions and 18 and 0 c./m. in the "central" sulfur fractions. The results indicate that this precipitation and dissolution did not induce exchange. (3) Throughout the detailed investigations of the exchange of sulfite with thiosulfate reported in this paper it was always observed that the equilibrium distribution of radioactivity was such as to indicate that only one sulfur in the thiosulfate can partake in the exchange. For example, in an experiment in which radioactive sulfite was heated with inactive thiosulfate at 100° and *p*H 12 for 7.5 hr. the final specific activities of the sulfite fraction, the central sulfur of the thiosulfate and the outer sulfur of the thiosulfate were 608, 598 and 6 counts min.$^{-1}$ (mg. S)$^{-1}$, respectively.

Calculations

The experimental data obtained from a typical run on the exchange reaction are given in Table

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(16) Foerster, Lange, Drossback and Seidel, *Z. anorg. u. allgem. Chem.*, **128**, 245 (1923).

(17) Andersen, *Z. physik. Chem.*, **B32**, 237 (1936).

(18) R. R. Williams, private communication.

II. The activity in the thiosulfate approaches an equilibrium value and the rate of growth of the activity is first order, as would be expected for an exchange reaction.[19]

TABLE II

EXCHANGE OF RADIOSULFUR BETWEEN SULFITE AND THIOSULFATE

	Analysis, moles liter^{-1} Initial	Analysis, moles liter^{-1} Final
Na_2SO_3[a]	0.2106	0.2086
$Na_2S_2O_3$	0.0638	0.0646
NaCl (added)	1.405	
*p*H	5.0	5.1

Ionic strength, 2.02; temp., 89.0 ± 0.3°.

Time, min.	$BaSO_4$, mg.	Exptl. $BaSO_4$ activity, counts min.$^{-1}$	Calcd. Spec. act., counts min. (mg. S)$^{-1}$	0.9 error, counts min.$^{-1}$
10	11.7	535	602	± 9
14	14.7	792	812	±13
18	11.8	944	1055	±15
22	16.9	1278	1261	±21
26	14.9	1374	1403	±22
30	14.4	1412	1458	±22
34	13.5	1415	1495	±22
38	14.4	1525	1576	±24
42	13.4	1525	1616	±24
46	18.0	1884	1830	±29

[a] Converted to NaCl + $NaHSO_3$ in adjusting the *p*H to 5, and considered as such in computing the ionic strength.

Data such as those of Table II for the rate of approach to equilibrium distribution of the radioactivity were used to determine the rate, R (in moles liters^{-1} min.$^{-1}$), at which sulfur atoms were transferred from thiosulfate to sulfite. For a given set of conditions and concentrations this rate is, of course, constant and independent of the presence of radioactivity. It is given by the expression[19]

$$Rt = \frac{-[SO_3^=][S_2O_3^=]}{[SO_3^=] + [S_2O_3^=]}\, 2.3 \log (1 - F)$$

where t is the time of reaction, brackets indicate the concentrations in moles liter^{-1} and F is the fraction of equilibrium distribution of the radioactivity attained at the time t. In this work $F = (\text{sp.a.})_t/(\text{sp.a.})_\infty$ where $(\text{sp.a.})_t$ and $(\text{sp.a.})_\infty$ are the specific activities of the central sulfur of the thiosulfate at time t and at equilibrium distribution of the radioactivity, respectively.

The value of R for any experiment may be calculated from the slope of a plot of $\log [1 - (\text{sp.a.})_t/(\text{sp.a.})_\infty]$ against time. Because, however, the experimental value for $(\text{sp.a.})_\infty$ is no more accurate than the individual values of $(\text{sp.a.})_t$ it is desirable to avoid its repeated use in the determination of R. This was accomplished by adapting a method proposed by Guggenheim.[20] The value of R was obtained from a plot of $\log [(\text{sp.a.})_{t+T} - (\text{sp.a.})_t]$ against time according to the equation

$$Rt = \frac{-2.3[SO_3^=][S_2O_3^=]}{[SO_3^=]+[S_2O_3^=]} \log[(\text{sp.a.})_{t+T} - (\text{sp.a.})_t]$$

The expression in the brackets represents the change in the specific activity of the central sulfur atom of the thiosulfate in a constant time interval of T min. beginning at any time t. The values of $(\text{sp.a.})_t$ and $(\text{sp.a.})_{t+T}$ were obtained from plots of the specific activity as a function of time, made from data such as given in Table II. The constant interval, T, was chosen as approximately twice the half-time of the reaction.

R is related to the rate constant of the reaction of transfer of sulfur atoms from thiosulfate to sulfite by the expression

$$R = k[SO_3^=]^n[S_2O_3^=]^m$$

or

$$\log R = \log k + n \log [SO_3^=] + m \log [S_2O_3^=]$$

where n and m indicate the order of the reaction with respect to sulfite and thiosulfate, respectively. Since k is a constant at constant temperature, the value of n may be determined from the slope of a plot of $\log R$ against $\log [SO_3^=]$ for experiments in which the thiosulfate concentration is held constant (Fig. 1), and the value of m may be similarly determined from the slope of a plot of $\log R$ against $\log [S_2O_3^=]$ for experiments in which the sulfite concentration is held constant (Fig. 2).

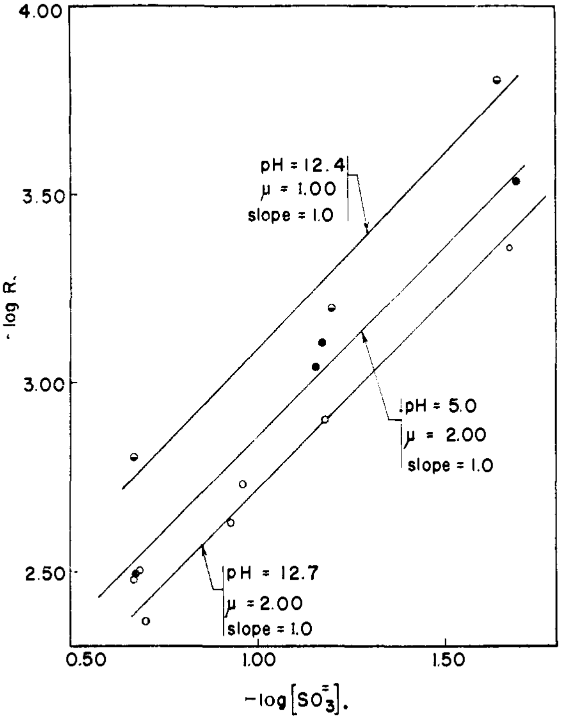

Fig. 1.—Lines whose slopes indicate the dependence of the rate of the exchange reaction on sulfite concentration. (Table III): ◒ *p*H 12.4, μ 1.00; ●, *p*H 5.0, μ 2.00; ○, *p*H 12.7, μ 2.

When n and m have been evaluated k may be calculated from the data. From data on the rate at different temperatures it is then possible to obtain the activation energy from the variation of $\log k$ with the reciprocal of the absolute temperature (Fig. 4).

Kinetics of Sulfite-Thiosulfate Exchange

Dependence of Rate on Sulfite Concentration.—Table III summarizes the results of fourteen ex-

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[19] See for example: (a) McKay, *Nature*, **142**, 997 (1938); (b) Roginsky, *Acta Physicochimie*, **14**, 1 (1941); (c) Duffield and Calvin, THIS JOURNAL, **68**, 557 (1946); (d) Friedlander and Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 285ff.

[20] Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

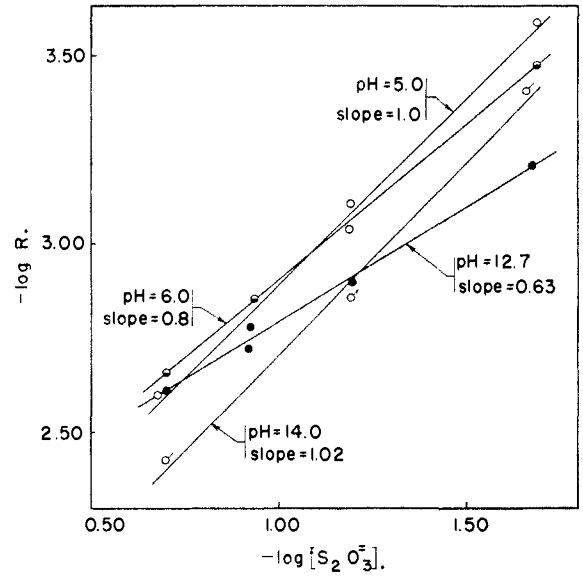


Fig. 2.—Lines whose slopes indicate the dependence of the rate of the exchange reaction on thiosulfate concentration (Table IV): O, *p*H 5; ⊖, *p*H 6; ●, *p*H 12.7; ♂, *p*H 14.0.

periments in which the thiosulfate concentration was held essentially constant while the sulfite concentration was varied at each of two *p*H values and two ionic strengths. When these results are plotted as $-\log R$ against $-\log [SO_3^=]$ (Fig. 1) they give lines which, within the accuracy of the experiments, have a slope of one for each of the three conditions used. This indicates that the rate of the sulfite–thiosulfate exchange is proportional to the first power of the sulfite concentration both at *p*H 5 and *p*H 12 and at ionic strengths of both 1 and 2.

TABLE III

EFFECT OF SULFITE CONCENTRATION, *p*H AND IONIC STRENGTH ON THE RATE OF SULFITE–THIOSULFATE EXCHANGE

Temp. 89.0 ± 0.3°; ionic strength adjusted with sodium chloride

$[SO_3^=]$, mole liter^{-1}	$[S_2O_3^=]$, mole liter^{-1}	*p*H	Ionic strength	*R*, mole liter^{-1} min.$^{-1}$ × 10^3	*k*, liter mole^{-1} min.$^{-1}$
0.2132	0.0642	12.8	2.04	3.32	0.243
.2064	.0623	12.0	2.01	3.14	.236
.1975	.0637	12.8	1.99	4.28	.340
.1168	.0631	12.2	2.01	2.34	.318
.1090	.0632	12.5	2.00	1.86	.270
.0658	.0632	12.8	2.00	1.26	.303
.0210	.0632	12.7	2.01	0.44	.332
.2104	.0647	12.0	1.05	1.58	.114
.0632	.0630	12.8	0.98	0.632	.159
.0227	.0618	12.4	1.01	0.158	.113
.2106	.0638	5.0	2.02	3.18	.237
.0675	.0646	4.8	2.00	0.782	.179
.0699	.0650	5.0	2.12	.910	.200
.0203	.0641	5.0	2.00	.293	.225

Dependence of the Rate on Thiosulfate Concentration.—The data of Table IV, plotted in Fig. 2, indicate that the rate of transfer of sulfur from thiosulfate to sulfite is proportional to the first power of the thiosulfate concentration when the *p*H of the solution is 5 or 14 but that the dependence is about 0.8 at a *p*H of 6 and about 0.6 at a *p*H of 12.7. The deviation from a slope of 1 at *p*H 12.7 was indicated by points determined from two independent sets of determinations using different solutions and the deviation seems to be much greater than the usual experimental error in this work. We have not, however, been able to arrive at any plausible explanation for such a minimum in the dependence on thiosulfate concentration as a function of *p*H. Additional experiments described in the next section showed a first power thiosulfate dependence in this *p*H region. We are, therefore, inclined to conclude, tentatively, that the rate of the exchange reaction may be proportional to the first power of the thiosulfate concentration throughout the *p*H range studied and that the experimental points which indicate otherwise may be in error.

TABLE IV

EFFECT OF THIOSULFATE CONCENTRATION AND *p*H ON THE RATE OF THE SULFITE–THIOSULFATE EXCHANGE

Temp. 89.0 ± 0.3°; ionic strength adjusted with sodium chloride

$[SO_3^=]$, mole liter^{-1}	$[S_2O_3^=]$, mole liter^{-1}	*p*H	Ionic strength	*R*, mole liters^{-1} min.$^{-1}$ × 10^3	*k*, liter mole^{-1} min.$^{-1}$
0.0617	0.1987	12.4	1.98	2.45	0.200
.0620	.1198	12.7	1.99	1.88	.253
.0656	.1180	12.7	2.00	1.65	.213
.0658	.0632	12.8	2.00	1.26	.303
.0617	.0211	12.3	1.99	0.615	.473
.0706	.1971	5.7	2.01	2.18	.157
.0592	.1164	5.9	1.98	1.40	.203
.0687	.0203	5.9	2.01	0.335	.240
.0723	.2002	5.0	2.02	2.44	.169
.0699	.0656	5.0	2.12	0.910	.200
.0675	.0646	4.8	2.00	.782	.179
.0741	.0206	4.5	2.02	.258	.169
.0649	.2002	14.0	2.01	3.72	.286
.0654	.0642	14.0	2.01	1.35	.322
.0646	.0221	14.0	2.01	0.389	.272

Effect of Changing Added Salt from Sodium Chloride to Sodium Sulfate.—In three series of runs, two at *p*H *ca.* 12.5 and one at *p*H *ca.* 4.8, sodium sulfate rather than sodium chloride was used to adjust the ionic strength to 2. The results of these experiments, given in Table V and plotted in Fig. 3 show a much more nearly first order dependence in the *p*H 12.5 range than is indicated by the data of Fig. 2. The three points obtained at *p*H 4.8 are not adequate to determine accurately the slope and probably do not exclude the possibility of a slope of 1. The average rate constant for the seven experiments at *p*H = 12 using sodium sulfate as the added salt is 0.168 liter mole^{-1} min.$^{-1}$ as compared to 0.272 liter mole^{-1} min.$^{-1}$ for eleven experiments at *p*H 12 using sodium chloride as the added salt (Tables III and IV). This is a ratio of 0.62. The ratio of average sodium ion concentrations in the two series of experiments was 0.73.

It was possible to neglect the possibility of an exchange of sulfur between sulfite and sulfate in these experiments because it has been demon-

TABLE V

EFFECT OF THIOSULFATE CONCENTRATION AND *p*H ON THE RATE OF SULFITE–THIOSULFATE EXCHANGE WHEN SODIUM SULFATE WAS USED TO ADJUST THE IONIC STRENGTH

Temp. 88.9 ± 0.2°; ionic strength adjusted with sodium sulfate

$[SO_3^=]$, mole liter^{-1}	$[S_2O_3^=]$, mole liter^{-1}	*p*H	Ionic strength	*R*, mole liter^{-1} min.$^{-1}$ × 10^3	*k*, liter mole^{-1} min.$^{-1}$
0.0631	0.1991	12.4	2.00	2.63	0.209
.0626	.0629	12.3	2.00	0.662	.168
.0617	.0217	12.7	2.00	0.229	.171
.0677	.1960	12.6	1.99	2.291	.173
.0665	.1184	13.0	2.01	1.01	.128
.0681	.0667	12.8	1.99	1.06	.233
.0658	.0216	12.6	2.00	0.135	.093
.0637	.1976	4.8	2.06	3.23	.257
.0633	.0628	5.1	2.06	0.485	.122
.0628	.0215	4.6	2.06	0.172	.127

strated[3] that such exchange does not occur in either acid or alkaline solutions up to 35 hr. at 100°.

Reaction at Higher Concentrations.—One determination of the rate of the exchange was carried out at sufficiently high sulfite and thiosulfate concentrations ($[SO_3^=] = 0.167$ *M*; $[S_2O_3^=] = 0.493$ *M*) to give an ionic strength of 2 without addition of a foreign salt. The *p*H was 12.4 and the temperature 88.9°. The rate constant calculated on the assumption that the rate was proportional to both the first power of the sulfite and first power of the thiosulfate concentrations was 0.189 liter mole^{-1} min.$^{-1}$.

Effect of *p*H on the Rate of the Exchange Reaction.—Inspection of Tables III, IV, V and VI and Figs. 1, 2, 3 and 4 shows that under the conditions of these experiments a variation in the concentration of hydrogen ion by a factor of 10^9 (from *p*H 5 to 14) has very little effect on the rate of the exchange reaction. The average of all of the rate constants given in Tables III and IV for the *p*H region of 4.8–5.9 and an ionic strength of 2 is 30% lower than the average for the experiments at *p*H 12 to 14.

Effect of Ionic Strength.—All experiments were carried out at an ionic strength of 2 except for one series of three runs which were made at an ionic strength of 1, using sodium chloride as the added salt. On the basis of these limited data (Table III and Fig. 1) the average rate constant is 0.47 as great at an ionic strength of 1 as at an ionic strength of 2. The average sodium ion concentration is 0.46 as great in the former case as the latter.

Effect of Surface Area.—In order to determine whether the walls of the Pyrex reaction flasks used in these experiments affected the rate of reaction an experiment was carried out in which enough Pyrex glass wool was present to increase the surface area in the flask about 30-fold. Before use the glass wool was cleaned in boiling concentrated nitric acid followed by thorough rinsing with distilled water. The reaction was carried out at ionic strength 2, *p*H 12.6, 89°, $[SO_3^=] = 0.0256$ *M*, $[S_2O_3]^= = 0.0626$ *M*. The observed rate constant was 0.441 as compared to 0.243, 0.246 and 0.340 for other experiments performed under similar conditions except for the presence of the glass wool, indicating that the reaction is affected only slightly if at all by a Pyrex surface.

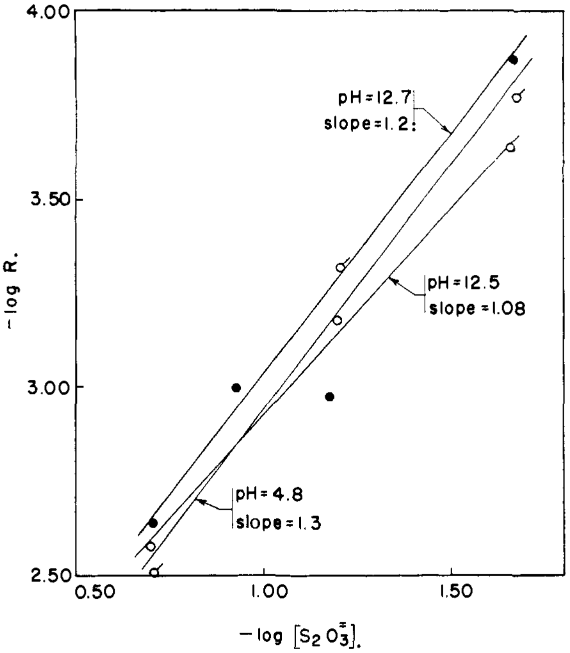


Fig. 3.—Lines whose slopes indicate the dependence of the rate of the exchange reaction on thiosulfate concentration with sulfate used to adjust the ionic strength (Table V): ♂, *p*H 4.8; ●, first series at *p*H *ca.* 12; ○, second series at *p*H 12.

Activation Energy and Frequency Factor.—Table VI shows the results of a series of five runs made at *p*H 5 at different temperatures but equivalent concentrations of reactants and another such series made at *p*H 12.7. These results are plotted in Fig. 4 as $-\log k$ (computed on the assumption that *n* and *m* in the expression $R = k[SO_3^=]^n[S_2O_3^=]^m$ are both unity) against $1/T$.

TABLE VI

EFFECT OF TEMPERATURE ON THE RATE OF SULFITE–THIOSULFATE EXCHANGE AT *p*H 5.0 AND *p*H 12.7

Ionic strength adjusted with sodium chloride

Temp., °C.	$[SO_3^=]$, mole liter^{-1}	$[S_2O_3^=]$, mole liter^{-1}	*p*H	Ionic strength	*R*, moles liter^{-1} min.$^{-1}$ × 10^3	*k*, liter mole^{-1} min.$^{-1}$
59.55	0.0646	0.1193	12.7	2.00	0.348	0.0452
69.95	.0643	.1194	12.7	2.00	0.810	.106
79.40	.0643	.1194	12.7	2.00	1.31	.171
88.90	.0620	.1198	12.7	1.99	1.88	.253
98.40	.0643	.1194	12.7	2.00	3.43	.447
61.98	.0719	.0650	5.0	2.00	0.173	.0370
69.88	.0719	.0650	5.0	2.00	.294	.0629
79.53	.0719	.0650	5.0	2.00	.461	.0989
89.03	.0699	.0650	5.0	2.12	.910	.200
96.20	.0719	.0650	5.0	2.00	1.36	.291

The values obtained at *p*H 5 are shown as open circles and those at *p*H 12.7 are closed circles. The slope of the line corresponds to an activation energy of 14.5 kcal./mole computed from all of the points by the method of least squares. The value of the frequency factor *A* (in the relation $k = Ae^{-E/RT}$),

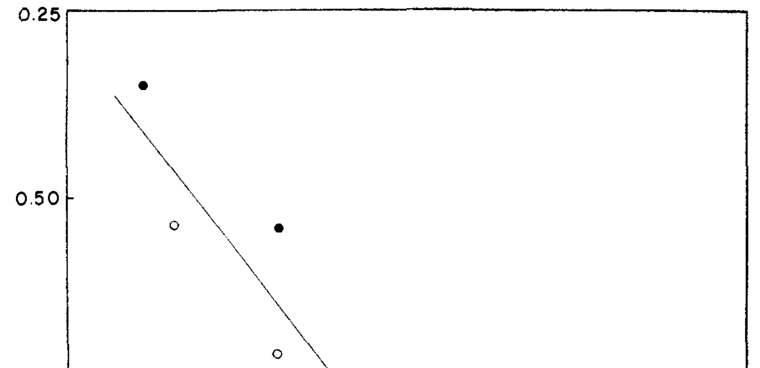
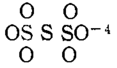


Fig. 4.—Effect of temperature on the rate constant of the exchange reaction: O, pH 5.0; ●, pH 12.7.

likewise computed from all the points, is 2.3×10^6 liters mole.$^{-1}$ sec.$^{-1}$.

Mechanism

Perhaps the two most obvious mechanisms which might be suggested for the transfer of a sulfur atom from a thiosulfate ion to a sulfite ion are: (1) the direct transfer, through collision of the two species, with  $\mathrm{O\overset{O}{\underset{O}{S}}S\overset{O}{\underset{O}{S}}O^{-4}}$ as the activated complex; and (2) an equilibrium dissociation of $S_2O_3^=$ to S and $SO_3^=$, the reverse of which could lead to conversion of radiosulfite in the solution to thiosulfate. If the latter mechanism prevailed, the rate controlling step would be the dissociation of $S_2O_3^=$ since the rate of the reverse reaction at the steady state must be equal to the rate of this dissociation and be controlled by it. The steady state concentration of sulfur is extremely small compared to that of thiosulfate. (The equilibrium constant for the reaction $S_2O_3^= = SO_3^= + S(r)$ is about 10^{-6}.)[21] In such a case the rate of the exchange reaction would be given by $R = k[S_2O_3^=]$ and would be independent of the sulfite concentration. The experimental results which show first order dependence on the sulfite concentration therefore rule out the dissociation mechanism. This conclusion is in agreement with the deductions of Voge[3] from a qualitative comparison of the rates of the sulfite–thiosulfate, sulfide–thiosulfate and sulfur–sulfide exchange reactions. The results are consistent with the hypothesis that the exchange occurs through collision of sulfite ions with thiosulfate ions, a mechanism which would require first order dependence on the concentrations of both sulfite and thiosulfate.

If the exchange occurs by direct transfer of the outer sulfur of the thiosulfate, it is pertinent to consider the evidence as to whether the preferred path of exchange is by collision between sulfite ions and thiosulfate ions as such or by collision of some related species such as HSO_3^-, H_2SO_3, $H_3SO_3^+$, SO_2 hydrate,[22] $HS_2O_3^-$, $H_2S_2O_3$, $H_3S_2O_3^+$, etc. In view of the fact that both the rate and the activation energy of the reaction are essentially independent of pH over the wide range studied it is possible to conclude that no one of these forms, which would vary in concentration with pH, is primarily responsible for the reaction.

The second ionization constant of thiosulfuric acid at 25° is given as[23] 2.7×10^{-2}. Therefore, the concentration of $HS_2O_3^-$ must have been extremely low even at pH 5, the lowest pH of these tests. The ionization constants of sulfurous acid at 25° are[24] $k_1 = 1.7 \times 10^{-2}$ and $k_2 = 6.2 \times 10^{-8}$ which leads to the conclusion that essentially all of the sulfite was present as HSO_3^- at pH 5 and essentially all of it as $SO_3^=$ at pH 9. From this fact and the fact that the rate of the sulfite-thiosulfate exchange is nearly independent of pH it must be concluded that a thiosulfate ion can collide with and transfer its sulfur to a sulfite ion or a bisulfite ion with approximately equal ease (or that ion pairs involving these ions react with equal ease).

Possibility of Ion Pair Formation with Sodium Ion.—In addition to sulfite, thiosulfate, hydrogen ion and hydroxyl ion the solutions studied in this work contained sodium ion and chloride or sulfate ion. It seems highly improbable that chloride or sulfate combines with sulfite or thiosulfate to form a species reactive in the exchange reaction but the possibility cannot be excluded that ion pairs between the latter ions and sodium ions are the actual reacting species. The fact that the mean activity

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(21) Bichowsky, THIS JOURNAL, **45**, 2225 (1923).

(22) Wright, *J. Chem. Soc.*, **105**, 2907 (1914); Schaefer and Kohler, *Z. anorg. Chem.*, **104**, 212 (1918); Walsh, *Quarterly Review*, **II**, 73 (1948).

(23) (*a*) Yui and Hagisawa, *Bull. Inst. Phys. Chem. Res. (Japan)*, **21**, 597 (1942); (*b*) Kolthoff, *Rec. trav. chim.*, **23**, 216 (1924).

(24) Tarter and Garretson, THIS JOURNAL, **63**, 808 (1941).

coefficients of sodium thiosulfate[25] and sodium sulfate[26] (and by analogy very probably sodium sulfite) are low may be[27] due to ion pair formation.

Measurements which we have made of the absorption spectra of aqueous thiosulfate and aqueous sulfite solutions indicate that the extinction coefficients depend on the concentration of the cation and are independent of the total ionic strength, and of the identity of the cation in the alkali metal series. The formation of ion pairs such as, for example, $NaS_2O_3^-$ is one possible explanation of such behavior.

Although no experiments have been made for the specific purpose of testing the effect of sodium ion concentration on the rate of the sulfite–thiosulfate exchange, there was an appreciable change in this concentration when the ionic strength was changed from 2 to 1 and also when the salt used to make up the ionic strength was changed from a 1,1 electrolyte to a 1,2 electrolyte. In the former case the average sodium ion concentration decreased by 54% and the average rate constant by 53%. In the latter case the average sodium ion concentration decreased by 27% and the rate constant by 38% (runs at *p*H 12). In contrast to these results the average rate constant for experiments at *p*H 5 was about 30% lower than the value for similar experiments at *p*H 12 although the average sodium ion concentration was about 10% higher at *p*H 5. The effect of the concentration and nature of positive ions on the sulfite–thiosulfate exchange should be investigated further. It is of particular interest in view of the recent discussion by Olson and Simonsen, of the effect of ions of opposite charge on rates of reaction between liked charged ions.[28]

Effect of Thiosulfate Concentration on Reaction Rate.—It has been pointed out in the presentation of the experimental results that the apparent dependence of the rate of the exchange reaction on the thiosulfate concentration at *p*H 6 was $[S_2O_3^=]^{0.8}$ and at *p*H 12 was $[S_2O_3^=]^{0.6}$ (Fig. 2) when the ionic strength was adjusted with sodium chloride. By contrast, identical determinations at *p*H 5 and *p*H 14 showed more nearly first power dependence as did also a determination at *p*H 12 when the ionic strength of 2 was achieved by the addition of sodium sulfate. We have not been able to reconcile these observations.

Variation of the thiosulfate concentration at constant ionic strength results in a change in the sodium ion concentration when sodium chloride is used to adjust the ionic strength but not when sodium sulfate is used. Consideration of this fact together with the observed first power dependence in the sulfate solutions suggested that the sodium ion concentration might be a controlling factor in the experimentally observed deviations from first power dependence. Both the fact that at lower and higher *p*H values sodium chloride solutions at ionic strength 2 gave much more nearly first power dependence, and the fact that the change in total sodium ion concentration resulting from variation in the relatively low thiosulfate concentration was slight (*ca.* 9% for a tenfold change in thiosulfate concentration) seem to eliminate this possibility.

Frequency Factor.—The frequency factor of 2.3×10^6 liters mole^{-1} sec.$^{-1}$ for the sulfite–thiosulfate exchange is about 10^{-5} of the most commonly observed frequency factors for bimolecular reactions between neutral molecules,[29a] but is in the range observed for a number of reactions between ions of like sign.[29b] The lowering of the value below the usual range for neutral molecules may be due in large part to coulombic repulsion.

The sulfite ion is believed to have a pyramidal structure[30] with the sulfur atom at the apex, and the thiosulfate ion to have a tetrahedral structure[30] with the exchangeable sulfur at one vertex. The orientation required for reaction between such molecules would be expected to reduce the frequency factor below the collision frequency but probably not by a factor of more than 10 or so. Both sulfite and thiosulfate ions may exist in a variety of states of hydration and ion pair formation in aqueous solution. It seems probable that exchange may proceed readily only through the reaction of one of the less predominant of these forms and that this fact may contribute largely to the reduction of the frequency factor.

Sulfide–Thiosulfate Exchange.—The exchange reaction between sulfide ion and thiosulfate ion has been shown to be slower[3] than the sulfite–thiosulfate exchange. For purposes of comparison we have made a preliminary determination which indicates that the activation energy is about 15 kcal./mole, *i.e.*, not far different from the value for the sulfite–thiosulfate reaction. This suggests that the rate determining step in the two reactions may be the same, *i.e.*, the splitting of the sulfur–sulfur bond in thiosulfate, although one reaction involves the transfer of a neutral sulfur atom from one ion to another while the other reaction involves the replacement of a sulfur atom accompanied by a transfer of electrons. If the sulfide–thiosulfate exchange is a bimolecular reaction, its frequency factor must be approximately 7×10^5 sec.$^{-1}$, which is somewhat lower than that of the sulfite–thiosulfate reaction.

Sulfite–Sulfate Exchange.—The structure of the sulfate ion is presumably similar to that of the thiosulfate ion except for the replacement of the outer sulfur atom by an oxygen atom. By analogy with the present work it might be supposed that the transfer of oxygen from sulfate to sulfite could be observed. It might be predicted that the frequency factor for the exchange would be somewhat higher than that for the sulfite–thiosulfate exchange because any one of the four oxygen atoms of the sulfate might be transferred, thus

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[25] R. A. Robinson, J. M. Wilson and R. H. Stokes, THIS JOURNAL, **63**, 1011 (1941).

[26] (a) G. Akerlöf, *ibid.*, **48**, 1160 (1926); (b) H. S. Harned and G. Akerlöf, *Physik. Z.*, **27**, 411 (1926).

[27] (a) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 421; I. L. Jenkins and C. B. Monk, THIS JOURNAL, **72**, 2695 (1950).

[28] Olson and Simonsen, *J. Chem. Phys.*, **17**, 1167 (1949).

[29] Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1947; (a) p. 71, (b) p. 94.

[30] (a) Zachariasen and Buckley, *Phys. Rev.*, **37**, 1295 (1931); (b) Gupta and Guha, *Proc. Natl. Inst. Sci.*, (*India*), **7**, 267 (1941); (c) Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1945, p. 305.

imposing somewhat less stringent orientation requirements. It might also be predicted that the activation energy would be higher because of the greater strength of the S–O bond than the S–S bond. If it is assumed that the activation energy is proportional to the strength of the bond broken,[31] a very rough estimate might be made from the relation

$$E_{(SO_3^{=} + SO_4^{=})} = E_{(SO_3^{=} + S_2O_3^{=})}\left(\frac{\text{strength of S–O bond in } SO_4^{=}}{\text{strength of S–S bond in } S_2O_3^{=}}\right)$$

by estimating the bond strengths from thermochemical values for the heat of formation of $SO_4^{=}$ and $S_2O_3^{=}$ from gaseous atoms (assuming hydration effects cancel or are negligible). Taking the values 215.8, 145.5, 148.5, −66.3 and −59.1 kcal. mole^{-1} as the heats of formation of sulfate, thiosulfate, sulfite, sulfur atoms and oxygen atoms, respectively,[32] the estimated bond strengths are S–O 126.4 and S–S 63.3 kcal./mole, and the estimated E for the sulfate exchange is 28.7 kcal. mole^{-1}. If the frequency factor is the same for the sulfate exchange as for the thiosulfate exchange, this would result in a half-time for the reaction in 0.1 M sulfite and 0.1 M sulfate of 3400 years at 100°, of 20 days at 250° and of 1 hr. at 400°. Voge[3] has shown that no exchange occurs between sulfite and sulfate on heating in 0.1 N acid or alkaline solution for 35 hours at 100° but has observed a slow exchange between sulfur dioxide and sulfur trioxide gases at 335°, which was catalyzed by water. Norris[33] has observed an exchange between sulfur dioxide and concentrated sulfuric acid with a readily measurable rate in the temperature range of about 200°, and with an apparent activation energy of 28.8 kcal. mole^{-1}. Huston and Norris[33] have found that the rate of exchange between intensively dried sulfur dioxide and sulfur trioxide gases is conveniently measurable in the range of 400 to 440° and, as indicated by Voge, that the reaction is heterogeneous and strongly catalyzed by water. It would be interesting to investigate the exchange of aqueous sulfite with sulfate in sealed tubes at temperatures above 250°.

Acknowledgments.—The authors wish to express their appreciation to Dr. E. L. King for helpful discussions during the course of these investigations.

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Summary

The transfer of the outer sulfur atom of thiosulfate ion to sulfite ion occurs in the temperature range of 60–100° at a rate which is proportional to the first power of the sulfite concentration and also of the thiosulfate concentration. The rate and activation energy appear to be essentially independent of pH in the range from pH 5 to 14. The second order velocity constant is given by the relation $k = 2.3 \times 10^6 e^{-14,500/RT}$ liters mole^{-1} sec.$^{-1}$.

The evidence indicates that the equilibrium of thiosulfate with sulfur and sulfite is not a part of the mechanism of sulfur transfer. Other factors to be considered with regard to the mechanism of this reaction are discussed.

A preliminary value of 15 kcal. mole^{-1} for the activation energy of the exchange of sulfide ion with thiosulfate has been determined.

Previous evidence indicating that the sulfur atoms of thiosulfate are not chemically equivalent has been confirmed and extended to show that exchange between them does not occur in 5 hours at 125° nor when the thiosulfate is precipitated as triethylenediaminenickel thiosulfate and subsequently dissolved in hydrochloric acid.

A reproducible routine method of determining the relative specific activity of S^{35} in barium sulfate precipitates is described.

Madison 6, Wis. Received June 26, 1950

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[31] J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

[32] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[33] Norris, This Journal, **72**, 1220 (1950).

[Contribution from the Cryogenic Laboratory and the Department of Chemistry, The Ohio State University]

Vapor Pressure of Inorganic Substances. IV. Tantalum between 2624 and 2943°K.[1]

By James W. Edwards, Herrick L. Johnston and Paul E. Blackburn

Although there have been two previous investigations of the vapor pressure of tantalum,[2,3] the results were in considerable disagreement. We have, therefore, redetermined the vapor pressure of tantalum, in this Laboratory, using the method of I. Langmuir. The method and techniques used by us have been described in earlier papers[4] from this Laboratory.

Procedure.—A sample of better than 99.9% pure tantalum was obtained from the Fansteel Metallurgical Corp. An analysis, conducted by the manufacturer, showed that the principal impurities were carbon and iron and that neither of these was present to more than 0.03%.

The rate at which the surface of a sample of tantalum evaporated *in vacuo* was determined. The sample was in the form of a hollow cylinder one inch high by one inch diameter with a 1/8 inch wall thickness. The ends of the cylinder were each covered with several split radiation shields made of tantalum sheet. This arrangement practically eliminated evaporation from the ends since the split shields did not heat efficiently. Three longitudinal holes drilled into the cylinder wall and one hole through the upper set of radiation shields served as black-body holes.

The sample was placed in an evacuated metal chamber and heated by radio frequency induction. Temperatures were measured by means of a carefully calibrated disappearing-filament optical pyrometer sighted on the four black-body

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[1] This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] D. B. Langmuir and L. Malter, *Phys. Rev.*, **55**, 743 (1949).

[3] M. D. Fiske, *ibid.*, **61**, 513 (1942).

[4] (a) H. L. Johnston and A. L. Marshall, This Journal, **62**, 1382 (1940); (b) R. B. Holden, R. Speiser and H. L. Johnston, *ibid.*, **70**, 3897 (1948); (c) R. Speiser and H. L. Johnston, Preprint No. 11, Thirty-First Annual Convention of the American Society for Metals, Cleveland, Ohio, Oct. 17–21, 1949.