THE KINETICS OF OXYGEN EXCHANGE
BETWEEN THE
SULFITE ION AND WATER

A Thesis
submitted to
the Faculty of Graduate Studies and Research
University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
MASTER OF SCIENCE

by
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August 1969

to my parents

ACKNOWLEDGEMENTS

I am pleased to acknowledge my gratitude to Dr. R.H. Betts for his constructive advice and guidance during the course of this research;
to my fellow worker, Steve Libich, for the numerous discussions with him;
and to the National Research Council and the Department of Chemistry for the financial assistance in the form of a scholarship and a demonstratorship respectively.

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ABSTRACT

Oxygen of mass 18 was used as a stable tracer to measure the rate of exchange between the sulfite ion and water as a function of pH and total sulfite concentration. A value for the rate constant of hydration of SO_2 in aqueous solution was determined. The gross rate constants k_1 and k_{-1} for the overall reaction

$$H^+ + HSO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_2 + H_2O$$

at 24.7°C and ionic strength = 0.9 were evaluated from exchange results to be

$$k_1 = 2.48 \pm 0.27 \times 10^9 \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

$$k_{-1} = 1.06 \pm 0.13 \times 10^8 \text{ sec.}^{-1}$$

and are one to two orders of magnitude larger than the values determined from relaxation measurements made earlier on this system by other workers.

Also, for the first time, rate constants for the pyrosulfite equilibrium

$$2\ HSO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} S_2O_5^= + H_2O$$

were obtained

$$k_2 = 7.00 \pm 0.21 \times 10^2 \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

$$k_{-2} \simeq 1 \text{ sec.}^{-1}$$

at 24.7°C and ionic strength = 0.9.

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1 - 1 ISOTOPIC EXCHANGE REACTIONS

Isotopic exchange is defined as the spontaneous reciprocal substitution of an atom (electrically neutral or charged, radioactive or stable) in a molecular entity by another atom of the same atomic number and of equal or different mass arising from another molecular entity.

Consider the overall exchange process

$$AX^* + BX_n \rightleftharpoons AX_n + BX^*$$

Let X_n, X^*, and X represent the normal or natural isotope, the tracer isotope, and all atoms X (whether like or different isotopes) respectively. Then AX and BX are the two exchanging species, and X is the atom undergoing exchange. Such an exchange is not observable unless one of the reactants is "tagged". X_n and X^* represent distinguishable forms of the same atom. X^* may be either a stable or radioactive isotope and will henceforth be referred to as the tracer atom. For a system "tagged" or labelled with a radioactive or stable isotope, the rate of exchange is assumed to be the same for all isotopic atoms, irrespective of their mass, that is, the species AX_n and AX^* are chemically identical.

To follow the progress of an isotopic exchange reaction in a homogeneous stable system, the chemically distinct species, one of which is labelled, are mixed for a certain period of time; then they are separated by some chemical or physical means, and the isotopic composition of the two fractions is determined. If the process of separating the species in itself brings about exchange, such exchange is said to be separation induced exchange. The question must always be considered, whenever instantaneous exchange is encountered, whether the exchange is really so fast that the rate cannot be measured, or whether the separation procedure has caused the exchange. If the overall exchange (that is, induced plus homogeneous) is incomplete after a certain period of time, this catalytic effect can be allowed for in establishing the kinetics by correcting for the exchange found at time $t = 0$. Regardless of the mechanism by which the exchange occurs, the number of exchangeable atoms in each species, or the concentration of the tracer atom, the rate of appearance of the tracer atoms in the initially unlabelled species is always first order with respect to time for homogeneous exchange reactions. Kinetic studies of exchange processes show that they may have extremely fast, medium, or zero rates depending on the particular system and the experimental conditions.

1 - 2 MATHEMATICS OF EXCHANGE REACTIONS

Consider a system involving two molecular species

AX and BX in dynamic equilibrium; let the first of these be labelled with an isotopic tracer. Consider the overall exchange process

$$AX^* + BX_n \rightleftharpoons AX_n + BX^*$$

where X^* represents the tracer isotope which can exchange with a normal or natural isotope X_n. Let R be the gross rate of exchange, that is, the rate at which X atoms (whether like or different isotopes) pass from AX to BX or vice versa. R will be a constant for a given set of conditions, although it is a function of the usual variables:

$$R = f\text{ (concentrations, temperature, pH, ionic strength, etc.)}$$

Also, the same R will apply to both forward and reverse reactions since no changes in chemical concentrations or other factors are involved during equilibration. One can now define various concentration variables and solve the equation describing the rate of isotopic exchange, the sole "driving force" for which is the increase in entropy obtained by complete randomization of isotope distribution.

Set

a = concentration of X in the AX form (g.-atom of X $l.^{-1}$) at time t

y_0 = initial concentration of X^* in the AX form (g.-atom $l.^{-1}$)

b = concentration of X in the BX form (g.-atom of X $l.^{-1}$) at time t

y = concentration of X* in the AX form (g.-atom $l.^{-1}$) at time t

z = concentration of X* in the BX form (g.-atom $l.^{-1}$) at time t

The rate ($\frac{dz}{dt}$) of increase in the concentration of tracer X in the form BX (assuming that the rate of change of isotopic distribution is determined purely on a statistical basis) is given by the rate at which X in the AX form is converted to X in the BX form (that is, R) multiplied by the fraction of AX that is labelled at time t ($= R\,\frac{y}{a}$). Similarly, the rate of disappearance of tracer X in the form of BX is given by the rate at which X in the BX form is converted to X in the AX form (that is, R) multiplied by the fraction of BX that is tracer at time t ($= R\,\frac{z}{b}$).

The net rate is given by the difference between these two quantities

$$\frac{dz}{dt} = \frac{-dy}{dt} = R\left(\frac{y}{a}\right) - R\left(\frac{z}{b}\right) = \frac{R}{ab}(by-az) \qquad (1)$$

But conservation of matter requires that:

$$y_o = y + z = y_\infty + z_\infty$$

$$y = (z_\infty + y_\infty) - z$$

Also at equilibrium no further change in z ensues, or

$$\frac{dz}{dt} = 0, \text{ or } (ay_\infty - bz_\infty) = 0, \text{ or } \frac{z_\infty}{a} = \frac{y_\infty}{b},$$

thus,

$$y = z_\infty + z_\infty \frac{b}{a} - z.$$

Substituting the above expression for y into equation (1),

$$\frac{dz}{dt} = \frac{R}{ab}\left[a(z_\infty + z_\infty \frac{b}{a} - z) - bz\right]$$

$$= \frac{R}{ab}\left[(a + b)(z_\infty - z)\right].$$

Rearranging,

$$\frac{dz}{z_\infty - z} = \frac{R}{ab}(a + b)\,dt.$$

Integrating the above,

$$-\ln(z_\infty - z) = \frac{R}{ab}(a + b)\,t + \text{constant}.$$

Since at $t = o$, $z = z_o$, the constant is equal to $-\ln(z_\infty - z_o)$, then,

$$\frac{R}{ab}(a + b)t = \ln \frac{[z_\infty - z_o] - [z - z_o]}{[z_\infty - z_o]} \qquad (2)$$

or

$$Rt = \frac{-ab}{(a + b)} \ln (1 - F) \qquad (3)$$

where F = fraction exchanged at time t:

$$F = \frac{z - z_o}{z_\infty - z_o} = \frac{y - y_o}{y_\infty - y_o} \qquad (4)$$

Consequently, if the logarithm of the fraction (1 - F) is plotted against time, a straight line passing through the origin should be obtained. Superficially this statement means that any true isotopic exchange reaction obeys a first order kinetic law. This observation was first recognized by McKay(1) in 1938. A convenient term that may be introduced is the half-life of exchange, $t_{\frac{1}{2}}$ (the time for half the equilibrium distribution of tracer to be obtained), the time necessary for the fraction of exchange, F, to reach a value of one half. Substitution of 0.5 for F and $t_{\frac{1}{2}}$ for t into equation (3) gives an expression relating the rate of exchange, R, to the half-life of exchange,

$$R = \frac{(ab) \quad (0.693)}{(a + b)(t_{\frac{1}{2}})} \,. \qquad (5)$$

1 - 3 USE OF O^{18}

In the study that was carried out here, namely, the oxygen exchange between sulfite ions and water, the tracer isotope was oxygen - 18, a stable isotope.

There are two methods of measuring the abundance of oxygen isotopes:

a) water density measurements, and

b) mass spectrometer methods.

Mass spectrometers which permit the simultaneous collection of ions of two different masses, as invented by Nier(2) in 1947, are universally used. The isotopic ratio of oxygen, $\frac{O^{18}}{O^{16}}$, was determined, in the present study, on a double collector type mass spectrometer. It is not convenient to measure the isotopic ratio of oxygen in water because it would necessitate baking out the instrument after each analysis. Nor is it desirable to use oxygen gas since it reacts with the filament. It is most suitable to measure the relative abundance of the isotopes of oxygen in the form of CO_2. The mass ratio of $\frac{C^{12}O^{16}O^{18}}{C^{12}O^{16}O^{16} + C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}} \left(\frac{46}{44 + 45}\right)$ was determined on the isotope ratio spectrometer. This ratio is referred to as the p-factor. The ratio $\frac{O^{18}}{O^{16}}$ is proportional to the measured p-factor. Measurement of the isotopic composition of the water is made either by equilibrating it with CO_2(3,4) or by converting the oxygen of the water into CO_2(5). The solute is generally converted to CO_2(5) in order to determine its isotopic composition. Once the p-factors have been determined, they are easily related to F, the fraction exchange, by substituting into equation (4) from section 1 - 2, then,

$$F = \frac{P_t - P_o}{P_\infty - P_o} \qquad (1)$$

Thus using a double collector type mass spectrometer, one can accurately determine the $\frac{O^{18}}{O^{16}}$ ratio; the next question then is, how does one best follow the progress of the exchange reaction. There are four methods which may be used: i) label the water, dissolve unlabelled solute, and follow the decrease of the O^{18} content of the water, or ii) follow the increase of the O^{18} content of the solute, and iii) label solute, dissolve in unlabelled water, and follow the increase of the O^{18} content of the water, or iv) follow the decrease of the O^{18} content of the solute. In each case the fraction of exchange, F, is related to the measured p-factors by equation (1), $F = \frac{P_t - P_o}{P_\infty - P_o}$. Since the concentration of oxygen atoms in the water($[H_2O] = 55.55$ moles $l.^{-1} \equiv 55.55$ g.-atom oxygen $l.^{-1}$) is generally much greater than the concentration of oxygen atoms in the solute (concentrations are in general less than 1 mole $l.^{-1}$), the water may be regarded as a large "reservoir" of oxygen atoms relative to the solute. From this type of analogy it is apparent that cases i) and iii) would be less sensitive than cases ii) and iv) to changes in the $\frac{O^{18}}{O^{16}}$ ratio. In fact cases i) and iii) are, in general, good only for semi-quantitative treatments, and whenever possible methods ii) and iv) are used to follow the progress of an isotopic exchange reaction.

1 - 4 WHY STUDY THE RATE OF EXCHANGE?

In its broad interpretation chemical kinetics has as its goal the understanding of the various factors affecting the velocity and course of a reaction. The approach to any one problem may involve such investigations as the determination of the rate constant and order of the reaction, the number and kinds of intermediate species, the effect of solvents, the determination of the activation energy, and the study of what bonds are broken in the reaction. For many years after the earliest investigation in 1850(6) the rates of chemical reactions in solutions were studied by simple methods. The reaction was initiated by mixing the reagent solutions, and its progress was followed by titrating samples, or making measurements of some physical property, after various intervals of time. The time required for mixing and for observation had to be short compared with the half-life of the reaction. Consequently, the fastest reactions that could be measured had half-lives of minutes or at least seconds. Many reactions, especially those of ions, were immeasurably fast by these standards, and their mechanisms could not be kinetically investigated.

The situation is now entirely changed. The first major advance was the introduction of the continuous-flow method by Hartridge and Roughton in 1923(7). This made possible the study of reactions with half-lives of a few milliseconds. The limiting factor was the rate of mixing. Since that time a whole range of techniques has emerged. The term "fast" is roughly applied to those reactions which would be too fast to investigate by conventional methods if conducted at "ordinary" temperatures and concentrations. Chemical events with half-lives as short as 10^{-7} sec. (and some of them 10^{-9} sec.) have been studied with reasonable accuracy using fast reaction techniques. Two types of fast reaction techniques will be discussed only briefly here, since they are discussed extensively elsewhere(8,9).

In the flow techniques the two reactant mixtures are rapidly mixed, and the reaction observed by one of several methods including i) conductometric, ii) photometric, iii) thermometric, and iv) potentiometric methods. The shortest half-life that can be measured by any of the preceding methods is determined by the least time of mixing, which is about a millisecond.

In the second type of method, called relaxation methods, use is made of small displacements from equilibrium. Consider a reversible reaction initially in equilibrium. If the conditions are then suddenly altered (temperature, pressure, or electric field), there is a time-lag while the system approaches the new position of equilibrium. This time lag is related to the rate constants of the forward and back reactions. For example, a sudden change of temperature has this effect on the dissociation of a weak acid. The course of the reaction is followed by a fast oscillographic method. A periodic change of temperature can also be affected, by means of ultrasonic waves; when the half-life of the reaction is comparable to the period of the disturbance, there is a sharp increase in the power absorbed. Using relaxation methods, mixing can be avoided altogether, and the range of half-lives accessible is about 10^{-9} to over 1 sec.

The answer to the question "why study the rate of exchange?" is that isotopic exchange study has revealed itself as another investigative approach (comparable to the relaxation techniques) for the evaluation of the rate constants of "fast" reactions. Fundamental to the understanding of the use of isotopic exchange for kinetic study, is the observation that the measured rate of exchange depends on the chemical reactions normally occurring. The investigation of reaction kinetics is made possible by this technique because of the chemical identity of isotopes. The rate of establishment of isotopic equilibrium is measured in a system in a steady state except for the distribution of isotopes. The chemical equilibrium ordinarily considered is concerned with the number of ions and molecules present. Isotopic equilibrium is concerned with the distribution of isotopes in the various ions and molecules. This latter equilibrium results in a uniform distribution of isotopes in all compounds. The time necessary to reach isotopic equilibrium is greater than that necessary to reach ordinary equilibrium. The last statement could possibly be made clearer by a hypothetical example. Suppose that the isotopic exchange between the species MO_2 and H_2O occurs by a hydration reaction

$$H_2O + MO_2 \rightleftharpoons H_2MO_3.$$

Now, although the time necessary for the attainment of ordinary equilibrium may be extremely fast (as short as 10^{-6} sec.) the time to reach isotopic equilibrium may involve times as great as seconds, minutes, hours, days, or years, depending on the particular system and the experimental conditions. This is so because the reaction (hydration reaction in this hypothetical case) must occur many times in order that there be a complete "scrambling" (isotopic equilibrium) of the isotopes among the species present. The use of isotopic exchange in kinetic studies will be made clearer in the next section (1 - 5) which discusses some of the systems that have been studied by means of this technique.

1 - 5 SOME SYSTEMS STUDIED

For a better understanding of the interpretation of the rate of exchange obtained from the present study (sulfite-H_2O), it is instructive to consider the kinetics for some related systems which have already been studied.

In 1952, Edwards(10), in a review article on oxygen exchange in oxyanions, pointed out that "although a considerable amount of qualitative work has been done in the studies on exchange of oxygen isotopes of oxyanions with the solvent water, few quantitative data on rate equations are found in the literature." The situation has not changed significantly since that time (three excellent review articles on research with isotopes of oxygen during the periods 1958-60, 1960-61 and 1963-66 have been prepared by Samuel and Stecker.)(11,12,13)

As in any kinetic study a necessary step is to establish precisely the dependence of the rate of exchange on the various factors (concentration, temperature, pH, ionic strength, etc.) involved. If a single reaction path is available for the reaction which leads to isotopic exchange, R may be expressed as

$$R = k[H^+]^m [AX]^n [BX]^p$$

where AX and BX are the exchanging species. Such a relationship is called the <u>rate law</u>. Once the rate law has been determined for a particular temperature and ionic strength, it is of interest to propose mechanisms for exchange consistent with the rate law. As pointed out in the previous section, the exchange can generally be explained in terms of equilibria which are known to be present; the rate of isotopic exchange then reflects the rate of all processes resulting in exchange. Isotopic exchange studies then offer the advantage of the determination of the rate of reaction under equilibrium conditions. The few systems discussed here will help to illustrate the manipulations involved. Consider the exchange between:

(i) Chromium (VI) Oxyanions and Water

Holyer and Baldwin(14) dissolved sodium chromate enriched in oxygen - 18 into water of normal isotopic composition and followed the isotopic composition of the water (aliquots withdrawn by vacuum distillation) by equilibration with carbon dioxide(3,4) and mass spectrometric analysis of the carbon dioxide. From their data they obtained the following rate laws as a function of pH:

$$\text{pH} > 10,\ R \propto [H^+]^{0.1}\,[\text{Cr(VI)}]^{1.2}$$

$$\text{pH } 8.4\text{–}10.0,\ R \propto [H^+]^{1.0}\,[\text{Cr(VI)}]^{2}$$

$$\text{pH } 6.7\text{–}8.4,\ R \propto [H^+]^{1.7}\,[\text{Cr(VI)}]^{2}$$

For each pH region they then proposed processes consistent with the rate laws:

pH >10,

$$CrO_4^{=} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrO_4^{=} + H_2O$$

pH 8.4-10,

$$HCrO_4^{-} + CrO_4^{=} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cr_2O_7^{=} + OH^{-}$$

pH 6.7-8.4,

$$2\ HCrO_4^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Cr_2O_7^= + H_2O$$

The rate law for oxygen exchange resulting from the three processes assumed is given by

$$R = k_1[CrO_4^=][H_2O] + k_2[CrO_4^=][HCrO_4^-] + k_3[HCrO_4^-]^2$$

$$= k_1'[CrO_4^=] + k_2[CrO_4^=][HCrO_4^-] + k_3[HCrO_4^-]^2$$

From a knowledge of the equilibrium relationships $K_1 = \frac{[HCrO_4^-]}{[H^+][CrO_4^=]}$ and $K_2 = \frac{[Cr_2O_7^=]}{[HCrO_4^-]^2}$, they were able to extract values for the rate constants k_1, k_2 and k_3 from the measured rates of exchange. Their values agreed quite well with the values obtained by other methods.

(ii) Bromate, Chlorate, and Iodate Ions and Water

To follow the oxygen exchange between bromate ions and water, Hoering et al(15) prepared oxygen - 18 tagged potassium bromate by the electrolytic oxidation of potassium bromide in O^{18} tagged water. The exchange was followed by precipitating the bromate as silver bromate, converting the precipitate to O_2 by thermal decomposition, and making an isotopic analysis of the O_2 on an isotope ratio mass spectrometer. In some experiments, samples of water were vacuum distilled from the reaction mixture. The water was allowed to reach isotopic equilibrium with CO_2, and the CO_2 was used for isotopic analysis. They found that the exchange of oxygen between the bromate ions and water followed a third order rate law

$$R = k[H^+]^2[BrO_3^-]$$

where k has the value $6.60 \pm 0.50 \times 10^{-3}$ $l.^2$ $mole^{-2}$ $sec.^{-1}$ at 30°C and ionic strength = 0.90. Edwards(10) had postulated that the exchange of water with bromate ions may occur by the equilibria

$$H^+ + BrO_3^- \rightleftharpoons HBrO_3 \quad \text{fast}$$

$$HBrO_3 + H^+ \rightleftharpoons H_2BrO_3^+ \quad \text{fast}$$

which may be followed by either a unimolecular

$$H_2BrO_3^+ \rightarrow BrO_2^+ + H_2O \text{ slow}$$

dissociation or by a nucleophilic displacement

$$H_2O^* + H_2BrO_3^+ \rightarrow H_2O + H_2BrO_3^{*+} \text{ slow.}$$

The authors assumed that a bimolecular nucleophilic displacement took place.

The isotopic exchange of oxygen between chlorate ions and water was shown(16) to follow the same type of rate law as for the bromate - water exchange, namely, $R = k[H^+]^2[ClO_3^-]$, where $k = 0.89 \times 10^{-3}$ $l.^2$ $mole^{-2}$ $sec.^{-1}$ at 100°C and ionic strength = 1.34. Once again the exchange process involved a cationic species; in this case, $H_2ClO_3^+$.

Hoering and co-workers(15) had also attempted to determine the kinetics of the isotopic exchange reactions between the iodate ion and water. They found the exchange to be complete, even in the alkaline region, in the time of mixing of one minute. Using an improved technique Anbar and Guttmann(17) were able to separate iodate from solution (before it had reached isotopic equilibrium with the solvent) and to follow the kinetics of the exchange. Their technique involved initiating the reaction by injecting small aliquots (0.01 - 0.25 ml.) of a 1 M solution of $LiIO_3$ (which had been allowed to attain isotopic equilibrium with H_2O^{18}) into 5 ml. of H_2O^{16} which was vigorously stirred; followed by quenching of the exchange reaction after a predetermined interval (1 sec. - 30 min.) by rapidly pouring 5 ml. of 0.5 M $Ba(ClO_4)$ solution in 80% ethanol into the well stirred reaction mixture. Such an experiment contributed only one point to the time versus ln(1-F) plot for each run. The $Ba(IO_3)_2$ precipitate was then thermally decomposed to O_2; the isotopic ratio $\frac{O_2^{16,18}}{O_2^{16,16}}$ was then determined by an isotopic ratio mass spectrometer. The results of IO_3^- - H_2O oxygen exchange in non-buffered solutions in the pH range 4.5-10.65 indicated that the rate of exchange is both acid and base catalyzed, passing through a minimum at about pH 7.7; see Fig. 1-1. The rate law was found to be $R = k_1[H^+][IO_3^-] + k_2[OH^-][IO_3^-]$, where

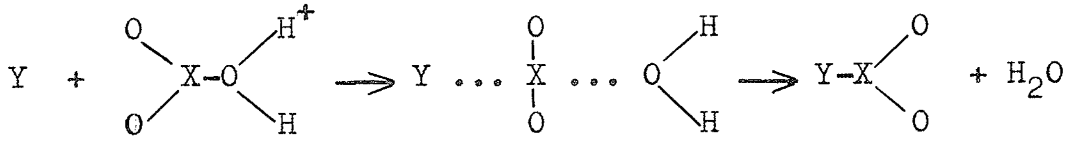
k_1, and k_2 have the values 3.24×10^4 l. mole sec.$^{-1}$, and 1.35×10^3 l. mole sec.$^{-1}$ respectively at 25°C. The suggested mechanism of exchange is via the reactions:

$$H_2IO_4^- \rightleftharpoons IO_3^- + H_2O, \text{ and}$$

$$O^*H^- + HIO_4^- \rightleftharpoons HIO_4^{*-} + OH^- .$$

When $H_2IO_4^-$ undergoes dissociation in more alkaline solutions $H_2IO_4^- \rightleftharpoons H^+ + HIO_4^=$, the $HIO_4^=$ formed cannot undergo a spontaneous and reversible dehydration like $H_2IO_4^-$.

In concluding this section on the exchange of oxygen between the oxyanions containing halogens and water, it is interesting to note that Anbar and Guttmann(18) found a catalytic effect of chloride ions on the isotopic oxygen exchange of both nitric and bromic acids with water. The mechanism that they suggested involved the nucleophilic replacement of a water molecule on the $H_2XO_3^+$ ion



where Y is H_2O or Cl^-. When $ClXO_2$ is formed it hydrolyzes rapidly to form again $Cl^- + HXO_3$. This observed catalysis confirms the mechanism suggested by Hoering et al(15) for the bromate - water exchange.

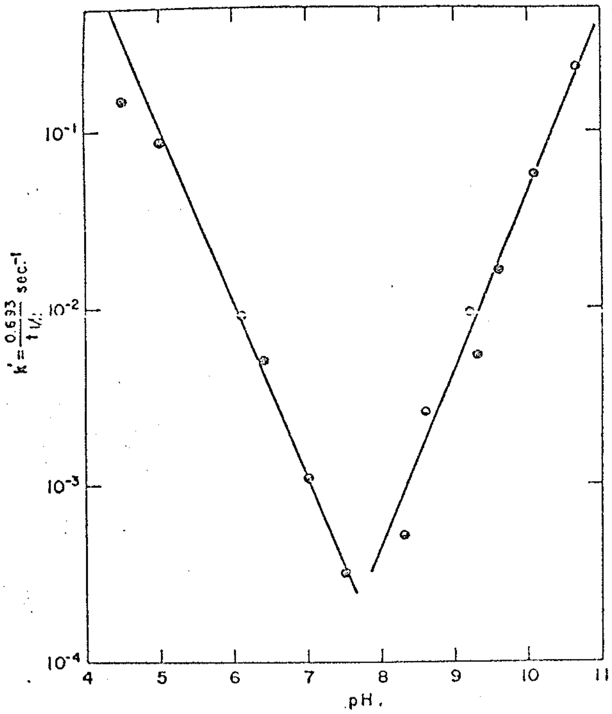
iii) the Sulfate Ion and Water

Hoering and Kennedy(19) found that the exchange

FIG. 1-1

The rate of iodate and water oxygen exchange in non-buffered solutions as a function of pH. [Reproduced from Ref. (17)].

FIG. 1-1



followed a rate law $R = k[H^+]^2[SO_4^=]$. On this basis they proposed that the oxygen exchange proceeded through the following reactions:

$$H^+ + SO_4^= \rightleftharpoons HSO_4^- \quad \text{fast}$$
$$HSO_4^- + H^+ \rightleftharpoons H_2SO_4 \quad \text{fast}$$
$$H_2SO_4 \rightleftharpoons H_2O + SO_3 \quad \text{slow.}$$

The dissociation of sulfuric acid into its anhydride and water was proposed as the rate determining step.

iv) Perrhenate Ion and Water

Murmann(20) in his work observed that the exchange of oxygen between the perrhenate ion and water occurred according to a non-catalyzed path as well as both acid and base catalyzed paths; see the pH dependence graph Fig. 1-2. The exchange obeyed the rate law

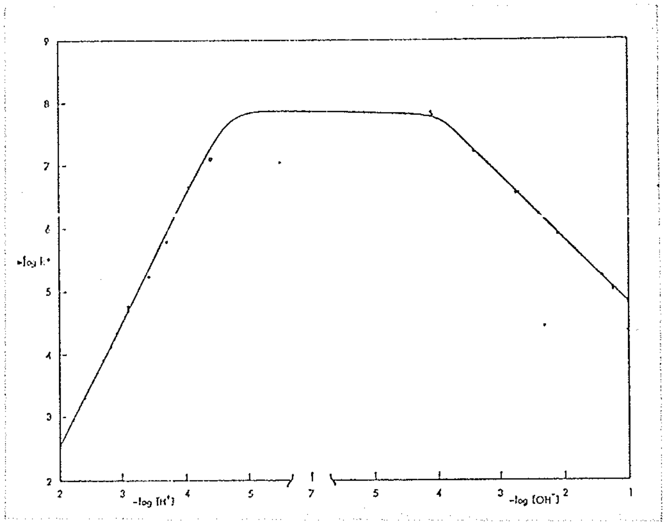
$$R = k_o[ReO_4^-][H_2O] + k_1[ReO_4^-][H_2O][H^+]^2$$
$$+ k_2[ReO_4^-][H_2O][OH^-]$$

where $k_o = 1.4 \pm 0.1 \times 10^{-8}$ l. mole^{-1} sec.$^{-1}$, $k_1 = 3.36 \pm 0.18 \times 10$ l.^{3} mole^{-3} sec.$^{-1}$, and $k_2 = 1.555 \pm 0.023 \times 10^{-4}$ l.^{2} mole^{-2} sec.$^{-1}$ at 25°C and ionic strength = 0.10.

For the many oxyanions such as NO_3^-, MnO_4^-, ClO_3^-, BrO_3^-, NO_2^-, and ReO_4^- which showed a second order rate dependence on H^+ ion concentration, Murmann proposed that a preassociation of the oxyanion with $2H^+$ ions occurs before the rate determining step. Three mechanisms are con-

FIG. 1-2
pH dependence for $ReO_4^- - H_2O$
oxygen exchange at 25°C and
ionic strength = 0.1.
[Reproduced from Ref. (20)]

FIG. 1-2



sistent with the rate law for this path. A general scheme is given below:

$$AO_m^{-1} + 2H^+ \rightleftharpoons H_2OAO_{m-1}^+ \quad \text{fast}$$

(a) $H_2OAO_{m-1}^+ + H_2O \rightleftharpoons H_2OAO_{m-1}^+ + H_2O$ slow

(b) $H_2OAO_{m-1}^+ + nH_2O \rightleftharpoons (H_2O)_{n+1}\ AO_{m-1}^+$ C.N. expansion

(c) $H_2O\ AO_{m-1}^+ \rightleftharpoons H_2O + AO_{m-1}^+$ slow.

Reactions (a) and (b) are nearly identical, differing only in whether the expanded coordination number (C.N.) has a finite stability or exists only in the transition state. The question with respect to whether both hydrogen ions reside on a single oxygen or are on two oxygens is unanswered. Mechanism (a) is most reasonable for NO_3^- and BrO_3^- since Cl^- catalysis has been observed, Cl^- apparently being effective in displacing H_2O from $H_2OAO_2^+$. Path (b) is suggested for ReO_4^-.

(v) the Carbonate and Bicarbonate Ions and Water

The CO_2-H_2O system is a particularly important one to consider in this discussion as it is analogous to the SO_2-H_2O system. Carbonic acid is unusual in that only a small fraction of the carbon dioxide dissolved in water exists as the diprotic acid H_2CO_3. The hydration equilibrium

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

$$K_h = \frac{[H_2CO_3]}{[CO_2]} = 2.6 \times 10^{-3}$$

is slow to be established (about 0.1 sec.) compared to the ionization equilibria

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$Ka_1' = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 1.7 \times 10^{-4}$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+$$

$$Ka_2 = \frac{[H^+][CO_3^=]}{[HCO_3^-]} = 5.6 \times 10^{-11},$$

which are established in about 10^{-6} sec. in dilute solutions. This difference in rates has made possible an analytical distinction between H_2CO_3 and the loosely hydrated CO_2 (aq); the ionization equilibria can be studied by very rapid flow techniques without appreciably disturbing the hydration equilibrium, and the separate equilibrium constants obtained. However, because $[H_2CO_3]$ is such a small fraction of $[CO_2]$, independent of concentration and pH, it is usually neglected in calculations. The first ionization constant of carbonic acid is generally given for the overall reaction

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$$

$$Ka_1 = Ka_1' \times K_h = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.4 \times 10^{-7}$$

at 25°C.

By the addition of HCl to dispersed $NaHCO_3$(21)

or Na_2CO_3(22) in anhydrous ethyl and methyl ether respectively, it has been shown that the anhydrous acid H_2CO_3 exists in ether solution at $\sim -30^\circ C$ as a stable entity. Corresponding etherates $OC(OH)_2 \cdot Et_2O$ and $OC(OH)_2 \cdot Me_2O$, which decompose above $-10^\circ C$ and $5^\circ C$ respectively, can be precipitated at $\sim -80^\circ C$ as white crystals. H_2CO_3, then, is quite generally recognized as a well defined compound in aqueous solutions of CO_2.

There is general agreement that the hydration of carbon dioxide may take place in two ways. When the pH is less than 8 only simple hydration is important

$$CO_2 + H_2O \rightleftharpoons H_2CO_3.$$

When the pH is greater than 10 a bimolecular reaction predominates

$$CO_2 + OH^- \rightleftharpoons HCO_3^-.$$

Between these limits both determine the rate of reaction.

Although only O^{18} studies of the hydration of CO_2 will be considered here, Kern(23) gave an excellent review of the various methods used to study the hydration. Working in the pH region <8, Mills and Urey(24) in 1940 found that under these conditions the bicarbonate ion exchanges oxygen with water only through the reversible formation of carbon dioxide by simple hydration

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2CO_3 \rightleftharpoons H^+ + HCO_3^-.$$

They reported a value of 2.75 x 10^{-2} sec.$^{-1}$ for the rate of hydration of CO_2 (k_1) at 25°C.

Poulton and Baldwin$^{(25)}$ in 1966 carried out an O^{18}- exchange study of the CO_2-H_2O system in the pH range ~ 7.5-~12.5. Their technique for the isotopic analysis of the carbonate-bicarbonate was unique. At various intervals, aliquots of the solution were withdrawn and placed in a flask attached to a high vacuum system. After proper degassing, concentrated sulfuric acid was added by means of a syringe through a rubber cap covering a short neck connected to the flask. The CO_2 driven off was collected and mass analyzed. They observed that the rate of exchange was proportional to the total concentration of carbonate plus bicarbonate ($[C(IV)] = [CO_3^=] + [HCO_3^-] + [CO_2]$) to the power 1.2 This led them to postulate contributions by processes second order in $[C(IV)]$. The pH dependence of exchange rate is shown in Fig. 1-3. For pH >10 the slope is approximately 1. The overall rate law $R \propto [H^+]^{\sim 1}[C(IV)]^{\sim 1}$ observed in this region is consistent with exchange taking place predominantly by way of the equilibria:

$$H^+ + CO_3^= \rightleftharpoons HCO_3^- \quad \text{fast}$$

FIG. 1-3

pH dependence of the rate of oxygen exchange between carbonate and bicarbonate ions and water at 25°C:

○ ionic strength = 0.5, [C(IV)] = 0.1

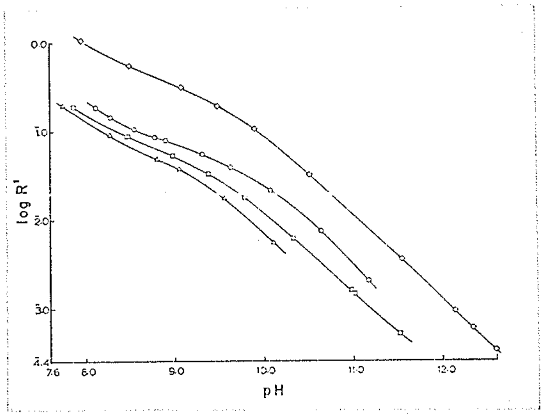
□ ionic strength = 1.5, [C(IV)] = 0.1

◇ ionic strength = 1.5, [C(IV)] = 0.5

△ ionic strength = 2.5, [C(IV)] = 0.1

[Reproduced from Ref. (25)]

FIG. 1-3



$$HCO_3^- \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} OH^- + CO_2 \quad \text{slow}$$

For the region pH $<$10 the observed dependence of exchange on the H^+ ion concentration is to the power $\sim$ 0.5. This observed dependence, intermediate between zero order and first order, may be explained as follows:

If the process

$$HCO_3^- \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} OH^- + CO_2$$

were the main one responsible for exchange, then the rate law expected would be $R \propto [H^+]^0[C(IV)]^{\sim 1}$.

However, if the process

$$H_2CO_3 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} CO_2 + H_2O$$

becomes important (as it does) in this region, require protonation as a first step,

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3.$$

One would then expect $R \propto [H^+]^1[C(IV)]^{\sim 1}$.

Since in the pH region 8-10 both of these processes of hydration are known to be important, one would expect a dependence on $[H^+]$ intermediate between first and zero order, as was observed. At 25°C and ionic strength = 0.5, Poulton and Baldwin reported values of 3.64×10^{-2} sec.$^{-1}$ and 8.4×10^3 mole^{-1} l. sec.$^{-1}$ for k_1 and k_2 respectively.

1 - 6 QUALITATIVE RULES FOR EXCHANGE

It is appropriate at this point to present some general statements on the relative lability of the oxygen atoms in different species. From the extensive qualitative studies that he carried out, Brodskii(26,27) drew the following general conclusions:

1. The rate of exchange decreases rapidly in the order:

acid > acid salt > neutral salt

Examples:

$H_2CO_3 > HCO_3^- > CO_3^=$

$RCOOH > RCOO^-$

$HNO_3 > NO_3^-$

$HReO_4 > ReO_4^-$

$H_2SO_4 > HSO_4^- \gg SO_4^=$

$H_2SO_3 > HSO_3^- > SO_3^=$

$H_2SeO_4 > SeO_4^=$

$H_3PO_2 > H_2PO_2^-$

$H_3PO_3 > HPO_3^=$

$H_3PO_4 \gg H_2PO_4^-, HPO_4^=, PO_4^\equiv$

2. For the same central ion the rate of exchange decreases when the number of oxygen or sulfur atoms which are bonded to the central ion increases.

For example:

$SO_3^= > S_2O_3^= > SO_4^=$

$SeO_3^= > SeO_4^=$

$H_3PO_2 > H_3PO_3 \gg H_3PO_4$

$$H_2PO_2^- > HPO_3^= \gg H_2PO_4^-, HPO_4^=$$

3. For a given group of the periodic table the rate of exchange increases with the atomic number:

$$CO_3^= < SiO_3^=$$

$$SO_4^= \ll SeO_4^= < TeO_4^=$$

$$CrO_4^= < MoO_4^=, WO_4^=$$

$$MnO_4^- < ReO_4^-$$

$$ClO_4^- \ll IO_4^-$$

$$ClO_3^- \ll BrO_3^- < IO_3^-$$

1 - 7 THE SO_2-H_2O SYSTEM

(i) Nature of the Species Present

In spite of the major importance of aqueous solutions of sulfur dioxide in a multitude of industrial processes, there remains a surprising uncertainty as to the nature of the equilibria between the molecular and ionic species in these solutions. Sulfur dioxide dissolves in water to the extent of about nine weight per cent at 25°C and atmospheric pressure(28). The resulting solution possesses well-known acidic properties and behaves as if it contained an acid, presumably H_2SO_3. However, although the ions, H_3O^+, HSO_3^-, and $SO_3^=$ are indeed present in the solution, the free acid itself has never been isolated or shown to exist. Nevertheless, its existence has been taken for granted by most chemists, the equilibria in the aqueous solutions being usually expressed as follows:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + H_2O \overset{K_1}{\rightleftharpoons} H_3O^+ + HSO_3^-$$

$$HSO_3^- + H_2O \overset{K_2}{\rightleftharpoons} H_3O^+ + SO_3^=$$

Assuming that these were the only equilibria involved, and that the first step is complete, that is, that all the un-ionized sulfur dioxide in solution is combined to form H_2SO_3, the two ionization constants from the above equations were calculated from electrical conductivity data to be K_1(29)= 1.72 x 10^{-2} and K_2(29)= 6.24 x 10^{-8} at 25°C. Many earlier workers(28,30,21)attempted to calculate the ratio of H_2SO_3 to "free" or uncombined SO_2 molecules in solution from the measurements of vapor pressures and electrical conductivities of the solution as a function of temperature and concentration. Campbell and Maass(30), for example, calculated that at 10°C the amount of "free" SO_2 amounted to about 20% of the total dissolved, whereas, at 25°C the amount of "free" SO_2 was about 50% of the total. These calculations appear to have relatively little merit, being based on such drastic assumptions as the use of Kohlrausch's law at fairly high concentrations, or the substitution of concentrations for activities. The above assumptions, however, were soon proved incorrect, as evidence from spectral studies, including Raman(32,33), infrared(34,35), and ultraviolet absorption(36) techniques showed that in aqueous solutions of SO_2 the unionized disulfur species consists mainly of uncombined sulfur dioxide molecules, with sulfurous acid (H_2SO_3) molecules, if present, in very minor amounts. The results from infrared spectra are the most convincing. Sulfur dioxide solutions in water show only the infrared bands typical of SO_2 molecules in the liquid and gaseous state. Falk and Giguère(34) set an upper limit for H_2SO_3 which could have escaped detection at approximately 3% of the sulfur dioxide concentrations. However, the actual concentration of H_2SO_3 may be expected to be very much smaller than that. Even at -190°C, where the formation of the compound H_2SO_3 would be much more likely to occur, there is no evidence from infrared measurements for a SO_2-H_2O combination(34). The term "sulfurous acid", established by long tradition, will continue to be used. It should be understood, however, that this hypothetical compound does not exist in detectable concentration even in solutions. In remarkable contrast to sulfur dioxide, selenium dioxide appears to react completely with water, forming the stable selenious acid, H_2SeO_3, both in solution and in the crystalline phase. Falk and Giguère(37) in an infrared investigation of SeO_2 (similar to the one they earlier made on SO_2) found evidence for the existence of selenious acid with the structure $(HO)_2SeO$. No evidence for free SeO_2 was found in solution.

Cotton(38) has discussed a useful generalization concerning the magnitude of the first dissociation constant, K_1, for oxyacids. Arguing that the value of K_1 seems to depend upon the charge of the central atom (since the greater the positive charge the more readily will the process of proton loss be favored), semi-quantitative correlations are possible if this positive charge is taken to be the so-called formal charge. Assuming that the structure of the oxyacid, H_nXO_m, is to be $O_{m-n}X(OH)_n$, the formal charge is given by the difference (m-n). For the case where (m-n) = 1, the pK_1 value is 2.8 ± 0.9. This relation holds for the following acids: H_3PO_4, H_3AsO_4, H_5IO_6, "H_2SO_3", $HClO_2$, and HNO_2 which have pK_1 values of 2.12, 3.5, 3.29, 1.90, 1.94, and 3.3 respectively.[a] Carbonic acid is exceptional in that the directly measured pK_1 = 6.38, does not refer to the process $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ since carbon dioxide in solution is only partly in the form H_2CO_3, and mainly as the loosely hydrated species, $CO_2(aq)$. When a correction is made for the equilibrium $CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq)$, the pK_1 value of 3.58 is

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(a) also H_2SeO_3 which has a value of 2.57 for pK_1

obtained which falls in the range for other (m-n) = 1 acids. It is particularly worth noting that "H_2SO_3" agrees well with the correlation. If sulfurous acid were formed in an amount determined by the limit for detection from I.R. studies (~3%), then the "real" K_1 could be calculated as follows:

$$\frac{[H_2SO_3]}{[SO_2]} \simeq 3 \times 10^{-2},$$

$$\frac{[H^+][HSO_3^-]}{[SO_2]} = 1.7 \times 10^{-2},$$

$$K_1 = \frac{[H^+][HSO_3^-]}{[SO_2]} \cdot \frac{[SO_2]}{[H_2SO_3]} = \frac{1.7 \times 10^{-2}}{3 \times 10^{-2}} \simeq 0.6.$$

It is interesting that the pK value ~ 0.2 does not fit the correlation for (m-n) = 1 oxyacids, and this is a further argument, admittedly inconclusive, suggesting the absence of sulfurous acid in aqueous solutions.

Recently an extensive Raman study by Simon and Waldmann(39,40,41) revealed for the first time in these solutions some lines due to the bisulfite ions, HSO_3^-, in very low concentrations, as well as pyrosulfite ions, $S_2O_5^=$, pointing to the hitherto unsuspected equilibrium $2\ HSO_3^- \rightleftharpoons S_2O_5^= + H_2O$. Golding(42) in his ultraviolet absorption studies of bisulfite solutions confirmed the preceding equilibrium and determined an approximate value of 7 x 10^{-2} for the equilibrium constant, $K = \frac{[S_2O_5^{=}]}{[HSO_3^{-}]^2}$. To explain the ultraviolet spectrum of the bisulfite solutions he postulated two kinds of H-attachment for the bisulfite ion; the $HO \cdot SO_2^-$ isomer of bisulfite at low total sulfur concentration, and the HSO_3^- isomer at high total sulfur concentration.

According to Cotton(43), the so-called hydrate of sulfur dioxide contains no H_2SO_3 but may be likened to a "clathrate" of the same type as other gas hydrates. According to this clathrate structure, the SO_2 molecules are retained or "clathrated" within cages or cavities provided by the water molecules. On this basis, the equilibria in aqueous solutions of SO_2 are best represented as:

$$SO_2 + xH_2O \rightarrow SO_2 \cdot xH_2O \text{ (hydrated } SO_2\text{, } x \sim 7)$$

$$[SO_2 \cdot xH_2O \rightleftharpoons H_2SO_3 \quad K \lll 1]$$

$$SO_2 \cdot xH_2O \rightleftharpoons HSO_3^-(aq) + H_3O^+ + (x-2)H_2O.$$

In any event from a macroscopic viewpoint, the overall equilibrium may be represented as:

$$SO_2 + H_2O \overset{K_1}{\rightleftharpoons} H^+ + HSO_3^-$$

and the first dissociation constant for "sulfurous acid" is properly defined as follows:

$$K_1 = \frac{[HSO_3^-][H^+]}{[\text{Total dissolved } SO_2] - [HSO_3^-] - [SO_3^=]} .$$

(ii) Review of O^{18}- Exchange Studies

Investigations of the exchange of oxygen between "sulfite"[a] and water are summarized in Table I. It is evident from the table that the story of sulfite-water exchange is a rather confusing one. Further discussion of this table will be taken up in section 5 - 3.

(iii) Kinetic Studies

It was pointed out earlier in section 1 - 5 that in the studies on the exchange of oxygen isotopes of oxyanions with the solvent water, few quantitative data on rate equations are found in the literature. This observation is once again apparent from the qualitative information tabulated in Table I. Two other independent studies, however, have been carried out to obtain rate data for the overall reaction $SO_2 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+ + HSO_3^-$.

In 1964, Wang and Himmelblau(49) reported that they had obtained "for the first time" forward, k_f, and reverse, k_r, rate constants for this system. The essence

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[a] The term "sulfite" will be used here to represent the total sulfite (SO_2, HSO_3^-, $S_2O_5^=$, $SO_3^=$) in solution.

Solute plus additives	Concentration of solute	pH	temp. °C	time	exchange	isotopic analysis	remarks	ref.
K_2SO_3			95	8 hrs.	complete	water density measurements	These early workers used very low O^{18} enrichments in their water.	44
K_2SO_3, NaOH			95	5 hrs.	none	water density measurements		44
K_2SO_3	4.3 M		19.3	(0.5 hr.) (24 hrs.)	none	water density measurements		45
K_2SO_3	4.1 M		100	24 hrs.	none	water density measurements		45
Na_2SO_3			room	72 hrs.	negligible	water density measurements		46
Na_2SO_3		6	80		$t_{\frac{1}{2}}$ 780hrs.	isotopic ratio from mass spectrometer analysis of SO_2		47
SO_2, 0.1M HCl	0.1 M		25	5 min.	complete	Barium sulfate heated with graphite at 1000°C to convert the oxygen to CO_2 which was mass analyzed.	Experiment was performed by passing SO_2 gas into enriched water adjusted to the desired acidity, then quenching the exchange by oxidizing with iodine.	48
SO_2, 0.4M NaOH	0.1 M		25	5 min.	complete			
K_2SO_3, 0.2N KOH	0.6g. per g. H_2O		20		$t_{\frac{1}{2}}$=210hrs.	Either by densiometric method or by quilibrating the water with CO_2.		26
K_2SO_3, 0.2N KOH	0.6g. per g. H_2O		100		$t_{\frac{1}{2}}$=2.5hrs.			26

of their procedure was to operate with the system at chemical equilibrium but isotopic disequilibrium with a radioactive tracer technique developed by Himmelblau and Babb(50). Tracer in the form of $NaHS^{35}O_3$ was injected into a solution containing $S^{32}O_2$, water, and $NaHS^{32}O_3$ which had been allowed to reach equilibrium under controlled conditions of temperature, pH, and pressure. Samples of solution were taken at periodical intervals after injection of the tracer. A portion of the sulfur dioxide in each sample was flashed out of solution and analyzed to determine the ratio of $S^{35}O_2$ at time t to that of a similar sample at isotopic quilibrium. Designating this ratio as R, they set up a linear relationship between the quantity ln(1-R) and the time of reaction from which the reaction rate constants were determined. From their data collected at temperatures 0 to 20°C, concentrations of $NaHSO_3$ from 0.02 to 0.8 mole $l.^{-1}$, and at pH ranges of 1.25 to 4.3, they obtained values of 2.2×10^{-2} $sec.^{-1}$ and 1.6 l. $mole^{-1}$ $sec.^{-1}$ for k_f and k_r respectively at 20°C. By analogy of SO_2 to CO_2, they presumed that a reaction with OH^- existed, but they were unable to detect such a reaction.

However, three years earlier, Eigen, Kustin, and Maass(51) had determined these rate constants from relaxation measurements. Their method was based on a periodic variation of temperature by means of ultrasonic waves propagated through the reaction vessel. They found that total equilibrium adjustment was reached in periods $<10^{-6}$ sec. depending on H^+ and HSO_3^- concentrations. The following reaction scheme was proposed by them:

$$\begin{tikzcd}
\text{(1)} & H^+ + HSO_3^- \arrow[rr, shift left] \arrow[dr, shift left] & & H_2SO_3 \arrow[ll, shift left] \arrow[dl, shift left] & \text{(2)} \\
& & SO_2 + H_2O \arrow[ul, shift left] \arrow[ur, shift left] & & \\
& & \text{(3)} & &
\end{tikzcd}$$

Whether the reaction goes on directly by way of (1) → (3) or indirectly by way of (1) → (2) → (3) they were not able to distinguish from their experiments. They preferred then to call the values that they determined, "gross" rate constants. At 20°C and ionic strength = 0.1, they reported values of 3.4×10^6 sec.$^{-1}$ and 2×10^8 sec.$^{-1}$ l. mole^{-1} for the rate constants for k_f and k_r respectively. The difference in values for k_f and k_r reported by the two independent groups of workers is remarkable! A summary of the results is given in Table II. Included in the table for comparison are corresponding values of k_f and k_r reported by Poulton and Baldwin$^{(25)}$ for the analogous CO_2-H_2O system at 25°C and ionic strength = 0.5.

TABLE II

VALUES REPORTED FOR RATE CONSTANTS OF THE REACTION $SO_2 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+ + HSO_3^-$ AND OF THE ANALOGOUS REACTION $CO_2 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2CO_3$ FOR THE CO_2-H_2O SYSTEM

System	Temp. (^oC)	k_f (sec.$^{-1}$)	k_r	Type of Study	Ref.
SO_2-H_2O	20	$2.2 x 10^{-2}$	1.6 l.mole^{-1}sec.$^{-1}$	S^{35} exchange	49
SO_2-H_2O	20	$3.4 x 10^{6}$	$2.8 x 10^{8}$ l.mole^{-1}sec.$^{-1}$	Relaxation	51
CO_2-H_2O	25	$3.6 x 10^{-2}$	14 sec.$^{-1}$(a)	O^{18} exchange	25

(a) Rate constant not reported, but calculated from forward rate constant and using a value of 2.6×10^{-3} for the hydration equilibrium constant $K_h = \frac{[H_2CO_3]}{[CO_2]}$.

PURPOSE OF THE INVESTIGATION

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In the light of the discrepancies reported in the literature in regards to both qualitative (O^{18}- exchange studies) and quantitative (determination of the rate constants for the overall equilibrium $SO_2 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+ + HSO_3^-$) studies of the SO_2- H_2O system, the present investigation on the rate of oxygen exchange between the sulfite ion(a) and water was carried out in the hope of removing some of the inconsistencies referred to above and also to obtain additional independent values for the rate constants k_f and k_r.

(a) To avoid any confusion that may arise on the part of the reader, it should be understood (1) that oxygen exchange is referred to the sulfite ion and water, only because the sulfite ion is the predominant species present under the alkaline conditions (pH 9- 10.5) of this study, and (2) that the actual exchange mechanism may involve derived species such as HSO_3^-, SO_2, or $S_2O_5^=$.

EXPERIMENTAL | 3

3 - 1 MATERIALS

Water enriched to approximately 1.6 atom °/o oxygen-18 (obtained from YEDA Research and Development Co. Ltd.) was distilled once from alkaline $KMnO_4$. Water of normal isotopic composition (containing approximately 0.2 atom °/o oxygen-18) was doubly distilled.

Acetone (obtained in bulk) was distilled once through a glass packed fractionation column.

Silver cyanide (AgCN, Baker, purified powder) was screened to remove larger granules; then stored under vacuum over phosphorous pentoxide.

The following reagents were used without further treatment:

NaOH pellets (reagent grade, Shawinigan), $Na_2B_4O_7\cdot 10H_2O$ ("borax", reagent, A.C.S., Anachemia Chemicals Ltd.), hydrochloric acid (~12 M, C.P. reagent, C.I.L.), $SrCl_2$ (certified, Fisher), NaCl (certified, A.C.S., Fisher), KNO_3 (N.F., Fisher), NH_4OH (~18 M, C.P. reagent, C.I.L.), argon (Matheson, H.P.), standard buffer solutions (pH 7.00 ± 0.02, Fisher, and pH 4.01 ± 0.01, Harleco), and Na_2SO_3 (certified A.C.S., Fisher).

A carbonate-free sodium hydroxide solution was prepared by taking advantage of the low solubility of sodium carbonate in concentrated solutions of alkali. NaOH pellets were dissolved in doubly distilled water to make an ~19 N solution. After the sodium carbonate settled out, the supernatant liquid was decanted and transferred, through Pyrex glass wool, into a plastic bottle equipped with a syphon and Ascarite (solid absorbent for CO_2, consisting of NaOH deposited on asbestos) guard tube. This solution was standardized by titrating against potassium acid phthalate ($KHC_8H_4O_4$) using phenolphthalein as an indicator. One liter of 0.100 N NaOH stock solution was prepared by dilution from this concentrated stock and stored in a plastic bottle.

Na_2SO_3 enriched in oxygen-18 was prepared as follows:

~3 g. of Na_2SO_3 was dissolved in ~15 ml. of O^{18}-enriched water. After degassing the solution three times by freeze-pump-thaw cycles under high vacuum at liquid nitrogen temperature (-196°C), the mixture was allowed to equilibrate overnight (which was known from previous work to be sufficiently long to allow complete exchange to occur). After equilibration, the solvent water was removed by distillation under vacuum to a side arm (maintained at -196°C in a liquid nitrogen bath) connected to the equilibration flask (Fig. 3-1b). After a large part of the water had been transferred to the side arm (~2 hr.), the equilibration flask was removed and attached to the high vacuum system where the final traces of water in the sodium sulfite was removed by occasional heating with a heat gun. A check on the purity and dryness of the enriched salt prepared in this way was made by comparing the infrared spectra of the original salt of normal isotopic composition with the infrared spectra of the final enriched salt. The salts were examined as Nujol mulls on a Perkin Elmer Model 337 grating infrared spectrophotometer in the region 400-4000 cm.$^{-1}$ (25 - 2.5 microns). The spectra appeared to be identical for the normal and labelled sodium sulfite, and the frequencies of the bands observed in both spectra agreed well with those reported(52,53,54) for the normal salt. Their infrared spectra did not noticeably contain the characteristic bands (450, 610, 981, 1100 cm.$^{-1}$) of sulfates, and, most important, bands near 3 and 6 microns, characteristic of hydration,(54) were absent in the labelled sulfite indicating that the salt was anhydrous sodium sulfite and not the hydrated form ($Na_2SO_3 \cdot 7H_2O$).

FIG. 3-1

3-1a reaction vessel

(stop watch included for scale)

3-1b apparatus for the preparation of oxygen-18 enriched Na_2SO_3

(pencil included for scale)

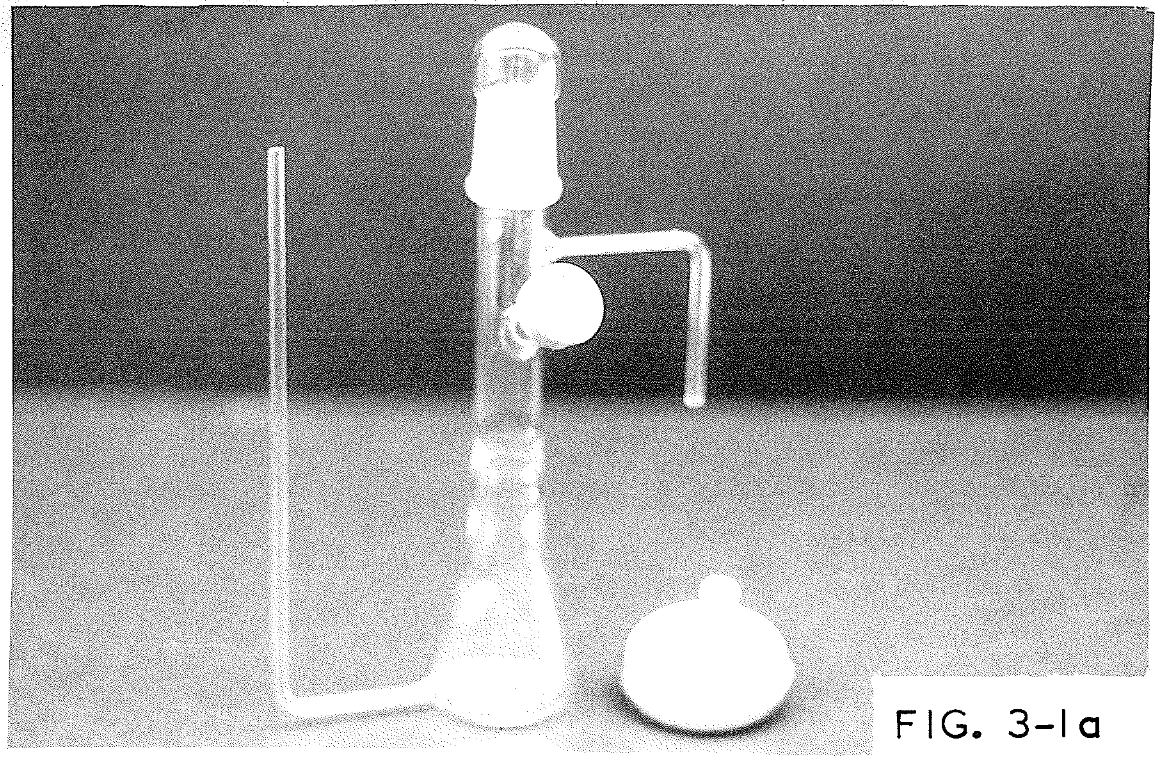


FIG. 3-1a

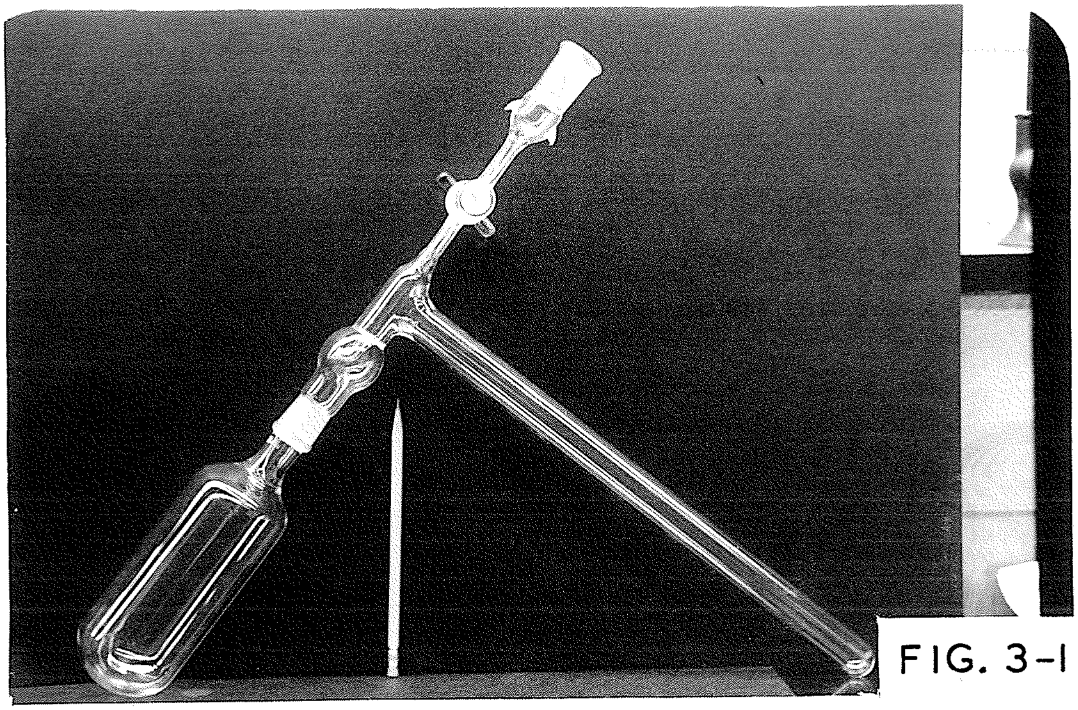


FIG. 3-1b

3 - 2 SAMPLE PREPARATION

Preliminary studies of the oxygen exchange between the sulfite ion and water were carried out using a "freeze dry" technique. The kinetic runs were followed by measuring either the increase or decrease of O^{18}-enrichment of Na_2SO_3. To start the exchange reaction a weighed amount of either normal or O^{18}-enriched Na_2SO_3 was added to 10 ml. of either O^{18}-enriched or normal water respectively. These solutions had been purged of oxygen by bubbling argon through them for ~5 min. in the apparatus shown in Fig. 3-1a. Argon was bubbled slowly through the solution while the reaction was in progress to preclude air oxidation of the sulfite. The pH of the solution was adjusted by adding minute quantities (1-125 micro liters) of conc. NH_4OH or con. HCl with a micro pipet. After starting the exchange reaction, approximately 4 ml. of the exchanging mixture was withdrawn, and its pH was measured using an Orion Model 801 digital pH meter (equipped with a Corning glass pH-electrode (No. 476022) and a Fisher calomel reference electrode (No. 13-639-62)) which was previously calibrated with the pH 7.0 and pH 4.01 buffers. At timed intervals aliquots of the mixture were withdrawn and transferred to pyrex tubes (~10 inches long, 12 mm. outer diameter) equipped with a glass joint for attachment to the vacuum line. The volume of the aliquots withdrawn was determined by the amount of oxygen (~0.05 x 10^{-3} moles CO_2) required for mass analysis. (The technique used to convert the oxygen in the sulfite to CO_2 will be discussed in the next section.) Most of the solutions were 0.3 M in sulfite and ~1 ml. aliquots were found to yield an adequate amount of carbon dioxide for isotopic analysis. The tubes were stoppered, placed in a liquid nitrogen bath (-196°C) to "stop" the exchange reaction, and then quickly attached to the vacuum line. The liquid N_2 bath was removed, and the frozen mixture was pumped on for ~4 hr. to remove the water (the heat expended in evaporation kept the mixture frozen).

Studies on the unbuffered solutions showed that the pH drifted as much as 0.2 pH units over the region pH 9 - pH 10.5. Since the drift was towards lower pH, it was suggested that air oxidation of sulfite occurred; consequently, a pH measuring cell, adapted to provide a "blanket" of argon during the pH measurement, was constructed. (Fig. 3-2b).

The "freeze dry" technique was not a very satisfactory one. The drying of the salt required a long time and the experimental reproducibility was not better than 4-5%. Furthermore, as it became desirable to control the

FIG. 3-2

3-2a breaker assembly for CO_2 collection (pencil included for scale).

3-2b pH measuring cell

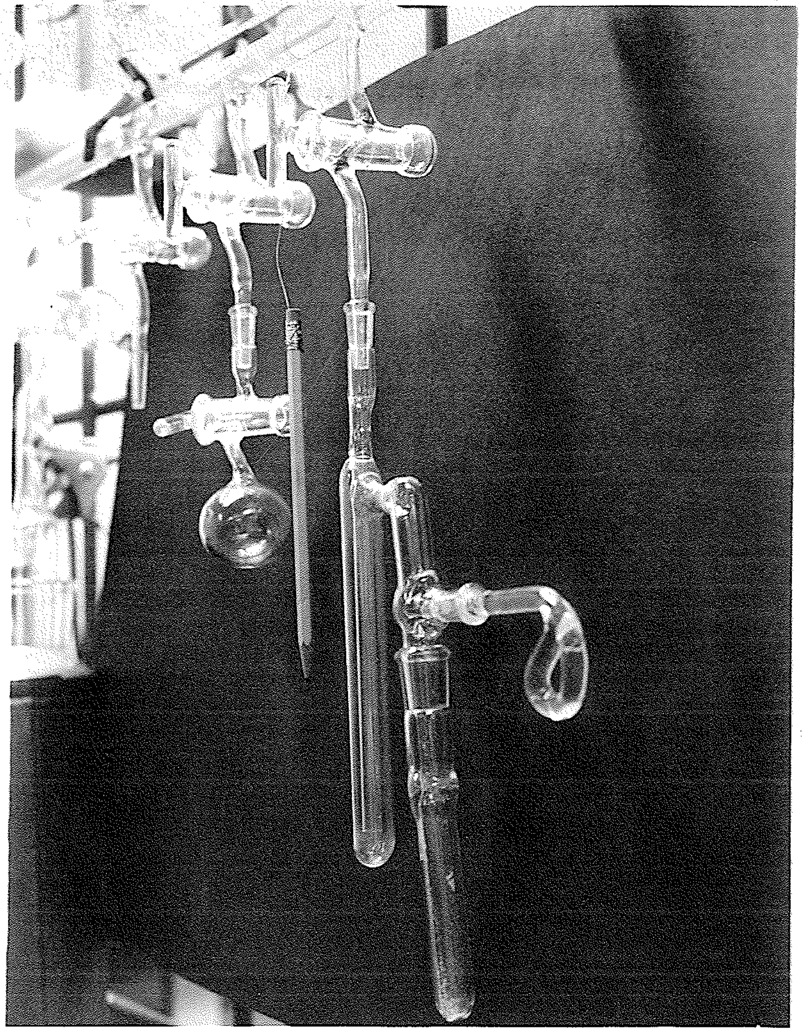


FIG. 3-2 a

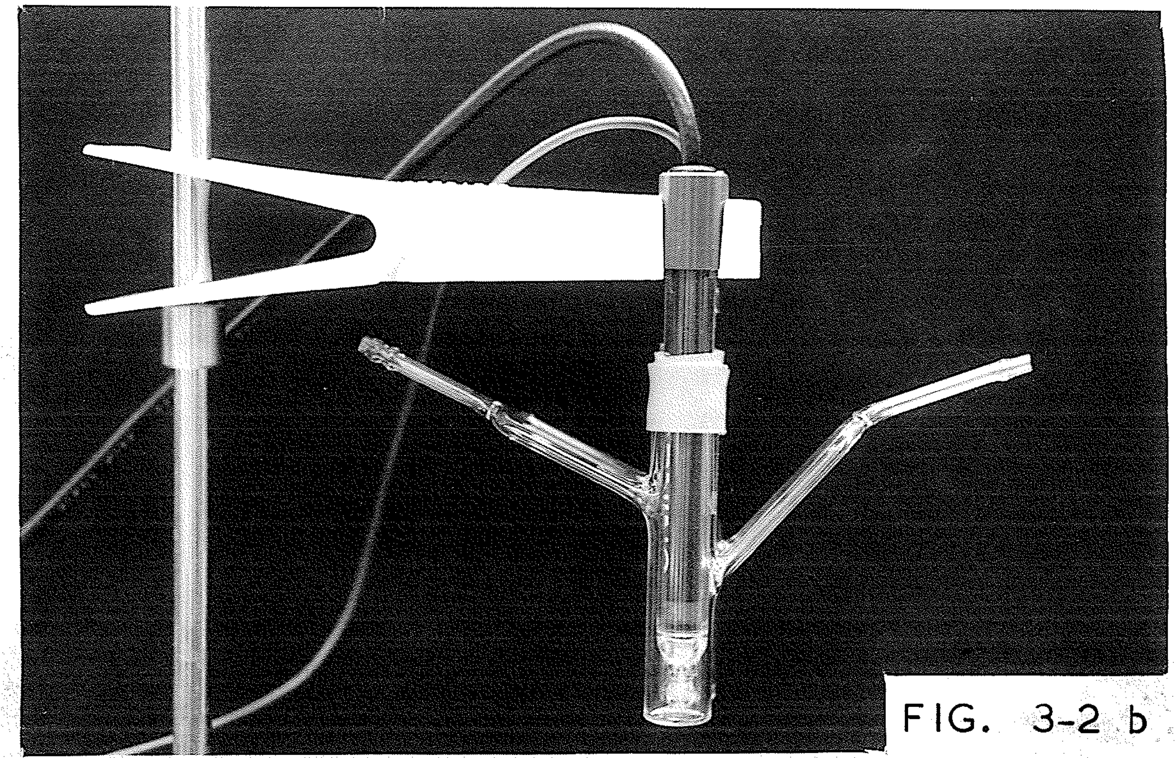


FIG. 3-2 b

pH with buffered solutions, the "freeze dry" technique was abandoned. It was decided upon, instead, to follow the progress of the exchange reaction by precipitating the sulfite present. Strontium sulfite was chosen as a precipitate since the solubility of strontium tetraborate allowed the solutions to be buffered with borax buffers in the pH region 8-10.8. The procedure used was as follows:

Borax buffer solutions were prepared by mixing different volumes of 0.100 N stock NaOH solution and 0.025 M borax solution as prescribed in the Handbook of Chemistry and Physics.(55) For most runs 10 ml. of the desired buffer solution was transferred to the reaction vessel (Fig. 3-1a) and placed in a constant temperature bath controlled at the desired temperature (usually 24.7 ± 0.05°C). Argon was bubbled through the solution for approximately 5 min. to remove any dissolved oxygen, and then was slowly bubbled through the solution to maintain an air-free atmosphere. A weighed quantity of O^{18}-enriched sodium sulfite (for most runs $[Na_2SO_3] = 0.3$ M) was quickly added by funnel through the top of the reaction vessel to initiate the exchange reaction. Once the salt was completely dissolved (~20 sec.), the stop watch was started. Approximately 4 ml. of the exchanging mixture was withdrawn and transferred to the pH measuring cell (Fig. 3-2b). The final adjusted pH of the solution was measured with the Orion digital pH meter. At timed intervals aliquots of the exchanging mixture (~1 ml. for 0.3 M Na_2SO_3) were removed from the reaction vessel by means of a Plastipak (trade name for plastic syringe manufactured by Becton, Dickinson and Co.) disposable syringe (2.5 ml. capacity) through the rubber serum cap covering the short side arm (see Fig. 3-1a) and released to a 15 ml. centrifuge tube containing ~5 ml. of 0.1 M strontium chloride solution. The $SrSO_3$ precipitated was centrifuged, decanted, washed with doubly distilled water, centrifuged, decanted, mixed with acetone, and filtered on a suction funnel with additional washing with acetone. The precipitates were finally dried for ~ 1 hr. under high vacuum. The technique that was used to convert the oxygen in the precipitate into a form suitable for isotopic analysis will be discussed in the next section.

3 - 3 ISOTOPIC ANALYSIS

The isotopic composition of the Na_2SO_3(obtained from the "freeze dry" technique or from equilibration with O^{18}-enriched water) and $SrSO_3$ salts was determined by a technique suggested by Shakhaskiri and Gordon(56). Their method consists of converting the oxygen in a compound to carbon dioxide by heating the sample with AgCN for ~ 2 hr. at 500°C. AgCN decomposes at 320°C to yield gaseous cyanogen and metallic silver. The cyanogen combines with the compound of unknown O^{18} content to form CO_2. Cyanogen, carbon monoxide, and nitrogen are among the other gaseous products. Most of the cyanogen is polymerized to solid paracyanogen by heating at 500°C. The procedure used in this work was to add the sample (containing approximately 0.45×10^{-3} moles of O_2) to approximately 3.6 times its weight of AgCN contained in a ten inch long pyrex tube (12 mm. outer diameter) adapted with a B 10/19 glass joint for attachment to the vacuum line. Before filling, the pyrolysis tubes were cleaned (by washing first with soap and water; then chromic acid), rinsed with doubly distilled water, and dried in the oven at ~140°C. After adding the sample and AgCN to the pyrolysis tube, it was constricted (approximately 3½ inch long narrow constriction) about half way up the tube with a torch and attached to the high vacuum line. After evacuation to approximately 10^{-4}-10^{-5} torr, the tube was sealed and heated for approximately 2 hr. at 500°C in a thermostated furnace. After cooling to room temperature, the tube was enclosed in the breaker assembly (Fig. 3-2a) which was evacuated under high vacuum. After approximately 5 min. the system was closed to the vacuum pump and the tube was opened by turning the handle of the breaker. Carbon dioxide was condensed with liquid nitrogen (-196°C) in the previously evacuated bulb, and traces of cyanogen gas were removed by the trap at -130°C (n-pentane slush) located between the "breaker" and the collection bulb. After the transfer of CO_2 was complete (approximately 2 min.) the non-condensible gases, carbon monoxide and nitrogen, were removed by opening the bulb to the vacuum pump. The isotopic ratio of the purified carbon dioxide was determined by measuring the ratio of 46 to the (mass 44 + mass 45) peaks [$C^{12}O^{16}O^{18}$ to $C^{12}O^{16}O^{16}$ + $C^{13}O^{16}O^{16}$ + $C^{12}O^{17}O^{16}$) ratio] by means of a Varian-Mat GD 150 isotope ratio mass spectrometer. This ratio was read directly by the double collector procedure and is referred to as the p-factor.

3 - 4 TREATMENT OF THE DATA

From equation (1) of section 1 - 3, the relationship between the measured p-factors and F, the fraction exchange, was given by

$$F = \frac{P_t - P_o}{P_\infty - P_o} ,$$

where P_t, P_o and P_∞ refer to the isotopic composition of the carbon dioxide samples taken at time t, zero, and infinity(a) respectively. For each run $-\log_{10}(1-F)$ was plotted versus time. The slope and intercept of the straight line plot were then determined by a least-squares

---

(a) that is, at isotopic equilibrium

treatment on an Olivetti Programma 101 desk computer. Ordinarily, one would obtain the half-life for the exchange ($t_{\frac{1}{2}}$) by reading off the graph the time (on the X-coordinate axis) corresponding to the point $\log_{10} 0.5$ (0.301 on the y-coordinate axis). However, the plots from this experimental work had a zero time intercept (~0.06-~0.09 for most runs). A brief discussion of this zero time exchange is given in the Appendix. To allow for this zero time exchange, the value 0.301 was added to the value of the intercept; then $t_{\frac{1}{2}}$ was obtained by feeding different values of X (time) back into the machine which calculated the corresponding y values $\left(-\log_{10}(1-F)\right)$. This process was repeated until the value of the sum (intercept plus 0.301) was generated; the corresponding X value (or time) then being $t_{\frac{1}{2}}$.

The rates of exchange were calculated by using equation (5) of section 1 - 2

$$R = \frac{[a][b] \quad 0.693}{([a] + [b]) \; t_{\frac{1}{2}}}$$

where [a] = number of g.-atom oxygen per l. in water = 55.55 g.-atom oxygen $l.^{-1}$, [b] is the number of g.-atom oxygen in the sulfite per l. = (3) x (concentration of Na_2SO_3 in moles $l.^{-1}$), and then R is in units of g.-atom oxygen $l.^{-1}$ $time^{-1}$. In most cases six samples, for each of which a P_t value was derived, were taken at intervals over two half-lives for each run.

Typical data treated in this way are given in the Appendix, pages 81-84.

RESULTS | 4

4 - 1 pH DEPENDENCE OF EXCHANGE RATE

From the preliminary studies carried out in the pH range 3-8 (3.0, 3.8, 5.9, 6.9, 8.2) using the "freeze-dry" technique, it was found to be impossible to "stop" the exchange reaction by freezing before isotopic equilibrium occurred. However, in the pH region 9-11 the exchange was found to be slow enough so that its kinetics could be followed. The few experiments carried out in this region suggested a pH dependence greater than first order.

For reasons discussed earlier, and since the rate of exchange appeared to be quite sensitive to changes in the H^+ ion concentration, the remainder of the work was carried out by using borax buffer solutions and precipitating the sulfite as strontium sulfite in order to follow the progress of the exchange reaction. The pH dependence of the exchange process was studied in a series of experiments in which the total concentration of "sulfite" ($[S_T] = [SO_3^{=}] + [HSO_3^{-}] + [SO_2] + 2\,[S_2O_5^{=}]$) was maintained constant ($[S_T]$ = 0.3 M, ionic strength = 0.90). Table III gives kinetic data for experiments carried out in borax buffers of differing pH at 25°C (runs 1 through 13). The rate of exchange, R, was obtained from

TABLE III

HYDROGEN ION DEPENDENCE OF THE RATE OF SULFITE-H_2O OXYGEN EXCHANGE ($t = 25^{\circ}C, [S_T] = 0.3$ M, $\mu = 0.9$)

Run	pH	$t_{\frac{1}{2}}$ (min.)	R (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)	$-\log_{10}$ R (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)
1	8.90	1.3	4.70×10^{-1}	0.328
2	8.97	1.7	3.60×10^{-1}	0.444
3	9.17	4.8	1.30×10^{-1}	0.886
4	9.30	7.8	7.90×10^{-2}	1.102
5	9.37	11.1	5.53×10^{-2}	1.247
6	9.45	14.2	4.32×10^{-2}	1.364
7	9.59	24.1	2.55×10^{-2}	1.594
8	9.73	43.7	1.40×10^{-2}	1.854
9	9.81	66.9	9.17×10^{-3}	2.038
10	9.98	143.5	4.28×10^{-3}	2.369
11	10.22	481.8	1.27×10^{-3}	2.896
12	10.34	868.8	7.06×10^{-4}	3.151
13	10.50	1518.0	4.04×10^{-4}	3.394
14*	9.00	4.5	1.36×10^{-1}	0.87
15*	9.60	83.6	7.34×10^{-3}	2.13
16*	10.44	1518.0	4.04×10^{-4}	3.39
17*	10.60	1510.0	4.04×10^{-4}	3.39
18*	10.75	3060.0	2.01×10^{-4}	3.70

*"Freeze-dry" technique used.

the half-life using equation (5) of section 1 - 2

$$R = \frac{[a][b]\ 0.693}{([a] + [b])\ t_{\frac{1}{2}}}$$

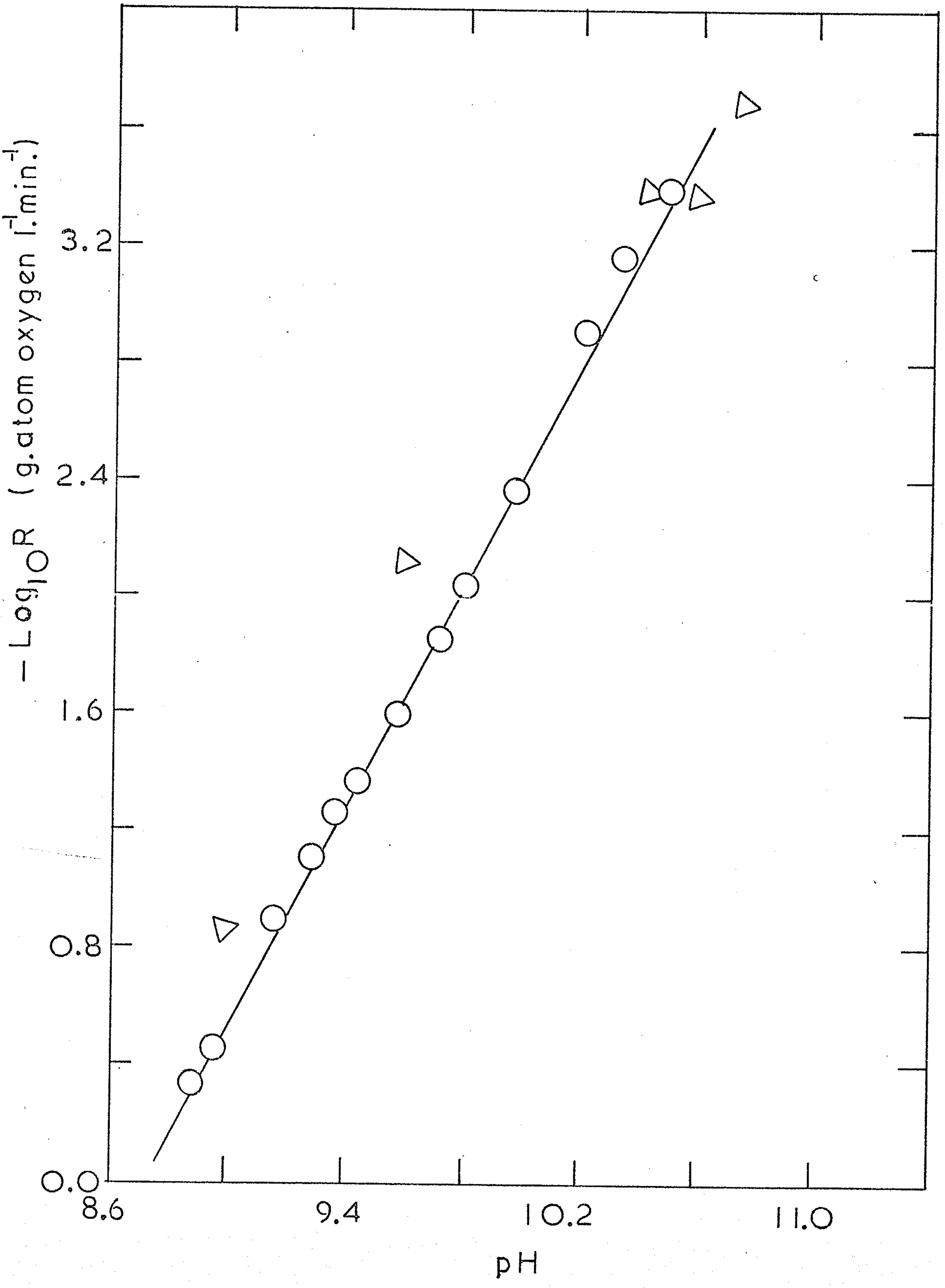
where [a] = number of g.-atom oxygen per l. in water = 55.55 g.-atom oxygen $l.^{-1}$, [b] is the number of g.-atom oxygen in the sulfite per l. = 0.90 g.-atom oxygen $l.^{-1}$, then

$$R = \frac{0.6138}{t_{\frac{1}{2}}} \qquad (1)$$

in units of g.-atom oxygen $l.^{-1}$ $min.^{-1}$ if $t_{\frac{1}{2}}$ is expressed in minutes.

Included in the table are kinetic data (runs 14-18) for experiments carried out in unbuffered solutions using the "freeze-dry" technique. A plot of $-\log_{10}$ R vs. pH ($-\log_{10}[H^+]$) for runs 1 through 13 was linear with an approximate slope of 2 (Fig.4-1). A linear least-squares treatment of all R values gave for the slope, which is the order with respect to H^+ ion concentration, a value of 1.93 ± 0.05. Values obtained from the "freeze-dry" experiments were also included on the graph. The treatment of the experimental results obtained from the experiment carried out at pH 9.98 is presented in the Appendix and is representative of the manner in which the other data were treated.

FIG. 4-1



3.2
2.4
1.6
0.8
0.0
8.6
9.4
10.2
11.0
pH
$-\mathrm{Log}_{10}R$ (g.atom oxygen l^{-1}.min.$^{-1}$)

4 - 2 SULFITE DEPENDENCE OF EXCHANGE RATE

The dependence on the total sulfite concentration, $[S_T]$, was determined by measuring the rate of exchange for different S_T concentrations maintaining the pH as close as possible to a value 9.52. The data obtained from five runs are given in Table IV. A plot of $-\log_{10} R^*$ versus $-\log_{10}[S_T]$ (Fig. 4-2) was linear with an approximate slope of 1.2. A least-square treatment of all R* values gave for the slope, which is the order with respect to $[S_T]$, a value of 1.15 ± 0.03.

4 - 3 TEMPERATURE DEPENDENCE OF EXCHANGE RATE

The rate of exchange at pH 9.62 and $[S_T] = 0.3$ M was studied at 10.0, 24.7, 35.9, and 50.3°C. The data obtained are given in Table V. A plot of $-\log_{10} R^*$ versus $\frac{1}{T}$ (Fig. 4-3) was linear with a slope (given by a least-squares treatment) of $1.94 \pm 0.17 \times 10^3$. According to the Arrhenius equation

$$\log_{10} R^* = \left(\frac{-Ea}{2.303Rg}\right) \frac{1}{T} + \log_{10} A$$

where Rg is the gas constant = 1.987 cal. $^{o}K^{-1}$ mole^{-1}, T = temperature in ^{o}K, and Ea and A are the Arrhenius parameters (activation energy and frequency factor respectively) to be determined. From the slope Ea was calculated to be 8.86 ± 0.80 k.cal. mole^{-1}, and from the intercept $\log_{10} A = 4.42$ (g.atom oxygen l.$^{-1}$ min.$^{-1}$).

TABLE IV

DEPENDENCE OF THE RATE OF SULFITE-H_2O OXYGEN EXCHANGE ON THE TOTAL SULFITE CONCENTRATION ($[S_T]$) AT 24.7°C.

Run	$[S_T]$(b)	R*(a) (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)	$-\log_{10}$ R* (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)	$-\log_{10}[S_T]$ (moles $l.^{-1}$)
1	0.600	6.63×10^{-2}	1.18	0.222
2	0.450	4.77×10^{-2}	1.32	0.347
3	0.300	3.09×10^{-2}	1.51	0.523
4	0.150	1.36×10^{-2}	1.87	0.824
5	0.075	6.00×10^{-3}	2.22	1.125

(a) R* represents the rate of exchange at pH 9.52 $[H^+] = 3.02 \times 10^{-10}$ mole $l.^{-1}$), which is the pH observed for the reaction carried out for $[S_T]$ = 0.60 M; the value of R* for $[S_T]$ = 0.3 M was obtained from the pH-dependence graph (Fig. 3-1), and all other values were normalized to pH 9.52 assuming that the rate of exchange is $\propto [H^+]^2$.

(b) The ionic strength for runs 3 through 5 was 0.90; that for runs 4 and 5 was adjusted by adding potassium nitrate. The ionic strength for runs 1 and 2 was 1.35 and 1.80 respectively. Since these points fitted so well on the sulfite dependence graph (Fig. 4-2), they were retained.

FIG. 4-2

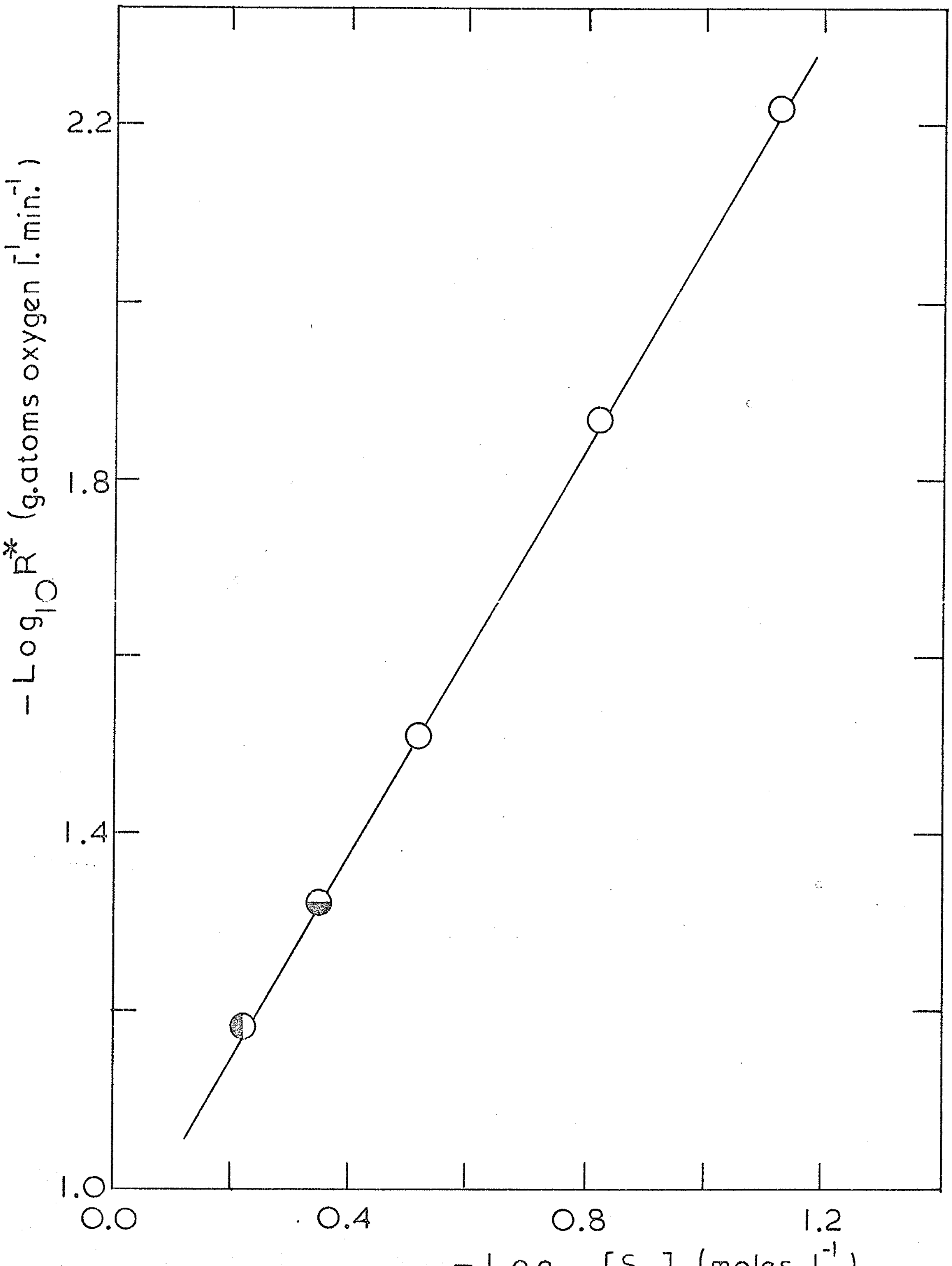
Total sulfite concentration ($[S_T]$) dependence of the rate of sulfite-H_2O oxygen exchange at $24.7^{\circ}C$:

○ $\mu = 0.9$

◒ $\mu = 1.35$

◐ $\mu = 1.80$

FIG.4-2



$-\mathrm{Log}_{10}R^*$ (g.atoms oxygen $l.^{-1}$ $min.^{-1}$)
2.2
1.8
1.4
1.0
0.0
0.4
0.8
1.2
$-\mathrm{Log}_{10}[S_T]$ (moles $l.^{-1}$)

TABLE V

TEMPERATURE DEPENDENCE OF THE RATE OF SULFITE-H_2O OXYGEN EXCHANGE ($[S_T]$ = 0.3 M, μ = 0.90)

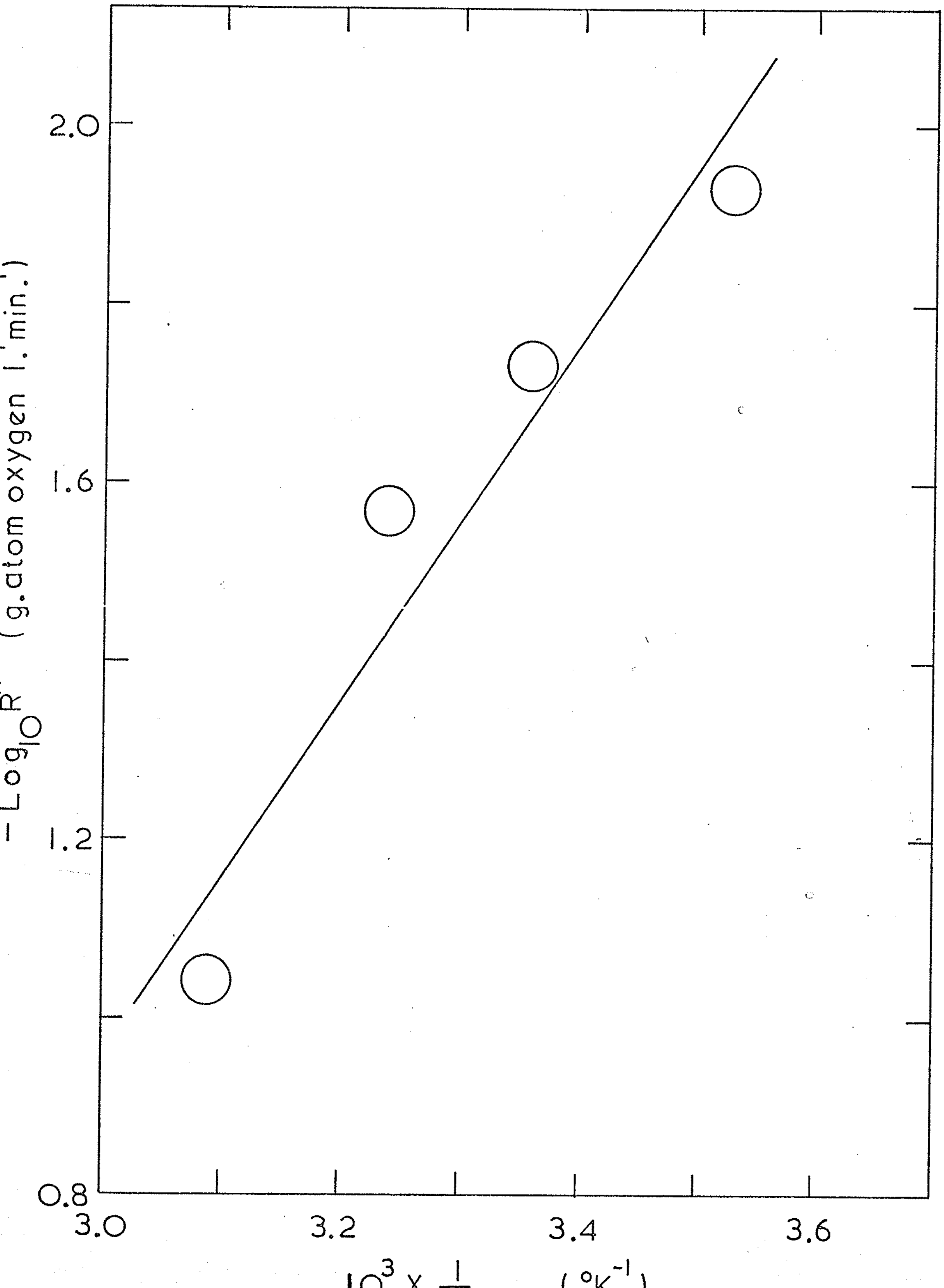
temp. (°C)	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	$pH_{expt'l}$	R*[(a)] (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)	$-\log_{10}$ R* (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)
10.0	3.53	9.62	1.18×10^{-2}	1.931
24.7	3.36	(9.62)	2.00×10^{-2}	1.703
35.9	3.24	9.74	2.70×10^{-2}	1.569
50.3	3.09	9.88	9.13×10^{-2}	1.040

(a) R* is the rate of exchange at pH 9.62. R* at 24.7°C was obtained graphically from Fig. 4-1, and R* at 35.9 and 50.3°C was obtained by normalizing the rate actually observed for the pH's given to pH 9.62 by assuming that the rate of exchange is proportional to the second power of the H^+ ion concentration.

FIG. 4-3

Arrhenius plot for sulfite-H_2O O^{18} exchange reaction.

FIG. 4-3


2.0
1.6
1.2
0.8
3.0
3.2
3.4
3.6
$-\mathrm{Log}_{10}R^*$ (g. atom oxygen l^{-1}. $\min.^{-1}$)
$10^3 \times \frac{1}{T}$ (°K^{-1})

DISCUSSION

5 - 1 RATE LAW AND MECHANISM FOR EXCHANGE

From the experimental work the rate law (at 24.7°C and ionic strength = 0.9) was found to be:

$$R = k[H^+]^{2.0}[S_T]^{1.15}$$

where $[S_T]$ represents the total sulfite ($[SO_2] + [HSO_3^-] + [SO_3^=] + 2\,[S_2O_5^=]$) in solution.

The rate of exchange reflects the rate of all processes resulting in exchange. It is desirable then to find the mechanisms consistent with the observed rate law.

One possible mechanism for the exchange of water and sulfite ions may involve the equilibrium

$$H^+ + SO_3^= \rightleftharpoons HSO_3^- \quad \text{fast}$$

followed by the hydration reaction

$$HSO_3^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_2 + H_2O \qquad (1)$$

Reaction (1) best represents the overall equilibrium present from a macroscopic viewpoint, although Cotton's explanation (in section 1 - 7) is believed to best represent the equilibria that are actually present, whereby the reaction (1) involves the breakdown of the "clathrate" structure of SO_2:

$$SO_2 \cdot xH_2O \rightleftharpoons HSO_3^-(aq) + H_3O^+ + (x-2)\,H_2O.$$

If the process (1) alone were responsible for isotopic exchange, the slope of the line through the experimental points plotted in Fig. 4-2 ($\log_{10}$ R vs. $\log_{10}$ $[S_T]$) would be unity. The observed slope of 1.15 suggests the contribution to isotopic exchange of a process or processes second order in $[S_T]$. The following process, second order in $[S_T]$ may be postulated:

$$2\ HSO_3^- \rightleftharpoons S_2O_5^= + H_2O. \qquad (2)$$

Golding(42) confirmed that this equilibrium was present and determined an approximate value of 7×10^{-2} for the equilibrium constant, $K' = \frac{[S_2O_5^=]}{[HSO_3^-]^2}$.

Equilibria (1) and (2) would yield terms in the exchange rate law of:

$R_1 = k_1\ [H^+][HSO_3^-]$ (first order in $[S_T]$)

$R_2 = k_2\ [HSO_3^-]^2$ (second order in $[S_T]$)

The total rate of oxygen exchange is given by the sum of these two terms

$$R = k_1\ [H^+][HSO_3^-] + k_2\ [HSO_3^-]^2. \qquad (3)$$

The rate of exchange expressed in this way is consistent with the observed experimental rate law, $R = k\ [H^+]^{2.0}$ $[S_T]^{1.15}$.

5 - 2 "EXTRACTION" OF THE RATE CONSTANTS

From a knowledge of the concentration of the species H^+ and HSO_3^- at a given pH, one should be able to determine values for the rate constants k_1 and k_2 for the two processes leading to oxygen exchange.

The concentration of H^+ ions was determined from the pH measurements, and the concentration of bisulfite ions was calculated simply as follows:

Fortunately a value for the equilibrium constant $K_{II} = \frac{[HSO_3^-]}{[H^+][SO_3^=]}$ was available in the literature for approximately the same ionic strength ($\mu = 1.0$) as in the present study ($\mu = 0.9$). This information eliminated the use of activity coefficients (which have not been very accurately determined) in the calculations. At 25°C and the ionic strength adjusted to 1 with $NaClO_4$, Sillén et al(57) obtained a value of 2.19×10^6 for K_{II}.

In the pH region (9-10.5) over which the oxygen exchange studies were carried out $[S_T] \simeq [HSO_3^-] + [SO_3^=]$[a] or in terms of $[HSO_3^-]$:

$$[S_T] = [HSO_3^-] + \frac{[HSO_3^-]}{[H^+]\,K_{II}}$$

$$= [HSO_3^-]\left(\frac{1 + [H^+]\,K_{II}}{[H^+]\,K_{II}}\right)$$

(a) the contribution of $[S_2O_5^=]$ to $[S_T]$ may safely be ignored in this pH region

$$\frac{[HSO_3^-]}{[S_T]} = \frac{[H^+]\ K_{II}}{1 + [H^+]\ K_{II}} \qquad (1)$$

Table VI gives the concentration of bisulfite ions at each pH for the runs 1 through 13 (from section 4 - 1) carried out at constant total sulfite concentration, $[S_T] = 0.3$ M.

If the pH is held constant as it was for the sulfite dependence studies at pH 9.52 (section 4 - 2), then the ratio $\frac{[HSO_3^-]}{[S_T]} = \frac{[H^+]\ K_{II}}{1 + [H^+]\ K_{II}}$ is a constant; call this constant r. Then the expression for the rate of exchange

$$R = k_1[H^+][HSO_3^-] + k_2[HSO_3^-]^2$$

becomes

$$R = k_1\ r'[S_T] + k_2\ r^2[S_T]^2$$

where $r' = r[H^+]$ = another constant. Dividing through the above expression by $[S_T]$,

$$\frac{R}{[S_T]} = k_1\ r' + (k_2\ r^2)[S_T]. \qquad (2)$$

From equation (2), a plot of $\frac{R}{[S_T]}$ vs. $[S_T]$ should give a straight line whose slope is <u>not</u> zero <u>if</u> there is a second order contribution to oxygen exchange. The pertinent data for runs 1 through 5 from section 4 - 2 given in Table VII. A plot of $\frac{R}{[S_T]}$ vs. $[S_T]$ (Fig.5-1) was linear with a slope and intercept, given by a least-squares treatment, having values of 0.0549 ± 0.0118 g.-atom oxygen

TABLE VI

HSO_3^- ION CONCENTRATION AND VALUES FOR THE PRODUCTS $[H^+][HSO_3^-]$ AND $[HSO_3^-]^2$ FOR A GIVEN pH AND TOTAL SULFITE CONCENTRATION ($[S_T]$) AT 24.7°C AND IONIC STRENGTH = 0.9

Run	pH	$[H^+]$ (mole l.$^{-1}$)	$\frac{[HSO_3^-]}{[S_T]} = \frac{[H^+]\,K_{II}}{1 + [H^+]\,K_{II}}$	$[HSO_3^-]$ for $[S_T]$=0.3M (mole l.$^{-1}$)	$[H^+][HSO_3^-]$ (mole^2 l.$^{-2}$)	$[HSO_3^-]^2$ (mole^2 l.$^{-2}$)
1	8.90	$1.26\text{x}10^{-9}$	$2.75\text{x}10^{-3}$	$8.25\text{x}10^{-4}$	$1.04\text{x}10^{-12}$	$6.81\text{x}10^{-7}$
2	8.97	$1.07\text{x}10^{-9}$	$2.33\text{x}10^{-3}$	$6.99\text{x}10^{-4}$	$7.48\text{x}10^{-13}$	$4.89\text{x}10^{-7}$
3	9.17	$6.76\text{x}10^{-10}$	$1.48\text{x}10^{-3}$	$4.44\text{x}10^{-4}$	$3.00\text{x}10^{-13}$	$1.97\text{x}10^{-7}$
4	9.30	$5.01\text{x}10^{-10}$	$1.10\text{x}10^{-3}$	$3.30\text{x}10^{-4}$	$1.65\text{x}10^{-13}$	$1.09\text{x}10^{-7}$
5	9.37	$4.27\text{x}10^{-10}$	$9.35\text{x}10^{-4}$	$2.81\text{x}10^{-4}$	$1.20\text{x}10^{-13}$	$7.90\text{x}10^{-8}$
6	9.45	$3.55\text{x}10^{-10}$	$7.77\text{x}10^{-4}$	$2.33\text{x}10^{-4}$	$8.27\text{x}10^{-14}$	$5.43\text{x}10^{-8}$
7	9.59	$2.57\text{x}10^{-10}$	$5.63\text{x}10^{-4}$	$1.69\text{x}10^{-4}$	$4.34\text{x}10^{-14}$	$2.86\text{x}10^{-8}$
8	9.73	$1.86\text{x}10^{-10}$	$4.07\text{x}10^{-4}$	$1.22\text{x}10^{-4}$	$2.27\text{x}10^{-14}$	$1.49\text{x}10^{-8}$
9	9.81	$1.55\text{x}10^{-10}$	$3.39\text{x}10^{-4}$	$1.02\text{x}10^{-4}$	$1.58\text{x}10^{-14}$	$1.04\text{x}10^{-8}$
10	9.98	$1.05\text{x}10^{-10}$	$2.30\text{x}10^{-4}$	$6.90\text{x}10^{-5}$	$7.25\text{x}10^{-15}$	$4.76\text{x}10^{-9}$
11	10.22	$6.03\text{x}10^{-11}$	$1.32\text{x}10^{-4}$	$3.96\text{x}10^{-5}$	$2.39\text{x}10^{-15}$	$1.57\text{x}10^{-9}$
12	10.34	$4.57\text{x}10^{-11}$	$1.00\text{x}10^{-4}$	$3.00\text{x}10^{-5}$	$1.37\text{x}10^{-15}$	$9.00\text{x}10^{-10}$
13	10.50	$3.16\text{x}10^{-11}$	$6.92\text{x}10^{-5}$	$2.08\text{x}10^{-5}$	$6.57\text{x}10^{-16}$	$4.33\text{x}10^{-10}$

TABLE VII

DATA FOR THE DETERMINATION OF THE SECOND ORDER CONTRIBUTION TO THE RATE OF EXCHANGE.

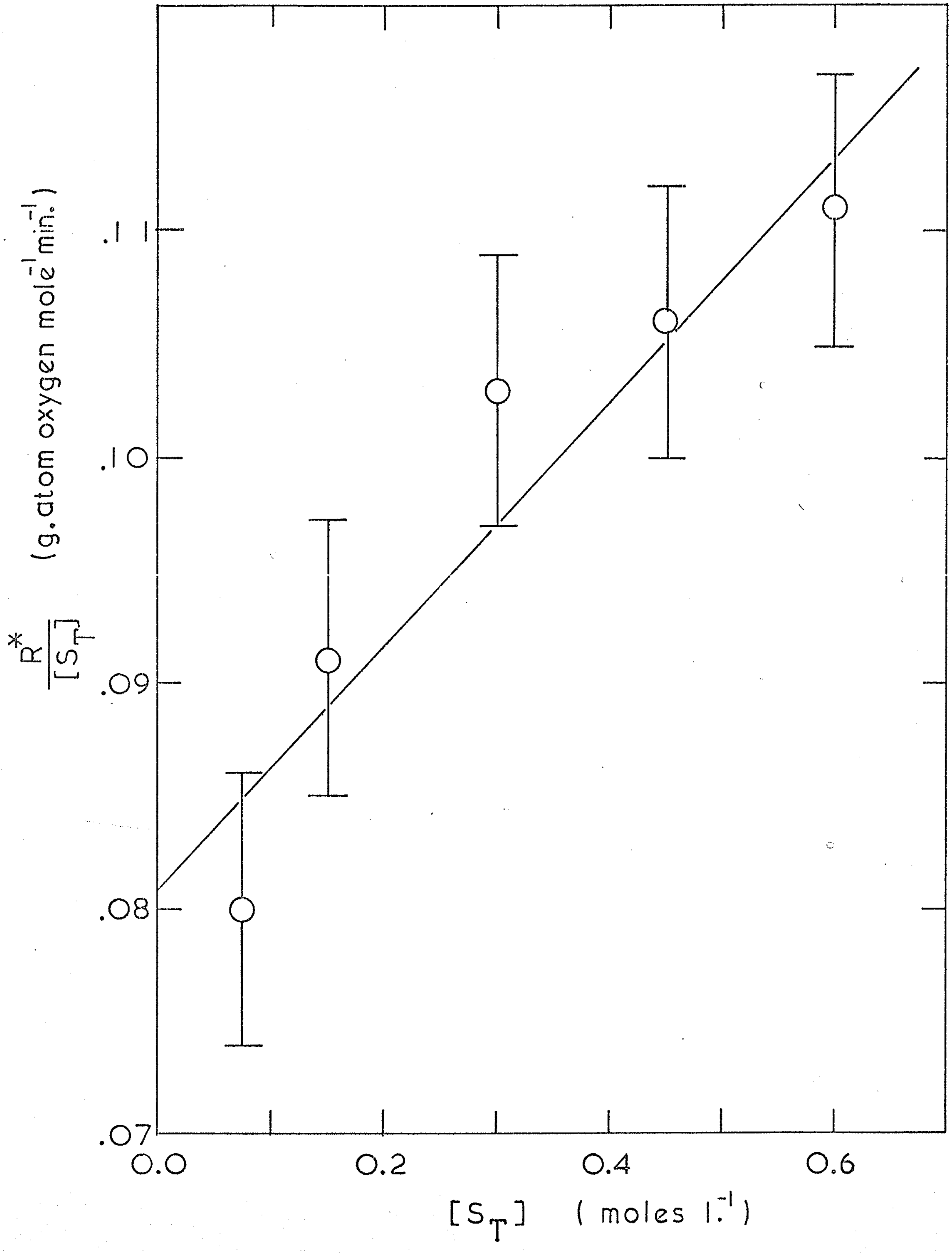
Run	$R^{*(a)}$ (g.-atom oxygen $l.^{-1}$ $min.^{-1}$)	$[S_T]$ (mole $l.^{-1}$)	$\frac{R^*}{[S_T]}$ (g.-atom oxygen $mole^{-1}$ $min.^{-1}$)
1	6.63×10^{-2}	0.600	0.111
2	4.77×10^{-2}	0.450	0.106
3	3.09×10^{-2}	0.300	0.103
4	1.36×10^{-2}	0.150	0.091
5	6.00×10^{-3}	0.075	0.080

(a) $R^* = R$ at pH 9.52.

FIG. 5-1

Determination of the second order contribution to the rate of sulfite-water oxygen exchange.

FIG. 5-1



$\frac{R^*}{[S_T]}$ (g. atom oxygen mole^{-1} min.$^{-1}$)
.07
.08
.09
.10
.11
0.0
0.2
0.4
0.6
$[S_T]$ (moles l.$^{-1}$)

mole^{-2} l. min.$^{-1}$ and 0.0807 ± 0.0023 g.-atom oxygen mole^{-1} min.$^{-1}$ respectively.

Knowing the value of r at pH 9.52 (calculated to be = 6.61×10^{-4}), values of the rate constants k_2 and k_1 were determined from the slope and intercept respectively. From the slope ($=k_2 r^2$) a value of 1.26×10^5 g.-atom oxygen mole^{-2} l. min.$^{-1}$ (= 2.10×10^3 g.-atom oxygen mole^{-2} l. sec.$^{-1}$) was obtained for k_2 or expressed in gram-mole rather than gram-atom units:

$$k_2 = 2.10 \times 10^3 \text{ g.-atom oxygen mole}^{-2} \text{ l. sec.}^{-1} \times \frac{1}{3 \text{ g.-atom oxygen mole}^{-1}}$$

$$= 7.00 \pm 0.21 \times 10^2 \text{ mole}^{-1} \text{ l. sec.}^{-1} .$$

From the intercept ($=[H^+] r k_1$) a value of 6.73×10^9 g.-atom oxygen mole^{-2} l. sec.$^{-1}$ was obtained for the rate constant k_1. Expressed in the units of gram-moles:

$$k_1 = 6.73 \times 10^9 \text{ g.-atom oxygen mole}^{-2} \text{ l. sec.}^{-1} \times \frac{1}{3 \text{ g.-atom oxygen mole}^{-1}}$$

$$= 2.24 \pm 0.06 \times 10^9 \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

Using the value obtained for $k_2 = 2.10 \times 10^3$ g.-atom oxygen mole^{-2} l. sec.$^{-1}$ a value for k_1 was found in another way using the data from the pH-dependence studies (section 4 - 1). If the second order contribution ($R_2 = k_2[HSO_3^-]^2$) is subtracted from the total rate of exchange ($R = k_1[H^+][HSO_3^-] + k_2[HSO_3^-]^2$), then k_1 can be determined simply from the first order term ($k_1 = \frac{R_1 = R - R_2}{[H^+][HSO_3^-]}$). Table VIII gives the values of the rate constant k_1 obtained in this way for each of the runs 1 through 13. The average value of k_1 was found to be $7.43 \pm 0.90 \times 10^9$ g.-atom oxygen $mole^{-2}$ l. $sec.^{-1}$ or expressed in units of gram-moles:

$$k_1 = 7.43 \times 10^9 \text{ g.-atom oxygen mole}^{-2} \text{ l. sec.}^{-1}$$
$$\times \frac{1}{3 \text{ g.-atom oxygen mole}^{-1}}$$
$$= 2.48 \pm 0.27 \times 10^9 \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

agreeing very well with the value ($2.24 \pm 0.06 \times 10^9$ $mole^{-1}$ l. $sec.^{-1}$) found from the intercept of the $\frac{R}{[S_T]}$ vs. $[S_T]$ plot (Fig. 5-1).

It would be interesting to know how significant is the contribution to oxygen exchange made by the second order term ($R_2 = k_2[HSO_3^-]^2$). The necessary data are given in Table IX. A plot of $\frac{R_2^*}{R}$ vs. $[S_T]$ is shown in Fig. 5-2. Approximately 30% of the exchange is carried by the second order process at $[S_T] = 0.6$ M. From Fig. 5-2, one would expect that for $[S_T] \simeq 2.0$ M the exchange would be predominantly due to the second order process ($2\ HSO_3^- \rightleftharpoons S_2O_5^= + H_2O$).

TABLE VIII

DETERMINATION OF THE RATE CONSTANT k_1

FOR THE EQUILIBRIUM $HSO_3^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_2 + H_2O$

FROM THE FIRST ORDER CONTRIBUTION TO THE RATE OF

OXYGEN EXCHANGE

Run	R (g.-atom oxygen $l.^{-1}$ $sec.^{-1}$)	$R_2 = k_2 [HSO_3^-]^2$ (a) (g.-atom oxygen $l.^{-1}$ $sec.^{-1}$)	$R_1 = R - R_2$ (g.-atom oxygen $l.^{-1}$ $sec.^{-1}$)	$k_1 = \frac{R_1}{[H^+][HSO_3^-]}$ (b) (g.-atom oxygen $mole^{-2} l.$ $sec.^{-1}$)
1	7.83×10^{-3}	1.43×10^{-3}	6.40×10^{-3}	6.15×10^{9}
2	6.00×10^{-3}	1.03×10^{-3}	4.97×10^{-3}	6.64×10^{9}
3	2.17×10^{-3}	0.41×10^{-3}	1.76×10^{-3}	5.87×10^{9}
4	1.32×10^{-3}	0.23×10^{-3}	1.09×10^{-3}	6.61×10^{9}
5	9.22×10^{-4}	1.66×10^{-4}	7.56×10^{-4}	6.30×10^{9}
6	7.20×10^{-4}	1.14×10^{-4}	6.06×10^{-4}	7.33×10^{9}
7	4.25×10^{-4}	0.60×10^{-4}	3.65×10^{-4}	8.41×10^{9}
8	2.33×10^{-4}	0.31×10^{-4}	2.02×10^{-4}	8.90×10^{9}
9	1.53×10^{-4}	0.22×10^{-4}	1.31×10^{-4}	8.29×10^{9}
10	7.13×10^{-5}	1.00×10^{-5}	6.13×10^{-5}	8.46×10^{9}
11	2.12×10^{-5}	0.33×10^{-5}	1.79×10^{-5}	7.49×10^{9}
12	1.18×10^{-5}	0.19×10^{-5}	9.90×10^{-6}	7.23×10^{9}
13	6.73×10^{-6}	0.91×10^{-6}	5.82×10^{-6}	8.86×10^{9}

(a) the product $[HSO_3^-]^2$ was obtained from Table VI, k_2 = 2.10×10^3 g.-atom oxygen $mole^{-2}$ l. $sec.^{-1}$.

(b) the product $[H^+][HSO_3^-]$ was obtained from Table VI.

TABLE IX

FRACTION OF OXYGEN EXCHANGE CONTRIBUTED BY THE SECOND ORDER TERM ($R_2 = k_2[HSO_3^-]^2$) IN THE RATE EXPRESSION

Run	R^{*} (a) (g.-atom oxygen l.$^{-1}$ sec.$^{-1}$)	$[S_T]$ (mole l.$^{-1}$)	$[S_T]^2$ (mole^2 l.$^{-2}$)	$[HSO_3^-]^2 = r^2[S_T]^2$ (b) (mole^2 l.$^{-2}$)	$R_2^{*} = k_2[HSO_3^-]^2$ (c) (g.-atom oxygen l.$^{-1}$ sec.$^{-1}$)	$\frac{R_2^{*}}{R^{*}}$
1	1.11×10^{-3}	0.600	0.3600	1.58×10^{-7}	0.33×10^{-3}	0.297
2	7.95×10^{-4}	0.450	0.203	8.93×10^{-8}	1.88×10^{-4}	0.236
3	5.15×10^{-4}	0.300	0.0900	3.96×10^{-8}	0.83×10^{-4}	0.161
4	2.23×10^{-4}	0.150	0.0225	9.90×10^{-9}	0.21×10^{-4}	0.094
5	1.00×10^{-4}	0.075	0.00563	2.48×10^{-9}	0.05×10^{-4}	0.050

(a) $R^{*} = R$ at pH 9.52.

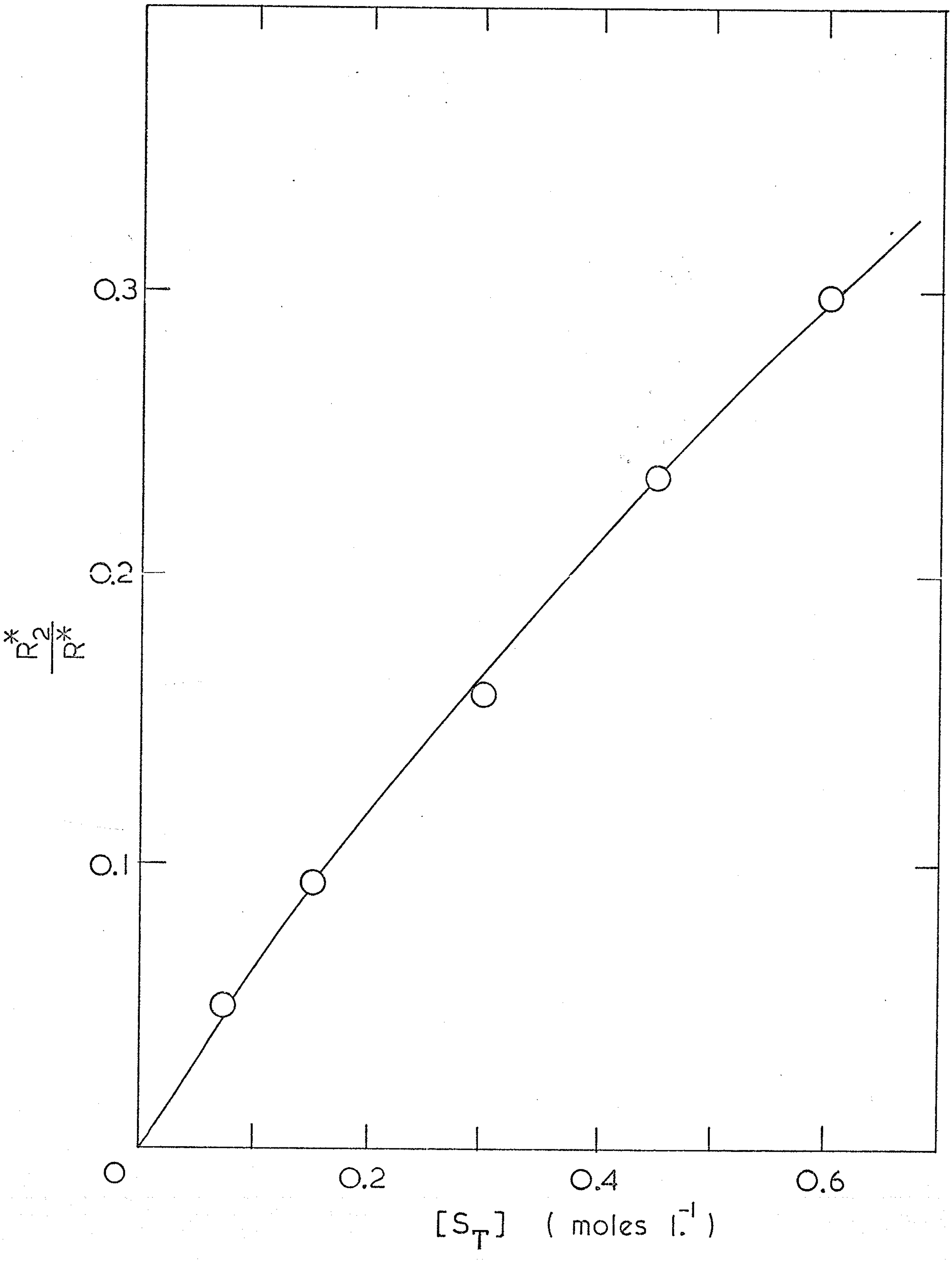
(b) $r^2 = (6.61 \times 10^{-4})^2 = 4.40 \times 10^{-7}$

(c) $k_2 = 2.10 \times 10^{3}$ g.-atom oxygen mole^{-2} l. sec.$^{-1}$

FIG. 5-2

Dependence of the second order contribution to the rate of exchange on the total sulfite concentration, $[S_T]$.

FIG. 5-2



To verify the form of the pH dependence of the second order term in the expression for the rate of exchange ($R = k_1[H^+]\,[HSO_3^-] + k_2[HSO_3^-]^2$) it would have been desirable to carry out pH dependence studies for different total sulfite concentrations ($[S_T]$). However the form of the rate expression was tested in another way from the data available. Substituting the expression for the sulfite concentration ($[HSO_3^-] = \dfrac{[S_T][H^+]K_{II}}{1 + [H^+]\,K_{II}}$) into the rate expression

$$R = k_1[H^+]\frac{[S_T]\,[H^+]K_{II}}{1 + [H^+]K_{II}} + k_2\frac{[S_T]^2[H^+]^2K_{II}^2}{(1 + [H^+]\,K_{II})^2}$$

$$= k_1[S_T][H^+]^2\,\frac{K_{II}}{1 + [H^+]\,K_{II}} + k_2[S_T]^2\,[H^+]^2\,\frac{K_{II}^2}{(1 + [H^+]K_{II})^2}$$

Setting $\dfrac{K_{II}}{1 + [H^+]K_{II}} = B$, the above becomes

$$R = k_1[S_T][H^+]^2\,B + k_2[S_T]^2\,[H^+]^2\,B^2$$

$$= R_1 + R_2.$$

The ratio of the first order to the second order contribution to the rate of exchange for a given pH is then

$$\frac{R_1}{R_2} = \frac{k_1[H^+]^2\,[S_T]}{k_2[H^+]^2\,[S_T]^2}\,\frac{B}{B^2} = \frac{k_1}{k_2}\,\frac{1}{[S_T]\,B}$$

When the total sulfite concentration ($[S_T]$) is held constant as it was for the pH dependence studies (section 4 - 1) the above ratio simplifies to

$$\frac{R_1}{R_2} = \frac{k_1}{k_2} \cdot \frac{1}{B}$$

However B is effectively constant for the pH range over which the pH dependence studies were made, since the largest value that the quantity $[H^+]K_{II}$ (run 1, Table VI) takes is $\simeq 3 \times 10^{-3}$ or $1 + K_{II}[H^+] \simeq 1.0$. Then for all values of $[H^+]$ (runs 1 through 13, Table VIII) would expect the ratio of R_1 to R_2 to be effectively constant. The observed constancy of the ratio $\frac{R_1}{R_2}$ (allowing for ± 20% error) for the runs 1 through 13 ($\frac{R_1}{R_2}$ = 4.46, 4.78, 4.29, 4.74, 4.55, 5.32, 6.10 6.52, 5.95, 6.13, 5.43, 5.20, 6.3 respectively) supports the form of the rate expression that was used, that is, the rate of the second order path is proportional to $[HSO_3^-]^2$ and no other terms involving $[H^+]$, $[OH^-]$ need be invoked.

5 - 3 COMPARISON WITH INVESTIGATIONS DONE BY OTHER WORKERS

(i) Comparison With Qualitative Studies

The results obtained by Hall and Alexander (Ref. 44, Table I) are compatible with those obtained in the present study. Mills(45) and Winter et al(46) did not observe exchange between K_2SO_3 or Na_2SO_3 and water probably due to the low sensitivity of the method they used (following the change in the isotopic composition of the solvent) as well as due to the low enrichment of the water used by the earlier workers. The higher sensitivity of the present method results from the fact that the isotopic composition of the sulfite ions was followed directly. Pryor and Tonellato(47) reported that their results "demonstrate unequivocally that, in the presence of thiosulfate, sulfite exchanges oxygens with water at least as slowly as does thiosulfate at 80° and pH 6." Their results contradict the order of exchange that is predicted (rule 2; section 1 - 6, $SO_3^{=} > S_2O_3^{=}$), and it appears that this discrepancy results from an inadequate interpretation of the mechanisms occurring. C.B. Amphlett(58) in his review article on the "Isotopic Exchange Between Different Oxidation States In Aqueous Solution" points out that "reports of complete exchange during the time of mixing and separation should be treated with caution." This observation seems to particularly apply to Halperin's and Taube's(48) observation that the exchange was complete in 5 min. when the water was 0.4 M in NaOH (pH probably lying somewhere in the region 12-14). The author of this thesis believes that the rapid exchange that Halperin and Taube observed is really induced exchange resulting from a second rapid homogeneous exchange involving an intermediate species which has a transient existence during the process of oxidation of all S^{IV} species present in solution to S^{VI} as sulfate. Brodskii(26) and also Hall and Alexander(44) reported that the exchange was slow in the basic region lending support for the present work. In fact for an experiment carried out (in the present studies) at pH $\simeq$ 12.7 (0.3 M Na_2SO_3, 0.1 M NaOH) no exchange was observed even after 17 days.

(ii) Comparison With Quantitative Studies

Table X summarizes rate constants for the processes distinguished in this study along with the results obtained by other methods. The values obtained from this study for k_1 and k_{-1} are one to two orders of magnitude larger than those reported by Eigen et al(51) from relaxation measurements. By the nature of this investigation, that is under conditions of very low concentrations of SO_2 and the necessary dependence on particular values for thermodynamic quantities (equilibrium constants),(a) the absolute accuracy of rate constants calculated is subject to debate.

(a) It is of interest that using Tartar's and Garretson's(29) values for $K_I (= 5.88 \times 10)$ and $K_{II} (= 1.6 \times 10^7)$ at zero ionic strength, values calculated from the oxygen exchange results for k_1 and k_{-1} (1.70×10^8 mole^{-1} l. sec.$^{-1}$, and 2.78×10^6 sec.$^{-1}$ respectively) agree remarkably well with those values reported by Eigen et al! These calculations illustrate quite well the marked sensitivity of the calculated rate constants on the values chosen for the equilibrium constants, K_I and K_{II}.

TABLE X

COMPARISON OF RATE CONSTANTS OBTAINED IN
THIS STUDY WITH VALUES DERIVED FROM OTHER METHODS

$$H^+ + HSO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_2 + H_2O$$

k_1 (mole^{-1}l. sec.$^{-1}$)	k_{-1} (sec.$^{-1}$)	Ref.	Temp. (^{o}C)	Ionic strength
2.48×10^9	$1.06 \times 10^{8\,(a)}$	This work	24.7	0.9
2.80×10^8	3.4×10^6	(51)	20	0.1
1.6	2.2×10^{-2}	(49)	20	?

$$2\ HSO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} S_2O_5^= + H_2O$$

k_2 (mole^{-1}l. sec.$^{-1}$)	k_{-2} (sec.$^{-1}$)	Ref.	Temp. (^{o}C)	Ionic strength
7.00×10^2	$\sim 1.0^{(b)}$	This work	24.7	0.9

(a) The value for k_{-1} was calculated from k_1 using the value reported for the equilibrium constant K_I $\left(= \frac{[SO_2]}{[H^+][HSO_3^-]}\right)$ $= 2.34 \times 10^1$ by Sillén et al at 25°C and ionic strength = 1(57).

(b) k_{-2} was calculated using the value for k_2 and the value reported by Golding(42) for the equilibrium constant $K = \frac{[S_2O_5^=]}{[HSO_3^-]^2} \simeq 7 \times 10^{-2}$.

The values reported by Wang and Himmelblau(49) for k_1 and k_{-1} are not anywhere near the values obtained from this study or from the relaxation measurements. Their values for k_1 and k_{-1} do not seem to be very acceptable since it was known(59) from flow studies that the hydration of SO_2 was "instantaneous" in contrast to the measurable rates of hydration and dehydration of CO_2. The experimental techniques that Wang and Himmelblau employed in their studies appear to be somewhat overcomplicated.

APPENDIX

SAMPLE RUN

Data for run number 10 from section 4 - 1 (temp. = 24.7°C, pH = 9.98, and $[S_T] = 0.3$ M) is presented in Table XI below:

TABLE XI

Aliquot No.	Time (min.)	p-factor	(1-F)	$-\log_{10}(1-F)$
1	20	0.02362	0.7861	0.1045
2	45	0.02152	0.7032	0.1529
3	90	0.01798	0.5635	0.2491
4	135	0.01508	0.4491	0.3477
5	180	0.01273	0.3564	0.4481
6	225	0.01092	0.2849	0.5453

From equation (1) of section 1 - 3 ($F = \frac{P_t - P_o}{P_\infty - P_o}$) the quantity (1-F) in Table XI is given by

$$(1-F) = \frac{P_t - P_\infty}{P_o - P_\infty} \qquad (1)$$

Substitution into the above expression the values 0.02904 and 0.00370 for the initial p-factor of the labelled sodium sulfite (P_o) and for the p-factor of the natural (unlabelled) sodium sulfite (P_∞) respectively, leads to the simpler expression

$$(1-F) = 39.463(P_t - P_\infty)$$

from which the values for (1-F) in Table XI were calculated. A plot of $-\log_{10}(1-F)$ vs. time is shown in Fig. I-1. A least-squares analysis of the straight line with the Olivetti Programma computer gave a value of 0.0572 for the intercept. Using the iterative technique discussed in section 3 - 4, a value of 143.5 min. was obtained for $t_{\frac{1}{2}}$ (that is, the number which when substituted back into the computer generated the value equal to the sum of 0.0572 and $\log_{10}$ 0.5 (0.3582). The rate of exchange was then obtained by substituting the value for $t_{\frac{1}{2}}$ into equation (1) from section 4 - 1

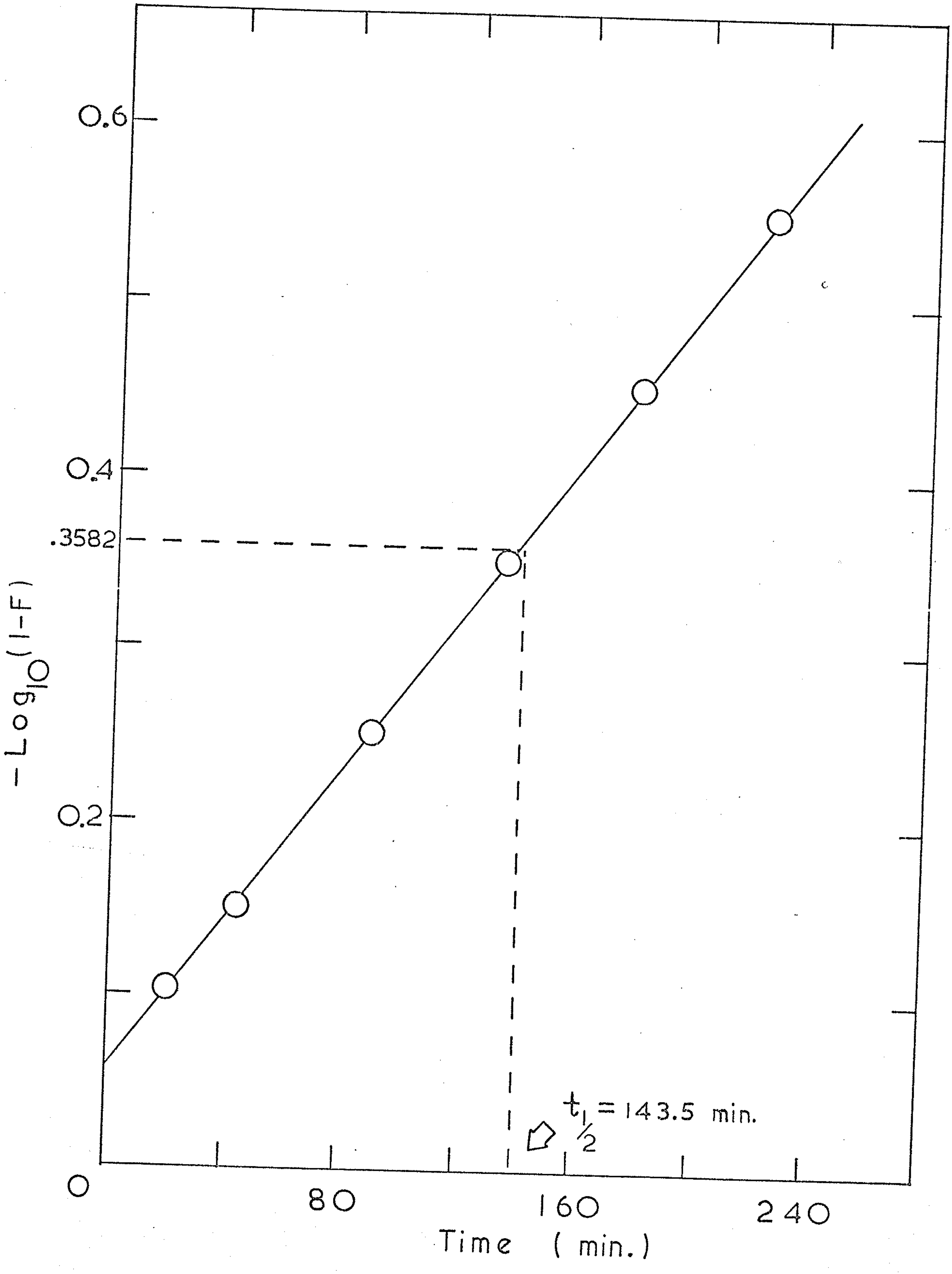
$$R = \frac{0.6138}{t_{\frac{1}{2}}} .$$

The cause of the induced exchange that was observed (~12%) is not understood, however, Prestwood and Wahl(60) have shown that, so long as the effects are reproducible and consistent techniques are used throughout, these effects may be eliminated. If F represents the fractional exchange at time t before separation, $\overline{F}$ that after separation at time t, and $\overline{F}_0$ the zero-time exchange after separation, and if P_0, P_t, and P_∞ are the p-factors of the separated fraction at zero time, time t, and at equilibrium respectively,

FIG. I-1

Sulfite-H_2O oxygen exchange reaction (temp. = 24.7°C, pH = 9.98, and $[S_T]$ = 0.3 moles $l.^{-1}$)

FIG. I-1



one can derive the following expression:

$$F = \frac{(P_t - P_o)}{(P_\infty - P_o)} = \frac{(\bar{F} - \bar{F}_o)}{(1 - F_o)} \qquad (2)$$

The quantities measured in an experiment are $\bar{F}$ and $\bar{F}_o$, the latter being obtained from a separation immediately after mixing; if values of F are calculated in this way, the points all lie on the same exchange curve passing through (1-F) = 1 at t = 0, whatever the method of separation. Uncorrected points give $F = \bar{F}_o$ at time t = 0. Alternatively if one plots $\ln(1-\bar{F})$ against t, values of R and $t_{\frac{1}{2}}$ may still be derived directly as for a separation procedure which does not induce exchange, since by substituting for F from equation (2) above into equation (3) from section 1 - 2, one obtains the expression

$$\ln(1-\bar{F}) = -R_t \frac{([a] + [b])}{[a][b]} + \ln(1-\bar{F}_o) \quad . \qquad (3)$$

The slopes of the corrected and the uncorrected curve are thus the same; in practice, uncorrected curves are usually employed, and the extent of induced exchange calculated from the intercept on the vertical axis (as was done in the treatment of the data in Table XI).

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