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KINETICS OF OXYGEN-18 EXCHANGE INVOLVING WATER, SULFUR OXYANIONS AND SOME POLYNUCLEAR CATIONS IN AQUEOUS MEDIA

BY

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
WINNIPEG, MANITOBA
FEBRUARY, 1971

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to my wife

ACKNOWLEDGEMENTS

I wish to express my gratitude and extend most sincere thanks to Dr. R.H. Betts for his excellent supervision and guidance throughout this research, and for his advice in other areas of my graduate studies.

I also acknowledge with thanks, the numerous discussions with my fellow worker, Ron Voss, concerning this research;
and Wayne Buchannon, for help in certain isotopic mass abundance measurements;
and the Department of Chemistry and the National Research Council for financial assistance in the form of a Teaching Assistantship and a bursary, respectively.

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ABSTRACT

Oxygen exchange measurements between the polynuclear hydroxy lead species, $Pb_4(OH)_4^{+4}$, or the hydroxy bismuth species, $Bi_6(OH)_{12}^{+6}$, and water have shown that the exchange has reached equilibrium in less than one minute for both species.

The possibility of oxygen exchange between tetrathionate and water catalyzed by sulfite was examined. This investigation was complicated by a chemical reaction which takes place between tetrathionate and sulfite to yield trithionate and thiosulfate. A semiempirical correlation which relates sulfur-sulfur bond length to activation energy for nucleophilic displacements on catenated sulfur bonds indicated that the catalyzed exchange process should proceed at least sixteen times faster than the chemical reaction leading to thiosulfate and trithionate as products. An explanation is proposed for the failure of the correlation in this system.

The nucleophilic displacement process on thiosulfate by sulfite has an important role in the kinetics of oxygen transfer between thiosulfate and sulfite. Subsequent oxygen transfer from sulfite to water then occurs, depending on the pH of the system. When the sulfite-water oxygen exchange is rapid then sulfite can be regarded as a catalyst in the thiosulfate-water oxygen exchange mechanism. The results at appropriate pH values provide a most interesting illustration of a system of reversible consecutive first order rate processes.

During the oxidation of thiosulfate to tetrathionate by a

variety of methods no large degree of exchange of the oxygens of thiosulfate with water occurs. In reactions where the radical anion, $S_2O_3^{\overset{-}{\cdot}}$ has been postulated as an intermediate, some exchange was observed but in other reactions the exchange was barely observable.

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INTRODUCTION

This thesis deals with a number of related, but distinct topics, all of which involve oxygen transfer of one kind or another. In this introduction, an account is given of the literature pertinent to these topics, some of which is further elaborated as required in the later parts of the thesis. The first part of the Introduction is concerned with cationic hydrates and oxycations; the second part introduces the particular bismuth and lead species examined. There follows a general discussion of the lability of oxygen in oxyanions, with particular reference to the thiosulfates and tetrathionates. The Introduction concludes with some account of the literature relating to the kinetics of oxidation of thiosulfate, and the role of oxygen tracer work in the possible elucidation of mechanism.

The enormous number of papers published which have utilized oxygen isotopes in chemical investigations attests to the importance and usefulness of oxygen tracer studies. A comprehensive bibliography of all research involving the isotopes of oxygen up to 1959 has been published by Samuel and Steckel(1) with subsequent supplements covering the period from 1959 to 1966(2-4). Many reviews on various aspects of research involving oxygen isotopes have appeared periodically in the literature. Reviews that specifically discuss inorganic reaction mechanisms and exchange of oxygen between inorganic oxygen containing species and water have been published by Dole(5), Edwards(6), Taube(7), Stranks and Wilkins(8), and Brodskii(9). In addition to these reviews, articles have appeared which discuss the methodology of oxygen isotopes(10) and the preparation of a large number of ^{18}O-labelled inorganic compounds(11).

1 - 1 CATIONIC HYDRATES AND OXYCATIONS:

It has long been known that ions in general interact strongly with water as solvent and may form definite structural hydrates. Some cations in aqueous solution exert sufficiently strong forces on water molecules to hold them in hydration spheres and therefore make them distinguishable from the water molecules of the solvent. Oxygen isotope tracer studies provide an excellent tool for the investigation of the lability of such water molecules or oxygen atoms with respect to solvent molecules and may provide evidence for the mechanism of exchange.

A general goal of such studies has been to learn the limits for which a distinction can be made between water molecules of hydration and the remaining solvent molecules or between oxygen atoms of ions and the oxygen atoms of solvent molecules. A specific goal, of particular interest for the chemistry of individual ions, is to determine the number of water molecules held by an ion, or the number of oxygen atoms held in an ion distinguishable from the solvent.

The structure of cationic hydrates and their stability has been investigated by many physical chemical methods and by oxygen isotope tracers. Oxygen isotope tracer studies include exchange methods(12-14), ^{17}O-nuclear magnetic resonance methods(15, 16), and equilibrium isotope fractionation effects(17). A factor of great importance in determining the behavior of complex ions in solution is the rate at which they undergo substitution in the inner sphere. It is, in fact, of greater importance for many of the observations which are made than is the factor of stability. It must be emphasized that a slower rate for substitution or oxygen exchange does not necessarily mean a greater stability. It only means that the time to reach equilibrium will vary greatly for the different ions.

A classic example of a cation holding back water molecules distinguishable from bulk solvent water molecules is the Cr(III) ion. Hunt and Taube(12, 14) found that Cr(III) holds six water molecules in its hydration sphere, thus justifying the formula $Cr(H_2O)_6^{+3}$. They also found that the half-time for exchange of these water molecules with solvent water molecules is approximately 40 hours at 25°C. Other ions such as Fe(III) and Al(III) exchange the water molecules of hydration with bulk solvent molecules within seconds(18).

Hold-back of oxygen by cations is not limited to that bound as H_2O but also has been observed for oxide oxygen atoms. Crandall(19) showed by means of oxygen exchange that U(VI) holds back two oxygen atoms, consistent with the formula UO_2^{+2}, but not with $U(OH)_4^{+2}$ which would otherwise also appear to be a reasonable formulation.

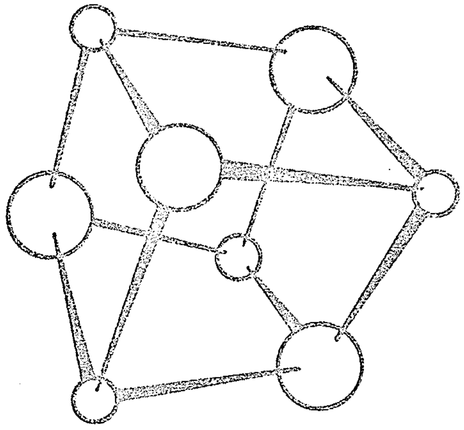
1 - 2 POLYNUCLEAR HYDROXY-CATIONS OF LEAD AND BISMUTH:

There is a good possibility that the oxygen exchange method can be used to distinguish bridge oxygen atoms in polynuclear ions from water which is singly bound. An oxygen atom bound to two or more other metal atoms in polynuclear polyhedra plays an important role in holding a particular structure intact and therefore it would seem reasonable to expect that such an oxygen atom would be rather inert to exchange with solvent oxygen atoms. The oxygen atoms in the polynuclear hydroxy cations, $Pb_4(OH)_4^{+4}$ and $Bi_6(OH)_{12}^{+6}$ are just such bridging oxygen atoms and therefore, it was of interest to examine the lability of these oxygens with respect to their exchangeability with the solvent.

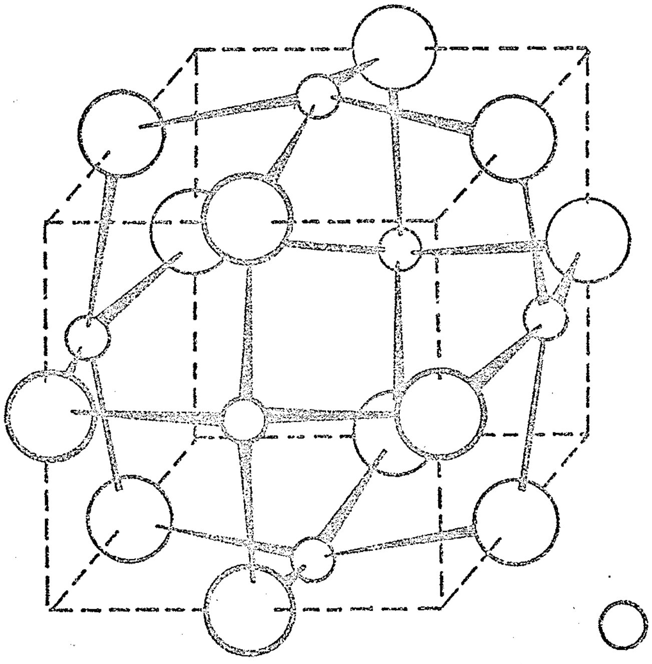
Pb(II) and Bi(III) are isoelectronic ions and both hydrolyze to give very soluble complexes whose structures are however, quite different. The main product of lead hydrolysis is the cubic tetramer, $Pb_4(OH)_4^{+4}$ while bismuth produces the octahedral hexamer $Bi_6(OH)_{12}^{+6}$. The structure of $Pb_4(OH)_4^{+4}$ ion was deduced from solution x-ray scattering measurements(20) and was confirmed by vibrational analysis of a Raman spectra by Maroni and Spiro(21) as a distorted cube consisting of lead and oxygen atoms each arranged tetrahedrally as shown in Fig. (1). The Raman spectrum provided evidence for weak metal-metal bonding, but from the structure it is seen that each oxygen atom provides a bridge between three lead atoms. From a molecular orbital analysis of this structure, Maroni and Spiro conclude that the average

Fig. 1

Arrangement of lead and oxygen atoms and of bismuth and oxygen atoms in the models assumed for $Pb_4(OH)_4^{+4}$ and $Bi_6(OH)_{12}^{+6}$ ions


○ — LEAD
○ — OXYGEN

$Pb_4(OH)_4^{+4}$


○ — BISMUTH
○ — OXYGEN

$Bi_6(OH)_{12}^{+6}$

Pb-O bond order is two-thirds.

The structure of the $Bi_6(OH)_{12}^{+6}$ ion, also shown in Fig. (1), was deduced from solution x-ray scattering study by Danford, Levy and Agron(22) and confirmed by Maroni and Spiro(23) by a Raman spectral correlation. The six bismuth atoms are located at the corners of a regular octahedron with twelve hydroxyl groups on the octahedral edges joining the bismuth atoms. The resulting structure can be described as a cuboctahedron with each bismuth atom lying just above the plane of four oxygen atoms. Maroni and Spiro predicted an average Bi-O bond order of one-half in this structure. The oxygen atoms act as bridges between the bismuth atoms but there is also evidence in the Raman spectrum for metal-metal bonding.

In view of the highly-ordered and well-defined structures for these oxygen-containing ions and the evidence for multiple bonding involving oxygen, it was of interest to examine the kinetic lability of the oxygen with respect to exchange with solvent oxygen as H_2O. Accordingly the perchlorate salts of these polynuclear hydroxy-cations were synthesized and the exchangeability of the hydroxyl oxygens with solvent was examined. The experimental details and results are given in Sections (3 - 1) and (3 - 2).

1 - 3 OXYANION EXCHANGE WITH WATER:

Oxygen atoms in oxyanions show large variations in rates of oxygen exchange with solvent water molecules. Investigations of the rates of exchange of oxygen in oxyanions are of great importance because the mechanisms and rates can quite often be linked to the reactions involving the displacement of a water molecule from the coordination sphere of the oxyanion by a different donor. Both exchange reactions of oxyanions and reactions of oxyanions with electron donors quite often involve hydrogen ion catalysis. Since oxyanions often have a large amount of resonance stabilization, it is necessary to overcome this resonance energy before a substitution or chemical reaction can take place. Addition of hydrogen ions converts the oxygen atoms of oxyanions to less stable form which can then undergo reaction. The function of hydrogen ion presumably is to strip off an oxide ion from the oxyanion as H_2O, or to withdraw electrons from the centre undergoing nucleophilic attack in an SN2 mechanism.

It has been said(24) that there does not seem to be any obvious relation between rates of oxidation and the oxidation potential of the oxyanions. The rates at which oxyanions oxidize species like halide or thiosulfate cover a vast range. Perchlorate, nitrate and selenate are very slow oxidants, while iodate, nitrite and selenite are rapid in acid solution. Periodate and hypochlorite are rapid oxidants even in alkaline solution. Thus something more than oxidizing power is involved. On the other hand, the available data indicate that there is a considerable correlation between the rates of oxidation and the rates of oxygen exchange with solvent water for the oxyanions(25). The rate of oxidation-reduction reactions involving oxyanions often have the same dependence on hydrogen ion concentration as is found in exchange reactions. The mechanism for these oxidation-reduction reactions indicates that the reducing agent first replaces a water molecule in the oxyanion and then electron transfer occurs after a bond between the reducing agent and the central atom of the oxyanion has been formed. In many of these oxidation-reduction reactions the replacement step may be the rate determining step, for replacement reactions in oxyanions generally have high energies of activation. For example, H_2SeO_3 oxidizes I^- to I_2(26) and $S_2O_3^=$ to $S_4O_6^=$(27) in dilute acid solution, while H_2SeO_4, which is a stronger oxidizing agent, does not oxidize either I^- or $S_2O_3^=$ unless the solution is strongly acidic. It is probable that the rate determining step in H_2SeO_3 and H_2SeO_4 oxidations is related to the ease of replacement of an oxide ion (as H_2O) by the reducing base and electron transfer is a rapid follow-up step. These observations about the rate of oxidation-reduction reactions are in good agreement with what is observed for the relative rates of oxygen exchange involving these ions(28).

More quantitative studies on the exchange of oxygen of oxyanions with solvent water are required to determine how generally these relations apply. In this connection, many general trends in these oxyanion exchanges have been observed by Edwards(29, 25) and by

Brodskii(30, 9) and a few generalized mechanisms have been proposed(6, 31) but many exceptions can be found and these must still be treated on an individual basis. For example, oxygen exchange reactions are as a rule catalyzed by acids and repressed by bases but for perrhenate(31) and iodate(32), a base catalysis has been observed.

For oxyanions that are derived from small, highly-charged central atoms, the leading rate law for exchange is

(1 - 1) $R = k(XO_m^{-n})(H^+)^2$

Many oxyanions such as $SO_4^=$, $SO_3^=$, NO_3^-, ClO_3^-, BrO_3^-, MnO_4^-, NO_2^-, ReO_4^- and possibly many others show such a second order dependence on (H^+). It is generally agreed that a pre-association of the oxyanion with two hydrogen ions occurs before the rate-determining step, thus greatly weakening the oxide bond to the central atom of the oxyanion. If the two hydrogen ions bond to one oxide ion of the anion then presumably that oxygen atom takes on properties which are very similar to oxygen atoms of water, and this may facilitate the exchange process. Three general mechanisms for this interchange have been proposed(6, 31). After a fast equilibrium step (Equation 1 - 2):

(1 - 2) $XO_m^{-n} + 2H^+ \rightleftarrows H_2OXO_{m-1}^{-n+2}$

the water exchange can take place by a concerted displacement by a second water molecule SN2 (Equation 1 - 3):

(1 - 3) $H_2OXO_{m-1}^{-n+2} + H_2O^* \rightleftarrows H_2O^*XO_{m-1}^{-n+2} + H_2O$ or,

by a co-ordination number expansion of the central atom of the anion (Equation 1 - 4):

(1 - 4) $H_2OXO_{m-1}^{-n+2} + xH_2O \rightleftarrows (H_2O)_{x+1}XO_{m-1}^{-n+2}$

or by SN1 elimination of a water molecule from the anion forming an anhydride (Equation 1 - 5):

(1 - 5) $H_2OXO_{m-1}^{-n+2} \rightleftarrows H_2O + XO_{m-1}^{-n+2}$

Evidence favoring the SN2 mechanism for exchange for NO_3^- and BrO_3^- is the catalysis by chloride observed in these systems(33), chloride apparently being effective in displacing H_2O from $H_2ONO_2^+$. Other evidence supporting the SN2 mechanism is the relative slowness of exchange of tetrahedrally substituted oxyanions as compared to the non-tetrahedrally substituted oxyanions. The oxygen tetrahedra around the central atom of the oxyanion act as a shield to prevent the nucleophilic attack by a water molecule. The slowness of oxygen exchange involving H_3PO_4, H_2SO_4 and $HClO_4$ as compared with H_3PO_3, H_2SO_3 and $HClO_3$ can be in part due to this factor.

Evidence for mechanism (1 - 4) is provided by oxyanions for which higher co-ordination numbers of the central atom are known to exist. Thus the rapid exchange for tungstates, molybdates, perrhenates, and periodates can be explained on the basis of this mechanism. Exchange in periodate, for example, could take place readily even without pH dependence, in view of the following known hydration reaction:

(1 - 6) $IO_4^- + 2H_2O \rightleftarrows H_4IO_6^-$

The SN1 anhydride formation (Mechanism 1 - 5) is probably the major exchange path for oxyanions such as sulfate, sulfite and carbonate for which the stable anhydrides SO_3, SO_2, and CO_2 are known to exist.

At this point it is appropriate to discuss some of the general trends observed by Brodskii(30, 9) and Edwards(25) in the relative lability of oxygen atoms in different oxyanions and to relate these to the mechanisms already discussed.

(i) Acidity of the Medium

Brodskii has stated that the rate of exchange decreases rapidly in the order: acid > acid salt > neutral salt. Examples of this trend are given by the following species:

$H_2SO_4 > HSO_4^- > SO_4^=$

$H_2SO_3 > HSO_3^- > SO_3^=$

$HNO_3 > NO_3^-$

$H_3PO_4 > H_2PO_4^-$, $HPO_4^=$, $PO_4^{\equiv}$, etc.

An increase in the acidity of the medium increases the relative concentration of the acid with respect to acid salt or neutral salt thus increasing exchange rate. The often observed second order dependence on hydrogen ion concentration in the rate laws for oxygen exchange of oxyanions can be related to the change in basicity of the oxide ion of the oxyanion as hydrogen ions are added to form successively hydroxyl ion and water. An increase in acidity of the solvent may influence the rate of exchange by a change in the medium from H_2O to H_3O^+ but no detailed study of this aspect has yet been made.

Although base catalysis has been observed for iodate and perrhenate oxygen exchange with water, the most likely explanation for this is the ability of hydroxyl ions to substitute for water molecules in the expanded co-ordination spheres of these ions.

(ii) Oxidation State of the Central Atom

In cases of elements which form several oxyanions in more than one oxidation state, the rate of oxygen exchange decreases as the oxidation state of the central atom increases. Examples are:

$H_3PO_2 > H_3PO_3 > H_3PO_4$

$SeO_3^= > SeO_4^=$

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

$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$

However some of the trends observed here may be related to steric effects rather than to oxidation state per se, since the geometry of the oxyanions change as more oxide ions are added.

(iii) Charge on the Central Atom

In a particular period of the periodic table it seems that the rate of oxygen exchange decreases as the charge increases on going from left to right. Examples:

$H_2SiO_4^= > HPO_4^= > SO_4^= > ClO_4^-$

$CO_3^= > NO_3^-$

$SO_3^= > ClO_3^-$

$SeO_3^= > BrO_3^-$

The variation of charge on the central atom of the above oxyanions may be related to other phenomena observed for these ions. For example the tendency of the oxyanions in the first series given above to polymerize decreases from left to right. The silicates and phosphates form a variety of polymeric species whereas sulfates form dimers and perchlorates only dehydrate to Cl_2O_7(81). Thus the oxygen exchange rate may be related to the ease of these oxyanions to form polynuclear species. The relative rates of oxygen exchange observed in the remaining three series of oxyanions given above may be related to the relative stability of their anhydrides. The anhydride species CO_2, SO_2 and SeO_2 are more readily formed and more stable than NO_2^+, ClO_2^+, and BrO_2^+. Also to lose water from or have a water molecule displaced from monoprotic acid it is necessary to have an additional proton present in the transition state (e.g. $H_2NO_3^+$) whereas diprotic acids have two protons already (e.g. H_2CO_3). Thus, the ease of protonation will have direct bearing on the relative rates of exchange in the series given above.

(iv) The Size of the Central Atom

For any given group in the periodic table there is an increase in the exchange rate for oxyanions as the atomic number of the central atom increases. Examples are:

$IO_4^- >> ClO_4^-$

$IO_3^- > BrO_3^- >> ClO_3^-$

$TeO_4^= > SeO_4^= >> SO_4^=$

$WO_4^{=}$, $MoO_4^{=} > CrO_4^{=}$, etc.

The increase in rate with increase in atomic number of the central atom can be attributed to the increase in size of the central atom. The larger the size of the central atom the more widely spaced the oxide atoms become therefore presenting less steric hindrance and also stabilizing the higher co-ordination numbers for these oxyanions.

The mechanisms presented so far are not the only routes by which oxygen can exchange between oxyanions and solvent water. Other routes of exchange are applicable to certain oxyanions only and are not as general as the mechanisms presented earlier. For example the dimerization of chromate and bisulfite (Equations 1 - 7 and 1 - 8):

(1 - 7) $2HCrO_4^{-} \rightleftarrows Cr_2O_7^{=} + H_2O$

(1 - 8) $2HSO_3^{-} \rightleftarrows S_2O_5^{=} + H_2O$

provide routes for the oxygen exchange and it has been shown that these routes contribute to the overall exchange rate of chromate(34) and sulfite(35).

Other mechanisms of exchange exist for sulfur oxyanions containing catenated sulfur-sulfur bonds. From the pioneering work of Foss(36-38) on the polythionates it is known that sulfur atoms in polythio compounds form unbranched chains and that many of the reactions of polythio compounds can be interpreted in terms of nucleophilic displacement reactions at the sulfur atom. For example if sulfite is mixed with polythionates then exchange of $SO_3^{=}$ groups can take place by an SN2 nucleophilic displacement as shown in Equation (1 - 9):

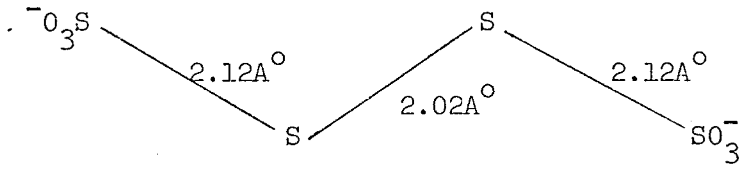
$$(1 - 9)\quad \overset{*}{S}O_3 + (O_3SS_nSO_3)^= \rightarrow (O_3SS_n\overset{*}{S}O_3)^= + SO_3^=$$

In effect this process corresponds to an exchange of three oxygens between the polythionate and sulfite. Since oxygen exchange between sulfite and water is rapid below pH 9(35) then sulfite would be expected to act as a catalyst for oxygen exchange between polythionates or thiosulfate and water. A further account of the literature on these subjects comprises the next two Sections of this thesis.

1 - 4 THE SULFITE-TETRATHIONATE SYSTEM:

Preliminary investigation by the author of oxygen exchange of tetrathionate with water indicated a very slow exchange (less than 3% exchange either in 8-10 days at 28°C or in 5 days at 53°C at pH 1.75). However, after this induction period a rapid decomposition of the tetrathionate occurred accompanied by rapid mixing of the oxygens of water with the polythionates in solution. Sulfite or thiosulfate were suspected as possible intermediate species that catalyzed the exchange and decomposition of the tetrathionate. However, thiosulfate is very unstable in this pH region. Therefore the reaction between sulfite and tetrathionate was examined more fully.

The structure of tetrathionate has been determined by Foss(37, 38) as a bent chain of sulfur atoms of differing S-S bond lengths and terminated by $-SO_3^-$ groups:



Sulfite can react with tetrathionate in an SN2 type of nucleophilic displacement by attacking either of the two inner sulfur atoms in the tetrathionate chain, the following two reactions being possible:

(1 - 10) $O_3S-S-S-SO_3^= + SO_3^= \rightarrow O_3S-S-SO_3^= + S-SO_3^=$

(1 - 11) $O_3S-S-S-SO_3^= + \overset{*}{S}O_3^= \rightarrow O_3\ S-S-S-\overset{*}{S}O_3 + SO_3^=$

Reaction (1 - 10) involves the displacement of thiosulfate from tetrathionate by sulfite and therefore involves a chemical change whereas reaction (1 - 11) only involves an exchange of sulfite groups. Reactions (1 - 10) and (1 - 11) do not differ in the point of attack by the incoming sulfite but differ in the site of S-S bond fission in the tetrathionate chain. Since the S-S bond lengths vary in the tetrathionate chain, then the semiempirical correlation of Davis(39, 40), which relates S-S bond lengths with nucleophilic displacement rates, can be used to predict the relative rates of reactions (1 - 10) and (1 - 11).

Some aspects of the kinetics of reaction (1 - 10) were studied many years ago by Foerster and Centner(41) who found the process to be first order in both sulfite (or bisulfite) and tetrathionate; however the effects of pH and ionic strength were not determined in this work. The kinetics of the sulfite-tetrathionate reactions were therefore determined in the pH range of 2.92-4.12 to extend the work in reference(41). In the same pH region an ^{18}O-labelling technique was used to check the relative rates of reactions (1 - 10) and (1 - 11) to form a basis for examining the validity of the Davis correlation. This pH range was used because it corresponds with the maximum chemical stability of tetrathionate(42), and moreover since the sulfite-water oxygen exchange reaction is extremely rapid in this region(35), a significant involvement of reaction (1 - 11) would lead to oxygen transfer between solvent and tetrathionate.

1 - 5 THE THIOSULFATE-SULFITE SYSTEM:

The isotopic exchange reaction of sulfur in the aqueous system sulfite-thiosulfate was examined some years ago by Ames and Willard(43). The outer sulfur of thiosulfate is transferred to sulfite at a measurable rate, the reaction being first order in both sulfite and thiosulfate, and zero order with respect to hydrogen ion. It will at once be evident that transfer of the outer S from thiosulfate converts the donor ion to sulfite and the acceptor ion to thiosulfate. As mentioned above, this is equivalent to transfer of oxygen from one species to the other. More recently, oxygen transfer between water and thiosulfate has been examined over a limited range of temperature and pH(44). The reaction is observable, but slow, e.g.

half-time of 20-30 hours at pH 6.0 and at a temperature of 80°C. In view of the known S atom transfer process(43), addition of sulfite would be expected to provide an alternate route for transfer of oxygen between thiosulfate and water, in pH regions where the sulfite-water oxygen exchange process (1 - 12) is reasonably rapid:

(1 - 11) $S_2O_2{}^{18}O^= + SO_3^= \rightarrow S_2O_3^= + SO_2{}^{18}O^=$

(1 - 12) $SO_2{}^{18}O^= + H_2O \rightarrow H_2{}^{18}O + SO_3^=$

The authors of Reference (44) have found no evidence of this coupled path, in that addition of 0.01M sulfite to 0.1M ^{18}O-thiosulfate produced no noticeable acceleration of oxygen transfer from water to thiosulfate. They suggested that the apparent lack of catalysis by sulfite was probably due to the slowness of the sulfite-H_2O exchange reaction. However, a recent study of the kinetics of the sulfite water exchange(35) shows that for the conditions of temperature and pH used in Reference (44) oxygen exchange between these latter species is very rapid, and indeed the oxygen in H_2O and sulfite would be always at isotopic equilibrium for the time scale (hours) used in Reference (44).

To resolve this discrepancy, the kinetics of ^{18}O-exchange in the system thiosulfate-sulfite-water was studied using ^{18}O-labelled thiosulfate, from pH 3 to 13, and for sulfite-thiosulfate ratios from 0.75 to 4.0. The results confirm that the S-atom transfer process provides an important route for interchange of oxygen between thiosulfate and water. As is outlined more fully below, the results at appropriate pH values, provide a most interesting illustration of a system of reversible, consecutive, first-order rate processes. Such systems have been examined theoretically a number of times, but to the best of our knowledge, no actual chemical systems of this kind have been described hitherto.

1 - 6 A SEARCH FOR REACTIVE INTERMEDIATES IN THE OXIDATION OF THIOSULFATE:

Most oxidation-reduction reactions involving oxyanions are believed to proceed in many steps of low molecularity. In writing mechanisms for such reactions different authors have postulated various intermediate species and in many of the cases these intermediates were believed to be more reactive than either reactants or products. If these intermediates are truly as reactive as is sometimes believed, then they might be expected to interact strongly with the solvent in their short lifetime.

It was mentioned earlier that the oxidation state of the central atom of an oxyanion strongly influences the oxygen exchange rate observed for a particular oxyanion. For example sulfite exchanges oxygen much more rapidly than thiosulfate or sulfate; however, the slow rate observed for the exchange in the latter two oxyanions may be due to their tetrahedral structure which accompanied the oxidation change. The oxidation of thiosulfate to tetrathionate or sulfate does not involve any great structural changes (all are approximately tetrahedral around the central sulfur atom) but a change in the oxidation state of the central atom takes place.

Thus a problem often encountered in oxidation reduction reactions of oxyanions is this: What is the co-ordination number of the central atom in the transition state and to what species is the central atom bound? It has been suggested(24) that the co-ordination number of the central atom often changes and that the substrate species often joins in a chemical bond with the central atom during or prior to the transition state of the oxidation-reduction reaction. If this is so, then the co-ordination number change may provide a route by means of which oxygen exchange may occur.

A number of intermediates have been postulated in the mechanism of oxidation of thiosulfate by various reagents. The uncharged species, S_2O_3, has been proposed by Foss(36) and by Edwards(45). The radical anion, $S_2O_3^{\overline{\cdot}}$, used to be postulated as an intermediate in reactions with iodine(46) but is now believed to exist only in the reaction of thiosulfate with peroxydisulfate(47), and also in the electrolysis of thiosulfate and in the photolysis of tetrathionate. The most commonly postulated intermediate in the oxidation of thiosulfate is a complex of thiosulfate with the donor such as $IS_2O_3^-$(48). A complete list of intermediate complexes of thiosulfate postulated in kinetic studies has been given by Edwards(6). In the reaction of Fe(III) with thiosulfate there is direct visual evidence of complex formation prior to electron transfer; a violet color appears upon mixing of these reagents followed by its gradual fading(49). Since all these oxyanions, thiosulfate, tetrathionate and sulfate, exchange oxygen with water very slowly then this system provides an excellent opportunity to check for reactive intermediates by means of exchange studies.

To examine some of these possibilities, thiosulfate was oxidized with a number of substrates including I_3^- , Fe(III), Cu(II), $CuPy_4^{+2}$, $S_2O_8^=$ and H_2O_2 under a variety of conditions. ($CuPy_4^{+2}$ represents a Copper (II) tetrapyridine complex). In addition, thiosulfate was oxidized electrolytically, and tetrathionate was photolyzed in ^{18}O-labelled water in an attempt to produce the radical anion, $S_2O_3^{\dot{-}}$ and to check thereby the lability of its oxygen atoms.

EXPERIMENTAL

2

2 - 1 MATERIALS:

Water enriched to approximately 1.6 atom percent ^{18}O (obtained from YEDA Research and Development Co. Ltd., Rehovoth, Israel) was distilled from alkaline permanganate through a glass-packed fractionation column. Water of normal isotopic composition was doubly distilled.

Silver cyanide (AgCN, purified powder, J.T. Baker Chemical Co.) was stored under vacuum over phosphorus pentoxide.

Sodium tetrathionate (K and K Laboratories Inc.) was analyzed by the procedure described by Jay(50). On the basis of infrared spectra of a Nujol mull and from the chemical analysis, it was found to be the dihydrate; $Na_2S_4O_6 \cdot 2H_2O$.

Tetrathionate was precipitated from aqueous solutions for isotopic oxygen analysis by a copper(II) tetrapyridine complex, $CuPy_4^{+2}$, (Py represents pyridine)(51). Copper(II) tetrapyridine tetrathionate precipitates readily after being stirred a few seconds as blue needles or elongated prisms of the formula $CuPy_4S_4O_6$. Copper(II) tetrapyridine reagent also precipitates trithionate and pentathionate, but only the pentathionate forms a hydrate, $CuPy_4S_5O_6 \cdot 2H_2O$. The copper(II) tetrapyridine trithionate forms rectangular violet crystals which may readily be distinguished from the tetrathionate precipitate. Of the three copper(II) tetrapyridine polythionate precipitates the most stable and at the same time the most insoluble is the tetrathionate.

This precipitate filters readily and when washed with acetone or ether gives a dry anhydrous product. Sulfite and sulfate do not interfere in these precipitations. Copper(II) tetrapyridine reagent was prepared by dissolving copper(II) acetate or nitrate in water and then adding an excess of pyridine to form the tetrapyridine complex of copper(II). The usual concentration of this reagent was 0.5M.

Thiosulfate was determined in the presence of sulfite by complexing the latter with formaldehyde and then titrating thiosulfate with iodine solution. Both sulfite and thiosulfate were determined in the sulfite-tetrathionate reaction by titrations with iodine. A 0.010M iodine solution was prepared by weight from solid iodine (resublimed U.S.P. Shawinigan). The concentration of the iodine solution was periodically checked against freshly-prepared sodium sulfite and sodium thiosulfate solution which were prepared from anhydrous reagents.

The following chemicals were used without any further treatment: sodium sulfite (Na_2SO_3 anhydrous, certified A.C.S. Fisher); sodium thiosulfate ($Na_2S_2O_3$, anhydrous, certified A.C.S. Fisher); sodium sulfate (Na_2SO_4 anhydrous, reagent, Shawinigan); copper acetate ($Cu(CH_3COO)_2$, reagent, A.C.S., Allied Chemical); lead oxide (PbO, mono-yellow, certified, Fisher); bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$ certified, Fisher); perchloric acid (C.P. reagent, C.I.L.); hydrochloric acid (C.P. reagent C.I.L.); citric acid ($H_3C_6H_5O_7 \cdot H_2O$, reagent A.C.S. powder, Matheson, Coleman & Bell); sodium chloride (NaCl, certified, A.C.S. Fisher); sodium hydroxide (NaOH, certified A.C.S. Fisher); sodium iodide (NaI, May and Baker); strontium chloride ($SrCl_2$, certified, Fisher); ammonium acetate (CH_3COONH_4, certified, Fisher); pyridine (C_5H_5N, "Baker Analyzed" reagent J.T. Baker Chemical Co.); barium chloride ($BaCl_2$, reagent A.C.S. Mallinckrodt); ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, certified, Fisher); mercuric chloride ($HgCl_2$, N.F. granular, Mallinckrodt); sodium fluoride (NaF, "Baker Analyzed" reagent, J.T. Baker Chemical Co.); sodium persulfate ($Na_2S_2O_8$, reagent, British Drug Houses); hydrogen peroxide (H_2O_2, 30% certified Fisher); argon (Matheson, H.P.).

2 - 2 SPECIAL PREPARATIONS:

Hydroxy lead perchlorate, $Pb_4(OH)_4(ClO_4)_4$, was prepared by the method of Maroni and Spiro(52). Lead oxide (yellow PbO) was dissolved in a slight excess of 6N perchloric acid. This solution was digested near the boiling point until clear. Then PbO was added to the boiling solution until it was neutral to litmus. This solution was then evaporated until crystallization occurred. The crystalline salt was recovered by filtration and pressed dry on filter paper. A sample of this salt was used to prepare a solution (3.2940 g/100 ml) which was analyzed for lead and perchlorate. Lead was determined as the sulfate precipitate with sulfuric acid. Total perchlorate was determined by titration with standard base solution of the acid liberated when a sample of the aqueous solution was passed through a cation exchange resin (AG-50W-X8, Bio-Rad). The ratio Pb:ClO_4^- was found to be 0.92. The measurement of weight loss following intensive drying under vacuum showed this prepared salt contained 3 moles of H_2O per mole of $Pb_4(OH)_4(ClO_4)_4$. This salt was finally dehydrated under vacuum at 100°C before use in the oxygen exchange experiments, described later.

Polynuclear hydroxy bismuth perchlorate, $Bi_6(OH)_{12}(ClO_4)_6$ was prepared by the methods described in the literature(53, 54). Bismuth oxide, Bi_2O_3 was prepared by hydrolysis of an aqueous solution of $Bi(NO_3)_3$. The hydroxide was heated at 700°C until yellow Bi_2O_3 was obtained. The Bi_2O_3 was then dissolved in concentrated perchloric acid in a molar ratio of 1:2. Dissolution was completed by digesting at 100°C until the solution became clear. The solution was concentrated by evaporation until precipitation occurred. Analyses for both bismuth and perchlorate were performed on a solution made from this prepared salt. Bismuth was determined as the insoluble BiOCl(55), while perchlorate was determined as described earlier for the corresponding lead compound. The Bi:ClO_4^- ratio was found to be 0.90. The excess perchlorate was due to unhydrolyzed bismuth as $Bi(ClO_4)_3$. Water of hydration was determined from the weight difference from analysis and weight of salt used to make up the solution. The hydroxy bismuth perchlorate prepared by this method corresponded to the formula $Bi_6(OH)_{12}(ClO_4)_6 \cdot 0.4Bi(ClO_4)_3 \cdot 10H_2O$.

Oxygen-18 labelled sodium thiosulfate was prepared from sodium sulfite according to the method of Hargreaves and Dunningham(56). Sodium sulfite was first equilibrated with ^{18}O-labelled water for a few hours at 60°-70°C. Then roll sulfur was added so that the mixture has a molar ratio of sulfite: water: sulfur of approximately 1:5:1.5 (excess sulfur was used). This mixture was digested at 80°C in a stoppered flask for several days. Sulfite rapidly reaches isotopic equilibrium with the labelled water and reacts with sulfur to form $Na_2S_2O_3 \cdot 5H_2O$. This material is a liquid above 48°C in which other materials present are insoluble. It was filtered through a sintered glass filter above 50°C and the separated liquid $Na_2S_2O_3 \cdot 5H_2O$ dehydrated under vacuum at 90°-100°C. Iodometric analysis of the product thiosulfate indicated it to be 99% $Na_2S_2O_3$ and less than 1% Na_2SO_3. The isotopic ^{18}O composition, determined by the procedure described in Section 2 - 3 was 1.24 atom percent ^{18}O. This material was used in experiments without further purification.

2 - 3 MASS SPECTROMETRY:

Oxygen-18 isotope abundances can be obtained from density measurements, infrared spectra, neutron activation and from mass spectrometry. The inherent precision of mass spectrometric techniques which involve simultaneous collection of two different masses(57), is much greater than the other methods so that mass spectrometry was used exclusively to determine the oxygen-18 content of the various compounds.

In most cases it is necessary to convert the oxygen in oxygen-containing compounds to a form which is suitable for mass spectrometry. Oxygen-18 content of water is not usually determined directly by mass spectrometry because of the difficulty of removing adsorbed water molecules from the walls of the mass spectrometer and because of its possible corrosive effects on the internal parts of the mass spectrometer. Carbon dioxide is the most suitable compound for mass spectrometric determination of oxygen-18 content because of its low or zero retention by surfaces and also because it is easily handled and purified in ordinary vacuum lines.

There are four general kinds of oxygen-18 tracer experiments in aqueous systems. These may be summarized as follows: (i) Label the water, dissolve an unlabelled solute, and follow the decrease of the ^{18}O content of the water, or (ii) Follow the increase of the ^{18}O content of the solute. (iii) Label the solute, dissolve in unlabelled water, and follow the increase of the ^{18}O content of the water, or (iv) Follow the decrease of the ^{18}O content of the solute. In this work all four methods have been applied. Since the concentration of oxygen atoms in the water (55.5 g-atoms oxygen $l.^{-1}$) is invariably much greater than the concentration of oxygen in the solute, then methods (i) and (iii), which follow the increase or decrease of oxygen-18 in water, are much less sensitive to changes in the $^{18}O/^{16}O$ ratio.

Measurement of the isotopic composition of water is made either by equilibrating it with CO_2 or by converting the oxygen of the water into CO_2 or O_2 by chemical means. Solutes are generally converted to CO_2 by chemical means in order to determine their oxygen-18 abundance.

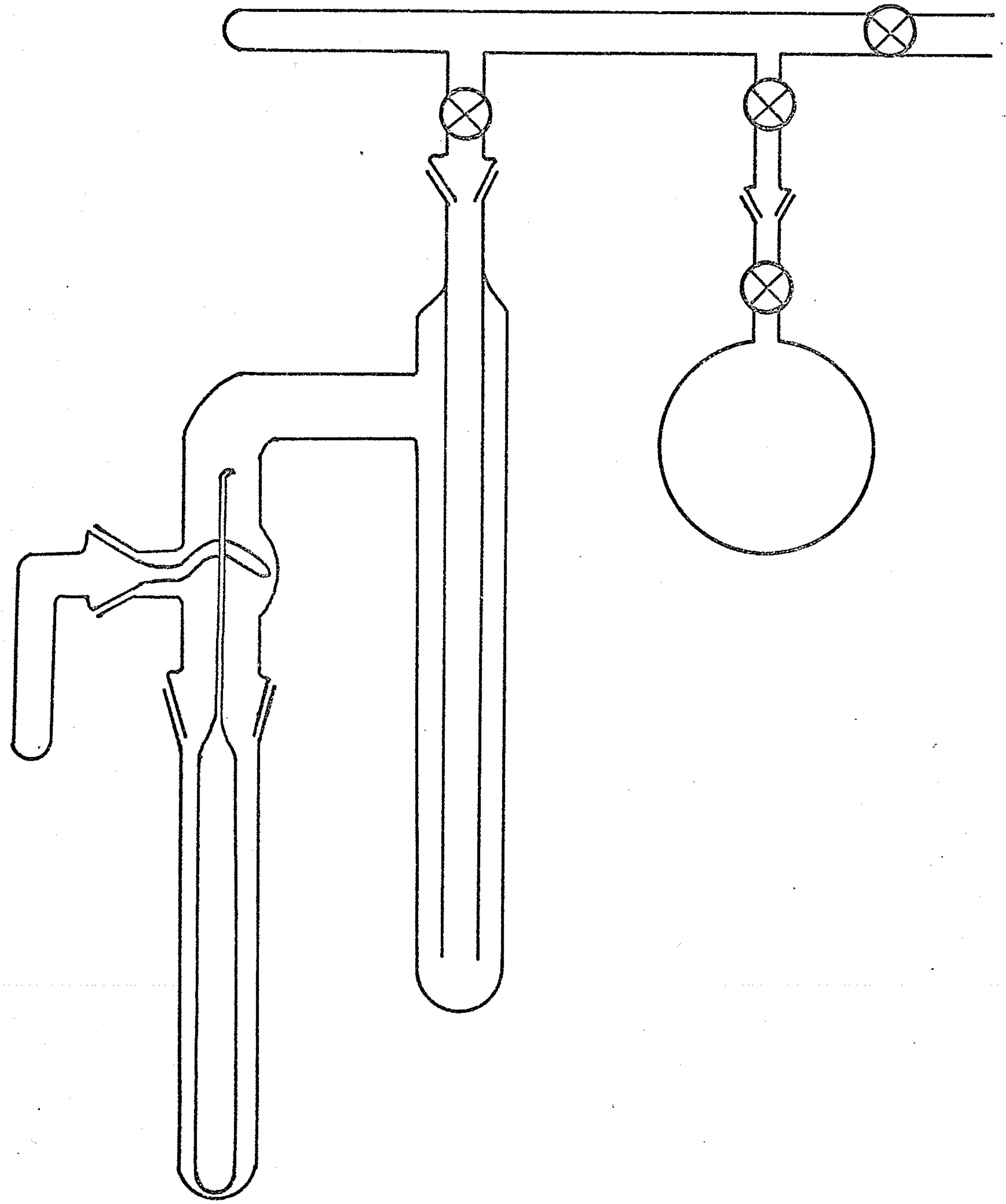
There is a large variety of methods for converting oxygen of oxygen-containing compounds into CO_2 for mass spectrometry some of which are specific for particular compounds, while others are more general. The method suggested by Shakhashiri and Gordon(58) for conversion of the oxygen of compounds into carbon dioxide is applicable to water and a large variety of inorganic compounds, and was used in this work.

This method involves conversion of the oxygen of the compounds to carbon dioxide by heating the sample with AgCN in an evacuated sealed ampoule for 2 hours at 500°C. Silver cyanide decomposes at 320°C into cyanogen gas and metallic silver. The cyanogen combines with the oxygen of the water or of the compound to form CO_2. Cyanogen, nitrogen and carbon monoxide are among the other major gaseous products formed. At 500°C, most of the excess cyanogen is polymerized to solid paracyanogen.

The procedure used throughout this work was to add the sample (containing usually 0.6 millimoles of oxygen) to 0.2 to 0.4 millimoles of silver cyanide (30-50 milligrams) in a pyrolysis tube. The pyrolysis tube was constructed of pyrex glass (20 cm. by 12 mm., o.d.), and fitted with a ground glass joint for attachment to the

Fig. 2

Breaker assembly for recovery of CO_2
after pyrolysis



vacuum line. The tube was then evacuated to $10^{-4} - 10^{-5}$ torr, and sealed off. For analysis of water, silver cyanide was placed in the tube which was then constricted and evacuated before water was transferred into it. Water transfer was made quantitative by cooling the lower end of the tube with liquid nitrogen before sealing and drawing off from the vacuum line. The sealed tubes were then placed in a furnace at 500°C for approximately 2 hours. When pyrolysis was complete, the tube was cooled to room temperature and enclosed in the breaker assembly shown in Fig. (2) for recovery of the carbon dioxide. The breaker assembly was evacuated under high vacuum for several minutes and then closed off to the vacuum pump. The tube was next opened by turning the handle of the breaker. Carbon dioxide along with other volatile products was first condensed in a purification trap maintained in a methylcyclohexane slush bath (-126°C) or in an n-pentane slush bath (-130°C). The slush baths were prepared by partially freezing the organic liquids with liquid nitrogen. Carbon dioxide was then sublimed from this trap to a bulb maintained at liquid nitrogen temperature (-196°C), leaving less volatile products (e.g., cyanogen) behind in the trap. Once transfer of carbon dioxide was complete (approximately 2 minutes), the non-condensible gases such as carbon monoxide, hydrogen and nitrogen were removed by pumping on the bulb for a few seconds. One purification was sufficient to produce carbon dioxide sufficiently pure for mass spectrometric analysis.

Isotopic analysis of the carbon dioxide was done with a

Varian-Mat GD-150 isotope ratio mass spectrometer. This spectrometer was specifically designed for precise isotope ratio determinations. It is equipped with a dual-inlet system for fast comparison of a particular sample against a standard sample of known isotopic composition and also with a double ion collector for the simultaneous collection of two isotopes for direct ratio determination.

In general there are two ways of admitting a gas sample to the ion source of a mass spectrometer, through a molecular leak or through a viscous leak. The GD-150 was equipped with a viscous leak. For isotope abundance measurements the molecular leak has the disadvantage that molecular effusion is mass dependent. For viscous flow to be dominant in a viscous leak, the gas must flow through the greater part of the length of the leak at a sufficiently high pressure for the mean free path of the gas to be much smaller than the dimensions of the leak. Under steady-state conditions, the ratio of the two components in the gas emerging from the viscous leak should be the same as their ratio in the reservoir. If the reservoir pressure drops too low, then the mean free path of the molecules will increase and molecular flow will occur.

For viscous flow to be dominant the pressure on the reservoir side of the tube must be much greater than on the inlet side of the tube. In the GD-150 spectrometer, reservoir pressures of 30 to 50 mm. Hg were used and since the pressure in the ion source was of the order of 10^{-6} to 10^{-7} mm. Hg, then conditions were appropriate for viscous flow. Since CO_2 was collected in 25 ml. bulbs, a sample size of 1 to 2 cc. of CO_2 at NTP was required to obtain this pressure in the reservoir of the mass spectrometer.

The accuracy of an abundance measurement depends in general on the magnitude of the ion current, and hence on the amount of sample available and on the abundance of the isotope under investigation. Therefore, high sample pressures were used when available. Moreover, the mass spectrometer has a relatively high density electron beam (250 μA) to ionize as much of the sample as possible. Also the ion source was equipped with an exit slit which was as wide as possible to give a high ion current in the analyzer and yet give a sufficiently high resolution to separate the isotopic masses under investigation. In this mass spectrometer an exit slit of 0.10 mm. was used giving a resolution of approximately 70. This was more than enough to separate the isotopic masses in carbon dioxide, namely masses 44, 45 and 46.

For precision isotope measurements a Faraday cup collector is a superior ion collector since the response of this collector is independent of ion mass, whereas the response of detectors such as electron multipliers are mass dependent and sometimes the output is non-linear with ion current as well. The Varion-Mat GD-150 was equipped with a double Faraday cup collector system. This system collects the abundant isotope on a wide slit collector and the less abundant isotope on a second collector placed behind a narrow slit in the first collector. Measurements for oxygen-18 content on carbon dioxide are done by focusing mass 46 (i.e., $^{12}C^{16}O^{18}O$), on the slit in the wide collector. Therefore the wide slit collector collected masses 41 to 49 except mass 46 which passed through the slit onto the second collector. The most abundant mass in the range 41 to 49 is mass 44 ($^{12}C^{16}O^{16}O$). Since ion currents generated by the sample were quite large as compared with background, the background contributed negligibly to the total ion current on the wide slit collector. The ion currents on these collectors were measured by using electrometer tubes to amplify the voltage drop produced by the ion current across a high ohmic resistor. The outputs of these amplifiers were made more similar by using a high resistance for the less intense current (10^{11} ohms for ion current due to mass 46 and 10^{10} ohms for ion current due to masses 44 and 45), thus producing a larger voltage drop and therefore eliminating some of the electronic difficulties in comparing the two markedly disparate voltages. The outputs of the two amplifiers was sent to an electrical bridge circuit, whereby the lower of the two ion currents was compensated by a portion of the higher current to yield a zero signal. A potentiometric recorder was used as a null instrument. The bridge thus gave a so-called P-factor which was the ratio of the ion currents on the two collectors. This P-factor is then the ratio of the abundance of carbon dioxide of mass 46 to that of masses 44 and 45 ($^{12}C^{16}O^{18}O$ to $^{12}C^{16}O^{16}O$ + $^{13}C^{16}O^{16}O$ + $^{12}C^{17}O^{16}O$ ratio). The P-factors are proportional to the abundance of oxygen-18 in the carbon dioxide samples.

The P-factors obtained from this instrument are not identical to calculated ratios from known naturally-occurring isotope abundances because the resistors in the two amplifiers were not perfectly matched. The P-factors were approximately 10% lower than the calculated ratios. For example, the measured P-factor for carbon dioxide containing 0.2039 atom percent oxygen-18 (natural abundance) was 0.00370 whereas the calculated ratio is 0.004043(59). This is of no consequence in this work, as we were not interested in absolute abundance ratios but only in the differences of oxygen-18 isotope abundances in different samples relative to each other, or to a standard. The P-factors were used directly in most of the comparisons of oxygen-18 abundance in various samples and in most of the calculations encountered in this work.

POLYNUCLEAR HYDROXY CATIONS OF LEAD AND BISMUTH

3

3 - 1 EXPERIMENTAL:

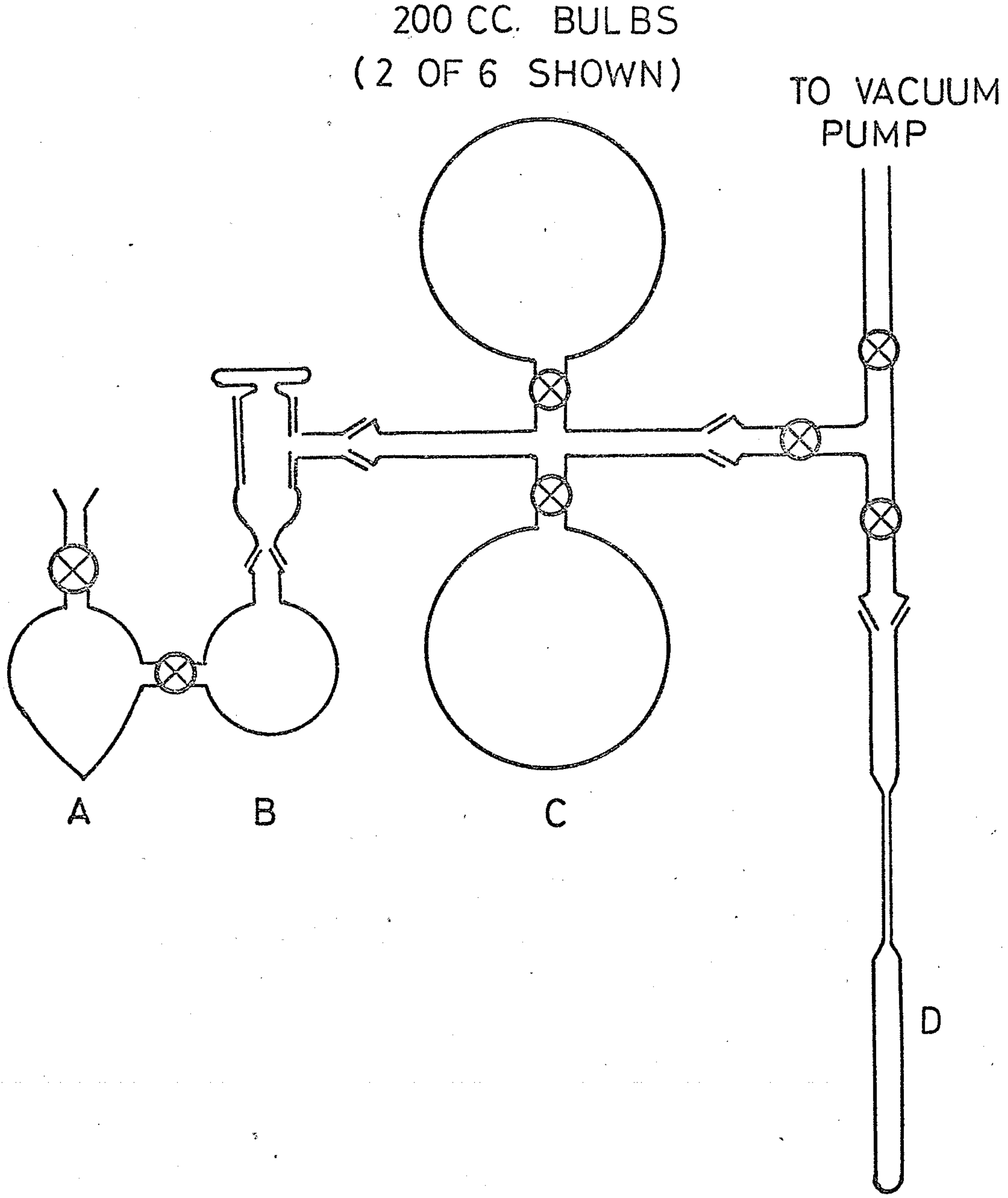
(i) $Pb_4(OH)_4(ClO_4)_4$ ^{18}O-Exchange with Water:

Oxygen-18 exchange between water and $Pb_4(OH)_4(ClO_4)_4$ was followed using the apparatus illustrated in Fig. 3. The actual exchange reaction was carried out in the two-compartment reaction flask, the volume of each compartment being approximately 25 cc. The compartments are designated by A and B in the Figure. In compartment A 3.0 ml. of oxygen-18 labelled water was placed and degassed prior to the start of the exchange reaction by freeze-pump-thaw cycles and then stored under vacuum in this compartment. Compartment B contained 3.8832 grams of vacuum dehydrated $Pb_4(OH)_4(ClO_4)_4$ salt which had been prepared for this experiment (see Section 2 - 2 for details of preparation). The whole procedure for this exchange study was carried out at room temperature. The whole apparatus including compartment B was evacuated to a high vacuum, and the six 200 ml. storage bulbs, (labelled C in Fig. 3), on the vacuum manifold, were closed off.

The exchange reaction was started by tilting the reaction cell suitably and opening the stopcock connecting compartments A and B so that the degassed water would flow into compartment B containing the lead salt. When half the salt dissolved (approximately 2 seconds) the clock used to time the sampling points was started. The reaction flask was agitated periodically, and especially before each sample was withdrawn, to ensure that vapor and liquid were in isotopic equilibrium.

Fig. 3

Apparatus for collecting water vapor samples in oxygen exchange experiments


200 CC. BULBS
(2 OF 6 SHOWN)
TO VACUUM PUMP
A
B
C
D

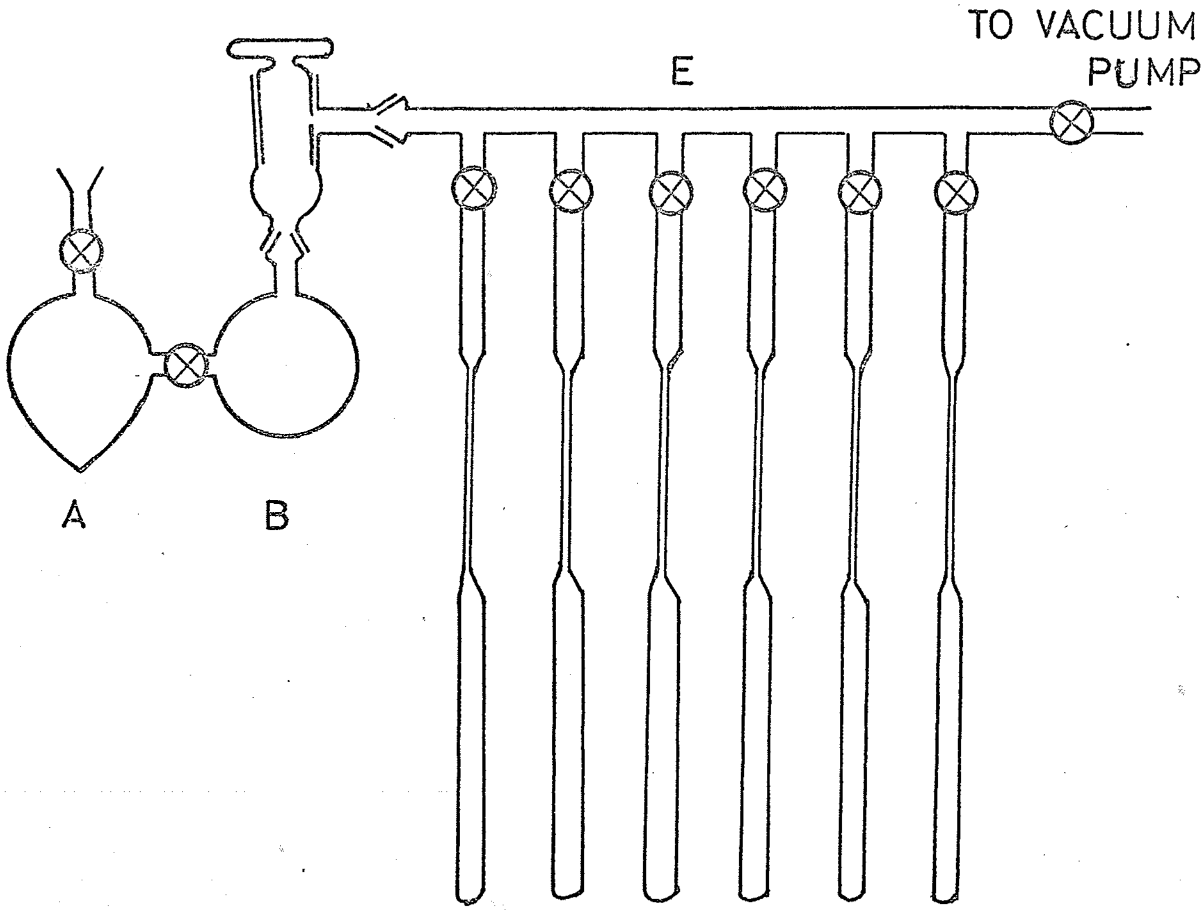
The progress of the exchange was followed by taking samples of water by evaporation under vacuum at suitably-timed intervals.

Each sample of water vapor was obtained in the following manner. The manifold connecting compartment B and the 200 ml. storage bulbs was first filled with water vapor from compartment B; this vapor was immediately pumped away. This was done to equilibrate the walls of the manifold with the water vapor currently being sampled and to reduce cross contamination between samples. Next compartment B was connected to one of the storage bulbs to collect a sample of water vapor from the reaction mixture. Only a few seconds were required to fill a given storage bulb, which was then closed off and the manifold evacuated in preparation for the next sample. This procedure was repeated until all the storage bulbs were filled. The water vapor from these storage bulbs was then transferred by vacuum transfer to pyrolysis tubes (labelled D in Fig. 3), which already contained silver cyanide. Pump out times of approximately 10 minutes between sample transfers was used to reduce cross contamination on the wall of the vacuum system. Procedure for conversion of the oxygen of water vapor to carbon dioxide and its subsequent isotopic analysis have been described in Section 2 - 3.

The reaction mixture used in the exchange experiment described above was allowed to equilibrate for several days and then the water was removed under vacuum, leaving oxygen-18 labelled hydroxy lead perchlorate; the oxygen-18 label being in the hydroxy positions,

Fig. 4

Modified apparatus for collection of water vapor samples in oxygen exchange experiments


TO VACUUM
PUMP
E
A
B

since perchlorate anions do not exchange oxygen with water at any appreciable rate. This oxygen-18 labelled hydroxy lead perchlorate was dried by vacuum pumping at room temperature overnight and then used in a reversed exchange reaction by using as solvent, water containing a natural abundance of oxygen-18. The procedure used for this reversed exchange reaction was the same as that already described above.

(ii) $Bi_6(OH)_{12}(ClO_4)_6$ Oxygen-18 Exchange with Water:

Oxygen exchange between water and $Bi_6(OH)_{12}(ClO_4)_6$ was examined using an apparatus similar to that used in the hydroxy-lead investigation but with the modifications shown in Fig. 4. The reaction flask was unchanged, but the collection manifold had been replaced. Instead of storing the water vapor sample in a storage bulb it was frozen down directly into the pyrolysis tube attached to the manifold (E). This change to direct sampling procedure was done to minimize cross contamination between successive samples. The manifold was flushed with a sample of water vapor before each sample for isotopic analysis was taken.

The procedure used in this experiment was similar to that used in the hydroxy lead exchange experiments. The exchange reaction was performed using 3.0 ml. of oxygen-18 labelled water in compartment A and 7.5640 grams of the hydroxy bismuth perchlorate prepared for this experiment (see Section 2 - 2 for synthesis procedure) in compartment B. The exchange was carried out at room temperature. In this case, however, the clock used to time the sample collection points was started before the water was let into the cell containing the salt. Preliminary experiments indicated the exchange was rapid so samples of water vapor were taken as rapidly as possible with this apparatus, the first sample was taken just after the salt had completely dissolved. The salt required 30-40 seconds to dissolve completely.

Following this series of measurements the reaction mixture was allowed to equilibrate at room temperature for two days and the water was removed by vacuum distillation. The salt was dried by pumping on it overnight at room temperature. This left oxygen-18 labelled hydroxy-bismuth perchlorate, the label being in the hydroxyl positions.

The reversed exchange was next examined using water of normal oxygen-18 abundance as solvent. The clock was again started just as the water was let in. It took slightly over a minute for the salt to completely dissolve because it had dried onto the walls of the reaction vessel during the vacuum drying procedure and, therefore, could not be mixed efficiently. The sampling procedure was the same as that used in the forward exchange experiment described above.

3 - 2 RESULTS:

As mentioned in Section 2 - 3 the P-factors obtained from the mass spectrometer are proportional to the $^{18}O/^{16}O$ ratio in the sample being analyzed. Therefore oxygen isotopic abundances were

TABLE I

^{18}O-EXCHANGE BETWEEN $Pb_4(OH)_4^{+4}$ AND H_2O AT ROOM TEMPERATURE

FORWARD EXCHANGE:

Time of Sample	Measured P-Factor
0	(0.0274)
35 seconds	0.0258
72 seconds	0.0255
30 minutes	0.0255
Calculated equilibrium§	0.0258
$H_2{}^{18}O$	0.0274
$Pb_4(OH)_4^{+4}$ (natural abundance)	0.00370

REVERSED EXCHANGE:

Time of Sample	Measured P-Factor
0	(0.00370)
24 seconds	0.00601
43 seconds	0.00622
78 seconds	0.00612
1 hour	0.00578
Calculated equilibrium§	0.00595
H_2O (natural abundance)	0.00370
$Pb_4(OH)_4^{+4}$ †	0.0258

§ See Appendix I for calculation of equilibrium P-factors.

† The P-factor for this material was taken as the calculated equilibrium value from the previous forward exchange.

compared in terms of P-factors in this section. The results of both the forward and reversed oxygen-18 exchange experiments between polynuclear hydroxy lead ions and water are given in Table I. The forward reaction involves net transfer of oxygen-18 from water to the polynuclear hydroxy lead species, while for the reverse reaction the net transfer is in the opposite direction. Since water was being analyzed for oxygen-18 abundance to follow the progress of the exchange reaction the oxygen-18 content of the water decreased in the forward reaction and increased in the reverse reaction.

The hydroxy lead perchlorate dissolved in water extremely rapidly (approximately 1-2 seconds for half the salt to dissolve and within 5 seconds for complete dissolution at room temperature). This salt was also extremely soluble, since the solutions used here were approximately 4M in Pb and this was by no means the maximum solubility of this salt.

The sampling technique used in this experiment was quite rapid. A single sample was taken in a time period of 1 to 2 seconds. The time between successive samples was 15 to 20 seconds. Since the hydroxy lead perchlorate dissolved so rapidly the start of the reaction could be defined quite accurately. Then the time of the first sample from the start of the reaction was also known quite accurately. As is seen from the results in Table I, the first sample could be collected within 25 seconds from the start of the reaction.

However, this sampling method was not fast enough as complete exchange had occurred within the time of the first sample and no further exchange could be observed after this first sample. The small variations that are observed amongst subsequent samples are most likely due to contamination effects in transferring water vapor samples in the vacuum system. The good agreement between the calculated equilibrium P-factors (see Appendix I for details of calculation) and the measured P-factors indicates that exchange equilibrium has been reached and that the contamination effects are random and not very large.

The results for the oxygen exchange between the polynuclear hydroxy bismuth ion and water are given in Table II. The sampling and timing procedures were changed from that used in the hydroxy lead experiments. Zero time here was taken as the instant the water was mixed with the salt. The bismuth salt, in contrast to the lead salt, took much longer to dissolve (approximately 30-40 seconds) and therefore there was much greater uncertainty in the true zero time. The sampling procedure was improved by going to direct sampling and eliminating the storage bulbs. Sufficient sample for an analysis (2-5 mg. H_2O) was frozen down into the pyrolysis tubes in the time taken for one twist of the stopcock. (The stopcock was actually in open position for only a fraction of a second). The greater uncertainty in the true sample time from zero time does not matter as the exchange was complete in the time of the first sample.

The low value for the first sample of the reversed exchange of the bismuth hydroxy ion was due to the fact that during drying of

TABLE II

^{18}O-EXCHANGE OF $Bi_6(OH)_{12}^{+6}$ WITH H_2O

FORWARD EXCHANGE:

Time of Sample	P-factor
0	(0.0295)
1 minute	0.0221
2 minutes	0.0222
4 minutes, 15 seconds	0.0223
Calculated equilibrium§	0.0223
Initial $H_2{}^{18}O$	0.0295
$Bi_6(OH)_{12}^{+6}$ (natural abundance)	0.00370

REVERSED EXCHANGE:

Time of Sample	P-factor
0	(0.00370)
1 minute	0.00723
5 minutes	0.00861
10 minutes 5 seconds	0.00860
15 minutes 10 seconds	0.00868
Calculated equilibium§	0.00902
H_2O (natural abundance)	0.00370
$Bi_6(^{18}OH)_{12}^{+6}$ †	0.00223

---

§ See Appendix I for details of calculation of equilibrium P-factor.

† The P-factor for this material was taken as the equilibrium P-factor from the forward exchange reaction.

the sample in the bulb from the previous run the salt had dried onto the walls of the flask. Therefore it was not completely dissolved when the first sample was taken. The rise in P-factor in the subsequent samples to a constant value after complete dissolution indicates the exchange is complete. The calculated equilibrium P-factors (see Appendix I for details of calculation) agree very well in the forward exchange with the measured P-factors, thus proving exchange equilibrium had been reached. The fact that the calculated P-factor for the reversed exchange is somewhat higher than the measured values is most likely due to the fact that the salt, when dried under vacuum overnight, partially dehydrated and therefore contained less than the 10 water molecules per mole of $Bi_6(OH)_{12}(ClO_4)_6$ that were present in the forward reaction.

If 0.00868 is taken as the equilibrium P-factor for the reversed exchange then the number of exchangeable oxygens per mole of $Bi_6(OH)_{12}(ClO_4)_6 \cdot xH_2O$ can be calculated. From such a calculation the number of exchangeable oxygens is 19.9 per mole of $Bi_6(OH)_{12}(ClO_4)_6$. Since 12 of these are in the hydroxyl positions then these results are consistent with there being 7.9 moles of water per mole of $Bi_6(OH)_{12}(ClO_4)_6$ starting material in the reversed exchange reaction.

3 - 3 .DISCUSSION:

The results have shown that the exchange of oxygen between either the polynuclear hydroxy lead or hydroxy bismuth ions and water has reached isotopic equilibrium before the first sample had been taken. The time of the first sample was one minute or less. The half-time for exchange must therefore be considerably less than a minute and could easily be as small as a fraction of a second.

A considerable fraction of the isotopic exchange must take place before the salt is completely dissolved. Therefore this method used here is inadequate for the time scale involved. Other methods of following this exchange reaction must be used if the true rate of exchange is to be measured. This method, however, has indicated that the exchange of oxygen between these closely-knit structures and water does take place extremely rapidly. We conclude that incorporation of oxygen (either as OH or H_2O) in highly-organized, multi-bonded structures, does not by itself, lead to measureably slow exchange with the solvent.

We may speculate about possible mechanisms of exchange. There is the possibility of hydrogen ion catalyzed exchange, since both the hydroxy lead and the hydroxy bismuth solutions were acidic. The pH of the hydroxy lead solution used in the exchange reaction was measured at 5.4 after the exchange was complete. The pH of the hydroxy bismuth solution was not measured although it was acidic to litmus. Thus hydrogen ions could catalyze exchange in ways already discussed.

Other possibilities of exchange are catalysis by the free Pb^{+2} and Bi^{+3} which were shown to be present in these solutions from the quantitative analysis. If the free Pb^{+2} or Bi^{+3} ions replace Pb or Bi atoms in the polynuclear structures then the hydroxy oxygen bonds must be broken to the metal atom being replaced and in this time oxygen exchange could take place with those oxygens not acting as bridge groups during the replacement. This form of catalysis is very unlikely however, since it would mean bringing highly positive-charged species together. Also several metal-metal and metal-oxygen bonds must be broken to eliminate one of the metal atoms from this closely-knit structure, and this seems unlikely.

The amazingly high solubility and the high positive charge of these polynuclear ions indicates there must be considerable interaction of water molecules with these ions. Each metal atom in the structure must have several water molecules attached to it in addition to the bonds to the hydroxyl bridge when they are dissolved in solution. The high positive charges would polarize attached water molecules and make the protons more acidic. Thus an attached water molecule outside the main structure of these polynuclear species could easily lose a proton and become a singly-attached hydroxyl group. Also the low bond order proposed for the metal oxygen bonds (two-thirds in the hydroxy lead species and one-half in the hydroxy bismuth species) in these polynuclear species would mean that one of the externally-attached water molecules could undergo rapid oxygen exchange with other OH groups in the structure. This method of exchange could account for the fast rate of exchange consistent with the retention of the polynuclear structure.

THE SULFITE-TETRATHIONATE SYSTEM

4

4 - 1 EXPERIMENTAL:

A kinetic analysis of the reaction between sulfite and tetrathionate was made by following the concentration of sulfite and thiosulfate in systems for which both pH and tetrathionate concentration were constant. This reaction, Equation (1 - 10);

$$(1 - 10) \quad SO_3^{=} + S_4O_6^{=} \rightarrow S_3O_6^{=} + S_2O_3^{=} \quad ,$$

involves a nucleophilic displacement of thiosulfate by sulfite. The changes in the concentration of sulfite and thiosulfate were followed by iodometric titrations of aliquots of the reaction mixture (see Section 2 - 1 for preparation and standardization of iodine solutions). Thiosulfate was measured in the presence of sulfite by first complexing sulfite with formaldehyde(60).

The buffers for the majority of the experiments were citrate buffers but ammonium acetate and sodium acetate buffers were used as well. Citrate buffers were prepared by partially neutralizing citric acid with sodium hydroxide:

(a) 0.50 moles citric acid + 0.25 moles NaOH per liter
pH = 2.825

(b) 0.50 moles citric acid + 0.50 moles NaOH per liter
pH = 3.455

(c) 0.50 moles citric acid + 0.75 moles NaOH per liter
pH = 4.035

Measurement of pH was made with 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 periodically calibrated with Fisher standard buffers of pH 7.00 and 4.01). The ionic strength of the buffers was adjusted with sodium chloride as required.

A typical run was done as follows: A 0.010M sodium sulfite solution was made up by weight from anhydrous sodium sulfite and dissolved in the appropriate buffer. This solution was brought to the desired temperature (usually 0°C) in a thermostated bath. The reaction was started by adding a previously weighed sample of $Na_2S_4O_6 \cdot 2H_2O$ to this buffered sulfite solution. Complete dissolution required less than 15 seconds. A portion of this solution was then taken for pH measurements. Aliquots of this reaction mixture were then withdrawn as required for iodometric analysis.

Two 10 ml. aliquots of this reaction mixture were withdrawn from the flask for each determination of sulfite and thiosulfate. The aliquots were withdrawn with a thermostated pipette and placed in two additional flasks labelled A and B which were kept in the bath until required for titration. Approximately 10 ml. of 40% formaldehyde solution was added to aliquot A to complex sulfite, and thiosulfate was then titrated with the 0.0101M iodine solution. The blank titration for 10 ml. of 0.010M sulfite with 10 ml. of 40% formaldehyde solution added was less than 0.1 ml. of the iodine solution taken to the starch end point and therefore no corrections were made for the blank. The time for the first sample was taken as the instant of addition of the formaldehyde and titration for thiosulfate was started immediately.

Aliquot B was titrated for total sulfite plus thiosulfate. The time for this sample was taken just as the starch-iodine end point appeared. Titrations generally required 30 to 40 seconds to complete.

The thiosulfate concentration, expressed in ml. of the iodine solution and obtained from aliquot A titrated in each time interval, was then plotted against time and from this plot the thiosulfate concentration corrected to the time of the aliquot B titration in each time interval could be determined. Subtracting this time-normalized thiosulfate concentration from the total sulfite plus thiosulfate titre obtained from aliquot B (both in terms of ml. of the iodine solution), gave the sulfite concentration. That is, B titre minus corrected A titre equals sulfite titre. This method of determining sulfite concentration gave a check on possible sulfite oxidation or thiosulfate decomposition in this pH region. The sum of the sulfite plus thiosulfate concentrations when converted to moles should be constant and equal to the original sulfite concentration of the run and this was found to be the case (see Appendix II for an example of a kinetic run).

The logarithm of the sulfite concentration, expressed in moles l^{-1}, was plotted against time for each kinetic run. These plots gave good straight lines, the slope of which were determined by linear regression analysis on a Hewlett-Packard Model 9100A desk computer.

The straight line plots indicated a first-order dependence of the reaction rate on the total sulfite concentration. The slopes of these plots gave the pseudo first-order rate constant for each kinetic run.

The dependence of the reaction rate on tetrathionate concentration was determined from a series of runs at different tetrathionate concentrations. The ionic strength in this series of runs was kept constant with sodium sulfate.

The reaction order with respect to hydrogen ion concentration was determined by runs at different pH using the citric acid buffers described previously and keeping the initial sulfite and tetrathionate concentrations constant. The ionic strength of the buffers was adjusted with sodium chloride in these runs.

The Arrhenius activation energy was determined from runs at 0.0°, 12.0°, and $25.2^{\circ}C$, for which the other parameters were constant. The pH of these runs was measured at the temperature of the run because the ionization constants of citric acid vary with temperature.

Oxygen exchange between sulfite and tetrathionate via the nucleophilic displacement of sulfite on tetrathionate by sulfite as illustrated by Equation (1 - 11):

$$(1 - 11) \quad O_3SSSSO_3^{=} + \overset{*}{S}O_3^{=} \rightarrow O_3SSS\overset{*}{S}O_3^{=} + SO_3^{=}$$

was checked for using oxygen-18 labelled sulfite. Approximately 0.01M solution of sodium sulfite was made up in 1.6 atom percent oxygen-18 labelled water. This solution was buffered to the desired pH using citric acid and sodium hydroxide. Sufficient of this solution (at 0°C) was added to a weighed portion of $Na_2S_4O_6 \cdot 2H_2O$ to yield 0.10M tetrathionate. At timed intervals, 1.2 ml. aliquots of this reaction mixture were added to 2 ml. of 1.0M copper(II) tetrapyridine acetate solution (see Section 2 - 1 for preparation of this complex). A blue precipitate which formed within 15 seconds was filtered by suction and washed first with water and then with acetone and ether. The precipitate was dried by sucking air through it for approximately one minute. It was further dried in the pyrolysis tubes later by heating the tubes to 150-200°C for a few minutes while connected to a high-vacuum pump. Separate oxygen-18 labelling experiments showed this precipitate to be anhydrous after the above treatment. Oxygen-18 abundance measurements were then performed on this precipitate by the method described in Section (2 - 3).

One additional experiment was done to check for oxygen exchange between sulfite and tetrathionate at a higher pH. Since the sulfite-tetrathionate chemical reaction (Equation 1 - 10) is very fast at higher pH, samples were taken only after the reaction was complete. A 0.2M sodium sulfite solution was prepared in 5.0 ml. of ^{18}O-labelled water and the pH was adjusted to approximately 8.0. This adjustment of pH added approximately 1.0 ml. of unlabelled water to this solution thus diluting the oxygen-18 labelling level in the final solution. This solution was then reacted with a stoichiometric weight of sodium tetrathionate, therefore no excess sulfite or tetrathionate remained in solution after reaction was complete. Unreacted sulfite was checked for with strontium nitrate solution and found to be absent. The thiosulfate formed was removed first by precipitation with lead acetate solution. Trithionate was then recovered by precipitation with the copper(II) tetrapyridine complex. Oxygen-18 abundance measurements were performed on both the lead thiosulfate and the copper(II) tetrapyridine trithionate precipitates.

4 - 2 RESULTS:

Kinetic data for the sulfite-tetrathionate reaction were obtained with total sulfite concentration at 0.010M and tetrathionate concentration ranging from 0.05M to 0.20M, pH of 2.92 to 4.70 and temperatures from 0°C to 25°C. The method of deriving rate constants from the iodometric titration data is given in Appendix II. Tetrathionate and hydrogen ion concentrations remained essentially constant throughout a particular run. The dependence of the reaction rate on sulfite concentration, for several runs, is shown in Fig. 5. These standard logarithmic plots are diagnostic of a first order reaction with respect to total sulfite, i.e.

$$(4 - 1) \quad -\frac{d[SO_3^=]_T}{dt} = k''[SO_3^=]_T$$

where $[SO_3^=]_T$ represents total sulfite, bisulfite and sulfurous acid, and k" is the first order rate constant. In the pH range of the kinetic experiments done here, greater than 99% of the total sulfite was bisulfite. Iodometric titrations of course determine only the total sulfite present. A compilation of pseudo-first order rate constants for a variety of experimental conditions is given in Column 5 of Table III from which the complete kinetics of the sulfite-tetrathionate reaction may be determined.

The pseudo-first order rate constants vary with the tetrathionate concentration (runs 1-4 in Table III also shown in Fig. 5) and also with the hydrogen ion concentration (runs 5-7 in Table III). Therefore, k" can be re-written in terms of a new rate constant k' as in Equation (4 - 2):

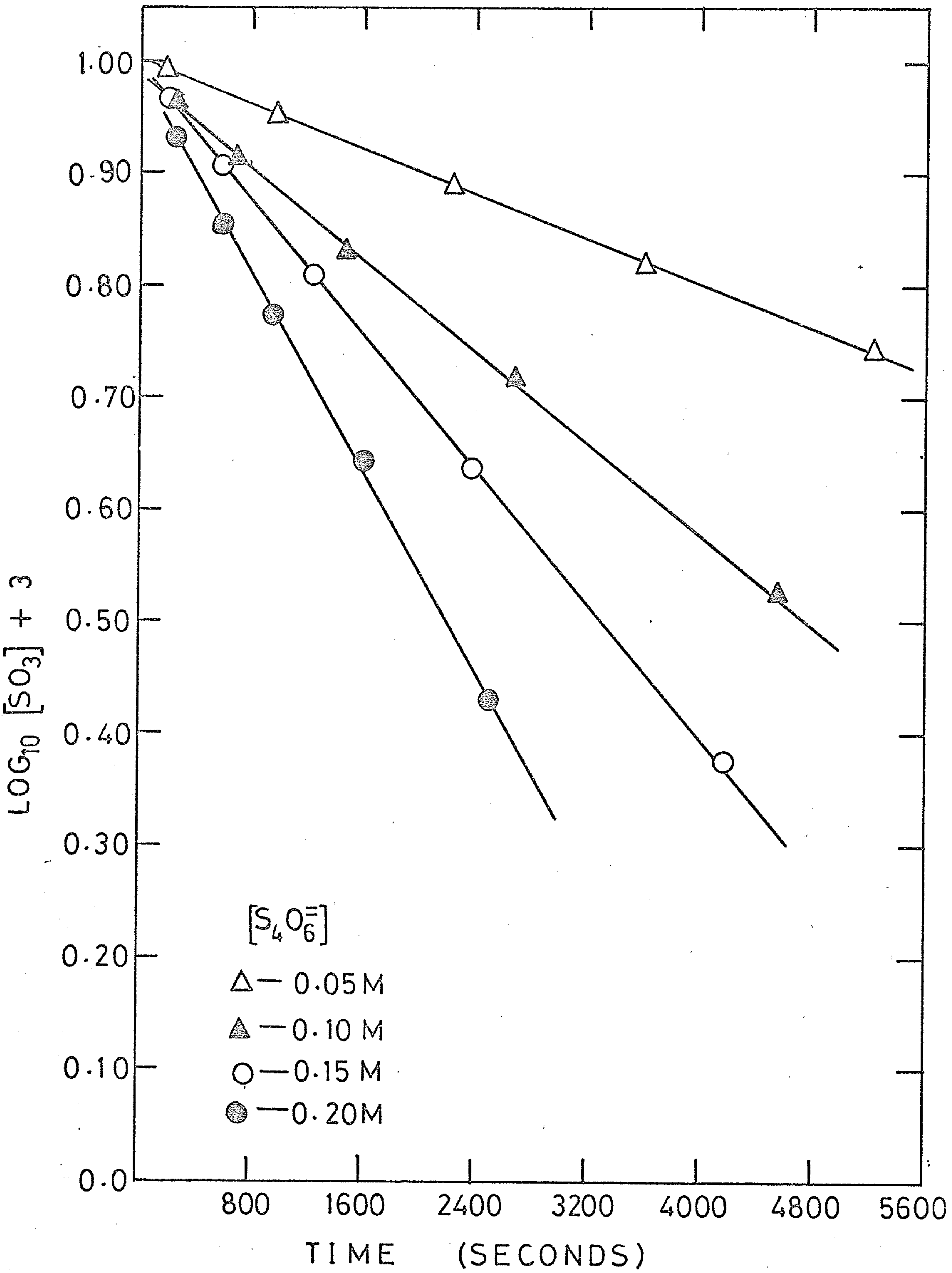
$$(4 - 2) \quad k'' = k'[S_4O_6^=]^a[H^+]^b$$

The values of a and b indicate the reaction order with respect to tetrathionate and hydrogen ion concentrations. The value of a was determined by plotting log k" versus log $[S_4O_6^=]$ in Fig. 6 for runs 1-4 for which the pH was constant. The slope of this line, as well as all the other slopes in this section, was determined by a least squares fit on a Hewlett-Packard Model 9100A calculator. The slope of the plot in Fig. 6 showed that $a = 1.00 \pm 0.03$. Therefore the reaction between sulfite and tetrathionate is first order with respect to tetrathionate concentration.

The reaction order with respect to hydrogen ion concentration was examined using the citric acid buffers described previously. From runs 5, 6, and 7 (Table III), it is evident that the reaction rate decreases with decreasing pH.

Fig. 5

Pseudo first order rate plots for the sulfite-tetrathionate reaction at different initial tetrathionate concentrations



1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.0
$LOG_{10}\ [SO_3] + 3$
800
1600
2400
3200
4000
4800
5600
TIME (SECONDS)
$[S_4O_6^=]$
△ — 0.05 M
▲ — 0.10 M
○ — 0.15 M
● — 0.20 M

TABLE III

KINETIC DATA FOR THE SULFITE-TETRATHIONATE REACTION

(Temperature = 0°C except where noted)

Run No.	pH	$[S_4O_6^=]$ moles $l.^{-1}$	Ionic Strength	$k'' \times 10^4$ (sec^{-1})	k $l.\ mole^{-1}\ sec.^{-1}$
1	3.54	0.200	1.13	4.71±0.06	1.48±0.02
2	3.54	0.150	1.13	3.46±0.05	1.46±0.02
3	3.54	0.100	1.13	2.34±0.04	1.48±0.03
4	3.54	0.050	1.13	1.17±0.02	1.47±0.03
5	4.12	0.100	1.33	9.79±0.27	1.63±0.05
6	2.92	0.100	1.33	0.645±0.025	1.67±0.06
7	3.54	0.100	1.33	2.61±0.06	1.65±0.04
8	3.54	0.100	0.83	1.76±0.03	1.11±0.02
9 §	3.49	0.100	0.83	3.35±0.09	2.38±0.06
10 †	3.45	0.100	0.83	6.12±0.18	4.75±0.14
11	3.54	0.150	0.98	3.08±0.05	1.30±0.02
12	4.30	0.100	0.38	3.36±0.04	0.368±0.004
13	4.70	0.088	0.80	24.1 ±0.3	1.06±0.01

§ Temperature = 12.0°C

† Temperature = 25.2°C

The value of b in Equation (4 - 2) was determined by plotting log k" versus pH in Fig. 7 for runs 5-7 (Table III). The slope of this plot was 0.98 ± 0.03, however, since pH equals -log $[H^+]$ then b = -0.98 ± 0.03. The reaction rate is therefore inversely proportional to the first power of hydrogen ion concentration.

Equation (4 - 2) can now be re-written as in (4 - 3):

$$(4 - 3) \quad k'' = \frac{k'[S_4O_6^=]}{[H^+]}$$

As mentioned earlier, in the pH range of these experiments greater than 99% of the sulfite in solution was bisulfite. The total sulfite concentration in Equation (4 - 1) can therefore be replaced with the bisulfite concentration to a very good approximation.

Combining Equations (4 - 1) and (4 - 3) the rate of reaction, R, can be written as:

$$(4 - 4) \quad R = \frac{k'[HSO_3^-][S_4O_6^=]}{[H^+]}$$

The inverse dependence of the reaction rate on hydrogen ion concentration seems a bit strange at first. However, it is known that the relative concentrations of sulfite, bisulfite and sulfurous acid vary with pH. From a knowledge of the equilibrium constants,

$K_1 = \frac{[H_2SO_3]}{[H^+][HSO_3^-]}$ and $K_2 = \frac{[HSO_3^-]}{[H^+][SO_3^=]}$, these relative concentrations may be calculated. Of the values for K_1 and K_2 available in the literature the values $K_1 = 2.34 \times 10^1$ and $K_2 = 2.19 \times 10^6$ (61)

Fig. 6

Determination of the reaction order of the sulfite-tetrathionate reaction with respect to tetrathionate concentration

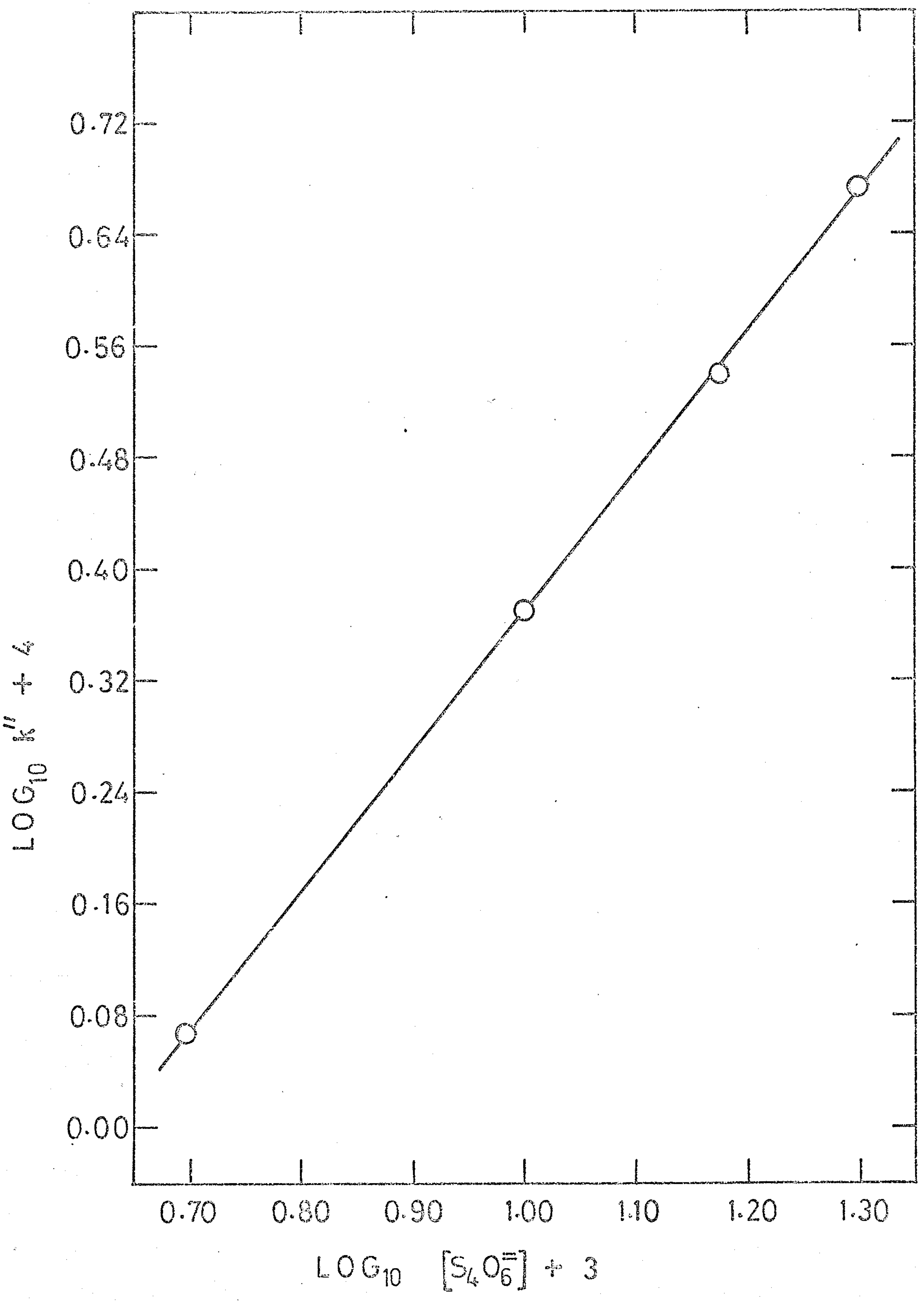
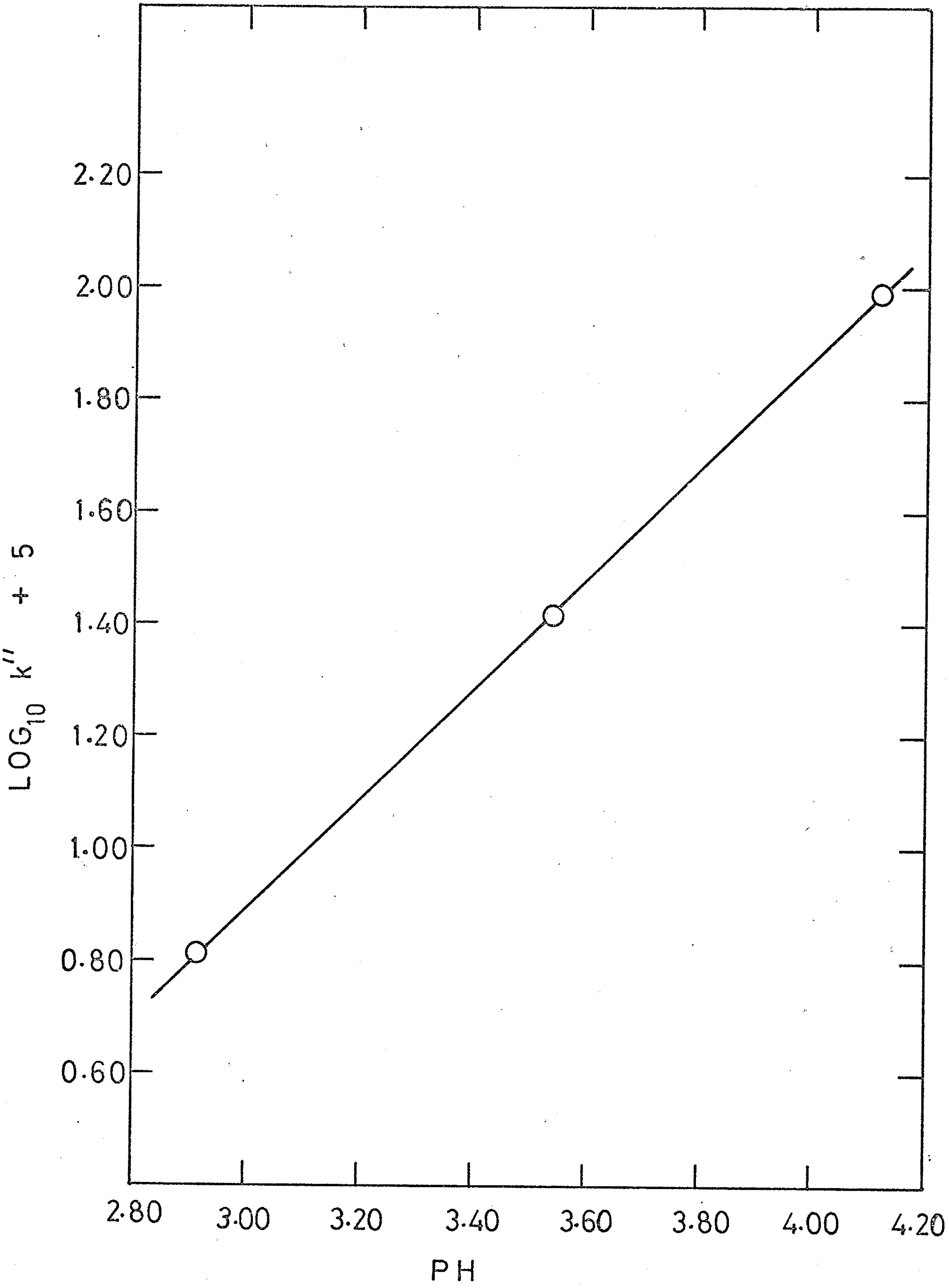

0·72
0·64
0·56
0·48
0·40
0·32
0·24
0·16
0·08
0·00
$\mathrm{LOG}_{10}\ k'' + 4$
0·70
0·80
0·90
1·00
1·10
1·20
1·30
$\mathrm{LOG}_{10}\ [S_4O_6^{=}] + 3$

Fig. 7

pH dependence of the sulfite-tetrathionate reaction in the pH region 2.92 to 4.12 and at 0°C


2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
$LOG_{10}\ k'' + 5$
2.80
3.00
3.20
3.40
3.60
3.80
4.00
4.20
PH

were chosen as appropriate for the ionic strength used in this work. The relative concentrations of sulfite, bisulfite, and sulfurous acid thus calculated are shown in Fig. 8. It is immediately evident that for the pH range used here (2.92 to 4.70) that the bisulfite concentration remains approximately constant and the sulfite concentration is inversely proportional to the hydrogen ion concentration in this pH region. Therefore the inverse dependence of the reaction rate on hydrogen ion concentration can be accounted for if one postulates that only the sulfite ion ($SO_3^=$), and not bisulfite ion (HSO_3^-), is capable of making nucleophilic displacements in the tetrathionate ion. Substituting the equilibrium relationship,

$K_2 = \frac{[HSO_3^-]}{[H^+][SO_3^=]}$ into the rate equation (4 - 4), the overall rate can be written in terms of the sulfite and tetrathionate concentrations only;

$$(4 - 5) \quad R = k'K_2[SO_3^=][S_4O_6^=]$$

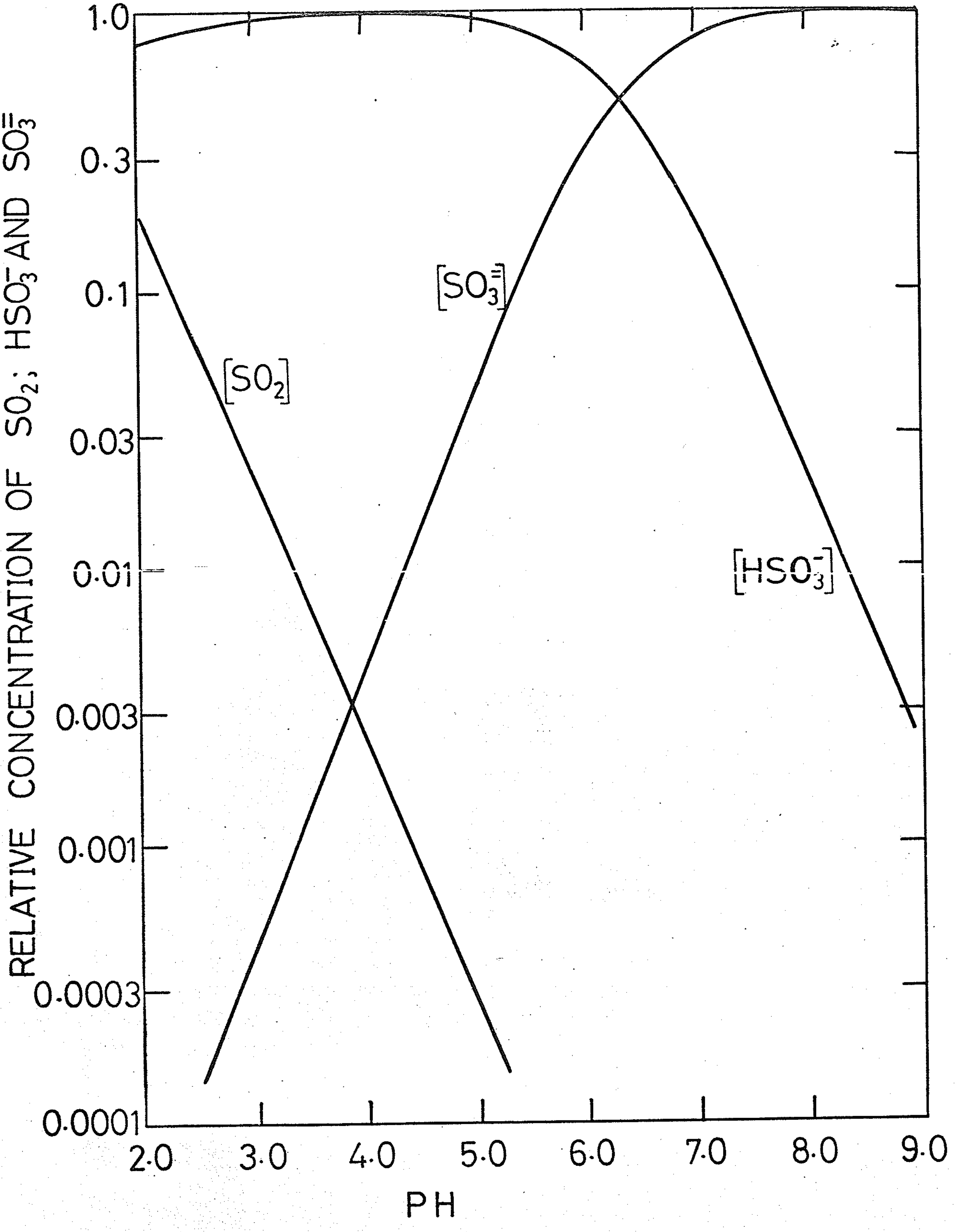
and if $k'K_2$ are combined into a single constant, k, the following rate equation is obtained:

$$(4 - 6) \quad R = k[SO_3^=][S_4O_6^=]$$

Further evidence that sulfite is the nucleophile acting on catenated sulfur-sulfur bonds is obtained from the investigation of Fava and Pajaro(62). They studied the radioactive sulfur exchange between sulfite and carboxymethyl thiosulfate over the pH range 4.1 to

Fig. 8

Relative concentrations of sulfite, bisulfite and sulfurous acid (sulfur dioxide) in aqueous solution as a function of pH



RELATIVE CONCENTRATION OF SO$_2$; HSO$_3^-$ AND SO$_3^=$
1.0
0.3
0.1
0.03
0.01
0.003
0.001
0.0003
0.0001
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
PH
[SO$_2$]
[SO$_3^=$]
[HSO$_3^-$]

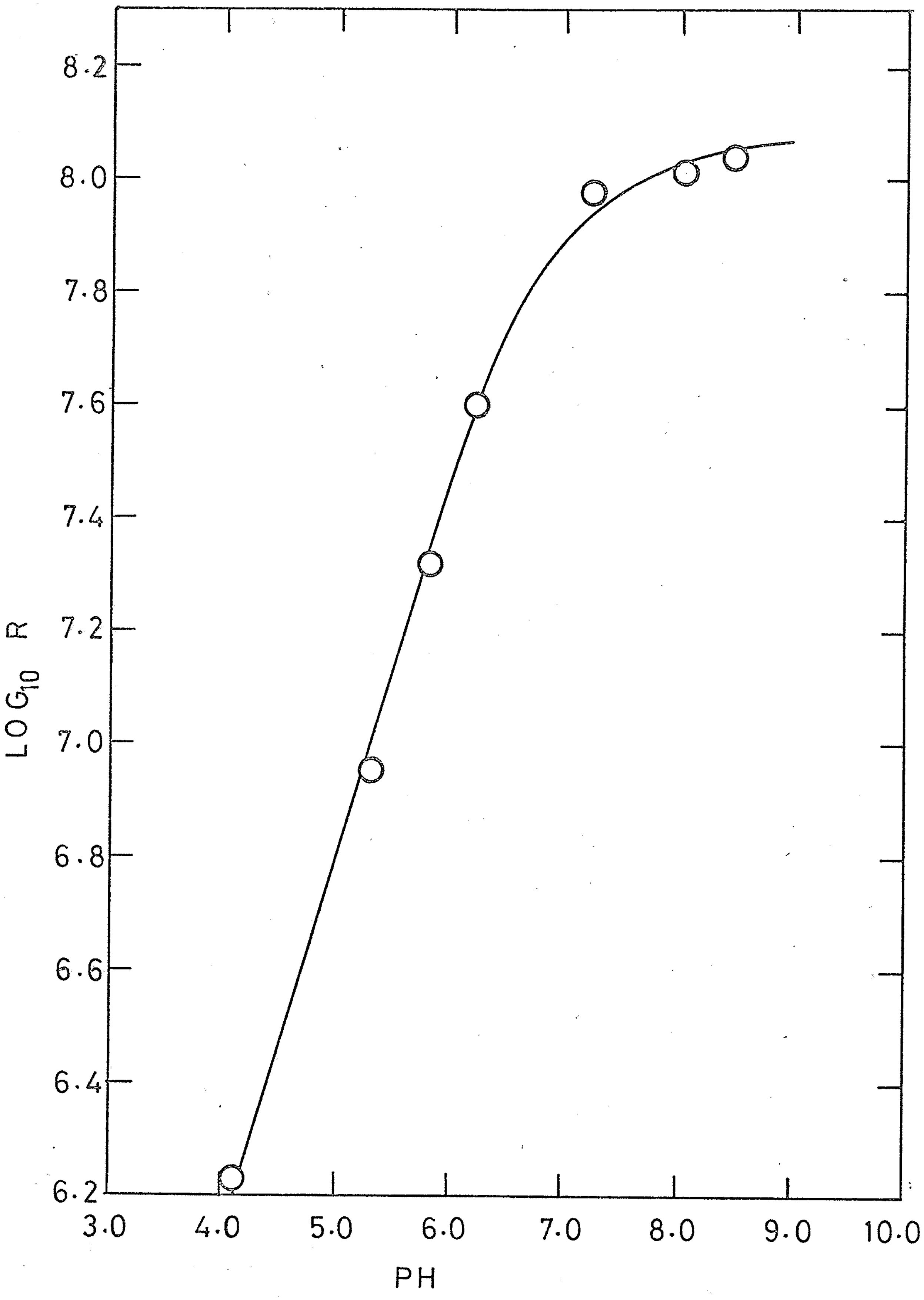
8.4. They, however, found that the exchange rate had a nonlinear dependence on the hydrogen ion concentration. When the logarithm of the exchange rates in their work is plotted against pH (Fig. 9), a curve is obtained. The shape of this curve is almost identical to the shape of the curve obtained for the relative sulfite concentration in Fig. 8 over the same pH region. Therefore, sulfite ion must be the major species responsible for the exchange process observed in that work via a nucleophilic displacement of a sulfite group on the carboxymethyl thiosulfate. Their analysis shows that sulfite is at least 100 times more effective than bisulfite as a nucleophile.

A high buffer capacity was required to keep the hydrogen ion concentration constant in the sulfite-tetrathionate reaction This resulted in high ionic strength and no quantitative treatment could be applied to ionic strength effects. However when the logarithm of the rate constant is plotted against square root of ionic strength (Fig. 10) there is a noticeable increase in rate with ionic strength, consistent with the fact that the reaction is taking place between similarly-charged species.

Measurement of pH of the buffered reaction mixtures at 0°, 12°, and $25.2^{\circ}C$ showed a pH change of almost 0.1 pH unit over this temperature range. This is proportional to the change in the ionization constant for citric acid over this temperature range(63).

The variation of the reaction rate with temperature is indicated by runs 8, 9 and 10 in Table III. The reaction rate

Fig. 9
Variation of rate of carboxymethylthiosulfate-sulfite exchange with pH (data of Fava and Pajaro; Reference 62)


8·2
8·0
7·8
7·6
7·4
7·2
7·0
6·8
6·6
6·4
6·2
LOG10 R
3.0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
PH

constant is related to temperature by the Arrhenius equation; $k = Ae^{-E_a/RT}$. A plot of $\log_{10}k$ versus the reciprocal of the temperature (in ^{o}K) is shown in Fig. 11. From the slope of this plot, the activation energy was found to be 9.3 Kcal./mole.

The exchange of oxygen between sulfite and tetrathionate, via sulfite group displacement, was measured under identical conditions as used in the sulfite-tetrathionate reaction studies. Under these conditions, as mentioned earlier, sulfite is in isotopic equilibrium with the oxygen-18 labelled water used ($P = 0.032$; 1.6 atom percent oxygen-18). The copper(II) tetrapyridine complex used to precipitate the tetrathionate from aliquots of the reaction mixture also precipitates trithionate and thiosulfate. Thiosulfate is precipitated because it is oxidized to tetrathionate by Cu(II). The sulfite-tetrathionate oxygen exchange experiments were done at $0^{o}C$ and at three different hydrogen ion concentrations. This provided variable conditions giving the exchange process an opportunity to proceed before the exchanging species, sulfite and tetrathionate, are consumed in the chemical reaction. The results of experiments at pH of 3.54, 2.92, and 4.12 are given in Tables IV, V, and VI. The measured P-factors are the relative oxygen-18 abundance in the copper(II) tetrapyridine precipitates, namely tetrathionate, trithionate and thiosulfate. The low values for the measured P-factors indicates immediately that little if any exchange has taken place between sulfite and tetrathionate. If exchange had taken place

Fig. 10

Variation of the rate constant for the sulfite-tetrathionate reaction with ionic strength

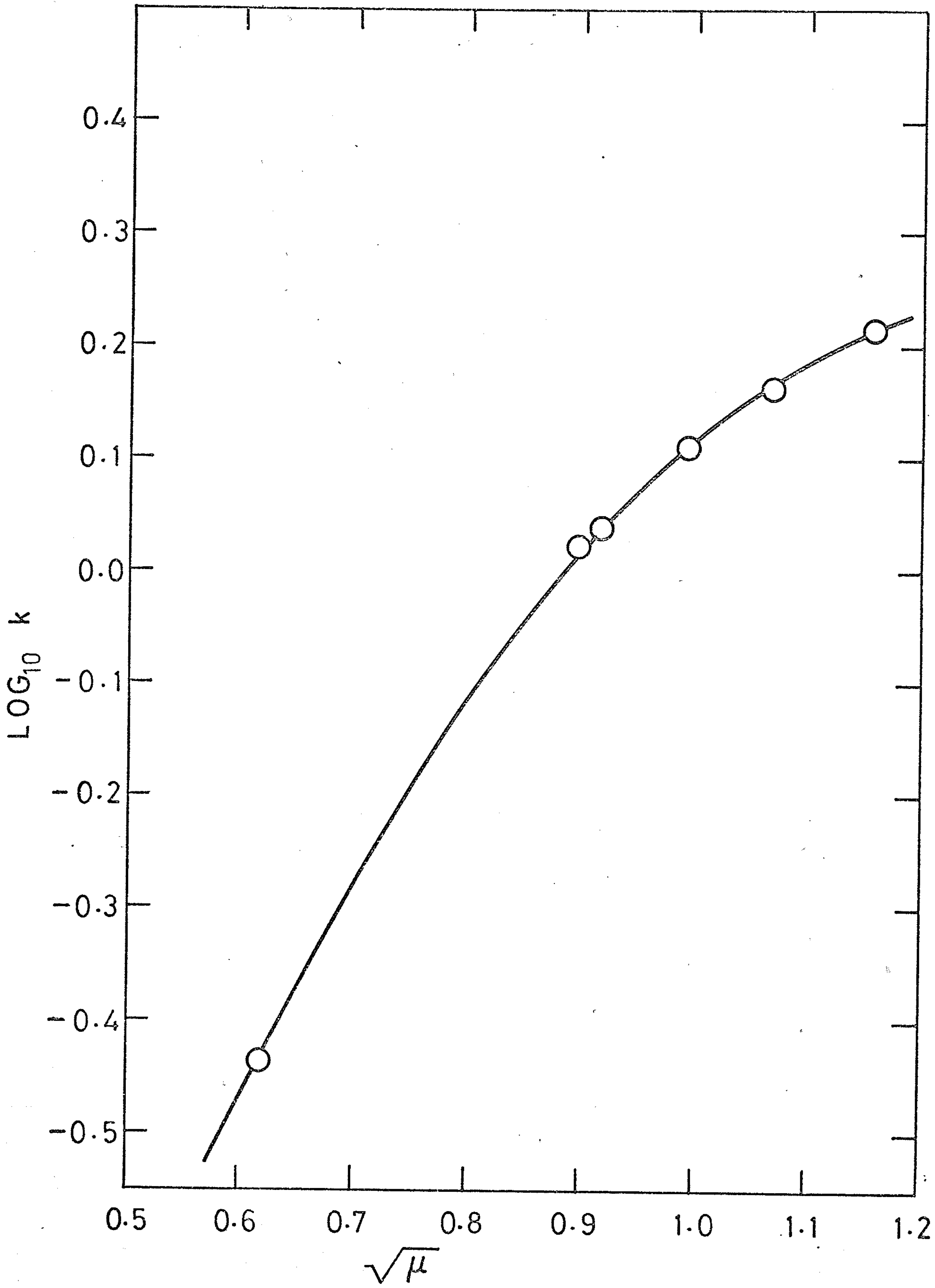
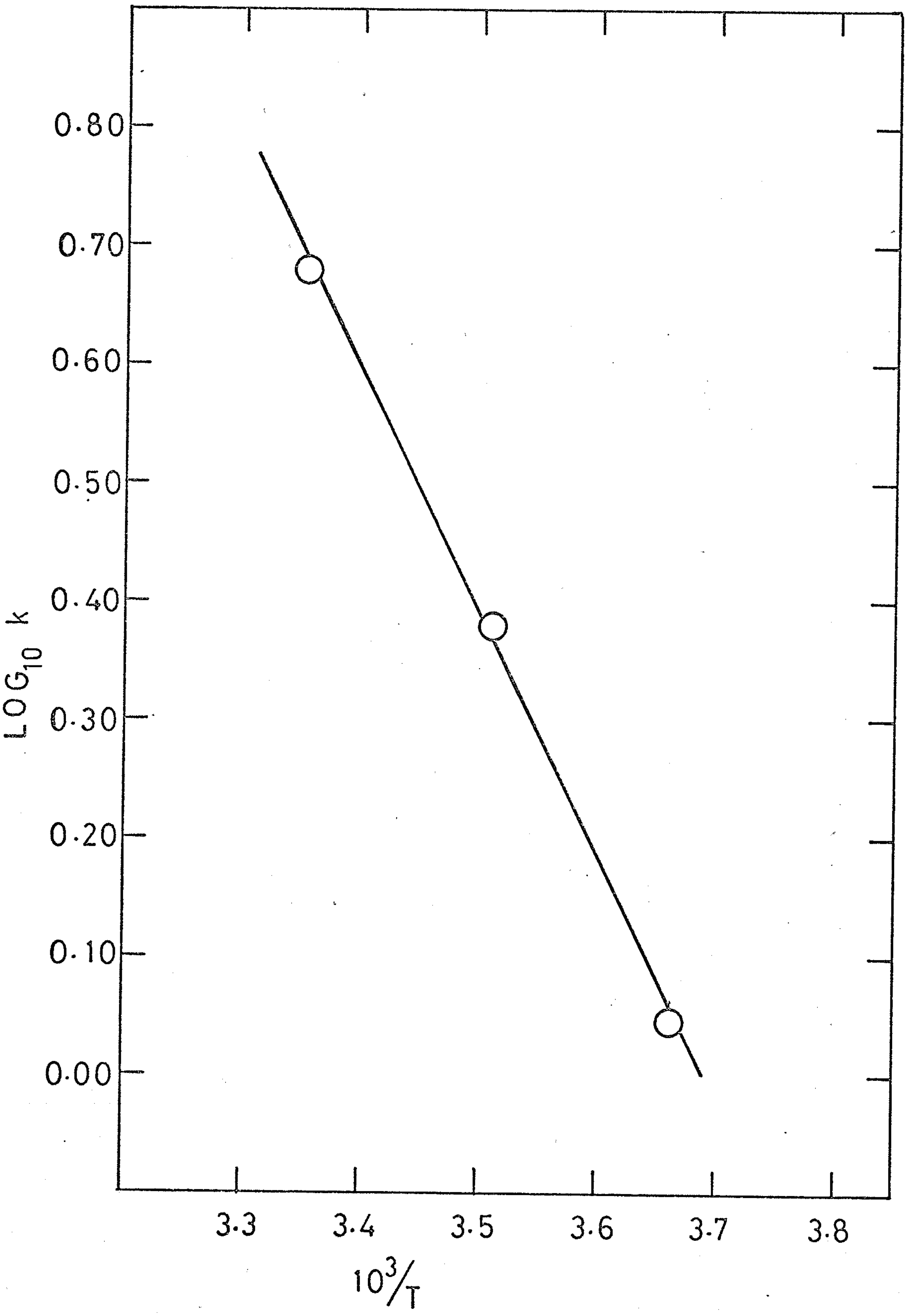

0·4
0·3
0·2
0·1
0·0
−0·1
−0·2
−0·3
−0·4
−0·5
LOG$_{10}$ k
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2
$\sqrt{\mu}$

Fig. 11

Arrhenius plot for the sulfite-tetrathionate reaction



0·80
0·70
0·60
0·50
0·40
0·30
0·20
0·10
0·00
$\log_{10} k$
3·3
3·4
3·5
3·6
3·7
3·8
$10^3/T$

rapidly then the P-factors of the tetrathionate would be expected to approach that of the water used, near 0.032. If no exchange at all took place between sulfite and tetrathionate, some oxygen-18 would still be expected to get into the precipitated trithionate via the chemical reaction:

$$(1 - 11) \quad SO_3^{=} + S_4O_6^{=} \rightarrow S_2O_3^{=} + S_3O_6^{=}$$

This chemical reaction involves sulfite displacement of thiosulfate on tetrathionate, thus forming a trithionate, in which half of the oxygens come from sulfite and are therefore labelled to the same extent with oxygen-18 as the water.

The calculated P-factors in Tables IV, V and VI were calculated assuming no exchange of oxygen between sulfite and tetrathionate had taken place and that the only oxygen-18 making its way into the precipitate was in the trithionate. The amount of trithionate formed at any given time was equated to the amount of sulfite reacted. The amount of sulfite reacted at any time was calculated from the expression:

$$(4 - 7) \quad [SO_3^{=}]_T \text{ reacted} = [SO_3^{=}]_o \, (1 - e^{-k''t})$$

since tetrathionate and hydrogen ion concentrations remain essentially constant. First order rate constants, k", were obtained from Table III for the conditions of ionic strength, and of tetrathionate and hydrogen ion concentrations used in these exchange experiments. The P-factor calculations were made assuming natural abundance P-factors (P = 0.0037)

TABLE IV

DETERMINATION OF EXCHANGE OF ^{18}O-LABELLED SULFITE WITH TETRATHIONATE

($T = 0^\circ C$; $\mu = 0.83$; $k'' = 1.76 \times 10^{-4}$ sec^{-1}; $[SO_3^=] = .0106M$; pH = 3.54)

Time (min.)	$(1 - e^{-k''t})$	$[SO_3^=]_T$ reacted§ moles l.$^{-1}$	P-factor (measured)	P-factor (calculated)†
1	0.0105	0.0001	0.00382	0.00372
10	0.10	0.0012	0.00383	0.00388
30	0.27	0.0029	0.00403	0.00411
70	0.53	0.0056	0.00443	0.00447
360	0.98	0.0104	0.00506	0.00511
370	0.98	0.0104	0.00510	0.00511
370	0.98	0.0104	0.00515	0.00511

§ The amount of $[SO_3^=]_T$ that had reacted was calculated from the appropriate first order rate constant, k", according to:

$$[SO_3^=]_T \text{ reacted} = [SO_3^=]_o \ (1 - e^{-k''t})$$

† The calculated P-factors assume no exchange of sulfite with tetrathionate had taken place, and that copper(II) tetrapyridine precipitated all the tetrathionate, trithionate and thiosulfate, leaving sulfite in solution, and that one-half of the oxygen in $S_3O_6^=$ comes from the solvent (P-factor for water = 0.032).

TABLE V

DETERMINATION OF EXCHANGE OF ^{18}O-LABELLED SULFITE WITH TETRATHIONATE

($T = 0^\circ C$; $\mu = 0.83$; $[SO_3^=]_o = 0.0155M$; pH = 2.92; $k'' = 4.22 \times 10^{-5}\ s^{-1}$)

Time (min.)	$(1 - e^{-k''t})$	$[SO_3^=]_T$ reacted moles l^{-1}	P-factor (measured)	P-factor (calculated)
1.5	0.01	0.0016	0.00384	0.00374
33	0.08	0.0012	0.00392	0.00388
60	0.14	0.0022	0.00412	0.00402
90	0.21	0.0033	0.00417	0.00417
120	0.26	0.0040	0.00426	0.00424
198	0.40	0.0062	0.00435	0.00454
201	0.40	0.0062	0.00449	0.00454
795	0.87	0.0135	0.00519	0.00549

The first order rate constant in this Table was calculated from the overall rate constant at this ionic strength (run 8 in Table III) but at the pH used here. The fraction of the sulfite reacted was then calculated from this rate constant as in Table IV. The P-factors in the last column of this Table were calculated assuming no contribution of the exchange reaction between sulfite and tetrathionate (Equation 1 - 11).

TABLE VI

DETERMINATION OF EXCHANGE OF ^{18}O-LABELLED SULFITE WITH TETRATHIONATE ($T = 0^{\circ}C$; $\mu = 0.83$; $[SO_3^{=}]_o = 0.023M$; pH = 4.12; $k'' = 6.68 \times 10^{-4} s^{-1}$)

Time (min.)	$(1 - e^{-k''t})$	$[SO_3^{=}]_T$ reacted moles l^{-1}	P-factor (measured)	P-factor (calculated)
1	0.04	0.0009	0.00413	0.00384
13	0.41	0.0097	0.00514	0.00501
35	0.75	0.0177	0.00540	0.00600
65	0.93	0.0220	0.00577	0.00648
120	0.99	0.0234	0.00579	0.00666
360	1.0	0.0236	0.00665	0.00668
370	1.0	0.0236	0.00665	0.00668

The first order rate constant in this Table was calculated from the overall rate constant at this ionic strength (run 8 in Table III) but at the pH used here. The fraction of the sulfite reacted was then calculated from this rate constant as in Table IV. The P-factors in the last column of this table were calculated as in Table IV assuming no contribution of the exchange reaction between sulfite and tetrathionate (Equation 1 - 11).

for all the oxygens of tetrathionate and thiosulfate and for three of the oxygens in trithionate; the remaining three oxygens of trithionate were assumed to have a P-factor identical to that of the water (P = 0.032).

The fact that the calculated P-factors agree so well with the measured P-factors clearly indicates that little if any oxygen exchange has taken place between sulfite and tetrathionate via a sulfite group exchange. All of the oxygen-18 (above natural abundance in the precipitate) is accounted for as being in the trithionate.

The results of the sulfite-tetrathionate experiment at pH ~ 8 are given in Table VII. The P-factor of the water was calculated to be 0.0273, taking into account the dilution by unlabelled water during the adjustment of pH. The P-factor of the trithionate was calculated assuming no exchange so that half the oxygens in trithionate were of natural abundance in oxygen-18 and the other half were labelled to the level of the water. The agreement is very good so there is no evidence for prior oxygen exchange between tetrathionate and sulfite. The small amount of labelling observed in the thiosulfate is due to the nature of the lead thiosulfate precipitate. This precipitate seems to induce some exchange during precipitation or possibly it retains some hydrated water which cannot be removed. Thus we have found in separate experiments that precipitation of unlabelled thiosulfate in oxygen-18 labelled water with lead acetate before any exchange could take place produced very similar P-factors for the thiosulfate oxygen-18 abundance as observed in Table VII.

TABLE VII

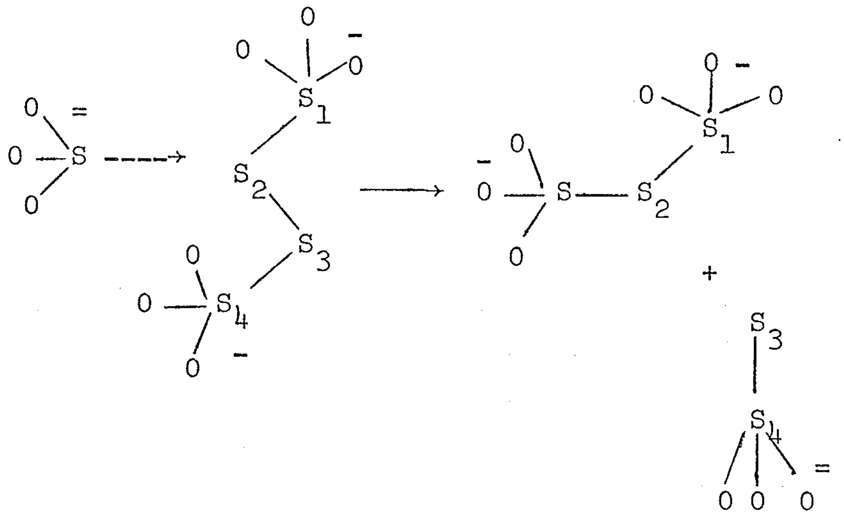
OXYGEN-18 EXCHANGE BETWEEN SULFITE AND TETRATHIONATE AT pH ~ 8

Time After Mixing Reactants	^{18}O content of $S_2O_3^=$ (P-factors)		^{18}O content of $S_3O_6^=$ (P-factors)	
	Measured	Calculated	Measured	Calculated
5 minutes	0.00431	0.00370	0.01465	0.0150
30 minutes	0.00455	0.00370	0.01453	0.0150

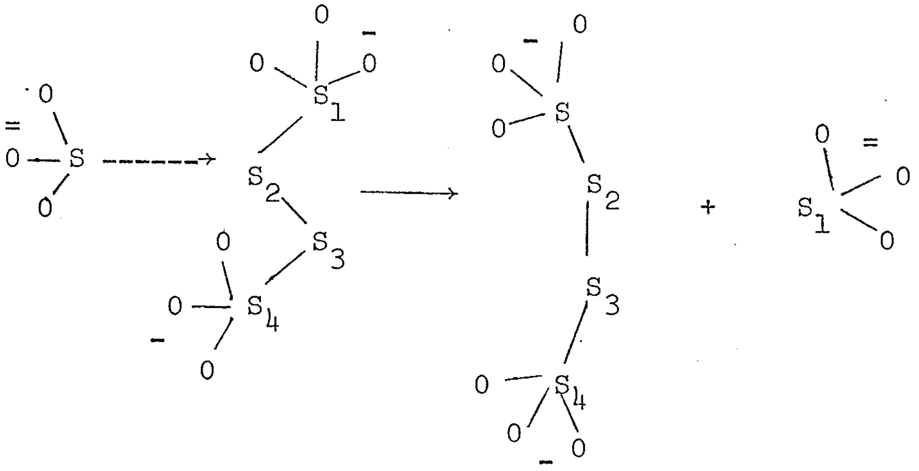
4 - 3 DISCUSSION:

The reactions investigated in this section are illustrated below:

(4 - 8)



(4 - 9)



In Reaction (4 - 8) the incoming sulfite attacks sulfur S_2 in the $S_4O_6^{=}$ chain, with S-S bond scission between S_2 and S_3 and trithionate and thiosulfate as products. In Reaction (4 - 9) the point of attack is the same, but S-S bond rupture is shown as occurring between S_1 and S_2 producing only sulfite group exchange. The reactions are shown with the sulfite attack on S_2 of the tetrathionate chain but the tetrathionate is symmetrical with S_2 and S_3 being identical. Exactly the same reactions would occur if sulfite attacked S_3 in the tetrathionate chain.

It has often been found that the bond lengths and bond strengths are related for a series of similar bonds usually by an r^{-3} dependence (where r is the length of the bond in question). Davis(39,40) has derived a semiempirical correlation which suggests that the activation energy of cleavage of catenated sulfur-sulfur bonds by cyanide or sulfite ions is directly proportional to the bond energy, of the S-S bond being broken in the rate-determining step. For displacements by sulfite ions the Davis correlation relating the activation energy of cleavage to the bond length is:

$$(4 - 10) \quad E_a = \frac{C}{r_{ss}^3}$$

where C = 110; and for displacements by cyanide ion C = 99.9. This correlation has been applied to a number of displacement reactions involving cyanide and sulfite and the data correlate well.

Since, as mentioned earlier, the bond lengths in the tetrathionate chain differ considerably the correlation given by Equation (4 - 10) can be used to predict the relative rates of reactions (4 - 8) and (4 - 9) above, by comparing the calculated activation energies for both reactions. In reaction (4 - 8) the S_2-S_3 bond of the tetrathionate chain is being broken. Its bond length is 2.02 A^o(38). The activation energy for displacement by sulfite ion calculated from Equation

(4 - 10) is 13.4 Kcal. In reaction (4 - 9) the S_1-S_2 bond in the chain is being broken. Its length is 2.12 A°(38) and the activation energy for displacement by sulfite ion is 11.6 Kcal from Equation (4 - 10).

The activation energy and the rate constants for reactions are related by the Arrhenius equation;

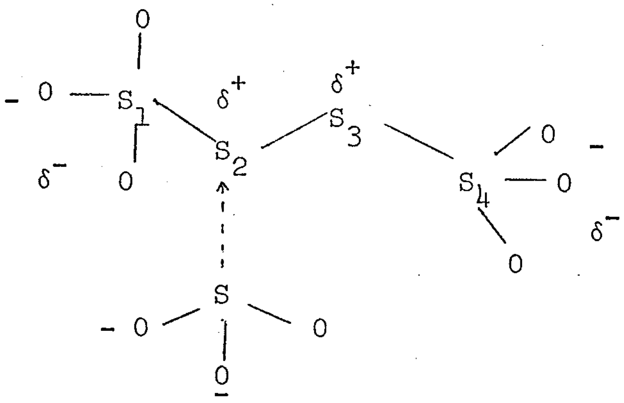
(4 - 11) $k = Ae^{-E_a/RT}$

The A factor in the Arrhenius equation contains a number of parameters such as steric effects, collision frequency, etc. The A factors involved in Reaction (4 - 8) and (4 - 9) would be expected to be very similar for the following reasons: Either Reaction (4 - 8) or (4 - 9) would be expected to occur by a single attack by sulfite ion on S_2 or S_3 of the tetrathionate chain. Stereochemically there is evidence that displacements at a sulfur atom require a linear transition state(64) with three sulfur atoms in a row. From models of tetrathionate and sulfite it is evident that there is little or no steric hindrance for either angle of attack by sulfite for Reactions (4 - 8) and (4 - 9). The sulfur atoms in tetrathionate form a bent chain with S-S-S bond angles of 104° and an SSS/SSS dihedral angle of 90.4°. The S_2 and S_3 atoms of the tetrathionate chain are out in the open with the oxygens at the ends of the chain well out of the way for sulfite attack. Steric effects should be almost identical in both reactions. Therefore taking a ratio of the rate constants given by Equation (4 - 11) for Reactions (4 - 8) and (4 - 9) the A factors cancel. Using the activation energies calculated above the ratio of the rate constants, k_1 and k_2 for Reactions (4 - 8) and (4 - 9) respectively, was calculated as $k_2/k_1 = 16.6$. The molecularity of these reactions is expected to be identical so this ratio predicts that the sulfite group exchange Reaction, (4 - 9), should proceed at least 16 times as fast as the chemical Reaction (4 - 8). This prediction is however contrary to our results. The data in Tables IV, V, VI, and VII indicate that the rate of the exchange reaction, relative to the chemical reaction, is practically zero during the lifetime of the chemical reaction. Some other effects, other than bond strengths, must therefore be involved in determining these reactions.

The possibility also arises that the end sulfur atoms, (S_1 and S_4) in the tetrathionate chain are different from S_2 and S_3. The end sulfur atoms in the tetrathionate chain are in different oxidation states as compared to the middle sulfur atoms. This would imply that a different type of S-S bond is being broken in Reaction (4 - 9) as compared with Reaction (4 - 8) and therefore the Davis correlation would not apply. Davis, however, has shown that cyanide attack on trithionate and sulfite attack on thiosulfate fit the correlation well. Both trithionate and thiosulfate have the type of bond under question in Reaction (4 - 9), one of the sulfur atoms having three oxygens attached to it. Therefore there can be no unusual effects attributed to the presence of these oxygen atoms in tetrathionate when the correlation is being applied.

The experimental activation energy, E_a, for Reaction (4 - 8) was determined from the plot in Fig. 11 as 9.3 Kcal/mole. The rate constant, k, used in this plot to determine the activation energy included the sulfite-bisulfite equilibrium constant, K_2, as indicated by Equations (4 - 5) and (4 - 6). However, data in the literature(65, 66) indicate that the sulfite-bisulfite equilibrium is independent of temperature so there is no enthalpy change associated with this equilibrium. Therefore the activation energy for the nucleophilic displacement by sulfite on tetrathionate (Reaction 4 - 8) is just the experimentally measured value of 9.3 Kcal/mole. This is much less than the value predicted from the Davis correlation (Equation 4 - 10) which was 13.4 Kcal/mole for breaking the S_2-S_3 bond in tetrathionate. This activation energy for Reaction (4 - 8) is even less than the predicted value for the exchange reaction (Equation 4 - 9). There must be some other factors involved which favor Reaction (4 - 8) over that of Reaction (4 - 9) thus altering the predicted activation energies so drastically.

The fact that Reactions (4 - 8) and (4 - 9) do not proceed at the relative predicted rates may be due to the electrostatics involved. The electron affinity of the oxygen atoms at the ends of the tetrathionate ion will leave the two central sulfur atoms of the tetrathionate chain with a slight positive charge:



The incoming sulfite will attack one of these two central sulfur atoms, i.e., S_2 or S_3, and electron transfer will occur along the bonds involved.

If Reaction (4 - 9), the exchange reaction, is to proceed then an electron will have to flow into one of the end $-SO_3^-$ groups which would then leave the tetrathionate to form a separate sulfite group. Since the end $-SO_3^-$ group already has a negative charge on it the electron has to flow against an electrostatic potential. If Reaction (4 - 8), the chemical reaction, occurs then the electron flow is in the other direction, from S_2 to S_3 on the tetrathionate chain. Since both these sulfur atoms have a positive charge on them, this will facilitate electron flow. Thus electrostatically Reaction (4 - 8) is greatly favored in this case and this effect may be large enough to overcome the bond strength effects which on the Davis correlation, should favor the exchange reaction.

THE THIOSULFATE-SULFITE-WATER SYSTEM

5

5 - 1 EXPERIMENTAL:

Oxygen exchange among the components in a system containing thiosulfate, sulfite and water was investigated by using oxygen-18 enriched thiosulfate. The preparation of oxygen-18 enriched thiosulfate from oxygen-18 enriched water was described in Section 2 - 1. This labelled thiosulfate was used in all kinetic runs in this Section.

Kinetic runs were done in the following way. A measured volume of water was freed of dissolved oxygen by bubbling with argon (Matheson H.P.) before adding sulfite, to prevent the oxidation of the latter. Then concentrated HCl or NaOH was added as required to obtain the desired pH. Oxygen-18 sodium thiosulfate was then added, the reaction vessel stoppered and the solution purged with argon for approximately one minute longer in order to have an argon atmosphere over the solution. This solution was placed in a water bath held at 50.3°C, the temperature used for all experiments in this Section. The reaction vessel had a side arm fitted with a serum cap through which aliquots of the solution could be withdrawn with a syringe without opening the reaction vessel to the atmosphere.

In some experiments, pH measurements were made at room temperature on duplicate solutions made up with unlabelled anhydrous sodium thiosulfate, while in other experiments the labelled solutions were used directly. A Model 801 Orion pH meter was used.

At timed intervals 1-2 ml. aliquots of the reaction mixture were removed, the pH adjusted to 11-12 with 2M sodium hydroxide and sulfite was precipitated and centrifuged down as $SrSO_3$ by addition of an aqueous solution of $SrCl_2$. The strontium sulfite precipitates were saved for oxygen-18 abundance measurements only in the experiment at pH 10.8. This precipitate was washed with acetone and recovered by filtration. The remaining solution was adjusted to pH 4.7 with a sodium acetate-acetic acid buffer, and thiosulfate was recovered by adding excess 0.5M Cu(II) tetrapyridine acetate solution. The preparation of this reagent has been described in Section 2 - 1. This method of recovering thiosulfate from solution for oxygen-18 abundance measurements (also used in Section 4) is rapid, quantitative and causes very little induced exchange (not more than 3% from blank experiments with ^{18}O-labelled water). The precipitate of $CuPy_4S_4O_6$ was filtered by suction and washed with ether or acetone.

In some experiments, thiosulfate was recovered as BaS_2O_3 precipitate after sulfite had been removed as $SrSO_3$. The barium thiosulfate precipitate, however, proved difficult to handle, since precipitation was very slow; often requiring addition of alcohol to encourage precipitation. This addition of alcohol sometimes caused some induced exchange thus giving erratic results in some of the runs. Moreover, this salt is difficult to dehydrate.

The oxygen-18 isotopic composition of the sulfite, thiosulfate and tetrathionate precipitates was determined as described in Section 2 - 3.

5 - 2 RESULTS AND DISCUSSION:

In an aqueous solution of thiosulfate and sulfite, there are several possibilities of oxygen-18 exchange among the various species. The direct exchange of ^{18}O between thiosulfate and water has been shown to be quite slow(44) and for the experimental conditions and times used here this possibility can be neglected. The remaining ^{18}O exchange possibilities are represented by Equations (5 - 1) and (5 - 2):

(5 - 1) $S_2O_2{}^{18}O^{=} + SO_3^{=} \rightarrow SO_2{}^{18}O^{=} + S_2O_3^{=}$

(5 - 2) $SO_2{}^{18}O^{=} + H_2O \rightarrow SO_3^{=} + H_2{}^{18}O$

with corresponding exchange rates R_1 and R_2. These equations had been given in the Introduction but are repeated here for convenience of discussion. Now if thiosulfate only is labelled with oxygen-18 initially, then one has the possibility of a system of two consecutive reversible reactions first order with respect to oxygen-18 exchange.

Oxygen exchange between thiosulfate and sulfite is effected through the sulfur atom transfer process studied by Ames and Willard(43).

(5 - 3) Rate of sulfur exchange $= k_1[SO_3^{=}][S_2O_3^{=}]$

(5 - 4) Rate of oxygen exchange $= R_1 = 3k_1[SO_3^{=}][S_2O_3^{=}]$

The rate of oxygen exchange is three times the rate of sulfur exchange. The differential equation for the oxygen-18 labelled thiosulfate concentration can be written as:

$$(5-5) \quad \frac{d[S_2O_2{}^{18}O^=]}{dt} = -k_1[S_2O_2{}^{18}O^=][SO_3^=] + k_1[S_2O_3^=][SO_2{}^{18}O^=]$$

Now, from Equation (5 - 4) one has:

$$(5-6) \quad k_1[SO_3^=] = \frac{R_1}{3[S_2O_3^=]}$$

and:

$$(5-7) \quad k_1[S_2O_3^=] = \frac{R_1}{3[SO_3^=]}$$

Substituting Equations (5 - 6) and (5 - 7), Equation (5 - 8) is obtained:

$$(5-8) \quad \frac{d[S_2O_2{}^{18}O^=]}{dt} = \frac{-R_1[S_2O_2{}^{18}O^=]}{3[S_2O_3^=]} + \frac{R_1[SO_2{}^{18}O^=]}{3[SO_3^=]}$$

For ease of handling these equations the following definitions are required:

$x = [S_2O_2{}^{18}O^=]$ $\qquad X = 3[S_2O_3^=]$

$y = [SO_2{}^{18}O^=]$ $\qquad Y = 3[SO_3^=]$

$z = [H_2{}^{18}O]$ $\qquad Z = [H_2O]$

where x, y, and z represent the molar concentrations of ^{18}O-labelled species. Because the ^{18}O level was low (~ 1%) doubly labelled oxy-anions can be neglected and x, y, and z will also be equal to the concentration of oxygen-18 in gram atoms $l.^{-1}$ of the indicated species. The quantities X, Y, and Z represent the concentration of oxygen-16 in gram atoms $l.^{-1}$ in the indicated species.

Using the above definitions Equation (5 - 8) can readily be re-written as follows:

$$(5 - 9) \qquad \frac{dx}{dt} = R_1 \frac{y}{Y} - R_1 \frac{x}{X}$$

Similarly differential equations for labelled sulfite and labelled water can be written as in (5 - 10) and (5 - 11):

$$(5 - 10) \qquad \frac{dy}{dt} = R_1 \frac{x}{X} - R_1 \frac{y}{Y} - R_2 \frac{y}{Y} + R_2 \frac{z}{Z}$$

$$(5 - 11) \qquad \frac{dz}{dt} = R_2 \frac{y}{Y} - R_2 \frac{z}{Z}$$

It is convenient to recast Equations (5 - 9), (5 - 10) and (5 - 11) in terms of the corresponding experimental P-factors, defined as follows:

$$P_x = k\frac{x}{X} \; ; \quad P_y = k\frac{y}{Y} \; ; \quad \text{and } P_z = k\frac{z}{Z}$$

(The term k in these definitions is a proportionality constant, the same for each definition, which allows for the fact that the P-factor is not an absolute measure of the corresponding $^{18}O/^{16}O$ ratio. It allows e.g., for instrumental calibration, and for the statistical factor of 2 involved in ^{18}O assay via CO_2 mass spectrometry. It cancels out of the following differential equations and also out of the F values used later in this Section). Substituting these definitions appropriately in Equations (5 - 9), (5 - 10), and (5 - 11) one has:

$$(5 - 12) \qquad \frac{dP_x}{dt} = \frac{R_1}{X} (P_y - P_x)$$

$$(5 - 13) \qquad \frac{dP_y}{dt} = \frac{R_1}{Y} (P_x - P_y) - \frac{R_2}{Y} (P_y - P_z)$$

$$(5-14) \quad \frac{dP_z}{dt} = \frac{R_2}{Z}(P_y - P_z)$$

The general solution of such a set of coupled rate equations has been given in the literature(67-72). The two methods of solving such coupled rate equations are: (a) converting these equations into second order differential equations of a single component and solving the resulting second order equation by standard methods, References (67-69) or (b) the above set of coupled differential equations can be solved in closed form, References (70-72). The second method has been used here, with the details of the solution being given in Appendix III.

The general solution of Equations (5 - 12), (5 - 13), and (5 - 14) from Appendix III is therefore simply:

$$(5-15) \quad P_i - P_\infty = A_i' e^{-\lambda_1 t} + A_i'' e^{-\lambda_2 t}$$

where P_i represents P_x, P_y or P_z as appropriate; A_i' and A_i'' are constants of integration satisfying initial conditions and P_∞ is the equilibrium isotopic ratio in all the components at infinite time (Equation 5 - 23 below). Both λ_1 and λ_2 are the same for P_x, P_y, or P_z and can be given in terms of the reaction rates R_1 and R_2 and of the concentration of the components X, Y, Z, as given by Equations (5 - 16) and (5 - 17):

$$(5-16) \quad \lambda_1 = \frac{1}{2}\left\{ \left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z}\right) + \left[\left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z}\right)^2 - 4R_1R_2\left(\frac{X+Y+Z}{XYZ}\right)\right]^{1/2} \right\};$$

$$(5-17)\quad \lambda_2 = \frac{1}{2}\left\{\left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z}\right) - \left[\left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z}\right)^2 - 4R_1R_2\left(\frac{X + Y + Z}{XYZ}\right)\right]^{1/2}\right\}$$

Equations (5 - 12), (5 - 13), and (5 - 14) describe the variation of the isotopic ratios in thiosulfate, sulfite and water as a function of time. Because water is overwhelmingly the main species, its isotopic composition is not a sensitive indicator of the exchange process and so was not measured.

The kinetics of Reactions (5 - 1) and (5 - 2) have been studied previously(43, 35). Reaction (5 - 1) has a first order dependence on thiosulfate and sulfite, and zero order dependence on $[H^+]$, whereas Reaction (5 - 2) has a first order dependence on sulfite, and is second order in $[H^+]$. Clearly there is available a greater degree of experimental control on R_2 than on R_1, since the former can be varied by many orders of magnitude, with respect to R_1, simply by alteration of the pH. Experimental measurements were made in the pH region 2.75 to 13, with the results up to pH 9.6 summarized in Table VIII.

It is convenient and useful to consider all the results in four groups, distinguished by the pH region. Each of these groups will now be discussed separately for sulfite and thiosulfate concentrations of the order of 0.5M.

Case I

In the pH range 5 to 10 the exchange of oxygens between water and sulfite is extremely rapid so that $R_2 >> R_1$. Therefore only the rate of oxygen atom transfer between thiosulfate and water is experimentally measurable by our method. Sulfite acts as a catalyst to exchange oxygen atoms between thiosulfate and water at a rate governed by the sulfur atom transfer between thiosulfate and sulfite as measured by Ames and Willard(43). Sulfite and water form a common pool of oxygen atoms which exchange with the oxygen atoms of thiosulfate. In this region of pH the sulfite is in ^{18}O isotopic equilibrium with water so $P_y = P_z$ at all times. Since no ^{18}O is lost from the system the following relation holds for infinite time:

$$(5 - 18) \qquad P_\infty(X + Y + Z) = XP_x + (Y + Z)P_y$$

Equation (5 - 18) can be used to eliminate P_y from Equation (5 - 12), and the resulting equation can be integrated directly to give:

$$(5 - 19) \qquad \ln \frac{P_x - P_\infty}{P_{x_o} - P_\infty} = -R_1 \frac{X + Y + Z}{X(Y + Z)} t$$

Here, P_{x_o} is the isotopic ratio in thiosulfate at zero time; P_x is the isotopic ratio in thiosulfate at time t; and P_∞ is the isotopic ratio in thiosulfate or in any of the other components at infinite time. In terms of the P-factors, the fraction exchanged, F, can be defined as $F = \frac{P_{x_o} - P_x}{P_{x_o} - P_\infty}$, hence $\frac{P_x - P_\infty}{P_{x_o} - P_\infty} = (1 - F)$ and Equation (5 - 19) is in the form of a conventional McKay relation(73). Equation (5 - 19) is also identical to an equation derived by Takaishi(67) for exchange processes involving an intermediate complex.

Plots of log (1 - F) versus time show linear behaviour as illustrated in Fig. 12 for run No. 1 in Table VIII. From the slopes of such plots, R_1 has been determined. Using the kinetic equation determined by Ames and Willard(43) given by (5 - 20):

$$(5 - 20) \quad R_1 = 3k_1[S_2O_3^=][SO_3^=]$$

values of k_1 shown in Table VIII have been calculated. As a comparison the rate constant k_1 calculated from the data of Ames and Willard(43) is 3.44×10^{-4} $l.m^{-1}s^{-1}$ at 50°C and for ionic strength of 2.0. Evidently the sulfur atom transfer process accounts very well for the interchange of oxygen between thiosulfate and water over this region of pH.

Case II

At a pH > 11, oxygen exchange between sulfite and water is effectively stopped(35). The only oxygen exchange is between thiosulfate and sulfite, via S atom transfer. The McKay equation(73) for ^{18}O exchange between these two species is given by Equation (5 - 21):

$$(5 - 21) \quad \ln \frac{P_x - P_\infty}{P_{x_o} - P_\infty} = -R_1 \frac{X + Y}{XY} t$$

where P_x and P_{x_o} have the same definition as in Case I but P_∞ now refers to the ^{18}O isotopic equilibrium between thiosulfate and sulfite only as given by Equation (5 - 22):

$$(5 - 22) \quad P_\infty = \frac{XP_{x_o} + YP_{y_o}}{(X + Y)}$$

A plot of log (1 - F) versus time for an experiment done at

Fig. 12

Fraction of ^{18}O exchange between thiosulfate and water catalyzed by sulfite at pH = 9.6 (see Equation 5 - 19)

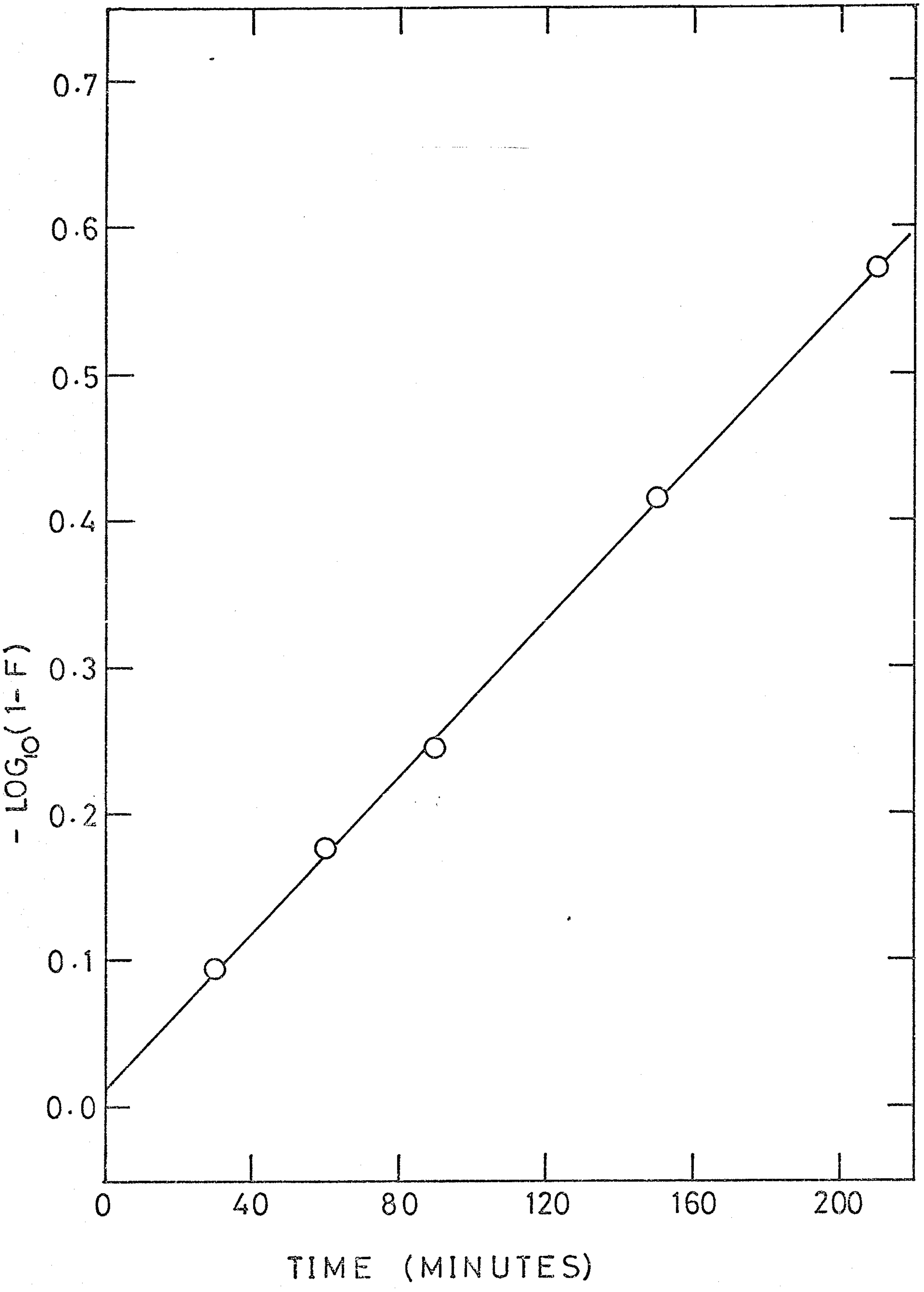

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
$-\mathrm{LOG}_{10}(1-F)$
0
40
80
120
160
200
TIME (MINUTES)

TABLE VIII

SUMMARY OF DATA ON OXYGEN TRANSFER BETWEEN THIOSULFATE AND WATER IN PRESENCE OF ADDED SULFITE

Run	$[S_2O_3^=]$ M	$[SO_3^=]$ M	pH	$R_1 \times 10^5$ (g-atoms O $l^{-1}s^{-1}$)	$k_1 \times 10^4$ ($l\ m^{-1}s^{-1}$)
1§	0.20	0.50	9.59	6.15	2.05
2§	0.20	0.50	7.31	6.10	2.03
3§	0.20	0.50	6.93	6.60	2.20
4§	0.20	0.50	6.44	6.30	2.10
5§	0.20	0.50	4.80	5.79	1.94
6§	0.20	0.50	7.60	6.37	2.11
7†	0.20	0.50	6.90	5.97	1.99
8†	0.20	0.50	6.90	6.20	2.07
9†	0.20	0.50	6.90	5.88	1.95
10†	0.20	0.50	6.90	5.60	1.87
11†	0.20	0.50	7.32	6.08	2.04
12†	0.20	0.50	7.32	6.42	2.14
13§	0.40	0.30	9.59	7.74	2.15
14†	0.30	0.40	9.60	6.75	1.88
15§,ϕ	0.20	0.80	9.59	14.6	3.05
16§,ϕ	0.50	0.50	9.59	20.2	2.71
17†,ϕ	0.50	0.50	7.3	24.9	3.30
18§	0.20	0.50	2.75	19.5	6.47

Temperature = 50.3°C for all runs.

§ Thiosulfate recovered as $CuPy_4S_4O_6$.

† Thiosulfate recovered as BaS_2O_3

ϕ Note higher ionic strength for these experiments.

$R_1 = 3k_1[SO_3^=][S_2O_3^=]$

k_1 in Reference (43) is given in terms of S atom transfer; for each such event, 3 oxygen atoms, in effect, transfer.

pH 13 is illustrated in Fig. 13. The good linearity of this plot is proof that oxygen in H_2O is not involved in any way. From the slope of this plot, R_1 was calculated as 5.75×10^{-5} gram atoms oxygen $l^{-1}s^{-1}$. This is in good agreement with the data of Table VIII, in which the thiosulfate exchange with water was catalyzed by sulfite, and R_1 was calculated from Equation (5 - 19). Evidently sulfur atom transfer is still the main process responsible for oxygen exchange. The insensitivity of this process to pH is to be expected from the work of Ames and Willard(43).

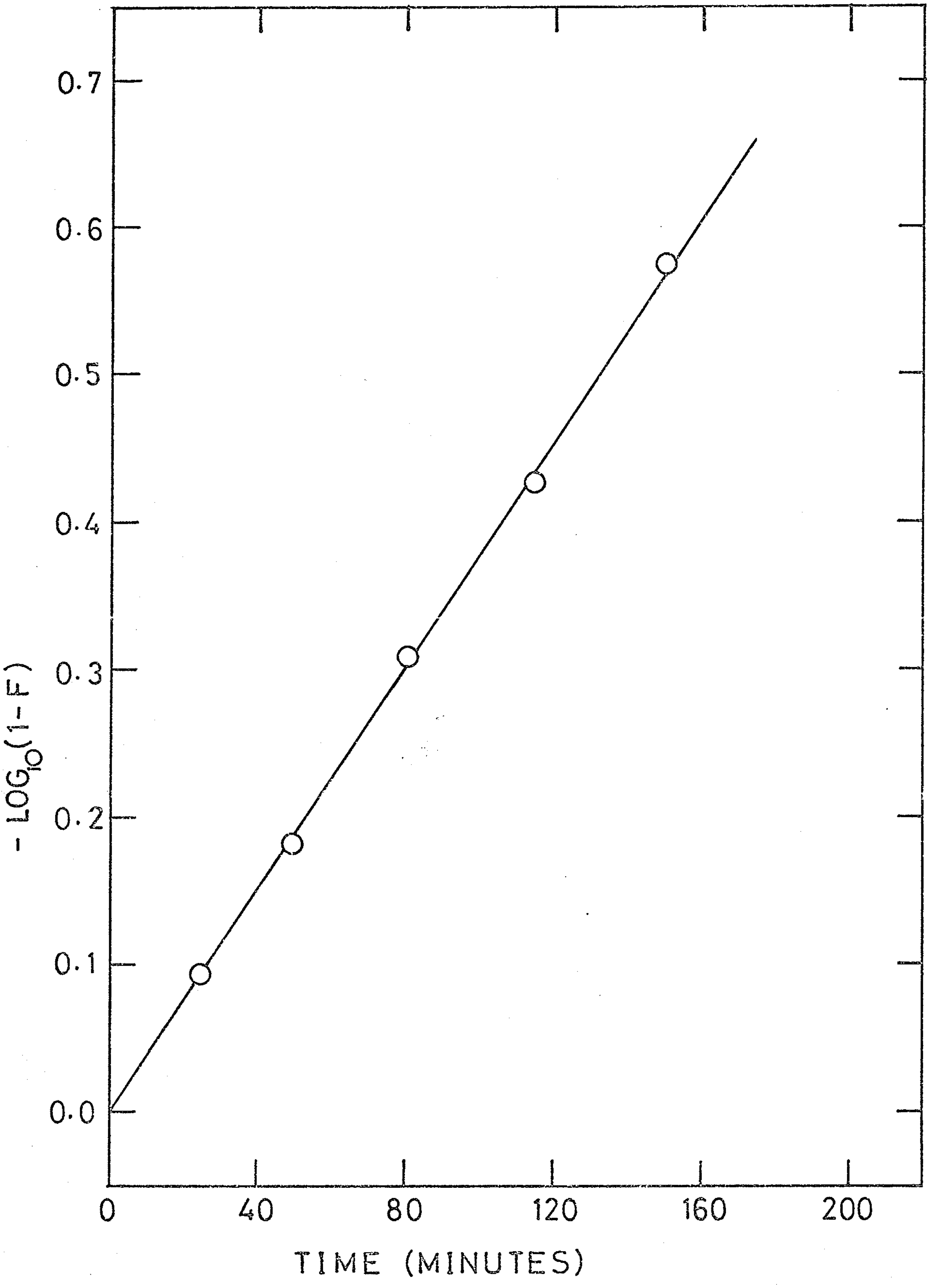
Case III

In the pH range 10 to 11 both R_1 and R_2 are within one or two orders of magnitude of each other. Thiosulfate and sulfite are exchanging oxygen atoms at a rate R_1 and sulfite is simultaneously exchanging oxygen atoms with water at a rate R_2. Since the ^{18}O isotopic label begins in thiosulfate, the oxygen-18 exchange in this system can best be described as two consecutive reversible first order reactions represented by Equations (5 - 1) and (5 - 2). The analytical solution of these equations has already been discussed and the general solution is given by Equation (5 - 15).

A graphical method can be used to evaluate λ_1, λ_2, A_x' and A_x'' in Equation (5 - 15), provided that R_1 and R_2 are sufficiently different so that λ_1 and λ_2 will differ by at least an order of magnitude. If $(P_x - P_\infty)$ is plotted against time on semi-log paper, then at sufficiently long times the curve should become a straight line,

Fig. 13

Fraction of ^{18}O exchange between thiosulfate and sulfite at pH 13 (see Equation 5 - 21), 0.2M $S_2O_3^=$, 0.5M $SO_3^=$

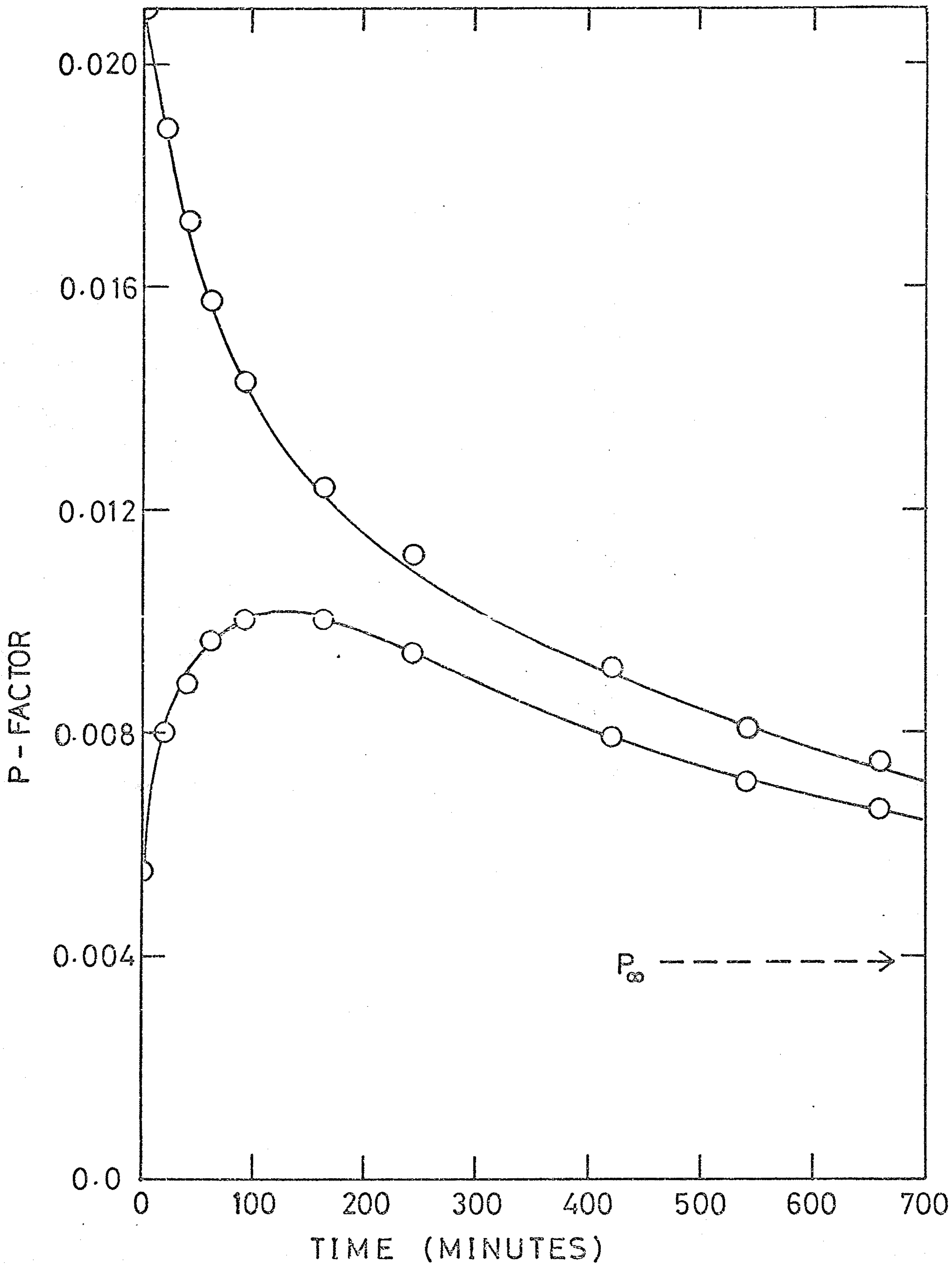

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
- LOG10(1- F)
0
40
80
120
160
200
TIME (MINUTES)

the exponential term with the smaller λ factor in Equation (5 - 15) being the main component at long times. The slope of this line segment will give the value of the smaller of the two λ's. If this line segment is extrapolated back to zero time and the ordinates of all points on this extrapolated line are now subtracted from the ordinates of the corresponding points on the original curve, and the resulting values replotted as before versus time, a straight line should result corresponding to the other exponential term in Equation (5 - 15). The slopes of these two resolved lines give λ_1 and λ_2 and the intercepts give the pre-exponential factors, $A_x^{'}$ and $A_x^{''}$. From this information R_1 and R_2 can be calculated. The data for $(P_y - P_\infty)$ can be treated in a similar way, and should give the same set of values for λ_1 and λ_2, and appropriate values for $A_y^{'}$ and $A_y^{''}$.

To indicate the validity of this analysis, an experiment was done at pH 10.8, $[S_2O_3^=] = [SO_3^=] = 0.5M$, a condition for which R_2 is expected to be less than R_1, but not zero. The ^{18}O-level in both thiosulfate and sulfite was determined experimentally as a function of time, i.e., values of P_x and P_y were obtained. (The quantity P_z (^{18}O-level in H_2O) was not followed, because as indicated earlier, this quantity does not change appreciably during the experiment.) Experimental values of P_x and P_y are shown in Fig. 14. In this Figure, the upper result shows the fall in level of ^{18}O in thiosulfate as the reaction proceeds. The lower curve shows very clearly the corresponding initial rise in ^{18}O abundance in sulfite.

Fig. 14

Variation of oxygen-18 in thiosulfate (upper curve) and sulfite (lower curve) as a function of time at pH 10.8. Open circles are experimental points and the lines are drawn from Equations (5 - 24) and (5 - 25)



P - FACTOR
0.020
0.016
0.012
0.008
0.004
0.0
0
100
200
300
400
500
600
700
TIME (MINUTES)
P_∞

A transient equilibrium is reached, as expected, followed by a decrease as the sulfite-water exchange proceeds towards isotopic equilibrium (shown as P_∞ in Fig. 14).

Plots of $(P_x - P_\infty)$ and $(P_y - P_\infty)$, on a logarithmic scale, versus time, are shown in Fig. 15, together with resolution of the curves into straight line components corresponding to the individual exponential terms comprising the curves as described above. The two sets of data lead to consistent values for λ_1 and λ_2, namely $\lambda_1 = 0.0193$ min^{-1}, $\lambda_2 = 0.00182$ min^{-1}, from the $(P_x - P_\infty)$ results, and $\lambda_1 = 0.0195$ min^{-1}, $\lambda_2 = 0.00186$ min^{-1} from the $(P_y - P_\infty)$ results. The quantities A_i' and A_i'' have been determined from the intercepts of the straight lines in Fig. 15. P_∞ was calculated from Equation (5 - 23).

$$(5 - 23) \qquad P_\infty = \frac{XP_{x_o} + YP_{y_o} + ZP_{z_o}}{X + Y + Z}$$

where P_{x_o} was the initial isotopic ratio in the thiosulfate at the start of the experiment and P_{y_o} and P_{z_o} are isotopic ratios for naturally occurring sulfite and water. The equations for variation of P_x and P_y as a function of time under our experimental conditions become:

$$(5 - 24) \qquad P_x = 0.0042 + 0.0065e^{-0.0194t} + 0.0106e^{-0.00184t}$$

$$(5 - 25) \qquad P_y = 0.0042 - 0.0060e^{-0.0194t} + 0.0082e^{-0.00184t}$$

(values of λ and t are in consistent units of min^{-1} and min, respectively.)

In Fig. 14 the open circles represent experimental values whereas the solid lines are drawn from Equations (5 - 24) and (5 - 25). The fit is very satisfactory.

From the average values of λ_1 and λ_2 determined in Fig. 15 and given above, R_1 and R_2 can be calculated from Equations (5 - 26) and (5 - 27):

$$(5 - 26) \quad \lambda_1 + \lambda_2 = \frac{R_1}{X} + \frac{R_1}{Y} + \frac{R_2}{Y} + \frac{R_2}{Z}\text{ , and}$$

$$(5 - 27) \quad \lambda_1\lambda_2 = R_1R_2 \frac{X + Y + Z}{XYZ}$$

from which $R_1 = 2.13 \times 10^{-4}$ gram atoms oxygen $l^{-1}\ s^{-1}$ and $R_2 =$ 1.00×10^{-4} gram atoms oxygen $l^{-1}s^{-1}$. From this value of R_1, k_1 (Equation 5 - 20) has been calculated as 2.82×10^{-4} l mole^{-1}s^{-1} which agrees with the values in Table VIII for similar thiosulfate and sulfite concentrations.

The value of R_2 (the rate of the sulfite-water exchange) derived in this analysis is not directly comparable to the data for this quantity from Reference (35) because of the large differences in the experimental conditions (ionic strength, sulfite concentration) between the two sets of results. Our best estimate of R_2 from Reference (35), extrapolated to the present conditions, is $\sim 1.4 \times 10^{-5}$ gram atom oxygen $l^{-1}s^{-1}$, in not unreasonable agreement with the value reported above.

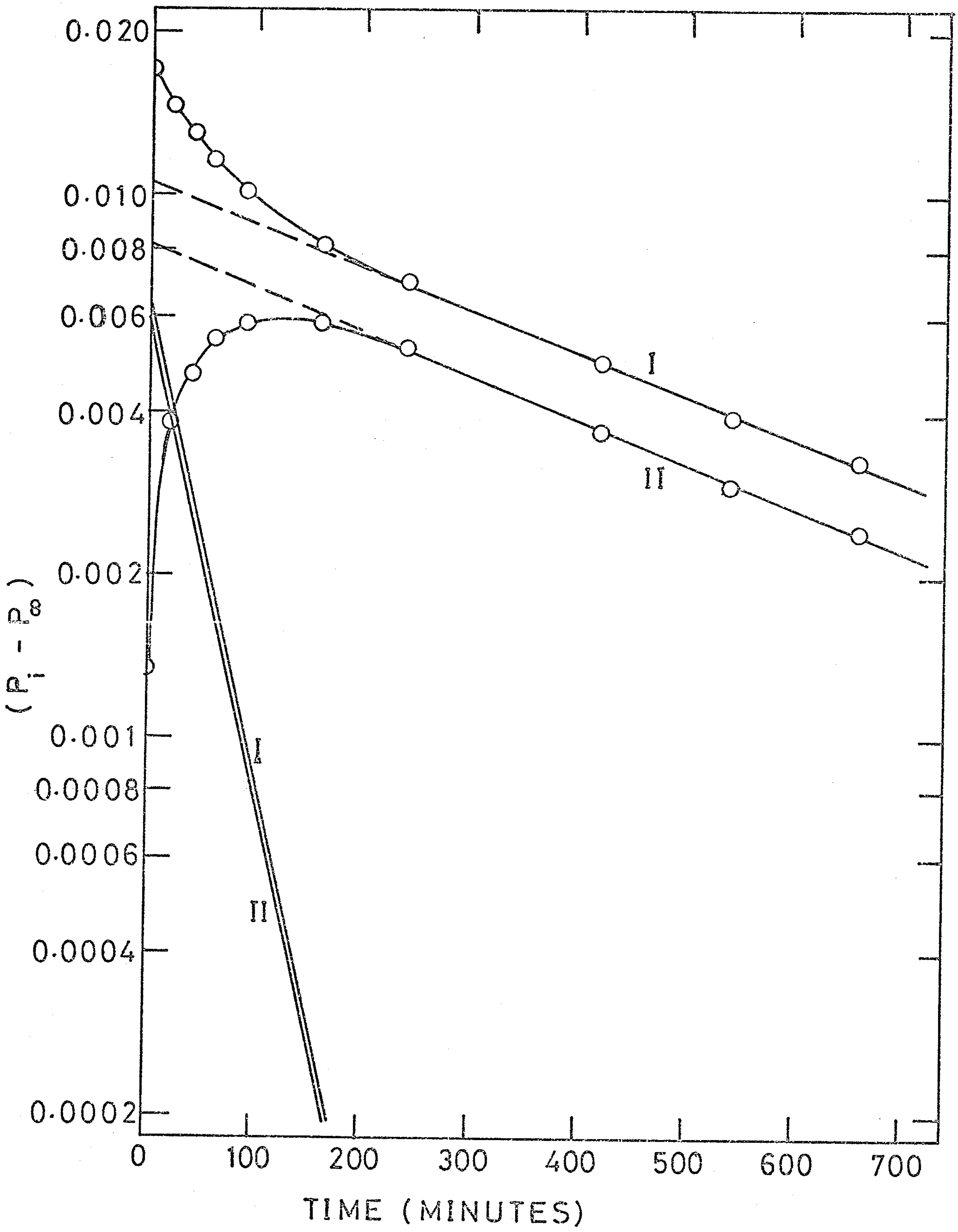
Case IV

In the acid region (pH < 4) thiosulfate by itself becomes increasingly unstable(74). However in the presence of sulfite which

Fig. 15

I - Data from measurement of ^{18}O content of thiosulfate;

II - ^{18}O content of sulfite. The corresponding straight line portions show the resolution of the two exponential terms (see text)


0·020
0·010
0·008
0·006
0·004
0·002
0·001
0·0008
0·0006
0·0004
0·0002
$(P_i - P_\infty)$
I
II
I
II
0
100
200
300
400
500
600
700
TIME (MINUTES)

in this pH region is mainly in the forms bisulfite and sulfurous acid (sulfur dioxide), the thiosulfate is stabilized and no sulfur appears even after several hours. In the absence of sulfite, precipitation of sulfur occurs within seconds. The unexpected stability of the thiosulfate in this acid medium may be related to the process:

$$(5 - 28) \quad H^+ + HSO_3^- + S_2O_3^= \rightleftarrows SO_2 \cdot S_2O_3^= + H_2O$$

Spectroscopic evidence for the complex $SO_2 \cdot S_2O_3^=$ has been found by Battaglia and Miller(74). Addition of thiosulfate to sulfite in a sufficiently acid medium produces a yellow color in the solution and this is thought to be due to the molecular complex shown in Equation (5 - 28).

The rate of oxygen atom transfer between thiosulfate and water is clearly accelerated at low pH, as is shown by run 18 in Table VIII made at a pH of 2.75. The value of k_1 is 6.46×10^{-4} $1\ m^{-1}\ s^{-1}$ and this is 3 times greater than for equivalent runs at higher pH. This acceleration at low pH may be due to direct exchange between thiosulfate and water; Pryor and Tonellato(44) indicate that this process is accelerated by a decrease in pH. Alternatively, the sulfur atom transfer process may show some slight dependence on pH; the work of Ames and Willard(43) did not go below pH 4.5. Also thiosulfate may decompose and the sulfur produced may react with the sulfite thus producing thiosulfate with an ^{18}O isotopic ratio equal to that of the water with which the sulfite is in equilibrium. Radioactive sulfur exchange measurements between sulfite and thiosulfate in acid medium are required to check for the presence of the latter processes.

5 - 3 CONCLUSION:

Evidently the sulfur atom transfer process of Ames and Willard(43) has an important role in the kinetics of oxygen transfer between thiosulfate and sulfite. The subsequent oxygen transfer from sulfite to water then occurs, depending on the pH of the system. The kinetics of the overall process are as predicted from independent studies of the two separate systems. Because of the differing kinetic orders of the two parts of the system, with respect to $[H^+]$, the overall kinetics can be varied at will. At each end of the pH range, the usual first order kinetics of simple isotopic exchange reactions is observed, while in the mid-region, one has two consecutive processes occurring at not dissimilar rates. This leads to the reversible consecutive first order behaviour illustrated in Figs. 14 and 15.

The exact reason for the disagreement between this work and that in Reference (44) is unknown. However there are some numerical inconsistencies in the earlier work. Also the conditions chosen there (low concentration of sulfite relative to thiosulfate) were not such as to allow the S atom transfer process to be clearly identified in the presence of the concurrent direct exchange of oxygen between water and thiosulfate.

THIOSULFATE OXIDATIONS 6

6 - 1 EXPERIMENTAL:

Thiosulfate was oxidized by various oxidizing agents in the hope of learning more about mechanisms by means of the oxygen exchange method. If the transition state in the oxidation is long lived or if active intermediates are formed in the oxidation process which may exchange their oxygen atoms with water then oxygen exchange methods should readily detect such species. The oxidations were performed with oxygen-18 enriched thiosulfate, dissolved in ordinary water or with unlabelled thiosulfate which was oxidized in the presence of oxygen-18 enriched water. Those oxidants which contained oxygen were of natural abundance, with respect to isotopic composition.

Tetrathionate was the main product encountered in these oxidations. It was separated by precipitation with copper(II) tetrapyridine complex for oxygen-18 abundance analysis. In many cases special problems were encountered in separating tetrathionate as a pure precipitate because the other products of the oxidations often interfered. These problems are discussed briefly below. The quantities used in the oxidations were such as to yield sufficient product for isotopic analysis; 1 to 2 ml. of 0.2M thiosulfate was sufficient.

The stoichiometry of the oxidation of thiosulfate by iodine is given by Equation (6 - 1):

(6 - 1) $2S_2O_3^{=} + I_3^{-} \rightarrow S_4O_6^{=} + 3I^{-}$

The reactions were carried out by mixing iodine and thiosulfate solutions in stoichiometric ratios. The iodine solutions were made sufficiently concentrated by addition of ethanol or of sodium iodide to form the I_3^{-} ion. Iodide interferes with the precipitation of tetrathionate and it was therefore removed by precipitation with bismuth nitrate. In other experiments iodide was removed with mercuric chloride, but this reagent had to be added in stoichiometric amount, since mercuric ions also interfere. In the low pH experiments thiosulfate was added to acidified iodine solutions but at high pH the order of mixing was varied.

Oxidation of thiosulfate by hydrogen peroxide was carried out by the addition of excess 30% H_2O_2 to thiosulfate. No problems of separating the tetrathionate were encountered here. Copper(II) tetrapyridine reagent used to precipitate tetrathionate also catalytically decomposed the excess hydrogen peroxide. At higher pH, sulfate was also a product of oxidation. It was separated as $SrSO_4$.

Oxidation of thiosulfate by either Cu(II) or $CuPy_4^{+2}$ was without complications. In the former case Cu(II) was added in excess and then pyridine was added to precipitate $CuPy_4S_4O_6$. In the latter case excess $CuPy_4^{+2}$ precipitated the tetrathionate. The copper(I) formed did not interfere with the precipitation of tetrathionate at the concentrations used here.

In the oxidation of thiosulfate by ferric ions, both Fe(III) and the product Fe(II) interfered in the recovery of tetrathionate with $CuPy_4^{+2}$. These problems were overcome by the addition of phosphoric acid which complexed ferric and ferrous ions sufficiently to permit the precipitation of $CuPy_4S_4O_6$.

Electrolysis of thiosulfate was carried out in a cell containing two compartments separated by a porous glass wall. A current of 10-15 mA for 2.5 hours was used in the electrolysis. Tetrathionate product was recovered as the $CuPy_4S_4O_6$ precipitate.

Oxidation of thiosulfate by peroxydisulfate is rather slow, requiring about 10 hours at 50°C for completion. Since peroxydisulfate is also precipitated by $CuPy_4^{+2}$ these reactions were run for 20 hours at 50°C to decompose any unreacted peroxydisulfate remaining in solution.

6 - 2 RESULTS AND DISCUSSION:

Sulfate is a by-product of the oxidation of thiosulfate by some oxidants, especially when hydrogen peroxide is used at higher pH. Copper(II) tetrapyridine recovered the product tetrathionate for oxygen-18 analysis without interference from the sulfate by-product.

Results of experiments in which iodine was the oxidant are given in Table IX. This reaction was carried out under a variety of conditions noted in the Table, and in all cases produced no appreciable

TABLE IX

THIOSULFATE OXIDATION WITH IODINE

($S_2O_3^{=}$ = 0.1M; I_2 = 0.1M; room temperature)

Run No.	pH of oxidation	P-factor of $S_2O_3^{=}$	P-factor for complete exchange	P-factor measured on $CuPy_4S_4O_6$
1	0.5	0.0225	0.0037	0.0218
2	1.0	0.0225	0.0037	0.0218
3	~6	0.0225	0.0037	0.0217
4	12	0.0225	0.0037	0.0213
5	13	0.0225	0.0037	0.0216
6	unadjusted	0.0225	0.0037	0.0217
7[§, †]	"	0.0037	0.032	0.0041[ψ]
8[§, φ]	"	0.0037	0.032	0.0064[ψ]

[§] Saturated I_2 solution in ethanol used as oxidant.

[†] T = 0°

[φ] T = 65°

[ψ] Tetrathionate recovered as $Na_2S_4O_6$ by adding excess EtOH.

exchange of thiosulfate oxygen with H_2O. The mechanism usually proposed for the iodine-thiosulfate reaction is(76):

(6 - 2) $S_2O_3^{=} + I_3^{-} \overset{\text{rapid}}{\rightleftarrows} S_2O_3I^{-} + 2I^{-}$

(6 - 3) $S_2O_3I^{-} + S_2O_3^{=} \xrightarrow{\text{slow}} S_4O_6^{=} + I^{-}$

Evidence from kinetic studies(76) of this reaction indicates that the intermediate, $IS_2O_3^{-}$, has a detectable lifetime in solution. It was also suggested that iodine was attached to the outer sulfur atom of the thiosulfate. The results in Table IX show that attachment of I^{+} to the thiosulfate has no great effect on the lability of the thiosulfate oxygens. In the basic pH region iodine is rapidly converted to IO^{-} which is thought to be the species responsible for oxidation of thiosulfate. This change in oxidant, however, did not influence the amount of oxygen exchange observed during the oxidation process.

The mechanism proposed for the hydrogen peroxide oxidation of thiosulfate(36, 77) is similar to the iodine oxidation.

(6 - 4) $H_2O_2 + S_2O_3^{=} \rightarrow HOS_2O_3^{-} + OH^{-}$

(6 - 5) $HOS_2O_3^{-} + S_2O_3^{=} \rightarrow S_4O_6^{=} + OH^{-}$

The mechanism of this reaction changes as the pH is increased. At pH 4.5 tetrathionate is the only product whereas at pH 13 no tetrathionate is produced and sulfate is the only product. At intermediate pH, around pH 9, tetrathionate and sulfate are produced in about equal yield. The amount of oxygen exchange observed, shown in Table X,

TABLE X

THIOSULFATE OXIDATION WITH H_2O_2

($S_2O_3^=$ ~0.2M; H_2O_2 = 30%; room temperature)

Run	pH at start of oxidation	P-factor of $S_2O_3^=$	P-factor for complete exchange	P-factor of $CuPy_4S_4O_6$	P-factor of $SrSO_4$
1	4.5	0.0225	0.0037	0.0214	---
2	8.7	0.0225	0.0037	0.0163	0.0071
3	9.6	0.0225	0.0037	0.0161	0.0083
4	13	0.0225	0.0037	---	0.0043

reflects this change in mechanism. As more sulfate is produced more exchange is observed. A P-factor of 0.0083 for sulfate represents 3 oxygens coming from water and one oxygen remaining from labelled thiosulfate. More knowledge of this mechanism is required before any conclusions can be made for exchange via active intermediates.

Oxidation of thiosulfate by Cu(II) and Fe(III) most likely proceeds by prior complex formation(78, 49). Oxidation by Cu(II) is very rapid and, as shown in Table XI, produces no appreciable exchange. The fact that oxidation of thiosulfate by copper(II) tetrapyridine complex produced no exchange in the recovered tetrathionate was made use of in the earlier part of this work. This meant that thiosulfate could be recovered from solution for oxygen-18 abundance measurements even in the presence of sulfate and sulfite in a form which required very little purification or dehydration. Other ions which precipitate thiosulfate such as barium and lead form hydrates which are extremely difficult to dehydrate.

There is visual evidence of the complex formation between thiosulfate and ferric ions. A deep purple color due to the complex $FeS_2O_3^+$ forms immediately upon mixing followed by gradual fading as the oxidation proceeds, possibly by electron transfer.

The proposed mechanism for this reaction is given as(49);

$$(6-6) \qquad Fe^{+3} + S_2O_3^{=} \rightleftarrows FeS_2O_3^{+}$$

$$(6-7) \qquad FeS_2O_3^{+} + S_2O_3^{=} \rightleftarrows FeS_2O_3^{\S} + S_2O_3^{\overset{-}{\cdot}}$$

TABLE XI

OXIDATION OF THIOSULFATE BY A VARIETY OF MEANS

($S_2O_3^{=}$ ~0.2M; Cu(II) = 0.2M; $CuPy_4^{+2}$ = 0.5M; Fe(III) = 0.2M; $S_2O_8^{=}$ = 0.1M)

Run No.	Oxidant	Temperature	P-factor of $S_2O_3^{=}$	P-factor for complete exchange	P-factor of $CuPy_4S_4O_6$
1	Cu^{+2}	Room	0.0037	0.032	0.0040
2	$CuPy_4^{+2}$	Room	0.0225	0.0037	0.0214
3	$CuPy_4^{+2}$	50°	0.0225	0.0037	0.0216
4	Fe^{+3}	0°	0.0037	0.032	0.0062
5	Fe^{+3}	24°	0.0037	0.032	0.0055
6	Fe^{+3}	53.7°	0.0037	0.032	0.0062
7	Fe^{+3}	-3°	0.0037	0.032	0.0056
8	electrolysis	Room	0.0037	0.032	0.0089
9	electrolysis§	Room	0.0037	0.032	0.0060
10	$S_2O_8^{=}$	50°	0.0225	0.0037	0.0156

§ Solution stirred by rotating electrode.

(6 - 8) $FeS_2O_3^{+} + S_2O_3^{-} \rightarrow Fe^{+2} + S_4O_6^{=}$

(6 - 9) $FeS_2O_3^{\S} + Fe^{+2} \rightleftarrows FeS_2O_3 + Fe^{+2}$

(6 - 10) $Fe^{+2} + S_2O_3^{=} \rightleftarrows FeS_2O_3$

Two reaction intermediates are proposed in the above mechanism; a singly-charged thiosulfuryl ion ($S_2O_3^{-}$), and an uncharged ion thiosulfate complex ($FeS_2O_3^{\S}$). This latter complex is regarded as a ferrous thiosulfate complex which, being formed by an electron transfer from a thiosulfatoferric ion, has the configuration of the latter ion. It is transformed to the normal ferrous thiosulfate complex by a slow reaction with a ferrous ion (Equation 6 - 9).

As seen in Table XI, oxidation of thiosulfate by ferric ions produces measurable exchange, but it is still far from complete. This exchange may be due to either of the two intermediates proposed in the mechanism. It was therefore of interest to examine other methods for production of the singly-charged thiosulfuryl ion ($S_2O_3^{-}$).

Electrolytic oxidation of thiosulfate to tetrathionate could proceed by either of two mechanisms(36). There could be a double electron transfer from one thiosulfate ion:

(6 - 11) $S_2O_3^{=} \rightarrow S_2O_3 + 2e$

followed by reaction between the discharged S_2O_3 species and thiosulfate ions

(6 - 12) $S_2O_3 + S_2O_3^{=} \rightarrow S_4O_6^{=}$

or a single electron transfer

(6 - 13) $S_2O_3^{=} \rightarrow S_2O_3^{\dot{-}} + e$

followed by reaction between two $S_2O_3^{\dot{-}}$ ion radicals. Here again there are two possible intermediates which may undergo oxygen exchange with water. Although electrolytic oxidation produced some exchange as shown by runs 9 and 10 in Table XI, the results were not very reproducible. The difference between runs 9 and 10 is that run 10 had a rotating platinum electrode to stir the solution as opposed to the stationary electrode in run 9. The solution was stirred so that if $S_2O_3^{\dot{-}}$ were in fact an intermediate, the possibility of its dimerization near the electrode would be reduced, thereby increasing its lifetime in solution.

Kinetic studies of the reaction represented by the equation

(6 - 14) $S_2O_8^{=} + 2S_2O_3^{=} \rightarrow S_4O_6^{=} + 2SO_4^{=}$

have shown that the rate is first order in peroxydisulfate and zero order in thiosulfate. A free radical mechanism has been proposed for this reaction as follows(79, 80):

(6 - 15) $S_2O_8^{=} \rightarrow 2SO_4^{\dot{-}}$

(6 - 16) $SO_4^{\dot{-}} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot}$

(6 - 17) $OH^{\cdot} + S_2O_3^{=} \rightarrow OH^{-} + S_2O_3^{\dot{-}}$

(6 - 18) $S_2O_3^{\dot{-}} + S_2O_8^{=} \rightarrow SO_4 \cdot S_2O_3^{=} + SO_4^{\dot{-}}$

(6 - 19) $S_2O_3^{\overline{\cdot}} + SO_4^{\overline{\cdot}} \rightarrow SO_4{\cdot}S_2O_3^{=}$

(6 - 20) $S_2O_3^{=} + SO_4{\cdot}S_2O_3^{=} \rightarrow S_4O_6^{=} + SO_4^{=}$

Run 10 in Table XI shows that some oxygen exchange between thiosulfate and water or peroxydisulfate has occurred during the oxidation process. There are two intermediates that could be responsible for this exchange; the radical anion, $S_2O_3^{\overline{\cdot}}$ or the complex $S_2O_3{\cdot}SO_4^{=}$.

Another method of producing the radical anion $S_2O_3^{\overline{\cdot}}$ is by photolysis of tetrathionate with light below 280 nm.(49). A sample of unlabelled tetrathionate (P = 0.0037) dissolved in labelled water (P = 0.032) was photolyzed with Hg light (253.7 nm.). The radical anions $S_2O_3^{\overline{\cdot}}$, if produced, recombined to form tetrathionate again. The P-factor of the tetrathionate after irridation of a 0.05M tetrathionate solution with 1.2 x 10^{15} photons/cm^2/sec for 4 hours was 0.0083. An ESR scan of this solution under photolysis in the cavity of an ESR spectrometer could detect no radicals, however, the lifetimes of these radicals could be so short that the steady-state concentration might be below the limit of detection by ESR methods. This experiment can hardly be regarded as definitive.

Another possibility for the absence of an ESR signal is that the tetrathionate could split into non-radical species; an uncharged S_2O_3 species and a thiosulfate ion during photolysis. However evidence for $S_2O_3^{\overline{\cdot}}$ as a product of photolysis is that when tetrathionate was mixed with acrylonitrile, and irridated with 253.7 nm light a small amount of polymer was formed. This polymer when examined by infrared spectroscopy showed evidence of a C-S link suggesting the polymerization was initiated by the $S_2O_3^{\overset{-}{\cdot}}$ radical(49).

CONCLUSIONS 7

Oxygen exchange measurements between the polynuclear hydroxy lead species, $Pb_4(OH)_4^{+4}$, or the hydroxy bismuth species, $Bi_6(OH)_{12}^{+6}$, and water have shown that the exchange rate is too rapid to be followed kinetically by the method used in this work. Complete isotopic oxygen equilibrium with solvent for both of these species occurs in less than one minute. The fast rate of exchange of the bridging oxygens in these polyhedra indicates that a highly-organized multiple-bonded structure, such as in these polyhedra, is not by itself a sufficient condition for inert oxygen atoms with respect to their exchange with the solvent. Possible mechanisms for this exchange have been proposed.

The possibility of oxygen exchange between tetrathionate and water catalyzed by sulfite, was examined. This system was complicated by the chemical reaction that takes place between tetrathionate and sulfite to yield trithionate and thiosulfate. A kinetic study of this chemical reaction showed the reaction to be second order overall; first order in tetrathionate concentration and first order in sulfite concentration. The rate constant was determined as 1.47 $l. mole^{-1} sec^{-1}$ at $0^{o}C$ and an ionic strength of 1.13. This study also showed that sulfite, and not bisulfite, was responsible for the nucleophilic displacement observed on tetrathionate.

The Davis correlation, which relates sulfur-sulfur bond length to activation energy for nucleophilic displacements on catenated sulfur bonds by sulfite or cyanide, suggested that the displacement of $-SO_3^=$ group on tetrathionate by sulfite should proceed at least sixteen times faster than the displacement of $S_2O_3^=$. However, no sulfite catalyzed exchange between tetrathionate and water was observed in the time period of the chemical reaction under a variety of conditions. A proposal based on electrostatics was given to show how the effects of bond energies could be modified during nucleophilic displacements.

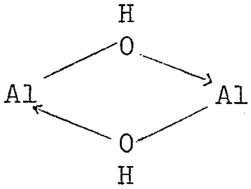
The nucleophilic displacement process on thiosulfate by sulfite has an important role in the kinetics of oxygen transfer between thiosulfate and sulfite. Subsequent oxygen transfer from sulfite to water then occurs, depending on the pH of the system. When the sulfite-water oxygen exchange is rapid then sulfite can be regarded as a catalyst in the thiosulfate-water oxygen exchange mechanism. The thiosulfate-sulfite oxygen exchange is independent of hydrogen ion concentration over a major portion of the pH region. The sulfite-water oxygen exchange has a second-order dependence on $[H^+]$. In the low pH range (2.75 - 10) the sulfite catalyzed oxygen exchange between thiosulfate and water is observed. In the high pH range (11 - 14) the usual first-order kinetics of simple isotopic exchange between thiosulfate and sulfite is observed, the sulfite-water oxygen exchange being virtually stopped. In the mid-region (pH 10 - 11), the two exchange processes occur at not dissimilar rates. For these conditions, the system provides an excellent example of a set of reversible consecutive first order rate processes. No large degree of scrambling of the oxygens of the thiosulfate with water was observed when thiosulfate is oxidized to tetrathionate. A few trends, however, were noticeable. For the very fast reactions (i.e., with I_3^-, Cu(II), $CuPy_4^{+2}$, and H_2O_2) very little or no exchange was observed. For reactions in which the radical anion, $S_2O_3^{\overline{\cdot}}$, is the postulated intermediate (i.e. with Fe(III), $S_2O_8^{=}$, electrolysis of $S_2O_3^{=}$ and photolysis of $S_4O_6^{=}$) some exchange was observed. Considering the very short lifetime of an intermediate, therefore if the observed exchange is due to this intermediate then the lability of the oxygen atoms in the radical anion, $S_2O_3^{\overline{\cdot}}$, must be greatly increased over that for thiosulfate or tetrathionate.

PROPOSALS FOR FURTHER RESEARCH 8

One of the main complications in the investigation of hydrated cations as oxyacids is the considerable tendency of hydrated ions of the type $MOH^{+(n-1)}$ (where n is the oxidation state of the ion) to polymerize. For example, in aluminum solutions, the equilibrium shown in Equation (8 - 1);

$$(8 - 1) \qquad 2Al(OH)^{+2} \rightleftarrows Al_2(OH)_2^{+4}$$

is set up. This dimer is thought to form the cyclic structure



Such polymers are essentially similar in structure to those already encountered in the polymerization of ordinary oxyacids in the sense that they contain oxygen bridges similar to those found in polyphosphates and silicates. In some polycations the bridges may be formed by hydroxyl groups but in others water may be eliminated as shown in Equation (8 - 2):

$$(8 - 2) \qquad 2MOH^{+(n-1)} \rightarrow M\text{-}O\text{-}M^{+2(n-1)} + H_2O$$

Mercuric solutions, for instance, contain species usually written as $Hg_2(OH)_2^{+2}$, but this could have split out water and be Hg_2O^{+2}. Of course it is presumably hydrated like other metal ions in solution, so it should really be written as $Hg_2(OH)_2(H_2O)_x^{+2}$ or $Hg_2O(H_2O)_x^{+2}$.

It might be expected that as a solution of a hydrated metal ion is made more alkaline, a monomeric ion, $MOH^{+(n-1)}$, would be produced first, then a dimer, $M_2(OH)_2^{+2(n-1)}$ and then higher polymers in a stepwise fashion as the total concentration of hydrolyzed species increases. This does not always seem to be so, at least for practical purposes. For example $Cu_2(OH)_2^{+2}$ is the main species formed in Cu(II) solutions, beryllium salts form $Be_3(OH)_3^{+3}$, lead forms $Pb_4(OH)_4^{+4}$ and bismuth forms $Bi_6(OH)_{12}^{+6}$ as the main species as these solutions are made more alkaline. Only traces of less complex species are thought to be present in these solutions. Thus there is more involved than just stepwise addition of partially hydrolyzed metal ions to form polymers. There appear to be definite structures favored by particular metal ions(81). For example dimers have been identified for the ions Be^{+2}, Al^{+3}, Sc^{+3}, La^{+3}, Th^{+4}, Sn^{+2}, In^{+3}, Cd^{+2}, Cr^{+3}, Fe^{+3}, Co^{+3} and Cu^{+2}; trimers are known for Be^{+2}, Sn^{+2} and Cu^{+2}; tetramers for Cu^{+2}, Pb^{+2} and Zn^{+4}; and Bi^{+3} gives the hexamer studied earlier.

Oxygen exchange methods still appear to be a useful tool in the investigation of such polymeric structures because such methods can usually indicate the number of oxygen atoms bound in these structures which are distinct from the solvent oxygen atoms. This may allow one to decide whether a particular structure contains hydroxyl bridges or oxygen bridges.

The investigation conducted in Section 3 on the lead and bismuth polynuclear species indicated that oxygen exchange between water as solvent and such polymerized species is very rapid. Therefore other methods must be used for following such rapid exchange reactions so that kinetic parameters may be determined and more information on the behavior of metal ions in aqueous solutions as a function of pH is to be revealed. Possible methods of following such rapid exchanges are flow dilution(18) or oxygen-17 NMR(82,83,15,16). The oxygen-17 NMR technique may be used to follow exchange rates with a half-life of 10^{-3} to 1 second. This may in some cases be fast enough to follow exchange of water of the hydration sphere of some of these complexes with the bulk solvent. The ideal case would be if one could measure both, the exchange of bridging oxygens or hydroxyl groups and exchange of water in hydration spheres with the bulk solvent.

Another fruitful field of research by oxygen exchange methods would be the study of ionic interaction in solution. The exchange rate of oxyanions and oxycations could be altered by other ions in their immediate environment. Charged particles are particularly sensitive to their environment. In addition to having thermodynamic and kinetic properties which depend heavily on the solvent, they will interact strongly with other ionic species in solution. The Debye-Huckel or the Bronsted-Bjerrum-Christiansen formulations give a reasonable interpretation of ionic interaction up to an ionic strength of 0.1. However because of experimental difficulties many reactions are studied at higher concentrations yielding solutions of ionic strength greater than 0.1. At higher concentrations the whole concept of the ionic strength principle breaks down, that is, the principle stating that the properties of an ion depend on the ionic strength only and not on the specific ions that constitute the environment. Thus the properties of ions could be altered greatly by the presence of other ions in its co-ordination sphere. For example in dilute aqueous solution an oxyanion (or oxycation) will have only water molecules in its inner co-ordination sphere. The oxygen exchange rate between the oxyanion and water will depend on the interaction of the water molecules with this oxyanion and in many cases the availability of protons to protonate the oxygens on the oxyanion. In more concentrated solutions the probability that this oxyanion will have cations in its co-ordination sphere are greatly increased. The cation-oxyanion pair could be co-ordinated or be separated by a water molecule. At any rate the presence of this cation should affect the exchange rate of the oxyanion since cations greatly affect the properties of water molecules in their co-ordination spheres, especially the dissociation constant of these water molecules thus making protons usually more available in their immediate vicinity. Thus on the molecular level the properties of water molecules in the co-ordination sphere of a cation-oxyanion pair will usually depend on the type and extent of interaction between the cation and oxyanion.

These interactions may range from simple ion pairs to complex formations with oxyanions acting as ligands for a variety of cations. Other interactions in solution include the $SO_2 \cdot S_2O_3^=$ complex ion given in Equation (5 - 28) or complexes formed between SO_2 and iodide ions.

There is physical chemical evidence in the literature for simple ion pair formation between cations and anions in aqueous solution. Spectroscopic evidence(84) indicates that thiosulfate forms ion pairs with metal ions of the form $MS_2O_3^-$. Evidence produced by NMR(15) indicates that the hydration numbers of sodium ions in solution is lowered in the presence of certain anions and this lowering was attributed to ion pairing.

There are some oxygen exchange studies which indicate that different cations influence the oxygen exchange rate of a particular oxyanion(30, 85). The nitrates, in particular, have been investigated because of the high solubility of a large variety of nitrate salts. These investigations, however, leave much to be desired because in most cases the solutions were extremely concentrated due to experimental methods used and ionic strength or pH effects were not controlled and therefore very few of the kinetic parameters in these exchange reactions were determined.

It is therefore desirable that a thorough kinetic investigation of the effects of different cations on the oxygen exchange rates of oxyanions with water be made. These effects can perhaps be related to the acid ionization constants of hydrated cations. The acid ionization constant, K_a, of hydrated M^{+n} is determined by the reaction.

$$(8-3) \quad M(H_2O)_x^{+n} + H_2O \rightleftarrows H_3O^+ + MOH(H_2O)_{x-1}^{+(n-1)}$$

and is given by

$$(8-4) \quad K_a = \frac{[H_3O^+][MOH(H_2O)_{x-1}^{+(n-1)}]}{[M(H_2O)_x^{+n}]}$$

These ionization constants are known for a variety of cations(81, 86). The pK_a values for these cations range from about 14 for sodium ions to 1.8 for Co(III) and 0.2 for Zr(IV). Thus the local acidity effects produced by some of these hydrated cations should markedly affect exchange rates of oxyanions if ion pairs are formed in solution.

Another type of interaction of ions in solution is complex formation where the oxyanion acts as a ligand. One result to be anticipated from the co-ordination of a ligand to a positively-charged metal ion is a distortion of the electronic distribution of that ligand toward the metal ion. This should result in a facilitation of attack by water molecules on the oxyanion leading to an increased rate of exchange. A preliminary experiment was carried out in an investigation of this effect by complexing La^{+3} ions with thiosulfate. Ionic strength was adjusted in a control experiment with sodium chloride. The lanthanum thiosulfate complex accelerated the oxygen exchange between thiosulfate and water by a factor of 4 over that of a control experiment. Other rare earth complexes of thiosulfate have even higher equilibrium constants(65). It would be of interest to examine the influence of complex formation on the oxygen exchange rate as a function of the equilibrium constant for these complexes. There is also the possibility of distinguishing whether the thiosulfate ligand is bonded through the sulfur or through an oxygen to the metal ion. Such linkage isomerism is known for some transition metal thiosulfate complexes(87). If co-ordination is through one of the oxygens on thiosulfate then there may be different exchange rates for the co-ordinated and unco-ordinated oxygens on thiosulfate. Such effects have been found for oxalate complexes with Co(III)(88).

One other possibility for a research topic is the investigation of the kinetic order with respect to water concentration of oxygen exchange reactions between oxyanions or other oxygen containing species and water by using non-aqueous solvents. Such experiments might also provide information about hydration of anions. Such information is at present rather scarce.

APPENDIX I

CALCULATION OF EQUILIBRIUM P-FACTORS FOR THE EXCHANGE STUDIES ON LEAD AND BISMUTH HYDROXY PERCHLORATES

The analysis of the hydroxy-lead perchlorate, $Pb_4(OH)_4(ClO_4)_4$ yielded a $Pb:ClO_4^-$ ratio of 0.92. This ratio corresponds to 9 atom percent of the Pb as unhydrolyzed Pb^{+2}. Also, thermogravimetric studies indicate that a trihydrate is initially formed which can be dehydrated by drying under vacuum at ~100°C. The equilibrium P-factor for the exchange study (Section 3 - 1) can be calculated from the above information and the weights of hydroxy lead perchlorate and water used.

The weight of dehydrated salt used was 3.8832 grams. Only 0.91 atom fraction of the lead is actually $Pb_4(OH)_4(ClO_4)_4$ the remainder being $Pb(ClO_4)_2$. The MW of $Pb_4(OH)_4(ClO_4)_4$ = 1294 while $Pb(ClO_4)_2$ = 406.

Therefore, the percent by weight that is $Pb_4(OH)_4(ClO_4)_4$ is:

$$\frac{(0.91 \times 1294/4)}{(0.91 \times 1294/4) + (0.09 \times 406)} \times 100 = \underline{89.8\%}$$

Therefore of the 3.8832 g. used in the exchange study (Section 3 - 1) only 3.485 grams is $Pb_4(OH)_4(ClO_4)_4$. This corresponds to 2.69×10^{-3} moles of $Pb_4(OH)_4(ClO_4)_4$ or to 1.08×10^{-2} g-atoms of exchangeable oxygen (considering that only the hydroxyl oxygens are exchangeable).

Since 3.0 ml. of water (0.167 g-atoms of oxygen) with an initial P-factor of 0.0274 was used while the oxygens in the hydroxyl groups has a P-factor of 0.00370 (natural abundance) then the equilibrium P-factor can be calculated as follows:

$$P_{\infty} = \frac{(0.0108 \times 0.0037) + (0.167 \times 0.0274)}{0.0108 + 0.167}$$

$$= \underline{0.0258} \text{ (see Table I, p. 41).}$$

For the reversed exchange the salt was only vacuum dried and not dehydrated at 100°C, thus it was assumed to be the trihydrate. In this case for each mole of $Pb_4(OH)_4(ClO_4)_4 \cdot 3H_2O$, there will be 7 exchangeable oxygens. The number of g-atoms of exchangeable oxygen will therefore be 1.88×10^{-2} g-atoms ($2.69 \times 10^{-3} \times 7$). These oxygens will have a P-factor of 0.0258 (the equilibrium value from the forward reaction). Since 3.0 ml. of water of P-factor 0.00370 was used in this exchange the equilibrium P-factor will be:

$$P_{\infty} = \frac{0.0188 \times 0.0258 + 0.167 \times 0.0037}{0.1858}$$

$$= \underline{0.00595} \text{ (see Table I, p. 41).}$$

The analysis of the hydroxy-bismuth perchlorate ($Bi_6(OH)_{12}(ClO_4)_6$) yielded a $Bi:ClO_4^-$ ratio of 0.90 or a $ClO_4^-:Bi$ ratio of 1.11. If the excess perchlorate over bismuth is due to $Bi(ClO_4)_3$ then 94.5 atom percent of the bismuth is from the $Bi_6(OH)_{12}(ClO_4)_6$ species. The molecular weight of $Bi_6(OH)_{12}(ClO_4)_6$ is 2055 and the MW of $Bi(ClO_4)_3$ = 507.2. The percentage of the bismuth by weight due to $Bi_6(OH)_{12}(ClO_4)_6$ is

$$\frac{(0.945 \times 2055/6)}{(0.945 \times 2055/6) + (0.055 \times 507.2)} \times 100$$

$$= \underline{92.2\%}$$

However, by the weight difference (i.e. the weight used for analysis and the weight of the products analyzed) showed there to be approximately ten molecules of hydration per mole of $Bi_6(OH)_{12}(ClO_4)_6$. Therefore the percentage by weight of the sample that is $Bi_6(OH)_{12}(ClO_4)_6 \cdot 10H_2O$ is:

$$\frac{\left(0.945 \times \underline{\frac{2055 + 180}{6}}\right)}{\left(0.945 \times \frac{2055 + 180}{6}\right) + (0.055 \times 507.2)} = \underline{90.2\%}$$

Therefore of the 7.5640 g. of the hydroxy bismuth perchlorate used in the exchange, only 6.83 grams was as $Bi_6(OH)_{12}(ClO_4)_6 \cdot 10H_2O$. This corresponds to 3.05×10^{-3} moles of bismuth hydroxy perchlorate · 10 hydrate or to 0.0672 moles of exchangeable oxygen (22 oxygens per formula weight were considered exchangeable). An amount of 3.0 ml. of water (0.167 g-atoms of oxygen) with an initial P-factor of 0.0295 was used in the exchange. The equilibrium P-factor can be calculated as follows:

$$P_\infty = \frac{(0.0672 \times 0.00370) + (0.167 \times 0.0295)}{0.167 + 0.0672}$$

$$= \underline{0.0223} \text{ (see Table II, p. 44).}$$

For the reversed exchange it was assumed that the number of exchangeable oxygens contained in the salt remained unchanged (0.0672 g-atoms of oxygen) with a P-factor of 0.0223. The 3.0 ml. of water used in the reversed exchange had a P-factor of 0.0037 (natural abundance). The equilibrium P-factor for the reversed exchange can be calculated as:

$$P_{\infty} = \frac{(0.0672 \times 0.0223) + (0.167 \times 0.00370)}{0.0672 + 0.167}$$

$$= \underline{0.00902} \text{ (see Table II, p. 44)}$$

APPENDIX II

SAMPLE KINETIC RUN ON THE SULFITE-TETRATHIONATE REACTION

The pseudo-first order rate constants for the sulfite-tetrathionate reaction (Section 4 - 1) were obtained as follows. Iodometric titration data for run No. 2 (Section 4 - 2) are given in Table XII. (Na_2SO_3 = 0.0104M; $Na_2S_4O_6$ = 0.150M; Na_2SO_4 = 0.050M; temperature = 0°C; buffer = 0.50M $NaH_2C_6H_5O_7$).

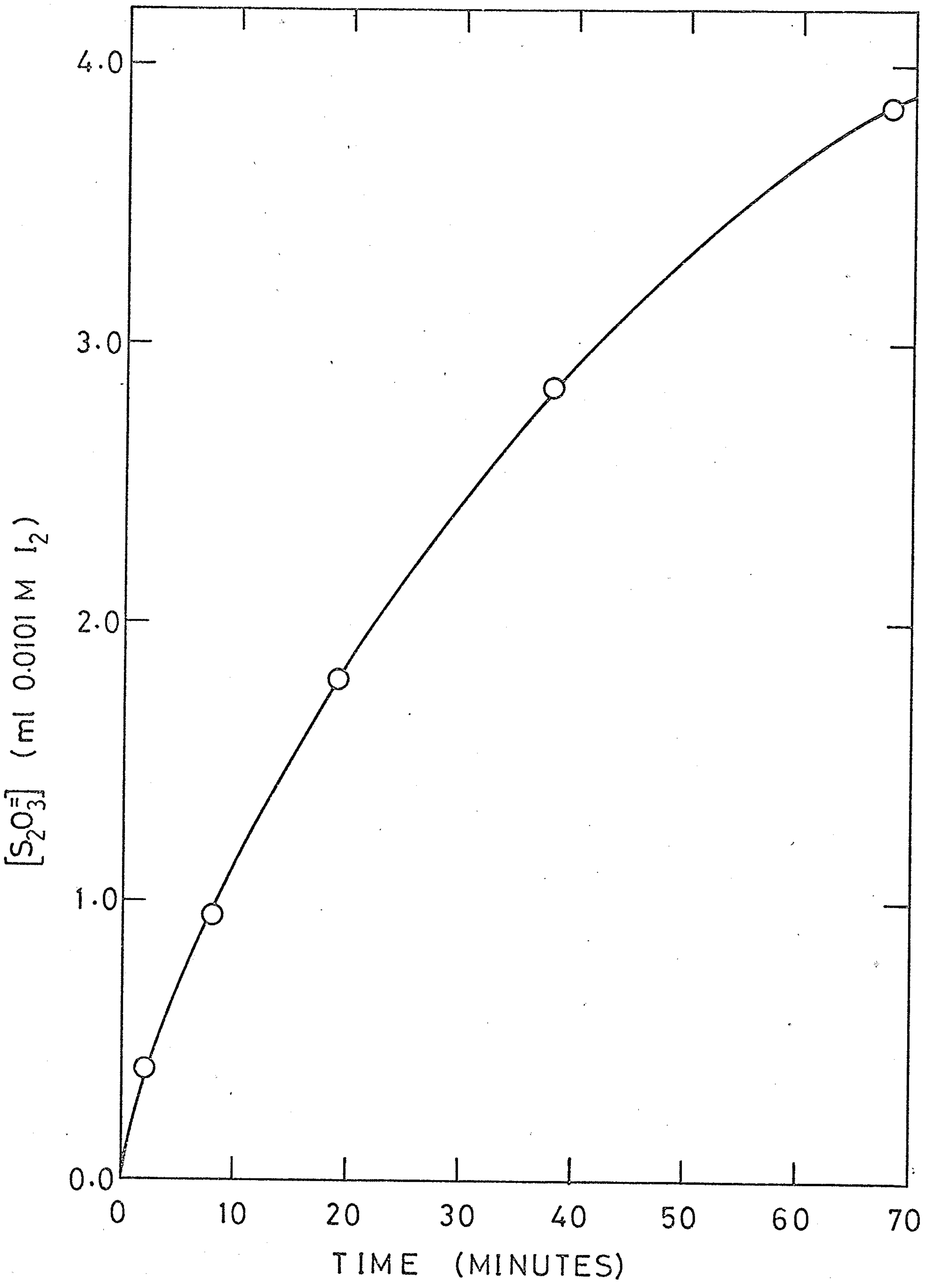
TABLE XII

TITRATION RESULTS IN ANALYSIS FOR THIOSULFATE AND SULFITE IN THE SULFITE-TETRATHIONATE REACTION (SECTION 4)

Aliquot A (10.0 ml.) Total $S_2O_3^=$		Aliquot B (10.0 ml.) Total $S_2O_3^= + SO_3^=$	
Time H_2CO added (sec)	ml. I_2 (0.0101M)	Time (seconds)	ml. I_2 (0.0101M)
120	0.40	200	9.65
480	0.95	560	9.10
1140	1.80	11230	8.30
2280	2.85	2370	7.20
4080	3.85	4170	6.25

Fig. 16

Formation of product thiosulfate in the sulfite-tetrathionate reaction



4.0
3.0
2.0
1.0
0.0
[S2O3=] (ml 0.0101 M I2)
0
10
20
30
40
50
60
70
TIME (MINUTES)

The results for thiosulfate (Aliquot A) were then plotted against time (Fig. 16). From this plot in Fig. 16 the thiosulfate titers at time of the second set of titrations (i.e. for Aliquot B) were read off. These are referred to as the time normalized thiosulfate titers and were subtracted from the total titers of Aliquot B. This difference corresponded to the sulfite concentration alone. Using the iodine concentration (Section 2 - 1) these titration volumes were converted to moles of thiosulfate and sulfite respectively, with the results shown in Table XIII.

TABLE XIII

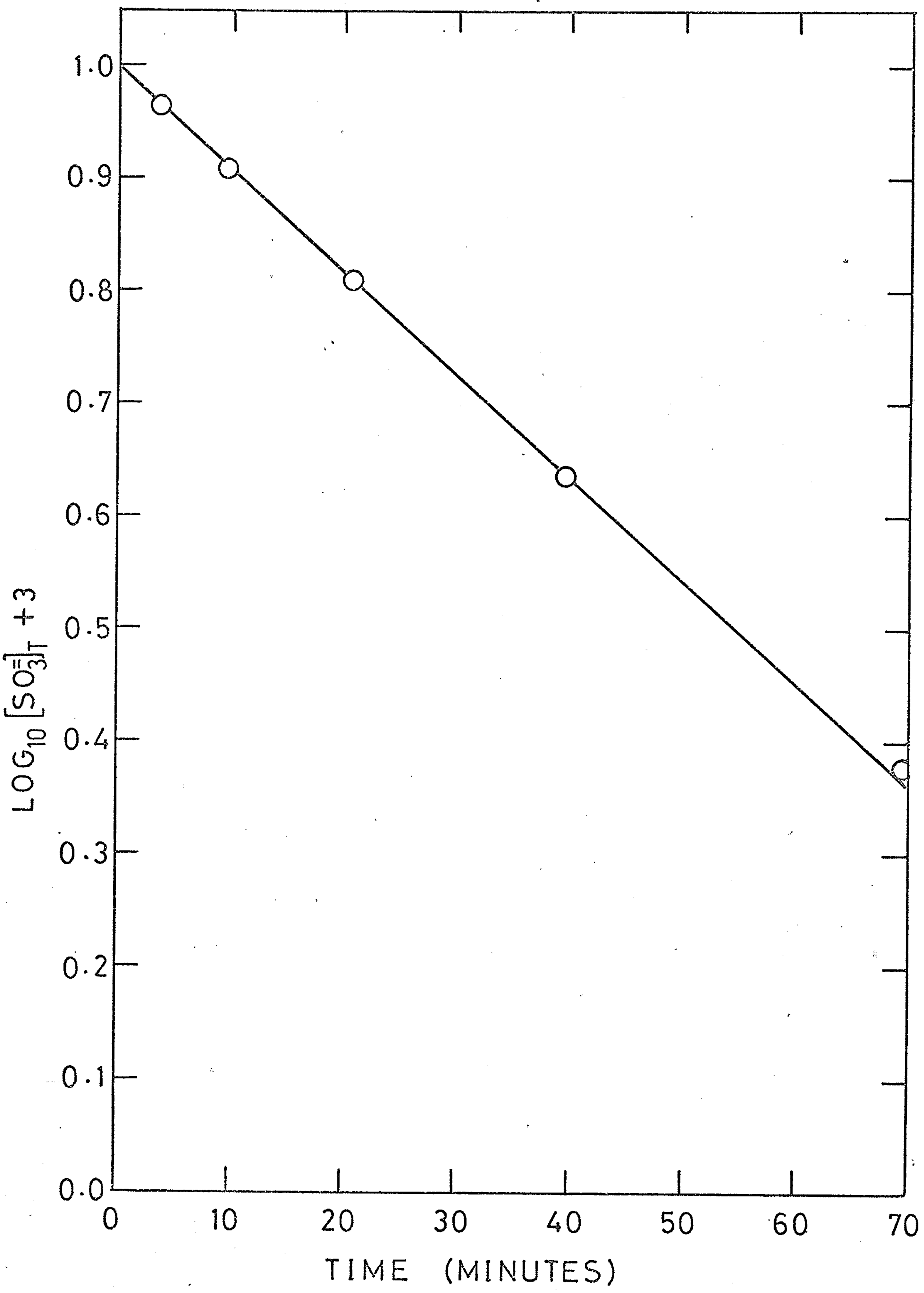
CALCULATED THIOSULFATE AND SULFITE CONCENTRATIONS FROM THE TITRATION DATA IN TABLE XII

Time (sec)	$S_2O_3^=$ in ml I_2 (graph)†	$S_2O_3^=$ moles/ 10 ml	$S_2O_3^=$ + $SO_3^=$ in ml I_2	$SO_3^=$ in ml I_2	$SO_3^=$ moles/ 10 ml	Σ moles $S_2O_3^=$ + moles $SO_3^=$
200	0.57	1.07×10^{-5}	9.65	9.12	9.21×10^{-5}	1.028×10^{-4}
560	1.08	2.18×10^{-5}	9.10	8.02	8.10×10^{-5}	1.028×10^{-4}
1230	1.90	3.84×10^{-5}	8.30	6.40	6.46×10^{-5}	1.030×10^{-4}
2370	2.92	5.90×10^{-5}	7.20	4.28	4.33×10^{-5}	1.023×10^{-4}
4170	3.88	7.84×10^{-5}	6.25	2.37	2.39×10^{-5}	1.023×10^{-4}

† Thiosulfate concentrations were determined from the graph in Fig. 16.

Fig. 17

Determination of pseudo first order rate constant in the sulfite-tetrathionate reaction (Section 4)


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
$\mathrm{LOG}_{10}[SO_3^=]_T + 3$
0
10
20
30
40
50
60
70
TIME (MINUTES)

As mentioned earlier, this method of determining sulfite concentration gave a check on oxidation of the sulfite to sulfate by molecular oxygen or the decomposition of the thiosulfate by acid. The constant value in the last column in Table XIII indicates that neither of these reactions has occurred. The initial concentration of the sulfite was 0.0104M which compares well with that last column obtained from titration results. Less than 0.2% of the sulfite was oxidized.

The logarithm of the sulfite concentrations were then plotted against time as shown in Fig. 17. The slope of this line was determined from a linear regression program on a Hewlett-Packard Model 9100A computer. The result for the line in Fig. 17 was $(3.46 \pm 0.05) \times 10^{-4}$ $\sec^{-1}$. This was the pseudo first order rate constant, k", for this kinetic run, and this information is recorded in Column 5 of Table III (of Section 4 - 2, p. 57).

APPENDIX III

METHOD OF INTEGRATION OF A COUPLED SET OF RATE EQUATIONS

General integrated equations may be readily derived for the rate Equations (5 - 12), (5 - 13), and (5 - 14) of Section 5 - 2 (repeated below):

$$(1) \quad \frac{dP_x}{dt} = \frac{R_1}{X}(P_y - P_x)$$

$$(2) \quad \frac{dP_y}{dt} = \frac{R_1}{Y}(P_x - P_y) - \frac{R_2}{Y}(P_y - P_z)$$

$$(3) \quad \frac{dP_z}{dt} = \frac{R_2}{Z}(P_y - P_z)$$

by methods described in the literature(70-72), which are similar to those used in solving the secular equations encountered in quantum mechanics. This set of three differential equations in three dependent variables P_i (where P_i represents P_x, P_y, or P_z) may be integrated in closed form.

First assume a particular solution of the form

$$(4) \quad P_i = B_i e^{-\lambda t}$$

where λ is a parameter to be determined and the B_i are constants. Substitution of (4) into Equations (1 - 3) and cancelling out the exponentials yields:

$$(5) \quad \left(\frac{R_1}{X} - \lambda\right)B_1 - \left(\frac{R_1}{X}\right)B_2 = 0$$

$$(6) \quad -\left(\frac{R_1}{Y}\right)B_1 + \left(\frac{R_1 + R_2}{Y} - \lambda\right)B_2 - \left(\frac{R_2}{Y}\right)B_3 = 0$$

$$(7) \quad -\left(\frac{R_2}{Z}\right) B_2 + \left(\frac{R_2}{Z} - \lambda\right) B_3 = 0$$

Equations (5 - 7) form a set of simultaneous homogeneous linear equations in B_1, B_2, and B_3. The conditions for a nontrivial solution for the B_i is that the determinant of the coefficients is zero.

$$(8) \quad \begin{vmatrix} \frac{R_1}{X} - \lambda & -\frac{R_1}{X} & 0 \\ -\frac{R_1}{Y} & \frac{R_1 + R_2}{Y} - \lambda & -\frac{R_2}{Y} \\ 0 & -\frac{R_2}{Z} & \frac{R_2}{Z} - \lambda \end{vmatrix} = 0$$

This determinantal equation, or secular equation, as it is often called, is a third degree algebraic equation in the parameter λ. Expanding (8), one obtains:

$$(9) \quad -\lambda \left[\lambda^2 - \left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z} \right) \lambda + \frac{R_1R_2}{XZ} + \frac{R_1R_2}{YZ} + \frac{R_1R_2}{XY} \right] = 0$$

from which the three solutions for λ_r are:

$$(10) \quad \lambda_1 = \frac{1}{2}\left\{ \left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z} \right) + \left[\left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z} \right)^2 - 4R_1R_2 \left(\frac{X + Y + Z}{XYZ} \right) \right]^{1/2} \right\}$$

$$(11) \quad \lambda_2 = \frac{1}{2}\left\{ \left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z} \right) - \left[\left(\frac{R_1}{X} + \frac{R_1 + R_2}{Y} + \frac{R_2}{Z} \right)^2 - 4R_1R_2 \left(\frac{X + Y + Z}{XYZ} \right) \right]^{1/2} \right\}$$

$$(12) \quad \lambda_3 = 0$$

Substitution of these λ_r into (5 - 7) gives three equations any two of which are independent. Making the arbitrary assumption that the various B_{1r} are unity, B_{2r} and B_{3r} can be solved for:

$$(13) \quad B_{1r} = 1$$

$$(14) \quad B_{2r} = \frac{R_1 - X\lambda_r}{R_1}$$

$$(15) \quad B_{3r} = \frac{R_2(R_1 - X\lambda_r)}{R_1(R_2 - Z\lambda_r)}$$

These particular solutions will not usually satisfy initial conditions of concentrations. A general solution is necessary and may be written as a linear combination of particular solutions. Any linear combination of particular solutions is also a solution of the differential Equations (1 - 3) since the latter are linear equations. The general solutions become:

$$(16) \quad P_x = \sum_r \overset{o}{Q}_r \, e^{-\lambda_r t}$$

$$(17) \quad P_y = \sum_r \overset{o}{Q}_r \, B_{2r} e^{-\lambda_r t}$$

$$(18) \quad P_z = \sum_r \overset{o}{Q}_r \, B_{3r} e^{-\lambda_r t}$$

where $\overset{o}{Q}_r$ are coefficients in the linear combinations and may be determined from initial conditions. Both $\overset{o}{Q}_r$ and B_{ir} are constants and may be combined into new constants as follows:

$$(19) \quad P_x = A'_x \, e^{-\lambda_1 t} + A''_x \, e^{-\lambda_2 t} + A_3$$

$$(20) \quad P_y = A'_y \, e^{-\lambda_1 t} + A''_y \, e^{-\lambda_2 t} + A_3$$

(21) $$P_z = A_z^{'} e^{-\lambda_1 t} + A_z^{''} e^{-\lambda_2 t} + A_3$$

At infinite time, $P_x = P_y = P_z = P_\infty = A_3$, so Equations (19 - 21) may be written as:

(22) $$P_i - P_\infty = A_i^{'} e^{-\lambda_1 t} + A_i^{''} e^{-\lambda_2 t}$$

which is the general solution used in Section 5 - 2, p. 85.

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