EQUILIBRIUM CONSTANTS FOR SULPHUR ISOTOPE EXCHANGE

THE EQUILIBRIUM CONSTANT FOR THE EXCHANGE OF THE SULPHUR ISOTOPES BETWEEN HYDROGEN SULPHIDE AND SULPHUR DIOXIDE

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TITLE: The Equilibrium Constant for the Exchange of the Sulphur Isotopes Between Hydrogen Sulphide and Sulphur Dioxide

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SCOPE AND CONTENTS: The equilibrium constant for the exchange of the sulphur isotopes between hydrogen sulphide and sulphur dioxide was measured at temperatures ranging from 700°K to 1300°K. For comparison with these measurements, values of the equilibrium constant were calculated, the calculations being based on the statistical mechanical theory of isotope effects and on spectroscopic data taken from the literature.

Although the experimental results were qualitatively consistent with theoretical predictions, there was a discrepancy between the experimental and calculated values. This discrepancy was tentatively ascribed to uncertainty in the vibrational isotope shifts of hydrogen sulphide.

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TABLE OF CONTENTS

I. INTRODUCTION

Page

(D) The Calculation of Vibrational Isotope Shifts

(E) The Reaction $H_2S^{34} + S^{32}O_2 \rightleftharpoons H_2S^{32} + S^{34}O_2$

(F) Scope of This Investigation

II. EXPERIMENTAL

(A) Sample Preparation

(B) Mass Spectrometry

(C) Corrections to the Data

III. CALCULATIONS

Page

IV. RESULTS AND DISCUSSION

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

(A) General

The development of quantum statistical mechanics has made possible the calculation of the thermodynamic properties of pure substances from the spectroscopically determined mechanical properties of the molecules, and hence equilibrium constants for a large number of reactions could be calculated. These calculations were of interest in two ways: comparison of the calculated equilibrium constants with values obtained experimentally provided a test for the hypothetical structure of the molecules, and estimates of equilibrium constants were available for systems in which direct experimental determinations were exceedingly difficult.

One of the most interesting results of this theory has been the prediction of deviations from unity for the equilibrium constants of isotope exchange reactions. Although these effects are small except in the case of the hydrogen isotopes, the development of mass spectrometers of high sensitivity in the detection of small variations in isotopic content has resulted in the observation of many such effects. Nevertheless, there have been few investigations undertaking an extended comparison over a wide temperature range between isotopic equilibrium constants obtained experimentally and those calculated from spectroscopic data.

The isotope exchange reaction studied in this work, the exchange of S^{32} and S^{34} between sulphur dioxide and hydrogen sulphide, was judged suitable for an investigation of this kind since variations in the relative abundance of S^{32} and S^{34} can be measured very accurately by mass spectrometric techniques and because good spectroscopic data for these molecules are now available for theoretical calculations. This isotope exchange is also of geochemical interest, since its occurrence in volcanos and fumaroles provides a possible mechanism for the fractionation of the sulphur isotopes in nature. In this work, therefore, the equilibrium constant for this reaction was measured over temperatures ranging from 700°K to 1300°K, and, in addition, values of the equilibrium constant were calculated for the same temperature range, the calculations being based on the best values of the molecular constants obtained from the literature.

(B) Differences in the Chemical Properties of the Isotopes

(1) Discovery of the Isotopes The name "isotope" was invented by Frederic Soddy in 1913 to designate elementary substances differing in radioactive properties but indistinguishable by ordinary chemical techniques. The existence of isotopes of non-radioactive elements was indicated by J. J. Thomson's positive ray experiments on neon, in which particles of mass 22 were observed along with the expected particles of mass 20. Unsuccessful attempts to isolate this unknown constituent by chemical methods followed, which, together with Aston's investigation of neon with the mass spectrograph, suggested that the constituent of mass 22 was an isotope of neon. Aston subsequently examined other elements with the mass spectrograph and found that many of them were composed of isotopic mixtures.

(2) Theoretical Predictions of Isotope Effects Although early workers were unable to distinguish between isotopes of an element by chemical means, it was already realized that a difference in atomic mass alone should result in a difference in the properties of an element. The kinetic theory

of gases indicated that various properties depend on the mass of the molecules of a gas: in particular, Lord Rayleigh (1) showed that particles differing only in mass should be separable by diffusion.

But since classical mechanics gave no information about the energy contained within the molecule, the question of whether the different isotopes of an element differed in their tendency to form a particular compound, i.e., whether the equilibrium constants for isotope exchange reactions differed from unity, could not be answered. With the advent of quantum mechanics, molecular energies could in principle be calculated, and, combining quantum mechanics with statistical mechanics, the differences in thermodynamic properties between molecules containing different isotopes of an element could be evaluated. This was done by Urey and Greiff (2), who calculated equilibrium constants for many isotope exchange reactions of the light elements. A variation of this method having considerable advantages in simplicity has been devised by Bigeleisen and Mayer (3).

In the case of kinetic phenomena, the transition state theory of reaction rates devised by Eyring and others (4) showed that the calculation of rate constants is related to that of equilibrium constants. The application of this theory to the calculation of the differences in reaction rates between different isotopic molecules has been made by Bigeleisen (5).

(3) <u>Experimentally Obtained Isotope Effects</u> The separation of isotopes by diffusion, predicted by Lord Rayleigh, was achieved to a considerable degree by Hertz (6) with the isotopes of neon. However, the most famous demonstration of this phenomenon has undoubtedly been the large-scale separation of the uranium isotopes for the atomic bomb project, using the diffusion rates of uranium-235 hexafluoride and uranium-238 hexafluoride.

Isotopic fractionation by chemical procedures was produced by Washburn and Urey (7), who found that deuterium was concentrated in the residual water during the electrolysis of water. Urey and Rittenberg (8) demonstrated that the differences in the equilibrium constant for the reaction $H_2 + I_2 = 2HI$ produced when deuterium is substituted for hydrogen agreed with their calculated values. Since that time, isotopic fractionation has been found to occur in many isotope exchange reactions (9), some of which have been successfully adapted to the large-scale production of separated isotopes, (e.g. the boron isotopes (10)).

(4) Isotope Effects in Natural Processes Several isotope exchange reactions have been postulated as the cause of variations in the isotopic content of the elements in natural samples. MacNamara and Thode (11) found differences in the sulphur isotopic content between sulphate and elemental sulphur from some Cyrenaican lakes in North Africa, in which isotope fractionation occurs through the mechanism of bacterial oxidation and reduction. Urey and others (12) demonstrated a fractionation of the oxygen isotopes in the slow crystallization of calcium carbonate and indicated that the temperature dependence of this effect could be used to estimate the temperatures of the deposition of limestone. Variations in the oxygen isotopic content of surface ocean water found by Epstein and Mayeda (13) were explained by the multiple-stage evaporation and condensation of water in the atmosphere.

The reaction studied in this work, the high-temperature exchange of sulphur between hydrogen sulphide and sulphur dioxide, occurring in volcanos and fumaroles has been postulated by Hitoshi Sakai (14) as a contributing cause of the variations of the natural isotopic content of sulphur.

(C) The Bigeleisen-Mayer Method for the Calculation of Isotopic Equilibrium Constants (3)

(1) Equilibrium Constants and Statistical Mechanics The calculation of equilibrium constants is made possible by the statistical mechanical relations between mechanical and thermodynamic quantities.

The thermodynamic condition for equilibrium for the homogeneous reaction

$$aA + bB = cC + dD \qquad (i)$$

is given by

$$c\mu_C + d\mu_D - a\mu_A - b\mu_B = 0 \qquad (ii)$$

where $\mu_A, \mu_B, \mu_C, \mu_D$ are the chemical potentials of components A, B, C, D.

If the system is an ideal gaseous mixture, the chemical potential of each component is of the form

$$\mu_i = \mu_i^o + RT \ln p_i \qquad (iii)$$

where p_i is the partial pressure of component i, T is the absolute temperature, R is the gas constant, and μ_i^o is a function of temperature only and is thus seen to be the Gibbs free energy of one mole of gas i at unit pressure (arbitrarily taken as 1 atm). Combining this equation with equation (ii), we obtain

$$c\mu_C^o + d\mu_D^o - a\mu_A^o - b\mu_B^o = - RT \ln \frac{p_C^c\, p_D^d}{p_A^a\, p_B^b} = - RT \ln K \qquad (iv)$$

The calculation of the equilibrium constant K requires that the μ^os, which are the standard free energies of the components, be calculated.

In order to find the statistical mechanical equivalent of the required thermodynamic quantities, we can use the relation,

$$A = - kT \ln Z \qquad (v)$$

where A is the Helmholz function, k is Boltzmann's constant, and Z is the canonical partition function, given by

$$Z = \sum_n e^{\frac{-E_n}{kT}} \qquad \text{(vi)}$$

where E_n is the energy of the system in quantum state n.

For the case of an ideal "dilute" gas, for which a Boltzmann distribution can be used, Z can be factored, and shown to be given by

$$Z = \frac{1}{N!}Q^N \qquad \text{(vii)}$$

where Q is the molecular sum-over-states and N is the number of molecules in the system. For 1 mole of gas, N becomes Avogadro's number N_o.

The Gibbs free energy per mole for an ideal gas is given by

$$\overline{F} = \overline{A} + PV = \overline{A} + RT \qquad \text{(viii)}$$

Using (v) and (vii) and approximating ln N_o! by $N_o \ln N_o - N_o$, we obtain

$$\overline{F} = -RT \ln \frac{Q}{N_o} \qquad \text{(ix)}$$

We must still find $\overline{F}$ for a pressure of one atmosphere. This can be simply done because the dependence on volume of Q is a simple proportionality. We can therefore write Q as Q'V where Q' is the sum-over-states per unit volume, and hence

$$\overline{F} = -RT \ln \frac{Q'V}{N_o} \qquad \text{(x)}$$

If the pressure is one atmosphere, V = RT, and

$$\mu^o = \overline{F}^o = -RT \ln \frac{Q'RT}{N_o} = -RT \ln Q'kT \qquad \text{(xi)}$$

Substituting this expression back into equation (iv), we can show

$$K = \frac{Q'^{c}_{C}\ Q^{d}_{D}}{Q'^{a}_{A}\ Q'^{b}_{B}} (kT)^{c + d - a - b} \qquad \text{(xii)}$$

Thus the equilibrium constant for an ideal gas reaction can be calculated if the molecular energy levels of the components are known.

(2) Absence of an Isotope Effect in Classical Statistics We can represent a general isotope exchange reaction by

$$A_1 + B_2 \rightleftharpoons A_2 + B_1 \qquad \text{(xiii)}$$

where A and B denote the two chemical species involved and the subscripts 1 and 2 denote the two isotopic substitutions.

The meaning of "no isotope effect" for this reaction is that, at equilibrium, the isotopic composition of the element under consideration is the same in substance A as in substance B.

A thermodynamic description can be made more simply if we consider the mechanism of an isotope exchange reaction, which can be written

$$A_1 + C \rightleftharpoons B_1 \qquad \text{(xiv)}$$

$$A_2 + C \rightleftharpoons B_2 \qquad \text{(xv)}$$

If these two reactions occur to the same extent under the same conditions, then there is no isotope effect.

We must consider two cases: the case where reactions (xiv) and (xv) are heterogeneous, and the case where they are homogeneous. Also, for simplicity in the statistical mechanical description of the system, we will consider the system at constant temperature and constant volume.

In the heterogeneous case, reaction (xiv) will be in equilibrium only if $\Delta \bar{A} = 0$. From (v) we therefore have

$$\frac{Z_{B_1}}{Z_{A_1} Z_C} = 1 \qquad \text{(xvi)}$$

If, under the same conditions, reaction (xv) is in equilibrium

$$\frac{Z_{B_2}}{Z_{A_2} Z_C} = 1 \qquad \text{(xvii)}$$

Therefore

$$\frac{Z_{A_1}}{Z_{A_2}} = \frac{Z_{B_1}}{Z_{B_2}} \qquad \text{(xviii)}$$

In discussing the partition function, we will assume that the electronic motions result in the formation of inter-atomic conservative forces and that the Hamiltonian of the system, $H(p,q)$, is thus the sum of a kinetic part dependent only on the momenta, p, of the atoms and a potential part dependent only on the co-ordinates, q, of the atoms. The classical canonical partition function

$$Z = \frac{1}{h^f} \int_p \cdots \int_q e^{\frac{-H(p,q)}{kT}} \, dp_1 \ldots dp_f dq_1 \ldots dq_f \qquad \text{(xix)}$$

(where h is Planck's constant and f is the number of degrees of freedom) can then be factored into two functions, one dependent on the momenta only and one dependent on the positions only. Furthermore, since $H(p) = \sum_i p_i^2/2m_i$, the momentum-dependent factor can be shown to be

$$Z(p) = \prod_i \left[\frac{2\pi m_i kT}{h^2}\right]^{3/2} \qquad \text{(xx)}$$

where the product is over the system.

Since the position-dependent factor, $Z(q)$, does not contain the atomic masses, the ratio

$$\frac{Z_{A_1}(p,q)}{Z_{A_2}(p,q)} = \frac{Z_{A_1}(p)}{Z_{A_2}(p)} = \left[\frac{m_1}{m_2}\right]^{3N_A/2} \qquad \text{(xxi)}$$

where m_1 and m_2 are the masses of isotopic atoms 1 and 2, and N_A is the number of the isotopically substituted atoms in a mole of A. Similarly,

$$\frac{Z_{B_1}}{Z_{B_2}} = \left[\frac{m_1}{m_2}\right]^{3N_B/2} \qquad \text{(xxii)}$$

where N_B is the number of isotopically substituted atoms in a mole of B.

The reaction (xiii) represents the exchange of one isotopic atom per molecule of A and B: therefore, $N_A = N_B$. (This is quite general, since any isotopic substitution can be represented by a succession of reactions of the form of (xiii).) The condition (xviii) is thus satisfied and there is no isotope effect.

In the case where reactions (xiv) and (xv) are homogeneous, the condition for equilibrium of either reaction is

$$\mu_B - \mu_A - \mu_C = 0 \qquad \text{(xxiii)}$$

where $u_i = \left.\frac{\partial A}{\partial n_i}\right]_{T,V}$ and n_i is the number of moles of component i.

From (v), this condition can be written

$$\frac{\partial \ln Z}{\partial n_B} - \frac{\partial \ln Z}{\partial n_A} - \frac{\partial \ln Z}{\partial n_C} = 0 \qquad \text{(xxiv)}$$

Again Z(p,q) can be factored into Z(p)Z(q), and Z(p) is given by

$$Z(p) = \frac{1}{N_B!}\left[\prod_i \frac{2\pi m_i kT}{h^2}\right]^{3N_B/2} \cdot \frac{1}{N_A!}\left[\prod_j \frac{2\pi m_j kT}{h^2}\right]^{3N_A/2} \cdot$$

$$\frac{1}{N_C!}\left[\prod_k \frac{2\pi m_k kT}{h^2}\right]^{3N_C/2} \qquad \text{(xxv)}$$

where N_B, N_A, N_C are the number of molecules of B, A and C in the system and the products $\prod_i$, $\prod_j$, $\prod_k$ are over all the atoms in a molecule of B, A and C respectively.

A typical term in (xxiv) is given by

$$\frac{\partial \ln Z}{\partial n_B} = \frac{\partial \ln Z(p)}{\partial n_B} + \frac{\partial \ln Z(q)}{\partial n_B}$$

$$= \frac{\partial \ln \frac{1}{N_B!}\left[\prod_i \frac{2\pi m_i kT}{h^2}\right]^{3N_B/2}}{\partial n_B} + \frac{\partial \ln Z(q)}{\partial n_B}$$

(using $N_B = n_B N_o$ and $\ln N_B! = N_B \ln N_B - N_B$)

$$= \frac{3N_o}{2} \ln \left[\prod_i \frac{2\pi m_i kT}{h^2} \right] - N_o \ln N_B + \frac{\partial \ln Z(q)}{\partial n_B} \qquad \text{(xxvi)}$$

With the other terms in (xxiv) calculated in the same way, we can see that the mass dependent term on the left side of equation (xxiv) is given by

$$\frac{3N_o}{2} \ln \frac{\prod_i \frac{2\pi m_i kT}{h^2}}{\prod_j \frac{2\pi m_j kT}{h^2} \prod_k \frac{2\pi m_k kT}{h^2}} \qquad \text{(xxvii)}$$

Since the atoms in a molecule of B are the same as those in a molecule of A added to those in a molecule of C, the same factors appear in both the numerator and denominator of the expression included in the logarithm. The term (xxvii) is thus 0, the condition (xxiv) is independent of atomic masses and therefore there is no isotope effect.

The usefulness of the above theorem lies in the fact that for systems of interest, the total energy can often be considered as the sum of energy terms arising from different modes of motion. The partition function can then be factored into terms arising from each independent mode of motion. From the above theorem, only those modes of motion for which the quantum mechanical partition function differs appreciably from the classical partition function will contribute to an equilibrium isotope effect.

For most systems at ordinary temperatures, vibrational modes are the only modes of motion for which this is the case; hence the explanation of equilibrium isotope effects is generally to be found in considering vibrational motions or motions interacting with vibrational motions.

(3) Isotope Exchange in Gases In the case of gaseous isotope exchange equilibria, the above approach can be used to deduce an explicit formula for the isotopic equilibrium constants.

From (xii), the equilibrium constant for the isotope exchange reaction (xiii) is given by

$$K = \frac{Q'_{A_2}Q'_{B_1}}{Q'_{A_1}Q'_{B_2}} = \frac{Q_{A_2}Q_{B_1}}{Q_{A_1}Q_{B_2}} \qquad \text{(xxviii)}$$

The molecular sum-over-states or molecular partition function Q is similar in form to the canonical partition function if the system is considered to be one molecule.

In quantum statistics

$$Q = \frac{1}{s}\sum_n e^{\frac{-\epsilon_n}{kT}} \qquad \text{(xxix)}$$

where s is the symmetry number of the molecule and ϵ_n is the energy of the molecule in state n.

In classical statistics

$$Q = \frac{1}{s}\cdot\frac{1}{h^f}\int_p \cdots \int_q e^{\frac{-H(p,q)}{kT}}\, dp..dq \qquad \text{(xxx)}$$

where the integral is now over the co-ordinates and momenta of the atoms in the molecule.

Assuming, as before, that the Hamiltonian can be separated into a momentum-dependent term and a position-dependent term, and following the same procedure as in the previous section, we can show that the classical partition function ratios are given by

$$\frac{s_{A_1}Q_{A_1}}{s_{A_2}Q_{A_2}} = \frac{s_{B_1}Q_{B_1}}{s_{B_2}Q_{B_2}} = \left[\frac{m_1}{m_2}\right]^{3/2} \qquad \text{(xxxi)}$$

It is now useful to introduce a function f, defined by

$$f = \left[\frac{m_2}{m_1}\right]^{3/2} \frac{Q_1}{Q_2} \qquad \text{(xxxii)}$$

We can see that the equilibrium constant for reaction (xiii) can be expressed as

$$K = \frac{f_B}{f_A} \qquad \text{(xxxiii)}$$

If the energy of the molecule can be separated into the sum of energies arising from different modes of motion, the partition function and hence f can be factored into a product made up of terms arising from each independent mode of motion.

$$f = \left[\frac{m_2}{m_1}\right]^{3/2} \prod_t \left[\frac{Q_1}{Q_2}\right]_t \qquad \text{(xxxiv)}$$

where the product is over all the independent modes of motion.

The classical equivalent of f will be factorable as well. Furthermore, from the definition of f,

$$\frac{s_1}{s_2} f_{\text{classical}} = 1 \qquad \text{(xxxv)}$$

Hence,

$$\frac{s_1}{s_2} f = \frac{s_1}{s_2} f / \frac{s_1}{s_2} f_{\text{classical}} = \prod_t \left[\frac{Q_1}{Q_2}\right]_t / \left[\frac{Q_1}{Q_2}\right]_{t\,\text{classical}} \qquad \text{(xxxvi)}$$

If the R.H.S. of (xxxvi) is 1 for both molecules, the equilibrium constant becomes the ratio of the symmetry number ratios for the two molecular species involved. Since the symmetry numbers represent the probabilities of forming each of the molecules assuming equal concentrations of isotopes 1 and 2 in substances A and B, this result indicates no isotope effect.

In order to calculate the equilibrium constant, it is only necessary to know the ratio of the quantum mechanical partition functions to the corresponding classical partition functions for the two isotopic species of each molecule for those modes of motion for which the quantum mechanical and classical partition functions are appreciably different. These will include vibrational motions for all molecules except at very high temperatures, and rotational motions for the hydrogen molecule at ordinary temperatures and some other molecules at low temperatures.

(4) Rotational Contribution to the Isotope Effect The partition function for a linear rigid rotator is given by

$$Q_r = \sum_J (2J + 1)e^{-BJ(J + 1)hc/kT} \qquad \text{(xxxvii)}$$

where J is the rotational quantum number and $B = h/8\pi^2cI$, where I is the moment of inertia.

There is no general analytic expression for the above sum. However, if the quantity σ, defined by

$$\sigma = hcB/kT \qquad \text{(xxxviii)}$$

is large, the expression (xxxvii) converges in a fairly small number of terms; if σ is small, Q_r can be calculated by the asymptotic expansion (15)

$$Q_r = \frac{1}{\sigma} + \frac{1}{3} + \frac{\sigma}{15} + \frac{4\sigma^2}{315} + \frac{\sigma^3}{315} + \cdots \qquad \text{(xxxix)}$$

If the sum in (xxxvii) is replaced by an integral, the classical rotational partition function is obtained, and found to be $1/\sigma$. The ratio of the quantum mechanical and classical partition functions is thus

$$\frac{Q_r}{Q_{r\,\mathrm{classical}}} = 1 + \frac{\sigma}{3} + \frac{\sigma^2}{15} + \frac{4\sigma^3}{315} + \cdots \qquad \text{(xl)}$$

In the more general case of the asymmetric rotor, the energy levels must be evaluated numerically and thus the calculation of the quantum-mechanical partition function is very difficult. The classical function is given quite simply as

$$Q_{\text{classical}} = \left[\frac{\pi}{\sigma_A \sigma_B \sigma_C}\right]^{1/2} \tag{xli}$$

Gordon (16) has shown that for the most unfavorable case likely to be encountered among ordinary molecules, an approximate formula

$$\frac{Q_r}{Q_{r\,\text{classical}}} = e^{\frac{\sigma_{BC}}{4}}\left[1 + \frac{\sigma_{BC}}{12} - \frac{\sigma_B \sigma_C}{12\sigma_A}\right] \tag{xlii}$$

where

$$I_A < I_B < I_C, \quad \sigma_i = \frac{h^2}{8\pi^2 I_i kT} \quad \text{and} \quad \sigma_{BC} = (\sigma_B \sigma_C)^{1/2}$$

gives Q_r accurate to 0.2% for temperatures above 100°K.

The effect of isotopic substitution on the rotational partition function results from changes in the moments of inertia. If the structure of the molecule is known, these changes can be calculated. For those compounds whose microwave spectrum has been studied, the moments of inertia of all the naturally occurring isotopic species of the molecule can be obtained directly from the experimental results without accurate knowledge of the structure of the molecule.

(5) <u>Vibrational Contribution to the Isotope Effect</u> The partition function for a harmonic oscillator with n normal modes of vibration is

$$Q_v = \prod_i \sum_{v_i} e^{\frac{-(v_i + 1/2)hc\omega_i}{kT}} = \prod_i \sum_{v_i} e^{-(v_i + 1/2)u_i}$$

$$= \prod_i \frac{e^{-u_i/2}}{1 - e^{-u_i}} \tag{xliii}$$

where the product is over all normal modes of the oscillator, v_i is the quantum number for the ith normal mode, ranging from 0 to ∞, ω_i is the classical frequency (called the "fundamental" frequency) of the ith normal mode in cm^{-1}, and, for convenience, u_i is defined by

$$u_i = \frac{hc\omega_i}{kT} \qquad \text{(xliv)}$$

The classical partition function for the same oscillator is given by

$$Q_{v_{classical}} = \prod_i \frac{1}{u_i} \qquad \text{(xlv)}$$

The ratio of the quantum mechanical and classical partition functions is therefore

$$\frac{Q_v}{Q_{v_{classical}}} = \prod_i \frac{u_i e^{-u_i/2}}{1 - e^{-u_i}} \qquad \text{(xlvi)}$$

The effect of isotopic substitution on the vibrational partition function results from the change in the fundamental frequencies of the molecule. To an approximation valid for most molecules, the interatomic forces of the molecule are unchanged by isotopic substitution: only the mass of the vibrating system is altered. The substitution of a heavier atom lowers the fundamental frequencies of the molecule whereas the substitution of a lighter atom raises them.

The vibrational contribution to the f function is thus given by

$$\frac{s_1}{s_2}f = \prod_i \frac{u_{i_1}}{u_{i_2}} e^{-(u_{i_1} - u_{i_2})/2} \cdot \frac{(1 - e^{-u_{i_2}})}{(1 - e^{-u_{i_1}})} \qquad \text{(xlvii)}$$

Writing $u_{i_1} = u_i$ and $u_{i_2} - u_{i_1} = \Delta u_i$, the above expression becomes

$$\frac{s_1}{s_2} f = \prod_i \frac{u_i}{u_i + \Delta u_i} \; e^{\Delta u_i/2} \, \frac{(1 - e^{-(u_i + \Delta u_i)})}{(1 - e^{-u_i})} \qquad \text{(xlviii)}$$

For small frequency shifts and fairly high temperatures, each Δu_i is small and the above expression can be expanded into a product of power series in each Δu_i. Approximating the resulting series by the first order terms*, we obtain

$$\frac{s_1}{s_2} f = 1 + \sum_i \left[\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1} \right] \Delta u_i \qquad \text{(xlix)}$$

The function in brackets, called $G(u_i)$, has been tabulated by Bigeleisen and Mayer (5). It is always positive and approaches $u_i/12$ as u_i becomes small and approaches 1/2 as u_i becomes large.

Since, from (xliv), both u_i and Δu_i are proportional to $1/T$, $((s_1/s_2)f - 1)$ is proportional to $1/T^2$ at high temperatures and to $1/T$ at low temperatures.

If isotopic molecule 2 contains the lighter isotope, Δu_i is positive and $s_1/s_2 . f$ is greater than 1. Thus, in any isotope exchange equilibrium between a molecule and the separated atoms, the heavier isotope will be concentrated in the molecule.

The above expressions have been derived for a rigid rotator and harmonic oscillator: the corrections for anharmonicity and rotational-vibrational interaction in actual molecules, although considerable in the calculation of the partition functions themselves, will be largely cancelled out in the ratio of the quantum mechanical to the classical partition function.

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*Bigeleisen (17) has since calculated higher terms in the power series.

(D) The Calculation of Vibrational Isotope Shifts

(1) Experimental and Theoretical Values In order to calculate the vibrational contribution to the isotope effect, we require the fundamental frequencies of both isotopic species of the molecules concerned. The fundamental frequencies of the most abundant isotopic species of a molecule can be determined spectroscopically. However, because of the complexity of vibrational spectra, the spectra of the less abundant species can only be observed through the use of separated isotopes, and, since the changes in the fundamental frequencies resulting from isotopic substitution (i.e. the isotope shifts) are small except in the case of the hydrogen isotopes, high resolution is required to measure them to the required accuracy. The isotope shifts can be calculated from the force constants of the molecule, but except for the case of diatomic molecules, the force constants cannot be rigorously determined from spectroscopic information on a single isotopic species. In the absence of other experimental information, the isotope shifts can be calculated only through the use of some fairly questionable assumptions about the force constants.

It is therefore preferable to use experimental isotope shifts in the calculation of isotopic equilibrium constants where these are available. This has been done by Bigeleisen and Friedman (18) and Begun and Fletcher (19) for the various substitutions of the nitrogen isotopes in the nitrous oxide molecule. As more pure isotopes of the elements become available, this procedure will become practical for most molecules.

(2) The General Quadratic Force Constants (20) The configuration of an N-atomic molecule can be described by 3N cartesian co-ordinates X_i. The potential energy V can be expanded in a Taylor series about the equilibrium configuration X_i^o of the molecule as:

$$V(x) = V(0) + \sum_{i=1}^{3N} V'_i(0)\, x_i + 1/2 \sum_{i,j=1}^{3N} V''_{ij}(0)\, x_i x_j$$

$$+ 1/6 \sum_{i,j,k=1}^{3N} V'''_{ijk}(0)\, x_i x_j x_k + \dots \qquad (1)$$

where $x_i = X_i - X_i^o$, and $V'_i(0)$, $V''_{ij}(0)$, etc., are the derivatives of V with respect to the co-ordinates taken at the equilibrium configuration.

At the equilibrium position, the potential energy is a minimum, and therefore all $V'_i(0)$ are zero; furthermore, the potential energy at the equilibrium position can be taken as zero, and hence the first non-zero term in the series is the quadratic term. In the harmonic oscillator approximation, higher terms in the series are ignored.

Of the 3N co-ordinates, six (for a non-linear molecule) are required to describe the position and orientation of the molecule as a whole. Since the potential energy depends only on the relative positions of the atoms, it can be written in terms of 3N - 6 "internal" co-ordinates S_i. Therefore, to the quadratic approximation, the potential energy is given by:

$$2V = \sum_{i,j=1}^{3N-6} F_{ij} s_i s_j \qquad (11)$$

where $s_i = S_i - S_i^o$ (S_i^o denoting the equilibrium configuration) and the F_{ij} are the quadratic force constants.

The number of different quadratic force constants for an asymmetric N-atomic molecule is the number of points in that portion of a square array with 3N - 6 points along the side obtained by taking the points on a diagonal together with all the points to one side of the diagonal. This gives 1 + 2 + 3 + 4 + ... (3N - 6) or $\frac{(3N - 6)(3N - 5)}{2}$.

(3) Calculation of the Fundamental Frequencies The fundamental frequencies are obtained by considering the molecule as a classical oscillator and solving the classical equations of motion for the system. In the Lagrangian form these are:

$$\frac{d\frac{\partial L}{\partial \dot{q}_i}}{dt} - \frac{\partial L}{\partial q_i} = 0 \qquad (1ii)$$

for each co-ordinate q_i where $L = T - V$, V being the potential energy and T the kinetic energy. In Cartesian co-ordinates, T has the familiar form:

$$T = 1/2 \sum_{i=1}^{N} m (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \qquad (1iii)$$

However, since we are not concerned with the motion of the molecule as a whole, we can impose the constraint that the position of the centre of mass remain constant and the total angular momentum be 0. The kinetic energy can now be written in terms of the 3N - 6 internal co-ordinates as:

$$2T = \sum_{i,j=1}^{3N-6} b_{ij} \dot{s}_i \dot{s}_j \qquad (1iv)$$

where the b_{ij} are functions of the masses of the atoms and the geometry of the molecule.

The Lagrangian equations of motion become:

$$\sum_{j=1}^{3N-6} b_{ij} \ddot{s}_j + \sum_{j=1}^{3N-6} F_{ij} s_j = 0 \qquad (1v)$$

$$i = 1, 2, \ldots (3N - 6)$$

A differential equation of this type has solutions of the form:

$$s_i = a_i e^{-2\pi i \nu t} \qquad (1vi)$$

Substitution of (lvi) into (lv) gives:

$$\sum_{j=1}^{3N-6} (F_{ij} - 4\pi^2\nu^2 b_{ij})\, a_j = 0 \qquad \text{(lvii)}$$

$$i = 1,\ 2,\ \ldots\ (3N - 6)$$

This is a set of 3N - 6 linear equations in the amplitudes a_i. The condition for a non-zero solution is given by the secular equation:

$$\begin{vmatrix} F_{11} - \lambda b_{11} & F_{21} - \lambda b_{21} & \cdots\cdots \\ F_{12} - \lambda b_{12} & F_{22} - \lambda b_{22} & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \end{vmatrix} = 0 \qquad \text{(lviii)}$$

where, for convenience, λ is substituted for $4\pi^2\nu^2$.

Solution of equation (lviii) for λ gives 3N - 6 roots for λ, and hence ν. The classical motion of the system can be seen from equation (lvi) to be a superposition of simple harmonic motions with the frequencies given by the values of ν, which are therefore the classical fundamental frequencies for the system.

The same argument applies to linear molecules, except that, since five co-ordinates suffice to describe the position of the molecule as a whole, 3N - 5 co-ordinates are required to describe the internal motion of the molecule.

Thus, for all molecules other than diatomic, there are many more force constants than fundamental frequencies. Since the vibrational spectrum of a single isotopic species of a molecule gives only the fundamental frequencies of that species, the force constants required to calculate isotope shifts must be obtained from additional experimental data or estimated through the use of a simplified model.

(4) The Case of the Bent XY_2 Molecule A bent triatomic molecule will have three internal co-ordinates, three fundamental frequencies and six force constants. A useful choice of the internal co-ordinates could be the two X-Y bond distances, denoted by r_1 and r_2, and the Y-X-Y bond angle, denoted by α. The potential energy can be written:

$$\begin{aligned} 2V = {} & c_1 \Delta r_1^2 + c_1' \Delta r_2^2 + c_2 r_1 r_2 \Delta\alpha^2 + 2c_3 r_1 \Delta r_1 \Delta\alpha \\ & + 2c_3' r_2 \Delta r_2 \Delta\alpha + 2c_4 \Delta r_1 \Delta r_2 \end{aligned} \tag{lix}$$

From the symmetry of the molecule, we can assume that $c_1' = c_1$, and $c_3' = c_3$. The number of distinct force constants is thus reduced to four.

The secular equation (lviii) has been worked out for this case by Glockler and Tung (21). From their formulae the relation between the frequencies and the force constants is given by:

$$\begin{aligned} \lambda_1 + \lambda_2 &= (c_1 + c_4)(1/\mu + \cos\alpha/M) + 2c_2(1/\mu - \cos\alpha/M) - 4c_3 \sin\alpha/M \\ \lambda_1\lambda_2 &= \left[2c_2(c_1 + c_4) - 4c_3^2\right]\left[1/\mu - 1/M^2\right] \\ \lambda_3 &= (c_1 - c_4)(1/\mu - \cos\alpha/M) \end{aligned} \tag{lx}$$

where M is the mass of atom X, m is the mass of atom Y, and $1/\mu = 1/M + 1/m$.

If the force constants of a molecule are known, the changes in the mass-dependent terms resulting from isotopic substitution can be calculated, and equations (lx) used to calculate the isotope shifts. When these changes are small, use can be made of a first-order approximation.

$$\begin{aligned} \Delta\lambda_1 + \Delta\lambda_2 &= (c_1 + c_4)\Delta(1/\mu + \cos\alpha/M) + 2c_2\Delta(1/\mu - \cos\alpha/M) - 4c_3\Delta(\sin\alpha/M) \\ \lambda_1\Delta\lambda_2 + \lambda_2\Delta\lambda_1 &= \left[2c_2(c_1 + c_4) - 4c_3^2\right] \Delta\left[1/\mu^2 - 1/M^2\right] \\ \Delta\lambda_3 &= (c_1 - c_4)\Delta(1/\mu - \cos\alpha/M) \end{aligned} \tag{lxi}$$

(E) The Reaction $H_2S^{34} + S^{32}O_2 \rightleftharpoons H_2S^{32} + S^{34}O_2$

(1) Mechanism of the Reaction The isotope exchange reaction studied in this investigation is the reaction,

$$H_2S^{34} + S^{32}O_2 \rightleftharpoons H_2S^{32} + S^{34}O_2 \qquad \text{(I)}$$

In order for this equilibrium to be set up, a reaction path must be provided for sulphur in hydrogen sulphide to be oxidized to sulphur dioxide and for sulphur in sulphur dioxide to be reduced to hydrogen sulphide under equilibrium conditions. One such path is provided by the reaction,

$$3S + 2H_2O \rightleftharpoons 2H_2S + SO_2 \qquad \text{(II)}$$

A mixture of dry hydrogen sulphide and sulphur dioxide does not react at ordinary temperatures even when condensed into a liquid solution, but in the presence of a moist surface, the reaction (II) goes quantitatively and rapidly to the left, as is shown in an elegant lecture demonstration (22). This phenomenon has been studied further by Albertson and Reynolds (23), who concluded that the reaction depends on the formation of the HS^- ion.

At higher temperatures, the reaction (II) has been studied by Udintseva and Chufarov (24). They found that in the neighborhood of 300°C the reaction takes place on the surface of the reaction vessel, being much faster in a glass vessel than in a metal vessel. At 350°C, in a glass vessel, the time required for the reaction to go to completion was from 3 to 6 hours.

(2) Thermodynamics of the $2H_2S + SO_2$ System At temperatures below the boiling point of sulphur, the equilibrium position of reaction (II) is almost quantitatively to the left, but above this temperature, consider-

able amounts of hydrogen sulphide and sulphur dioxide are present at equilibrium. The thermodynamic functions of the gases in this system have been calculated from spectroscopic data by Evans and Wagman (25). Using these results, they calculated the equilibrium composition of the system for a total pressure of 1 atm. and various temperatures.

In addition to reaction (II), the reaction

$$H_2S + 2\,H_2O \rightleftharpoons SO_2 + 3\,H_2 \qquad \text{(III)}$$

can occur in the sulphur dioxide-hydrogen sulphide system, but the equilibrium position for this reaction is far to the left at temperatures below 1200°K.

(F) Scope of This Investigation

(1) Experimental and Theoretical Studies of Isotope Exchange Although many isotope exchange reactions have been studied either experimentally or theoretically, there are comparatively few exchange systems for which the ideal-gas theory given in section (I) (C) can be rigorously applied, and which can also be set up and studied in the laboratory. In particular, the study of gaseous isotope exchanges at high temperature, where the simplified forms of the expression for the equilibrium constant should be valid, has seldom been undertaken.

The exchange $H_2O + HT \rightleftharpoons HTO + H_2$ was studied by Black and Taylor (26) at temperatures from 16°C to 300°C, and their results compared with the results of very rigorous calculations by Libby (27). They found excellent qualitative agreement between measured and calculated values, with a displacement between the two curves slightly greater than their estimated experimental error. A similar investigation was carried out by

Stranks (28) for the exchange $C^{14}O + C^{12}OCl_2 \rightleftharpoons C^{12}O + C^{14}OCl_2$ in the range 10°C to 500°C, who found discrepancies between his measured and calculated values at the higher temperatures.

The exchange of the oxygen isotopes between calcite and water has been studied by Clayton (29, 30) and Epstein and others (12) at temperatures ranging from 7°C to 750°C, but since this exchange takes place in a condensed system, only a very qualitative comparison with theory was possible.

The extension of these studies to higher temperatures requires increasing sensitivity in the methods of isotopic assay, since the isotope effects become small. The simultaneous-collection mass spectrometer (31) has greatly increased the sensitivity with which variations in isotopic content can be detected, although its full advantages can only be realised for a small number of elements. It was therefore considered of interest to study an exchange system at high temperatures for which the products can be isotopically analysed by the simultaneous-collection mass spectrometer. The system chosen had the advantages that it could be set up at fairly high temperature, variations in the ratio of the two most abundant sulphur isotopes could be measured to 0.01% of the isotope ratio, and since the vibrational constants of the hydrogen sulphide and sulphur dioxide molecules are fairly well known, a significant comparison of experimental and theoretical values of the equilibrium constant was possible.

The temperature range in this investigation was from 500°C to 1000°C, the lower limit being set by the condensation of sulphur, and the upper limit by the maximum working temperature of the fused silica reaction vessel.

(2) The Experimental Problem The equilibrium constant for the isotope exchange reaction (I) is equal to the S^{34}/S^{32} ratio for sulphur dioxide divided by the S^{34}/S^{32} ratio for hydrogen sulphide when the two gases have come to isotopic equilibrium. The measurement of the equilibrium constant required that samples of the two gases be withdrawn from the system, separated, prepared for isotopic analysis, and introduced into the mass spectrometer without further change being produced in the isotopic content of the samples.

The working gas in the mass spectrometer is sulphur dioxide. The sulphur dioxide obtained from the equilibrium mixture could thus be used in the mass spectrometer provided it was sufficiently pure, but the hydrogen sulphide had to be converted to sulphur dioxide.

Both the sulphur dioxide and the hydrogen sulphide removed from the equilibrium mixture had to be converted to the sulphur dioxide used in the mass spectrometer quantitatively and without contamination if errors were to be avoided. Contamination of the sample with sulphur of a different isotopic content could occur either through incomplete separation of the initial mixture or through contamination from sulphur-containing impurities in the apparatus at any stage of the process. Error could result from any chemical step giving less than quantitative yields, since the material lost could be expected to differ in isotopic content from the remaining material as a result of chemical isotope effects. Chemical isotope effects are in general larger at lower temperatures: thus, even small losses occurring during steps carried out at room temperature or below could produce errors of appreciable size in comparison to the high temperature isotope effect being measured.

Since hydrogen sulphide and sulphur dioxide are unstable together at ordinary temperatures, it is not surprising that failure to separate the two gases without losses from chemical reaction was found to be the most serious source of error.

II. EXPERIMENTAL

(A) Sample Preparation

(1) Equilibration of the System The equilibrium reaction (II) was set up by heating sulphur and water in a fused quartz vessel of about 500 ml. capacity. A weighed quantity of sublimed sulphur was added to the vessel through the side-arm; the side-arm was then sealed to a vacuum system, the vessel evacuated, and water distilled into it. The neck on the side-arm was then sealed off with a torch. It was found that 0.2 gms. sulphur and 0.1 ml. water gave adequate samples of sulphur dioxide and hydrogen sulphide without producing dangerous pressure in the reaction vessel.

The water used in the first runs was ordinary distilled water. However, to eliminate corrections required by the difference in the oxygen isotopic content (see section (I)(C)) between distilled water and the tank oxygen used to convert the hydrogen sulphide to sulphur dioxide, some water was prepared by burning this tank oxygen in an excess of hydrogen.

The reaction vessel was then placed in a furnace and heated to the temperature at which the reaction was to be studied (see Fig. 1). To test for the attainment of equilibrium, the final temperature was approached from both directions. Half of the runs were carried out by heating the furnace from room temperature to the final temperature and maintaining it at this temperature for 24 hours before samples were taken; in the remaining runs, the furnace was heated to 100° above the final temperature, held there for 24 hours, cooled to the final temperature, and again held there for 24 hours before samples were taken. Temperatures were measured with a platinum-platinum rhodium thermocouple.

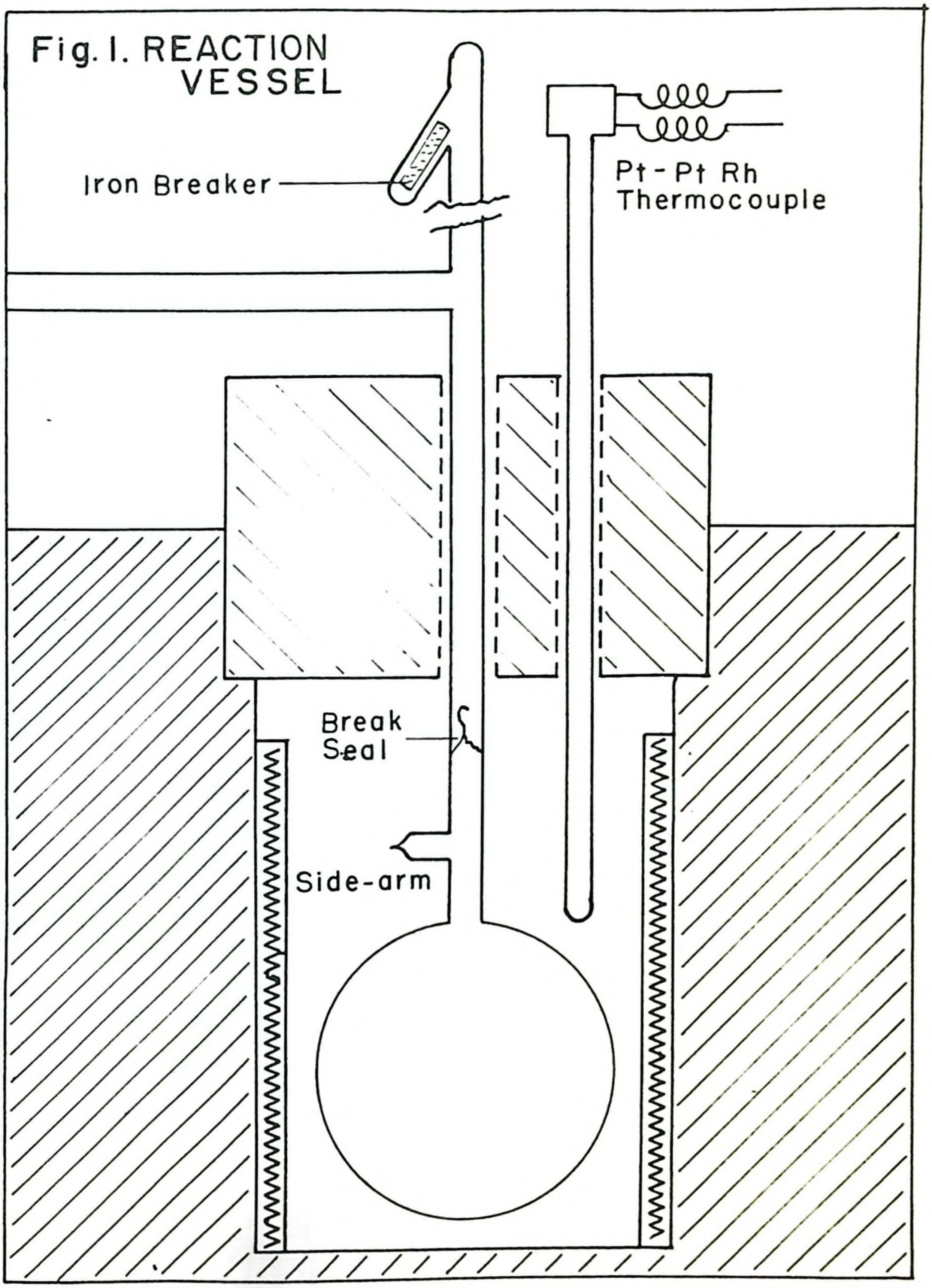
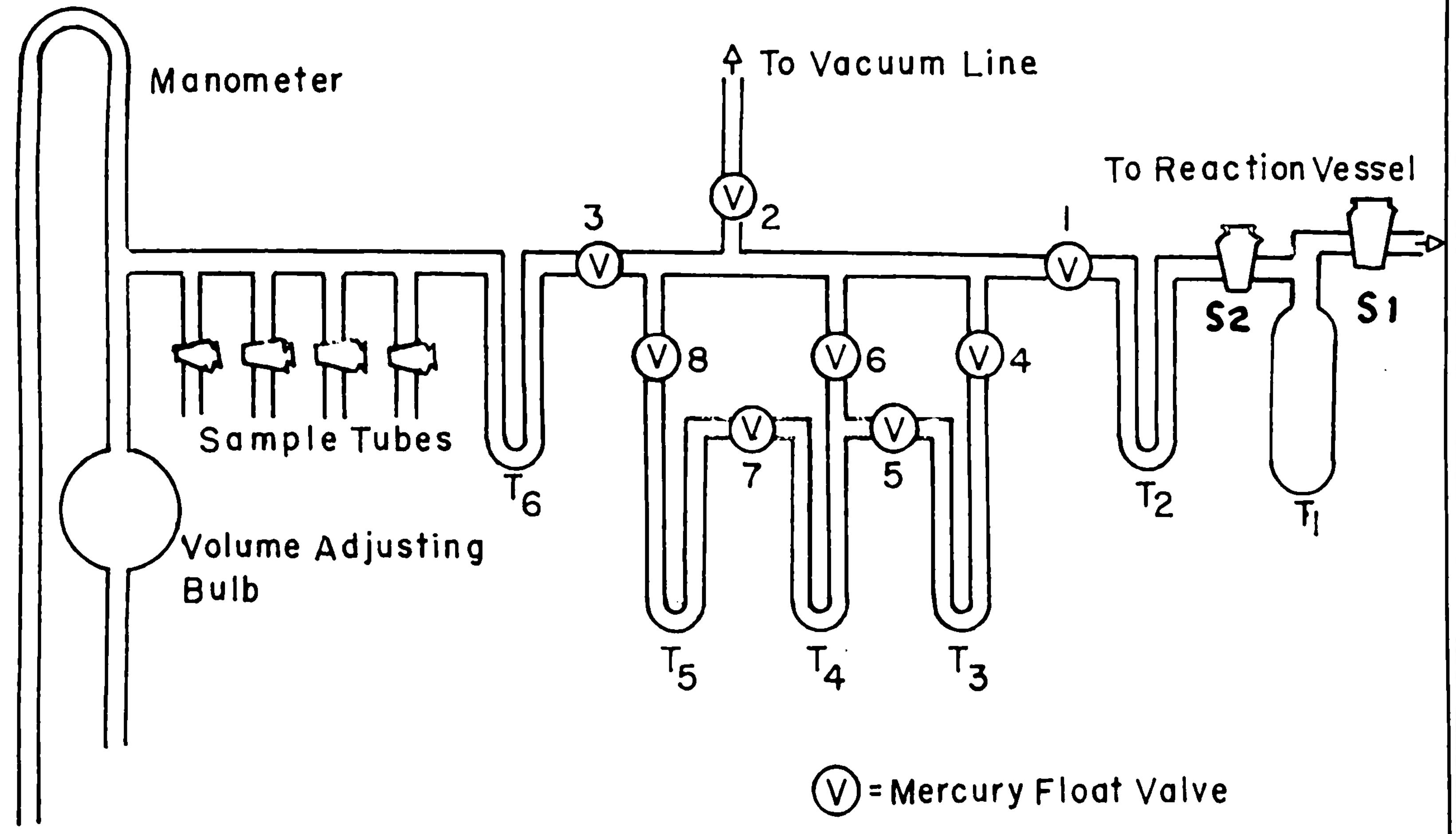


Fig. 1. REACTION VESSEL

Fig. 2. DISTILLATION and SAMPLING APPARATUS



(2) <u>Separation of Hydrogen Sulphide and Sulphur Dioxide</u> When equilibration was completed, the break-seal on the reaction vessel was broken and the escaping gases condensed in the large bore trap, T_1, at liquid air temperature (see Fig. 2). It was now necessary to separate the hydrogen sulphide, sulphur dioxide, and water present in the trap such that no further chemical reaction could occur. The separation was carried out by high-vacuum trap-to-trap distillation, using low temperature baths at -190°C, -135°C, and -78°C, obtained from liquid air, melting ethyl chloride, and dry ice-acetone respectively. The vapour pressures of hydrogen sulphide and sulphur dioxide at -135°C are about 1 mm. and 10^{-3} mm. Hg respectively, while at -78°C, the vapour pressures of sulphur dioxide and water are about 8 mm. and 0.5×10^{-3} mm. Hg respectively.

The steps in the separation were as follows:

(1) with stopcock S_1 closed, S_2 open, trap T_1 was opened to the vacuum line for about 15 sec. Then with mercury float valves V_1, V_8 open, and the others closed, T_1 was allowed to warm slowly with T_2 at -135°C and T_5 at -190°C. At the end of this step, most of the hydrogen sulphide was in T_5, and the sulphur dioxide and water in T_2.

(2) with V_5, V_7 open, the others closed, T_4 at -135°C, and T_3 at -190°C, T_5 was raised to -135°C. The hydrogen sulphide was now in T_3, further purified from sulphur dioxide.

(3) with V_1, V_7, and V_8 open, T_2 was raised to - 78°C. When most of the sulphur dioxide appeared to be condensed in T_3, V_1 was partially closed and T_2 allowed to warm until the mercury level in V_1 indicated a few mm. pressure. The trap was then re-cooled to -78°C. Failure of the mercury to go down promptly to the 0 position indicates the presence of

sulphur dioxide or hydrogen sulphide entrained in the relatively large amount of ice. V_1 was then opened. If the presence of entrained gas was indicated, this step was repeated.

(4) with V_5 and V_7 open, the others closed, T_5 was allowed to warm to room temperature. The sulphur dioxide was now in T_4, while traces of hydrogen sulphide which might have remained behind in step (1) should have passed through to T_3.

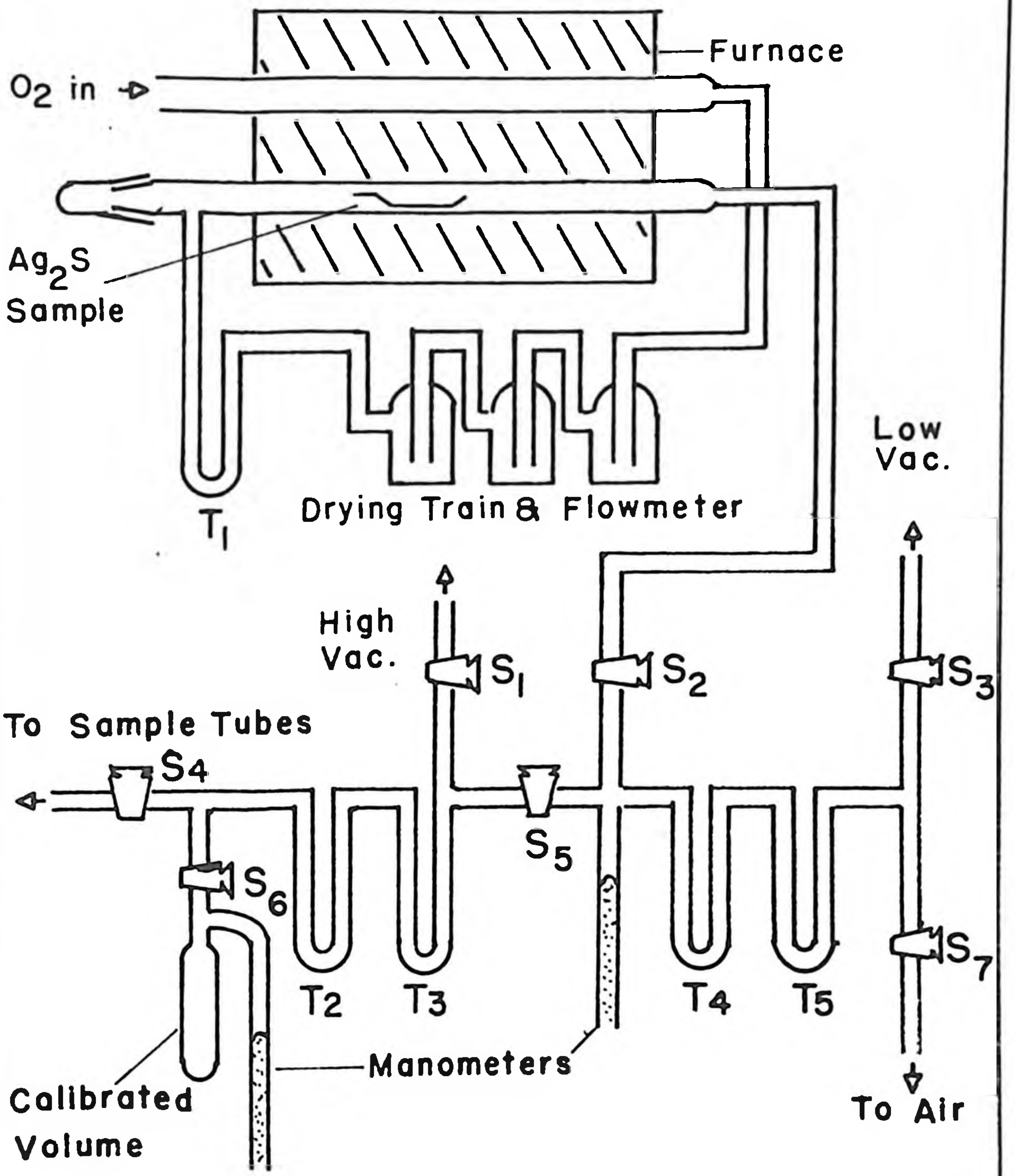
(5) with V_2, V_3, and V_4 open, T_3 was opened to the vacuum line for about 5 sec., then V_2 was closed and the hydrogen sulphide frozen in T_6. V_3 was then closed, and the gas allowed to warm to room temperature for a yield measurement. It was then frozen and sealed into a sample tube constructed with a thin bulb at one end.

(6) with V_2, V_3, and V_6 open, T_4 was opened to the vacuum line for about 5 sec., then V_2 was closed, and the sulphur dioxide frozen in T_6. The yield was measured as above and the gas sealed in a sample tube suitable for use on the mass spectrometer.

(3) Conversion of Hydrogen Sulphide to Sulphur Dioxide The hydrogen sulphide had to be converted to sulphur dioxide to be compared directly with the sulphur dioxide obtained above on the mass spectrometer. This process was carried out by conversion of the hydrogen sulphide to silver sulphide, which was then burned in a stream of oxygen to give sulphur dioxide.

The bulb of the sample tube was broken beneath the surface of a silver nitrate solution. After the solution containing the silver sulphide precipitate was boiled to coagulate the precipitate, the precipitate was filtered on glass wool and dried in an oven overnight.

Fig.3. SULPHIDE BURNING APPARATUS



The conversion of the silver sulphide to sulphur dioxide was carried out on the apparatus shown in Fig. 3. A stream of oxygen was set to flow through the combustion tube, stopcocks S_2 and S_7, and traps T_4 and T_5, at a rate of about 0.2 litres per minute. Trap T_1 was cooled by liquid oxygen to condense any water which might have passed the drying train, and T_4 and T_5 were cooled by liquid oxygen to condense the sulphur dioxide produced in the combustion tube. The combustion furnace, a Leco silicon carbide-heated furnace, was maintained at about 1300°C. The steps in the procedure were as follows:

(1) the silver sulphide sample was inserted into the hot combustion tube and the oxygen flow maintained for an additional 10 minutes. At the end of this time, stopcocks S_2 and S_7 were closed, and the traps evacuated slowly through S_3. When the evacuation was almost complete, the traps were opened to the high vacuum system for about 1 minute.

(2) with S_2, S_3, S_5, and S_7 closed, T_4 was allowed to warm to room temperature. When all the sulphur dioxide was condensed in T_5, the traps were again opened to high vacuum to remove the last traces of oxygen.

(3) it was found necessary to remove impurities of carbon dioxide and water which persisted in spite of efforts to purify the oxygen stream and the silver sulphide precipitate. This was done by a modified trap-to-trap distillation technique. With S_5 open, the others closed, trap T_3 was cooled to -135°C with melting ethyl chloride, T_2 to -190°C with liquid air, and T_5 allowed to warm to room temperature. The carbon dioxide was thus condensed in T_2, and the sulphur dioxide and water in T_3.

(4) S_5 was closed and S_1 opened, and T_2 allowed to warm. After an interval of about 15 sec. after the last carbon dioxide was observed to leave T_2, S_1 was re-closed.

(5) T_2 was then maintained at -78°C with dry ice-acetone, the calibrated volume cooled with liquid air, S_6 opened, and T_3 allowed to warm. When all the sulphur dioxide and water had evaporated from T_3, S_6 was re-closed, and the calibrated volume warmed to room temperature for a measurement of the yield of sulphur dioxide.

(6) the sulphur dioxide was then frozen and sealed in a sample tube for use on the mass spectrometer.

(B) Mass Spectrometry

(1) The Mass Spectrometer The instrument used in this investigation was a 6-inch Nier type 90° mass spectrometer equipped for simultaneous collection, the design and operation of which has been described by Wanless and Thode (32). Two identical sample storage systems are connected to the inlet of the mass spectrometer through nickel capillary leaks. Gas from the leaks is passed through an arrangement of magnetically switched valves which directs the gas from one of the sample storage systems into the ion source of the mass spectrometer and the gas from the other into an auxiliary pumping system. This part of the apparatus has been designed for the minimum disturbance of the gas flow into the ion source when the position of the valves is changed.

Ion currents from masses 64 and 66 are collected, and the voltages developed by the ion currents across very large resistors are amplified by Vibrating Reed Electrometer amplifiers. The signals from the ion currents can be displayed directly on a chart recorder, or, using the circuit described by Wanless and Thode (32), a fraction of one signal may be tapped off from a potentiometer, balanced against the other, and deviations from the balance point displayed on the recorder.

(2) Operating Procedure Throughout this work, one of the sample systems contained a standard sample of sulphur dioxide, against which all the other samples studied were compared. The pressure of the standard sample was adjusted to give nearly full scale deflection of the 64 amplifier. The valves were then switched to collect the samples to be studied and the pressure of this sample adjusted to give the same signal on the 64 amplifier as was obtained with the standard sample. In order to obtain the most stable operation during measurements, it was found desirable to allow gas to flow into the spectrometer under operating conditions for about half an hour before measurements were started, and thereafter to avoid interrupting the flow of gas until measurements were completed.

With the standard sample flowing into the instrument, the detection circuit was now switched to measure the balance point between the two ion currents. Final adjustments were made in the magnetic field to give the maximum 66/64 ion current ratio: the potentiometer was then adjusted to give a null signal on the recorder, indicating the balance point. In order to determine the sensitivity of the recorder for the off-balance condition, the potentiometer setting was changed a few steps (to give a signal approximately the same as that given by the sample under study) and the deflection between the recorder traces measured.

With the potentiometer at its original setting, the valves were changed to admit the sample under study into the spectrometer. The deflection produced in the recorder trace was measured, then the standard sample re-admitted and the deflection measured. This procedure was repeated several times. A finite time is required for the ion currents to come to a steady state after a sample change: therefore, in order to minimise the effect of drifting, these operations were carried out at regular time intervals. It was found that for samples differing by not more than 1% in isotope ratio from the standard sample, a period of 15 seconds appeared adequate to re-establish a steady state. The routine adopted was a 15 second pause after changing the valve setting, a 30 second interval in which a recorder trace was taken, followed by a change in the valve setting, and so on.

About eight or ten measurements, depending on the scatter of the results, were taken in each set of comparison of the standard and unknown samples, and about six in each set for sensitivity determination. The scatter in the measurements in the "sensitivity" sets is usually less than in the sets involving sample changes, since there is no time lag between the drawing of the traces.

A complete measurement of a sample consisted of three sets of comparison of the standard and unknown samples and four sensitivity sets arranged such that each "comparison" set is bracketed by two "sensitivity" sets. This procedure gives three values for the comparison of the standard and unknown samples, calculated as follows: if R is the 66/64 ion current ratio and δR is the difference in this ratio between the standard and unknown samples,

$$\frac{\delta R}{R} = \frac{d'}{d}\,\frac{\delta X}{X} \qquad \text{(lxii)}$$

where d' is the average deflection between traces in the "comparison" set, d is the same quantity averaged between the two bracketing "sensitivity" sets, X is the fraction of the 64 signal tapped off on the potentiometer to balance the 66 signal, and δX is the difference in this ratio used to produce the deflection in the "sensitivity" sets.

If the mass spectrometer was operating satisfactorily (which could be clearly seen from the appearance of the traces), the three results for $\delta R/R$ obtained in this manner almost invariably fell within a range of 0.02% and usually within a range of 0.01%.

(C) Corrections to the Data

(1) The Oxygen Correction The mass spectrometer gives values for variations in the ratio of the ion current at mass 66 to that at mass 64. The mass 64 ion current is produced by the single species $S^{32}O_2^{16}$, but the mass 66 ion current is produced by two species, $S^{34}O_2$ and $S^{32}O^{16}O^{18}$, which are present in significant amounts. If R denotes the (66)/(64) ratio, R_s the S^{34}/S^{32} ratio, and R_o the O^{18}/O^{16} ratio, it can be seen that

$$R = R_s + 2R_o \qquad \text{(lxiii)}$$

The approximate values of these ratios for natural materials are 0.0452 for R_s, and 0.00204 for R_o. (33).

The observed relative differences in the (66)/(64) ratios must be converted into relative differences in the S^{34}/S^{32} ratios, which are the quantities giving the desired equilibrium constants. From (lxiii), it follows that

$$\frac{\delta R_s}{R_s} = \left[\frac{\delta R}{R}\right]\left[\frac{R_s + 2R_o}{R_s}\right] \qquad \text{(lxiv)}$$

where the samples being compared differ in sulphur isotopic content but not in oxygen isotopic content. The correction factor, based on the natural abundance ratios quoted above, is 1.090.

If, however, there is a difference in the O^{18}/O^{16} ratios of the samples being compared as well, the effect of this difference on the relative difference in the (66)/(64) ratios must first be determined and corrected for. From (lxiii) the relative difference in the (66)/(64) ratio resulting from a difference in the oxygen isotope ratio (assuming the sulphur isotope ratio is held constant) is given by:

$$\frac{\delta R}{R} = \left[\frac{\delta R_o}{R_o}\right]\left[\frac{2R_o}{R_s + 2R_o}\right] \qquad \text{(lxv)}$$

This quantity must be subtracted from the observed $\delta R/R$ to obtain the value used in equation (lxiv). From the natural abundance ratios quoted, the factor $(2R_o)/(R_s + 2R_o)$ was found to be 0.083.

The oxygen in the sulphur dioxide formed in the equilibration came from the water initially placed in the reaction vessel, whereas the oxygen in the sulphur dioxide produced from the hydrogen sulphide came from the tank oxygen used in the combustion of silver sulphide. It was assumed that the isotopic content of the oxygen in the sulphur dioxide obtained from the equilibration was not significantly different from that of the oxygen in the water used, since calculations by Urey (9) predicted a very small isotope effect for the exchange of oxygen between water and sulphur dioxide. The difference in the O^{18}/O^{16} ratio between oxygen in the distilled water used for most of the runs and the tank oxygen used in the combustion of silver sulphide was determined as follows: water was prepared from the tank oxygen by combustion in a stream of hydrogen, the two water samples equilibrated with carbon dioxide following the method of Urey and Cohn (34), and the carbon dioxide analysed on the mass spectrometer. The O^{18}/O^{16} ratio for the tank oxygen was found to be 1.1% larger than that for the distilled water, hence the (66)/(64) ratio for the sulphur dioxide obtained from the equilibration was corrected upward by 0.09%.

Some of the water prepared from tank oxygen was used for further equilibration runs. The results of these runs were consistent with the corrected values of the previous runs to within the precision of the measurements.

(2) Correction for the Sulphur Dioxide-Trioxide Reaction In the combustion of silver sulphide, it is not possible to convert the sulphur quantitatively to sulphur dioxide because of the reaction:

$$SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3 \qquad (IV)$$

This reaction also serves as a mechanism for the exchange of the sulphur isotopes between sulphur dioxide and sulphur trioxide, which has an isotope effect. The isotopic content of the sulphur dioxide obtained differs from that of the silver sulphide by an amount which increases with the amount of sulphur trioxide formed and the deviation of the equilibrium constant for the isotope exchange from unity. Both these effects are reduced by increasing temperature. However, the temperature which determines these effects is not the maximum temperature of the furnace, but the lowest temperature at which reaction (IV) can proceed at an appreciable rate before the gases are swept out of the combustion tube.

The correction was estimated in the following way: from the measured yield of sulphur dioxide, the temperature at which reaction (IV) took place was deduced, on the assumption that chemical equilibrium had been established. The equilibrium constant for the isotope exchange was calculated at this temperature from spectroscopic data. From these quantities, the change in isotopic content of the sulphur dioxide from that of the starting material could be calculated.

With the maximum furnace temperature at 1300°C or 1570°K, the yield of conversion of silver sulphide to sulphur dioxide was found to be about 90%. From the equilibrium data of Rice-Jones (35), the corresponding temperature was 1310°K. The isotopic equilibrium constant at this temperature was calculated to be 1.0025, where the sulphur trioxide is enriched in the heavy isotope. The sulphur dioxide obtained was therefore depleted in the heavy isotope over the starting material by 0.025% of the isotope ratio.

(3) Systematic Errors in the Separation Procedure In order to determine any changes produced by the separation procedure described in section II (A) (2) in the isotopic content of the sulphur dioxide and hydrogen sulphide formed in the reaction vessel some test runs were carried out in the following way. Samples of sulphur dioxide and hydrogen sulphide were prepared from a sample of ferrous sulphide, the former from the combustion of a portion of the ferrous sulphide in the apparatus described in section II (A) (3), and the latter from the reaction of a portion of the ferrous sulphide with hydrochloric acid, the hydrogen sulphide formed being swept by a nitrogen stream through a dry ice trap and condensed in a trap cooled with liquid air. Samples of sulphur dioxide, hydrogen sulphide, and water, in approximately the amounts in which they were present in the equilibrium mixture, were sealed in separate sample tubes on the distillation and sampling apparatus (Fig. 2) in place of the reaction vessel. With trap T_1 cooled by liquid air, the samples were released simultaneously into the trap. The gases were then separated by means of the procedure described in section II (A) (2). The hydrogen sulphide recovered, as well as hydrogen sulphide samples reserved for comparison, was converted to sulphur dioxide as described in section II (A) (3).

The yields of recovery for both gases in the separation procedure were about from 75% to 80%. A small quantity of sulphur was observed in trap T_1 after the separation. Comparison of the isotopic content of the gases before and after the separation step indicated that the sulphur dioxide was fairly consistently enriched in S^{34} by about 0.08% whereas the hydrogen sulphide was changed in an erratic manner, the changes averaging to a slight depletion in S^{34}. The net difference in the S^{34}/S^{32} ratio between the sulphur dioxide and hydrogen sulphide produced by the separation procedure was 0.12% with an average deviation of 0.06% for six determinations. This difference is therefore a systematic error which must be corrected for in the results of the equilibration runs.

It is also evident that the scatter produced by this step is much larger than the scatter of the mass spectrometric results (see section II (B) (2)). Investigation of the conversion of hydrogen sulphide to sulphur dioxide indicated that, with the exception of infrequent large errors, the scatter resulting from this step was of the order of ±0.02% or less. Thus the inability of the present procedure to separate hydrogen sulphide from sulphur dioxide without losses from chemical reaction appears to be the chief limitation on the precision of the results. Modifications made on the separation procedure in an attempt to reduce these errors had little effect either on the systematic error or on the scatter.

III. CALCULATIONS

(A) Molecular Constants

The molecular constants required for the calculation of the isotopic equilibrium constant are the fundamental frequencies for both isotopic species of sulphur dioxide and hydrogen sulphide. The frequencies used for $S^{32}O_2$ were the zero-order frequencies (i.e., corrected for anharmonicity) reported by Shelton, Nielsen and Fletcher (36), and those for H_2S^{32} were zero-order frequencies reported by Allen and Plyler (37).

Since no experimental values were available for the species containing S^{34}, these values had to be calculated with the use of the quadratic force constants. These force constants were taken from recent estimates in the literature.

The evaluation of the four force constants for these molecules is based on the three observed frequencies of the most abundant isotopic species and one other property of the molecule. Kent Wilson and Polo (38) and Kivelson (39) determined the force constants of sulphur dioxide, the former authors by measuring the fundamental frequencies of $S^{32}O^{16}O^{18}$, and the latter author by the use of the centrifugal stretching constants obtained from the micro-wave rotational spectrum. The agreement between the force constants obtained was well within their estimated error. The force constants for hydrogen sulphide have been estimated by Smith and Linnett (40), who based their estimate on the fundamental frequencies of D_2S^{32} and analogy with similar molecules.

The values of the four force constants (defined in equation (lix) section I (D) (4)), for the two molecules are given in Table I.

TABLE I

Force Constants for H_2S, SO_2

Molecule	dy/cm. x 10^{-5}				Ref.
	c_1	c_2	c_3	c_4	
SO_2	10.006	0.7933	0.169	0.0256	(39)
H_2S	4.4 ± 0.2	0.55 ± 0.05	0.2 ± 0.2	-0.15 ± 0.05	(40)

From the above force constants and equation (lxi), the isotope shifts were calculated. The isotope shifts obtained, together with the fundamental frequencies for the S^{32}-containing molecules, are shown in Table II.

TABLE II

Frequencies and Frequency Shifts

Mode	SO_2		H_2S	
	cm.$^{-1}$		cm.$^{-1}$	
	ω	$\delta\omega$	ω	$\delta\omega$
1	1167.60	7.40	2721.92	1.69
2	526.27	4.00	1214.51	1.90
3	1380.91	16.8	2733.36	2.70

The uncertainty in the frequency shifts is difficult to estimate. The relative error in ω_3 is about the same as that of the force constant c_1, but the other two frequency shifts can vary quite sharply with modest changes in c_3 and c_4. For example, using Smith and Linnett's estimated lower limits for the absolute values of c_3 and c_4 for hydrogen sulphide, one obtains 2.24, 1.82, and 2.64 cm.$^{-1}$ for $\delta\omega_1$, $\delta\omega_2$ and $\delta\omega_3$ respectively.

(B) Calculation of the Equilibrium Constant

From equations (xxxiii) and (xlix), section I (C), the equilibrium constant is given by:

$$K = 1 + \sum_i G(u_i)\Delta u_i \,_{(SO_2)} - \sum_i G(u_i)\Delta u_i \,_{(H_2S)} \qquad \text{(lxvi)}$$

By means of equation (lxvi), the equilibrium constant was calculated at 50° intervals from 700°K to 1400°K. A Bendix G-15 digital computer was used in the calculation.

Limitations to the accuracy of equation (lxvi) arise from the approximation involved in obtaining (xlix) from (xlviii), the neglect of anharmonicity, and the assumption of classical rotation. The most unfavorable case for the approximation mentioned above is that of the f function for sulphur dioxide at the lowest temperature used. The f function was calculated for sulphur dioxide at 700°K using the exact equation (xlviii) and compared with the value obtained from equation (xlix). The values differed by 0.01%. Since the exponentials in equation (xlviii) were obtained through the use of five-figure logarithms, this difference may be within the uncertainty of the calculation.

Urey (9) has suggested, as a correction for the effects of anharmonicity, the multiplication of the f function by the factor exp $(E_2^o - E_1^o)$anh./kT, where $(E_2^o - E_1^o)$anh. is the contribution to the zero-point energy difference between isotopic molecules 1 and 2 resulting from the anharmonic contributions to the energy levels. This correction is inexact for two reasons. As a correction for the quantum-mechanical factor in the f function, it amounts to the assumption that all the vibrational levels are lowered by anharmonicity by the same amount as the ground state. Thus it is nearly exact at low temperatures, where the contribution to the partition function of the ground state is predominant, but is too small (in absolute value) for higher temperatures, since the anharmonic effects on the higher levels are much larger. However, as a correction for the f function as a whole, the factor does not take into account that the classical partition function ratio is also changed by anharmonicity. Therefore, at low temperatures, where the correction is exact for the quantum-mechanical factor in the f function, it is too large in absolute value as a correction for the f function as a whole. Since, in the high temperature limit, the quantum-mechanical partition function must equal the classical partition function, it is probable that the correction suggested by Urey is too large in absolute value throughout the entire temperature range.

The zero-point energy differences were calculated in order to arrive at an upper limit to the effect of anharmonicity. Anharmonicity coefficients for the S^{32}-containing species were obtained from Allen and Plyler (37) and Shelton, Nielsen and Fletcher (36), and the anharmonicity coefficients for the S^{34}-containing species calculated by means of the formula of Dennison and Darling (41):

$$\frac{X_{ij}}{X'_{ij}} = \frac{\omega_i\omega_j}{\omega'_i\omega'_j} \qquad \text{(lxvii)}$$

where the X_{ij} are the anharmonicity coefficients, and the primes refer to the isotopic substitution. This formula was found by Dennison and Darling to represent the anharmonicity coefficients of H_2O and D_2O quite accurately. From this data, the correction factor to be applied to the equilibrium constant was found to be exp -(0.071)/T, which is 0.01% at 700°K. Since this correction is probably too large, as explained above, it was concluded that the effect of anharmonicity could be neglected. (It should be noted that this correction does not take into account the errors, probably much more serious, that arise from the assumption of a harmonic potential in the calculation of the isotope shifts.)

In the assumption of classical rotation, the most unfavorable case is that of hydrogen sulphide. Gordon (16) has shown that for a hypothetical rotor with moments of inertia 1 x 10^{-40} gm.cm.^{2}, 2 x 10^{-40} gm.cm.^{2}, and 3 x 10^{-40} gm.cm.^{2}, the difference between the classical and quantum mechanical partition functions is about 2% at 300°K. The moments of inertia of both isotopic species of the hydrogen sulphide molecule have been determined from microwave measurements by Burrus and Gordy (42) and are shown in Table III.

TABLE III

Moments of Inertia of H_2S

Species	In Units of 10^{-40} gm.cm.^{2}		
	I_A	I_B	I_C
H_2S^{32}	2.6522	3.0399	5.6861
H_2S^{34}	2.6615	3.0399	5.6954

It can be seen that, firstly, the moments of inertia are larger and hence the rotation more nearly classical than in the case of the hypothetical rotor investigated by Gordon. Secondly, the changes in the moments of inertia produced by substitution of the sulphur isotopes is a fraction of 1%. It seems therefore safe to neglect non-classical rotation of hydrogen sulphide.

IV. RESULTS AND DISCUSSION

(A) Experimental Values for the Equilibrium Constant

The equilibrium constant is given by:

$$K = \frac{\left[S^{34}O_2\right]\left[H_2S^{32}\right]}{\left[S^{32}O_2\right]\left[H_2S^{34}\right]} = \frac{R_s(SO_2)}{R_s(H_2S)} = 1 - \frac{R_s(SO_2) - R_s(H_2S)}{R_s} \qquad \text{(lxviii)}$$

and, therefore, the relative difference in the S^{34}/S^{32} ratio for the hydrogen sulphide and sulphur dioxide in the equilibrium mixture gives (K - 1). The values obtained directly from the mass spectrometry are the relative differences in the (66)/(64) ratio between the operating standard sample and the two sulphur dioxide samples obtained from the separation and subsequent processing of the hydrogen sulphide and sulphur dioxide originally taken from the equilibrium mixture. To obtain the required equilibrium constants, the mass spectrometric results must be corrected for any differences in the oxygen isotopic content of the samples, converted to S^{34}/S^{32} ratios, and corrected for the systematic errors produced by the conversion of hydrogen sulphide to sulphur dioxide and by the separation procedure. These corrections are described in section II (C), and illustrated for one of the measurements of the equilibrium constant in Table V. The values of the equilibrium constant obtained in this way are tabulated as (K - 1) in Table IV.

Theoretically, in the high temperature limit, the quantum mechanical partition function becomes identical to the classical partition function, and hence all isotope effects in isotope exchange reactions disappear.

TABLE IV

Experimental Values for the Equilibrium Constant for $H_2S^{34} + S^{32}O_2 \rightleftharpoons H_2S^{32} + S^{34}O_2$

T(°K)	(K - 1) x 1000	Dir.[1]
768	7.9	B
775	7.0	A
813[2]	7.0	A
838[2]	5.8	B
880	4.0	A
883	4.1	B
978	3.6	A
985	4.4	B
986	4.7	B
1053[2]	3.5	B
1063[2]	4.1	A
1069	2.1	B
1110	3.2	A
1175	2.9	B
1191	2.9	A
1269	2.1	A
1279	2.7	B

[1] B denotes those runs in which the final temperature was approached from below, and A denotes those runs in which the final temperature was approached from above.

[2] In these runs, the water used in the equilibration was that prepared from tank oxygen. In the other runs, distilled water was used.

TABLE V

Example of Experimental Results

Mass Spectrometer Values and Corrections for First Value in Table IV. (All Values in Parts Per 1000.)

Comparison with Operating Standard			
Sample	$\delta R/R$	av. $\delta R/R$	After O_2 Corr.[1]
SO_2 from H_2S	-1.52 -1.50 -1.44 -1.38	-1.46	
SO_2 from Equ'm	+6.20 +6.20 +6.15	+6.18	+7.10

Comparison of SO_2 with H_2S			
$\delta R/R$	$\delta R_s/R_s$[1]	After Corr. for H_2S Conversion[2]	After Corr. for Separation[3]
8.56	9.34	9.09	7.9

R is (66)/(64) ratio, and R_s is S^{34}/S^{32} ratio.

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[1] See section II (C) (1).

[2] See section II (C) (2).

[3] See section II (C) (3).

Furthermore, the theory given in section I (C) (5) predicts that the vibrational contribution to the isotope effect should be proportional to $1/T^2$. Hence a graph of (K - 1) against $1/T^2$ should give a straight line passing through the origin. To test this prediction, the measured values of (K - 1) were therefore plotted against $1/T^2$ and are shown, with the calculated values for comparison, in Fig. 4.

It can be seen that, qualitatively, the experimental points appear to lie on a straight line through the origin, although the scatter of the points would obscure a small curvature.

A least-squares fit of the data was made to a function of form:

$$(K - 1) = a/T^2 + b \qquad \text{(lxix)}$$

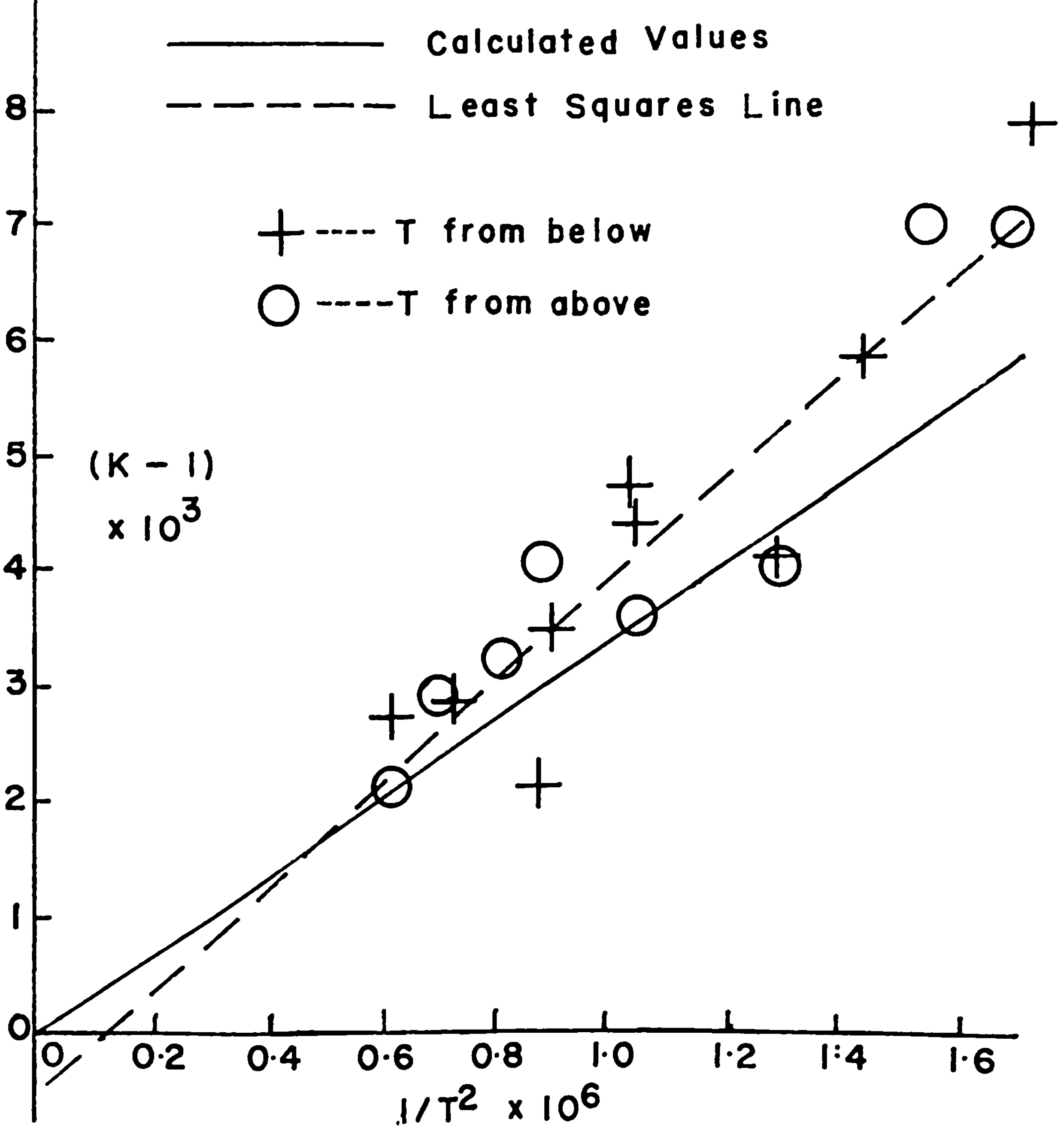
and the values of the parameters determined to be $a = (4.5 \pm 0.5) \times 10^3 \text{deg.}^2$ and $b = -0.0006 \pm 0.0006$. The errors are standard deviations calculated by means of the formulae quoted in Margenau and Murphy (43). When the errors in the applied corrections are taken into account as well as the error due to the scatter of the points, the standard deviation in the intercept becomes ±0.0009. The least-squares line can therefore be considered to pass through the origin to within the precision of the measurements.

Since the scatter of the points around the least-squares line is similar in size to the scatter obtained in the tests of the separation procedure, and since the scatter produced by the silver sulphide burning step has been found to be usually less than ± 0.02% of the isotope ratio, it is probable that the separation step is the principal source of error.

Fig. 4

The Equilibrium Constant for

$H_2S^{34} + S^{32}O_2 \rightleftharpoons H_2S^{32} + S^{34}O_2$



This error is likely due to the loss of some of the hydrogen sulphide and sulphur dioxide by chemical reaction before the separation was complete.

The amounts of sulphur dioxide and hydrogen sulphide obtained in the equilibration runs, after taking into account the losses found in the separation procedure, were roughly consistent with the equilibrium concentrations for this system calculated from the data of Evans and Wagman (25): thus, it is likely that no further serious losses have occurred.

(B) Calculated Values for the Equilibrium Constant

The calculated values of the equilibrium constant are shown plotted as (K - 1) against $1/T^2$ in Fig. 4. The values fall very close to a straight line through the origin with slope about 3.4×10^3 deg.^{2}, although at the low-temperature end, the slope begins to increase. The high-temperature approximation, obtained by replacing G(u) by u/12 in equation (lxvi), gives a line with slope 3.39×10^3 deg.^{2}. The good agreement between this value and that obtained by the more exact equation must be regarded as the result of a fortuitous cancellation of errors, since the individual G(u) terms differ from the u/12 approximation by from 2% to 25% in the temperature range studied.

The uncertainty in the calculated values resulting from the uncertainty in the calculated isotope shifts must be considered. Errors were assigned somewhat arbitrarily to the isotope shifts, (the assignments being based on the uncertainties in the force constants reported in the literature) and the effect on the equilibrium constant calculated. The assigned errors were as follows:

for sulphur dioxide,

$\delta\omega_1$ ... ±10%, $\delta\omega_2$ ... ± 10%, $\delta\omega_3$ ... ±5%,

for hydrogen sulphide,

$\delta\omega_1$ ... ±25%, $\delta\omega_2$ ... ±25%, $\delta\omega_3$ ... ±5%.

On the basis of these assumed errors in the isotope shifts, and with the use of the high-temperature approximation, the error in (K - 1) was calculated to be ±10%.

The largest contribution to this error came from the terms containing $\delta\omega_3$ for both molecules, in spite of the fact that this isotope shift is the least uncertain of the three. This is because the term $G(u_3)\delta u_3$ is much larger for both molecules than the corresponding terms for the other two modes.

(C) Comparison of Experimental and Calculated Values

Both the experimental and the calculated values for (K - 1) gave approximately straight lines passing through the origin when plotted against $1/T^2$, and were thus consistent with the general prediction of the theory that the equilibrium constant must be 1 in the high temperature limit. However, the experimental and calculated values of the slope differed somewhat, the two values being $(4.5 \pm 0.5) \times 10^3$ deg.^{2} and $(3.4 \pm 0.3) \times 10^3$ deg.^{2} respectively. If the error in the calculated slope is treated as a standard deviation, the difference between the two slopes is $(1.1 \pm 0.6) \times 10^3$ deg.^{2}, or about two standard deviations. The two slopes therefore coincide only at the 95% confidence limit.

There thus appears to be a real discrepancy between the experimental and calculated values. The most probable source of error in the calculated values would be the isotope shifts for hydrogen sulphide, since the force constants for hydrogen sulphide are not known with a high degree of certainty. This question could be resolved by direct spectroscopic measurement of the isotope shifts through the use of hydrogen sulphide enriched in S^{34} (which would also permit an improved estimate of the force constants), or the determination of the centrifugal stretching constants from the microwave rotational spectrum and the calculation of improved force constants following the method of Kivelson (35).

Temperature-dependent systematic errors could arise in the experimental values if some reaction occurred as the equilibrium mixture was withdrawn from the reaction vessel and condensed into the trap, or if the hydrogen sulphide and sulphur dioxide sampled were not present in the equilibrium system as the free gaseous molecules. In the first case, the increment or decrement of the hydrogen sulphide and sulphur dioxide produced in such a reaction would have a different isotopic content than the remainder of these gases as a result of a kinetic isotope effect. However, any kinetic isotope effect could be expected to be at the most of the same order of magnitude as the equilibrium isotope effect being measured, and since the yield measurements showed no great discrepancy in the amount of gas sampled from the expected equilibrium amounts (except for the losses found in the separation procedure), errors from this effect were probably small.

The states of the hydrogen sulphide and sulphur dioxide present in the equilibrium mixture could differ from that of the free molecules either through dissociation or through some form of molecular interaction. In the dissociation of a molecule, the lighter isotopic species is always favored in the dissociation products, and therefore in an isotope exchange reaction, a partially dissociated compound will be more enriched in the lighter isotopic species than it would be if no dissociation took place. The extent of dissociation of hydrogen sulphide and sulphur dioxide can be estimated through the use of the thermodynamic data of Evans and Wagman (25). Sulphur dioxide can dissociate into sulphur monoxide and oxygen, but this reaction occurs only to a negligible extent at 1500°K or below. Hydrogen sulphide, however, begins to dissociate in the temperature range covered by this investigation, being 6% dissociated at 1000°K, and 15% dissociated at 1200°K under a total pressure of one atmosphere. The presence of a large concentration of sulphur vapour in the equilibrium mixture would tend to suppress this dissociation somewhat. The effect on the measured isotopic equilibrium constant would be to give high values of (k - 1) at the higher temperatures studied. The observed discrepancy between the measured and calculated values is, however, greater at the lower end of the temperature range.

Molecular interaction energies are mass-dependent, as is shown by the difference in vapour pressure of different isotopic species. Vapour pressure isotope effects tend to be almost an order of magnitude smaller than chemical isotope exchange effects, and, since the energies involved in deviations from ideal gas behaviour are much smaller than the interaction energies in condensed systems, the effect of non-ideal gas behaviour on the isotopic equilibrium constant should be negligible.

(D) Conclusions

From the above considerations, it can be claimed that the experimentally obtained values for the equilibrium constants should be more reliable than the calculated values, and that the discrepancy between them can be attributed to errors in the estimation of the isotope shifts. If the isotope shifts were accurately known, however, the theory used in this work should give values for the equilibrium constants accurately to 0.1% for the system studied: therefore, the accurate experimental determination of the isotope shifts should resolve this question conclusively.

Equilibrium constants for isotopic exchange reactions have been used in several fields. In naturally occurring chemical processes, especially, the isotopic content of the substances involved may often be determined more easily than the chemical composition of the system, and isotopic equilibrium constants used to estimate the conditions under which the process was occurring. The results of this investigation suggest that calculated equilibrium constants should be used with caution, unless experimental isotope shifts are available for the molecular species under consideration.

APPENDIX I

Equilibrium Constants for the Reaction $S^{34}O_2 + S^{32}O_3 \rightleftharpoons S^{32}O_2 + S^{34}O_3$

Experiments are in progress for the measurement of the equilibrium constant for the exchange of the sulphur isotopes between sulphur dioxide and sulphur trioxide. In order to have theoretical results available for comparison, calculations have been carried out on the partition function ratios of $S^{32}O_3$ and $S^{34}O_3$ in a similar manner to those on the isotopic hydrogen sulphide and sulphur dioxide molecules.

Since there are no spectroscopic measurements available for $S^{34}O_3$, the isotope shifts must be calculated from normal vibration theory. A general non-linear 4-atomic molecule has six fundamental frequencies and twenty-one independent quadratic force constants. However, in the case of a planar XY_3 molecule such as sulphur trioxide, the high degree of symmetry present reduces the number of frequencies to four, two of which are doubly degenerate, and the number of independent quadratic force constants to five. The four fundamental frequencies obtained from spectroscopic measurements on $S^{32}O_3$ are insufficient to determine the five force constants; hence, the number of force constants must be reduced through the use of an approximate model.

In the simple valence-force treatment (15), three force constants are assigned to the molecule, corresponding to S-O bond stretch, to change in the O-S-O bond angle in the equilibrium plane of the molecule, and to deflection of the central sulphur atom from the plane of the three oxygen atoms. The secular equation (lviii) is then set up in terms of these force constants and the corresponding internal co-ordinates and solved for the fundamental frequencies. Tudge and Thode (44) calculated the isotope shifts of sulphur trioxide using this procedure.

The solution of the secular equation gives four equations relating the fundamental frequencies to the force constants. Three would be sufficient to determine the three simple valence-force constants: the fourth can be used as a consistency check (which will usually be somewhat inexact), or a fourth parameter can be introduced in addition to the three valence-force constants in the hope that this will give an improved approximation to the potential energy.

One method of introducing such a parameter is a potential energy function of the Urey-Bradley type, in which a term representing the repulsive interactions of non-bonded atoms is added. Janz and Mikawa (45) have calculated Urey-Bradley force constants for a number of planar XY_3 molecules for the in-plane vibrations only. (The simple valence-force constant for the vibration of the sulphur atom perpendicular to the plane of the three oxygen atoms is unchanged in this treatment, since, from symmetry considerations, there can be no interaction terms between this motion and the motions of the molecule in the plane.)

The potential energy for the in-plane motions of the molecule is given by:

$$V = \sum_{i=1}^{3} \left[K_i' r_i \Delta r_i + 1/2\, K_i \Delta r_i^2 \right] + \sum_{i<j}^{3} \left[H_{ij}' r_{ij}^2 \Delta\alpha_{ij} + 1/2\, H_{ij} (r_{ij} \Delta\alpha_{ij})^2 \right] + \sum_{i<j}^{3} \left[F_{ij}' q_{ij} \Delta q_{ij} + 1/2\, F_{ij} (\Delta q_{ij})^2 \right] \qquad \text{(lxx)}$$

where r is the S-O bond length, α is the O-S-O bond angle, and q is the distance between unbonded atoms. Since these co-ordinates are not all independent, only four of the six force constants are independent.

Janz and Mikawa have derived the relations between the frequencies and the force constants for this case. These relations are:

$$\lambda_1 = \mu_Y(K + 3F)$$

$$\lambda_3 + \lambda_4 = (K + \tfrac{3}{4}F' + \tfrac{3}{4}F)(\tfrac{3}{2}\mu_X + \mu_Y) - \tfrac{9}{4}(F' + F)\mu_X + (H - \tfrac{3}{4}F' + \tfrac{1}{4}F)(\tfrac{9}{2}\mu_X + 3\mu_Y)$$

$$\lambda_3\lambda_4 = \left[(K + \tfrac{3}{4}F' + \tfrac{3}{4}F)(H - \tfrac{3}{4}F' + \tfrac{1}{4}F) - \tfrac{3}{16}(F' + F)^2\right] \cdot (3\mu_Y^2 + 9\mu_X\mu_Y) \qquad \text{(lxxi)}$$

where $1/\mu_X$ is the mass of the sulphur atom and $1/\mu_Y$ is the mass of the oxygen atom. The values obtained by Janz and Mikawa for the force constants K, H, F, and F' were 9.08, 0.521, 0.555, and -0.0426 x 10^5 dy./cm. respectively.

It can be seen that there is no sulphur isotope shift for the normal vibration ω_1. This vibration is the symmetric stretch in which the central atom does not move. The isotope shifts for the vibrations ω_3 and ω_4 were calculated by means of equations (lxxi), the force constants reported by Jans and Mikawa, and the fundamental frequencies reported by Stockmayer, Kavanagh and Mickley (46). The isotope shift for the out-of-plane vibration was calculated by means of the valence-force formula given by Herzberg (15). The isotope shifts, together with the fundamental frequencies for the most abundant isotopic species, are shown in Table VI.

TABLE VI

Isotope Shifts for SO_3

Mode	ω (cm.$^{-1}$)[a]	$\Delta\omega$ (cm.$^{-1}$)[b]	$\Delta\omega$ (cm.$^{-1}$)[c]
1	1068	0	0
2	530	9.55	11.60
3 (2)	1332	18.1	19.35
4 (2)	560	2.23	1.96

[a] Stockmayer, Kavanagh and Mickley (46).

[b] This work.

[c] Tudge and Thode (44).

With the use of these molecular constants and equation (xlix), values of the f function for sulphur trioxide were calculated for temperatures ranging from 400°K to 1400°K, and are shown, along with the corresponding values for hydrogen sulphide and sulphur dioxide, in Table VII, Appendix II.

APPENDIX II

TABLE VII

Partition Function Ratios and Calculated Equilibrium Constants for the Exchange of S^{32} and S^{34} Among Sulphur Trioxide, Sulphur Dioxide and Hydrogen Sulphide

T(°K)	(f − 1)[1] SO_3 (x 10^3)	(f − 1) SO_2 (x 10^3)	(f − 1) H_2S (x 10^3)	(K − 1) SO_3 − SO_2 (x 10^3)	(K − 1) SO_2 − H_2S (x 10^3)
400	46.18	27.81	....	18.37	....
500	31.85	19.27	....	12.58	....
600	23.16	14.05	....	9.11	....
700	17.55	10.67	3.66	6.88	7.01
800	13.73	8.35	2.98	5.38	5.38
900	11.01	6.70	2.45	4.31	4.26
1000	9.03	5.50	2.06	3.53	3.44
1100	7.50	4.58	1.74	2.92	2.84
1200	6.35	3.88	1.50	2.47	2.38
1300	5.45	3.32	1.29	2.13	2.03
1400	4.72	2.88	1.14	1.84	1.74

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[1] See section I (C) (3).

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