CALCULATED EQUILIBRIUM CONSTANTS

FOR

ISOTOPIC EXCHANGE REACTIONS

INVOLVING

SULFUR-CONTAINING COMPOUNDS

By

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Scope and contents of this thesis:

Partition function ratios and exchange constants are calculated for isotopic compounds involving sulfur. These calculations are discussed in the light of variations in the abundance of the sulfur isotopes found in naturally occurring substances. Equilibrium constants are predicted for many exchange reactions.

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ABSTRACT

Recent investigations by H.G. Thode, J. Macnamara and C. Collins[1] have shown that the S^{32}/S^{34} ratio in natural sulfur-containing compounds varies by as much as five percent. These wide-spread variations suggest that fractionation of the sulfur isotopes occurs in natural processes due to differences in the chemical properties of isotopic molecules. In order to determine the magnitude of the effects that could be expected, partition function ratios for isotopic molecules containing sulfur and equilibrium constants for many isotopic exchange reactions involving sulfur have been calculated by methods of statistical mechanics. The results of these calculations are discussed.

INTRODUCTION

Historical

Soon after the discovery of deuterium, it was found that the isotopes of hydrogen and other light elements differed slightly in chemical properties. In 1932, Urey and Rittenburg^{2} showed from statistical theory that the equilibrium constants for hydrogen isotope exchanges involving hydrogen and hydrogen halides differed from unity. Later, Farkas and Farkas^{3} applied this method to calculate exchanges involving hydrogen and deuterium in water. Urey and Greiff^{4} were the first to show from theoretical considerations that isotopes of the light elements other than hydrogen had different chemical properties. According to their calculations, exchange constants for isotopic reactions differed from unity thus showing that slight fractionation of the isotopes could be expected. There is, therefore, a theoretical basis for the differences in the chemical properties of isotopic molecules. The introduction of a heavy isotope into a molecule lowers the frequency of the internal vibrations and thereby changes the free energy, entropy and other thermodynamic properties of a molecule. The equilibrium constant for a reaction depends on the thermodynamic partition functions of each of the molecules involved. Since the partition functions of isotopic molecules are different, it is seen that equilibrium constants for isotopic reactions will differ from unity.

H.C. Urey[5] has recently used a relatively simple relation for the calculation of partition function ratios for isotopic molecules that involves only the vibrational frequencies. By a combination of these ratios, equilibrium constants for specific exchange reactions are obtained. He has made a comprehensive study of many possible exchanges involving oxygen, hydrogen, nitrogen, boron and the halogens.

Similar calculation of the partition function ratios and equilibrium exchange constants for sulfur compounds have been calculated. An attempt has been made to explain the wide-spread variations of S^{34} that have been reported by H.G. Thode, J. Macnamara and C. Collins[1].

Theoretical

Partition Functions

In an ideal system of N molecules, different numbers of them are in different energy levels. The number of molecules having energy $\mathcal{E}_i$ is given by statistical mechanics as

$$n_i = n_o e^{-\mathcal{E}_i/kT} \qquad 1E$$

where n_o is the number of molecules having zero point energy. If g_i is the number of quantum states having nearly equal energy, then the total number of molecules N is given by

$$N = g_o n_o + g_1 n_1 + g_2 n_2 + \text{———} \qquad 2E$$

or

$$N = n_o \sum_{i=0}^{\infty} g_i e^{-\mathcal{E}_i/kT} \qquad 3E$$

The summation in the above equation is defined as the "partition function" and is given the symbol Q. Any thermodynamic text will give a complete development of the partition function and show how such thermodynamic properties as specific heat, free energy, entropy, etc. are dependent upon Q[6,7].

For example the free energy is given by

$$F = E_0 + RT \ln N - RT \ln Q \qquad 4E$$

where E_0 is usually the zero point energy of the molecule and the other symbols have their usual physical meaning. The total energy $\mathcal{E}$ of a molecule is made up of the sum of translational, rotational, vibrational, and electronic energies such that

$$\mathcal{E} = \mathcal{E}_t + \mathcal{E}_r + \mathcal{E}_v + \mathcal{E}_e \qquad 5E$$

Thus $$e^{-\mathcal{E}/kT} = e^{-\mathcal{E}t/kT} \cdot e^{-\mathcal{E}r/kT} \cdot e^{-\mathcal{E}v/kT} \cdot e^{-\mathcal{E}e/kT} \qquad 6E$$

and $$Q = Q_t \cdot Q_r \cdot Q_v \cdot Q_e \qquad 7E$$

$$= \sum_{i=0}^{\infty} e^{-\mathcal{E}t/kT} \cdot g_t \cdot \sum_{i=0}^{\infty} e^{-\mathcal{E}v/kT} \cdot g_v \cdot \sum_{i=0}^{\infty} e^{-\mathcal{E}r/kT} \cdot g_r \cdot \sum_{i=0}^{\infty} e^{-\mathcal{E}e/kT} \cdot g_e \qquad 7E'$$

Values for $\mathcal{E}_t$, $\mathcal{E}_r$ etc. can be obtained by imposing certain quantum mechanical conditions on the Schrödinger wave equation. If these values are placed in equation 7E and other certain valid assumptions are made[7], we obtain the following relationships for diatomic molecules.

$$Q_t = \frac{(2\pi MkT)^{3/2}}{h^3} \cdot \frac{RT}{P} \qquad 8E$$

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2} \qquad 9E$$

$$Q_v = \frac{e^{-\frac{u}{2}}}{1 - e^{-u}} \quad \text{where} \quad u = \frac{hc\omega}{kT} \qquad 10E$$

$$Q_e = 1 \qquad 11E$$

where M = molecular weight of the molecule

I = moment of inertia of the molecule

σ = symmetry number of the molecule

ω = fundamental vibration frequency of the molecule

Thus the only variables in equation 8E to 11E are M, I, σ and ω while the remaining symbols are constants and have their usual physical meaning.

Equilibrium Constants in Terms of Partition Functions

A typical exchange reaction may be written

$$aA_1 + bB_2 = aA_2 + bB_1 \qquad 12E$$

where A and B are molecules which have some one element as a common constituent and subscripts 1 and 2 indicate that the molecule contains only the light or the heavy isotope respectively. It is well known that the equilibrium constant, K, for any reaction is given by

$$-RT \ln K = \Delta F^\circ \qquad 13E$$

where F° is the STANDARD free energy. For a reaction of the type 12E we would get

$$-RT \ln K = aF_{A_2} + bF_{B_1} - aF_{A_1} - bF_{B_2} \qquad 14E$$

On substituting 4E in 14E and simplifying, one gets the relation

$$K = \left[\frac{Q_{A2}}{Q_{A1}}\right]^{a} \Big/ \left[\frac{Q_{B_2}}{Q_{B_1}}\right]^{b} e^{-\left[\frac{aE_{o_{A_2}} + bE_{o_{B1}} - aE_{o_{A_1}} - bE_{o_{B_2}}}{RT}\right]} \qquad 15E$$

Instead of taking E_o as the "zero point energy" (which is unique for any molecule), one can take E_o as the bottom of the "potential energy curve". Since the potential energy curves are practically identical for isotopic molecules, then E_{oA_2} equals E_{oA_1} and E_{oB2} equals E_{oB_1}. Thus the exponential term in 15E become unity and

$$K = \left[\frac{Q_{A_2}}{Q_{A_1}}\right]^{a} \Bigg/ \left[\frac{Q_{B_2}}{Q_{B_1}}\right]^{b} \qquad 16E$$

Therefore, in order to calculate the value of K, it is first necessary to find the Q_2/Q_1 ratio for substances A and B.

Formulas for Partition Function Ratios of Isotopic Molecules

The problem resolves itself into one of evaluating Q_2/Q_1 for various isotopic compounds. By making use of equations 7E to 11E, it is possible to obtain formulas for Q_2 and Q_1. If one now divides Q_2 by Q_1 and cancels the constant terms, the resulting equation is identical with that given by H. C. Urey[5].

$$\frac{Q_2}{Q_1} = \frac{I_2 \ \sigma_1 \ M_2^{3/2} \ e^{\frac{-u_2}{2}} \ (1 - e^{-u_1})}{I_1 \ \sigma_2 \ M_1^{3/2} \ (1 - e^{-u_2}) \ e^{\frac{-u_1}{2}}} \qquad 17E$$

The following reasoning is then used by H.C. Urey[5] to obtain further simplification. If the right and left sides of equation 17E are multiplied by $(m_1/m_2)^{3/2n}$ (where m_1 and m_2 are the atomic weights of the isotopic atoms being considered and n is the number of isotopic atoms being exchanged), and if the right side of 17E is multiplied and divided by the ratio u_1/u_2, it is possible to simplify this expression. Thus 17E becomes

$$\frac{Q_2}{Q_1}\left[\frac{m_1}{m_2}\right]^{3/2n} = \frac{\sigma_1\, u_2\, e^{\frac{-u_2}{2}}\,(1 - e^{-u_1})}{\sigma_2\, u_1\,(1 - e^{-u_2})\, e^{\frac{-u_1}{2}}} \qquad 18E$$

since

$$\frac{I_2\ M_2^{3/2}\ m_1^{3/2n}\ u_1}{I_1\ M_1^{3/2}\ m_2^{3/2n}\ u_2} = 1 \qquad 19E$$

according to the Teller and Redlich theorem. New partition functions are defined where

$$\frac{Q_2'}{Q_1'} = \frac{Q_2}{Q_1}\left[\frac{m_1}{m_2}\right]^{3/2n} \qquad 20E$$

It is obvious that the equilibrium constant K is given by

$$\left[\frac{Q_{A_2}'}{Q_{A_1}'}\right]^a \Bigg/ \left[\frac{Q_{B_2}'}{Q_{B_1}'}\right]^b = K \qquad 21E$$

Equation 18E can be put in a more convenient form for purpose of calculation. Defining

$$x = \frac{u_1 + u_2}{4} \quad \text{and} \quad \delta = \frac{u_1 - u_2}{2} \qquad 22E$$

and expanding in terms of δ, we obtain

$$\ln\frac{Q_2'}{Q_1'} = \ln\frac{\sigma_1}{\sigma_2} + \ln\frac{u_2}{u_1} + (\coth x)\,\delta \qquad 23E$$

Although the entire proceeding treatment has been given for diatomic molecules, one can go through similar reasoning for polyatomic molecules and obtain an equation related to 23E.

$$\ln \frac{Q_2'}{Q_1'} = \ln \frac{\sigma_1}{\sigma_2} + \sum_i \ln \frac{u_{2_i}}{u_{1_i}} + \sum_i (\coth x_i)\,\delta_i \qquad 24E$$

$$\text{where } u_i = \frac{hc\omega_i}{kT} \qquad x_i = \frac{u_{2_i} + u_{1_i}}{4} \qquad \delta_i = \frac{u_{1_i} - u_{2_i}}{2} \qquad 25E$$

ω_i are the various vibrational frequencies (in cm.$^{-1}$) of the isotopic molecules, σ_1 and σ_2 are the symmetry numbers of the molecules. For nearly all molecules studied in this paper, the ratio of the symmetry numbers is equal to unity. Therefore, although the calculations for a single Q would be extremely complicated (see equation 7E to 11E), the partition function <u>ratio</u> for <u>isotopic molecules</u> is easily obtained from a <u>knowledge of vibrational frequencies alone</u>.

In order to determine Q_2'/Q_1', it is necessary to obtain the vibrational frequencies of the molecules containing the most abundant isotope from spectroscopic data and then to calculate the frequencies of the rare isotopic molecules by means of well known "normal vibration equations".[8] This method must be used because, in general, the rare isotopic molecule is in such low concentration that its vibrational frequencies cannot be experimentally determined.

"Normal vibration equations" have been known for many molecules for some time and these equations approximately relate the frequencies to "force constants" and atomic weights.[8] If one assumes these same "force constants" to hold for both the abundant and the rare molecule, then it is possible to calculate frequencies for both isotopic molecules (by putting in the appropriate atomic weights) and then find the differences in the frequencies. While these calculated frequencies may be slightly in error (since the normal vibration equations are only approximate), the differences can be evaluated quite accurately by this method[9]. Using these differences and the experimentally observed fundamental frequencies for the abundant molecule, it is possible to determine the fundamental frequencies for the molecule containing the rare isotope.

As pointed out by Urey[5], the partition functions for polyatomic molecules may be slightly in error because only the fundamental frequencies are known (i.e. no anharmonic terms). Also, errors will be introduced when we apply statistical mechanical formulae relating to ideal gaseous substances to condensed phases or solids in solution.

Isotope Effects in Unidirectional Processes

Considerable work has been done recently on the experimental determination of the effect of isotopes on the specific reaction rates.[10,11,12] These researches have mainly been on the decomposition of organic compounds. It has been shown conclusively that isotopic molecules have different rates of reaction and that, in general, the molecule containing the lighter isotope reacts faster.

The problem of reaction rates has also been approached from a theoretical point of view. Eyring, Evans and Polanyi[13] have treated rate reactions from a statistical viewpoint and their method is called "theory of absolute rates". J. Bigeleisen[14] in a recent paper has considered the ratio of rate constants for competitive reactions of isotopic molecules and has derived the following formula which gives the approximate ratio of the rate constants.

$$\frac{k_1}{k_2} = \frac{Q_{R_2}}{Q_{R_1}} \Bigg/ \frac{Q_2^{\ddagger}}{Q_1^{\ddagger}} \left[\frac{m_2^*}{m_1^*}\right]^{\frac{1}{2}} \qquad 26E$$

The k's are the specific rate constants, Q_R and $Q^{\ddagger}$ are the partition functions for the reactants and "activated complex" respectively, m^* is the effective mass of the activated complex and the subscripts 1 and 2 refer to the light and heavy isotopic species respectively.

Thus we see that the k_1/k_2 ratio really depends on the differences in chemical properties of the isotopes (as determined by the partition function ratios). However, it is not yet possible to calculate k_1/k_2 because the values of the partition function ratios for the activated complexes are unknown. Also, it is not at all certain what values should be given to m_2^*/m_1^*.

RESULTS AND DISCUSSION

Numerical Results

Table I contains a list of the frequencies of the diatomic molecules used in the calculations while Table II gives the corresponding data on the polyatomic molecules. Appendices I and II contain sample calculations for the determination of fundamental frequencies of typical diatomic and polyatomic molecules.

The values of the partition function ratios and equilibrium constants are given in Table III (See appendix III for a sample calculation of Q_2'/Q_1' for a typical molecule). The method of tabulation in Table III is the same as that employed by Urey[5]. The Q_2'/Q_1' ratios are given at two temperatures, while the equilibrium constants are contained at the intersection of the appropriate row and column. In all cases, the heavy isotope will concentrate in the compound listed at the left.

TABLE I

Molecular Frequencies

Molecule	ω_e	$\omega_e x_e$	Reference
PbS^{32}	428.14	1.20	Herzberg I[15], p. 491
PbS^{34}	417.10	1.14	Calculated. Herzberg I, p. 71, 151
$S^{32} - S^{32}$	725.8	2.85	Herzberg I, p. 492
$S^{34} - S^{34}$	704.2	2.70	Calculated. Herzberg I, p. 71, 151
$S^{32} - S^{34}$	715.1	2.77	Calculated. (Note that the symmetry number is not equal to those for $S^{32} - S^{32}$ and $S^{34} - S^{34}$)

TABLE II

Molecular Frequencies

(The numbers in brackets represent the degree of degeneracy of a frequency)

Molecules	Frequencies w_1	w_2	w_3	w_4	References
H_2S^{32}	2611.	1290.	2684.		Herzberg II[16], p. 170
H_2S^{34}	2610.77	1287.90	2679.45		Calc. Herzberg II, p. 169
H_2S^{36}	2610.57	1286.02	2675.38		Calc. Herzberg II, p. 169
$S^{32}CN^-$	2065.53	398.18 (2)	752.81		Calc. Herzberg II, p. 174
$S^{34}CN$	2064.99	397.58 (2)	743.02		
$S^{32}CO$	2081.82	529.24 (2)	859.09		Calc. Herzberg II, p. 174
$S^{34}CO$	2080.47	528.42 (2)	847.77		
CS_2^{32}	655.79	396.55 (2)	1522.64		Calc. Herzberg II, p. 172
CS_2^{34}	636.24	394.70 (2)	1515.56		
$S^{32}O_2$	1151.	519.	1361.		Herzberg II, p. 285
$S^{34}O_2$	1142.84	514.93	1343.75		Calc. Herzberg II, p. 169
$S^{32}O_3$	1069.	652.	1330. (2)	532. (2)	Herzberg II, p. 178
$S^{34}O_3$	1069.	640.40	1310.65 (2)	530.04 (2)	Calc. Herzberg II, p. 178
$S^{32}O_4^{=}$	980.	451. (2)	1113.60 (3)	618.90 (3)	Urey and Bradley[17], p. 1977
$S^{34}O_4^{=}$	980.	451. (2)	1097.56 (3)	615.55 (3)	Calc. Urey and Bradley
$S^{36}O_4^{=}$	980.	451. (2)	1083.21 (3)	612.30 (3)	
S_8^{32*}					
S_8^{34}					

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*	S_8^{32}	470.	216.	267.	557.	465. (2)	200. (2)	243. (2)	434. (2)
	S_8^{34}	455.98	209.56	259.04	540.39	451.13 (2)	194.04 (2)	235.75 (2)	421.06 (2)

S_8^{32}	152. (2)	542. (2)	185. (2)	Bhagavantam and Venkatarayudu[18]
S_8^{34}	147.47 (2)	525.84 (2)	179.48 (2)	

TABLE III

Equilibrium Constants For Sulfur Exchanges

	$\frac{S^{34}O_4^=}{S^{32}O_4^=}$	$\frac{S^{34}O_3}{S^{32}O_3}$	$\frac{S^{34}O_2}{S^{32}O_2}$	$\frac{S^{34}CO}{S^{32}CO}$	$\left[\frac{CS_2^{34}}{CS_2^{32}}\right]^{\frac{1}{2}}$	$\left[\frac{S_8^{34}}{S_8^{32}}\right]^{\frac{1}{8}}$	$\frac{S^{34}CN^-}{S^{32}CN^-}$	$\left[\frac{S_2^{34}}{S_2^{32}}\right]^{\frac{1}{2}}$	$\frac{H_2S^{34}}{H_2S^{32}}$	$\frac{PbS^{34}}{PbS^{32}}$	$\frac{S^{=34}}{S^{32=}}$	°C
Q_2'/Q_1'	1.101	1.096	1.053	1.022	1.021	1.018	1.015	1.015	1.015	1.010	1.000	0
	1.088	1.084	1.045	1.019	1.019	1.016	1.014	1.013	1.013	1.009	1.000	25
$\frac{S^{34}O_4^=}{S^{32}O_4^=}$	1.000	1.005	1.046	1.077	1.078	1.082	1.084	1.085	1.085	1.090	1.101	0
		1.004	1.041	1.068	1.063	1.071	1.073	1.074	1.074	1.078	1.088	25
$\frac{S^{34}O_3}{S^{32}O_3}$		1.000	1.041	1.072	1.073	1.077	1.079	1.080	1.080	1.085	1.096	0
			1.037	1.064	1.064	1.067	1.069	1.070	1.070	1.074	1.084	25
$\frac{S^{34}O_2}{S^{32}O_2}$			1.000	1.030	1.031	1.034	1.036	1.037	1.037	1.043	1.053	0
				1.026	1.026	1.029	1.031	1.032	1.032	1.036	1.045	25
$\frac{S^{34}CO}{S^{32}CO}$				1.000	1.001	1.003	1.006	1.007	1.007	1.012	1.022	0
					1.000	1.003	1.005	1.006	1.006	1.010	1.019	25
$\left[\frac{CS_2^{34}}{CS_2^{32}}\right]^{\frac{1}{2}}$					1.000	1.003	1.005	1.006	1.006	1.011	1.021	0
						1.003	1.005	1.006	1.006	1.010	1.019	25
$\left[\frac{S_8^{34}}{S_8^{32}}\right]^{\frac{1}{8}}$						1.000	1.002	1.003	1.003	1.008	1.018	0
							1.002	1.003	1.003	1.007	1.016	25
$\frac{S^{34}CN^-}{S^{32}CN^-}$							1.000	1.001	1.001	1.006	1.016	0
								1.001	1.001	1.005	1.014	25
$\left[\frac{S_2^{34}}{S_2^{32}}\right]^{\frac{1}{2}}$								1.000	1.000	1.005	1.015	0
									1.000	1.004	1.013	25
$\frac{H_2S^{34}}{H_2S^{32}}$									1.000	1.005	1.015	0
										1.004	1.013	25
$\frac{PbS^{34}}{PbS^{32}}$										1.000	1.010	0
											1.009	25
$\frac{S^{34=}}{S^{32=}}$											1.000	0
												25

Perhaps special reference ought to be made to the Q_2'/Q_1' ratio of 1.000 for $S^=$ ion. The rigorous partition function ratio for a molecule which has only translational freedom is $Q_2/Q_1 = (M_2/M_1)^{3/2}$ where M_2 and M_1 are the molecular weights of the heavy and light molecules respectively. Following Urey's method of simplification (outlined earlier) one obtains

$$\frac{Q_2}{Q_1}\left[\frac{m_1}{m_2}\right]^{3/2n} = \left[\frac{M_2}{M_1}\right]^{3/2}\left[\frac{m_1}{m_2}\right]^{3/2n} \qquad 27E$$

In the case of $S^=$ ion, n equals unity, and M equals m so that when new partition functions are defined, one obtains

$$\frac{Q_2'}{Q_1'} = \frac{Q_2}{Q_1}\left[\frac{m_1}{m_2}\right]^{3/2n} = 1.000 \qquad 28E$$

By analogy, the values of Q_2'/Q_1' for many monatomic ions and molecules should be unity. Values for Li^+, Cl^-, Br^- and I^- could be added to Urey's tables of exchange constants.

When partition functions are calculated for S_2^{32}, $S^{32} - S^{34}$ and S_2^{34}, it is found that the equilibrium constant (at 0° C) for the reaction

$$S_2^{32} + S_2^{34} = 2\ S^{32} - S^{34}$$

is 4.0004. If there were no chemical differences in the sulfur isotopes, the value of K would be 4.0000.

It is interesting to note that the enrichment factors (K - 1) for exchanges involving S^{36} are twice those involving S^{34}. This is seen in the following reactions.

$S^{32}O_4^{=} + H_2S^{34} = S^{34}O_4^{=} + H_2S^{32}$ $K_{(\text{calc.})} = 1.074$ at 25° C

$S^{32}O_4^{=} + H_2S^{36} = S^{36}O_4^{=} + H_2S^{32}$ $K_{(\text{calc.})} = 1.145$ at 25° C

This effect has been observed experimentally (on other exchanges) by H.G. Thode, R.L. Graham and J.A. Zeigler[19].

Possible Exchanges

When an attempt is made to correlate the theoretically calculated constants with experimentally observed constants, considerable difficulty is encountered. In the first place, many of the listed compounds (or ions) will not exchange under normal conditions and low temperatures. Secondly, for those compounds that do exchange, no vibrational data is known.

No chemical exchanges are known to involve the stable $SO_4^{=}$ ion[20,21]. Cooley, Yost and McMillan [22] report that there is no transfer of sulfur atoms between free sulfur and carbon disulfide at temperatures up to 100° C.

Even though the following exchanges are known to occur, no partition function ratios can be calculated for HS^-, $SO_3^{=}$, $SSO_3^{=}$ and HSO_3^- due to lack of spectroscopic data.

$HS^{32}O_3^- + S^{34}O_2 = HS^{34}O_3^- + S^{32}O_2$ (19) $K_{(\text{Exp't})} = 1.019 \pm 0.002$ at 25° C

$HS^{34-} + H_2S^{32} = H_2S^{32\,-} + H_2S^{34}$ (23) $K_{(\text{Exp't})} = 1.006$ at 0° C

$S^{32}O_3^{=} + S^{34}SO_3^{=} = S^{34}O_3^{=} + S^{32}SO_3^{=}$ 20

$S^{32=} + S^{34}SO_3^{=} = S^{34=} + S^{32}SO_3$ 20

Although none of the above reactions afford the means of substantiating the theory, it is felt that some of the following exchanges could be used for this purpose. A possible reaction is one analogous to the oxygen exchange between CO_2 and H_2O namely,

$$H_2S^{34} + \tfrac{1}{2}\ CS_2^{32} = H_2S + \tfrac{1}{2}\ CS_2^{34} \quad K_{(calc)} = 1.006 \text{ at } 25^\circ \text{ C}$$

Although Douglas, Cooley and Yost [24] state that the above substances do not exchange in benzene solution, it is felt that an exchange might take place in CS_2 solution. This reaction could proceed through the interchange

$$H_2S + CS_2 = H_2CS_3$$

because the sulfur atoms in H_2CS_3 are all equivalent. A reaction somewhat similar to the above has been reported by Edwards and Nesbitt[25] who found $S^{=}$ and CS_2 to exchange by the formation of the intermediate $CS_3^{=}$.

$$S^{34=} + \tfrac{1}{2}\ CS_2^{32} = S^{32=} + \tfrac{1}{2}\ CS_2^{34} \quad K_{(calc)} = 1.019 \text{ at } 25^\circ \text{ C}$$

Another exchange that could be measured experimentally is the following

$$PbS^{32} + S^{34=} = PbS^{34} + S^{32} \quad K_{(calc)} = 1.009 \text{ at } 25^\circ \text{ C}$$

Other equilibrium exchanges may be brought about by reversible oxidation-reduction reactions.

Viz: $2\ H_2S + 2\ I_2 = S_2 + 4\ HI$

The exchange for this reaction would be

$$H_2S^{32} + S_2^{34} = H_2S^{34} + S_2^{32} \quad K_{(calc)} = 1.000 \text{ at } 25^\circ \text{ C}$$

Explanation of the Natural Variations of S^{34}

Reference is made here to the work of H.G. Thode, J. Macnamara and C. Collins[1] (See Figure I). On studying their results, it is found that the partition function ratios give at the most a semi-qualitative explanation of the experimental data. The S^{32}/S^{34} ratios needed for the following discussion will be found in Table IV.

From the S^{32}/S^{34} ratios for $SO_4^{=}$ and H_2S in well water, the above workers[1] found that $SO_4^{=}$ was enriched in S^{34} in each of four cases by amounts ranging from 4.5% to 2.2% (with an average enrichment of 3.3%). Now if it were possible to establish exchange between H_2S and $SO_4^{=}$, then from Table III one could predict that the $SO_4^{=}$ should be enriched by 7.4% *when equilibrium is attained*. Although it is unlikely that sulfates could be reduced in nature by chemical agents, it is known that certain anaerobic bacteria reduce sulfates to hydrogen sulfide. Since it is unlikely that $SO_4^{=}$ and H_2S are completely in equilibrium, then the enrichment of S^{34} should be in the compound indicated by the HIGHEST Q'_2/Q'_1 ratio but the *amount* of enrichment would be less than that indicated by the equilibrium constant. This reasoning seems to be in agreement with the experimental data.

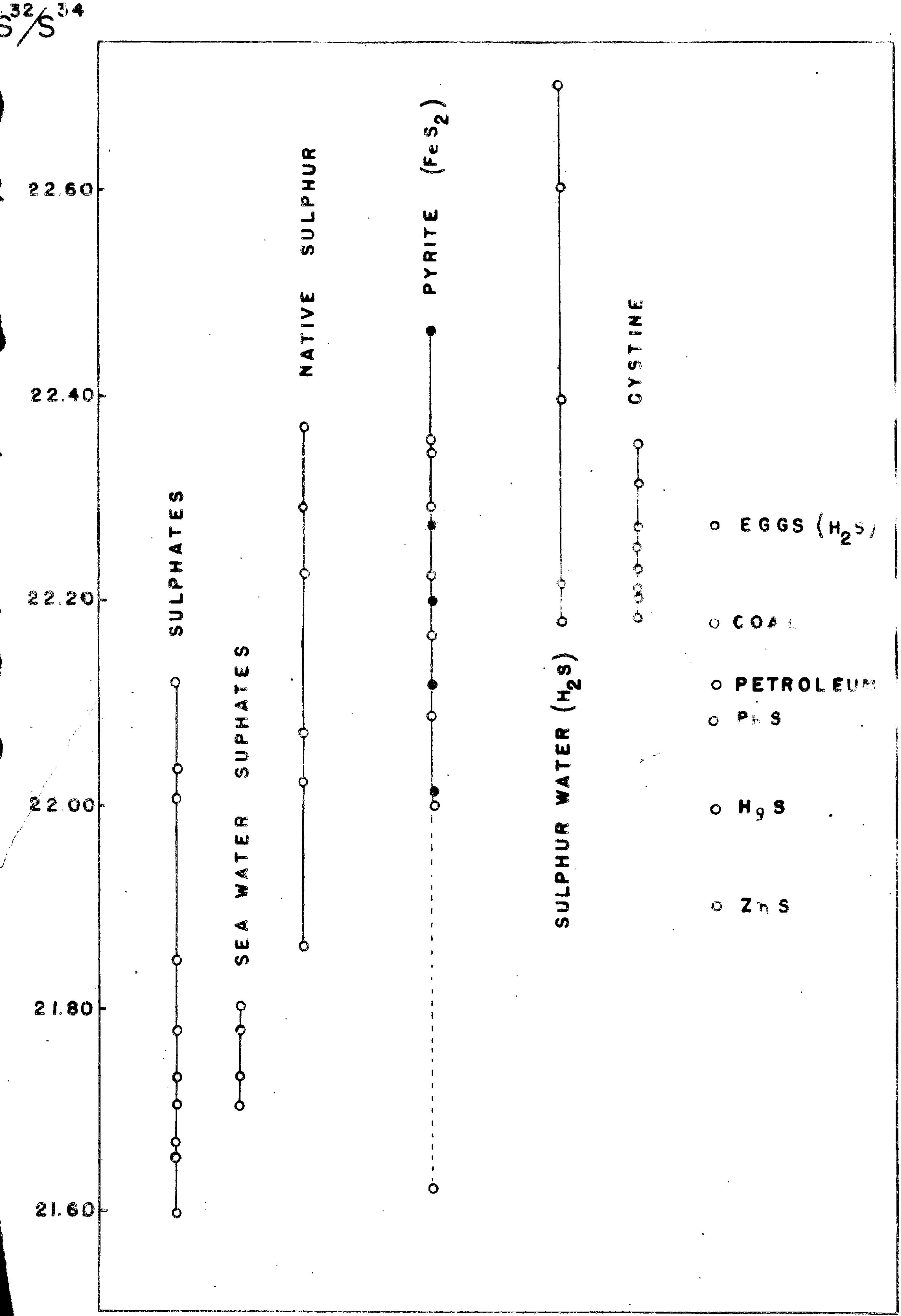
These workers also report that the isotopic abundances of sulfur are the same for H_2S in solution and native sulfur on rocks at the outpouring of sulfur-water wells. This is what we would predict for the reactions

$$H_2S + O_2 = H_2O + S_2$$

$$4\,S_2 \rightarrow S_8$$

from the partition functions for S_2 and H_2S. The exchange reaction in the

FIGURE I



S^{32}/S^{34}
22.60
22.40
22.20
22.00
21.80
21.60
SULPHATES
SEA WATER SUPHATES
NATIVE SULPHUR
PYRITE (FeS_2)
SULPHUR WATER (H_2S)
CYSTINE
EGGS (H_2S)
COAL
PETROLEUM
PbS
HgS
ZnS

TABLE IV

S^{32}/S^{34} Ratios

Sample Number	Source	Sulfur Compound	Location	Ratio
1	Well Water	H_2S	Dorchester, Ont.	22.705 ± 0.010
1	" "	$SO_4^=$	" "	21.735 ± 0.010
1	" "	S^o	" "	22.705 ± 0.005
2.	" "	H_2S	Tillsonburg, Ont.	22.190 ± 0.010
2	" "	$SO_4^=$	" "	21.715 ± 0.010
2	" "	S^o	" "	22.285 ± 0.010
3	" "	H_2S	Port Ryersee, Ont.	22.400 ± 0.010
3	" "	$SO_4^=$	" " "	21.650 ± 0.010
4	" "	H_2S	Port Stanley, Ont.	22.215 ± 0.010
4	" "	$SO_4^=$	" " "	21.585 ± 0.010
5	Native Sulfur	S	Gulf of Mexico	22.370 ± 0.010
6	" "	S	" " "	22.290 ± 0.005
7	Sea-Water	$SO_4^=$	Atlantic Ocean	21.75 ± 0.02

above would be

$$H_2S^{34} + \tfrac{1}{2} S_2^{32} \quad = \quad H_2S^{34} + \tfrac{1}{2} S_2^{32} \quad K_{(calc)} = 1.000$$

The only other way to explain this result is to say that no fractionation occurs. However, this is not probable since we know from many sources[11,12,26] that fractionation occurs whenever a chemical reaction is carried out whether the reaction is reversible or unidirectional.

Recent investigations[27] have shown that the S^{34} content of sea-water sulfates from different oceans is fairly constant. Also, the S^{32}/S^{34} ratio for Atlantic sea-water sulfates is very nearly the same as the average S^{32}/S^{34} ratio of Ontario gypsum deposits (laid down from the sea[29]). From these facts, we may assume that the isotopic abundances of sulfur in sea-water are constant and furthermore, that these sulfates have had these ~~sulfates have had these~~ same abundances for some time in the past. If the sulfur deposits in the Gulf of Mexico were due to bacterial action on sea-water sulfates, then we would predict that the native sulfur would be depleted in S^{34} by a factor of 1.082 (Table III). The experimental results show that this sulfur is lower in S^{34} than sea sulfates by a factor of 1.03.

Probably most natural variations of S^{34} in nature are caused by this "desirability" of the heavier isotopes to be found in certain compounds. It is known that sulfates are reduced to hydrogen sulfide in the muds at the bottom of lakes. Some of this H_2S escapes into the atmosphere, some is reoxidized by aerobic bacteria to $SO_4^{=}$, some is oxidized to free sulfur by oxygen and the rest reacts with iron silicates to produce pyrite or mascarite. Pyrite sulfur can be converted to H_2S by acids or changed to SO_2 by heat and oxidizing conditions (volcanoes). This H_2S and SO_2 can react together at volcano vents to produce free sulfur. By means of a "sulfur cycle" in nature where the sulfur atoms in sulfates, hydrogen sulfide, free sulfur, pyrite, sulfur dioxide, organic sulfur etc. are interchanged many times, it is possible to produce the variations in S^{34} that have been reported.[1]

SUMMARY

Partition function ratios and exchange reaction constants have been calculated for isotopic compounds containing sulfur in an attempt to discover the amount of fractionation that is theoretically possible in nature. These theoretical calculations are compared to experimentally observed data and we find that the semi-quantitative correlation between the two is very encouraging. Thus we feel that the differences in the chemical properties of isotopic substances are sufficient to cause wide-spread variations of the sulfur isotopes.

APPENDIX

I. Calculation of Vibrational Frequencies for S_2^{32} and S_2^{34}

Equations are given in Herzberg I[15], p. 151 for the calculation of vibrational frequencies for diatomic molecules. They are

$$\omega = (\omega_e - \omega_e x_e) V - \omega_e x_e V^2$$

$$\omega' = (\rho \omega_e - \rho^2 \omega_e x_e) V - \rho^2 \omega_e x_e V^2$$

where ω_e = fundamental vibration frequency

$\omega_e x_e$ = anharmonic vibration frequency

ω = vibration frequency of "abundant" molecule

ω' = vibration frequency of "rare" molecule

V = unity

ρ = $\sqrt{u/ u'}$

u = reduced mass of "abundant" molecule

u' = reduced mass of "rare" molecule

For these calculations,

ω_e = 725.8 cm.$^{-1}$ Herzberg I, p. 492

$\omega_e x_e$ = 2,85 cm.$^{-1}$

$$\rho = \sqrt{\frac{S^{32} \cdot S^{32}}{S^{32} + S^{32}} \Bigg/ \frac{S^{34} \cdot S^{34}}{S^{34} + S^{34}}} = \sqrt{\frac{S^{32} + S^{32}}{2\, S^{34}}}$$

$S^{32} = 31.9809 \times 1.6600 \times 10^{-24}$ gm.[28]

$S^{34} = 33.9771 \times 1.6600 \times 10^{-24}$ gm.

Using the above values and equations, one obtains

$$\omega = 720.1 \text{ cm.}^{-1}$$

$$\omega' = 698.8 \text{ cm.}^{-1}$$

II. Calculation of Vibrational Frequencies for $S^{32}O_3$ and $S^{34}O_3$

Normal vibration equations for SO_3 are given in Herzberg II[16], p.178.

They are

$$\lambda_1 = \frac{k_1}{m_Y}$$

$$\lambda_2 = \left[1 + \frac{3m_Y}{m_X}\right] \cdot \frac{k_\Delta}{l^2} \cdot \frac{1}{m_Y}$$

$$\lambda_3 + \lambda_4 = \left[1 + \frac{3m_Y}{2m_X}\right] \cdot \left[\frac{k_1}{m_Y} + \frac{3k_\delta}{l^2\, m_Y}\right]$$

$$\lambda_3 \cdot \lambda_4 = 6\left[1 + \frac{3m_Y}{2m_X}\right] \cdot \frac{k_\delta \cdot k_1}{l^2\, m_Y}$$

Where λ_i = normal vibration frequency (in t^{-2})

$k_1 = 10.77 \times 10^5$ dynes per cm.

$\frac{k_\delta}{l^2} = 0.46 \times 10^5$ dynes per cm.

$\frac{k_\Delta}{l^2} = 1.60 \times 10^5$ dynes per cm.

m_Y = mass of oxygen atom
= 16.000 x 1.6600 x 10^{-24} gm.

m_X = mass of sulfur atom

$m_X (S^{32})$ = 31.9809 x 1.6600 x 10^{-24} gm.

$m_X (S^{34})$ = 33.9771 x 1.6600 x 10^{-24} gm.

It is possible from the above data to calculate λ_i for both $S^{32}O_3$ and $S^{34}O_3$ molecules. (NB. - use six significant figures throughout the calculations.) By using the following relation, it is then possible to determine the vibrational frequencies (ω_i) for the molecule.

$$\omega_i = \frac{\sqrt{\lambda_i}}{2 \pi C}$$

where C = velocity of light in cms.

The calculated values of ω_i are given in the following table. Using these calculated frequencies, the differences in the frequencies are determined; these differences are then used to find the fundamental vibrational frequencies of the rare isotopic molecule.

	ω_1	ω_2	ω_3 *(2)	ω_4 *(2)	
$S^{32}O_3$	1069.10	651.66	1432.89	451.54	Calculated
$S^{34}O_3$	1069.10	640.06	1413.54	449.58	Calculated
	0	11.60	19.35	1.96	Differences
$S^{32}O_3$	1069	652	1330	532	Observed. See Herzberg II, p 178
$S^{34}O_3$	1069	640.4	1310.65	530.04	

These last set of frequencies are the ones used in the calculation of Q_2' / Q_1' .

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* 3 and 4 are doubly degenerate and so must be taken twice in the calculations of Q_2' / Q_1'

III. Calculation of Q_2' / Q_1' for SO_3

From the values of ω_i (Table II) and from the following relations, it is possible to calculate the information needed.

$$u_i = \frac{hc\,\omega_i}{kT} = 4.8256 \times 10^{-3} \cdot \omega_i \quad (\text{at } 25^\circ \text{ C})$$

$$x_i = \frac{u_{1_i} + u_{2_i}}{4} \qquad \delta_i = \frac{u_{1_i} - u_{2_i}}{2}$$

The calculations may be tabulated in the following manner. (Note the double degeneracy of ω_3 and ω_4).

i	u_{1_i}	u_{2_i}	x_i	δ_i	$(\coth x_i)\ \delta_i$
1	5.15857	5.15857	2.57928	0.000000	0.000000
2	3.14629	3.09031	1.55915	0.027990	0.030582
3	6.41805	6.32467	3.18568	0.046690	0.046854
3	6.41805	6.32467	3.18568	0.046690	0.046854
4	2.56722	2.55776	1.28125	0.004730	0.005521
4	2.56722	2.55776	1.28125	0.004730	0.005521
					0.135332 $= \sum_i (\coth x_i)\ \delta_i$

The above values may be placed in equation 24E to obtain Q_2' / Q_1'.

$$\ln \frac{Q_2'}{Q_1'} = \ln \frac{\sigma_1}{\sigma_2} + \sum_i \ln \frac{u_{2_i}}{u_{1_i}} + \sum_i (\coth x_i)\ \delta_i \qquad 24E$$

$$\ln \frac{Q_2'}{Q_1'} = \ln \frac{1}{1} + \ln \frac{(5.15857)\ (3.09031)\ (6.32467)^2\ (2.55776)^2}{(5.15857)\ (3.14629)\ (6.41805)^2\ (2.56722)^2} + 0.135332$$

$$\ln \frac{Q_2'}{Q_1'} = \ln 0.946820 + 0.135332$$

$$= \ln 0.946820 + \ln 1.1449$$

$$\frac{Q_2'}{Q_1'} = 0.946820 \times 1.1449 = 1.084 \quad \text{(See Table III)}$$

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