SELENIUM ISOTOPE FRACTIONATION IN MATURE AND IN THE LABORATORY

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Бу

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A method was developed for the accurate comparison of selenium isotope ratios for various samples using selenium hemafluoride gas in a mass spectrometer.

Calculations were made to determine the extent of selenium isotope fractionation that can be expected in isotope exchange processes.

The selenium isotope ratios for 16 naturally occurring samples have been compared using meteoritic selenium as a standard. These results showed small variations for samples obtained from massive sulphide ores, including those of igneous origin. However, in selenium samples entracted from plant material and soil, variations of up to 1.5 percent were found in the Se³²/Se⁷⁶ ratio. Undoubtedly, these large variations are due to oxidation and reduction processes.

A kinetic isotope effect of 1.5 percent was found in the laboratory reduction of selenite to elemental selenium. This effect is of the same order of magnitude as that predicted by a simple model of the reduction mechanism.

11

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TABLE OF CONTENTS

INTRODUCTION	
Equilibrium Isotope Effects	2
Kinctic Isotope Effects	4
Isotope Abundance Variations in Nature	5
Geochemistry of the Sulphur Isotopes	11
Selenium	18
Absolutes Abundances of the Isotopes of Selenium	25
THEORY	
Theory of Equilibrium Isotope Effects	29
Theory of Kinetic Isotope Effects	35
Results of Theoretical Calculations	39
EXPERIMENTAL	
Sample Preparation	43
Extraction of Selenium	43
Preparation of SeF ₆	48
The Mass Spectrometer	52
New Mass Spectrometer Tube	54
All-metal Sample Line	56
Procedure	56
Fractionation Studies	59
Frocedure for Reduction of Sodium Selenite	60
RESULTS AND DISCUSSION	
Natural Abundance Studies	6 1
Reduction of Sodium Selenite	64
APPENDIX I	
Calculation of Isotopic Vibrational Frequency Shifts for Selenium-containing Molecules Diatomic Molecules Selenate Ion (SeO Selenium Hexafluoride (SeF) Hydrogen Selenide (H2Se)	67 67 70 72 75

APPENDIX II

Calculations of $\frac{92}{91}$ for Selenium-containing Holecules Page 78

List of Tables

I.	Selenium Containing Hinerals	page 22	
II.	Selenium Deposits of the World 2		
III.	Absolute Abundances of the Isotopes of Selenius 2		
IV.	Equilibrium Constants for Se ⁷⁶ - Se ⁸² Exchange Reactions	41	
٧.	Results of Se ⁷⁶ /Se ⁸² Ratics in Natural Samples	62	
VI.	Calculations of Vibrational Frequencies for Se ⁷⁶ and Se ⁵² Containing Distancic Holecules	69	
VII.	Calculations of 92/276 for Selenium-containing Diatomic Nolecules	78	
VIII.	Calculations of Q'_2/Q'_1 for SeO ² at O ^O C	79	
IX.	Calculations of 2/21 for Sect at 25°C	7 9	
Х.	Calculations of $\frac{1}{2}/\frac{1}{2}$ for SeO ^{$=$} at 100 ^o C	80	
XI.	Calculations of $\frac{1}{2}/\frac{1}{4}$ for SeU ² ₄ at 250°C	80	
XII.	Calculations of $\frac{1}{2}/\frac{1}{2}$ for SeF ₆ at 0°C	81	
XIII.	Calculations of 2/21 for SeF ₆ at 25°C	62	
XIV.	Calculations of $\frac{1}{2}/\frac{1}{2}$ for SeF ₆ at 100° C	83	
XV.	Calculations of $u_2^{\prime}/v_1^{\prime}$ for SeF ₆ at 250°C	84	
XVI.	Calculations of $\frac{1}{2}/\frac{1}{1}$ for H_2 se at $0^{\circ}C$	85	
XVII.	Calculations of $\frac{1}{2}/\frac{1}{2}$ for H_2 se at 25°C	85	
XVIII.	Calculations of $\frac{1}{2}/\frac{1}{2}$ for H_2 so at 100° C	85	
XIX	Calculations of 4/41 for H25e at 250°C	86	

vi

List of Figures

Following page

1 Sulphur Isotope Distribution in Nature 12 Fig. Fig. 2 HEr-Br. Distillation Apparatus for Selenium 445 Extraction 45 3 S-Se Combustion Tube Mg. 48 FIR. 4 Steel-Cabinet Housing of Fluorine Cylinder 5 Fluorine Line (Schematic) 50 Fig. 6 Fluorine Line (Photograph) 50 Fig. 7 Principle of Metron Speed Changer 53 Fig. 8 Clutch for Scanner 53 Fig. 53 Fig. 9 Scanner Fig. 10 Comparison of Se and Se by Skip-Scanning 53 54 Fig. 11 Monel Sample Line (Photograph) 54 Fig. 12 Mass Spectrometer with New Tube Fig. 13 Monel Sample Line (Schematic) 55 Fig. 14 Hg Spectrum (Marrow Collector Slit) 55 Fig. 15 SeF5 Spectrum (Wide Collector Slit) 55 Fig. 16 SeF5⁺ Spectrum (Wide Collector Slit) 55 Fig. 17 Collector with Stains from SeF5⁺ during Simultaneous Collection 55 Fig. 18 Monel Sample Tube 57 Fig. 19 SeF₅ Spectrum Scanned with Collector Electronics Set for Simultaneous Collection 57

Following page

Fig.	20	(a) and (b) Plots of Recorded Data for Two Identical and Two Different Samples	58
Fig.	21	Variations in the Se ⁸² /Se ⁷⁶ Ratio found in Natural Samples	63

viii

INTRODUCTION

At the turn of the century the study of redicactivity revealed that some of the radioactive substances could not be separated chemically from the known elements.

In 1910, Soddy (1) suggested that such substances, differing in physical properties but having the same chanical properties, be called "isotopes". This term is derived from the Greek "isos" meaning "equal" and "topos" meaning "place" to signify that these elementary substances should occupy the same place in the periodic table. In 1913, Soddy (2) and Fajans (3) independently extended this concept. It is interesting to note that as far back as 1885, Sir William Crookes (4) suggested the possibility of isotopes: "I conceive therefore that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have atomic weight 40, there are not a few which are represented by 39 and 41."

The possible existence of isotopes among the stable elements was first noticed by Thomson (5) in 1912, who found that the positive ion beam formed from neon was resolved into two beams in his positive-ray parabola apparatus. Furification of the neon revealed no change in this observation. In 1920, Aston (6) provided definite proof with his mass spectrograph that neon consisted of at least two isotopes of mass 20 and 22. Aston (6) and Dempster (7) then identified and measured the abundances of the isotopes of many elements with their mass spectrographs.

The heavy isotopes of carbon, hydrogen, nitrogen and oxygen were missed by the early mass spectrographic studies and were first found by molecular spectroscopy between 1928-32 (8, 9, 10).

-1-

It was found in the radioactive disintegration studies that the uranium and thorium radioactive series terminated in Fb^{205} and Fb^{203} respectively. Consequently, Richards (11) found that the lead associated with thorium ores had a higher atomic weight than that associated with uranium ores. Therefore, it was known quite early in the history of isotopes that variations in the isotopic abundances of an element in a deposit could be altered by radioactive decay.

Further, from the theory of radioactive decay, the amount of radioactively-produced product in a deposit, relative to the amount of radioactive parent mineral present, is indicative of the age of the parent mineral. Thus, isotopic analysis of the lead present in uranium and thorium deposits has been used to determine the age of these deposits. Similarly, Aldrich and Nier (12) found that the argon associated with potassium minerals had up to three times the A^{40} concentration present in atmospheric argon. The amount of this A^{40} which is produced by the radioactive decay of K^{10} has been used to date the time of formation of potassium minerals.

In the two decades following the discovery of isotopes, many data were accumulated to suggest that the isotopes of an element were identical chemically and, with the exception of radioactively produced species, were of constant abundance in nature. However, these conclusions were based on mass spectrographic and atomic weight measurements of insufficient sensitivity as well as on unsuccessful attempts to separate isotopes chemically.

Equilibrium Isotope Effects: The discovery of deuterium by Ursy, Brickwedde, and Murphy (13) in 1932, led to a change in the concepts

-2-

concerning the chemical behaviour of isotopes. It seemed impossible that deuterium, with twice the weight of protium, should behave chemically the same as protium. About this time, Baeléus et al. (14) found variations of up to 8 parts per million in the densities of waters from various sources, which they attributed to variations in the abundances of the hydrogen isotopes. Using the methods of statistical mechanics, Urey and Rittenberg (15) then calculated the equilibrium constants for the reaction

 H_2 (g) \div D_2 (g) \Longrightarrow 2 HD (g)

at different temperatures. They found these to differ from unity which indicated that the isotopes of hydrogen were different chemically. Rittenberg, Bleekney and Urey (16) then determined the equilibrium constants for the reaction experimentally at different temperatures and found the emerimental values close to the theoretical ones. Urey and Greiff (17) also calculated equilibrium constants for some isotopic reactions of the elements, lithium, boron, carbon, mitrogen, chlorine, and browine. Their results indicated equilibrium isotope fractionations varying from 1 to 10% and experimental confirmations of these were soon obtained. For example, Weber, Nahl, and Urey (18) found Cop in equilibrium with water to be enriched in 0¹⁸ by 4.6% at 0°C as compared with the value of 4.4% predicted by theory. Other equilibrium isotope effects and data are sumarized by Usey (19). Many isotope exchange reactions involving the isotopes of the light elements have been studied in recent years and the agreement between theory and experiment has been excellent.

Isotope exchange reactions have found application in the separation

-3-

of isotopes. Whereas the fractionation is small in a simple exchange, counter-current extraction columns with large numbers of theoretical plates can result in an almost complete separation. Separated isotopes continue to play a large role in all creas of scientific research.

<u>Kinetic Isotope Effects</u>: It was also found soon after the discovery of deuterium, that isotopic molecules react at different rates and therefore, kinetic isotope effects exist. The first notable demonstration of a kinetic isotope effect was the discovery by Urey and Washburn (20) in 1932 that partially electrolyzed water was enriched in deuterium, protium having been evolved faster than deuterium at the cathode. Two years later Bach, Bonhoeffer, and Fajans (21) showed that the rate of reaction of H₂ with bromine was over three times faster than that of P₂ with bromine. Farkas and Farkas (22) in the same year reported similar results with the photochemical reactions of hydrogen and deuterium with chlorine.

The work done on the relative rates of reaction of hydrogenand deuterium-containing compounds has been reviewed by Urey and Teal (23) and more recently by Eidinoff (24).

Kinetic isotope effects for elements other than hydrogen were not reported until 1949. In that year, Lindsay, McElcheran, and Thode (25) and Bigeleisen and Friedman (26) reported carbon isotope effects in the decomposition of exalic acid and the decarboxylation of malonic acid. These results were reported on further by Lindsay, Bourns, and Thode (27,23) in 1951. These results were in excellent agreement with theory and contrary to the very high values reported by Yankwich and Calvin (29). Whereas, the latter used c^{14} -labelled compounds and counting techniques, Thode et al. used compounds of normal isotopic composition and mass spectrometry. The

-4-

latter method evolded the difficulties of synthesizing labelled compounds and minimized errors due to normal contamination. Yankwich and his coworkers (30) repeated their experiment later with mass spectrometry and finally obtained $C^{14} - C^{12}$ isotope effects in agreement with those $C^{13} - C^{12}$ isotope effects reported previously (23). The decomposition of oxalic acid was interesting because of the symmetry of the molecule and its two possible modes of reaction. Heglecting the rare molecule containing two C^{13} , the molecules decomposed as follows:

(A)
$$c^{12}_{00H} \xrightarrow{k_1} c^{12}_{0_2} + c^{12}_{0_2} + H_2^{0}$$
 (mode 1)

(B)
$$c^{12}_{00H} \xrightarrow{k_2} c^{13}_{0_2} \div c^{12}_{0} \div H_2^{0}$$
 (mode 2)
(B) $c^{13}_{00H} \xrightarrow{k_3} c^{12}_{0_2} \div c^{13}_{0} \div H_2^{0}$ (mode 3)

Lindsay, McElcheran, and Thode (25) observed two isotope effects. Firstly, species (A) reacted 3.4% faster than species (B). This was termed an intermolecular effect (27). Secondly, when species (B) decomposed, k_2/k_3 was found to be 1.032, that is mode 2 was favoured over mode 3 by 3.2%. This was termed an intramolecular effect (27).

The ratio of rate constants for reactions of isotopic molecules can be calculated by formulae given by Eyring (31). More recently, Bigeleisen (32) has revised this to an expression for the ratio of the isotopic rate constants which is more convenient to use.

Several authors (33, 34, 35) have written reviews on kinetic isotope effects.

Isotope Abundance Variations in Nature: Since the isotopes of the lighter elements differ in their chemical properties, fractionation in natural chemical processes can be expected. Previous mention has been made of

-5-

the fractionation of the hydrogen isotopes found in water samples by Emeleus (14). Since then, variations in the abundances of the isotopes of many of the lighter elements in nature have been found and studied extensively.

Numerous methods have been used to analyse the deuterium content of water including differences in densities, indexes of refraction, thermal conductivity, spectra, and analysis by mass spectrometry. Bleakney and Gould (36) initiated the determination of the H/D ratio mass spectrometrically in 1933. Other workers who have since carried out this study include Friedman (37) who showed water samples to have a variation of 165 in the H/D ratio. Ocean waters near the equator were enriched in deuterium. This was ascribed by Friedman to the preferential evaporation of H_0 over D_0. A further study of North American rainfall samples, progressing from the Pacific coast inland across the Rocky Mountains, showed a gradation in deuterium content. The further inland the rainfall was examined, the lower was the deuterium content found. This Friedman attributed to the preferential condensation of the heavier water molecules which enriched the coastal rainfall in deuterium. The remaining vapour, depleted in deuterium, moved further inland before condensing, accounting for the gradation in the deuterium content noted. Friedman also found sea plants depleted by 9% in deuterium relative to the deuterium content of the surrounding ocean water, and sought evidence for organic fractionation of hydrogen isotopes. A study of fumaroles in Yellowstone Park showed the deuterium content to be very low (depletion of 20 to 45%). Friedman suggested this might be the result of the equilibrium exchange reaction

H2 + HDO ==== HD + H2O

-6-

If this hypothesis is the only contributing factor, theoretical considerations, based on the observed douterium depletions, place the temperature of these fumaroles above 400°C.

Grygen was the next element shown to vary in its isotopic composition in nature. Dole and his co-workers (33-45) made a careful and extensive study from 1935 onwards of the 0¹⁸ content in samples of water, the atmosphere, iron ore and carbonate rock. Atmospheric oxygen was found to be enriched in 0¹³ by 3.15 compared with the 0¹³ content of fresh waver and stroopheric CO, was enriched by 3.9% in the 0¹⁸ compared with that of fresh water. Many extensive studies have been made on the chundances of oxygen isotopes. In this connection Urey (46, 47, 48), Epstein (46, 48, 49, 50), and Hmiliani (51, 52) emong others, have carried out studies. An interesting concept which has been applied in some of the many studies made, is that of a paleo temperature scale. Urey (19) suggested in 1947 that a measurement of isotopic fractionation due to a known isotopic reaction, might determine the temperature at which the fractionation occurred, if the temperature dependence of the isotopic reaction were large enough. The isotopic equilibrium reaction

$$1/3 \operatorname{co}_{3 \operatorname{ calcite}}^{16^{-}} \stackrel{*}{\xrightarrow{}} \operatorname{H}_{2}^{16}(1) \stackrel{K}{\xleftarrow{}} 1/3 \operatorname{co}_{3}^{13^{-}} \stackrel{*}{\xrightarrow{}} \operatorname{H}_{2}^{0}^{16}(1)$$

has been studied in detail (Urey (47), Urey et. al., (48), McCrea (53) and Epstein et al. (46)) with the motive of establishing a paleo temperature scale. Clayton (54) found K to bel.03187 at 25°C and to have a temperature dependence given by

$$\ln K = 2725 \, T^{-2}$$

-7-

This result means that carbonate shells are enriched in O¹⁸ over the surrounding water. In this connection Epstein (49) studied the fossil of Jurassic Belemite, a marine animal of the mesozoic age (1.2 x 108 years ago). Carbon dioxide derived from the carbonate in successive layers of the shell was analysed for the 0¹⁸/0¹⁶ ratio. An enrichment in 0^{18} was found along with variations of the $0^{18}/0^{16}$ ratio in successive levers, in accordance with the above isotopic equilibrium equation. These variations were attributed to seasonal changes in the temperature of the water in which the animal existed and corresponded to temperature fluctuations between 18°C and 24°C on the basis of the isotopic equilibrium above. This experiment was valuable in proving that original carbonate layers are retained through history and therefore a study of this kind is feasible. Along with other theoretical considerations of this type of experiment, there is also the problem of the constancy of the 0¹⁸ content of the ocean over geological time. Although many studies have resolved this to an extent, the best colution seems to be to use the above reaction in conjunction with another one involving oxygen exchange, so that the oxygen dependence can be eliminated from the data. Determinations of this type are being carried out currently.

In 1939, three years after Dole's first reports on the variations in the oxygen isotopes, Nier and Gulbransen (55) and, two years later, Nier and Murphy (56) reported variations of up to 5% in the C^{12}/C^{13} abundances. In general, limestones were enriched and plants depleted in the heavier carbon isotope. These results have been since reaffirmed and interesting information has been gained from reports by West (57), Pankama (53), Trofimov (59), Baertschi (60), Wickman (61, 62, 63),

-8-

von Ubish (61), Mars (64), Manther and Dansgaard (65), Craig (66), Landergren (67), Silverman and Epstein (68), Thole, Wanless, and Wallouch (69), Feely and Kulp (70). Of these, Craig (66) made a most extensive and detailed investigation. Many additional interesting results were obtained from these investigations. For example, both land and marine plants tend to concentrate C^{12} , although the latter do this to a lesser degree. This phenomenon may be attributed to differences in the cellular structures of the two types of plant, assuming that the concentration of the C^{12} is due to kinetic and/or equilibrium isotope effects in the photosynthesis of atmospheric CO_2 . Further, the work of Silverman and Epstein (68) with petroleums showed that petroleums of marine origin have less C^{12} than petroleums of non-marine origin, indicating that marine plants of ages ago also concentrated less C^{12} than their contemporary land plants.

Practionation of the isotopes of boron in nature was reported by Thole, Macmanara, Lossing, and Collins (71) in 1948. Although others, notably Parwell, von Ubish, and Wickman (72), did not find this, and expressed doubt concerning the work of Thole et al., recent work by McMillen (73) in this laboratory confirms the original findings.

In 1949, variations in the abundances of naturally-occurring sulphur isotopes were reported by Thede, Macmanura, and Collins (74). Although variations of up to 5% in the $3^{32}/3^{34}$ ratio were observed in this early work, subsequent investigations have widened this variation to 8% which would indicate a 16% variation in the $3^{32}/3^{36}$ ratio. This work on the geochemistry of sulphur isotopes will be discussed more fully below.

-9-

In 1951, Graham, Macnamara, Crocker, and MacFarlane (75) found the Ge^{76}/Ge^{70} ratio in naturally-occurring germanium samples to vary by as much as 0.7%.

About the same time, Edwards (76) found a 0.5% variation in the Cl^{35}/Cl^{37} ratio in two different salt deposits.

The study of silicon isotope abundances also began at this time. Marsden (77) made the initial study, followed by Reynolds and Verhoogen (78) and Allenby (79). However, for the same types of sample, Reynolds et al. found a 0.3% overall variation in the $51^{28}/51^{30}$ ratio, while Allenby found variations of as much as 1.3%. Tilley (80) has recently found overall variations similar to those obtained by Reynolds.

In 1953 and 1954, Cameron (81) reported a variation of up to 3.3% in the Li⁶/Li⁷ ratio of lithium minerals.

In the following year Hoering reported on the first of a series (82, 83, 84) of studies on the isotopes of nitrogen. In these, he found nitrogen in the atmosphere and rocks to have the same N^{14}/N^{15} ratio. He also found variations ranging from a 1.3% emrichment of N^{14} in bottled methane to a 1.3% enrichment of N^{15} in sel samoniac from Paracutin, Maxico, as compared to atmospheric nitrogen. Further studies have shown that the nitrogen content of natural gas is richer in N^{14} than the nitrogen found in the associated crude oil. Hoering has suggested that this resulted from the migration of the oil and gas through porous deposits. Migration by molecular flow, in which the mean free path of the gas is greater than the pore dimensions,

-10-

results in flow rates of the isotopic molecules which are inversely proportional to the square root of their masses. Hearing set up laboratory diffusion experiments with powdered Torpedo limestone and obtained isotopic fractionations which gave some credence to his theory. Hearing has also found daily variations in the N^{14}/N^{15} ratio in the nitrate ion and amonia in rainfall. No entirely satisfactory explanation of these variations has been offered.

Recently, the Cu^{63}/Cu^{65} ratio in minerals has been shown to vary by as much as 0.9 percent. (Walker et al. (85)).

It has therefore been established that many of the lighter elements vary in their natural isotopic composition, and that a study of these variations can provide solutions to many problems in geology, geochemistry, and other branches of science.

Geochemistry of the Sulphur Isotopes: The study of sulphur isotopes has proved most interesting because of its chemical forms and its wide distribution in nature. Since selenium is to some extent chemically similar to sulphur, one would expect to find similar fractionations of the selenium isotopes in some studies. On the other hand, there are some physical and chemical differences between selenium and sulphur which should yield new and interesting information from a study of the selenium isotopes. Since information already obtained from the extensive study of variations in the isotopic abundances of sulphur will be helpful in explaining anomalies found in a selenium isotope abundance study, the geochemistry of the isotopes of sulphur is now discussed.

As montioned previously, the initial data published by

-11-

Macmanara, Collins, and Thode (74) showed that the S32/S34 ratio in terrestrial comples varied by as much as 5%. In general, sulphates vere found to be enviced in S34 while hydrogen sulphide from sulphurated well waters was depleted in the heavier isotope. Later, Machanara and Thode (85) reported that the sulphur in meteorites had a remarkably constant S³²/S³⁴ ratio. This constancy was later reaffirmed (87, 88, 89). Two facts stood out in the investigation of meteoritic subhur: firstly, the constancy of the S³²/3³⁴ ratio suggested that meteoritic sulphur was not subject to the same isotopic fractionations as terrestrial sulphur; and secondly, the meteoritic value for the S³²/S³⁴ ratio was close to the average value of the s³²/s³⁴ ratio for terrestrial semples. These facts led Thode and Macmanara (86) to postulate that the meteoritic S³²/S³⁴ ratio represented the princedial abundance of terrestrial subphur before any fractionation processes occurred. In this connection, subpur of imeous origin, which has had less chance to be fractionated since its formation, should have a S³²/S³⁴ ratio close to the meteoritic value. This has been confirmed experimentally (Machemara et al. (90). Vincenadov et al. (91), Kulp et al. (92) and Sakai (93)).

Figure 1 summarizes most of the sulphur isotope abundance data, 6 is the per mil enrichment of 5³⁴ compared with meteoritic sulphur and is defined by

$$\delta = \frac{5^{34}/5^{32} \text{ comple} - 5^{34}/5^{32} \text{ meteoritic}}{5^{34}/5^{32} \text{ meteoritic}} \times 1000$$

The constancy of the meteoritic 5³²/5³⁴ ratio is immediately noticeable and the igneous sulphides are noted to have 5³²/5³⁴



ratios close to the meteoritic value. It is to be noted that most of the sedimentary sulphides are enriched in S^{32} while the sedimentary sulphates are depleted in S^{32} . Sea water sulphate has been shown to be fairly constant in its S^{32}/S^{34} ratio as has been found by Trofimov (87), Szabo, Tudge, Macmanaza, and Thode (94), Kulp (92), Sakai (93) and Thode, Monster, and Dunford (95). Extensive work by Thode, Monster, and Dunford (95) who have izvestigated over fifty samples of sea water sulphate from the Atlantic, Pacific, and Arctic oceans gives a value of + 20.1 \ddagger 0.5 for δ .

The total variation of the $5^{32}/5^{34}$ isotope ratio in Fig. 1 is seen to be $\wedge 8\%$. Tudge and Thode (96) noted that this was close to the equilibrium isotope effect for the exchange reaction

 $s^{32}o_{l_{4}}$ + $H_{2}s^{3l_{4}}$ = $s^{3l_{4}}o_{l_{4}}$ + $H_{2}s^{32}$

for which the calculated equilibrium constant was found to be 1.075 at 25°C. This value has been revised to 1.071 by the more recent calculations of Harrison (97). Since this exchange does not take place under normal conditions (Voge and Libby (98)), it was suggested by Tudge and Thode (96) that the following biological sulphur cycle might well provide a mechanism for this fractionation in nature.

-13-



Many studies have been made of the isotope fractionation in the sulphur cycle. Direct evidence for the fractionation of sulphur in the above cycle was obtained by investigating the Cyrenaican Lakes in Africa. Anserobic reducing and photosynthetic hydrogen sulphide oxidizing bacteria abound in these lakes and produce a sedimentary layer of elemental sulphur (Butlin (99), Butlin and Postgate (100)). While analysing samples from these lakes, Macmanara, and Thode (101) found the 3^{34} content of the elemental sulphur to be 3.2% less than that of the soluble sulphate from the same lake; Harrison (97), in the samples with which he worked found the deplotion in the 3^{34} content of the elemental sulphur to be 1.5%.

Other evidence of the biological sulphur cycle producing fractionation of the sulphur isotopes was found in the salt domes of

-14-

Louisiana and Texas (Thode, Wanless, and Wallouch (102)) where elemental sulphur was depleted by about 4% and sulphide by about 5% in s³⁴ relative to the associated gypsum. Two possibilities exist for the formation of this sulphur by reduction of the sulphate, the high temperature reduction of the sulphate by organic matter (oil fields associated with the salt domes) or the bacterial reduction of the sulphate with petroleum providing a source of carbon and free energy for life. The first of these mechanisms, however, seems incapable of causing the large fractionation observed whereas the latter is quite capable of doing so, as shown by the Cyrenaican Lake study. The isolation of anacrobic sulphate-reducing bacteria in these deposits by Miller (103) added further weight to the concept that the sulphur in these deposits came from the bacterial reduction of sulphate. Further, organic matter, necessary for bacterial life, is converted to carbon dioxide and water by these. This changes the calcium sulphate to a porous calcitic linestone with elemental sulphur embedded in it, which is the very type of deposit that is present in these salt domes today.

The hypothesis that sulphate reducing bacteria were responsible for the sulphur isotope fractionation has been substantiated by Inboratory experiments. Those, Kleerekoper, and McElcheran (104) showed that <u>Desulphovibrio desulphuricans</u> while reducing sulphate, produced H_2S which was 1% richer in S³² than the mitrient. Subsequently, Wallauch (105), Jones, Starkley, Feely, and Kulp (106) and Jones (107) found a temperature coefficient associated with this reduction which was too large to be explained by any simple theory of isotopes. Harrison and Thode (103) subsequently studied the fractionation of the sulphur isotopes with <u>Desulphovibrio desulphuricans</u> over a wide range of

-15-

temperatures, concentrations and growth conditions and found $5^{32}C_{l_1}^{**}$ was reduced faster than $5^{34}O_{l_1}^{**}$ by anounts varying between 0 and 2.5%. These results were interpreted by a mechanism involving two steps. The first step involves pickup of sulphate by the enzyme to form an enzyme complex. It has been proposed that this step has little or no isotops effect. The second step is the sulphur-oxygen bondbracking step and involves a large effect as shown by Harrison and Thede (109) who report a 2.3% kinetic isotope effect in the chemical reduction of sulphate. It was therefore suggested that the isotope effect in the bacterial reduction will vary depending on the ther the first or second step is rate controlling. If the first step is rate controlling, there is no isotope effect and the maximum isotope effect results when the second step is rate controlling. Intermediate isotope effects result when the two steps are both exercising some influence on the reduction rate.

Other parts of the sulphur cycle have received study from the point of view of isotope fractionation. Tahii (110) found that plant notabolism of sulphate in mustard and algae produced no isotope effect in nature or the laboratory. This observation was startling in comparison to the results found with bacteria, but has a possible explanation by the above postulate of Thode and Harrison. It is possible that the first step, which in this case would be the diffusion of sulphate through a cell membrane by an enzyme reaction, is always rate controlling and results in a negligible isotope effect. Mollcharan (111) found no fractionation in the oxidation of sulphur to sulphate by Thiobscillus. Ford (112) found the same results with T. tio-oxidans.

-16-

Ford (112) also examined sulphur isotope fractionation in mixed cultures of the oxidizing bacteria chromatium and the reducing <u>D. des-</u> <u>ulphuricans</u>, thus setting up conditions similar to those of the Cyrenaican Lakes.

Other reactions have been suggested for the fractionation of the sulphur isotopes. Vinogradov (89) suggested the following reactions to be good possibilities

> $3 8_2^{32}, 3^4 + 4 H_2^0 \implies 4 H_2^{32} + 2 3^{34} 0_2$ $4 H_2^{3^{34}}, 3^2 + 0_2 \implies 2 H_2^0 + 2 H_2^{3^2} + 2 3^{34}$

Cragg (113) used the first of these reactions to study the exchange of sulphur isotopes between H_2S and SO_2 over the temperature range $600^{\circ}C$ to $1000^{\circ}C$. He has found results slightly higher than those predicted by theoretical calculations (0.25% enviciment of S^{32} in H_2S at $1000^{\circ}C$).

Sakai and Magasawa (93) have measured the $5^{34}/5^{32}$ ratios in SO₂ and H₂S from fumaroles of Japanese velcances at sites of different temperatures. From their results and theoretical calculations, they suggest that the fractionation found can be attributed to the reaction,

 $H_2^{H_2} + 2H_2^{H_2} = 30_2 + 3H_2$

Another finding of note, in the studies of sulphur isotopes in volcances, was the fact that, when all the sulphur containing compounds arising from these fumaroles were collected and analysed, the average $8^{34}/8^{32}$ value was very close to the meteoritic value. This further suggests that meteoritic sulphur gives the primordial $8^{34}/8^{32}$ ratio for terrestrial sulphur. (Rafter, 149). Shima (115) has found that, when FcS₂ undergoes partial thermal decomposition according to the reaction,

FeS₂ -----> FeS + S

the 3^{32} tends to concentrate in the pure sulphur rather than the pyrite. This is due to the different bond energies of Fe-S³⁴ and Fe-S³². This decomposition is similar to that of oxalic acid previously mentioned, in that the symmetry of the FeS₂ molecule makes both inter- and intra-molecular isotope effects possible. It is interesting to point out that a large intra-molecular isotope effect has been found for this reaction, but the inter-molecular isotope effect appears to be negligible.

In conclusion, it is seen that the sulphur isotope studies show many processes whereby sulphur isotopes are fractionated in nature and in the laboratory. Analogous processes may result in the fractionation of the selenium isotopes, particularly in those cases where selenium and sulphur behave similarly.

Selenium: (116, 117, 118, 119, 155) Selenium is an element of relative rarity and multiferious uses. A general review of selenium is now included to present many of its interesting aspects, including its geochemical behaviour, and thus to gain some insight into possible mechanisms for the fractionation of selenium isotopes in nature.

In 1817, J. J. Berzelius and J. G. Gahn (120) discovered a red deposit in the sulphuric acid plant at Gripsholm, Sweden, in which they owned shares. It was first thought to be a new compound of sulphur and tellurium, but further investigations by Berzelius led to the conclusion that a new element had been found. Berzelius

-18-

named it selenium (Greek, selene--moon) since Klaproth had previously named tellurium after the earth (Latin--tellus). Selenium remained a laboratory curiosity until Willoughby Smith found its electrical resistence to be light dependent. Its photoelectric properties and its ability to rectify alternating current account for the use of over half of the world's production. The next largest use is that of pigments for paint, ceramics and leather. As well as decolourising glass by counteracting the blue tones, it is used to colour glass red for such products as automobile tail-lights. Other uses include those of a degaser in stainless steel production, vulcanizing agent in rubber production, catalyst in the drug industry, antioxident in labricating oils, toner in photography, as well as in insecticides and fungicides.

The most important connercial source of selenium is copperrefinery-enode-alines where it is recovered as a by-product. Therefore the domand for copper determines the price of selenium. It is also a by-product of flash reasting of pyrites in the manufacture of subpluric acid.

Solenium exists in a number of allotropic forms which are not as well defined as those of subpur. Amorphous selenium may be obtained as a red powder by the reduction of selenious acid. If this powder is heated until fluid and quickly cooled, a deep ruby-red vitreous form results which is very brittle. Notallic selenium is the most stable allotrops and the only one with a definite making point $(217^{\circ}C)$. This form is grey in colour and of hemsgenal crystalline structure. Crystallization of selenium from earbon disulphide yields another allotrops which is deep red, translucent and of memoclinic crystalline structure.

-19-

Selenium has chemical properties between those of sulphur and tellurium. Ferrous selenide is formed by heating iron filings with selenium. This on treatment with hydrochlorio acid gives hydrogen selenide.

FeSe + 2 HCl = H_2 Se + FeCl₂

 H_2 Se, like hydrogen sulphide (H_2 S), is a gas at room temperature. Whereas hydrogen sulphide is recognized as having a "rotten-egg" odour, that of hydrogen selenide is described as having a "rotten-horse-radish" odour.

Heating of selenium in the presence of oxygen yields selenium dioxide (SeO_2) . Unlike SO_2 , selenium dioxide is a solid at room temperature. SeO_3 , compared to SO_3 , is very difficult to prepare and extremely hygroscopic. Selenious acid (H_2SeO_3) is formed when selenium dioxide is dissolved in water or elemental selenium is reacted with nitric acid. The dissociation constant of selenious acid is 0.25 times that of sulphurous acid. The dissociation constant of selenic acid (H_2SeO_4) however, is about twice that of sulphuric acid. Hydrogen peroxide or ozone is necessary to produce selenic acid because of the high oxidation potential necessary to oxidize selenium to the +6 state as shown below. Consequently selenic acid is a very powerful oxidizing agent capable of liberating chlorine from hydrochloric acid in dilute solution.

Selenium combines with the halogens to produce selenium halides. Of particular interest in this work is the relatively unreactive selenium hexafluoride (SeF₆) gas and its possible use in mass spectrometric determinations of the selenium isotopes. Selenium tetrafluoride (SeF₄) also exists and is a colourless liquid at room temperature.

Many other chemical similarities between sulphur and selenium exist in both inorganic and organic compounds. Of particular consequence. is the substitution of selenium for sulphur in cysteine and other sulphurcontaining emino acids. Humerous legunes, chiefly of the species "Astrogalus" thrive in selenium rich soils. Whereas some plants use selenium as an alternative for sulphur, others such as <u>Astrogalus</u> <u>Peetimetus</u> and <u>Alpipappus Femontli</u> need selenium for survival.

Selenium-containing albumin is polsonous and animals eating these plants contract "alkali disease". Marco Polo (121) in the 13th century witnessed its affects when he was in Mestern Ghina. Madison (122), a surgeon in the United States Gavalry, reported its affects in 1850 on horses feeding along the Missouri River. Alkali disease is characterized by softening of the horns and hoots and loss of hair or feathers. This is believed due to the decomposition of the hermitins. Franke (123) in 1928 prompted the investigation which led to the uncovering of selenium by Robinson (124) in these plants and its subsequent identification as the etiological agent. It is estimated that the loss to agriculture in the Southwastern United States outweighs economically the benefits derived from selenium. Flexing and Walch (125) have found a similar selenium problem in certain counties in Treland.

Besides complex organic forms, selenium is found in nature in crystalline and anorphous elemental forms; in solid solution with sulphur and tellurium; as selenides, selenites, and rarely as selenates. Table I lists many of the selenium-containing minerals. It is seen that many of these minerals have analogies in the corresponding sulphur containing minerals.

In notweally cocurring subplur minorals, selentum is found replacing subplur at its sites in the crystal lattice because of the eloseness of their ionic radii (Se⁻ = $1.94A^{\circ}$) and (S⁻ = $1.74A^{\circ}$)

-21-

TABLE I

Minerals of Selenium

Selenides PeSe(?) Achavalite Aguilarite Agases Cu2Se Derzelianite (Co, Cu, M1), Sou(?) Pornhardtite Cedmoselite Cd(Se, S) Pose (The most common) Cleusthelite (Gu, TL, Ag), Se Crookesite CuFe3Sel (?) Eskeboznite Eucairite CuAgeo Pese, Ferroselite Guanajustite (frenzelite, Castillite) Bl2Be3 (Co, Fe) Seg Hastite CuSe Klocknannite Big (Se, 3), Se:S 2:1 Laltakarite Metaciumabar, selenian (onofrite, guadalcazarite) Mg (S, Se) Naumennite (cacheutaite) Acoso Bi2Se3 Paraguanajuatite Penroseite (blockite) (Mi, Cu, Pb) Sep Stilleite ZnSe Ticmann1te McSe. Trogtalite Colles Unangite Cu3Se2 Unnamed CoSe(?) continued

Selenites

Ablfedite

Chalcomentie

Cobaltomenite

Selenite or Selencte

Kerstenite (molybdomenite)

INISCO3.6H20 (?) CuSeO3.2H20 Hydrous cobalt selenite

Lydrous lead selenite or lead selenate

Orde

Selenolito

Martures

Lehrbachite

Zorgite "scebachite"

Tilkerodite, selenkobaltblei

Se02

Tiemanite, clausthalite

Clausthelite, tiemannite, unangite

Clausthelite, cobaltite, hometite

This substitution seems to occur more readily at high temperatures since the ratio of selenium to sulphur atoms ranges from 1:70,000 -250,000 in low temperature magnetic sulphides, but from 1:400 - 20,000 in high temperature sulphides. Goldschmidt (118) has estimated the average abundance of selenium in magnetic rock to be 0.09 ppm.

Because of the oxidation potentials involved, selenium is not oxidized as readily as sulphur. The relative oxidation potentials of

S	>	H2S03	-0.41 volts
Se	>	H2SeO3	-0.74 volte
H2SO3	\rightarrow	H2SOL	-0.17 volts
H2Se03	>	H2ScOL	-1.15 volts

These differences in oridation potentials separate sulphur and selenium in the leaching and weathering cycle of primary ores. The oridation potential under which weathering occurs, although capable of cridizing sulphur to sulphate, cannot oxidize selenium to selenate. Whereas sulphate ion is present in the sea, selenate ion is not. No selenium is found in the depths of the occans except near the mouths of tributaries (125, 127). The reason for this is that the small amount of selenium which is oxidized to selenite by weathering and goes into solution is precipitated by iron and manganese hydroxides as hydrosolenitos, e.g. $Fe(HSeO_3)_3.nH_2O$. Therefore all secondary sulphate and sulphide beds contain very little selenium. In gypsum the ratio of selenium to sulphur is 1:500,000 (117). Marine deposits and clays containing iron possess more selenium than gypsum. The formation of hydroselenites by iron hydroxide is believed to be the reason that seleniferous soils of Hawaii and Puerto Rice are incepable of supporting

-24-

soluniferous vegetation. The available selenium has been chemically bound to the iron as insoluble hydroselenite.

Table II summarizes the various types of deposits in which selenium is found, and some of the better known deposits in the world for each category including igneous, sedimentary, soil, and volcano sources. Most of the selenium in the soils of the United States is believed to have had its primary source in volcances of ancient geological times. A maximum in volcanic activity occurred in Permian, Triassic, and Cretacious times with the deposition of material for the Rocky Mountains. Similarly selenium in the soils of Hawaii is thought to have its source in the volcances currently active there.

Finally, selenium has been found in meteorites (128). Stony meteorites contain from 3 to 15 ppm. selenium. Tron alloy from octahedrite meteorites contain no selenium, but the troilite from these contain 23 to 200 ppm. In Canyon Diablo troilite, the ratio 5:30 was found to be h_{2} 215. (64) corresponding to 235 ppm.

Absolute Abundances of the Isotopes of Selenium: Table III summarizes the selenium isotope abundance measurements. Historically, Johnson (132) predicted isotopes 79 and 81 in addition to those found by Aston (129). However, Bainbridge (133) confirmed those isotopes found by Aston and found no trace of those predicted by Johnson.

-25-

TARLE II

Selenium Deposits of the World

Type of Deposit	Better Known Geographical Locations
Hydrothernel bese netel sulphide deposits	Trondheim Area, Norway; Naime, South Aust- ralia; Broken Hill, N.S.V.; Nt.Isa, Queens- Lend.
Copper Deposits 1. Disseminated 2. Replacement and vein deposits	 Ray and Morenci, Arizona; Ely, Nev.; Binghan, Utah; Chino, New Marico; Cananca, Marico. Butte, Montana; Cerro de Pasco, Peru; Northern Enodesia; Belgian Congo.
Nasoive Sulphide	Rio Muto, Spain; Mt.Lyell, Temanie; Mt.Isq Queensland; Bor, Yugoslavia; Bolidan,Swedan; Flin Flon, Manitoba; Sudbury, Ontario; Ducktorn, Tenn.
Sulphide Vein 1. Copper-silver-lead 2. Ritchblende-bearing	 Skrikerun, Sweden; Eurz Mountains, Gennang Copiepo, Chile; Colquechaca, Bolivia. Coldfields, Saskatcherun; Shinkolobwe, Belgian Congo.
Epithemal gold-silver	Bilver City, Idaho; Comstock Lode and Jar- bridge, Nev.; Guannjunto, Maxico; Radjang Leboug, Sumatra.
Epithermal Mercury	Euckakin Feak, Nev.; Abbot Mine, Californie; Lucky Boy Mine, Flute County, Utah; Guadalcazar and Hiutzuco, Maxico.
Sclendo minerals with no sulphides	Heico Mine, Colquechaca, Bolivia; Cerro de Cacheuta, Argentina.
Sandstone with uranium	Western U.S.A.
(Volcenic)	Valley of 10,000 Smokes, Alaska; Krisuvik, Iceland; Vesuvius, Lipari Island, Sicily; Kilausa, T.H.; New Zealand; Tateyama and Iowa , Japan.

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TABLE II (continued)

Selenium Deposits of the World

Type of Deposit	Better Known Geographical Locations				
Soils of unusually high content	Ireland, Japan, Mexico, Cuba, Columbia, Puerto Rico, Havaii, Southvestern U.S.A.				
Coal	England, Bolgium.				
Phosphate Rock Deposits	Phosphoria Deposit of Wyoming				

TABLE III

Absolute Abundances of the Isotopes of Selenium

WORKER	ASTON (129)	CAMERON	HIBES (131)					
YEAR	1923	1	1948					
LISTRUMENT	Mass Spectrograph	60° Mass Spect	Samo as C. and W.					
DEFECTION	Photometric	Elec	Electronic					
SOURCE	Se Vapour Discharge	SeF6 Electron Impact	Se Vapour Electron Imp.	Avorago	SeF6 Electron Imp.			
34 ⁵⁰ 74	0.9%	0.86\$	0.88\$	0.87±0.01\$	0.96-0.03%			
59 ⁷⁶	9.5%	9.08\$	8.95%	9.02 [±] 0.07%	9.12 [±] 0.03%			
50 ⁷⁷	8.3%	7.51\$	7.65\$	7.58±0.07\$	7.50 [±] 0.03%			
59 ⁷⁸	24.0%	23.54%	23.51\$	23.52 [±] 0.02%	23.61 [±] 0.05%			
80 Se	48.0%	50.02%	49.62\$	49.82 [±] 0.20¢	49.96 [±] 0.21%			
8°82	9.3%	8.99%	9.39%	9.19 [±] 0.20%	8.84-0.08%			

-28-

THEONY

The principles of isotopic frestionstion are now well-known and it is possible to calculate, from a knowledge of the fundamental vibrational frequencies of selenium-containing compounds, the extent to thich the selenium isotopes might be expected to fractionate in a naturally occurring procees. The question of the magnitude of the rossible isotope effect which can be expected with selenium isotopes now arises. In the case of the selenium isotopes Se⁷⁶ and Se⁸², there is a mass difference of 6 or a percentage mass difference of 3 percent. This is to be compared with a mass difference of 2 or a percentage mass difference of 7 percent in the case of the two sulphur isotopes 532 and 534. Since large isotope effects are found for these two sulphur isotopes, some fractionation of the selenium isotopes is expected. Calculations of exchange constants for isotopic reactions involving Se⁷⁶ and Se⁵² have therefore been carried out to determine the entent of scleaium isotope fractionation that can be expected in the laboratory and in natural processes.

Theory of Bouilibrium Isotope Effects: Urey and Crieff (17) first applied statistical mechanics to the calculation of equilibrium exchange constants. Further simplification by Urey (19) and Bigeleisen and Mayer (134) has made it possible to calculate these from a knowledge of the vibrational frequencies of the isotopic molecules alone.

Consider a typical exchange reaction of the form

 $eA_1 \leftrightarrow bB_2 \longrightarrow aA_2 + bB_1$ (1) where A and B are molecules containing the element under consideration and subscripts 1 and 2 refer to light and heavy isotopes respectively

-29-

of the element in the molecules.

From thermodynamics, the standard free energy change for the above reaction is given in terms of the equilibrium constant by

0ľ

From statistical mechanics an expression for the free energy in terms of the "partition function" Q is evailable.

 $F = E_0 + RT \ln N - RT \ln Q \qquad(4)$ where N is Avogedro's number,

E, is the zero point energy of the molecule.

If only one molecule is considered in unit volume instead of one mole, N is replaced by unity and the second term of (4) disappears. Substitution of (4) in (3) and simplification gives.

$$K = \left[\frac{Q_{AB}}{Q_{A_{1}}}\right]^{a} \left[\frac{Q_{B_{2}}}{Q_{B_{1}}}\right]^{b} \qquad e^{-\frac{aE_{0A_{2}} + bE_{0B_{1}} - aE_{0A_{1}} - bE_{0B_{2}}}{RT}}{RT} \qquad(5)$$

The potential energy curves of isotopic molecules have been found to be essentially identical. Therefore, choosing the bottom of the potential energy curve for E_0 rather than the zero point energy leads to further simplification of (5) as $E_{0A_2} = E_{0A_1}$ and $E_0 = E_0$

The exponential becomes unity and

Thus, the equilibrium constant becomes the ratios of the "complete" partition functions for the two isotopically substituted molecules.

Since ratios of partition functions are being considered, many factors cancel to give for distance molecules

$$\frac{v_2}{v_1} = \frac{\sigma_1 I_2}{\sigma_2 I_1} \left| \frac{M_2}{M_1} \right|^{3/2} = \frac{e^{-u_2/2}}{e^{-u_2/2}} \cdot 1 - e^{-u_1} \cdots (7)$$

and for polyatomic molecules

$$\frac{\sqrt{2}}{\sqrt{1}} = \frac{\sigma_{1}}{\sigma_{2}} \left[\frac{A_{2}}{A_{1}} \frac{B_{2}}{B_{1}} \frac{c_{2}}{c_{1}} \right] \left[\frac{M_{2}}{M_{1}} \right] \Pi_{1} \frac{e^{-u_{2}i/2}}{1 - e^{-u_{2}i}} \frac{1 - e^{-u_{1}i}}{e^{-u_{1}i/2}} \dots (8)$$

The I's are the moments of inertia of the distonic molecules. The A's, B's and C's are the principle moments of inertia of the polyatomic molecules.

 $u = \frac{hcy}{kT}$ where y is the vibrational frequency in cm⁻¹ units (wave number) and the product T_1 for polyatomic molecules is taken over "1" such frequencies.

 σ_1 and σ_2 are symmetry numbers.

Thuse formulae assume that hT is large compared to the rotational energy levels.

Vrey simplified (7) and (8) by the following:

Both sides of equations (7) and (8) are multiplicity

 $(M_1/M_2)^{3/2n}$ where M_1 and M_2 are the stonic weights of the isotopic

atoms being exchanged and "n" is the number being exchanged. The right hand sides of (7) and (8) are multiplied and divided by u_1/u_2 and $\prod_i u_{1_i}/u_{2_i}$ respectively. By the Teller-Redlich Theorem (90),

$$\frac{I_{2}}{I_{1}} \begin{bmatrix} \frac{M_{2}}{M_{2}} \end{bmatrix}^{3/2} \begin{bmatrix} \frac{M_{1}}{M_{2}} \end{bmatrix}^{3/2n} \frac{u_{1}}{u_{2}} = \begin{bmatrix} \frac{A_{2}}{L_{2}} \frac{B_{2}}{C_{2}} \\ \frac{A_{1}}{L_{1}} \frac{B_{1}}{C_{1}} \end{bmatrix} \begin{bmatrix} \frac{M_{2}}{M_{2}} \end{bmatrix}^{3/2n} \prod_{i} \frac{u_{1i}}{u_{2i}} = 1$$

With this (7) and (8) become

$$\frac{q_2'}{q_1'} = \frac{\sigma_1}{\sigma_2} \frac{u_2}{u_1} = \frac{e^{-u_2}/2}{1 - e^{-u_2}} \frac{1 - e^{-u_1}}{e^{-u_1}/2} \dots (7')$$

and

$$\frac{q_2'}{q_1'} = \frac{\sigma_1}{\sigma_2} \prod_{i} \frac{u_{2i}}{u_{1i}} = \frac{e^{-u_{2i}/2}}{1 - e^{-u_{2i}}} + \frac{1 - e^{-u_{1i}}}{e^{-u_{1i}/2}} \cdots (8')$$

where

by

For reaction (1) the equilibrium constant K is obviously given by

$$K = \begin{bmatrix} \frac{Q_{2}' A}{Q_{1}' A} \end{bmatrix} \begin{bmatrix} \frac{Q_{2B}' B}{Q_{1B}'} \end{bmatrix}$$

Therefore K can be calculated from a knowledge of the vibrational frequencies of the isotopic species. This involves direct observation, or in the case of a rarer isotope, calculation from observations on a more abundant isotope by means of force equations. The above derivation has assumed the energy levels to be harmonic. If the rotational partition functions have not reached classical values, a further correction is necessary. Bigeleisen and Mayer (13^k) show that classical partition functions cannot lead to an isotope effect, and arrive at equations 7 and 8 from this consideration and other cancellations by showing the ratio of the complete partition functions can be expressed simply as the ratio of vibrational partition functions.

The symmetry numbers ratio ${}^{C}_{1}/{}^{C}_{2}$ is unity if the molecule under consideration contains only one atom of the element being exchanged or more than one atom occupying indistinguishable positions in the molecule.

(7) and (8) have been further simplified by geometrical expausions. Urey (19) used an expansion of the form

$$\lim_{u \to u_{2}} \frac{Q_{2}}{Q_{1}} = \lim_{u \to u_{2}} \frac{G_{1}}{G_{2}} + \leq \lim_{u \to u_{1}} \frac{u_{2i}}{u_{1i}} + \leq_{i} \left[\operatorname{coth} x_{i} \delta_{i} + \frac{1}{G_{2}} \operatorname{coth} x_{i} (\operatorname{coth}^{2} x_{i} - 1) + \delta_{i}^{3} + \cdots - \right]$$

where
$$x_{1} = \frac{u_{1_{1}}}{h} = \frac{u_{2_{1}}}{h} = \frac{u_{1}}{2} \dots (11)$$

For molecules not containing hydrogen or deuterium, with small u's, the δi^3 term can be neglected and further expansion gives

$$\frac{Q_{2}}{Q_{1}^{2}} = \frac{\sigma_{1}}{\sigma_{2}} \prod_{i} \left[1 - \frac{1}{2\psi} (u_{2i}^{2} - u_{1i}^{2}) \right] \text{for}$$
(8') (1 = 1 for diatomic case) (7)(12)

Bigeleises and Mayer (134) used another geometrical expansion which gives a more convenient form. They let $u_{11} = u_{21} + \Delta u_1$ where u_{11} corresponds to the lighter molecule to make Δu_1 always positive. Then (8') becomes

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod_{i} \frac{u_{2i}}{u_{2i} + u_1} \cdot e^{\frac{\Delta u_1}{2}} \frac{1 - e^{-u_2}i + \Delta u_1}{1 - e^{-u_2}i} \dots (13)$$

 Δu_1 is negligible for every case except hydrogen and further simplification gives

The function $(\frac{1}{2} - \frac{1}{u} + \frac{1}{c^{u}2_{i-1}})$ has been termed the free energy function G(u) by Bigeleisen and Mayer who have tabulated it for values of u from 0 to 25 (134).

In the summation over "i" vibrational frequencies of the molecule, an n- degenerate frequency must be counted n times. <u>Kinetic Isotope Effects</u>: Byring (31) and Evans and Polanyi (135) have applied a statistical treatment to the problem of reaction rates in a method known as the "theory of absolute rates". From this theory and collision theory, Bigeleisen (32) has developed the following theory of kinetic isotope effects.

Consider two isotopic molecules A_1 and A_2 possessing the lighter and heavier isotope respectively reacting with B, C, etc., to give products P_1 and P_2 .

$$A_1 * B * C * \cdots * B_1 \longrightarrow P_1$$

$$A_2 * B * C * \cdots * B_2 \longrightarrow P_2 \qquad \cdots \cdots (15)$$

According to the Eyring method (136), the rate constants k_1 and k_2 are given by

$$k_{1} = K_{1} \frac{c_{1}^{\dagger}}{c_{A1}c_{B}} \frac{\left[kT + \frac{1/2}{2\pi M_{1}^{\dagger}}\right]}{\frac{kT}{2\pi M_{1}^{\dagger}}} \cdot \frac{1}{\delta_{1}} \dots (16a)$$

$$k_{2} = K_{2} \frac{c_{2}^{\dagger}}{c_{A2}c_{B}} \frac{\left[kT + \frac{1/2}{2\pi M_{2}^{\dagger}}\right]}{\frac{kT}{2\pi M_{2}^{\dagger}}} \cdot \frac{1}{\delta_{2}} \dots (16b)$$

K is the transmission coefficient

 G^{\ddagger} is the concentration of the activated complex M^{\ddagger} is the effective mass of the complex along the co-

ordinate of decomposition

8 is the length of the top of the potential barrier which the complex traverses.

-35-

Since the potential energy surfaces for isotopic molecules are essentially the same, $\delta_1 = \delta_2$ and

From statistical mechanical considerations, the ratios of the concentrations of the individual molecules can be replaced by the corresponding ratios of the complete partition functions. The minimum of the potential energy curve of the normal molecules is chosen as the zero of the energy scale for the normal molecules. The minimum in the saddle of the potential energy surface of the activated complex is a suitable zero for the calculation of the ratio of the partition functions of the isotopic activated complex.

As mentioned previously, Bigeleisen and Mayer (134) have shown that the ratio of the complete partition functions for the two isotopic molecules can be empressed as a simple function of the vibrational energy levels of the two molecules. For molecules whose rotation is not classical at the reaction temperature, a correction is necessary.

Hence	<u>k1</u> =	$\frac{K_1}{K_2} \cdot \frac{r}{r^*}$		
where	2 =	$\frac{Q_{A_2}}{Q_{A_1}}$ $\frac{T_1}{1}$ $\begin{bmatrix} 1\\ 1\\ 1\\ 1 \end{bmatrix}$	$\frac{4(1)}{4(2)}$ 3/2	(18)
and	2 [‡] =	$\frac{Q_1^*}{Q_2^*} \prod_i \begin{bmatrix} 1\\ 1\\ 1 \end{bmatrix}$	$\frac{4}{4}(1)}{3/2}$	

-30-

M₁ are the masses of the isotopic atoms in the isotopic molecules. From the theory of equilibrium isotope effects, the ratio of the partitions functions can be represented by

$$\frac{Q_{A_2}}{Q_{A_1}} = \frac{\sigma_1}{\sigma_2} \left[1 + \sum_{1}^{3n-6} G(u_1) \Delta u_1 \right]$$

and

G(u) has been previously defined.

(18) can be rearranged to give

Bigeleisen has gone further to add tunnel effect corrections.

Hirschfelder and Wigner (137) have conducted a theoretical study to show that the transmission coefficients ratio is very nearly unity for systems above room temperature having a distribution in the velocities of the reacting isotopic molecules.

In general, because the $\frac{M_2^{\#}}{M_1^{\#}}$ term is larger than unity, the lighter molecule reacts at the faster rate. If the activated complex is very tightly bound however such that

$$\sum_{i}^{3n'-6} G(u_{\underline{i}}^{\dagger}) \Delta u_{\underline{i}}^{\dagger} > \sum_{i}^{3n-6} G(u_{\underline{i}}) \Delta u_{\underline{i}}^{\dagger} + \frac{1}{2} \ln \frac{M_{\underline{i}}^{\dagger}}{M_{\underline{i}}^{\dagger}}$$

the rate constant for the heavier molecule is greater.

 N_2°/N_2° is the reduced mass of the transition state along the resetion co-ordinate. In practice, this is usually considered to be the reduced mass of the single bond directly involved in the reaction. This is the result of two different approaches of Slater (133) and Byring (135). However, Digoleisen and Wolfsberg (139) have suggested that because the molecule is being torm into two frequents, the reduced mass of these two frequents should be considered. In principle, this controvency can be resolved at higher temperatures because Digoleisen's approach gives an ensuer lower than Slaber'6.

Wolffeberg (100) has since discussed this controversy as follows. If the A-B bond is bothen in the molecule X-A-B-Y and the B-Y and X-A bonds are weak compared to the A-B bond, they will shorten as the A-B bond lengthens. In this case, the reduced mass term is closer to that of A and B, i.e. = $\frac{AB}{A+D}$. If, however, the A-B bond is considerably weaker than the X-A and D-Y bond, then the decomposition is that of tearing the centures of mass of XA and BY apart and the reduced mass term is closer to = $\frac{W_A}{M_{HY}}$.

Wolfsberg concludes by saying a knowledge of the potential energy surface is necessary in order to make any definite statement concoming the reduced mass ratio.

The most serious drawheelt of the equation is our ignorance of the mature of the activated complex and hence the innbility to calculate its partition function ratio. We are certain, however,

-33=

that it is somewhere between reactants and products in its nature, and thus there are two limiting cases.

<u>Case I</u> The activated complex is like the reactant. In this case the bond being ruptured is not the rate-controlling step; the two G(u) terms are equal and cancel; the ratio of the rate constants is simply the ratio of the reduced masses.

<u>Case II</u> The activated complex is like the products. In this case the bond is completely ruptured and $G(u^{\dagger}) \Delta u^{\dagger}$ will be given its smallest possible value or the ratio of the rate constants is a maximum. We expect the activated complex and the observed effect to be intermediate of these two cases.

<u>Results of Theoretical Calculations</u>: It was shown previously that equilibrium constants for isotope exchange reactions can be calculated from the partition function ratios for isotopic molecules and are the product of two such ratios. Fartition function ratios for various isotopic molecules involving Se⁷⁶ and Se³² have therefore been calculated, to determine the magnitude of selenium isotope fractionation that can be expected in selenium isotopic exchange processes.

Appendix I contains calculations of vibrational frequencies for Se⁷⁶ and Se⁸² containing compounds. Experimental values of vibrational frequencies were assumed to apply to the compounds containing the most abundant Se⁸⁰ isotope. From these observed values, the frequencies for the Se⁷⁶ and Se⁸² containing molecules were calculated by means of (currently known) "normal force equations".

-39-

For a molecule of a particular symmetry type, several sets of force equations are available from the assumption of various models describing that particular symmetry type. The application of some of these derived sets of equations to selenium-containing molecules gave inconsistent results whereas their application had been satisfactory for describing other molecules of the same symmetry type. Often, more equations than are necessary to establish all of the assumed force constants are derivable from a model. These extra equations serve as a check on the validity of the model's application to the selenium-containing molecule whose symmetry the model described. On this basis, the sets of normal force equations used for the calculations in Appendix I were selected.

Appendix II contains calculations of the ratios of the partition functions of Se^{62} and Se^{76} -containing molecules at 0°C, 25° C, 100° C and 250° C mode with the Bigeleisen-Mayer equation and tabulation of the G(u) function (134).

Table IV summarizes these calculated partition function ratios with the exception of some selenides whose calculated ratios were very close to those selenides in the table. In addition, equilibrium constants have been calculated for possible isotopic exchange reactions involving the compounds in this table.

At the top of the table underneath the symbol for the compound, the values of $Q_2^{\prime}/Q_1^{\prime}$ are listed for the four temperatures considered. It is noted that these ratios differ from unity by as much as 6 percent.

-40-

		2	sidie i	V			
Fguilibrium	Constants	2027	Se76	50 ⁶²	Eschenge	Reactions	

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	-	126	still pol		100000000	F7. Oa	canacerson of the	76-	
	Sererg	Salog	Sel ¹⁰ Selle	Se 'O	I_Se'	SerSe	Phee	Se	
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2	1.059	1.044	1.012	1.009	1.605	1.000	2.005	1.000	0
1	201224	1.023	1.007	2.005	2.003	2.003	2.603	1.000	100
J.	1.019	2.024	2.004	2.003	1.002	2.002	2.001	1.000	250
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762	*	1.011	2.027	2.029	2.032	1.032	1.031	2.034	200
00aC		1.005	2.015	2.025	2.017	2.027	1.013	1.019	253
32 =		3.000	1.032	1.035	2.039	3038	1.039	2.04	G
De Ul	-		2.027	2.690	1.033	2.033	2.034	1.033	25
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C.A.			a constant and	2 000	3 004	3 002	3 00%	1.000	0
Se ⁰² 0				20000	2.003	2.003	1.004	1.003	25
-760					3.002	1.002	1.002	1.005	100
		June 199			1.001	1.001	2.002	1.003	250
20.01				3213ZN	1.000	0.999	1.000	1.005	0
n200						1.000	3.002	1.005	25
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									100
Se ^{ro}									250
1									and the second

In the main body of the table, equilibrium constants for isotopic exchange between the compounds listed at the top and compounds listed in the far left column are calculated for the temperatures listed in the far right column. An equilibrium constant greater than unity in the table means that the heavier isotope is concentrated in the compound listed in the left column.

For an example, consider SeQ_{ij} in the left hand column and H_2Se at the top of the table. The value 1.033 is found at 25°C in the table where the SeQ_{ij} row and H_2Se column intersect. This is the equilibrium constant for the reaction

$$H_2$$
 se⁸² + se⁷⁶ $=$ H_2 se⁷⁶ + se⁶ Q_1

at 25°C. This means that provided a mechanism for this isotopic exchange can be found, a 3.3 percent selenium isotope effect is predicted.

-42-

DESPERIDENTAL

Selenium hexafluoride gas was chosen for the mass spectrometric analysis of the selenium isotopes because of its stability, ease of quantitative preparation and the simplicity of its mass spectrum.

Other gases considered were hydrogen selenide H_2 Se, selenium dioxide SeO₂ and selenium carbonyl SeCO. The mass spectrum of the first of these is complicated by the overlapping of ion species, e.g., Se⁷⁸⁺, Se⁷⁷H⁺ and Se⁷⁶H₂⁺ at mass 78. Computations on such a spectrum are tedious and subject to considerable error. The second compound, SeO₂ has a very low vapour pressure at room temperature and its usage would necessitate maintenance of the source and sample line of the mass spectrometer at a constant elevated temperature. Finally, selenium carbonyl SeCO decomposes very readily and is unsuitable.

<u>Sample Preparation</u>: The preparation of selenium hexafluoride was carried out in two steps: (1) extraction of elemental selenium from natural samples, and (2) fluorination of the extracted selenium to SeF_6 in a fluorine line.

Extraction of Selenium: The well-known hydrobromic acid-bromine distillation method was used to extract quantitatively elemental selenium from the natural samples. The relatively high volatility of selenium tetrabromide essential to this procedure was recognized as far back as 1896 when Gooch and Peirce (141) separated selenium from tellurium on the basis of the different volatilities of their tetrabromides. Noyes and Bray (142) have outlined the principles of this distillation

-43-

technique and its ability to separate selenium, arsenic and germanium from most of the other elements. Robinson et al (143) and subsequently Williams and Lakin (144) adapted the method to the determination of selenium in natural samples and their method was generally used in this work.

The distillation apparatus used is shown in Fig. 2. The sample to be analyzed is placed in the distillation flask along with 100 ml. of 48% HBr and 2 ml. of Br. The addition of bromine is necessary to ensure that the selenium is in its hexavalent state since $SeBr_{I_L}$ cannot be formed quantitatively from sclenium in any of its lower oxidation states. The mixture is then distilled into a flask containing 20 ml. of bromine water. At very low temperatures the excess bromine is distilled off and, as the temperature is raised, it is followed by SeBr_h (formed by the reduction of hexavalent Selenium with the HBr) and any excess HBr present. About 80 ml. of distillate are collected and sulphur dioxide gas is then passed through it to remove bromine. Although the SO₂ sometimes precipitates out the elemental selenium, 0.5 gm of hydroxylamine hydrochloride are added to the distillate to ensure quantitative precipitation. The treated distillate is then warmed on a steam bath for thirty minutes and allowed to stand for two days. precipitation is assumed to be complete after this time and the supernatant solution is poured off. The precipitated selenium is then transferred to a centrifuge tube, centrifuged and washed alternately with water to remove inorganic ions and with ethyl ether to remove any possible organic contaminants. After washing, the selenium is dried in an oven at 80°C.

-44-



Various natural samples required different methods of preparation prior to distillation.

Plant materials were prepared according to the method of Williams and Lakin (144). 10 gms of well-ground plant material were added slowly to a solution of 50 ml of concentrated sulphuric acid and 100 ml. of concentrated nitric acid in a 600 ml. beaker which had been previously cooled by an ice bath. The cooling was to minimize frothing, to retard the rate of nitrogen percende evolution, and to keep the reacting mixture below 120°C, at which temperature considerable loss of selenium could occur. After this initial treatment, the beaker was gradually heated on a hot plate to 115°C and maintained there until the nitrogen percende ceased to evolve. The mixture was then allowed to cool and transferred to the distillation flask to be distilled with HBr-Br₂.

Solemidos, solemites, and mative solemium samples were finely ground and added slowly to an excess of concentrated mitric acid contained in a 600 ml. beaker in an ice bath. After 50 ml. of concentrated sulphuric acid was added carefully to the mixture it was varmed gradually to 115°C and kept at that temperature until mitregen peroxide was no longer formed. After cooling, the mixture was ready for distillation.

Elemental sulphur containing selenium was oxidized by the method of Marvin and Schumb (145). The apparatus (see Fig. 3) consisted of a combustion section (34 nm pyrex tubing) fitted with an oxygan inlet and a filtering section (12 nm pyrex tubing) packed with Gooch-quality asbestos fiber and surrounded with a water cooling jacket. In operation, up to 100 gm of finely ground sulphur was placed in a pyrex boat

-45-



(3.4 cm x 20 cm) in the combustion section. Oxygen was then passed through the apparatus, the inlet stopper removed, one end of the sulphur sample ignited, the inlet stopper replaced, and the oxygen flow maintained to provide a reasonable combustion rate. The sulphur was oxidized to SO, SO, and S, O, gases which passed through the filtering section*, while the less volatile SeO, wassolidified and trapped by the asbectos in the cooled filtering section. The oxygen flow was continued after the combustion was completed until the whole apparatus had cooled. After the boat had been washed with hot concentrated nitric acid, the combustion tube was mounted vertically over a filter flash and additional hot nitric acid was poured through the system to dissolve all SeO2. The boat rinsings and the combustion tube filtrates were combined, 50 ml. of concentrated sulphurle acid addad and the mixture heated and distilled as described previously. Since SeO, attacked the inlet rubbar stopper during combustion, the inlet tube was terminated in a bulb in order to minimize back diffusion of Sco₂ (see Fig. 3).

In the case of samples dissolved in water, the solutions were made alkaline with sodium peroxide and evaporated to the point of dryness. Then the residue was taken up with 100 ml. of HEr-Er₂ solution, and added to the distilling flash for distillation.

fince gypsum contains only 1 part in 500,000 of selenium (117), a large quantity of gypsum had to be treated in order to obtain a suitable sample of selenium.

* S_2O_3 , sulphur sesquioxide is sometimes trapped as a blue solid in the asbestos filter. However, further passa e of oxygen converts it to SO_4 .

-46-

Since the solubility of $CaSe_4.2H_2^{0}$ (99 gm./litre) is about 40 times larger than that of $CaSO_4.2H_2^{0}$ (2.58 gm./litre) at 25°C (146), attempts were made to extract the selenate from finely powdered gypsum by stirring an aqueous suspension of it for several days and then filtering it. However, the yields of selenium obtained in this way were much smaller than expected and it appeared that most of the selenium remained trapped in the $CaSO_4$ crystals. However, gypsum treated directly with HBr-Br₂ solution, then distilled, resulted in a much larger recovery of selenium.

In the case of natural samples which contained selenium in more than one form, attempts were made to extract the different forms separately. For example, plants may contain water soluble selenium (SeO_3^{-}) in addition to selenium in complex organic compounds. The former could be extracted with water and the solution treated as already described above for aqueous solutions. The remainder of the plant was processed by the method described for plant materials. In inorganic samples containing selenium, two or more selenium minerals may often be identified by their colour. As an example, unangite, CuSe.Cu₂Se, which is dark red in colour and chalcomenite, CuSeO₃.2H₂O, which is light blue, frequently occur together. It was found that these two minerals could be separated mechanically by their colour and therefore elemental selenium could be extracted from each separately.

In the digestion of samples prior to distillation, all nitrogen oxides must be removed. Otherwise, HBr may be oxidized to Br₂ in the distillation or nitroxyl tribromide may be formed and distilled. Nitroxyl tribromide is not decolourized when SO₂ is passed through the distillate.

-47-

It was found that all the oxides of nitrogen could be removed by the digestion of the samples containing H_2SO_4 until white fumes of SO_3 appeared, but prolonged evolution of SO_3 fumes might result in some loss of selenium. Another method used for the removal of nitrogen oxides was the addition of urea to the digested sample prior to distillation; this destroyed the nitrogen oxides by reactions such as

$$(\mathrm{NH}_2)_2$$
 CO + 2HNO₂ \rightarrow 2H₂ + CO₂ $+$ 5H₂O

Preparation of SeF Fluorination of elemental selenium can result in the production of both SeF_{l_1} and SeF_6 , the former being produced preferentially at temperatures close to $0^{\circ}C$. In the method to be described, however, fluorine was present in a large excess and this resulted in the quantitative conversion of selenium to SeF_6 at room temperature.

The fluoring line built for this preparation is shown in Figures 5 and 6. Its construction may be better understood when it is recalled that fluorine, the most reactive of the elements, reacts with everything except inert gases and already fully fluorinated compounds. High heats of reaction always result and hence many precautions are required and the choice of materials for a fluorine line is limited. Since the reaction of fluorine with some metals (e.g. copper, monel) is retarded after an initial fluoride coating is formed, these metals can be safely used in the construction of a fluorine line. Class is resistant to dry fluorine but breaks easily and should definitely not be used where the pressure of fluorine is significant. The most inportant precautions to be taken are the placement of the fluorine cylinder behind a barricade and the operation of the cylinder valve by

43-



remote control. The barricade built for this purpose is shown in Fig. 4 and Fig. 6. It was simply a welded steel cabinet (1-1/4") angle stock frame and 1/8" steel sheeting) designed to hold the fluorine cylinder securely. Remote control of the main cylinder valve was effected through lever A, while a Matheson #55 needle valve was rotated by extension B (Fig. 4).

-49-

In preliminary experiments with a fluorine line containing many pyrex components it was found impossible to prepare SeF_6 samples free of SiF_4 contamination. Therefore, the fluorine line was reconstructed of monel tubing with monel valves in the sample preparation section. All joints were argon arc welded and overlayed with silver solder to eliminate all possible leaks.

With the exception of V_4 (Fig. 5), the Hoke values used were the M440 type since their teflon seats could be easily replaced. V4 was a Hoke 413 metal diaphragm type value which would not absorb SeF₆ in this section and cause intercontamination of samples. The line could be uncoupled and recoupled in the necessary places by Hoke 410 couplings.

All glass stopcocks in the line were lubricated with Kel-f. 90 or Hooker Fluorolube GR470 grease.

Since commercial fluorine may contain up to 0.2 percent hydrogen fluoride, it was desirable to remove this in order to protect certain essential pyrex components in the line, e.g., the flowmeter. This was accomplished by the sodium fluoride trap (Fig. 5) according to the reaction

 $IIaF + IIF \longrightarrow IIaHF_2$

The sodium fluoride used in this trap was prepared by heating $1/4^{\circ}$ sodium bifluoride pellets at 275° in a mitrogen stream till all the HF was removed. This provided a highly efficient porcus surface for reabsorption of hydrofluoric acid from the fluorine cylinder.

Another component of the line, the mercury manometer (Fig. 5) served as a pressure indicator and as a safety blowout device if the internal pressure of the line should become excessive. A layer of Kel-f oil on the mercury surface in the capillary reduced the reaction of the mercury with fluorine.

A conventional, U-tube design, pyrex 2lowmeter, (Fig. 5), halffilled with Kel-f #3 oil was used to measure flow-rates. The capillary joining the two arms of the flowmeter was selected so that a pressure difference of 1 cm of oil corresponded to a flow rate of 0.5 mole/hr. The bulbs in each of the arms of the flowmeter served as reservoirs to prevent loss of oil during indivertently high flow rates.

Other equipment used in conjunction with the fluorine line included a polyethylene wash bottle of amonium hydroxide so that fluorine leaks might be detected by the formation of amonium fluoride, a mixture of glycerine and magnesium dioxide for fluorine burns and protective clothing, including rubber gloves, coat, and a face mask, which was worn during fluorinations.

The procedure for fluorinating small samples of elemental selenium is now discussed with reference to Fig. 5.

Elemental selenium was inserted in a monel boat at coupling C2. Prior to this incertion, it was found absolutely necessary to evacuate the line, flame the line and fill the volume between

-90-





 V_3 and V_{l_1} with mitrogen before disconnecting C_1 and C_2 , in order to minimize contaminations. Immediately upon insertion of the selenium and recoupling of the line, V_{l_1} was opened slowly to re-evacuate the section back to V_2 .

During the rest of the procedure all values had to be turned slowly to avoid blowing powleved selenium along the line. The mercury monometer served as a visual means of accomplishing this.

Liquid air was now placed around U-tubes 2 and 6. The purpose of these traps was to eliminate previously found contaminants which had been identified with the mass spectrometer as fluorecombons (e.g. \mathbb{CP}^{4+} , \mathbb{CP}^{4+} , \mathbb{CP}_{3}^{-4+} $\mathbb{C}_{3}^{-1/2}\mathbb{F}_{7}^{-4}$ Mass 169) etc.) and were believed to have their origin in the creaking of the tellon packing of the Matheson #55 needle value due to high pressures of fluorine. These traps had the disadvantage of freesing out some fluorine (D.F. - 168.14°C), but both traps were necessary to remove the low molecular weight fluorecarbons. All U-tube traps had packings of michel sheaves to increase their efficiency. Liquid air was also placed around U-tube A to freeze out SeF, as it was formed.

Nitrogen, which was used as a dilutant, was then introduced into the system. Notter control of the mitrogen flow rate resulted if the disphrage value on the mitrogen cylinder was set at 5 to 10 lbs. pressure and V_2 was used to set the desired flow rate of 0.4 mole/hr. as read on the flowmeter.

After five minutes the main value of the fluorine cylinder was partially opened (<u>Matheson #55 needle value closed</u>). The needle value was then adjusted so that the total flow rate was 0.6 mole/hr. i.e., N₂ : $F_2 \sim 2$: 1. When fluorine was first observed at the exit (armonium

-51-

hydroxide), the main value of the fluorine cylinder was closed and the modile value gradually opened to maintain the flow rate, thus suppoing the modile value of fluorine. The modile value was then closed, and mitrogen flow continued for 10 minutes after which V_{2} , V_{3} , V_{4} , and V_{8} were closed. Next, the line was evacuated to V_{4} , V_{5} closed, and the scientum hemafluoride transferred from U-tube A to the sample tube. The sample tube (value closed) of SeF₆ was them removed and taken for analysis with the mass spectrometer.

The Mass Spectrometer: The following ions: SeF_5^* , SeF_3^* , SeF_3^* , SeF₂^{*}, SeF^{*}, and Se^{*} appeared when SeF₆ gas was bombarded by electrons in the ion source of the mass spectrumeter. It is known that in the electron bombardment of the englagous gas SF₆, the undissociated ion SF₆^{*} is also found in very low concentrations which suggests that SeF₆^{*} was also present, but undetected. Of the ion species formed, SeF₅^{*} was present in the highest concentration (> 85% of the total ion species with SO volt electrons) and therefore, this ion species was used for all measurements.

In the study, Se^{7b} and Se⁸² would have shown the largest effect in any fractionation of the selenium isotopes because these isotopes have the largest percent mass difference. However, it was more convenient to measure the two isotopes with the next largest percent mass difference, Se⁷⁶ and Se⁸² because they occur in relatively high abundances (both~95) in nature.

Initial studies were made with a 90° , 6 inch radius mass spectrometer which had a tube with terion "0"-ring gashets and a glass sample line with measury reservoirs. With this mass spectrometer, the

-92-

 GeF_5^* mass spectrum was scanned by varying the magnetic field and the Se⁷⁶F₅⁺ and Se⁸²F₅⁺ ion surrents were measured by single collection.

The magnetic field scamer built for these measurements is shown in Fig. 9. The Helinot (9) set the voltage at the grid of the magnet supply's sories control tube. It was desired to rotate this Helipot at various specis above and below 2 r.p.m. This speed variation was accomplicited with a Netwon variable speed changer, the principle of which is shown in Fig. 7. Figure 7.B and C shows how the tipping of the intermediate theois between the hendepherical shells connected to the cutout that insit seems the cutout that is the to retain an or faster than the input shaft. It was found accessary to drive this type of speed charger with an 1900 r.p.s. synchronous motor and then use an 800:1 goar reducer to drive the Helipot, in order to achieve amoth, consistant seaming of the magnetic field. A simple springloaded, dry-plate clutch (Fig. 8) was connected between the gear-reducer and the Religion to permit moment sesanting and to protect the Heliyot from being driven past its terminals. The complete scamer layout is phone in Figure 9 and its components are listed on the page following the discreme

To improve upon the precision of the measurements, a skip-seen technique was developed so that the Se⁷⁶F₅⁺ and the Se⁵²F₅⁺ ion currents could be measured quickly without the interference of the intervening ion currents. This technique involves the superimposition of a stepvise change in the megnetic field upon the regular megnetic seaming of the ion currents. Fig. 10 shows the resultant recover trace of Se⁷⁶F₅⁺ and Se⁸²F₆⁺ with this type of scaming.

-530





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Components of the Scamer (Figure 9)

- 1. Reversing condenser for motor.
- 2. Westinghouse Type FL, 1/100 N.P., 1800 r.p.m., 60 cycle single phase synchronous motor (U.S.A.).
- 3. Cooling fee.
- 4. Tygon couplings.
- 5. Metron Variable Speed Changer.
- 6. 800 to I gear reducer.
- 7. Flexible metal coupling.
- 8. Clutch.
- 9. 20 K Helipot.
- 10, 11, 12. Rotation of knob K, turns the thread rot (11) through gearing (10) to nove block (12) connected to the speed control of the Metron.


Using this method of scanning, and single collection, the $5e^{76}/5e^{82}$ ratios could be measured with a precision of ± 0.25 .

The preliminary results indicated that a mass spectrometer with terflon gaskets and a glass comple line was not suitable for analysis of the selenium isotopes using SeFg. Firstly, with a glass sample line equipped with glass stopcocks and mercury reservoirs, it was impossible to introduce SeFg into the mass spectrometer free of contamination, and in particular, free of SiFg. SiFg is a troublesame contaminant in view of the fact that it cannot be removed by distillation procedures since SiFg and SeFg have similar vapour pressures over a wide temperature range. Since it was also apparent that some of the contamination resulted from impurities in the walls of the mass spectrometer tube itself, both a new tube and an all metal mass spectrometer sample line wave built.

The New Mass Spectrometer Tube: The new tube of the mass spectrometer (Fig. 12) had metal flanges and aluminium gashets which allowed the tube to be baked at very high temperatures, thereby attaining low pressures ($< 10^{-7}$ nm Hg).

Similtaneous collection as described by Wanless and Thode (147) was also incorporated into the new tube to improve upon the precision and reproduction of the comparison measurements of the Se⁷⁶/Se⁶² isotope ratio. Se⁷⁶ F₅, and Se⁸² F₅⁺ ion currents were collected with two slits simultaneously. The output of the vibrating road electrometer measuring the Se⁸² F₅⁺ ion current was placed across a lOK put-and-take potentionster and a measured portion of this cutput was fed back inversely to cancel the Se⁷⁶ F₅⁺ ion current at the input of its

-51-



FIGURE 11 MONEL SAMPLE LINE (mass spectrometer)



FIGURE 12 MASS SPECTROMETER (New tube with heavy flam es for aluminum gaskets. The source cover has been removed to expose the source)

vibrating reed electrometer to give a null reading.

The spacing of the collector slits was calculated from the wellknown dispersion formula for the magnetic analyzer

- d = dispersion between masses m and m + An
- r = radius of mass spectrometer analyzer tube

For masses 171 and 177 (Se⁷⁶ F_5^+ and Se⁸² F_5^+) and a six inch radius mass spectrometer, this spacing is calculated to be 5.36 m.

The widths of these slits had to be calculated in conjunction with the width of the source slit to give the desired resolutions. A narrow slit in the collector is necessary to resolve Se⁷⁶ F_5^+ from the neighbouring Se⁷⁷ F_5^+ ion beam, thereas a wider slit can be used for the collection of Se⁸² F_5^+ to permit easier setting up of similtaneous collection since the nearest ion current, Se⁸⁰ F_5^+ is two mass units away. Using the well-known formula for the resolution.

where R = resolution

r = radius of magnetic analyzer

 \geq s = the sum of the source slit and the collector slit the choice of 0.15 mm width for the source alit, 0.5 mm width for the narrow collector slit and 1.0 mm width for the wide collector slit, results in a calculated resolution of 234 and 132 with the narrow and wide slits respectively. The actual resolution obtained with the narrow slit is indicated by the single collection recorder traces shown in Figures 14 and 15, while the resolution obtained with the wide slit



:

1.200





is indicated by the single collection recorder trace in Fig. 16. The stains on the collector plate (Fig. 17) caused by routine analysis of the SeF_5^+ mass spectrum by simultaneous collection indicate that both the slit spacings and the resolution were satisfactory for simultaneous collection.

All-netal Sample Line: The all-metal cample line which was constructed of monel 1/8" N.P.T. pipe and Hoke 413 metal diaphragm type valves is shown in Figures 11 and 13. These valves removed any possible contanination due to grease, and allowed the line to be flamed thoroughly for the elimination of moisture. The whole line was built smell to climinate memory effects and could be used for the comparison of two samples in the mass spectrometer. V_3 and V_3' (Fig. 13) are the sample tubes (Fig. 18) of SeF6 which have been removed from the fluorine line after sample preparation and attached here with Hoke 410 couplings C and C'. Whereas specific pairs of these couplings had been heliumleak tested, their interchangeability was questioned and therefore aluminum foil gaskets were made for use with these couplings. B in Fig. 13, is a small nickel trap into which a very small cample of SePs can be transferred and used within the volume bounded by valves V1, V2, and V_2 , to give a upable pressure behind the mass spectrometer leak. Normally, the samples occupied a larger volume of the system when examined.

<u>Procedure</u>: Before the introduction of a sample into the monel sample line it is evacuated and thoroughly flamed. The nickel leak is also flamed. With reference to Figure 13, the sample contained by V_3 is

-56-

now admitted. Initially, a coarse adjustment of the sample pressure behind the leak of the mass spectrometer results from careful manipulation of the sample value V_3 with values V_2 open and V_1 and V_2' closed. If the sample pressure behind the leak is ancessively high, another coarse adjustment is made by freezing the gas between V_3 and V_2 back into the sample tube and then allowing the gas behind the leak to expand into this volume (V_2 open, V_3 closed). A very fine adjustment of the sample pressure behind the leak can be made by pumping a small amount of sample through value V_1 with value V_2 closed. With the closing of V_1 and the reopening of V_2 , the gas adjusts to a slightly reduced pressure.

When the pressure is adjusted, the magnetic field is seamed to search for undesirable contaminants. With a negative result, the instrument is now checked to see if it is properly focussed for simultaneous collection. This check is accomplished by setting the collector electronics for simultaneous collection and scanning the SeF₅⁺ mass range. The asterisk on the resulting recorder trace in Figure 19 indicates the proper setting of the magnet current for simultaneous collection of the Se⁷⁶₅⁺ and Se³²₅⁺ ion currents. It is significant that this portion of the recording trace is flat.

Since the volume of the sample tube is small, the pressure drops noticeably in time. Because the balance point obtained in the comparison of the two ion currents changes alightly with the signal, and therefore, the pressure, the accurate comparison of two samples demands that the balance point obtained be compared under identical conditions. The balance point and the Se ${}^{82}F_{5}$ signal for a sample under examination

-57-



FIGURE 13 MONEL SAMPLE TORE (Hoke 413 type valve and Ecke 410 coupling)



FIGURE 19 RECORDER TRACE SeF5⁺ SPECTRUM which results that the magnetic field is scanned and the collector electronics set for simultaneous collection.

are therefore recorded every three minutes for 15 minutes. At the end of this time the sample is stored between valves V2 and V2 and after thorough fluming of the volume behind the mass spectrometer leak, the other sample is similted as described above. Its pressure must be carefully adjusted in relation to the pressure of the sample which was previously examined. After proper initial adjustments, both samples can be stored in the sample line and examined many times without further pressure adjustments. The pressure adjustment is better understood by referring to Figure 20 (a) which shows an actual comparison of two samples. Note how the set of measurements (2) is centrally located between sets of measurements (1) and (3). Similarly (3) is centered between (2) and (4), etc., because of correct initial pressure adjustment. This was found to be the only way in which two identical samples could be shown to have the same Se⁷⁶/Se⁸⁰ ratio as ung the case in Figure 20 (a). Figure 20 (b) shows an actual case where two samples of different Se⁷⁶/Se⁸² ratios did not have their pressures properly adjusted till observation (6). It is obvious from these results that slight changes in the balance point results from both changes in signal and changes in time after the introduction of the sample and these changes are due to changing conditions in the mass spectrometer tube. The procedure used effectively compared the isotope ratios for the two samples over the same signal range and the same period of time.

Two methods were used to determine the difference in isotope ratio between two samples from the recorded data. The first method was that of a graphical plot as shown in Figures 20 (a) and (b). The best line was drawn through the points obtained for each sample and the

-58-

FIGURE 20(a)

Nexulto obtained by comparing two identical samples. The balance point was plotted against the voltage developed by the So³²T5⁴ ion current across the input resistor to the vibrating read electrometer. The initial sample pressures have been properly adjusted to give meaningful data.

FIGURE 20(b)

The same as 20(a) with the exceptions that the two samples are inotopically different and the pressure has not been properly adjusted until observation (6).



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vertical distance between these two lines was measured at intervals along the plot. This measured difference and the balance point of the standard sample give directly the isotopic composition difference of the two samples.

In the second method, every balance point is taken into account in the analysis of the data. Referring to Figure 20, 1, 2, 3, etc., are "sets of observations". For each of these the recorded balance points were averaged. Then $\frac{1(ev)+3(ev)}{2}$ was compared to $(2)_{ev}$, etc., 2 to give an isotope ratio difference for the two samples.

A "run" consisted of some 6 or 8 such measurements. In a run, a standard deviation of 20.0005 in the measurements was obtainable. When several runs on the same sample were carried out, the reproducibility of the measurements could be obtained to 20.0005 or better.

The same samples compared on different days gave results which were reproducible to \$ 0.0005. Also separate proparations of the same samples were found to be reproducible within these same limits indicating that the sample proparation methods were quantitative and little or no fractionation of the isotopes occurred in the preparation.

In the earlier stages of this investigation, it was found that after a vigorous baking of the mass spectrometer, well-resolved, flattopped peaks resulted as shown in Figures 14 and 15. However, after a period of about a week of stendy operation, the peak shape and resolution deteriorated. Subsequently, however, it was found that, by keeping the analyzer tube warm ($\sim 60^{\circ}$ C) during analysis of the samples, the good peak shape and resolution could be retained indefinitely.

-59-

Fractionation Studies

Harrison et al (109) reported large kinetic s^{32}/s^{34} isotope effects in the domical reduction of sulphate and sulphite to hydrogen sulphide. The corresponding isotope effects in the bacterial reduction of sulphate and sulphite are responsible for a large part of the sulphur isotope fractionation which occurs in nature. For this reason, it was of considerable interest to determine the critent to which selenium isotopes fractionate in the reduction of sodium selenite to elemental selenium.

Procedure for Reduction of Sodium Selenite: Hydroxylamine hydrochloride was found to be a satisfactory reducing agent for the study of isotope effects in the reduction of sodium selenite according to the reaction

$$2^{\text{E}} \div 2^{\text{MH}_20\text{H}} \div 5 \circ 0_3 \longrightarrow 5 \circ \downarrow \div 1 \circ 2^{\text{O}} \div 4 \circ 2^{\text{O}}$$

if the reduction occurred in dilute solutions.

5.0 gm of sodium selenite are discolved in 500 ml of water. Enough hydroxylamine hydrochloride (~ 0.04 gm) in solution is added to precipitate about 1 percent of the total selenium. The solution turns pink after a period of about an hour, indicating the slow precipitation of selenium. The solution is then allowed to stand overnight and the precipitated selenium is separated with a centrifuge since finely precipitated selenium in the red form goes through very fine filters. This selenium is then washed and drish at 80° C.

The rest of the selenium (99%) present as selenite in the supernatant solution is now quantitatively recovered by the addition of excess hydroxylamine hydrochloride, after which it is contrifuged, whiched, and dried. The se^{76}/se^{82} ratios for these two samples of element^B1 selenium are then compared.

RESULES AND DISCUSSION

Natural Abundance Studies

In view of the remarkable uniformity in the $5^{32}/5^{34}$ ratio in meteorites of all types, and the considerable evidence, that this ratio represents, the primordial ratio of the sulphur isotopes in terrestrial sulphur, it seemed reasonable to assume in the first instance that the selenium isotope ratio for meteorites was also constant and represented the primordial ratio of the selenium isotopes.

Therefore, in the comparison of the selenium isotope ratios in various samples, selenium entracted from troilite in Canyon Diablo meteorite was used as a standard. In practice, however, a sample of selenium from Noranda was used as a secondary standard because of the small sample of meteoritic selenium available.

Table V and and Figure 21 summarize the selenium isotope abundance data obtained for a variety of natural samples. S is the eurichment of Se⁸² in $^{\circ}/_{\circ\circ}$ defined by

$$\delta = \frac{\frac{82}{5e^{76}} \frac{76}{\text{sample} - 5e^{76}} \frac{82}{5e^{76}} \frac{76}{\text{meteoritic}}}{\frac{82}{5e^{76}} \frac{82}{5e^{76}} \frac{1000}{\text{meteoritic}}}$$

The distribution of the selenium isotopes found in the samples investigated to date (Fig. 21) would seem to justify the choice of meteoritic selenium as a standard for comparison and suggest that the meteoritic value of the isotope ratio is indeed the primordial or base value from which isotopic fractionation has occurred in geological and biological processes.

It is seen, from the data, that the Se⁸²/Se⁷⁵ ratio in the samples examined varies by 1.5 percent. The selenium samples from

TABLE V

Results of the Variations of the Se⁸²/Se⁷⁶ Ratio in Natural Samples

Sample No.	Location	Alleged Type of Deposit	8 gz %.
l	Canyon Diablo Meteorite	Selenium in Troilite	0.000
2	Noranda, Quebec	Hypothermal or Nagmatic Hydrothermal Massive Sulphide (151)	+0.5 ± 0.5
3	Murdochville, Quebec	Hypothermal or Magmatic Hydrothermal Massive Sulphide (151)	+1.0 <u>+</u> 0.5
4	Flin Flon, Manitoba	Hypothermal or Magmatic Hydrothermal Massive Sulphide (151)	+0 . 5 <u>+</u> 0.5
5	Sudbury, Ontario	Molten Magma or Igneous Origin (151)	+0 . 5 <u>+</u> 0.5
6	Mt. Lyell, Australia	Mesothermal (151)	-1.0 + 1.0
7	Mt. Wingen, N. S. W.	Selenium precipitated below pyrite	-1.0 ± 1.0
8	Beaverlodge Lake, Saskatchewan	Umangite (Cu2Se Cu Se) in Hydrothermal Pitchblende bearing sulphide vein	0.0 <u>+</u> 0.5
9	Beaverlodge Lake, Saskatchewan	Chalcomenite (Cu Se 03.2H2 in Association with 8	0) +0.5 <u>+</u> 0.5
10	Unknown	Refined selenium, Phelp's Dodge Refining Corp. New York	+0.5 ± 0.5
11	Unknown	Refined selenium, American Smelting and Refining Co.	10.5 <u>+</u> 0.1

-62-

-62A-

Sample No.	Location	Alleged Type of Deposit	δ ₈₂ %.
12	Unknown	Commercial SeF6, Allied Chemical and Dye Corp., Baton Rouge, Louisiana Selenium was purchased from Company in #11	10.5 <u>+</u> 0.5
13	Unknown	Astragalus Bisulcatus plant containing selenite and complex organic selenium compounds	+2 . 0 <u>+</u> 0 . 5
14	Unknown	Astragalus Pattersoni plant containing selenite and complex organic selenium compounds	-11.0 <u>+</u> 1.0
15	County Meath, Ireland	Soil Sample containing selenite and complex organic selenium compounds	+4.0 <u>+</u> 0.5
16	Mt. Shirane, Japan	Elemental selenium in volcanic sulphur	-2.0 + 1.0

TABLE V (continued)

plant materials and soil show the largest variations in the selenium isotope ratios whereas the massive sulphide ores (probably igneous and magmatic hydrothermal deposits) show little or no variation with respect to meteoritic selenium.

It is interesting to compare these selenium isotope results with similar results obtained in the sulphur isotope studies.

The selenium extracted from massive sulphide ore appears to be slightly enriched in the heavy isotope Se^{82} ($\delta = +0.5$). Sulphur in similar ores has been shown to be enriched in the heavy isotope S^{34} although the results in this case are more pronounced (90). For example, Sudbury igneous ore is enriched by 0.5 and 2.5% or in Se⁸² and S³⁴ respectively, the meteoritic values being taken as standard in each case.

The Se⁸²/Se⁷⁶ ratio for elemental selenium from Mt. Shirane, Japan (volcanic) is, of course, not indicative of the average ratio for volcanic selenium, since selenium is present in other compounds and some fractionation between these compounds in volcanic gases is possible. Sulphur studies have shown wide variations in isotopic ratios for various volcanic sulphur containing samples (150,87,74), however, when all the compounds arising from a volcano vent are collected and analysed, an average S^{34}/S^{32} ratio very close to the meteoritic standard is obtained (149). The fact that the elemental selenium sample investigated is depleted in Se⁸² by 2 °/oo indicatos that some fractionation of the selenium isotopes has occurred in the volcanic gases. Elemental sulphur from the same volcano was also found to be depleted in the heavy isotope (8 = -5 (114)).

The sample from Beaverlodge Lake, Sackatchewan, which contains



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umangite (Cu_2 Se.CuSe) and chalcomenite ($CuSeO_3.2H_2O$). (Samples 8 and 9 Table V), is considered to have been derived from primary sulphide ore as the selenide and subsequently partially condized (Robinson 152). The results show little or no fractionation of the selenium isotopes in this natural process.

The variations found in the Se³²/Se⁷⁶ ratios for selenium extracted from plant material and soils indicates large isotope effects which have occurred probably in oxidation and reduction processes in biological systems. It is now fairly well established that the major portion of sulphur isotope fractionation in biological systems occurs in the bacterial reduction of sulphate. Anaerobic bacteria are known to reduce selenates and selenites as well, and large selenium isotops effects under certain conditions are to be expected.

Although the kinetic isotope effects obtained in the bacterial reduction of sulphate varies with the metabolic rate, the maximum value of this isotope effect at low metabolic rates approaches that obtained in a direct chemical reduction (103, 109). The results from the determination of the selenium isotope effect in the chemical reduction of selenite are reported below.

Reduction of Sodium Selenite

Three runs were carried out in which Ma₂SeO₃ was reduced by enough hydroxylamine hydrochloride in dilute solution at 3°C to precipitate 1 percent of the total selenite as elemental selenium. The isotope fractionation which occurred in this 1 percent reaction may be expressed in terms of

-64-

$$R = \frac{Se^{76}/Se^{82} \text{ reduced portion (Seo)}}{Se^{76}/Se^{82} \text{ remainder (Seo_3^{-1})}}$$

The results obtained were as follows:

तिस्य	R
1	1.014
2	1.016
3	2.016
Average	1.015 ± 0.001

These results indicate a kinetic isotope effect of (R-1) x 100 = 1.5 percent in the chamical reduction of selenite to elemental selenium. The question arises as to whether this is a true kinetic isotope effect in which case $R = k_1/k_2$ for

$$se^{76}o_3 = \frac{k_2}{5e_0^{76}}$$
 se_0^{76}

or whether some isotopic exchange of selenium has also occurred between the reactant and the product in the course of the experiment. A slow exchange of the selenium isotopes between selenite and elemental selenium would result in a gradual increase of (R-1) since the equilibrium isotope effect for the exchange

$$se^{76}o_3 = se_0^{82} = se_0^{76}se_0^{76}$$

would be considerably larger than the kinetic isotope effect in the reduction process.

In this connection, Haissinsky and Pappas (153) have observed

-65-

with tracer experiments that anorphous selenium exchanges with its ions in a 5.5N HCl solution 0.1M with respect to SeO₂. The rate was found to increase with acid concentration approaching ¹O percent in 1 hour at 10 N HCl. Since the exchange was found to take place only at high acid concentrations, no appreciable exchange of the selenium isotopes would be expected in the almost neutral, dilute solutions of this reduction experiment.

Although the possible exchange in neutral solutions should be investigated further, the results indicate a 1.5 percent isotope 50^{75} - 52^{82} effect in the chemical reduction of solenite.

The kinetic isotope effect for the reduction of selenite to elemental selenius may be calculated using the equation of Bigeleisen (page 37 no. 20) providing we have the normal vibrational frequencies for the reactants and the activated complex. However, in the absence of any information about the activated complex for the reaction, it is necessary to make certain assumptions. By considering the breaking of the Se-O bond in a simple distoric model and assuming the bond to be completely broken in the activated complex; k_1/k_2 from the Highleisen equation is found to be 1.015 at 0°C.

The agreement between the experimental and the theoretical result is fortuitous in view of the single model assumed. Mevertheless, this model shows that the result is of the order expected.

-66-

APPENDIX I

Calculation of Isotopic Vibrational Frequency Shifts for Selenium-containing Nolecules

Experimental values for the normal vibrational frequencies of many selenium-containing molecules are available. Since Se^{80} is the most abundant (about 50%) of the selenium isotopes, these experimental values are assumed to apply to the Se⁸⁰ containing compound. The vibrational frequencies of the Se⁷⁶ and Se⁸² containing molecules are now calculated from these observed frequencies with available "normal force equations" which describe molecules of different symmetries.

<u>Diatomic Molecules</u>: The assumption is made that the diatomic molecule is an anharmonic oscillator with a potential energy function of the form

$$U = f(r - r_e)^2 - g(r - r_e)^3$$
 etc. (1)

where r_e represents the equilibrium internuclear distance and $(r - r_e)$ represents the displacement from this equilibrium position.

If the anharmonicity is small ($g \ll f$), it is found that the energy values (eigenvalues) of the Schrödinger equation

$$\nabla \psi + \frac{8\pi^2}{h^2} \mu (E - u) \psi = 0$$
(2)

are given by

$$E_{v} = hc \quad u_{e}(v + \frac{1}{2}) - u_{e}x_{e}(v + \frac{1}{2})^{2} + u_{e}y_{e}(v + \frac{1}{2})^{3} + \dots (3)$$

where v is the vibrational quantum number, w_{e} is the classical vibrational frequency in cm⁻¹ units and μ is the reduced mass of the two atoms $\frac{m_{1}m_{2}}{m_{1} + m_{2}}$.

The classical vibrational frequency of a harmonic oscillator for a diatomic molecule in units of \sec^{-1} is given by

$$V_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where $-k(r - r_e)$ is the restoring force for the displacement $(r - r_e)$ and μ is the reduced mass of the two atoms. -67Assuming that the force constant "k" is the same for isotopic molecules, the classical vibrational frequency for an isotopic molecule is given in terms of the frequency of the more abundant molecule by

$$\frac{v^2}{v} = \sqrt{\frac{\mu}{\mu_i}} = \rho$$

and from the relationship v = cv, it follows that

$$\frac{w_{e}^{1}}{w_{e}} = ($$

The assumption that "k" is the same for isotopic molecules is based on the observation that the potential energy curves for isotopic diatomic molecules have been found alike to a very high degree.

The selection rule for vibrational energy transitions is given by $\Delta \mathbf{v} = \frac{1}{2} \mathbf{1}$ and the energy change in the vibrational transition $\mathbf{v} = \mathbf{1}$ to $\mathbf{v} = 0$ is given by equation (3) as

$$\Delta E_{v} = he \left[v_{e} - 2u x_{e} + \cdots \right] = hev \qquad \dots \qquad (5)$$

From (4), the energy levels for the isotopic molecule are given in terms of the abundant molecule by

and the energy change in the transition v = 1 to v = 0 is given by

$$\delta S_{v}^{i} = hc \left[ev_{e}^{i} - 2\rho^{2} v_{e}^{i} x_{v} + \frac{1}{2} \right] = hc v_{i}^{i} \qquad (7)$$

The calculations for the vibrational frequencies of Se' and Se⁵²-containing distomic molecules then proceed as follows:

 w_e and $w_e x_e$ for the Se⁶⁰-containing molecule is obtained from observed data (Herzberg (148)). Then

-63-

TABLE VI CALCULATION OF VIERATIONAL FREDUENCY SHIFTS FOR Se⁷⁶ and Se⁸² - CONTAINING DIATOMIC SPECIES

MOLIECULE	80 We-1 cm	(we_1) ⁸⁰	80,76 سرا مر	V 10 1 76	80, 82 سرا سر	1/80, 82 مرا بر	76 we-1 cm-1	82 e_1	(ve.1) m	(ve_1) (me_1)	75 w_1 cm	82
PbSe	277.6	0.51	1.038	1.019	0.9824	0.9912	282.9	275.2	0.53	0.50	281.8	274.2
GeSe	406.8	1.20	1.025	1.013	0.9883	0.9941	411.9	404.3	1.21	1.18	410.5	403.0
SnSe	331.2	0.736	1.032	1.016	0.9854	0.9927	336.4	328.8	0.759	7.25	334.9	327.3
C Se	1036.0	4.8	1.007	1.003	0.9968	0.9984	1039.5	1034.3	4.83	4.78	1029.8	1024.7
SiSe	580.0	1.78	1.014	1.007	0.9937	0.9968	583.9	578.2	1.80	1.77	580.3	574.7
se ⁸² se ⁸⁰ se ⁷⁶ se ⁸⁰	391.77	1.06	1.026	1.013	0.9878	0.9939	396.9	389.4	1.09	1.05	394.7	387.3
8e ⁸² 5e ⁸² 8e ⁷⁶ 5e ⁷⁶	391.77	1.06	1.053	1.025	0.9756	0.9377	402.0	386.97	1.12	1.03	399.76	384.9
Se0 ¹⁶	907.1	4.61	1.009	1.004	0.9959	0.9980	911.1	905.3	4.65	4.59	901.79	896.12

-65-

$$(w_{e}x_{e})^{76} = \rho_{76}^{2} (w_{e}x_{e})^{80}$$

From these

$$w_{82} = w_e^{-82} - 2(w_e x_e)^{-82}$$

 $w_{76} = w_e^{-76} - 2(w_e x_e)^{-76}$

Table VI summarizes the calculations made to determine the vibrational frequencies of some Se⁷⁶ and Se⁸²-containing molecules.

Selenate Ion (SeU,). This ion is of tetrahedral structure. Heath and Linnett (156) have compared the assumptions of "Simple Valence Force Fields (SVFF)" with those of "Orbital Valency Force Fields (OVFF)" in their application to tetrahedral XYL compounds and have found the latter to be superior. In particular, with other compounds, they considered SeO_h^{-1} and found the calculated and the observed frequencies to be in excellent agreement as shown:

5e0 ₄ ⁼	^{II} 1	¹¹ 2	и ₃	Rip
Observed Frequencies (161)	834cm-1	875om-1	416cm ⁻¹	339cm ⁻¹
OVFF Calculated Frequencies	834cm-1	875an ⁻¹	406cm ⁻¹	346cm ⁻¹

It is seen that there are four normal acdes for molecules of this symmetry type. Of these modes, N_1 and N_{l_2} are non-degenerate while modes N_2 and N_3 are triply-degenerate.

From the OVFF approach the following equations were given for $SeO_{l_{\mu}}$ by Heath and Linnett (154).

$$\lambda_{1} = \frac{1}{m_{o}} (k_{1} + \theta \Lambda) \qquad \dots \dots \dots (1)$$

$$\lambda_{2} + \lambda_{3} = \left[\frac{1}{m_{o}} + \frac{4}{3m_{s}}\right] \left[k_{1} + \frac{\theta}{3}\Lambda - \frac{4}{3} \frac{B}{R}\right]$$

$$+ \left[\frac{1}{m_{o}} + \frac{\theta}{3m_{s}}\right] \left[k_{2} + \frac{4}{3}\Lambda + \frac{10}{3} \frac{B}{R}\right]$$

$$- \frac{\theta}{3m_{s}} \left[\frac{\theta}{3}\Lambda - \frac{4}{3} \frac{B}{R}\right] \dots \dots (1)$$

-70-

$$\lambda_{2}\lambda_{3} = \left[\frac{1}{m_{o}^{2}} + \frac{4}{m_{o}n_{se}}\right] \left\{ \left[k_{1} + \frac{3}{3} - \frac{4}{3}\frac{B}{R}\right] \left[k_{1}^{*} + \frac{4}{3}i + \frac{10}{3}\frac{B}{R}\right] \\ - \frac{1}{2} \left[\frac{3}{3}i - \frac{4}{3}\frac{B}{R}\right]^{2} \right\}$$

$$(3)$$

$$\lambda_{4} = \frac{1}{m_{o}} \left[k_{1}^{*} + 2\lambda + \frac{B}{R}\right]$$

$$(4)$$
where $\lambda_{1} = 4\pi^{2}c^{2}w_{1}^{2}$

$$w_{1} = \text{frequency in cm}^{-2}$$

$$m_{so} = \text{meas of colonium stom}$$

$$m_{o} = \text{meas of colonium stom}$$

$$k_{1} = \text{bend stretching constant for Se = 0 bank}$$

$$= (5.40 \times 10^{5} \text{ dynes/cm})$$

$$x^{2}k_{1}^{*} = \text{bending constant of the 0 = 58 = 0 angle}$$

$$(k^{4}a = 0.64 \times 30^{5} \text{ dynes cm})$$

-B and 2. are the first and second differentials of the potential energy function representing regulation between non-bonded atoms. For $\sec \theta_{4}^{=}$ A = 0.135 x 10⁵ dynes/cm $\frac{3}{R} = 0.21 x 10^{5}$ dynes/cm

It is firstly noted that λ_1 and λ_4 are not dependent upon the mass of solenium and therefore remain the same with isotopic substitution of solenium. $\lambda_2 + \lambda_3$ and $\lambda_2 \lambda_3$ can now be calculated from equations (2) and (3) using the values of the constants given by Heath and Linnott (156). Then, λ_1 and λ_2 and subsequently v_1 and v_2 can be obtained by using the equation:

$$\lambda^{2} = (\lambda_{2} + \lambda_{3})\lambda + \lambda_{2}\lambda_{3} = 0,$$

whose roots are given by

$$2\lambda = \lambda_2 + \lambda_3 = \sqrt{(\lambda_3 + \lambda_2)^2 + \lambda_2^{\lambda_3}}$$

These values are found to be the following:

- - - 72-

	λ2 + λ3	$\lambda_{2\lambda_{\overline{3}}}$	42	₩3	
Se7604=	5.5354 x 10 ⁴ sec=2	$4.4593 \times 10^8 \text{ sec}^{-4}$	379.6 cm ⁻¹	407.7 cm-1	
50 ⁸⁰ 04=	5.4717 x 10 ⁴ sec ⁻²	4.3537 x 10 ⁸ sec ⁻⁴	874.6 cm ⁻¹	405.1 cm-1	
Se ⁸² 04=	5.4421 x 10 ⁴ sec=2	4.3100 x 10 ⁸ sec ⁻⁴	872.2 cm ⁻¹	4C4.2 cm ⁻¹	

Now if the calculated normal vibrational frequencies, w_2 and w_3 for Se⁸⁰04⁼ are compared to the observed values, a discrepancy is noted for w_3 .

Se ⁸⁰ OL= observed	<u>875</u>	cm-l		416	cm-1
Se ⁸⁰ 04 ⁼ calculated	874.6	c=-1		405.1	c a -1
Therefore, a correction	factor	of 416 405.1	is now	applie	ed to the

calculated w_3 's for Se⁷⁶04⁼ and Se⁸²04⁼ to align their values with the observed value for Se⁸⁰04⁼. After doing this, the normal frequencies for Se⁷⁶04⁼ and Se⁸²04⁼ are found to be:

	<u>se7601,=</u>	Se ⁸²⁰⁴ =		
wl	834 cm ⁻¹	834 cm ⁻¹		
¥2	880.0 cm-1	872.6 cm ⁻¹		
w3	418.6 cm-1	415.1 cm ⁻¹		
w4	339 cm-1	339 ca-1		

SeF₆: Sclenium hexafluoride is of octahedral structure of O_h symmetry. Heath and Linnett (156) have applied the SVFF and the OVFF method to molecules of this structure, in particular SeF6, and found the OVFF method to give better agreement. The calculated values and the observed values of the fundamental frequencies were compared as follows:

Sef 6	^N L	11 ₂	113	15/24	^N 5	и _б
Observed (157)	708 cm ⁻¹	662 cm ⁻¹	767 -21-1	461 cm ⁻¹	/105 cm ⁻¹	245 cm ⁻¹
Calculated OVFF	720 as ^{~2}	650 cm ⁻¹	802 cm ^{~1}	46; cm ^{~1}	402 cm ⁻¹	350 cm ⁻¹

-73-

Of these 6 normal modes, N, is non-degenerate, N_2 is doubly degenerate and N_3 , N_4 , N_5 , and N_6 are triply degenerate. N_1 , N_2 , and N_3 are associated with valency vibrations while N_4 , N_5 , and N_6 are associated with deformation vibrations.

 N_1 , N_2 , and N_5 appear in the Haman spectrum while N_3 and N_4 appear in the infra red spectrum. N_6 , however, is forbidden in either spectrum and cannot be observed spectroscopically. It must be calculated by combination tones or obtained from specific heat data. It is noted that this normal vibration is not satisfactorily considered in the OVEF approach.

Heath and Linnett (156) give the following equations for SeP from the CVFF approach.

$$\lambda_{1} = (k_{1} + 8A)/n_{p} \qquad (1)$$

$$\lambda_{2} = (k_{1} - \frac{8}{3}\frac{3}{R} + \frac{8}{3}A)n_{p} \qquad (2)$$

$$\lambda_{3} + \lambda_{4} = f_{11}'\frac{1}{m_{p}} + \frac{2}{m_{59}} + f_{22}(\frac{4}{m_{59}} + \frac{1}{m_{p}})$$

$$-4\sqrt{2} \times f_{12}'n_{59} \qquad (3)$$

$$\lambda_{5}\lambda_{4} = (f_{11}f_{22} - f_{12}^{2})(\frac{1}{m_{p}^{2}} + \frac{6}{m_{59}}) \cdots (4)$$

whore

-74-

 $\lambda_{6} = (k_{0} + 2\Lambda)/m_{\rm p}$ (6)

where

^mSo = mass of selenium atem

mp = mass of fluering atom

The constants have been calculated by Heath and Linnett to be as follows:

$$k_1 = 4.3 \times 10^5 \text{ dyns/cm}.$$

 $k_p = 1.00 \times 10^5 \text{ dyns/cm}.$
 $A = 0.1875 \times 10^5 \text{ dyns/cm}.$
 $B/R = 0.0290 \times 10^5 \text{ dyns/cm}.$

It is immediately seen from the equations that λ_1 , λ_2 , λ_5 , and λ_6 are independent of the mass of selenium and therefore remain the same for isotopic substitution of selenium. In isotope shift calculations, therefore, the poor agreement of the calculated λ_6 with the observed value no longer presents a problem. Using equations (5) and (4), $\lambda_5 + \lambda_4$ and $\lambda_5 \lambda_4$ are obtained. As before, λ_5 and λ_4 and subsequently w_5 and w_4 can be determined. The results are as follows:

	$\lambda_3 + \lambda_4$	2324	w _j	ч _{!+}
se ⁷⁶ F6	5.1150 x 1.0 ⁴ eec ⁻²	4.6872 x 10 ⁸ sec ⁻¹	607.9 cm ⁻¹	464.7 cm ⁻¹
30 ⁶⁰ P6	5.0289 x 10 ⁴ see ⁻²	4.7405 x 10 ⁸ 300-4	800.3 cc ⁻¹	461.9 ca ^{~1}
Se ⁸² F6	5.0289 x 10 ⁴ sec ⁻²	4.7405 x 2.0 ⁸ seo ⁻⁴	800.3 cm ⁻¹	461.9 om ⁻¹

The calculated values of w_{3} and $\beta_{l_{2}}$ for Se⁶⁰ P₆ are now conserved with the observed values, and

Se ⁸⁰ F _G	w ₃	$u_{l_{\lambda}}$		
Observed	787 cm ⁻¹	461 co ⁻¹		
Calculated	800.3 m ⁻¹	461.9 cm ⁻¹		

correction factors $(\frac{787}{800.3} \text{ and } \frac{l_{461}}{l_{461.9}})$ are used to align the calculated vibrational frequencies for Se⁷⁶ P_6 and Se⁸² P_6 with the observed vibrational frequencies for Se⁸⁰ P_6 .

Summarizing:

	ษา	^U 2	^w 3	w _l	^w 5	^w 6
Se ⁷⁶ F6	708 cm ⁻¹	662 cm ⁻¹	794.7 cm ⁻¹	463.8 cm ⁻¹	405 cm ⁻¹	245 cm ⁻¹
^{Se⁸²⊮6}	708 cm ⁻¹	662 cm ⁻¹	783.9 cm ⁻¹	459.7 cm ⁻¹	405 cm ⁻¹	245 cm ⁻¹

H_Se: Triatomic non-linear molecules have been studied by Glocker and Tung (158) with the assumption of general force fields which produce three equations with four force constants for isoceles non-linear triatomic molecules as follows:

$$\lambda_{1} + \lambda_{2} = L_{11} + L_{12} + L_{33}$$

$$\lambda_{1}\lambda_{2} = L_{33}(L_{11} + L_{12}) - 2L_{13}L_{31}$$

$$\lambda_{3} = L_{11} - L_{12}$$
where $-L_{11} = \frac{c_{1}}{M} \Rightarrow \frac{c_{2}}{M} \sin \alpha - \frac{c_{4}}{M} \cos \alpha$

$$L_{12} = \frac{c_{1}}{M} \cos \alpha - \frac{c_{2}}{M} \sin \alpha + \frac{c_{4}}{M}$$

$$-L_{13} = \frac{c_{1}}{M} \sin \alpha - 2c_{3}\left[\frac{1}{M} - \frac{\cos \alpha}{M}\right] + \frac{c_{4}}{M} \sin \alpha$$

$$-L_{31} = \frac{c_{2}}{M} \sin \alpha - c_{3}\left[\frac{1}{M} + \frac{\cos \alpha}{M}\right]$$

$$L_{33} = 2c_{2}\left[\frac{1}{M} - \frac{\cos \alpha}{M}\right] - \frac{2c_{3}}{M} \sin \alpha$$
where M = mass of central atom
$$m = mass of terminal atoms$$

$$\frac{1}{\mu} = \frac{1}{\mu} + \frac{1}{\mu}$$

-75-

The observed angle α for H_2 is close to 90° while the two symmetric frequencies observed are 2260 and 1074, and the antisymmetric frequency observed is 2350 (). Since α is 90°, the equations are simplified because:

$${}^{-L}11 = \frac{-c_1}{\mu} + \frac{c_3}{M}$$

$${}^{L}12 = \frac{-c_3}{M} + \frac{c_4}{\mu}$$

$${}^{-L}13 = \frac{c_1}{M} - \frac{2c_3}{\mu} + \frac{c_4}{M}$$

$${}^{-L}31 = \frac{c_2}{M} - \frac{c_3}{\mu}$$

$${}^{L}33 = \frac{2c_2}{\mu} - \frac{2c_3}{M}$$

which gives

by

$$\lambda_{1} + \lambda_{2} = \frac{1}{\mu} \left[2c_{2} + c_{4} + c_{1} \right] - \frac{4c_{3}}{M}$$

$$\lambda_{1}\lambda_{2} = \left[2c_{2}(c_{1} + c_{4}) - 4c_{3}^{2} \right] \left[\frac{1}{\mu^{2}} - \frac{1}{M^{2}} \right] \dots (2)$$

$$\lambda_{3} = (c_{1} - c_{4})(\frac{1}{\mu})$$

Smith and Linnett () have subsequently applied these equations to $\rm H_2Se$ and found the following force constants

$$c_1 = 3.4 \pm 0.1 \times 10^5$$
 dynes/cm
 $c_2 = 0.36 \pm 0.06 \times 10^5$ dynes/cm
 $c_3 = 0.15 \pm 0.03 \times 10^5$ dynes/cm
 $c_4 = -0.15 \pm 0.15 \times 10^5$ dynes/cm

It is seen from (2) that the isotopic frequencies for w_j are related

$$\frac{\lambda_3^1}{\lambda_3} = \frac{\mu}{\mu'} \text{ or } \frac{\mu'}{\mu_3} = \sqrt{\frac{\mu}{\mu'}}$$

Assuming that the observed frequency value of w_3 applies to $\Pi_2 \text{Se}^{80}$, w_3 for $\Pi_2 \text{Se}^{76}$ and $\Pi_2 \text{Se}^{82}$ is calculated to be 2350.7 cm⁻¹ and $\Pi_2 \text{Se}^{82}$ is calculated to be 2350.7 cm⁻¹ and 2349.7 cm⁻¹ respectively ($w_3^{60} = 2350 \text{ cm}^{-1}$).

-77-

If the constants of Smith and Linnett (160) are used to find $\lambda_1 \lambda_2$ and $\lambda_1 + \lambda_2$, u_1 and u_2 for the isotopic molecules are found to be

	¹¹ 2 ^{Se} 76	^{II} 2 ^{Se⁸⁰}	123e ⁸²
v ₁	2430.7 cm ⁻¹	2430.1 cm ⁻¹	2429.8 cm ⁻¹
¥2	960.1 cm ⁻¹	959.7 cm ⁻¹	959.5 cm ⁻¹

The observed values of w_1 and w_2 are 2260 cm⁻¹ and 107⁴ cm⁻¹ respectively. If these frequencies are assumed to be those for $H_2 Se^{80}$, the calculated values are corrected to the observed values to give

	^{H2Se} 76	^H 2 ^{Se⁸⁰}	H23082
₩1	2260.7 cm ⁻¹	2260.0 cm ⁻¹	2259.8 cm ⁻¹
¹⁴ 2	1074.4 cm ⁻¹	1074.0 cm ⁻¹	1073.8 cm ⁻¹

The errors between the observed values and the calculated values of w_1 and w_2 result because four force constants cannot be determined uniquely with three frequencies. However, this method is considered to be more accurate than other methods which assume fewer force constants.

AFFE DIA II

Calculations of $\frac{1}{2}/\frac{1}{4}$ for Se⁸² and Se⁷⁶ containing compounds were made using the isotopic vibrational frequencies found in Appendix I and the Bigeleisen Nayer Equation (No. 14, page 34). The G(u) values were taken from the table of Eigeleisen and Hayer (134).

TABLE VII

Calculation of $2'$	/ '1'	for	Se-containing	Diatonio	Species
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	in the second		and the second se	the second se	the second second	And the second state of th	
Moleculo	Tenp °C	^u 76	^u 82	Ĺu	G(u ₀₂)	G(u)/u	2/1 ⁼ 1.6(u)/u
Pb3e82 Fb3e76	0°0 25 100 250	1.4639 1.3595 1.0862 0:7748	1.44+39 1.3228 1.0569 0.7539	0.0401 0.0367 0.0234 0.0209	0.1165 0.1071 0:0891 0.0621	0.0047 0.0039 0.0026 0.0013	1.0047 1.0039 1.0026 1.0013
<u>Gese</u> 82 Gese76	0 ⁰ C 25 1C0 250	2.1616 1.9804 1.5625 1.1207	2.1221 1.9442 1.5534 1.1080	0.0395 0.0362 0.0289 0.0206	0.1669 0.1499 0.1243 0.0899	0.0069 0.005½ 0.0036 0.0019	1.0069 1.0054 1.0036 1.0019
<u>BnSe</u> 82 SnSe76	0 ⁰ 0 25 100 250	1.7635 1.6156 1.2909 C.9208	1.7235 1.5790 1.2616 0.8999	0.0400 0.0367 0.0293 0.0309	0.1355 0.1245 0.1017 0.0740	0.0054 0.0046 0.0030 0.0023	1.005% 1.0046 1.0030 1.0023
05082 03076	0 ⁰ U 25 100 250	5.4227 4.9680 3.9695 2.8514	5•3959 4•9434 3•9499 3•8174	0.0269 0.0246 0.0197 0.0140	0.5193 0.3047 0:2665 0.2605	0.0036 0.0075 0.0052 0.0037	1.0096 1.0075 1.0052 1.0037
<u>SiSe</u> 82 SiSe76	0 ⁰ 3 25 100 250	3.0557 2.7995 2.2369 1.5995	3.0262 2.7725 2.2153 1.5601	0.0295 0.0270 0.0216 0.0154	0.2205 0.2060 0.1711 0.1265	0.0065 0.0056 0.0037 0.0020	1.0065 1.0056 1.0037 1.0020
3082 20 3076 3000	0 ⁰ 0 25 100 250	2.0784 1.9041 1.5214 1.0652	2.0394 1.0684 1.4929 1.0649	0.0390 0.0357 0.0285 0.0203	0.1592 0.1473 0.1200 0.0571	0.0062 0.0055 0.0055 0.0055 0.0015	1.0062 1.0053 1.0054 1.0016
<u>50</u> 82 82 3076 80 3076 80 80	0°0 25 100 250	2.1051 1.9285 1.5409 1.0991	2.0269 1.8569 1.4837 1.0583	0.0782 0.0716 0.0572 0.0108	0.1584 0.1465 0.1195 0.0898	0.0124 0.0105 0.0068 0.0037	1.0124 1.0105 1.0069 1.0037
3076016	0 ⁰ 0 25 100 250	4.7406 4.3505 3.4761 2.4794	4.7108 4.5251 5.4542 2.4638	0.0299 0.0274 0.0219 0.015	0.2971 0.2821 0.2430 0.1872	0.0089 0.0077 0.0055 0.0029	1.0089 1.0077 1.0053 1.0029

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TABLE VIII

	and the second second		6 1	Sector Sector	4		
i	u ₂₁ (cm ⁻¹)	w _{li} (cm ⁻¹)	$\Delta v_i(cm^{-1})$	u ₂₁	Δu _i	0(u ₂₁)	€(u∐u
1	034	834	0.00				
2	872.6	038	7.4	4.5946	0.03896	0.29256	0.0114
2	872.6	880	7.4	4.5946	0.03896	0.29256	0.0114
2	872.6	880	7.4	4.5946	0.03896	0.29256	0.0114
3	415.1	1:18.6	3.5	2.1857	0.01843	0.16910	0.0031
3	415.1	418.6	3.5	2.1857	0.01843	0.16910	0.0031
3	415.1	416.6	3.5	2.1857	0.01843	0;16910	0.0031
4	339	539	0.0				
			the second se	the second se	the second second second second		

Calculation of $Q_{2}^{\prime}/Q_{1}^{\prime}$ for $\operatorname{SeO}_{b_{1}}^{=}$ at $O^{O}C$

 $\frac{1}{2}/\frac{1}{1} = 1.044$ at 0°C

TABLE IX

			21		4 -	and the second second	Same States
i	w ₂₁ (cm ⁻¹)	v _{li} (cm ⁻¹)	$\Delta v_i (cm^{-1})$	u _{2i}	۵ ^u i	c(u ₂₁)	G(u Au
1	834	834	0.00				
2	872.6	890	7.4	4.2095	0.03570	0.27750	0.00990
2	872.6	880	7.4	4.2093	0.03570	0.27750	0.00990
2	872.6	880	7.4	4.2093	0.03570	0.27750	0.00990
3	415.1	418.6	3.5	2.002'	0.01688	0.15666	0.00264
3	415.1	418.6	3.5	2.0024	0.01666	0.15666	0.00264
3	415.1	418.6	3.5	2.0024	0.01688	0.15666	0.00264
4	339	330	0.0				

Calculation of $2^{\prime}_{\mu}/2^{\prime}_{\mu}$ for SeO₄ at 25°C

 $\sum G(u) \Delta u = 0.038$

 $\sum G(u) \Delta u = 0.0' t'$

21/21 = 1.038 at 25°C

-700

-80-

TABLE X

Calculation of Q_1^2/Q_1^2 for SeV, at $100^{\circ}C$

i	W ₂₁ (cm ⁻¹)	$u_{11}(cm^{-1})$	LM _i (cm ⁻¹)	¹² 21	i.u ₁	0(u ₂₁)	G(u)4u
1	634	834	0.00				
2	872.6	880	7.4	3.3633	0.02147	0.24609	0.00602
2	872.6	060	7.4	3.3633	0.02447	0.24609	0.00602
2	872.6	8SO	7.4	3.3633	0.02447	0.24609	0.00602
3	415.1	418.6	3.5	2.6000	0.01200	0.12797	0.00164
3	415.1	416.6	3.5	1.6000	0.01280	0.12797	0.00164
3	41.5.1	418.6	3.5	1.6000	0.01280	0.12797	0.00164
4	339	539	ΰ₀O				4.

 $\sum C(u) \Delta u = 0.023$

4/41 = 1.025 at 100°C

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				and and the second in	and and the second second		
i	w _{2i} (cm ⁻¹)	v ₁₁ (cm ⁻¹)	(mi(ca-1)	u ^{SI}	Δu _i	C(u21)	6(u) <i>i</i> u
1	834	85 ⁴ +	0.0				
5	872.6	880	7.4	2.3990	0.02035	0.18304	0.00372
2	872.6	053	7.4	2.3990	0.02035	0.18304	0.00372
2	872.6	860	7.4	2.3990	0.02035	0.18304	0.00372
3	415.1	418.6	3.5	1.1412	0.00962	0.09509	04000896
3	415.1	41.0.6	3.5	1,1412	0.00962	0.09309	
3	415.1	410.6	3.5	1.1412	0.00962	0.09309	
4	339	339	0.0				
						A REAL PROPERTY AND INCOME.	The second second second second

Calculation of $\frac{1}{2}/\frac{1}{4}$ for $\frac{1}{2}$ at 250°C

 $\Sigma G(u) \Delta u = 0.014$

	-		Change and an and an and a state		And the Real Property lies of the		
i	^u 2i	^{1/} 11	∆w _i	u _{2i}	∆ u _i	G(u ₂)	G(u2)an
1	cm ⁻¹ 708	cm ⁻¹ 708	cm ⁻¹ 0.0				
2	662	662	0.0				
2	662	662	0.0				
3	783.8	794•7	11.1	4.1273	0.05698	0.27410	0.01562
3	783.8	794.7	11.1	4.1273	0.05698	0.27410	0.01562
3	763.8	794.7	11.1	4.1273	0.05698	0.27420	0.01562
4	459+7	463.8	4.1	2.4205	0.02155	0.26455	0.00398
4	459.7	465.8	4.7	2.4205	0.02155	0.18455	36500°0
lş.	459.7	463.0	4.1	2.4205	0.02155	0.16455	0.00398
5	405	405	0.0				
5	405	405	0.0				
5	405	405	0.0				
6	245	245	0.0				
6	245	245	0.0				
6	2 ⁴ +5	245	0.0				

Calculation of 2/21 for SoF6 at 0°C

∑0(u)au = 0.059

 $0'_2/0'_1 = 1.059 \text{ at } 0^{\circ}C$

TABLE XIII

i	^v 21	v ٦;	A <i>w</i>	^u 21	Δu.	C(u_2)	0(u_)4u
1	cm-1 708	em-1 708	cm ⁻¹ O				
2	662	662	о				
5	662	662	0				
3	783.8	79407	11.2	3.7613	0.05220	0.25006	0.01351
3	783.8	794.07	21.1	3.7015	0.05220	0.25886	0.01351
3	783.8	794.07	32.1	3.7813	0.05220	0.25886	0.01351
4	459.7	463.8	1:.1	2.2178	0.02974	0.17124	0.00558
4	459.7	463.8	4.02	2.2178	0. 1974	0.1712'+	0.00538
4	459.7	463.8	4.2	2.2178	0.01974	0.17124	0.00558
5	405	405	0.0				
5	405	405	0.0				
5	405	405	6.0				
6	245	245	0.0				
6	245	245	0.0				
6	245	245	0.0				

Calculation of $\frac{1}{2}/\frac{1}{4}$ for eF_6 at 25°C

ZG(u)au = 1.051

2/31 = 1.051 at 25°0

TABLE XIV

Calculation of $\frac{1}{2}/\frac{1}{2}$ for SeF₆ at 100°C

i	N.ST	v li	∆ <i>u</i> _j	u _{2i}	∆u <u>₁</u>	G(u ₂)	С(u ₂)Ди
1	cm-I 708	cm ⁻¹ 708	cm ⁻¹ 0.0				
2	662	662	0.0				
2	662	662	0.0				
3	783.7	794.7	11.1	3.0215	0.04171	0.22024	0.00919
3	783.7	794.7	21.2	3.0213	0.04171	0.22024	0.00919
5	783.7	794.7	12.1	3.0215	0.04171	0.22024	0.00919
4	459.7	463.0	4 <u>, 1</u>	1.7719	0.01577	0.14046	0.00215
l _k	459.7	463.8	14.2	1.7719	0.01577	0.14046	0:00215
4	459.7	463.8	4,2	1.7719	0.01577	0.14046	0.00215
5	405	405	0.0		1.0.1		
5	405	405	0.0				
5	405	405	0.0				
6	245	245	0.0				
6	245	245	0.0				
6	245	245	0.0				

 $\Sigma G(u) \Delta u = 0.034$

2/1 = 1.034 at 100°C

TABLE XV

Calculation	oî	21	3	for	SeF	zt	250°C	
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i	^W 2i	^{v/} li	۵۷ <u>i</u>	u ₂₁	Δu _i	G(u ₂)	G(u ₂)Au
1	cm-1 708	cm ⁻¹ 708	cm ⁻¹ 0.0				
2	662	662	0.0			-	
2	662	662	0.0				
3	783.8	794•7	11.1	2.1846	0.02975	0.16904	0.00503
3	783.8	79 ⁴ •7	11.1	2,1846	0.02975	0.1690%	0.00503
5	783.8	794.7	11.1	2.1848	0,02975	0.16904	0.00503
Ļ	450:1	463.8	4.1	1.2639	0.01125	0.1.0262	0.00115
4	459.7	463.8	4.1	1.2639	0.01125	0.10262	0.00115
4	459.7	463.8	4.1	1.2639	0.01125	0.10262	0.00115
5	4:05	4:05	0.0				
5	405	405	0.0				
5	405	405	0.0				
6	245	245	0.0				
6	245	245	0.0				
6	245	245	0.0				

∑C(u)4u = 0.029

$$Q_{1}^{1}/Q_{1}^{1} = 1.019 \text{ at } 250^{\circ}C$$

PARLE XVI

Calculation of $\frac{1}{\sqrt{2}}/\frac{1}{\sqrt{2}}$ for H Se at $0^{\circ}C$

i	۳J	^w 2	ĹM	^u 2	Ĺu	0(u ₂)	G(u)Lu
1	cm-1 2260.7	cm-1 2259.6	cm-1 0.9	11.8988	0.00/4739	0.41597	0.0020
2	1074.4	1073.8	0.6	5.6540	0.002977	0.32671	0.0010
3	2350.7	2349.7	2.0	12.3721	0.005265	0.41917	0.0022

ΣG(u)/m = 0.0052

 $\frac{1}{2}$ for H_2 se at $0^{\circ}C = 1.005$

TABLE NVII

Calculation of $\frac{1}{2}/\frac{1}{1}$ for H_2 is at 25°C

i	^U l	^w 2	Ĺч	^u 2	<i>L</i> 11	6(u ₂)	C(u)Lu
1	cm ⁻¹ 2260.7	cm-1 2259.8	cm-1 0.9	10.9010	0.004342	0.40829	0.0013
2	1074.4	1073.8	0.6	5.1800	0.002894	0.31263	0.0009
3	2350.7	2349.7	1.0	21.3347	0.004824	0.41178	0.0020

 $\Sigma G(u)/u = 0.0047$

 $u_2^{1/2}$ for u_2^{30} at $25^{\circ}c = 1.005$

TABLE XVIII

Calculation of $\frac{1}{2}/\frac{1}{2}$ for H_2 at $100^{\circ}C$

i	w1	w 2	ĹIJ	u ₂	Δu	G(u ₂)	C(u)&u
1	cm-1 2260.7	cm-1 2259.8	ст- 0.9	8.7102	0.003469	0.38556	0.0013
2	1074.4	1073.8	0.6	4.1369	0.002313	0.27458	0.0006
5	2350.7	2349.7	1.0	9.0567	0.003854	0.38970	0.0015
5	2350.7	2349.7	1.0	9.0567	0.003854	0.38970	0

-85-

3/4 for Hose at 100°C = 1.003

TAPLE XIX

i	w ₁	л ^S	ÈM	^u 2	ĹIJ	G(u ₂)	G(u)/u
1	cm 2260.7	cm 2259.8	cm Ui9	6.2129	0.002474	0.34119	0.0008
2	1074.4	1073.8	0.6	2.9522	0.001650	0.21636	0.0004
3	2350.7	2349.7	1.0	6.4600	0:002749	0.34676	0.0010

Calculation of 01/01 for H2Se at 250°C

 $\sum G(u) du = 0.0022$

 $\frac{1}{2}$ for H_2 Se at 250°C = 1.002

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-96-