THE STUDY IN THE LABORATORY

OF

SELENIUM ISOTOPE EFFECTS

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SCOPE AND CONTENTS: The methods available for the calculation of ratios of partition functions for isotopic molecules were examined critically and compared. A number of calculations were made for carbon as well as for selenium systems using the exact method rather than an approximate one.

Improvements were made to the sample handling system of the mass spectrometer to prevent sample cross-contamination and to reduce the time needed for sample changeover.

Four sets of experiments were performed. The kinetic isotope effects in the reductions to Se^{o} of Se^{Vl} and Se^{lV} were studied as were the isotope exchange reactions between Se^{o} and Se^{lV} and between Se^{lV} and Se^{Vl}. Estimates were made of the ratios of rate constants and isotope exchange equilibrium constants for ^{82}Se and ^{76}Se in these systems and these were compared with the theoretical values.

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TABLE OF CONTENTS

II. THEORY

III. EXPERIMENTS

IV. RESULTS AND DISCUSSION

V. APPENDICES

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

During the last quarter of a century many studies have been made of the differences in chemical properties of isotopic molecules and of the variations in nature of isotopic abundances. On the one hand, the chemical studies have provided information regarding the nature of chemical reactions and of the activated complexes postulated by the transition state theory, while on the other, they have been useful in suggesting the mechanisms which must be invoked in order to explain the abundance variations observed in nature.

In 1960 Krouse (1) reported the study of a number of selenium samples of geological and biological origin which revealed that the isotopes of selenium are fractionated in nature. The fractionations reported are smaller than those which have occurred in sulphur from similar sources, but the general trends for both elements are the same.

The present work is concerned with the study of selenium isotope fractionations brought about in chemical processes in the laboratory. Apart from their intrinsic interest such studies are of importance from two points of view. Firstly, because of the general chemical similarities between sulphur and selenium, it is of interest to compare their respective isotope fractionations in similar chemical reactions, while secondly, a study of selenium isotope fractionations in the laboratory is necessary if the fractionations occurring in nature are to be explained satisfactorily.

Four experiments have been performed, in which two kinetic and two equilibrium isotope effects have been studied. These are the isotope effects in:

The reduction of selenite (Se^{IV}) to Se^{o}

The reduction of selenate (Se^{VI}) to Se^{o}

The equilibrium between Se^{IV} and Se^{VI}

The equilibrium between Se^{IV} and Se^{o}

The reductions of sulphate and sulphite have been studied (2) and while the reduction of selenite has been examined under similar conditions, because the reduction of selenate is difficult, the conditions under which it has been studied are rather different from those commonly used for sulphate reductions.

Attempts have been made (3,4) to detect exchange between sulphate and sulphite in chemical systems, but very little evidence for such exchange has been found. The corresponding selenium exchange has been studied, equilibration being allowed to proceed for longer periods of time than has been attempted in the sulphur experiments.

Haissinsky and Pappas (5) reported isotopic exchange between Se^{VI} and Se^{IV} in strong HCl solutions and have pointed out that it is much faster than the corresponding sulphur exchange. An experiment has been performed to determine whether there is isotope fractionation involved in the equilibrium.

Analyses of variations in the $^{82}Se:^{76}Se$ ratios of selenium samples have been made using selenium hexafluoride in the mass spectrometer described by Krouse. A number of improvements have been made in the sample preparation procedure and to the gas handling system of the mass spectrometer as well as to the mass spectrometer itself. Comparisons of selenium samples have been made using the "del" notation, where, for a sample X:

$$\delta^{82}\mathrm{Se} = \frac{\left(\frac{^{82}\mathrm{Se}}{^{76}\mathrm{Se}}\right)_X - \left(\frac{^{82}\mathrm{Se}}{^{76}\mathrm{Se}}\right)_S}{\left(\frac{^{82}\mathrm{Se}}{^{76}\mathrm{Se}}\right)_S} \times 1000 \ ^{o}/oo$$

Rather than use the same standard throughout the work, it has been found convenient to use a number of standards, each one appropriate to the experiment under consideration at the time.

Calculations have been made, using spectroscopic data, of the theoretical values of the isotope effects studied. The results of these calculations are presented in the Results and Discussion section. A number of improvements have been made in the methods used for the calculation of isotope effects, and these are illustrated by calculations of carbon isotope effects as well as being incorporated into the selenium calculations.

A set of tables has been prepared of the fractionation resulting in the substrate and product material for different fractions of reaction and ratios of rate constants for first order competing isotopic reactions. These tables are useful in the interpretation of observed isotope effects and are extensively referred to in the Results and Discussion section.

II. THEORY

An isotope effect, or isotope fractionation, is said to occur when the relative abundances of the isotopes of an element in some system are altered by chemical means, and is a result of slight differences in the chemical properties of these isotopes. Such an effect may occur when two chemical systems containing the element in question co-exist in chemical equilibrium (equilibrium isotope effect) or when one or more such systems change their identity in the course of a chemical reaction (kinetic isotope effect). The principles governing isotope fractionation are well understood, and it is possible, using the data of molecular spectroscopy, to predict the extent to which fractionation may be expected to occur in both the equilibrium and kinetic cases.

2.1 Equilibrium Isotope Effects

Although chemical equilibrium may be considered as that condition of a chemical system where the rate at which a forward reaction is taking place is exactly balanced by the rate of the reverse reaction, the theory of equilibrium isotope effects is best considered in terms of the statistical mechanics of a system of particles in dynamic equilibrium. It should be noted that such a treatment does not consider the time taken to attain equilibrium or whether there in fact exists a mechanism or series of mechanisms by which equilibrium may be attained.

Consider the isotope exchange reaction:

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1$$

where the subscripts 1,2 refer to light and heavy isotopes of the element under consideration and A and B are molecules containing this element. Numerous workers (6,7,8,9,10) have derived the following expression for the equilibrium constant:

$$K = \left(\frac{Z'_{A_2}}{Z'_{A_1}}\right)^{a} \Big/ \left(\frac{Z'_{B_2}}{Z'_{B_1}}\right)^{b} = \left(\frac{N_{A_2}}{N_{A_1}}\right)^{a} \Big/ \left(\frac{N_{B_2}}{N_{B_1}}\right)^{b}$$

where, for example, Z'_{A_2} represents the partition function for the molecule A when it contains the heavy isotope of the element in question, and N_{A_2} is the number of molecules of the type A_2. Such an expression for K in terms of partition function ratios is simply an alternative statement of the law of mass action for a mixture of perfect gases, and instead of ratios of the numbers of molecules it is, of course, permissible to consider ratios of partial pressures, activities or chemical potentials.

2.2 Evaluation of Partition Function Ratios

The partition function of a molecule depends upon its mass, moments of inertia, fundamental vibrational frequencies, the temperature of the enclosure and the nuclear spins of the constituent atoms. It is, however, possible to evaluate ratios of partition functions for isotopic molecules using only vibrational frequencies.

Following Herzberg (11):

$$Z' = \frac{(2\pi Mk'T)^{3/2}}{h^3} \cdot \frac{Vk'T}{hcB} \prod_{i}^{3n-5} \frac{e^{-u_i/2}}{1-e^{-u_i}} \left[\frac{1}{\sigma} \prod (2I+1) \prod \frac{(2I'+1)^2}{2} \right]$$

$$Z' = \frac{(2\pi M k' T)^{3/2}}{h^3} V \sqrt{\frac{\pi}{ABC}\left(\frac{k'T}{hc}\right)^3} \prod_i^{3n-6} \frac{e^{-u_i/2}}{1-e^{-u_i}} \left[\frac{1}{\sigma} \prod (2I+1) \prod \frac{(2I'+1)^2}{2}\right]$$

for diatomic (or linear polyatomic) and polyatomic molecules respectively, where

n is the number of atoms in the molecule

M is the total molecular mass

k' is the Boltzmann constant

A,B,C are the rotational constants of the molecule, related to its principal moments of inertia by equations of the type

$$A = \frac{h}{8\pi^2 c I_A}$$

The term u_i is related to ν_i the i^{th} fundamental frequency of the molecule by the equations:

$$u_i = \frac{\epsilon_i}{k'T} = \frac{h\nu_i}{k'T}$$

and the bracketed terms are symmetry and nuclear spin factors which cancel out in later expressions and have no effect on the estimation of isotope effects. Their precise nature is discussed by Herzberg (11). A number of assumptions are implied in these expressions, of which the following should be mentioned:

1. For the rotational contributions to Z', the rigid rotor model is adopted and it is supposed that in all cases this term will have reached its high temperature or classical limit. The implications of this approximation have been discussed by Herzberg (11) and Cragg (10). It is further assumed that there are no vibration-rotation interactions.

2. For the vibrational contributions to Z', the harmonic oscillator model is used. The vibrations of real molecules are not harmonic, but the approximation is not greatly in error when considering the ratios of partition functions for isotopic molecules, provided the observed fundamental frequencies are used rather than the zero order frequencies, and that the temperature is low enough so that only low lying vibrational states have appreciable populations. Hulston (12) has shown how anharmonicity corrections can be of significance at high temperatures. For the majority of molecules, only the observed fundamentals are available, since it is in only a few cases that anharmonicity constants have been studied.

3. The only energies which require evaluation are those of molecular vibrations. Since the potential energy curves for isotopic molecules are essentially identical, the vibrational energies for a given molecule may be measured relative to the bottom of this curve, since the correction term relating this energy to the arbitrary common zero for all molecules considered would appear in both the numerator and denominator of the expression for an equilibrium constant.

Thus for two isotopic, polyatomic molecules, omitting for convenience, the nuclear spin and symmetry terms:

$$\frac{Z'_2}{Z'_1} = \left(\frac{M_2}{M_1}\right)^{3/2} \left(\frac{I_{A_2}\; I_{B_2}\; I_{C_2}}{I_{A_1}\; I_{B_1}\; I_{C_1}}\right)^{1/2} \prod_{i}^{3n-6} \frac{e^{-u_{2i}/2}}{1-e^{-u_{2i}}} \quad \frac{1-e^{-u_{1i}}}{e^{-u_{1i}/2}}$$

Urey (13) and Bigeleisen and Mayer (7) have shown by different approaches how it is possible to evaluate this type of expression without knowledge of the moments of inertia. Urey considers the Teller-Redlich product rule (14,15) which states that the quantity:

$$\frac{\prod_{i}^{3n-6} u_i^2 \prod_{j} m_j^3}{M^3 I_A I_B I_C}$$

(where the m_j's are the atomic masses in the molecule) is invarient under isotopic substitution. Thus for two isotopic species:

$$\left(\frac{M_2}{M_1}\right)^{3/2} \left(\frac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}}\right)^{1/2} = \prod_{i}^{3n-6} \frac{u_{2i}}{u_{1i}} \prod_{j} \left(\frac{m_{2j}}{m_{1j}}\right)^{3/2}$$

so that

$$\frac{Z'_2}{Z'_1} = \prod_{j} \left(\frac{m_{2j}}{m_{1j}}\right)^{3/2} \prod_{i}^{3n-6} \frac{u_{2i}}{u_{1i}} \cdot \frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}} \cdot \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}$$

Now the terms $\left(\frac{m_{2j}}{m_{1j}}\right)^{3/2}$ will not affect the expression for an equilibrium constant since they will appear in both numerator and denominator, so it is convenient to calculate the modified ratio

$$\frac{Z_2}{Z_1} = \prod_{i}^{3n-6} \frac{u_{2i}}{u_{1i}} \cdot \frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}} \cdot \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \qquad (1)$$

Bigeleisen considers the relationship between the ratio $\frac{Z'_2}{Z'_1}$ and its classical limit, arriving at the same expression for $\frac{Z_2}{Z_1}$.

Two simplifications have been widely used for the evaluation of equation (1), due to Urey (13) and Bigeleisen and Mayer (7). These may be written:

$$\ln \frac{Z_2}{Z_1} = \sum_{i}^{3n-6} \ln \frac{u_{2i}}{u_{1i}} + \sum_{i}^{3n-6} \delta_i \coth x_i \qquad (2)$$

where

$$x_i = \frac{u_{1i} + u_{2i}}{4} \quad \text{and} \quad \delta_i = \frac{u_{1i} - u_{2i}}{2}$$

and

$$\frac{Z_2}{Z_1} = 1 + \sum_{i}^{3n-6} G(u_i)\Delta u_i \qquad (3)$$

where

$$G(u_i) = \frac{1}{2} - \frac{1}{u_{2i}} + \frac{1}{e^{u_{2i}}-1} \quad \text{and} \quad \Delta u_i = u_{1i} - u_{2i}$$

Two other approximations have been developed due to Tatevsky (16) and Kuznetsova et al (17). That of Tatevsky involves substituting for the vibrational partition function ratio the product of the ratios of fundamental frequencies. Application of the Teller Redlich product rule in this case yields

$$\frac{Z_2}{Z_1} = 1$$

so that the deviation of an equilibrium constant from unity is attributed solely to the symmetry number ratios. Kuznetsova and his coworkers assume diatomic point mass molecules and derive expressions for $\left(\frac{M_2}{M_1}\right)^{3/2}$ and $\frac{I_{A2}}{I_{A1}}$ in terms of the reduced masses of the molecules and the isotopic mass difference and then make further assumptions about the temperature variation of the equilibrium constant. Their results are then extended to polyatomic molecules. Neither of these approximations give satisfactory agreement between their predictions and predictions based upon the exact expression.

For all calculations, unless otherwise stated, the exact expression was evaluated using an I.B.M. program due to Hulston (12).

2.3 Comparison of the Expressions of Urey and Bigeleisen

While Bigeleisen's expression is somewhat more convenient for purposes of computation, especially in view of the fact that values of the function G(u) are tabulated (7), Urey's expression is, in fact, a more accurate approximation. Both expressions involve power series expansions in terms of a Δ_i, a number proportional to $(\nu_{1i} - \nu_{2i})$ the frequency shift in the ith fundamental frequency of the molecule, caused by isotopic substitution, and normally these expressions are terminated at the 1st order term in Δ_i. However, in the logarithmic expression developed by Urey, the term in Δ^2 has a zero coefficient, so that the errors involved are due to terms in Δ^3 and higher, while the expression developed by Bigeleisen has a non-zero term in Δ^2.

To demonstrate the improved accuracy of the Urey expression over the more generally used Bigeleisen expression, a sample set of calculations has been performed for the carbon isotope exchange reaction

$$\left. {}^{12}CO_2 + {}^{13}CO_3^{=} \xrightleftharpoons{K} {}^{13}CO_2 + {}^{12}CO_3^{=} \right]_{25^\circ C}$$

K has been evaluated in three different ways, using the "exact" expression in equation (1) and equations (2) and (3), the results being presented in Table I.

TABLE I

Calculations of Partition Function Ratios and the ^{13}C Exchange Equilibrium Constant for the CO_2-$CO_3^{=}$ System at 25°C

	Method		
	Exact	Urey	Bigeleisen
$\frac{z(^{13}CO_3^{=})}{z(^{12}CO_3^{=})}$	1.19263	1.1926	1.1750
$\frac{z(^{13}CO_2)}{z(^{12}CO_2)}$	1.18371	1.1837	1.1678
K	1.00754	1.0075	1.0062

Table I shows that the value of the equilibrium constant calculated using Urey's expression is essentially in agreement with that obtained by the exact method, while calculations using Bigeleisen's expression introduce a slight error. The value of K given above differs from the value 1.012 calculated by Urey (13) because here the calculation was made using more recent frequency data. The frequencies used, together with the results of further calculations over a range of temperatures, are presented in Appendix 5.2. and 5.3.

2.4 Theory of Kinetic Isotope Effects

The theory of isotope fractionation in the course of chemical kinetics is considered in terms of the theory of absolute reaction rates and was first treated in detail by Bigeleisen (18). The theory of absolute reaction rates was developed by Eyring (19), Evans and Polanyi (20) and others (21) while certain aspects of it have been reconsidered by Slater (22) who arrives at essentially the same results by applying more rigorous arguments to the problem.

The theory rests upon two postulates. Firstly, that there is an initial state of the reactants and a final state of the products between which exists an intermediate activated state which is in chemical equilibrium with the initial state. Secondly, that the "activated complexes" of the activated state decompose at a definite rate to form the products of the reaction.

The expression for the rate constant, k, derived from these postulates may be written (21):

$$k = \frac{k'T}{h} \cdot \kappa t K$$

where κ represents a transmission coefficient

t represents a quantum mechanical tunnelling correction

and K represents the equilibrium constant for the equilibrium between the reactants and activated complexes.

Considering now the case where the reactants contain either the light or heavy isotope of the element of interest:

$$\frac{k_1}{k_2} = \frac{\kappa_1}{\kappa_2} \cdot \frac{t_1}{t_2} \cdot \frac{K_1}{K_2}$$

The assumptions are made that $\kappa_1 = \kappa_2$

and that $t_1 = t_2$

(The validity of these identities is discussed by Bigeleisen and Wolfsberg (23)).

so that:

$$\frac{k_1}{k_2} = \frac{K_1}{K_2}$$

and from the previous discussion of equilibrium constants:

$$\frac{K_1}{K_2} = \frac{Z'^{\ddagger}_1}{Z'^{\ddagger}_2} \cdot \frac{Z_2}{Z_1}$$

where Z_1, Z_2 refer to partition functions for the reactants and $Z'^{\ddagger}_1$, $Z'^{\ddagger}_2$ refer to partition functions for the activated complexes where, if there are several reactant molecules, A, B, C, participating in the reaction,

$$Z = Z(A) \, . \, Z(B) \, . \, Z(C) \ldots$$

The ratio $\frac{Z_2}{Z_1}$ may be evaluated in the manner discussed previously, but before considering the evaluation of $\frac{Z'^{\ddagger}_1}{Z'^{\ddagger}_2}$ it is necessary to consider the nature of the activated complex. It is supposed by the theory that one of the vibrational degrees of freedom of the activated complex is non-genuine, corresponding to the cleavage (or formation) of a bond, and is equivalent to a translation along the reaction coordinate. Suppose that in the activated complex the Lth vibrational mode is non-genuine, so that u_L has a pure imaginary value

The vibrational contribution to the partition function of an activated complex will then take the form

$$\prod_{i\neq L}^{3n^{\ddagger}-7} \frac{e^{-u_i/2}}{1-e^{-u_i}}$$

where $n^{\ddagger}$ is the number of atoms in the activated complex, and i does not take the value L

so that

$$\frac{Z'^{\ddagger}_{2}}{Z'^{\ddagger}_{1}} = \left(\frac{M_2^{\ddagger}}{M_1^{\ddagger}}\right)^{3/2} \left(\frac{I_{A_2}^{\ddagger}\, I_{B_2}^{\ddagger}\, I_{C_2}^{\ddagger}}{I_{A_1}^{\ddagger}\, I_{B_1}^{\ddagger}\, I_{C_1}^{\ddagger}}\right)^{1/2} \prod_{i\neq L}^{3n^{\ddagger}-7} \frac{e^{-u^{\ddagger}_{2i}/2}}{1-e^{-u^{\ddagger}_{2i}}}\; \frac{1-e^{-u^{\ddagger}_{1i}}}{e^{-u^{\ddagger}_{1i}/2}}$$

The Teller Redlich product rule still applies for all $3n^{\ddagger}-6$ vibrations, i.e.

$$\frac{u_L^{\ddagger 2} \prod_{i\neq L}^{3n^{\ddagger}-7} u_i^{\ddagger 2} \prod_j m_j^3}{M^{\ddagger 3}\, I_A^{\ddagger}\, I_B^{\ddagger}\, I_C^{\ddagger}}$$

is invariant under isotopic substitution, so that:

$$\left(\frac{M_2^{\ddagger}}{M_1^{\ddagger}}\right)^{3/2} \left(\frac{I_{A_2}^{\ddagger}\, I_{B_2}^{\ddagger}\, I_{C_2}^{\ddagger}}{I_{A_1}^{\ddagger}\, I_{B_1}^{\ddagger}\, I_{C_1}^{\ddagger}}\right)^{1/2} = \frac{u^{\ddagger}_{2L}}{u^{\ddagger}_{1L}} \prod_{i\neq L}^{3n^{\ddagger}-7} \frac{u^{\ddagger}_{2i}}{u^{\ddagger}_{1L}} \prod_j \left(\frac{m_{2j}}{m_{1j}}\right)^{3/2}$$

and

$$\frac{Z'^{\ddagger}_{2}}{Z'^{\ddagger}_{1}} = \prod_{j}\left(\frac{m_{2j}}{m_{1j}}\right)^{3/2}\frac{u^{\ddagger}_{2L}}{u^{\ddagger}_{1L}}\prod_{i\neq L}^{3n^{\ddagger}-7}\frac{u^{\ddagger}_{2i}}{u^{\ddagger}_{1i}}\cdot\frac{e^{-u^{\ddagger}_{2i}/2}}{e^{-u^{\ddagger}_{1i}/2}}\cdot\frac{1-e^{-u^{\ddagger}_{1i}}}{1-e^{-u^{\ddagger}_{2i}}}$$

and as before, for purposes of evaluation, it is only necessary to consider the modified ratio:

$$\frac{Z''^{\ddagger}_{2}}{Z''^{\ddagger}_{1}} = \frac{u^{\ddagger}_{2L}}{u^{\ddagger}_{1L}}\prod_{i\neq L}^{3n^{\ddagger}-7}\cdot\frac{u^{\ddagger}_{2i}}{u^{\ddagger}_{1i}}\cdot\frac{e^{-u^{\ddagger}_{2i}/2}}{e^{-u^{\ddagger}_{1i}/2}}\cdot\frac{1-e^{-u^{\ddagger}_{1i}}}{1-e^{-u^{\ddagger}_{2i}}}$$

writing this as

$$\frac{Z''^{\ddagger}_{2}}{Z''^{\ddagger}_{1}} = \frac{u^{\ddagger}_{2L}}{u^{\ddagger}_{1L}}\cdot\frac{Z_{2}^{\ddagger}}{Z_{1}^{\ddagger}} = \frac{\nu^{\ddagger}_{2L}}{\nu^{\ddagger}_{1L}}\cdot\frac{Z_{2}^{\ddagger}}{Z_{1}^{\ddagger}}$$

it can be seen that

$$\frac{k_{1}}{k_{2}} = \left(\frac{Z_{2}}{Z_{1}}\Big/\frac{Z_{2}^{\ddagger}}{Z_{1}^{\ddagger}}\right)\cdot\frac{\nu^{\ddagger}_{1L}}{\nu^{\ddagger}_{2L}}$$

The expression in the bracket has the form of an equilibrium constant, and may be evaluated as such. This term is temperature dependent and tends to the value unity as the temperature increases. The other term represents the high temperature limit of the ratio of the rate constants.

It is possible to regard this second term as the ratio of two imaginary frequencies which are determined by force constant analysis of the activated state "molecules" for the two isotopic cases, or, as the ratio of the inverses of the square roots of the effective masses of the activated complexes as they traverse the critical region of the reaction coordinate. These two approaches are equivalent since the frequency which is considered to take on an imaginary value and a non-genuine character is the stretching frequency of the various components of the activated complex. The former approach has been discussed by Eyring (21) while the latter has been developed by Slater (22) for unimolecular reactions involving a single bond rupture. For reactions involving two bond extensions and/or contractions, known as three centre reactions, Bigeleisen and Wolfsberg (23) have developed appropriate expressions for effective mass ratios.

III. EXPERIMENTS

The procedures for the isotope fractionation studies, the method for preparing mass spectrometer samples, the mass spectrometer and the isotopic analysis procedure are described below.

In all the fractionation studies the same stock solutions of sodium selenite (Na_2SeO_3) and sodium selenate (Na_2SeO_4) were used. B.D.H. selenite (lot 25611) and selenate (lot 15711) were made up into half molar solutions, the molality being determined by direct weighing and confirmed by gravimetric determination of selenium.

A number of experiments were performed for which the resultant selenium was not analysed. This was because it was found necessary to concentrate on repeat analyses rather than to perform single analyses of all the selenium samples available. Only those experiments are described for which isotopic analyses were performed.

Selenium samples were converted to SeF_6 for mass spectrometer analysis. It was found that samples prepared from 100% reductions of aliquots from the stock selenite and selenate had the same $^{82}Se:^{76}Se$ ratio as the cylinder SeF_6, so that any of these could be used as an isotopic standard.

3.1 Fractionation Studies

Before beginning the selenium isotope effect studies it was necessary to perform a number of preliminary experiments to determine conveniently fast and simple methods for reducing selenate and selenite to selenium and for separating Se^{VI} from Se^{IV} in mixtures containing both these oxidation states of the element. The reduction of selenite or selenium dioxide to selenium is simple and a number of reagents may be used, while the reduction of selenate is more difficult. Table II lists the reducing agents for selenate and selenite that have been reported in the literature.

3.1.1 The Reduction of Selenite

The most convenient reducing agent for selenite was found to be ascorbic acid ($C_6H_8O_6$) which gives quantitative reductions quickly at room temperature. The efficiency of reduction is not affected by the presence of selenate or sulphate and is constant between pH8 and pH2. For fractional reductions the percentage reaction can be easily and predictably controlled by the quantity of ascorbic acid added, the stoichiometry of the reaction being:

$$SeO_3^{=} + 2H^+ = H_2SeO_3$$

$$H_2SeO_3 + 2C_6H_8O_6 = Se^0 + 2C_6H_6O_6 + 3H_2O$$

Two sets of reductions were performed, one, at 24°C, varying the percentage reduction, and the other a set of 20% reductions at 3°C and 40°C. These experiments are summarised in Table III. In all cases the procedure was as follows: Na_2SeO_3 and H_2SO_4 in the quantities indicated are mixed with 150 ml of distilled water in a 600 ml beaker. The beaker is immersed in a constant temperature water bath, and after the solution has attained the required temperature, 100 ml of water, at the same temperature and containing the required quantity of $C_6H_8O_6$, is added. The solution is kept in the water bath until the red colloidal Se has settled, after

TABLE II

Reported Reducing Agents for Selenite and Selenate

Agent	Selenite		Selenate		References
	Yes or No	Comments	Yes or No	Comments	
$C_6H_8O_6$	Y				24,25
$FeSO_4$	Y				25
$Fe(OH)_3$	Y		N		26
NH_2NH_2	Y				25,27
$NH_2NH_2H_2SO_4$	Y	In HCl	Y		25,28
$NH_2OH \cdot HCl$	Y	In H_2O			1
HBr			Y	In HCl	29
HCl			Y	To $SeO_3^=$	30
H_2S			Y	To Se+S	31
KI	Y	In HCl			27,28,29,32
SO_2	Y	In HCl	N		25,28
SO_2	Y	H_2SO_4+H_2SO_3	Y	H_2SO_4+H_2SO_3	33
SO_2	Y	In HCl+ $NH_2OH \cdot HCl$	Y	In HCl+ $NH_2OH \cdot HCl$	34

TABLE III

Experimental Plan for Partial Reductions of Sodium Selenite with Ascorbic Acid

Experiment	T°C	% Reduction	Total Se,mg	ml4.2N H_2SO_4	Product Se,mg
1	24	10	1980	12.5	198
2	24	20	990	6.3	198
3	3	20	990	6.3	198
4	40	20	990	6.3	198

which it is filtered through a fine gooch crucible. In cases where the substrate is required, after the initial filtering an excess of $C_6H_8O_6$ is added to the remaining solution and after nucleation the Se collected by further filtering.

3.1.2 The Reduction of Sodium Selenate

In preliminary experiments on the reduction of sodium selenate to selenium, it was found difficult to achieve satisfactory results with some of the methods cited in the literature, notably that of Caley and Henderson (33). A modification of this method, due to de Salas (34), was found to give quantitative reductions. For up to 50 mg Se^{V1}, the solution is diluted to 20 ml; 100 mg $NH_2OH.HCl$ and 30 ml conc. HCl are added and the solution allowed to cool to room temperature. 20 ml of 7% H_2SO_3 is added and the solution left to stand until nucleation of the precipitated Se^o has proceeded to the point where filtration may be performed. For larger quantities of selenium the reagent quantities must be increased proportionately in order to give quantitative reduction.

A more satisfactory method was found, using the fact that HCl can reduce Se^{V1} to Se^{1V} (30, 31), and this was used in all subsequent experiments. Concentrated HCl is added to the selenate solution until it is 30% with respect to HCl. $C_6H_8O_6$ is then added. Production of red Se^o is almost immediate, and when excess $C_6H_8O_6$ is used, recovery of Se^o is quantitative.

In order to study possible isotope effects in the reduction of Se^{V1} it is necessary to perform partial reductions, and attempts to do this in a controlled manner have met with considerable difficulties. Upon the addition of a small amount of $C_6H_8O_6$, sufficient to produce only partial reduction, red Se^o is formed but after a short time disappears. It is either taken up into solution or re-oxidised (25) by a mechanism discussed in section 4.2.

Three experiments were performed, at 22°C in each case, in which partial reductions were achieved. In each of these 10 ml of 0.5 M Na_2SeO_4 together with 50 ml H_2O and 120 ml conc. HCl was used.

1. 881 mg $C_6H_8O_6$ (2.5 meq.) was added to the solution. After the formation of red Se^o, 300 ml H_2O was added. No depletion of the red Se was observed.
2. 881 mg $C_6H_8O_6$ was added to the solution. Red Se^o was formed and at the end of an hour had virtually disappeared. A further 881 mg $C_6H_8O_6$ was added, and more red Se^o formed.
3. The solution was allowed to stand overnight before the addition of 881 mg $C_6H_8O_6$. Red Se^o was formed, some of which was lost back into solution.

In each of the three experiments, the red Se was allowed to nucleate and was recovered for analysis by filtering the solution.

3.1.3 Equilibration of Selenite and Selenate

Previous experiments (3) have shown that exchange between S^{lV} and S^{Vl} in chemical systems either does not occur or is very slow. To study the similar exchange between Se^{lV} and Se^{Vl} two experiments were performed in which equilibration was permitted to proceed for 59 days and 146 days respectively.

The solutions used were in each case 5 ml 0.5 M Na_2SeO_3 and 5 ml 0.5 M Na_2SeO_4 together with 7.5 ml 4.2N H_2SO_4 and 2.5 ml H_2O. The solutions were in sealed 50 ml weighing bottles which were kept in a constant temperature water bath at 25°C for the periods of time mentioned above.

Recovery of Se^o from such mixtures of Se^{lV} and Se^{Vl} is effected using the previously described methods for the reduction of selenium in these oxidation states. $C_6H_8O_6$ is added to reduce the Se^{lV} and then, after filtration, HCl is added to reduce the Se^{Vl}.

In these experiments selenium was present in equimolar quantities in the two oxidation states. The selective reduction procedure has been found, however, to permit quantitative determinations of Se^{lV} and Se^{Vl} when the Se^{lV} to Se^{Vl} ratio is as high as 100:1 or as low as 1:100.

3.1.4 Equilibration of Selenite and Selenium

The experiments of Haissinsky and Pappas (5) indicate that there is isotopic exchange between Se^o and Se^{lV} in strongly acid solutions. A preliminary experiment has been performed to determine whether or not there is isotope fractionation associated with this exchange.

Because rapid exchange only occurs between amorphous Se^o and Se^{lV}, while the exchange between metallic Se^o and Se^{lV} is slow, it is necessary to use freshly reduced selenium. 5 ml 0.5 M Na_2SeO_3 with 12 ml H_2O were added to 105 ml conc. HCl in a 250 ml beaker (giving $\sim$ 10N HCl). 881 mg $C_6H_8O_6$ was added to the solution giving quantitative reduction of the Se^{lV}. After 10 minutes a further 5 ml 0.5 M $NaSeO_3$ was added and the solution stirred for about an hour, until the red Se^o had turned black. The experiment was performed at 10^oC. After the transformation of the Se^o to the metallic form, the solution was filtered to remove Se^o and then the Se^{lV} reduced by the addition of further $C_6H_8O_6$.

3.2 Production of Selenium Hexafluoride

The procedure used is basically the same as that described by Krouse (1) although some details have been changed to increase the efficiency of the process and to reduce the contaminants in the samples.

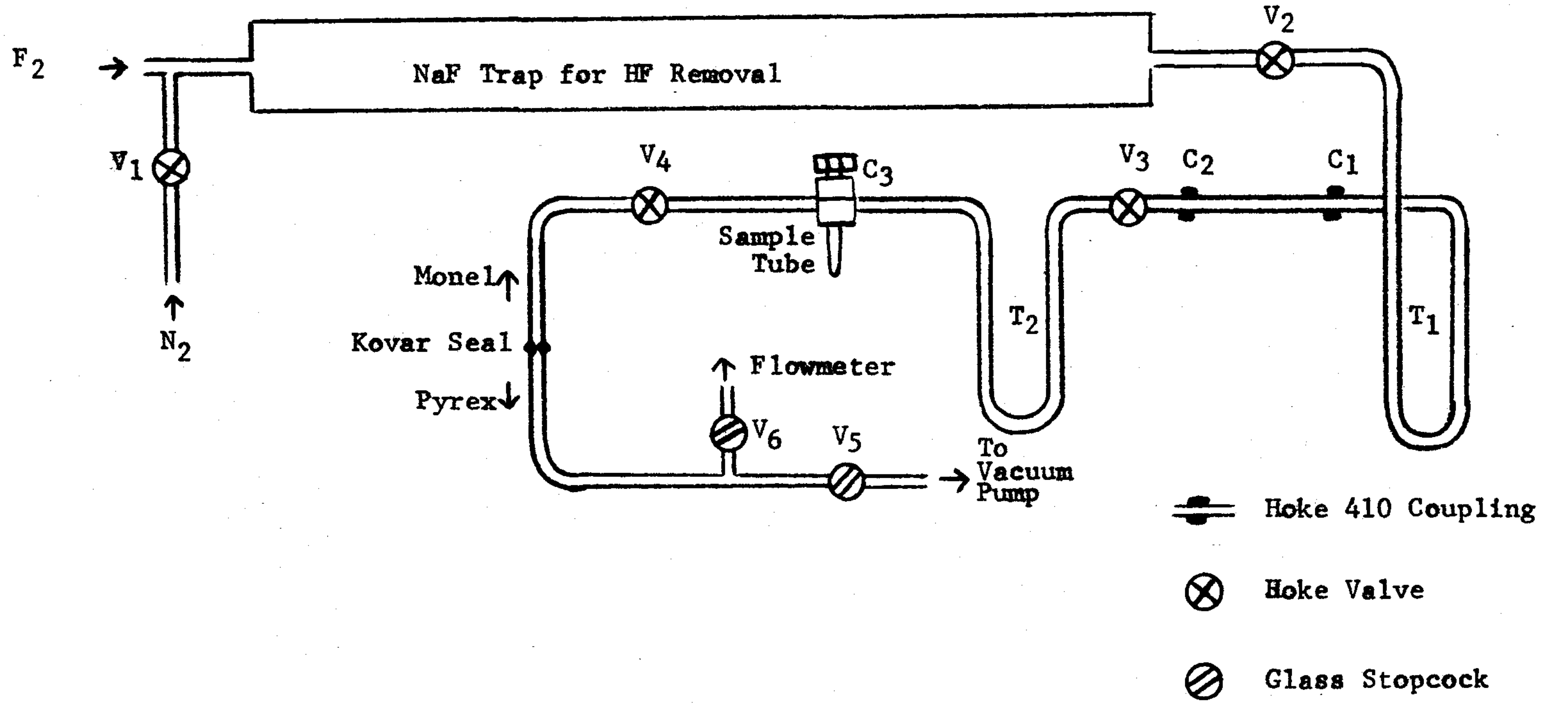
Liquid oxygen is used in the cold traps, rather than liquid air, because it was found that liquid air tended to condense fluorine. Liquid oxygen at -183°C permits the flow of fluorine, boiling point -187°C, without condensation.

The fluorination line is shown schematically in Fig. 1 and the fluorination procedure is as follows. The Se sample ($\sim$10 mg finely powdered elemental Se) is placed, in a boat, of nickel sleeving, in the reaction chamber, and the section of line between C_1 and C_2 is replaced and the couplings tightened. The sample tube is attached to the line at the coupling C_3 and the line evacuated as far as the valve V_2. After pumping on the sample to dry it thoroughly and testing the coupling points for vacuum tightness, the valve V_5 is closed and V_1, V_2 and V_6 opened to give a flow of nitrogen. The flow is adjusted by manipulation of V_1 to give a measured flow rate of 0.2 mole/hr. The two traps T_1 and T_2 are now cooled with liquid oxygen.

With the needle valve of the fluorine cylinder closed, the main valve is opened and closed, and the needle valve adjusted to give a total flow of 0.6 mole/hr after which the main valve of the cylinder is again opened. Fluorine is allowed to pass through the system until detected at the exit of the flowmeter, after which the main valve to the cylinder is closed and the needle valve gradually opened, so as to remove the over-pressure of fluorine from the

FIG. 1

FLUORINE LINE



small volume between these valves.

After fluorination the nitrogen flow is maintained at 0.2 mole/hr for 30 minutes and at 0.4 mole/hr for a further 30 minutes to ensure scavenging of elemental fluorine from the system.

After scavenging, V_2 and V_6 are closed and the line is evacuated. V_3 and V_4 are closed and the liquid oxygen dewar moved from T_2 to the sample tube. T_2 is gently heated to speed the sample transfer, and V_4 is opened briefly, to remove any air which may have leaked in at C_3, before closing the sample tube and removing it from the line.

3.3 Mass Spectrometer

3.3.1 General

The mass spectrometer used in these studies is a 6" radius instrument employing 90° magnetic deflection with first order direction focussing. The spectrometer tube is metal with pyrex pumping leads, cold traps and single stage mercury diffusion pumps at the source and collector. Ions are produced from the gaseous sample in an electron impact source, are accelerated through 2000 volts in the ion gun and enter the analyser tube from an inlet slit 0.15 mm in width. If desired, any accelerating voltage between 1000 and 3000 volts may be used, the higher limit being for low mass number work. Mass separation is effected by an electromagnet with continuous variation in four ranges from $\sim$1000 gauss to $\sim$6000 gauss which covers mass numbers 7 to $\sim$220 at 2000 volts. There is a double collection arrangement with a wide high mass slit of 1.0 mm and a narrow low mass slit of 0.5 mm with a separation of 5.36 mm. For the narrow slit the theoretical resolution is 235 while that attained in practice is 200, adjacent mercury peaks being just resolved.

Ion currents are measured using vibrating reed electrometers while isotope abundances are compared using the null method described by Wanless and Thode (35), a fraction of the signal at the wide slit being fed back to reduce to zero that at the narrow slit. The grid leak resistors used at these collectors are 5 x 10^9 ohms. and 3 x 10^9 ohms. respectively while the feedback resistance at the narrow slit is 6 x 10^9 ohms. The SeF_6 samples yield SeF_5^+ as the most abundant of the ionic species present. $^{76}SeF_5^+$ and $^{82}SeF_5^+$ are collected at the narrow and wide slits respectively. This arrangement gives an instrument sensitivity of 2 ^{o}/oo per cm on the recorder chart with a 1 volt signal at the wide collector.

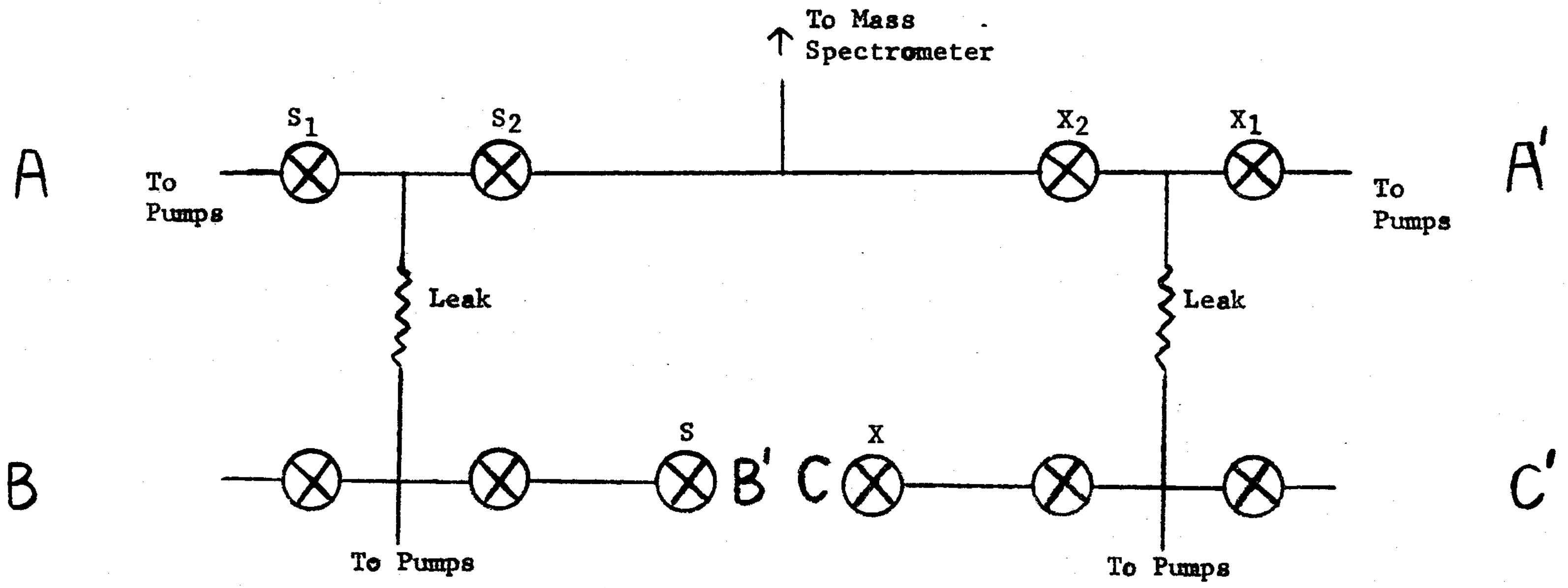
3.3.2 Sample Line

Because of the nature of the sample gas, it is necessary to use an all-metal admission system, which must, of course, have provision for rapid changeover from standard to unknown samples. This was originally attempted with an all-metal magnetic valve, similar in design to the glass model described by Wanless and Thode (35), with stainless steel coated iron bearings resting on conical seats. It was found impossible to attain sufficiently good seating and the minimum leakage obtained was 16% with a sample changeover time of 4 minutes.

A new sample handling system has been constructed, illustrated schematically in Fig. 2, where sample changeover is effected by an array of four Hoke valves. This arrangement gives zero leakage, and so no sample cross-contamination, with an operating time of less than 10 seconds and a sample changeover time of less than 20 seconds.

FIG. 2

SCHEMATIC DIAGRAM OF THE NEW MASS SPECTROMETER SAMPLE HANDLING SYSTEM



Monel and copper tubing were used in the construction of the sample handling system together with Hoke 413 and 411 metal diaphragm valves. The system consists of two sample gas reservoirs (BB' and CC') for the standard and unknown samples, connected by nickel leaks of 5/1000" I.D. and 12" in length to the sample changeover system (AA') and from there by 1/4" I.D. copper tubing to the mass spectrometer ion source. Referring to the valves labelled in AA' and defining $\overline{S_1}$ and S_1 as referring to the valve S_1 in its shut and open states, then the mode ($\overline{S_1}$, S_2, $\overline{X_2}$, X_1) admits the standard to the spectrometer while (S_1, $\overline{S_2}$, X_2, $\overline{X_1}$) admits the unknown.

The sample tubes S and X are attached to the gas reservoirs by Hoke 410 couplings. Full use can be made of the freeze-down fingers for adjustment of sample pressures by using empty sample tubes at the opposite ends of the reservoirs.

The adjustment of sample pressures is necessary because although the balance point for a given sample is independent of sample pressure over a fairly wide range, the sensitivity of the instrument to differences in isotope ratio is directly proportional to it. So, for the comparison of two samples where the null or balance condition only holds for the standard, or possibly is only closely approached for the standard, it is necessary that the instrument sensitivity be exactly the same for standard and unknown.

Because the use of SeF_6 as the sample gas precludes the use of glass reservoirs and of mercury cut-offs and pressure adjustment devices, it is necessary to adjust a sample's pressure by partial freezing or pumping. The possibility of isotope fractionation occurring during such a process cannot be ignored. A series of tests was performed with identical samples for S and X where the pressure of one was altered by freezing or pumping while that of the other was changed by evacuation of one section of the sample line, so that the gas then reoccupied the whole line at a reduced pressure. These experiments showed very little disturbance of the balance point and no appearance of a del between the samples.

3.3.3 Analysis Procedure

The monel sample tube X containing the unknown sample is attached to the sample inlet system at C while the standard is attached at B'. The standard may be either a sample prepared on the fluorine line or SeF_6 from a cylinder of the gas that was reserved for use as a mass spectrometer standard. After evacuation of the sample inlet lines, the two samples are frozen down with liquid air and pumped on for a short time to remove any small amount of air that might have leaked into the sample tubes. The standard and unknown samples are then admitted alternately into the mass spectrometer and their pressures in the sample line adjusted until they give equal signals at the wide collector, after which analysis is performed by the method described by Wanless and Thode.

It was found necessary to perform the analyses rapidly (in $\sim$1/2 hr) and to flush the system with argon between runs to prevent rapid deterioration of the tungsten filament and consequent increase in the noise level on the null trace. This deterioration was caused either by the SeF_6, or F^- remaining after the production of SeF_5^+, attacking the filament. Rapid sample handling combined with argon scavenging of the ion source increases the useful filament life from 3 or 4 analyses to $\sim$ 20.

IV. RESULTS AND DISCUSSION

Each experimental isotope effect quoted below is the mean value of several observations. The experimental precision of individual analyses was improved during the course of this work, initially being ± 1 °/oo and later being brought up to ± 0.1 or 0.2 °/oo. This improvement was made possible by frequent renewal of the filament in the mass spectrometer, and by synchronisation of the Wien oscillator circuits in the vibrating reed electrometers. When the same SeF_6 sample was analysed on two different occasions, the reproducibility was ± 0.2 °/oo. The error limits in the quoted results are indicative of the reproducibility for repeat fluorination and analysis and are the standard deviations of the observations.

4.1 Reduction of Sodium Selenite

4.1.1 Results

Table IV shows the results of the reduction experiments. Column 4 shows the observed isotope effects comparing product Se with the starting material, and Column 5 lists the ratio of rate constants for the reactions:

$$^{76}Se^{1V} \xrightarrow{k_1} {}^{76}Se^{o}$$

$$^{82}Se^{1V} \xrightarrow{k_2} {}^{82}Se^{o}$$

the ratio being estimated using the tables in Appendix 54. Fig. 3 shows the experimental temperature variation of k_1/k_2.

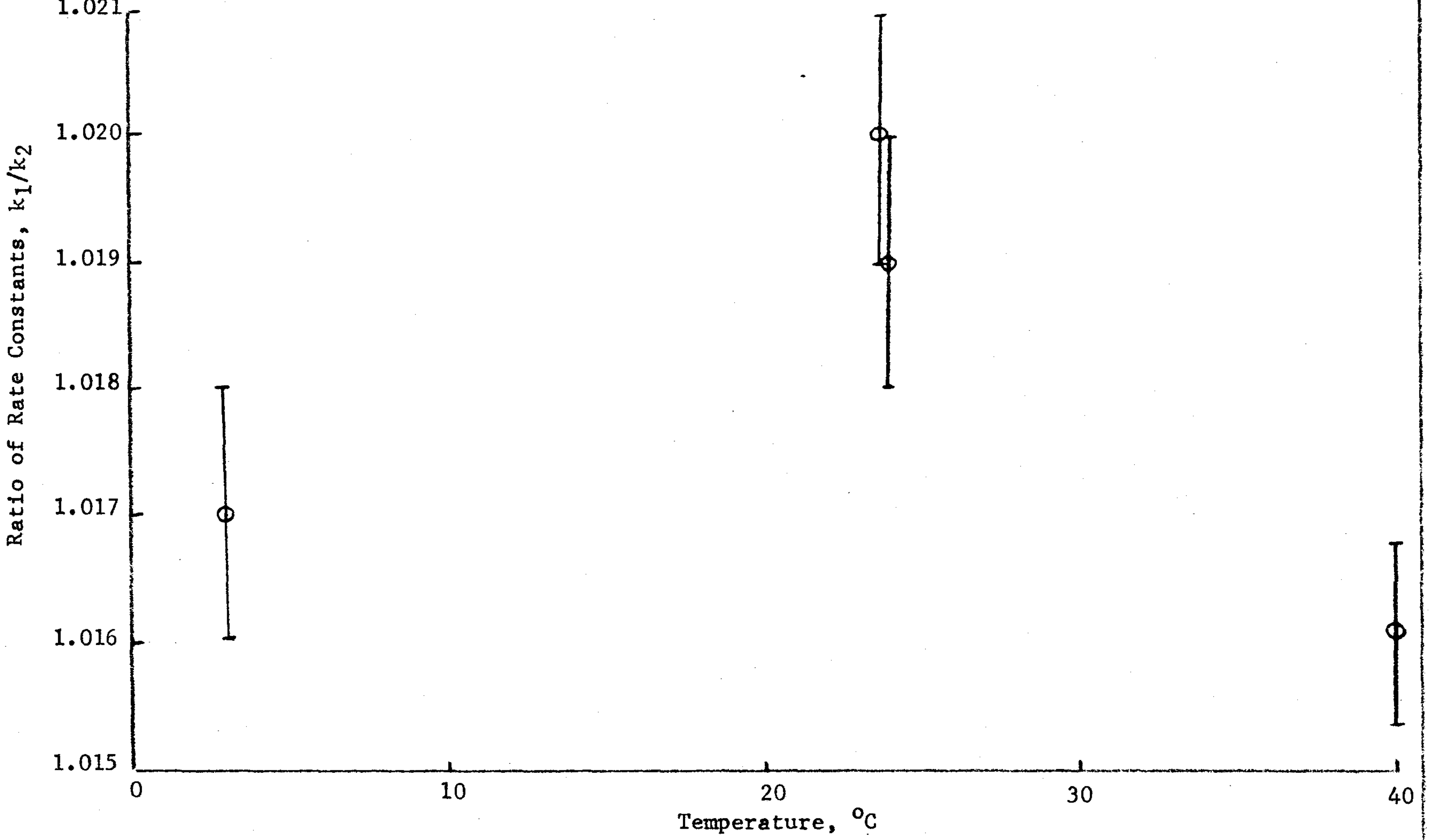
TABLE IV

The Partial Reduction of Sodium Selenite: Experimental Results

Experiment	T^oC	% Reduction	δ $^o/oo$	k_1/k_2
1	24	10	-18.4 ± 1	1.020 ± 0.001
2	24	20	-16.9 ± 1	1.019 ± 0.001
3	3	20	-14.6 ± 1	1.017 ± 0.001
4	40	20	-14.2 ± 0.7	1.016 ± 0.0007

FIG. 3

THE TEMPERATURE DEPENDENCE OF k_1/k_2
FOR THE REDUCTION OF SODIUM SELENITE



4.1.2 Theoretical Considerations

Referring to the expression developed in the theory section for the ratio of rate constants it may be seen that the theoretical estimation of such a ratio depends upon precise knowledge of the form of the activated complex. Such information is not available and it is necessary to consider models in which the nature of the activated complex is assumed to be known. The merits of such models are gauged by their appropriateness to the physical conditions and the agreement between predictions based on them and the observed isotope effects.

In the past it has been common to estimate theoretical values for the ratios of rate constants by considering two limiting cases:

I. Where the activated complex is identical to the starting material and there is no stretching of the bond which is considered to break in the rate controlling step for the reaction. In this case it is said that:

$$\frac{Z_2}{Z_1} = \frac{Z_2^{\ddagger}}{Z_1^{\ddagger}}$$

and so

$$\frac{k_1}{k_2} = \left(\frac{m_2^{\ddagger}}{m_1^{\ddagger}}\right)^{1/2}$$

and this mass ratio is evaluated by considering the effective mass to be the reduced mass of the "diatomic molecule", defined by the bond to be broken, either atomic masses or mass fragments being considered.

II. Where the activated complex is identical to the product material, and the bond which breaks in the rate controlling step is considered to be completely ruptured. In this case it is said that:

$$\frac{k_1}{k_2} = \left(\frac{Z_2}{Z_1}\right)_{\text{reactants}} \Bigg/ \left(\frac{Z_2}{Z_1}\right)_{\text{products}} \cdot \left(\frac{m_2^{\ddagger}}{m_1^{\ddagger}}\right)^{1/2}$$

where the mass term is the same as in case I.

The argument against these approaches rests on the fact that the theory for the determination of rate constant ratios depends upon the idea of an activated complex in which one of the vibrational frequencies, because of the shape of the potential surface, has changed character and has become a translation. This change gives rise to the term involving the ratio of two imaginary frequencies which is commonly evaluated as a mass term. If, however, the activated complex is identified with either the starting or product material, then strictly speaking, it does not have a vibration which changes character, and so there is no mass term in the expression for k_1/k_2. This being the case the two extreme models outlined above, while giving values for k_1/k_2 which generally lie lower and higher than the experimental value, have limited physical significance.

The approaches discussed below have been developed to follow the formalism of the theory and to incorporate the idea that in the transition state, the vibrational frequencies of the activated complex are the same as those of the reactant molecule except for that corresponding to bond cleavage or formation. Of the revised approaches, number III is the most important and represents the best possible description of the physical situation, while numbers IV and V are included to give the extreme lower and upper values that might be expected for the ratio of rate constants. The numerical results obtained from the revised approaches do not differ very much from those obtained by the methods described above, but it is felt that they are to be preferred since they follow the formalism more closely.

III. Where the activated complex is identical to the starting material, with the exception that the frequency associated with the breaking bond is missing. In this case:

$$\frac{Z_2}{Z_1} \Bigg/ \frac{Z_2^{\ddagger}}{Z_1^{\ddagger}} = \frac{Z(\nu_{2L})}{Z(\nu_{1L})}$$

where this ratio is the same as the partition function ratio for diatomic isotopic molecules with frequencies ν_{2L} and ν_{1L}, ν_L being that frequency in the starting material which is missing in the activated complex. The mass ratio is evaluated as before.

IV. Where the partition function ratio term is very close to unity, which occurs when the temperature is high.

In the high temperature limit;

$$\frac{k_1}{k_2} = \left(\frac{m_2^{\ddagger}}{m_1^{\ddagger}}\right)^{1/2}$$

V. Where the activated complex has some structure which is strictly speaking unknown, but for which the value of the partition function ratio lies between that for the starting material (with the omission of a frequency term) and unity. The extreme case of unity may be approached if in the transition state there is complexing of the reacting molecule with other material, so that a complicated structure is formed in which not many of the vibrational frequencies are sensitive to isotopic substitution. In this case:

$$\frac{k_1}{k_2} = \frac{Z_2}{Z_1} \cdot \left(\frac{m_2^{\ddagger}}{m_1^{\ddagger}} \right)^{1/2}$$

These three approaches III, IV and V give, for a particular model of the activated complex an intermediate (III) as well as extreme (IV and V) estimates for the ratio of rate constants.

Considering now the reduction of sodium selenite, and supposing the rate determining step to be the cleavage of a Se-O bond:

According to III. The activated complex is the same as the starting material with the exception that one vibrational mode has taken on a non-genuine character. This mode is most probably one component of the doubly degenerate E type asymmetric stretching vibration ν_3 ($\sim$ 730 cm^{-1}). The ratio of partition functions for the activated complex is simply that for $SeO_3^=$ with the contribution for one component of ν_3 omitted, and

$$\frac{Z_2}{Z_1} \Bigg/ \frac{Z_2^{\ddagger}}{Z_1^{\ddagger}} = \begin{array}{l} 1.008 \text{ at } 0^\circ C \\ 1.007 \text{ at } 25^\circ C \\ 1.006 \text{ at } 50^\circ C \end{array}$$

The mass term may be evaluated either for atomic masses or mass fragments in the "diatomic molecule" SeO_2 — O, for which the values 1.006 and 1.004 may be calculated. The values for k_1/k_2 are shown in Table V.

According to IV. The high temperature limit for k_1/k_2 is simply the mass term, 1.004 or 1.006 depending on whether mass or atom fragments are considered.

According to V. The upper limit for k_1/k_2 is given by

TABLE V

Values of the Ratio of Rate Constants for the Reduction of Se^{IV}, Calculated According to Argument III

$T^{o}C$	k_1/k_2 Mass Fragments	k_1/k_2 Atomic Fragments
0	1.012	1.014
25	1.011	1.013
50	1.010	1.012

$$\frac{k_1}{k_2} = \frac{Z(^{82}SeO_3^{=})}{Z(^{76}SeO_3^{=})} \cdot \left(\frac{m_2^{\ddagger}}{m_1^{\ddagger}}\right)^{1/2}$$

for which the values of k_1/k_2 are shown in Table VI.

The results of the three methods of calculation are summarised in Table VII.

All these simple models give a regular decrease in the value of k_1/k_2 with increase of temperature. If the reduction is first order with respect to selenite and is moreover a single step process, then the experimentally observed temperature dependence is anomalous and cannot be explained in terms of the simple model considered here. The model is, however, adequate to explain the order of magnitude of the isotope effect in the reduction of Se^{1V} to Se^{o}.

The anomalous temperature dependence could possibly be explained in terms of the temperature variation of a partition function ratio term (c.f. the CO_2 - $CO_3^{=}$ equilibrium constant and its variation with temperature, as shown in the Appendix). However, the overall temperature variation of k_1/k_2 is probably rather too extreme to be explained satisfactorily in this manner, so that it may be supposed that at low temperatures some other factor, solvent effects for example, is causing the value of k_1/k_2 to be depressed. If this is the case, then the temperature coefficient observed between 24°C and 40°C is quite consistent with the theoretically derived values. It may be noted that, in Table VII, proceeding from the intermediate case to the high estimate, the value for k_1/k_2 becomes closer to the experimental value and at the same time the temperature coefficient gives better agreement with that observed between 24°C and 40°C.

TABLE VI

Values of the Ratio of Rate Constants for the Reduction of Se^{IV}, Calculated According to Argument V

T^oC	k_1/k_2	
	Mass Fragments	Atomic Fragments
0	1.033	1.035
25	1.029	1.031
50	1.025	1.027

TABLE VII

Summary of the Calculated Ratios of Rate Constants for the Reduction of Se^{IV}

T^oC	k_1/k_2					
	Low		Intermediate		High	
	Mass	Atom	Mass	Atom	Mass	Atom
0	1.004	1.006	1.012	1.014	1.033	1.035
25	1.004	1.006	1.011	1.013	1.029	1.031
50	1.004	1.006	1.010	1.012	1.025	1.027

4.2 Reduction of Sodium Selenate

4.2.1 Results of Experiments

Table VIII shows the yields of selenium from the experiments described on page 22 together with the del values for the product selenium, compared to the starting material. The following four points are of importance in considering the results of these experiments:

i. For the reaction

$$Se^{VI} \longrightarrow Se^{IV}$$

in hydrochloric acid solution we may write, for one-molar solutions, using the oxidation potentials compiled by Latimer (47):

$$SeO_4^{=} + 4H^+ + 2Cl^- = H_2SeO_3 + H_2O + Cl_2 \quad - 0.21$$

The negative value of E_o shows that components on the left of the equation are favoured in the equilibrium. However, it is known that in strong solutions of HCl, Se^{VI} is reduced to Se^{IV} (30, 31). This is reasonable since in an open system where Cl_2 is removed and where the hydrogen ion concentration is high, the equilibrium constant can be such that H_2SeO_3 is favoured over $SeO_4^{=}$.

ii. After the formation of Se^o by the $C_6H_8O_6$ reduction of Se^{IV}, Se^o is lost. This is caused by the reaction:

$$2Se^{VI} + Se^o \longrightarrow 3Se^{IV}$$

for which we may write, for one-molar solutions:

$$2SeO_4^{=} + Se^o + H_2O + 4H^+ = 3H_2SeO_3 \quad + 0.41$$

The positive value of the potential indicates that the reaction should proceed to the right. In practice this will be the case only if the Se^o is present in the red active form. It is known that the loss of

TABLE VIII

Experimentally Observed Isotope Effects in the Reduction of Se^{VI}

Experiment	Se Recovery mg	Se Recovery %	δ °/oo
1	122	32.5	-14.0±1.4
2	233	59.2	-8.3±0.5
3	72	18.0	-10.4±0.7

Se^{o} cannot be due to a reaction of the form

$$Se^{o} \longrightarrow Se^{IV}$$

without any participation of the Se^{VI}, since in the equilibrium experiments described below it was possible to have coexisting Se^{IV} and red Se^{o} in strong acid solution without any loss of Se^{o}.

iii. If $C_6H_8O_6$ remains after the reduction

$$Se^{VI} \longrightarrow Se^{IV} \longrightarrow Se^{o}$$

it will reduce to Se^{o} the Se^{IV} formed by the reaction

$$2Se^{VI} + Se^{o} \longrightarrow 3Se^{IV}$$

iv. The oxidation of Se^{o} is considered to proceed until all the Se^{VI} has been reduced.

Considering the three experiments in turn, but out of order:

Experiment 1. With 400 mg Se^{VI} in HCl solution, 2.5 meq $C_6H_8O_6$ was added and after one minute the solution reduced in acidity so as to quench the oxidation of Se^{o}.

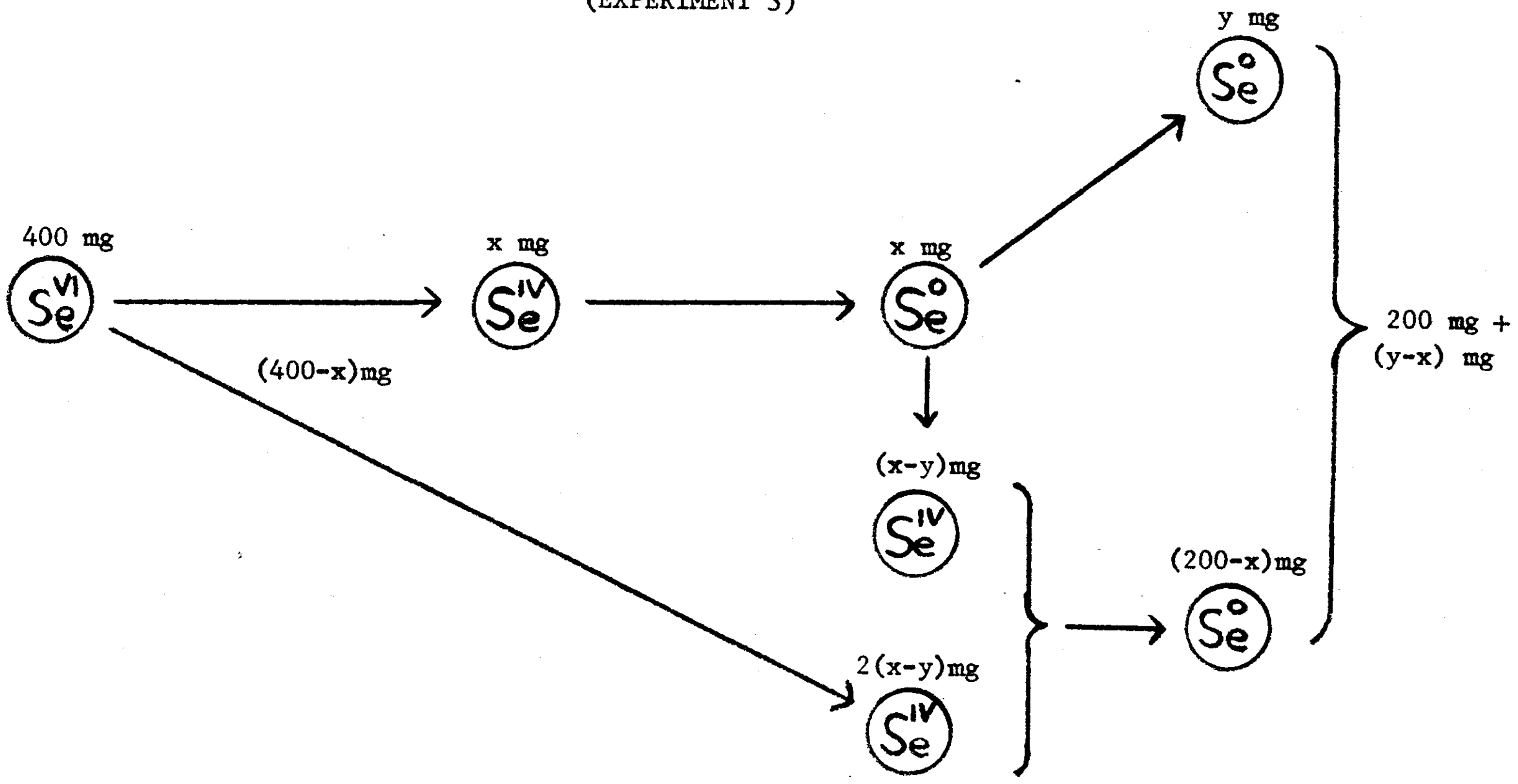
$$Se^{VI} \xrightarrow{32.5\%} Se^{IV} \xrightarrow{100\%} Se^{o}$$

There is no isotope effect in the second step. The observed isotope effect is -14 $^{o}/oo$ for a 33% reduction, which corresponds to a value of 1.018 for the ratio of rate constants in the reduction of Se^{VI} to Se^{IV}.

Experiment 3. 400 mg Se^{VI} in hydrochloric acid solution was allowed to stand for 24 hrs. before 2.5 meq $C_6H_8O_6$ was added. No attempt was made to prevent the oxidation of the Se^{o} formed and 72 mg of Se^{o} was recovered. The proposed reaction scheme is shown in Fig. 4. x mg Se^{VI} is reduced to Se^{IV} and 100% of the Se^{IV} is reduced to Se^{o}. Of the x mg Se^{o}, y mg remains unoxidised while (x-y) mg is

FIG. 4

PROPOSED REACTION SCHEME FOR THE
REDUCTION OF SODIUM SELENATE
(EXPERIMENT 3)



is oxidised to Se^{IV}. In this oxidation, twice this quantity, the total remaining, of Se^{VI} is reduced to Se^{IV}. So 3(x-y)mg of Se^{IV} are produced. There was sufficient $C_6H_8O_6$ added to reduce 200 mg Se^{IV} and x mg was reduced, so that now a further (200-x)mg are reduced to Se^o, giving a total of (200-x) + y mg Se^o, experimentally 72 mg.

From the above considerations:

$$(200-x) + y = 72$$

$$2(x-y) = 400-x$$

so that

$$x = 144 \text{ mg}; \qquad y = 16 \text{ mg}$$

Figure 5 shows the complete reaction scheme.

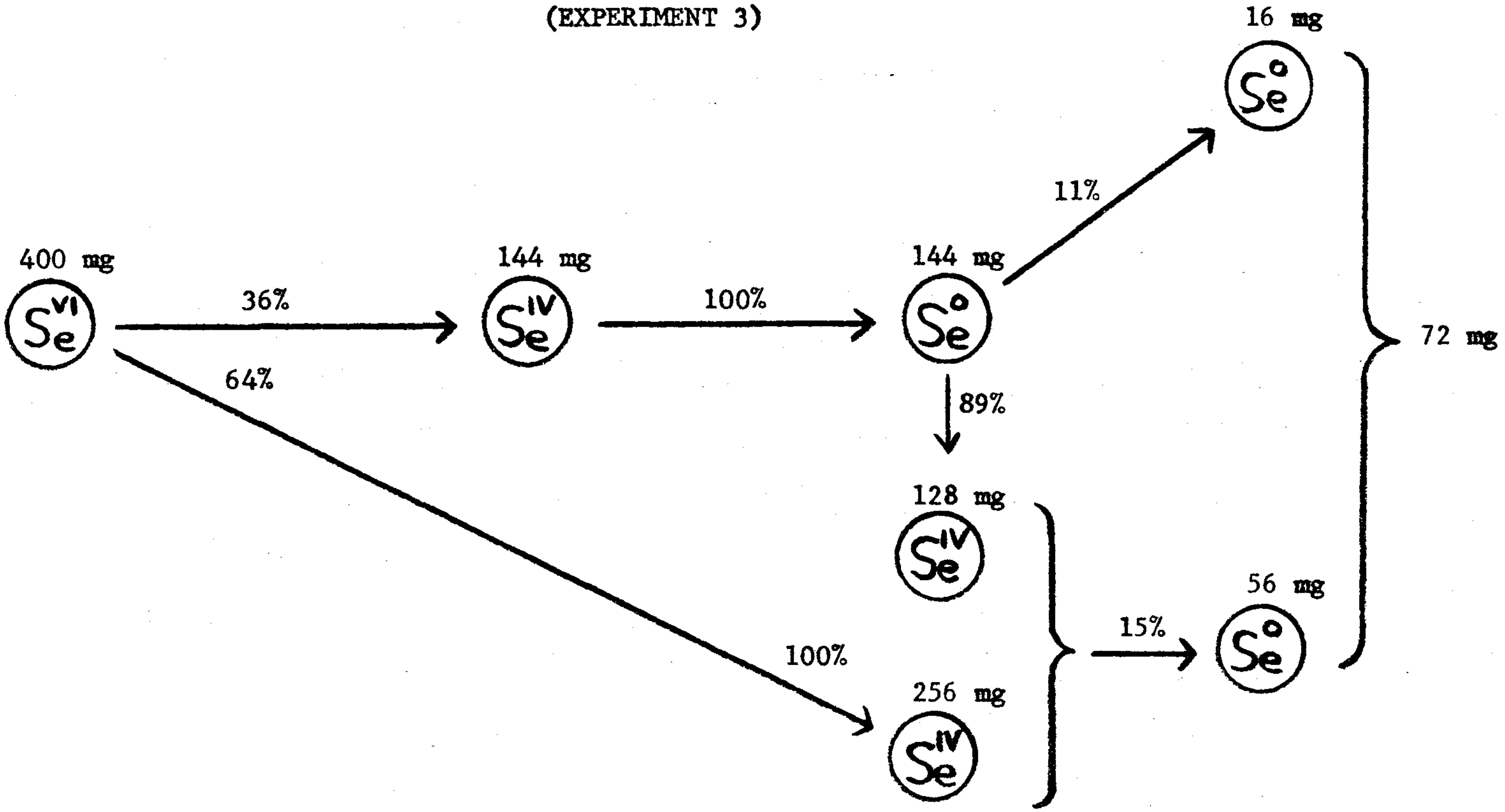
If in the oxidation of Se^o, one considers the substrate to be at + Δ °/oo with respect to the original Se^o, so that the 128 mg Se^{IV} formed from the Se^o is at $-\frac{16}{128}\Delta$ °/oo with respect to it, and if one considers k_1/k_2 for the selenite and selenate reductions to be 1.015 and 1.018 respectively, then taking into account the observed del value of the final product Se^o (-10.4 °/oo), it is possible to work through the reactions and derive Δ= 17 °/oo, so that k_1/k_2 for the oxidation of Se^o to Se^{IV} is 1.007.

Experiment 2. With 400 mg Se^{VI} in HCl solution, 215 meq $C_6H_8O_6$ was added, and red Se^o formed, some of which was reoxidised, and after one hour a further 2.5 meg $C_6H_8O_6$ was added, more red Se^o being formed. The final yield of Se^o was 233 mg.

Here x mg Se^{VI} was reduced to Se^{IV} and to Se^o. Much of the Se^o was oxidised to Se^{IV} accompanied by the reduction to Se^{IV} of all the remaining Se^{VI}. When the second addition of $C_6H_8O_6$ was made,

FIG. 5

COMPLETE REACTION SCHEME FOR THE
REDUCTION OF SODIUM SELENATE
(EXPERIMENT 3)



only Se^{1V} and Se^{o} remained, and the $C_6H_8O_6$ was sufficient to reduce 200 mg Se^{1V} to Se^{o}, there being no further oxidation. This being the case the amount of Se^{o} not oxidised by the presence of Se^{V1} must have been 33 mg.

The proposed reaction scheme is shown in Fig. 6. From the above considerations:

$$2(x-33) + x = 400$$

so that

$$x = 155 \text{ mg}$$

Fig. 7 shows the complete reaction scheme.

Using $Se^{V1} \longrightarrow Se^{o}$: $k_1/k_2 = 1.018$

$Se^{1V} \longrightarrow Se^{o}$: $k_1/k_2 = 1.015$

$Se^{o} \longrightarrow Se^{1V}$: $k_1/k_2 = 1.007$

and working through the various reactions leads to the result that the recovered selenium should have a del value of -6.9 ^{o}/oo, compared to the experimental value of -8.3 ^{o}/oo.

The same procedure may be repeated in interpreting the results of experiments 2 and 3, with different values for k_1/k_2 for the selenite reduction. The results of such calculations are shown in Table IX.

In each case the ratio of rate constants for the reduction of Se^{V1} to Se^{1V} has been taken as 1.018. The ratio of rate constants for the reduction of Se^{1V} to Se^{o} has been assigned the three values in Column 2. Column 3 shows the ratio of rate constants for the oxidation Se^{o} to Se^{1V}, as estimated from the results of experiment 3, and Column 4 shows the expected del value in the Se^{o} recovered in experiment 2. The row of Table IX enclosed by asterisks is in best

FIG. 6

PROPOSED REACTION SCHEME FOR THE
REDUCTION OF SODIUM SELENATE
(EXPERIMENT 2)

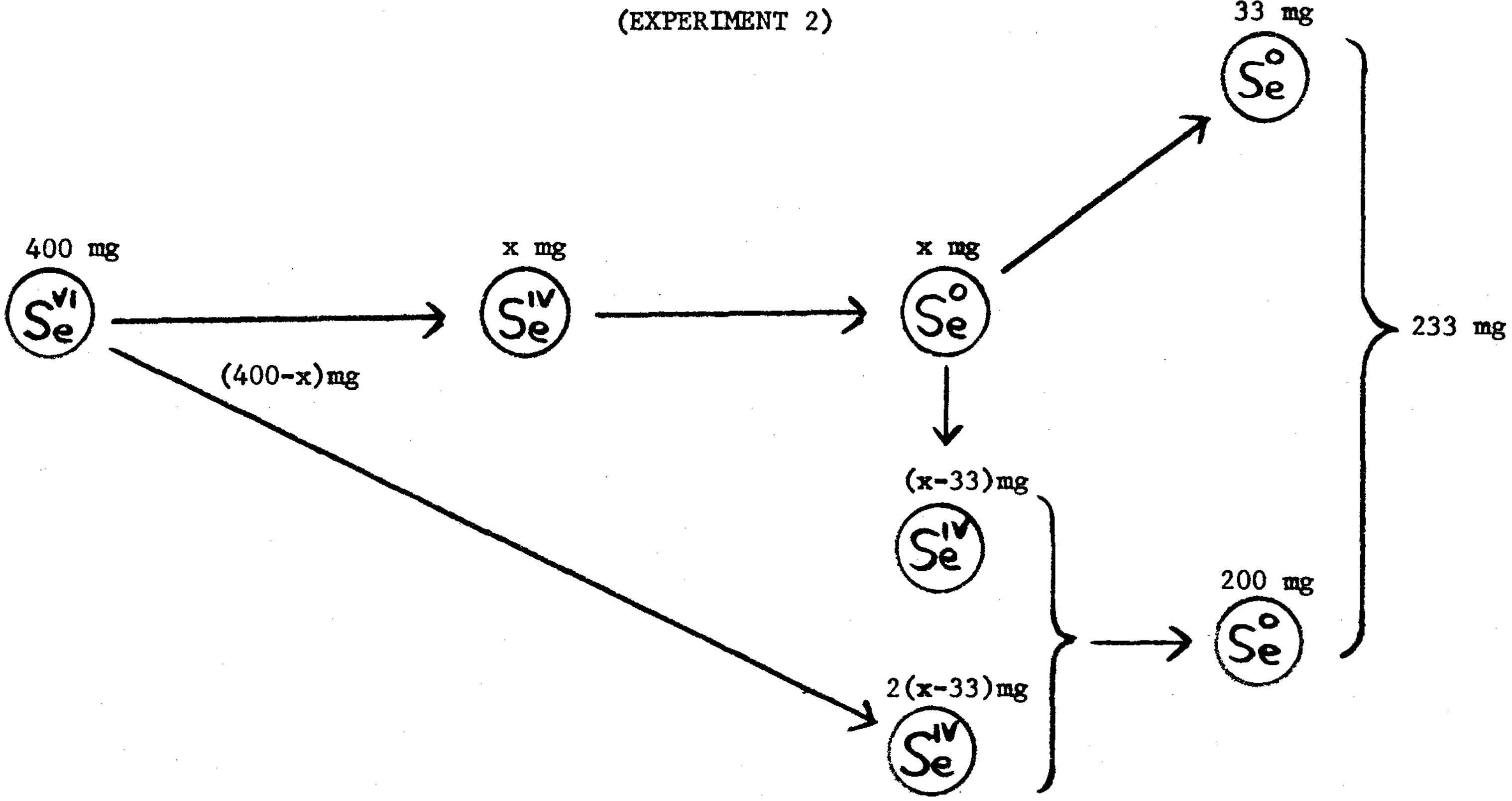


FIG. 7

COMPLETE REACTION SCHEME FOR THE
REDUCTION OF SODIUM SELENATE
(EXPERIMENT 2)

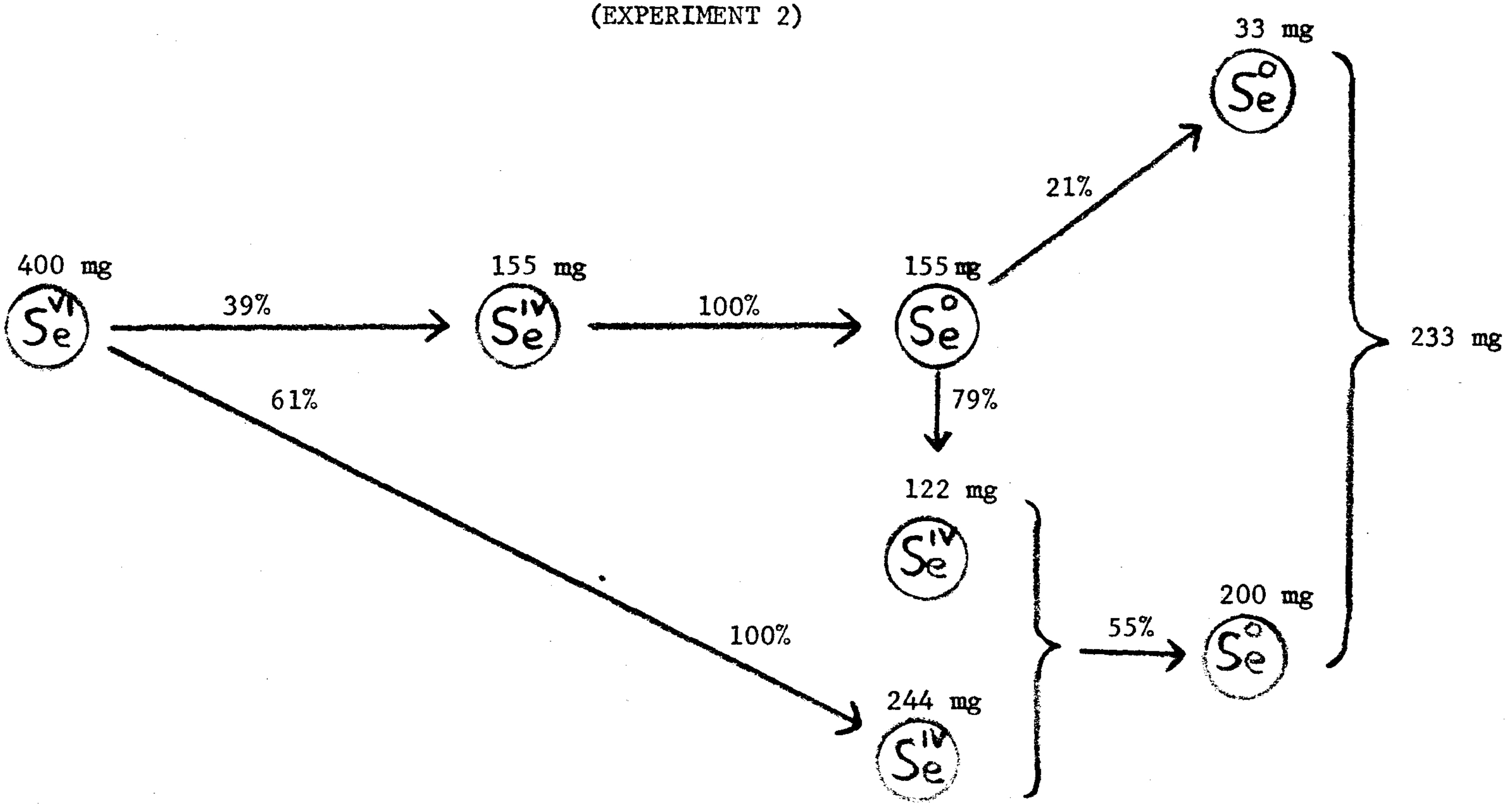


TABLE IX

Interpretation of the Se^{VI} Reduction Experiments

k_1/k_2			
$\mathrm{Se}^{VI} \rightarrow \mathrm{Se}^{IV}$	$\mathrm{Se}^{IV} \rightarrow \mathrm{Se}^{o}$	$\mathrm{Se}^{o} \rightarrow \mathrm{Se}^{IV}$	$\delta(\mathrm{Se}^{o})$ °/oo
1.018	1.015	1.007	-6.9
* 1.018	1.017	1.010	-9.1 *
1.018	1.019	1.013	-9.6

agreement with experiment.

It has been suggested (48) that in view of the negative E_o value for the reduction of selenate to selenite by chloride ion, that in hydrochloric acid solutions, Se^{VI} is reduced to Se^{IV} by the reaction

$$SeO_4^{=} + 8Cl^{-} + 8H^{+} \longrightarrow SeCl_6^{=} + Cl_2 + 4H_2O$$

and that $SeCl_6^{=}$ is reduced to elemental selenium by $C_6H_8O_6$ as is $SeO_3^{=}$.

If this is the case, there is no alteration of the conclusions reached in the preceding sections if in the reduction of $SeO_4^{=}$ to $SeCl_6^{=}$ the rate determining step is still the cleavage of an Se-O bond in $SeO_4^{=}$. In each case, 100% of the Se^{IV} so formed is reduced to Se^{o}, with no isotope effect, and the oxidation of Se^{o} to Se^{IV} is followed by rapid reduction to Se^{o} (by the action of $C_6H_8O_6$) and this Se^{IV} will be in the form of $SeO_3^{=}$.

4.2.2 Theoretical Considerations for the Reduction of Se^{VI} to Se^{IV}

Following the arguments outlined in section 4.1 and supposing the rate determining step in the reaction to be the cleavage of a Se-O bond:

According to III. The activated complex is the same as the starting material with the exception that one vibrational mode has taken on a non-genuine character. This mode is most probably one component of the triply degenerate F_2 type vibration ν_3 (~ 880 cm^{-1}). The ratio of partition functions for the activated complex is simply that for $SeO_4^{=}$ with the contribution for one component of ν_3 omitted, and

$$\frac{Z_2}{Z_1} \Bigg/ \frac{Z_2^{\ddagger}}{Z_1^{\ddagger}} = 1.013 \text{ at } 25^{\circ}C$$

The mass term may be evaluated either for atomic masses or mass fragments in the "diatomic molecule" SeO_3-O for which the values 1.006 and 1.002 may be calculated, so that k_1/k_2 at 25°C is either 1.019 or 1.015.

According to IV. The high temperature limit for k_1/k_2 is simply the mass term, 1.006 or 1.002 depending on whether atom or mass fragments are considered.

According to V. The upper limit for k_1/k_2 is given by

$$\frac{k_1}{k_2} = \frac{Z(^{82}SeO_4^{=})}{Z(^{76}SeO_4^{=})} \cdot \left(\frac{m_2}{m_1}\right)^{1/2}$$

which gives, at 25°C, 1.053 and 1.049 for atom and mass fragments.

The results of the three methods of calculation are summarised in Table X.

TABLE X

Summary of the Calculated Ratios of Rate Constants for the Reduction of Se^{VI} at 25°C

	k_1/k_2		
	Low	Intermediate	High
Mass Fragments	1.002	1.015	1.049
Atomic Fragments	1.006	1.019	1.053

There is no temperature variation data with which to further narrow down the choice of a preferred ratio.

4.2.3 Theoretical Considerations for the Oxidation of Se^{o} to Se^{lV}

It is possible to make a number of reasonable assumptions about the nature of the activated complex in the oxidation of Se^{o} to Se^{lV}:

a) That it is just elemental selenium

b) That it is a diatomic Se-O molecule in the process of forming

c) That the rate controlling step is the breaking of an Se atom from an Se chain

d) That the reaction is three centred, with a selenium breaking from an Se chain as an oxygen attaches itself

All these possibilities require, for the computation of k_1/k_2, information on the partition function ratio for open ended selenium chains. This information is not available.

All that may be reasonably said at the moment concerning this reaction is that if the activated complex is simply selenium or a diatomic molecule containing selenium, so that $Z_2^{\ddagger}/Z_1^{\ddagger}$, is unity and so that the reduced mass term is either unity or greater than unity, then the predicted ratio k_1/k_2 will be greater than unity, as is observed experimentally.

4.3 The Equilibration of Se^{Vl} and Se^{lV}

The results of the two experiments were as follows:

59 days, fractionation = 2.7 ± 0.6 °/oo

146 days, fractionation = 4.2 ± 1.0 °/oo

The fractionation referred to is the comparison of the final Se^{Vl} to the final Se^{lV}, the initial phases being isotopically identical.

The chemical yields of Se^{1V} and Se^{V1} were very nearly quantitative being 198 mg and 197 mg in the 59 day experiment and 197 mg and 200 mg in the 146 day experiment, compared to the theoretical figure of 198 mg.

Assuming a simple mechanism for the equilibration so that the observed fractionation factor approaches the exchange constant asymptotically with an experimental time dependence:

$$1 + \delta = K(1 - e^{-t/\Upsilon})$$

the experimental results yield

$$K = 1.005$$

and

$$\Upsilon = 73 \text{ days}$$

However, taking the error limits of the observed fractionation yields:

$$1.003 \lesssim K \lesssim 1.015$$

$$30d \lesssim \Upsilon \lesssim 300d$$

The error limits are large, but could only be reduced by performing experiments over still longer times, a year being a suitable period.

In view of the small fractionation observed over a period of 60 days, it is not surprising that the experiments of Ford (3) did not yield measurable fractionations over a period of 100 hrs. for the exchange between sulphate and sulphite.

The theoretical value of the exchange constant is given in TableXIII in the Appendix, but in view of the wide error limits on the experimental figure little can be said about the agreement between theory and experiment except that it appears that the theoretical estimate may be somewhat high.

4.4 The Equilibration of Se^{o} and Se^{lV}

In this experiment the yields of selenium from each phase were essentially quantitative, 189 mg and 198 mg for Se^{o} and Se^{lV} respectively, compared to the theoretical value of 198 mg. The selenium from the selenite was compared with the tank standard and found to be +3.5 ± 0.3 °/oo so that, compared to the selenium phase, the enrichment is +7.0 ± 0.6 °/oo.

This experiment confirms the findings of Haissinsky and Pappas (5) that there can be isotope exchange between Se^{lV} and Se^{o}, and shows that there is an isotope effect associated with the exchange.

Haissinsky and Pappas found in their experiments that it was difficult to achieve complete exchange because exchange only occurs when the Se^{o} is in the red active form. In the presence of Se^{lV} in strong acid solutions, red selenium changes to the black less active form fairly rapidly. The fact that the change only takes place rapidly in the presence of Se^{lV} suggests that the mechanism of the exchange might itself be responsible for the conversion of Se^{o} (red) to Se^{o} (black).

At 10°C, in the acid solution used in this experiment, Haissinsky and Pappas indicate that exchange will only be about half completed by the time the red Se changes to black and "freezing-in" occurs. This being the case, the exchange constant for the reaction

$$^{82}Se^{o} + {}^{76}Se^{lV} \rightleftharpoons {}^{76}Se^{o} + {}^{82}Se^{lV}$$

is 1.014.

It is not possible to predict theoretically the equilibrium constant, since the partition function ratio for open-ended chains of selenium is not available. However, since

$$K = \frac{Z(^{82}(SeO_3^{=})}{Z(^{76}SeO_3^{=})} \Bigg/ \frac{Z(^{82}Se^{o})}{Z(^{76}Se^{o})}$$

and the unknown partition function ratio will be greater than unity, the upper limit for K is the partition function ratio for selenite, i.e. 1.027 at 10°C.

V. APPENDICES

5.1 Derivation of Urey's and Bigeleisen's Expressions for Z_2/Z_1

Urey (13) developed from the exact expression the following power series expression to facilitate the estimation of ratios of partition functions:

$$\ln \frac{Z_2}{Z_1} = \sum_{i}^{3n-6} \ln \frac{u_{2i}}{u_{1i}} + \sum_{i}^{3n-6} \left[\delta_i \coth x_i + \frac{1}{12} \coth x_i (\coth^2 x_i - 1) \delta_i^3 + \cdots \right]$$

In order to show that

$$S = \ln \frac{e^{-u_2/2}}{1-e^{-u_2}} \cdot \frac{1-e^{-u_1}}{e^{-u_1/2}} = \delta \coth x + \frac{1}{12} \coth x(\coth^2 x-1)\delta^3 + \cdots$$

it is necessary to substitute for u_1 and u_2 in terms of the previously defined x and δ, which yields

$$S = \ln e^{\delta} \frac{1-e^{-2x}e^{-\delta}}{1-e^{-2x}e^{\delta}}$$

Now, supposing that S may be written:

$$S = \sum_{r=0}^{\infty} a_r \delta^r$$

differentiating n times with respect to δ the expressions for S, and setting δ equal to zero gives an equation for a_n, and doing this for $n = 0,1,2,3$ yields the required form for S.

Bigeleisen's expression for Z_2/Z_1 (7) may be derived from the exact expression by substituting

$$u_{1i} = u_{2i} + \Delta u_i$$

and by expanding the various exponential factors in terms of Δu_i, terminating each expansion at the first order term in Δu_i.

5.2 Vibrational Frequency Assignments and Force Constant Calculations

In order to calculate the partition function ratios for isotopic molecules it is necessary to know, or estimate, the fundamental vibrational frequencies for these molecules. In most cases, experimental determinations of vibrational frequencies have been performed only for the naturally most abundant isotopes of the molecular constituents. The fundamental frequencies for a molecule containing a less abundant isotope must be determined by a two step process: firstly a set of force constant equations must be set up, using the observed vibrational frequencies, to determine the molecular force constants, and secondly these same equations must then be used again, with the calculated force constants and the isotopic mass value to determine the new set of frequencies. Except in the case of extremely simple molecules, there are more force constants than fundamental frequencies, so that approximations must be made, some of the constants being set to zero in order to provide a solvable set of equations.

5.2.1 Carbon Dioxide (Gaseous)

The fundamental frequencies for both $^{12}CO_2$ and $^{13}CO_2$ have been measured, so that no force constant analysis is necessary. A compilation of the frequencies has been made by Wentink (36) and his estimated best values are listed in Table XI.

5.2.2 Carbon Dioxide (Aqueous)

Jones and McLaren (37) measured the value of ν_3 for $^{12}CO_2$ dissolved in water. They did not determine ν_1 or ν_2 under the same conditions since ν_1 is not active in the infra-red and presumably ν_2 was too low to be measured on their instrument. ν_1 and ν_2 have been estimated by assuming them to be displaced from the gaseous $^{12}CO_2$ values by the same fractional amounts as is ν_3. The values of ν_1, ν_2, ν_3 for dissolved $^{13}CO_2$ were estimated by assuming the same fractional isotope shifts as for gaseous $^{13}CO_2$. These frequency assignments are listed in Table XI.

5.2.3 Carbonate Ion

The fundamental frequencies for $^{12}CO_3^{=}$ quoted by Kujumzelis (38) are shown in Table XI. The force constant analysis due to Heath and Linnett (39) has been used to calculate the frequencies for $^{13}CO_3^{=}$, also shown in Table XI. Heath and Linnett employed the Orbital Valence Force Field approach for determining force constants, the following equations being used:

$$\lambda_1 = (k_1 + 6A)\frac{1}{my}$$

$$\lambda_2 + \lambda_3 = \left(k_1 - \frac{3}{4}\frac{B}{Re} + \frac{3}{2}A\right)\left(\frac{1}{my} + \frac{3}{2mx}\right) + \left(k_\beta + \frac{9}{4}\frac{B}{Re} + \frac{3}{2}A\right)\left(\frac{1}{my} + \frac{3}{2mx}\right) - \left(2A - \frac{B}{Re}\right)\frac{9}{4mx}$$

$$\lambda_2\lambda_3 = \left[\left(k_1 - \frac{3}{4}\frac{B}{Re} + \frac{3}{2}A\right)\left(k_\beta + \frac{9}{4}\frac{B}{Re} + \frac{3}{2}A\right) - \frac{9}{16}\left(2A - \frac{B}{Re}\right)^2\right]\left[\frac{1}{m^2y^2} + \frac{3}{m_xm_y}\right]$$

$$\lambda_4 = \left(k_\beta + \frac{3B}{Re}\right)\left(\frac{1}{my} + \frac{3}{mx}\right)$$

TABLE XI

Vibrational Frequency Assignments

Molecule	ν_1	(D)	ν_2	(D)	ν_3	(D)	ν_4	(D)
$^{12}CO_2$(gaseous)	1342.86	1	667.30	2	2349.30	1		
$^{13}CO_2$(gaseous)	1344.66	1	648.65	2	2283.46	1		
$^{12}CO_2$(aqueous)	1338.70	1	665.20	2	2342.00	1		
$^{13}CO_2$(aqueous)	1340.49	1	646.61	2	2276.37	1		
$^{12}CO_3^{=}$	1063.00	1	1415.00	2	680.00	2	879.00	1
$^{13}CO_3^{=}$	1063.00	1	1375.75	2	677.49	2	851.38	1
$^{80}SeO_3^{=}$	805.00	1	432.5	1	735.0	2	376.0	2
$^{76}SeO_3^{=}$	807.97	1	435.17	1	738.99	2	376.75	2
$^{82}SeO_3^{=}$	803.59	1	431.30	1	733.15	2	375.65	2
$^{80}SeO_4^{=}$	835	1	341	2	875	3	421	3
$^{76}SeO_4^{=}$	835	1	341	2	881.80	3	422.62	3
$^{82}SeO_4^{=}$	835	1	341	2	871.84	3	420.24	3

N.B. The frequencies quoted above are not of course as accurate as implied by the number of significant figures. The machine calculations were designed to handle two places of decimals and the figures above represent the input data used for these calculations.

where $\lambda_i = 4\pi^2\nu_i^2c^2$ and the suffices x, y refer to carbon and oxygen respectively.

For $CO_3^=$:

$$k_1 = 5.4 \times 10^5 \text{ dyne. cm}^{-1}$$

$$k_\beta = 1.055 \times 10^5 \text{ dyne. cm}^{-1}$$

$$A = 0.875 \times 10^5 \text{ dyne. cm}^{-1}$$

$$B/Re = 0.135 \times 10^5 \text{ dyne. cm}^{-1}$$

5.2.4 Selenite Ion

The fundamental frequencies listed in Table XI are the means of values reported by Rocchiccioli (40) and Walrafen (41). The selenite ion has pyramidal XY_3 structure and a force constant analysis must take into account the apex angle of the pyramid. Wells and Bailey (42) determined the structure of the SeO_3 groups in crystals of selenious acid, finding the pyramids to be non-regular. Using their data the mean apex angle is 100.6°, and this value has been used in the analysis.

The Wilson F G Matrix method has been used to determine the force constants. Following Nakomoto (43) the F and G matrix elements are:

F matrix elements

For A_1 vibrations:

$$F_{11} = f_r + 2f_{rr}$$

$$F_{12} = r(2f_{r\alpha} + f_{r\alpha}')$$

$$F_{22} = r^2(f_\alpha + 2f_{\alpha\alpha})$$

For E vibrations:

$$F_{11} = f_r - f_{rr}$$

$$F_{12} = r(-f_{r\alpha} + f_{r\alpha'})$$

$$F_{22} = r^2(f_\alpha - f_{\alpha\alpha})$$

G matrix elements

For A_1 vibrations:

$$G_{11} = \mu_y + (1 + 2\cos\alpha)\mu_x$$

$$G_{12} = -\frac{2}{r}\,\frac{(1 + 2\cos\alpha)(1 - \cos\alpha)}{\sin\alpha}\mu_x$$

$$G_{22} = \frac{2}{r^2}\,\frac{1 + 2\cos\alpha}{1 + \cos\alpha}\left[\mu_y + 2\mu_x(1 - \cos\alpha)\right]$$

For E vibrations:

$$G_{11} = \mu_y + \mu_x(1 - \cos\alpha)$$

$$G_{12} = -\frac{1}{r}\,\frac{(1 - \cos\alpha)^2}{\sin\alpha}\mu_x$$

$$G_{22} = \frac{1}{r^2(1 + \cos\alpha)}\left[(2 + \cos\alpha)\mu_y + (1 - \cos\alpha)^2\mu_x\right]$$

The secular equation for both A_1 and E vibrations is:

$$\lambda^2 - \lambda(F_{11}G_{11} + 2F_{12}G_{12} + F_{22}G_{22}) + (F_{11}F_{22} - F_{12}^2)(G_{11}G_{22} - G_{12}^2) = 0$$

There are six force constants but only four distinguishable frequencies so in performing the analysis it has been assumed that $f_{r\alpha}$ and $f_{r\alpha'}$ may be neglected, leaving f_r, f_{rr}, f_α and $f_{\alpha\alpha}$ to be determined. Using the frequency data for $^{80}SeO_3^=$, the following set of force constants were selected:

$$f_r = 4.497 \times 10^5 \text{ dyne. cm}^{-1}$$

$$f_\alpha = 0.629 \times 10^5 \text{ dyne. cm}^{-1}$$

$$f_{rr} = 0.420 \times 10^5 \text{ dyne. cm}^{-1}$$

$$f_{\alpha\alpha} = 0.092 \times 10^5 \text{ dyne. cm}^{-1}$$

These have been used to determine the frequencies for $^{76}SeO_3^=$ and $^{82}SeO_3^=$ quoted in Table XI

5.2.5 Selenate Ion

The fundamental frequencies for $^{80}SeO_4^=$ listed in Table XI are the means of values reported by Heath and Linnett (39), Pistorius (44) and Walrafen (45): $SeO_4^{=}$ has T_d symmetry giving 1 non-degenerate A_1 vibration (ν_1) 1 doubly degenerate E vibration (ν_2) and 2 triply degenerate T_2 vibrations (ν_3, ν_4). The Wilson F G matrix approach employed by Pistorius has been used to evaluate the force constants, the F and G matrix elements being:

F matrix elements

For A_1 vibrations:

$$F_{11} = f_r + 3f_{rr}$$

For E vibrations:

$$F_{11} = r^2(f_\alpha + f_{\alpha\alpha'} - 2f_{\alpha\alpha})$$

For T_2 vibrations:

$$F_{11} = r^2(f_\alpha - f_{\alpha\alpha'})$$

$$F_{12} = \sqrt{2}\ r\ (f_{r\alpha} - f_{\alpha\alpha'})$$

$$F_{22} = f_r - f_{rr}$$

G matrix elements

For A_1 vibrations:

$$G_{11} = \mu_y$$

For E vibrations:

$$G_{11} = 3\mu_y/r^2$$

For T_2 vibrations:

$$G_{11} = 2\mu_y + \frac{16}{3}\mu_x/r^2$$

$$G_{12} = -\ \frac{8}{3}\ \frac{\mu_x}{r}$$

$$G_{22} = \mu_y + \frac{4}{3}\mu_x$$

The secular equations are:

For A_1 vibrations:

$$\lambda_1 = F_{11}G_{11}$$

For E vibrations:

$$\lambda_2 = F_{11}G_{11}$$

For T_2 vibrations:

$$\lambda^2 - \lambda(F_{11}G_{11} + 2F_{12}G_{12} + F_{22}G_{22}) + (F_{11}F_{22} - F_{12}^2)(G_{11}G_{22} - G_{12}^2) = 0$$

Following Pistorious, f_{rr} is assumed to be 0.347 and the equations for f_r, $f_{r\alpha} - f_{r\alpha}'$, $f_\alpha - f_{\alpha\alpha}'$ and $f_{\alpha\alpha} - f_{\alpha\alpha}'$, yielding:

$$f_r = 5.529 \times 10^5 \text{ dyne. cm}^{-1}$$

$$f_{r\alpha} - f_{r\alpha}' = -0.195 \times 10^5 \text{ dyne. cm}^{-1}$$

$$f_\alpha - f_{\alpha\alpha}' = 0.660 \times 10^5 \text{ dyne. cm}^{-1}$$

$$f_{\alpha\alpha} - f_{\alpha\alpha}' = 0.148 \times 10^5 \text{ dyne. cm}^{-1}$$

These have been used to determine the frequencies for $^{76}SeO_4^=$ and $^{82}SeO_4^=$ quoted in Table XI.

5.3 Results of Calculations of Partition Function Ratios

5.3.1 Carbon

Table XII shows the values of the partition function ratios for aqueous and gaseous carbon dioxide and for the carbonate ion for ^{12}C and ^{13}C. Also shown is the equilibrium constant for exchange between gaseous carbon dioxide and carbonate ion. The agreement between these values and experimental determinations is discussed by Thode et al (46).

5.3.2 Selenium

Table XIII shows the values of the partition function ratios for selenite and selenate ions for ^{76}Se and ^{82}Se. Also shown is the equilibrium constant for exchange between these ions.

5.4 Isotope Fractionation During First Order Competing Reactions

Bigeleisen and Wolfsberg (23) have developed expressions

TABLE XII

Results of Partition Function Ratio and ^{13}C Exchange Constant Calculations

T°C	(1) $\frac{Z(^{13}CO_2\,(a))}{Z(^{12}CO_2\,(a))}$	(2) $\frac{Z(^{13}CO_2\,(g))}{Z(^{12}CO_2\,(g))}$	(3) $\frac{Z(^{13}CO_3^{=})}{Z(^{12}CO_3^{=})}$	K (1-2)	K * (1-3)
0	1.2077	1.2211	1.2086	1.0008	1.0103
10	1.1971	1.2090	1.1980	1.0008	1.0092
20	1.1874	1.1978	1.1883	1.0008	1.0081
30	1.1785	1.1875	1.1793	1.0007	1.0071
40	1.1702	1.1781	1.1710	1.0007	1.0061
50	1.1625	1.1693	1.1633	1.0007	1.0052
60	1.1554	1.1612	1.1561	1.0007	1.0044
70	1.1488	1.1536	1.1495	1.0007	1.0036
80	1.1426	1.1465	1.1433	1.0006	1.0029
90	1.1368	1.1400	1.1374	1.0006	1.0023
100	1.1314	1.1338	1.1320	1.0006	1.0016
200		1.0894	1.0922		0.9975
300		1.0638	1.0682		0.9959
400		1.0476	1.0526		0.9953
500		1.0368	1.0417		0.9954
600		1.0293	1.0338		0.9957
700		1.0238	1.0279		0.9961
800		1.0198	1.0235		0.9964
900		1.0167	1.0200		0.9968

* Cross over at 130°C

Minimum at 450°C

TABLE XIII

Results of Partition Function Ratio and ^{82}Se-^{76}Se Exchange Constant Calculations

T°C	(1) $\frac{Z(^{82}SeO_3^{=})}{Z(^{76}SeO_3^{=})}$	(2) $\frac{Z(^{82}SeO_4^{=})}{Z(^{76}SeO_4^{=})}$	K (1-2)
0	1.0285	1.0541	1.0250
10	1.0267	1.0510	1.0236
20	1.0252	1.0481	1.0224
30	1.0238	1.0454	1.0212
40	1.0224	1.0430	1.0201
50	1.0212	1.0407	1.0191
60	1.0201	1.0387	1.0182
70	1.0191	1.0367	1.0174
80	1.0181	1.0349	1.0166
90	1.0172	1.0333	1.0158
100	1.0164	1.0317	1.0151
200	1.0106	1.0207	1.0100
300	1.0074	1.0145	1.0071
400	1.0054	1.0107	1.0053
500	1.0042	1.0082	1.0041
600	1.0033	1.0065	1.0032
700	1.0027	1.0053	1.0026
800	1.0022	1.0043	1.0022
900	1.0019	1.0037	1.0018

relating initial isotopic abundances to those existing in the reaction products and substrate material after a fraction f of the starting material has reacted. Simpler relations may be derived by considering the conjugate, D, of f, and in particular the depletion in the substrate of the heavy isotope.

Consider the competing reactions

$$A_1 + B + C\ldots \xrightarrow{k_1} P_1 + \ldots$$
$$A_2 + B + C\ldots \xrightarrow{k_2} P_2 + \ldots$$

for which

$$-\frac{dA_1}{dt} = k_1 A_1 BC\ldots$$

$$-\frac{dA_2}{dt} = k_2 A_2 BC\ldots$$

Solution of these simultaneous differential equations yields:

$$\left(\frac{A_2}{A_{20}}\right)^{1/k_2} = \left(\frac{A_1}{A_{10}}\right)^{1/k_1}$$

This may be rewritten as

$$\frac{A_1}{A_{10}} = D^{k_1/k_2}$$

where

$$D = \frac{A_2}{A_{20}}$$

Defining δ as the del value for products compared with starting material and δ' as that for substrate compared with starting material it may be easily shown that

$$\delta = \frac{D - D^{k_1/k_2}}{1 - D^{k_1/k_2}}$$

and

$$\delta' = \frac{D}{D^{k_1/k_2}} - 1$$

A series of calculations has been made for δ and δ' using the McMaster University IBM 7040 computer. These quantities are tabulated in Table XIV for values of D between 0 and 1 and for values of k_1/k_2 between 1.000 and 1.050.

The layout of the tables is as follows:

Rate
Ratio ....54.00 ← % Reaction (% Depletion = 100 - % Reaction) Measured wrt. Heavy Isotope

1.012 .... 7.84 ← - Observed δ value

1.012 9.37 ← Observed δ' value

Although the table is accurate enough for most practical purposes it may be desired to relate the depletion with respect to the heavy isotope to the total depletion, and similarly for fractions of reaction. Now

$$D_T = \frac{A_1 + A_2}{A_{10} + A_{20}}$$

and it may be easily shown that

$$D = \frac{D_T}{1 - x'} \quad \text{and} \quad f = \frac{f_T}{1 - x}$$

where:

$$x' = N \frac{\delta'}{1 + \delta'} \quad \text{and} \quad x = N \frac{\delta}{1 + \delta}$$

and

$$N = \frac{\frac{A_{10}}{A_{20}}}{1 + \frac{A_{10}}{A_{20}}}$$

Depending on the value of $\frac{A_{10}}{A_{20}}$, N will have some value between zero and unity. The difference between D and D_T is a maximum for N equal to unity, in which case

$$\frac{D - D_T}{D_T} = \delta' \qquad \text{and} \qquad \frac{f - f_T}{f_T} = \delta$$

or for an observed isotope effect of 50 ^{o}/oo, the maximum error in D or f will be 5%.

TABLE XIV

Isotope Fractionation Factors for First Order Competing Reactions

(Pages 71-82 Inclusive)

RATE	PERCENT REACTION									
RATIO	10.00	9.00	8.00	7.00	6.00	5.00	4.00	3.00	2.00	1.00
1.001	0.95	0.96	0.96	0.97	0.97	0.98	0.98	0.99	0.99	1.00
1.001	0.11	0.10	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02
1.002	1.90	1.91	1.92	1.93	1.94	1.95	1.96	1.97	1.98	1.99
1.002	0.22	0.19	0.17	0.15	0.13	0.11	0.09	0.07	0.05	0.03
1.003	2.84	2.86	2.87	2.89	2.90	2.92	2.94	2.95	2.97	2.98
1.003	0.32	0.29	0.26	0.22	0.19	0.16	0.13	0.10	0.07	0.04
1.004	3.78	3.80	3.83	3.85	3.87	3.89	3.91	3.93	3.95	3.97
1.004	0.43	0.38	0.34	0.30	0.25	0.21	0.17	0.13	0.09	0.05
1.005	4.72	4.75	4.78	4.80	4.83	4.85	4.88	4.90	4.93	4.95
1.005	0.53	0.48	0.42	0.37	0.31	0.26	0.21	0.16	0.11	0.06
1.006	5.66	5.69	5.72	5.76	5.79	5.82	5.85	5.88	5.91	5.94
1.006	0.64	0.57	0.51	0.44	0.38	0.31	0.25	0.19	0.13	0.07
1.007	6.60	6.63	6.67	6.71	6.74	6.78	6.82	6.85	6.89	6.92
1.007	0.74	0.67	0.59	0.51	0.44	0.36	0.29	0.22	0.15	0.08
1.008	7.53	7.57	7.62	7.66	7.70	7.74	7.78	7.82	7.86	7.90
1.008	0.85	0.76	0.67	0.59	0.50	0.42	0.33	0.25	0.17	0.09
1.009	8.46	8.51	8.56	8.60	8.65	8.70	8.74	8.79	8.83	8.88
1.009	0.95	0.85	0.76	0.66	0.56	0.47	0.37	0.28	0.19	0.10
1.010	9.39	9.45	9.50	9.55	9.60	9.65	9.70	9.76	9.81	9.86
1.010	1.06	0.95	0.84	0.73	0.62	0.52	0.41	0.31	0.21	0.11
1.011	10.32	10.38	10.44	10.50	10.55	10.61	10.66	10.72	10.78	10.83
1.011	1.16	1.04	0.92	0.80	0.69	0.57	0.45	0.34	0.23	0.12
1.012	11.25	11.31	11.38	11.44	11.50	11.56	11.62	11.68	11.74	11.80
1.012	1.27	1.14	1.01	0.88	0.75	0.62	0.49	0.37	0.25	0.13
1.013	12.17	12.24	12.31	12.38	12.44	12.51	12.58	12.64	12.71	12.77
1.013	1.38	1.23	1.09	0.95	0.81	0.67	0.54	0.40	0.27	0.14
1.014	13.10	13.17	13.24	13.32	13.39	13.46	13.53	13.60	13.67	13.74
1.014	1.48	1.33	1.17	1.02	0.87	0.72	0.58	0.43	0.29	0.15
1.015	14.02	14.10	14.18	14.25	14.33	14.41	14.48	14.56	14.63	14.71
1.015	1.59	1.42	1.26	1.09	0.93	0.77	0.62	0.46	0.31	0.16
1.016	14.94	15.02	15.11	15.19	15.27	15.35	15.43	15.51	15.59	15.67
1.016	1.69	1.52	1.34	1.17	1.00	0.83	0.66	0.49	0.33	0.17
1.017	15.86	15.94	16.03	16.12	16.21	16.30	16.38	16.47	16.55	16.64
1.017	1.80	1.61	1.42	1.24	1.06	0.88	0.70	0.52	0.35	0.18
1.018	16.77	16.87	16.96	17.05	17.14	17.24	17.33	17.42	17.51	17.60
1.018	1.90	1.70	1.51	1.31	1.12	0.93	0.74	0.55	0.37	0.19
1.019	17.69	17.78	17.88	17.98	18.08	18.18	18.27	18.37	18.46	18.56
1.019	2.01	1.80	1.59	1.38	1.18	0.98	0.78	0.58	0.39	0.20
1.020	18.60	18.70	18.81	18.91	19.01	19.11	19.21	19.32	19.42	19.51
1.020	2.11	1.89	1.67	1.46	1.24	1.03	0.82	0.61	0.41	0.21
1.021	19.51	19.62	19.73	19.84	19.94	20.05	20.16	20.26	20.37	20.47
1.021	2.22	1.99	1.76	1.53	1.31	1.08	0.86	0.64	0.43	0.22
1.022	20.42	20.53	20.65	20.76	20.87	20.98	21.09	21.20	21.31	21.42
1.022	2.33	2.08	1.84	1.60	1.37	1.13	0.90	0.68	0.45	0.23
1.023	21.32	21.44	21.56	21.68	21.80	21.92	22.03	22.15	22.26	22.37
1.023	2.43	2.18	1.92	1.68	1.43	1.19	0.94	0.71	0.47	0.24
1.024	22.23	22.35	22.48	22.60	22.72	22.85	22.97	23.09	23.21	23.32
1.024	2.54	2.27	2.01	1.75	1.49	1.24	0.99	0.74	0.49	0.25
1.025	23.13	23.26	23.39	23.52	23.65	23.77	23.90	24.03	24.15	24.27
1.025	2.64	2.37	2.09	1.82	1.55	1.29	1.03	0.77	0.51	0.26

RATE	PERCENT REACTION									
RATIO	10.00	9.00	8.00	7.00	6.00	5.00	4.00	3.00	2.00	1.00
1.026	24.03	24.17	24.30	24.44	24.57	24.70	24.83	24.96	25.09	25.22
1.026	2.75	2.46	2.18	1.89	1.62	1.34	1.07	0.80	0.53	0.27
1.027	24.93	25.07	25.21	25.35	25.49	25.63	25.76	25.90	26.03	26.16
1.027	2.85	2.55	2.26	1.97	1.68	1.39	1.11	0.83	0.55	0.28
1.028	25.83	25.98	26.12	26.27	26.41	26.55	26.69	26.83	26.97	27.10
1.028	2.96	2.65	2.34	2.04	1.74	1.44	1.15	0.86	0.57	0.29
1.029	26.73	26.88	27.03	27.18	27.32	27.47	27.62	27.76	27.90	28.05
1.029	3.07	2.74	2.43	2.11	1.80	1.49	1.19	0.89	0.59	0.30
1.030	27.62	27.78	27.93	28.09	28.24	28.39	28.54	28.69	28.84	28.98
1.030	3.17	2.84	2.51	2.18	1.86	1.54	1.23	0.92	0.61	0.31
1.031	28.52	28.68	28.84	28.99	29.15	29.31	29.46	29.62	29.77	29.92
1.031	3.28	2.93	2.59	2.26	1.92	1.60	1.27	0.95	0.63	0.32
1.032	29.41	29.57	29.74	29.90	30.06	30.22	30.38	30.54	30.70	30.86
1.032	3.38	3.03	2.68	2.33	1.99	1.65	1.31	0.98	0.65	0.33
1.033	30.30	30.47	30.64	30.81	30.97	31.14	31.30	31.47	31.63	31.79
1.033	3.49	3.12	2.76	2.40	2.05	1.70	1.35	1.01	0.67	0.34
1.034	31.18	31.36	31.53	31.71	31.88	32.05	32.22	32.39	32.56	32.72
1.034	3.59	3.22	2.84	2.48	2.11	1.75	1.39	1.04	0.69	0.35
1.035	32.07	32.25	32.43	32.61	32.79	32.96	33.14	33.31	33.48	33.65
1.035	3.70	3.31	2.93	2.55	2.17	1.80	1.43	1.07	0.71	0.36
1.036	32.95	33.14	33.32	33.51	33.69	33.87	34.05	34.23	34.40	34.58
1.036	3.81	3.41	3.01	2.62	2.23	1.85	1.48	1.10	0.73	0.37
1.037	33.84	34.03	34.22	34.40	34.59	34.78	34.96	35.14	35.33	35.51
1.037	3.91	3.50	3.09	2.69	2.30	1.90	1.52	1.13	0.75	0.38
1.038	34.72	34.91	35.11	35.30	35.49	35.68	35.87	36.06	36.24	36.43
1.038	4.02	3.60	3.18	2.77	2.36	1.96	1.56	1.16	0.77	0.39
1.039	35.60	35.80	36.00	36.19	36.39	36.59	36.78	36.97	37.16	37.35
1.039	4.12	3.69	3.26	2.84	2.42	2.01	1.60	1.19	0.79	0.40
1.040	36.47	36.68	36.88	37.09	37.29	37.49	37.69	37.88	38.08	38.27
1.040	4.23	3.78	3.35	2.91	2.48	2.06	1.64	1.22	0.81	0.41
1.041	37.35	37.56	37.77	37.98	38.18	38.39	38.59	38.79	38.99	39.19
1.041	4.33	3.88	3.43	2.98	2.55	2.11	1.68	1.25	0.83	0.42
1.042	38.22	38.44	38.65	38.87	39.08	39.29	39.49	39.70	39.91	40.11
1.042	4.44	3.97	3.51	3.06	2.61	2.16	1.72	1.29	0.85	0.43
1.043	39.10	39.32	39.54	39.75	39.97	40.18	40.40	40.61	40.82	41.02
1.043	4.55	4.07	3.60	3.13	2.67	2.21	1.76	1.32	0.87	0.44
1.044	39.97	40.19	40.42	40.64	40.86	41.08	41.30	41.51	41.73	41.94
1.044	4.65	4.16	3.68	3.20	2.73	2.26	1.80	1.35	0.89	0.45
1.045	40.84	41.07	41.30	41.52	41.75	41.97	42.19	42.41	42.63	42.85
1.045	4.76	4.26	3.76	3.28	2.79	2.32	1.84	1.38	0.91	0.46
1.046	41.70	41.94	42.17	42.40	42.63	42.86	43.09	43.32	43.54	43.76
1.046	4.86	4.35	3.85	3.35	2.86	2.37	1.88	1.41	0.93	0.47
1.047	42.57	42.81	43.05	43.28	43.52	43.75	43.98	44.21	44.44	44.67
1.047	4.97	4.45	3.93	3.42	2.92	2.42	1.93	1.44	0.95	0.48
1.048	43.43	43.68	43.92	44.16	44.40	44.64	44.88	45.11	45.34	45.58
1.048	5.08	4.54	4.02	3.49	2.98	2.47	1.97	1.47	0.98	0.49
1.049	44.30	44.55	44.79	45.04	45.28	45.53	45.77	46.01	46.25	46.48
1.049	5.18	4.64	4.10	3.57	3.04	2.52	2.01	1.50	1.00	0.50
1.050	45.16	45.41	45.66	45.92	46.16	46.41	46.66	46.90	47.14	47.38
1.050	5.29	4.73	4.18	3.64	3.10	2.57	2.05	1.53	1.02	0.51

RATE	PERCENT REACTION									
RATIO	20.00	19.00	18.00	17.00	16.00	15.00	14.00	13.00	12.00	11.00
1.001	0.90	0.90	0.91	0.91	0.92	0.93	0.93	0.94	0.94	0.95
1.001	0.23	0.22	0.20	0.19	0.18	0.17	0.16	0.14	0.13	0.12
1.002	1.79	1.80	1.81	1.82	1.83	1.84	1.85	1.87	1.88	1.89
1.002	0.45	0.43	0.40	0.38	0.35	0.33	0.31	0.28	0.26	0.24
1.003	2.67	2.69	2.71	2.73	2.74	2.76	2.78	2.79	2.81	2.83
1.003	0.67	0.64	0.60	0.56	0.53	0.49	0.46	0.42	0.39	0.35
1.004	3.56	3.58	3.61	3.63	3.65	3.67	3.70	3.72	3.74	3.76
1.004	0.90	0.85	0.80	0.75	0.70	0.66	0.61	0.56	0.52	0.47
1.005	4.45	4.47	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.70
1.005	1.12	1.06	1.00	0.94	0.88	0.82	0.76	0.70	0.64	0.59
1.006	5.33	5.36	5.40	5.43	5.46	5.50	5.53	5.56	5.60	5.63
1.006	1.34	1.27	1.20	1.12	1.05	0.98	0.91	0.84	0.77	0.70
1.007	6.21	6.25	6.29	6.33	6.37	6.41	6.45	6.48	6.52	6.56
1.007	1.57	1.48	1.40	1.31	1.23	1.14	1.06	0.98	0.90	0.82
1.008	7.09	7.13	7.18	7.22	7.27	7.31	7.36	7.40	7.44	7.49
1.008	1.79	1.69	1.59	1.50	1.40	1.31	1.21	1.12	1.03	0.94
1.009	7.97	8.02	8.07	8.12	8.17	8.22	8.27	8.32	8.37	8.41
1.009	2.02	1.90	1.79	1.68	1.58	1.47	1.36	1.26	1.16	1.05
1.010	8.84	8.90	8.96	9.01	9.07	9.12	9.18	9.23	9.29	9.34
1.010	2.24	2.11	1.99	1.87	1.75	1.63	1.51	1.40	1.28	1.17
1.011	9.72	9.78	9.84	9.90	9.96	10.02	10.09	10.14	10.20	10.26
1.011	2.46	2.33	2.19	2.06	1.92	1.79	1.67	1.54	1.41	1.29
1.012	10.59	10.66	10.72	10.79	10.86	10.92	10.99	11.06	11.12	11.18
1.012	2.69	2.54	2.39	2.24	2.10	1.96	1.82	1.68	1.54	1.40
1.013	11.46	11.53	11.61	11.68	11.75	11.82	11.89	11.96	12.04	12.10
1.013	2.91	2.75	2.59	2.43	2.27	2.12	1.97	1.82	1.67	1.52
1.014	12.33	12.41	12.49	12.56	12.64	12.72	12.80	12.87	12.95	13.02
1.014	3.13	2.96	2.79	2.62	2.45	2.28	2.12	1.96	1.80	1.64
1.015	13.19	13.28	13.36	13.45	13.53	13.61	13.70	13.78	13.86	13.94
1.015	3.36	3.17	2.99	2.80	2.62	2.45	2.27	2.10	1.92	1.75
1.016	14.06	14.15	14.24	14.33	14.42	14.51	14.59	14.68	14.77	14.85
1.016	3.58	3.38	3.19	2.99	2.80	2.61	2.42	2.24	2.05	1.87
1.017	14.92	15.02	15.12	15.21	15.31	15.40	15.49	15.58	15.67	15.77
1.017	3.81	3.59	3.38	3.18	2.97	2.77	2.57	2.38	2.18	1.99
1.018	15.79	15.89	15.99	16.09	16.19	16.29	16.39	16.48	16.58	16.68
1.018	4.03	3.81	3.58	3.36	3.15	2.93	2.72	2.51	2.31	2.10
1.019	16.65	16.75	16.86	16.97	17.07	17.18	17.28	17.38	17.48	17.58
1.019	4.25	4.02	3.78	3.55	3.32	3.10	2.87	2.65	2.44	2.22
1.020	17.50	17.62	17.73	17.84	17.95	18.06	18.17	18.28	18.39	18.49
1.020	4.48	4.23	3.98	3.74	3.50	3.26	3.03	2.79	2.56	2.34
1.021	18.36	18.48	18.60	18.71	18.83	18.95	19.06	19.17	19.29	19.40
1.021	4.70	4.44	4.18	3.93	3.67	3.42	3.18	2.93	2.69	2.46
1.022	19.22	19.34	19.46	19.59	19.71	19.83	19.95	20.07	20.18	20.30
1.022	4.93	4.65	4.38	4.11	3.85	3.59	3.33	3.07	2.82	2.57
1.023	20.07	20.20	20.33	20.46	20.58	20.71	20.83	20.96	21.08	21.20
1.023	5.15	4.86	4.58	4.30	4.02	3.75	3.48	3.21	2.95	2.69
1.024	20.92	21.06	21.19	21.32	21.46	21.59	21.72	21.85	21.98	22.10
1.024	5.37	5.08	4.78	4.49	4.20	3.91	3.63	3.35	3.08	2.81
1.025	21.77	21.91	22.05	22.19	22.33	22.47	22.60	22.74	22.87	23.00
1.025	5.60	5.29	4.98	4.67	4.37	4.08	3.78	3.49	3.21	2.92

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RATE          PERCENT  REACTION
RATIO     20.00     19.00     18.00     17.00     16.00     15.00     14.00     13.00     12.00     11.00

1.026     22.62     22.77     22.91     23.06     23.20     23.34     23.48     23.62     23.76     23.90
1.026      5.82      5.50      5.18      4.86      4.55      4.24      3.93      3.63      3.33      3.04
1.027     23.47     23.62     23.77     23.92     24.07     24.22     24.36     24.51     24.65     24.79
1.027      6.05      5.71      5.38      5.05      4.72      4.40      4.09      3.77      3.46      3.16
1.028     24.31     24.47     24.63     24.78     24.94     25.09     25.24     25.39     25.54     25.69
1.028      6.27      5.92      5.58      5.24      4.90      4.57      4.24      3.91      3.59      3.27
1.029     25.16     25.32     25.48     25.64     25.80     25.96     26.11     26.27     26.42     26.58
1.029      6.50      6.13      5.78      5.42      5.07      4.73      4.39      4.05      3.72      3.39
1.030     26.00     26.17     26.33     26.50     26.66     26.83     26.99     27.15     27.31     27.47
1.030      6.72      6.35      5.98      5.61      5.25      4.89      4.54      4.19      3.85      3.51
1.031     26.84     27.01     27.19     27.36     27.53     27.69     27.86     28.03     28.19     28.35
1.031      6.95      6.56      6.18      5.80      5.42      5.06      4.69      4.33      3.98      3.62
1.032     27.68     27.86     28.03     28.21     28.39     28.56     28.73     28.90     29.07     29.24
1.032      7.17      6.77      6.38      5.99      5.60      5.22      4.84      4.47      4.10      3.74
1.033     28.51     28.70     28.88     29.06     29.24     29.42     29.60     29.78     29.95     30.12
1.033      7.40      6.98      6.58      6.17      5.78      5.38      4.99      4.61      4.23      3.86
1.034     29.35     29.54     29.73     29.92     30.10     30.28     30.47     30.65     30.83     31.01
1.034      7.62      7.20      6.78      6.36      5.95      5.55      5.15      4.75      4.36      3.97
1.035     30.18     30.38     30.57     30.77     30.96     31.15     31.33     31.52     31.70     31.89
1.035      7.85      7.41      6.97      6.55      6.13      5.71      5.30      4.89      4.49      4.09
1.036     31.02     31.22     31.42     31.61     31.81     32.00     32.20     32.39     32.58     32.77
1.036      8.07      7.62      7.17      6.74      6.30      5.87      5.45      5.03      4.62      4.21
1.037     31.85     32.05     32.26     32.46     32.66     32.86     33.06     33.26     33.45     33.64
1.037      8.30      7.83      7.37      6.92      6.48      6.04      5.60      5.17      4.75      4.33
1.038     32.68     32.89     33.10     33.31     33.51     33.72     33.92     34.12     34.32     34.52
1.038      8.52      8.04      7.57      7.11      6.65      6.20      5.75      5.31      4.87      4.44
1.039     33.50     33.72     33.94     34.15     34.36     34.57     34.78     34.99     35.19     35.39
1.039      8.75      8.26      7.77      7.30      6.83      6.36      5.90      5.45      5.00      4.56
1.040     34.33     34.55     34.77     34.99     35.21     35.42     35.64     35.85     36.06     36.27
1.040      8.97      8.47      7.97      7.49      7.00      6.53      6.06      5.59      5.13      4.68
1.041     35.15     35.38     35.61     35.83     36.05     36.27     36.49     36.71     36.92     37.14
1.041      9.20      8.68      8.17      7.67      7.18      6.69      6.21      5.73      5.26      4.79
1.042     35.98     36.21     36.44     36.67     36.90     37.12     37.35     37.57     37.79     38.01
1.042      9.42      8.89      8.37      7.86      7.35      6.85      6.36      5.87      5.39      4.91
1.043     36.80     37.03     37.27     37.51     37.74     37.97     38.20     38.43     38.65     38.87
1.043      9.65      9.11      8.57      8.05      7.53      7.02      6.51      6.01      5.52      5.03
1.044     37.62     37.86     38.10     38.34     38.58     38.81     39.05     39.28     39.51     39.74
1.044      9.87      9.32      8.78      8.24      7.71      7.18      6.66      6.15      5.65      5.15
1.045     38.43     38.68     38.93     39.17     39.42     39.66     39.90     40.14     40.37     40.60
1.045     10.10      9.53      8.98      8.43      7.88      7.35      6.82      6.29      5.77      5.26
1.046     39.25     39.50     39.76     40.01     40.25     40.50     40.75     40.99     41.23     41.47
1.046     10.32      9.75      9.18      8.61      8.06      7.51      6.97      6.43      5.90      5.38
1.047     40.06     40.32     40.58     40.84     41.09     41.34     41.59     41.84     42.08     42.33
1.047     10.55      9.96      9.38      8.80      8.23      7.67      7.12      6.57      6.03      5.50
1.048     40.88     41.14     41.41     41.67     41.92     42.18     42.44     42.69     42.94     43.19
1.048     10.77     10.17      9.58      8.99      8.41      7.84      7.27      6.71      6.16      5.61
1.049     41.69     41.96     42.23     42.49     42.76     43.02     43.28     43.54     43.79     44.04
1.049     11.00     10.38      9.78      9.18      8.58      8.00      7.42      6.85      6.29      5.73
1.050     42.50     42.77     43.05     43.32     43.59     43.85     44.12     44.38     44.64     44.90
1.050     11.22     10.60      9.98      9.36      8.76      8.16      7.57      6.99      6.42      5.85
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RATE          PERCENT  REACTION
RATIO    30.00     29.00     28.00     27.00     26.00     25.00     24.00     23.00     22.00     21.00

1.001     0.84      0.84      0.85      0.85      0.86      0.87      0.87      0.88      0.88      0.89
1.001     0.36      0.35      0.33      0.32      0.31      0.29      0.28      0.27      0.25      0.24
1.002     1.67      1.68      1.69      1.70      1.72      1.73      1.74      1.75      1.76      1.77
1.002     0.72      0.69      0.66      0.63      0.61      0.58      0.55      0.53      0.50      0.48
1.003     2.49      2.51      2.53      2.55      2.57      2.59      2.60      2.62      2.64      2.66
1.003     1.08      1.03      0.99      0.95      0.91      0.87      0.83      0.79      0.75      0.71
1.004     3.32      3.35      3.37      3.39      3.42      3.44      3.47      3.49      3.51      3.54
1.004     1.43      1.38      1.32      1.26      1.21      1.16      1.10      1.05      1.00      0.95
1.005     4.15      4.18      4.21      4.24      4.27      4.30      4.33      4.36      4.39      4.42
1.005     1.79      1.72      1.65      1.58      1.51      1.44      1.38      1.31      1.25      1.18
1.006     4.97      5.01      5.04      5.08      5.12      5.15      5.19      5.22      5.26      5.29
1.006     2.15      2.06      1.98      1.90      1.81      1.73      1.65      1.57      1.50      1.42
1.007     5.79      5.83      5.88      5.92      5.96      6.00      6.05      6.09      6.13      6.17
1.007     2.50      2.41      2.31      2.21      2.11      2.02      1.93      1.84      1.75      1.66
1.008     6.61      6.66      6.71      6.76      6.81      6.85      6.90      6.95      7.00      7.04
1.008     2.86      2.75      2.64      2.53      2.42      2.31      2.20      2.10      1.99      1.89
1.009     7.43      7.48      7.54      7.59      7.65      7.70      7.76      7.81      7.86      7.91
1.009     3.22      3.09      2.97      2.84      2.72      2.60      2.48      2.36      2.24      2.13
1.010     8.24      8.31      8.37      8.43      8.49      8.55      8.61      8.67      8.73      8.78
1.010     3.58      3.44      3.30      3.16      3.02      2.89      2.75      2.62      2.49      2.36
1.011     9.06      9.13      9.19      9.26      9.33      9.39      9.46      9.52      9.59      9.65
1.011     3.94      3.78      3.63      3.47      3.32      3.17      3.03      2.88      2.74      2.60
1.012     9.87      9.95     10.02     10.09     10.17     10.24     10.31     10.38     10.45     10.52
1.012     4.29      4.12      3.95      3.79      3.62      3.46      3.30      3.15      2.99      2.84
1.013    10.68     10.76     10.84     10.92     11.00     11.08     11.16     11.23     11.31     11.38
1.013     4.65      4.47      4.28      4.10      3.93      3.75      3.58      3.41      3.24      3.07
1.014    11.49     11.58     11.67     11.75     11.84     11.92     12.00     12.08     12.17     12.25
1.014     5.01      4.81      4.61      4.42      4.23      4.04      3.85      3.67      3.49      3.31
1.015    12.30     12.39     12.49     12.58     12.67     12.76     12.85     12.93     13.02     13.11
1.015     5.37      5.16      4.94      4.74      4.53      4.33      4.13      3.93      3.74      3.55
1.016    13.11     13.21     13.31     13.40     13.50     13.59     13.69     13.78     13.88     13.97
1.016     5.73      5.50      5.27      5.05      4.83      4.62      4.41      4.20      3.99      3.78
1.017    13.91     14.02     14.12     14.23     14.33     14.43     14.53     14.63     14.73     14.83
1.017     6.09      5.84      5.61      5.37      5.14      4.91      4.68      4.46      4.24      4.02
1.018    14.72     14.83     14.94     15.05     15.16     15.26     15.37     15.47     15.58     15.68
1.018     6.45      6.19      5.94      5.69      5.44      5.20      4.96      4.72      4.49      4.26
1.019    15.52     15.64     15.75     15.87     15.98     16.09     16.21     16.32     16.43     16.54
1.019     6.80      6.53      6.27      6.00      5.74      5.49      5.23      4.98      4.74      4.49
1.020    16.32     16.44     16.57     16.69     16.81     16.92     17.04     17.16     17.28     17.39
1.020     7.16      6.88      6.60      6.32      6.05      5.78      5.51      5.25      4.99      4.73
1.021    17.12     17.25     17.38     17.50     17.63     17.75     17.88     18.00     18.12     18.24
1.021     7.52      7.22      6.93      6.64      6.35      6.06      5.78      5.51      5.24      4.97
1.022    17.92     18.05     18.19     18.32     18.45     18.58     18.71     18.84     18.97     19.09
1.022     7.88      7.57      7.26      6.95      6.65      6.35      6.06      5.77      5.49      5.20
1.023    18.71     18.85     18.99     19.13     19.27     19.41     19.54     19.67     19.81     19.94
1.023     8.24      7.91      7.59      7.27      6.95      6.64      6.34      6.03      5.74      5.44
1.024    19.51     19.65     19.80     19.94     20.09     20.23     20.37     20.51     20.65     20.79
1.024     8.60      8.26      7.92      7.59      7.26      6.93      6.61      6.30      5.99      5.68
1.025    20.30     20.45     20.60     20.75     20.90     21.05     21.20     21.34     21.49     21.63
1.025     8.96      8.60      8.25      7.90      7.56      7.22      6.89      6.56      6.24      5.92
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RATE	PERCENT REACTION									
RATIO	30.00	29.00	28.00	27.00	26.00	25.00	24.00	23.00	22.00	21.00
1.026	21.09	21.25	21.41	21.56	21.72	21.87	22.02	22.18	22.33	22.47
1.026	9.32	8.95	8.58	8.22	7.86	7.51	7.17	6.82	6.49	6.15
1.027	21.88	22.04	22.21	22.37	22.53	22.69	22.85	23.01	23.16	23.32
1.027	9.68	9.30	8.91	8.54	8.17	7.80	7.44	7.09	6.74	6.39
1.028	22.67	22.84	23.01	23.18	23.34	23.51	23.67	23.83	24.00	24.15
1.028	10.04	9.64	9.25	8.86	8.47	8.09	7.72	7.35	6.99	6.63
1.029	23.45	23.63	23.81	23.98	24.15	24.32	24.49	24.66	24.83	24.99
1.029	10.40	9.99	9.58	9.17	8.78	8.38	8.00	7.61	7.24	6.86
1.030	24.24	24.42	24.60	24.78	24.96	25.14	25.31	25.49	25.66	25.83
1.030	10.76	10.33	9.91	9.49	9.08	8.67	8.27	7.88	7.49	7.10
1.031	25.02	25.21	25.40	25.58	25.77	25.95	26.13	26.31	26.49	26.66
1.031	11.12	10.68	10.24	9.81	9.38	8.96	8.55	8.14	7.74	7.34
1.032	25.80	26.00	26.19	26.38	26.57	26.76	26.95	27.13	27.32	27.50
1.032	11.48	11.02	10.57	10.13	9.69	9.25	8.83	8.40	7.99	7.58
1.033	26.58	26.78	26.98	27.18	27.38	27.57	27.76	27.95	28.14	28.33
1.033	11.84	11.37	10.90	10.44	9.99	9.54	9.10	8.67	8.24	7.81
1.034	27.36	27.57	27.77	27.98	28.18	28.38	28.57	28.77	28.97	29.16
1.034	12.21	11.72	11.24	10.76	10.30	9.83	9.38	8.93	8.49	8.05
1.035	28.14	28.35	28.56	28.77	28.98	29.18	29.39	29.59	29.79	29.99
1.035	12.57	12.06	11.57	11.08	10.60	10.12	9.66	9.19	8.74	8.29
1.036	28.91	29.13	29.35	29.56	29.78	29.99	30.20	30.40	30.61	30.81
1.036	12.93	12.41	11.90	11.40	10.90	10.42	9.93	9.46	8.99	8.53
1.037	29.69	29.91	30.13	30.36	30.57	30.79	31.01	31.22	31.43	31.64
1.037	13.29	12.76	12.23	11.72	11.21	10.71	10.21	9.72	9.24	8.76
1.038	30.46	30.69	30.92	31.15	31.37	31.59	31.81	32.03	32.25	32.46
1.038	13.65	13.10	12.57	12.04	11.51	11.00	10.49	9.99	9.49	9.00
1.039	31.23	31.47	31.70	31.93	32.16	32.39	32.62	32.84	33.06	33.28
1.039	14.01	13.45	12.90	12.35	11.82	11.29	10.77	10.25	9.74	9.24
1.040	32.00	32.24	32.48	32.72	32.96	33.19	33.42	33.65	33.88	34.10
1.040	14.37	13.80	13.23	12.67	12.12	11.58	11.04	10.51	9.99	9.48
1.041	32.77	33.02	33.26	33.51	33.75	33.99	34.22	34.46	34.69	34.92
1.041	14.74	14.15	13.56	12.99	12.43	11.87	11.32	10.78	10.24	9.72
1.042	33.54	33.79	34.04	34.29	34.54	34.78	35.02	35.27	35.50	35.74
1.042	15.10	14.49	13.90	13.31	12.73	12.16	11.60	11.04	10.49	9.95
1.043	34.30	34.56	34.82	35.07	35.32	35.58	35.82	36.07	36.31	36.56
1.043	15.46	14.84	14.23	13.63	13.04	12.45	11.88	11.31	10.75	10.19
1.044	35.06	35.33	35.59	35.85	36.11	36.37	36.62	36.87	37.12	37.37
1.044	15.82	15.19	14.56	13.95	13.34	12.74	12.15	11.57	11.00	10.43
1.045	35.83	36.10	36.37	36.63	36.90	37.16	37.42	37.67	37.93	38.18
1.045	16.18	15.54	14.90	14.27	13.65	13.03	12.43	11.84	11.25	10.67
1.046	36.59	36.86	37.14	37.41	37.68	37.95	38.21	38.47	38.74	38.99
1.046	16.55	15.88	15.23	14.59	13.95	13.33	12.71	12.10	11.50	10.91
1.047	37.35	37.63	37.91	38.19	38.46	38.73	39.01	39.27	39.54	39.80
1.047	16.91	16.23	15.56	14.91	14.26	13.62	12.99	12.36	11.75	11.15
1.048	38.10	38.39	38.68	38.96	39.24	39.52	39.80	40.07	40.34	40.61
1.048	17.27	16.58	15.90	15.23	14.56	13.91	13.27	12.63	12.00	11.38
1.049	38.86	39.15	39.45	39.73	40.02	40.31	40.59	40.87	41.14	41.42
1.049	17.64	16.93	16.23	15.55	14.87	14.20	13.54	12.89	12.25	11.62
1.050	39.61	39.91	40.21	40.51	40.80	41.09	41.38	41.66	41.94	42.22
1.050	18.00	17.28	16.57	15.86	15.17	14.49	13.82	13.16	12.51	11.86

RATE	PERCENT REACTION									
RATIO	40.00	39.00	38.00	37.00	36.00	35.00	34.00	33.00	32.00	31.00
1.001	0.77	0.78	0.78	0.79	0.80	0.80	0.81	0.82	0.82	0.83
1.001	0.52	0.50	0.48	0.47	0.45	0.44	0.42	0.41	0.39	0.38
1.002	1.53	1.55	1.56	1.58	1.59	1.60	1.61	1.63	1.64	1.65
1.002	1.03	0.99	0.96	0.93	0.90	0.87	0.84	0.81	0.78	0.75
1.003	2.30	2.32	2.34	2.36	2.38	2.40	2.42	2.44	2.46	2.48
1.003	1.54	1.49	1.44	1.39	1.34	1.30	1.25	1.21	1.16	1.12
1.004	3.06	3.08	3.11	3.14	3.17	3.19	3.22	3.24	3.27	3.30
1.004	2.05	1.98	1.92	1.85	1.79	1.73	1.67	1.61	1.55	1.49
1.005	3.82	3.85	3.88	3.92	3.95	3.98	4.02	4.05	4.08	4.11
1.005	2.56	2.48	2.40	2.32	2.24	2.16	2.08	2.01	1.94	1.86
1.006	4.57	4.62	4.66	4.70	4.74	4.78	4.82	4.85	4.89	4.93
1.006	3.07	2.98	2.88	2.78	2.69	2.59	2.50	2.41	2.32	2.23
1.007	5.33	5.38	5.43	5.47	5.52	5.57	5.61	5.66	5.70	5.75
1.007	3.59	3.47	3.36	3.24	3.13	3.02	2.92	2.81	2.71	2.61
1.008	6.09	6.14	6.19	6.25	6.30	6.35	6.41	6.46	6.51	6.56
1.008	4.10	3.97	3.84	3.71	3.58	3.46	3.33	3.21	3.10	2.98
1.009	6.84	6.90	6.96	7.02	7.08	7.14	7.20	7.26	7.31	7.37
1.009	4.61	4.46	4.32	4.17	4.03	3.89	3.75	3.62	3.48	3.35
1.010	7.59	7.66	7.73	7.79	7.86	7.92	7.99	8.05	8.12	8.18
1.010	5.13	4.96	4.80	4.64	4.48	4.32	4.17	4.02	3.87	3.72
1.011	8.34	8.41	8.49	8.56	8.64	8.71	8.78	8.85	8.92	8.99
1.011	5.64	5.46	5.28	5.10	4.93	4.75	4.59	4.42	4.26	4.09
1.012	9.09	9.17	9.25	9.33	9.41	9.49	9.57	9.64	9.72	9.80
1.012	6.15	5.95	5.76	5.56	5.37	5.19	5.00	4.82	4.64	4.47
1.013	9.84	9.92	10.01	10.10	10.18	10.27	10.35	10.44	10.52	10.60
1.013	6.67	6.45	6.24	6.03	5.82	5.62	5.42	5.22	5.03	4.84
1.014	10.58	10.68	10.77	10.86	10.96	11.05	11.14	11.23	11.32	11.41
1.014	7.18	6.95	6.72	6.49	6.27	6.05	5.84	5.63	5.42	5.21
1.015	11.32	11.43	11.53	11.63	11.73	11.83	11.92	12.02	12.11	12.21
1.015	7.70	7.45	7.20	6.96	6.72	6.49	6.26	6.03	5.81	5.59
1.016	12.07	12.18	12.28	12.39	12.50	12.60	12.70	12.81	12.91	13.01
1.016	8.21	7.94	7.68	7.42	7.17	6.92	6.68	6.43	6.19	5.96
1.017	12.81	12.92	13.04	13.15	13.26	13.37	13.48	13.59	13.70	13.81
1.017	8.73	8.44	8.16	7.89	7.62	7.36	7.09	6.84	6.58	6.33
1.018	13.55	13.67	13.79	13.91	14.03	14.15	14.26	14.38	14.49	14.61
1.018	9.24	8.94	8.65	8.36	8.07	7.79	7.51	7.24	6.97	6.71
1.019	14.29	14.41	14.54	14.67	14.79	14.92	15.04	15.16	15.28	15.40
1.019	9.76	9.44	9.13	8.82	8.52	8.22	7.93	7.64	7.36	7.08
1.020	15.02	15.16	15.29	15.42	15.56	15.69	15.82	15.94	16.07	16.20
1.020	10.27	9.94	9.61	9.29	8.97	8.66	8.35	8.05	7.75	7.45
1.021	15.76	15.90	16.04	16.18	16.32	16.45	16.59	16.72	16.86	16.99
1.021	10.79	10.44	10.09	9.75	9.42	9.09	8.77	8.45	8.14	7.83
1.022	16.49	16.64	16.79	16.93	17.08	17.22	17.36	17.50	17.64	17.78
1.022	11.31	10.94	10.58	10.22	9.87	9.53	9.19	8.85	8.53	8.20
1.023	17.22	17.38	17.53	17.69	17.84	17.99	18.13	18.28	18.42	18.57
1.023	11.82	11.44	11.06	10.69	10.32	9.96	9.61	9.26	8.91	8.58
1.024	17.95	18.12	18.28	18.44	18.59	18.75	18.90	19.06	19.21	19.36
1.024	12.34	11.94	11.54	11.16	10.77	10.40	10.03	9.66	9.30	8.95
1.025	18.68	18.85	19.02	19.18	19.35	19.51	19.67	19.83	19.99	20.14
1.025	12.86	12.44	12.03	11.62	11.22	10.83	10.45	10.07	9.69	9.32

RATE	PERCENT REACTION									
RATIO	40.00	39.00	38.00	37.00	36.00	35.00	34.00	33.00	32.00	31.00
1.026	19.41	19.59	19.76	19.93	20.10	20.27	20.44	20.60	20.77	20.93
1.026	13.38	12.94	12.51	12.09	11.68	11.27	10.87	10.47	10.08	9.70
1.027	20.14	20.32	20.50	20.68	20.85	21.03	21.20	21.37	21.54	21.71
1.027	13.89	13.44	13.00	12.56	12.13	11.70	11.29	10.88	10.47	10.07
1.028	20.86	21.05	21.24	21.42	21.61	21.79	21.97	22.14	22.32	22.49
1.028	14.41	13.94	13.48	13.03	12.58	12.14	11.71	11.28	10.86	10.45
1.029	21.59	21.78	21.97	22.17	22.35	22.54	22.73	22.91	23.09	23.27
1.029	14.93	14.44	13.96	13.49	13.03	12.58	12.13	11.69	11.25	10.82
1.030	22.31	22.51	22.71	22.91	23.10	23.30	23.49	23.68	23.87	24.05
1.030	15.45	14.94	14.45	13.96	13.48	13.01	12.55	12.09	11.64	11.20
1.031	23.03	23.24	23.44	23.65	23.85	24.05	24.25	24.44	24.64	24.83
1.031	15.97	15.45	14.93	14.43	13.94	13.45	12.97	12.50	12.03	11.57
1.032	23.75	23.96	24.17	24.39	24.59	24.80	25.00	25.21	25.41	25.61
1.032	16.49	15.95	15.42	14.90	14.39	13.89	13.39	12.90	12.42	11.95
1.033	24.47	24.69	24.91	25.12	25.34	25.55	25.76	25.97	26.17	26.38
1.033	17.01	16.45	15.91	15.37	14.84	14.32	13.81	13.31	12.81	12.33
1.034	25.18	25.41	25.63	25.86	26.08	26.30	26.51	26.73	26.94	27.15
1.034	17.52	16.95	16.39	15.84	15.29	14.76	14.23	13.71	13.20	12.70
1.035	25.90	26.13	26.36	26.59	26.82	27.04	27.27	27.49	27.71	27.92
1.035	18.04	17.46	16.88	16.31	15.75	15.20	14.65	14.12	13.59	13.08
1.036	26.61	26.85	27.09	27.32	27.56	27.79	28.02	28.25	28.47	28.69
1.036	18.56	17.96	17.36	16.78	16.20	15.63	15.08	14.53	13.99	13.45
1.037	27.32	27.57	27.81	28.06	28.30	28.53	28.77	29.00	29.23	29.46
1.037	19.09	18.46	17.85	17.25	16.65	16.07	15.50	14.93	14.38	13.83
1.038	28.03	28.29	28.54	28.79	29.03	29.28	29.52	29.76	29.99	30.23
1.038	19.61	18.97	18.34	17.72	17.11	16.51	15.92	15.34	14.77	14.21
1.039	28.74	29.00	29.26	29.51	29.77	30.02	30.26	30.51	30.75	30.99
1.039	20.13	19.47	18.82	18.19	17.56	16.95	16.34	15.75	15.16	14.58
1.040	29.45	29.72	29.98	30.24	30.50	30.76	31.01	31.26	31.51	31.76
1.040	20.65	19.97	19.31	18.66	18.02	17.39	16.76	16.15	15.55	14.96
1.041	30.16	30.43	30.70	30.97	31.23	31.49	31.75	32.01	32.27	32.52
1.041	21.17	20.48	19.80	19.13	18.47	17.82	17.19	16.56	15.94	15.33
1.042	30.86	31.14	31.42	31.69	31.96	32.23	32.50	32.76	33.02	33.28
1.042	21.69	20.98	20.29	19.60	18.93	18.26	17.61	16.97	16.33	15.71
1.043	31.57	31.85	32.13	32.41	32.69	32.97	33.24	33.51	33.77	34.04
1.043	22.21	21.49	20.77	20.07	19.38	18.70	18.03	17.37	16.73	16.09
1.044	32.27	32.56	32.85	33.14	33.42	33.70	33.98	34.25	34.53	34.80
1.044	22.74	21.99	21.26	20.54	19.84	19.14	18.46	17.78	17.12	16.47
1.045	32.97	33.27	33.56	33.86	34.14	34.43	34.72	35.00	35.28	35.55
1.045	23.26	22.50	21.75	21.01	20.29	19.58	18.88	18.19	17.51	16.84
1.046	33.67	33.97	34.27	34.57	34.87	35.16	35.45	35.74	36.02	36.31
1.046	23.78	23.00	22.24	21.49	20.75	20.02	19.30	18.60	17.90	17.22
1.047	34.37	34.68	34.99	35.29	35.59	35.89	36.19	36.48	36.77	37.06
1.047	24.30	23.51	22.73	21.96	21.20	20.46	19.73	19.01	18.30	17.60
1.048	35.06	35.38	35.70	36.01	36.31	36.62	36.92	37.22	37.52	37.81
1.048	24.83	24.01	23.22	22.43	21.66	20.90	20.15	19.41	18.69	17.98
1.049	35.76	36.08	36.40	36.72	37.04	37.35	37.65	37.96	38.26	38.56
1.049	25.35	24.52	23.71	22.90	22.11	21.34	20.57	19.82	19.08	18.35
1.050	36.45	36.78	37.11	37.43	37.75	38.07	38.39	38.70	39.01	39.31
1.050	25.88	25.03	24.19	23.38	22.57	21.78	21.00	20.23	19.48	18.73

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RATE           PERCENT  REACTION
RATIO     50.00     49.00     48.00     47.00     46.00     45.00     44.00     43.00     42.00     41.00

1.001      0.70      0.71      0.71      0.72      0.73      0.73      0.74      0.75      0.76      0.76
1.001      0.70      0.68      0.66      0.64      0.62      0.60      0.58      0.57      0.55      0.53
1.002      1.39      1.40      1.42      1.43      1.45      1.46      1.48      1.49      1.51      1.52
1.002      1.39      1.35      1.31      1.28      1.24      1.20      1.17      1.13      1.10      1.06
1.003      2.08      2.10      2.12      2.15      2.17      2.19      2.21      2.23      2.25      2.28
1.003      2.09      2.03      1.97      1.91      1.86      1.80      1.75      1.69      1.64      1.59
1.004      2.77      2.80      2.83      2.86      2.89      2.92      2.94      2.97      3.00      3.03
1.004      2.78      2.70      2.62      2.55      2.47      2.40      2.33      2.26      2.19      2.12
1.005      3.45      3.49      3.53      3.57      3.60      3.64      3.68      3.71      3.75      3.78
1.005      3.48      3.38      3.28      3.18      3.09      3.00      2.91      2.82      2.73      2.65
1.006      4.14      4.18      4.23      4.27      4.32      4.36      4.41      4.45      4.49      4.53
1.006      4.17      4.05      3.94      3.82      3.71      3.60      3.49      3.38      3.28      3.18
1.007      4.82      4.88      4.93      4.98      5.03      5.08      5.13      5.18      5.23      5.28
1.007      4.87      4.73      4.59      4.46      4.33      4.20      4.07      3.95      3.83      3.71
1.008      5.50      5.57      5.63      5.69      5.74      5.80      5.86      5.92      5.97      6.03
1.008      5.57      5.41      5.25      5.10      4.95      4.80      4.65      4.51      4.37      4.23
1.009      6.19      6.25      6.32      6.39      6.46      6.52      6.59      6.65      6.71      6.78
1.009      6.26      6.08      5.91      5.74      5.57      5.40      5.24      5.08      4.92      4.76
1.010      6.87      6.94      7.02      7.09      7.16      7.24      7.31      7.38      7.45      7.52
1.010      6.96      6.76      6.57      6.37      6.19      6.00      5.82      5.64      5.47      5.30
1.011      7.54      7.63      7.71      7.79      7.87      7.95      8.03      8.11      8.19      8.26
1.011      7.66      7.44      7.22      7.01      6.81      6.60      6.40      6.21      6.01      5.83
1.012      8.22      8.31      8.40      8.49      8.58      8.67      8.75      8.84      8.92      9.01
1.012      8.36      8.12      7.88      7.65      7.43      7.20      6.99      6.77      6.56      6.36
1.013      8.90      8.99      9.09      9.19      9.28      9.38      9.47      9.56      9.66      9.75
1.013      9.06      8.80      8.54      8.29      8.05      7.81      7.57      7.34      7.11      6.89
1.014      9.57      9.68      9.78      9.88      9.99     10.09     10.19     10.29     10.39     10.48
1.014      9.76      9.48      9.20      8.93      8.67      8.41      8.16      7.91      7.66      7.42
1.015     10.24     10.36     10.47     10.58     10.69     10.80     10.91     11.01     11.12     11.22
1.015     10.46     10.16      9.86      9.57      9.29      9.01      8.74      8.47      8.21      7.95
1.016     10.91     11.03     11.15     11.27     11.39     11.51     11.62     11.73     11.85     11.96
1.016     11.16     10.84     10.52     10.21      9.91      9.62      9.33      9.04      8.76      8.48
1.017     11.58     11.71     11.84     11.97     12.09     12.21     12.33     12.45     12.57     12.69
1.017     11.86     11.52     11.18     10.86     10.54     10.22      9.91      9.61      9.31      9.01
1.018     12.25     12.39     12.52     12.66     12.79     12.92     13.05     13.17     13.30     13.42
1.018     12.56     12.20     11.85     11.50     11.16     10.82     10.50     10.17      9.86      9.55
1.019     12.92     13.06     13.20     13.35     13.48     13.62     13.76     13.89     14.02     14.16
1.019     13.26     12.88     12.51     12.14     11.78     11.43     11.08     10.74     10.41     10.08
1.020     13.59     13.74     13.89     14.03     14.18     14.32     14.47     14.61     14.75     14.89
1.020     13.96     13.56     13.17     12.78     12.40     12.03     11.67     11.31     10.96     10.61
1.021     14.25     14.41     14.56     14.72     14.87     15.02     15.17     15.32     15.47     15.61
1.021     14.67     14.25     13.83     13.43     13.03     12.64     12.26     11.88     11.51     11.15
1.022     14.91     15.08     15.24     15.40     15.57     15.72     15.88     16.04     16.19     16.34
1.022     15.37     14.93     14.50     14.07     13.65     13.24     12.84     12.45     12.06     11.68
1.023     15.57     15.75     15.92     16.09     16.26     16.42     16.59     16.75     16.91     17.07
1.023     16.07     15.61     15.16     14.71     14.28     13.85     13.43     13.02     12.61     12.21
1.024     16.23     16.42     16.59     16.77     16.95     17.12     17.29     17.46     17.63     17.79
1.024     16.78     16.30     15.82     15.36     14.90     14.46     14.02     13.59     13.16     12.75
1.025     16.89     17.08     17.27     17.45     17.63     17.81     17.99     18.17     18.34     18.51
1.025     17.48     16.98     16.49     16.00     15.53     15.06     14.61     14.16     13.72     13.28
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RATE	PERCENT REACTION									
RATIO	50.00	49.00	48.00	47.00	46.00	45.00	44.00	43.00	42.00	41.00
1.026	17.55	17.75	17.94	18.13	18.32	18.51	18.69	18.87	19.06	19.23
1.026	18.19	17.67	17.15	16.65	16.15	15.67	15.19	14.73	14.27	13.82
1.027	18.21	18.41	18.61	18.81	19.01	19.20	19.39	19.58	19.77	19.95
1.027	18.90	18.35	17.82	17.29	16.78	16.28	15.78	15.30	14.82	14.35
1.028	18.86	19.07	19.28	19.49	19.69	19.89	20.09	20.29	20.48	20.67
1.028	19.60	19.04	18.48	17.94	17.41	16.89	16.37	15.87	15.37	14.89
1.029	19.52	19.73	19.95	20.16	20.37	20.58	20.79	20.99	21.19	21.39
1.029	20.31	19.72	19.15	18.59	18.03	17.49	16.96	16.44	15.93	15.42
1.030	20.17	20.39	20.62	20.84	21.05	21.27	21.48	21.69	21.90	22.10
1.030	21.02	20.41	19.82	19.23	18.66	18.10	17.55	17.01	16.48	15.96
1.031	20.82	21.05	21.28	21.51	21.73	21.96	22.17	22.39	22.61	22.82
1.031	21.73	21.10	20.48	19.88	19.29	18.71	18.14	17.58	17.03	16.50
1.032	21.47	21.71	21.95	22.18	22.41	22.64	22.87	23.09	23.31	23.53
1.032	22.43	21.79	21.15	20.53	19.92	19.32	18.73	18.16	17.59	17.03
1.033	22.12	22.37	22.61	22.85	23.09	23.32	23.56	23.79	24.02	24.24
1.033	23.14	22.47	21.82	21.18	20.55	19.93	19.32	18.73	18.14	17.57
1.034	22.77	23.02	23.27	23.52	23.76	24.01	24.25	24.48	24.72	24.95
1.034	23.85	23.16	22.49	21.83	21.18	20.54	19.91	19.30	18.70	18.11
1.035	23.41	23.67	23.93	24.19	24.44	24.69	24.94	25.18	25.42	25.66
1.035	24.56	23.85	23.16	22.47	21.81	21.15	20.51	19.87	19.25	18.64
1.036	24.06	24.33	24.59	24.85	25.11	25.37	25.62	25.87	26.12	26.37
1.036	25.27	24.54	23.83	23.12	22.44	21.76	21.10	20.45	19.81	19.18
1.037	24.70	24.98	25.25	25.52	25.78	26.05	26.31	26.57	26.82	27.07
1.037	25.98	25.23	24.50	23.77	23.07	22.37	21.69	21.02	20.36	19.72
1.038	25.34	25.62	25.90	26.18	26.45	26.72	26.99	27.26	27.52	27.78
1.038	26.69	25.92	25.17	24.42	23.70	22.98	22.28	21.60	20.92	20.26
1.039	25.98	26.27	26.56	26.84	27.12	27.40	27.67	27.95	28.21	28.48
1.039	27.41	26.61	25.84	25.07	24.33	23.59	22.88	22.17	21.48	20.80
1.040	26.62	26.92	27.21	27.50	27.79	28.08	28.36	28.63	28.91	29.18
1.040	28.12	27.30	26.51	25.73	24.96	24.21	23.47	22.74	22.03	21.33
1.041	27.26	27.56	27.87	28.16	28.46	28.75	29.04	29.32	29.60	29.88
1.041	28.83	28.00	27.18	26.38	25.59	24.82	24.06	23.32	22.59	21.87
1.042	27.90	28.21	28.52	28.82	29.12	29.42	29.71	30.01	30.29	30.58
1.042	29.54	28.69	27.85	27.03	26.22	25.43	24.66	23.89	23.15	22.41
1.043	28.53	28.85	29.17	29.48	29.79	30.09	30.39	30.69	30.98	31.28
1.043	30.26	29.38	28.52	27.68	26.85	26.05	25.25	24.47	23.70	22.95
1.044	29.17	29.49	29.82	30.13	30.45	30.76	31.07	31.37	31.67	31.97
1.044	30.97	30.08	29.20	28.33	27.49	26.66	25.85	25.05	24.26	23.49
1.045	29.80	30.13	30.46	30.79	31.11	31.43	31.74	32.05	32.36	32.67
1.045	31.69	30.77	29.87	28.99	28.12	27.27	26.44	25.62	24.82	24.03
1.046	30.43	30.77	31.11	31.44	31.77	32.09	32.42	32.73	33.05	33.36
1.046	32.40	31.46	30.54	29.64	28.75	27.89	27.04	26.20	25.38	24.57
1.047	31.06	31.41	31.75	32.09	32.43	32.76	33.09	33.41	33.73	34.05
1.047	33.12	32.16	31.22	30.29	29.39	28.50	27.63	26.78	25.94	25.11
1.048	31.69	32.05	32.40	32.74	33.09	33.42	33.76	34.09	34.42	34.74
1.048	33.84	32.85	31.89	30.95	30.02	29.12	28.23	27.35	26.50	25.65
1.049	32.32	32.68	33.04	33.39	33.74	34.09	34.43	34.77	35.10	35.43
1.049	34.55	33.55	32.57	31.60	30.66	29.73	28.82	27.93	27.06	26.20
1.050	32.95	33.32	33.68	34.04	34.40	34.75	35.10	35.44	35.78	36.12
1.050	35.27	34.25	33.24	32.26	31.29	30.35	29.42	28.51	27.62	26.74

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RATE          PERCENT  REACTION
RATIO    60.00     59.00     58.00     57.00     56.00     55.00     54.00     53.00     52.00     51.00

1.001     0.62      0.62      0.63      0.64      0.65      0.66      0.67      0.67      0.68      0.69
1.001     0.92      0.90      0.87      0.85      0.83      0.80      0.78      0.76      0.74      0.72
1.002     1.22      1.24      1.26      1.28      1.29      1.31      1.33      1.34      1.36      1.37
1.002     1.84      1.79      1.74      1.69      1.65      1.60      1.56      1.52      1.47      1.43
1.003     1.83      1.86      1.88      1.91      1.93      1.96      1.98      2.01      2.03      2.05
1.003     2.76      2.68      2.61      2.54      2.47      2.40      2.34      2.27      2.21      2.15
1.004     2.44      2.47      2.51      2.54      2.57      2.61      2.64      2.67      2.70      2.74
1.004     3.68      3.58      3.48      3.39      3.29      3.20      3.12      3.03      2.95      2.86
1.005     3.04      3.09      3.13      3.17      3.21      3.25      3.30      3.34      3.37      3.41
1.005     4.60      4.47      4.35      4.23      4.12      4.01      3.90      3.79      3.68      3.58
1.006     3.65      3.70      3.75      3.80      3.85      3.90      3.95      4.00      4.04      4.09
1.006     5.52      5.37      5.22      5.08      4.94      4.81      4.67      4.55      4.42      4.29
1.007     4.25      4.31      4.37      4.43      4.49      4.54      4.60      4.66      4.71      4.77
1.007     6.44      6.27      6.10      5.93      5.77      5.61      5.46      5.30      5.16      5.01
1.008     4.85      4.92      4.99      5.06      5.12      5.19      5.25      5.32      5.38      5.44
1.008     7.36      7.16      6.97      6.78      6.59      6.41      6.24      6.06      5.89      5.73
1.009     5.45      5.53      5.61      5.68      5.76      5.83      5.90      5.97      6.05      6.12
1.009     8.29      8.06      7.84      7.63      7.42      7.22      7.02      6.82      6.63      6.45
1.010     6.05      6.14      6.22      6.30      6.39      6.47      6.55      6.63      6.71      6.79
1.010     9.21      8.96      8.72      8.48      8.25      8.02      7.80      7.58      7.37      7.16
1.011     6.65      6.74      6.84      6.93      7.02      7.11      7.20      7.29      7.37      7.46
1.011    10.14      9.86      9.59      9.33      9.08      8.83      8.58      8.34      8.11      7.88
1.012     7.24      7.35      7.45      7.55      7.65      7.75      7.84      7.94      8.03      8.13
1.012    11.06     10.76     10.47     10.18      9.91      9.63      9.37      9.11      8.85      8.60
1.013     7.84      7.95      8.06      8.17      8.28      8.38      8.49      8.59      8.69      8.80
1.013    11.99     11.66     11.35     11.04     10.73     10.44     10.15      9.87      9.59      9.32
1.014     8.43      8.55      8.67      8.79      8.90      9.02      9.13      9.24      9.35      9.46
1.014    12.92     12.57     12.22     11.89     11.56     11.25     10.94     10.63     10.33     10.04
1.015     9.02      9.15      9.28      9.41      9.53      9.65      9.77      9.89     10.01     10.13
1.015    13.84     13.47     13.10     12.74     12.40     12.05     11.72     11.39     11.08     10.76
1.016     9.61      9.75      9.89     10.02     10.15     10.28     10.41     10.54     10.67     10.79
1.016    14.77     14.37     13.98     13.60     13.23     12.86     12.51     12.16     11.82     11.48
1.017    10.20     10.35     10.49     10.64     10.78     10.92     11.05     11.19     11.32     11.45
1.017    15.70     15.28     14.86     14.46     14.06     13.67     13.29     12.92     12.56     12.21
1.018    10.79     10.95     11.10     11.25     11.40     11.55     11.69     11.83     11.97     12.11
1.018    16.63     16.18     15.74     15.31     14.89     14.48     14.08     13.69     13.30     12.93
1.019    11.38     11.54     11.70     11.86     12.02     12.17     12.33     12.48     12.63     12.77
1.019    17.57     17.09     16.62     16.17     15.73     15.29     14.87     14.45     14.05     13.65
1.020    11.97     12.14     12.31     12.47     12.64     12.80     12.96     13.12     13.28     13.43
1.020    18.50     18.00     17.51     17.03     16.56     16.10     15.66     15.22     14.79     14.37
1.021    12.55     12.73     12.91     13.08     13.26     13.43     13.60     13.76     13.93     14.09
1.021    19.43     18.90     18.39     17.89     17.39     16.91     16.45     15.99     15.54     15.10
1.022    13.13     13.32     13.51     13.69     13.87     14.05     14.23     14.40     14.57     14.74
1.022    20.37     19.81     19.27     18.75     18.23     17.73     17.24     16.75     16.28     15.82
1.023    13.72     13.91     14.11     14.30     14.49     14.68     14.86     15.04     15.22     15.40
1.023    21.30     20.72     20.16     19.61     19.07     18.54     18.03     17.52     17.03     16.55
1.024    14.30     14.50     14.71     14.91     15.10     15.30     15.49     15.68     15.87     16.05
1.024    22.24     21.63     21.04     20.47     19.90     19.35     18.82     18.29     17.78     17.27
1.025    14.88     15.09     15.30     15.51     15.72     15.92     16.12     16.32     16.51     16.70
1.025    23.18     22.54     21.93     21.33     20.74     20.17     19.61     19.06     18.52     18.00
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RATE	PERCENT REACTION									
RATIO	60.00	59.00	58.00	57.00	56.00	55.00	54.00	53.00	52.00	51.00
1.026	15.46	15.68	15.90	16.11	16.33	16.54	16.75	16.95	17.15	17.35
1.026	24.11	23.46	22.82	22.19	21.58	20.98	20.40	19.83	19.27	18.73
1.027	16.03	16.27	16.49	16.72	16.94	17.16	17.37	17.59	17.80	18.00
1.027	25.05	24.37	23.70	23.05	22.42	21.80	21.19	20.60	20.02	19.45
1.028	16.61	16.85	17.09	17.32	17.55	17.77	18.00	18.22	18.44	18.65
1.028	25.99	25.28	24.59	23.92	23.26	22.61	21.99	21.37	20.77	20.18
1.029	17.19	17.43	17.68	17.92	18.16	18.39	18.62	18.85	19.07	19.30
1.029	26.93	26.20	25.48	24.78	24.10	23.43	22.78	22.14	21.52	20.91
1.030	17.76	18.02	18.27	18.52	18.76	19.00	19.24	19.48	19.71	19.94
1.030	27.87	27.11	26.37	25.65	24.94	24.25	23.57	22.91	22.27	21.64
1.031	18.33	18.60	18.86	19.11	19.37	19.62	19.86	20.11	20.35	20.59
1.031	28.82	28.03	27.26	26.51	25.78	25.07	24.37	23.69	23.02	22.37
1.032	18.90	19.18	19.45	19.71	19.97	20.23	20.48	20.73	20.98	21.23
1.032	29.76	28.95	28.15	27.38	26.62	25.89	25.17	24.46	23.77	23.09
1.033	19.47	19.76	20.03	20.30	20.57	20.84	21.10	21.36	21.62	21.87
1.033	30.70	29.86	29.05	28.25	27.47	26.71	25.96	25.23	24.52	23.82
1.034	20.04	20.33	20.62	20.90	21.18	21.45	21.72	21.99	22.25	22.51
1.034	31.65	30.78	29.94	29.12	28.31	27.53	26.76	26.01	25.27	24.56
1.035	20.61	20.91	21.20	21.49	21.78	22.06	22.34	22.61	22.88	23.15
1.035	32.59	31.70	30.83	29.98	29.16	28.35	27.56	26.78	26.03	25.29
1.036	21.18	21.48	21.79	22.08	22.38	22.66	22.95	23.23	23.51	23.79
1.036	33.54	32.62	31.73	30.85	30.00	29.17	28.35	27.56	26.78	26.02
1.037	21.74	22.06	22.37	22.67	22.97	23.27	23.56	23.85	24.14	24.42
1.037	34.49	33.54	32.62	31.72	30.85	29.99	29.15	28.33	27.53	26.75
1.038	22.31	22.63	22.95	23.26	23.57	23.87	24.18	24.47	24.77	25.06
1.038	35.44	34.47	33.52	32.60	31.69	30.81	29.95	29.11	28.29	27.48
1.039	22.87	23.20	23.53	23.85	24.17	24.48	24.79	25.09	25.39	25.69
1.039	36.39	35.39	34.42	33.47	32.54	31.64	30.75	29.89	29.04	28.22
1.040	23.43	23.77	24.11	24.44	24.76	25.08	25.40	25.71	26.02	26.32
1.040	37.34	36.31	35.31	34.34	33.39	32.46	31.55	30.67	29.80	28.95
1.041	24.00	24.34	24.68	25.02	25.35	25.68	26.00	26.32	26.64	26.95
1.041	38.29	37.24	36.21	35.21	34.24	33.29	32.35	31.44	30.55	29.68
1.042	24.56	24.91	25.26	25.60	25.94	26.28	26.61	26.94	27.26	27.58
1.042	39.24	38.16	37.11	36.09	35.09	34.11	33.16	32.22	31.31	30.42
1.043	25.11	25.48	25.83	26.19	26.54	26.88	27.22	27.55	27.88	28.21
1.043	40.19	39.09	38.01	36.96	35.94	34.94	33.96	33.00	32.07	31.15
1.044	25.67	26.04	26.41	26.77	27.12	27.48	27.82	28.17	28.50	28.84
1.044	41.15	40.01	38.91	37.84	36.79	35.76	34.76	33.78	32.83	31.89
1.045	26.23	26.61	26.98	27.35	27.71	28.07	28.43	28.78	29.12	29.46
1.045	42.10	40.94	39.81	38.71	37.64	36.59	35.57	34.56	33.58	32.63
1.046	26.78	27.17	27.55	27.93	28.30	28.67	29.03	29.39	29.74	30.09
1.046	43.06	41.87	40.72	39.59	38.49	37.42	36.37	35.35	34.34	33.36
1.047	27.34	27.73	28.12	28.51	28.89	29.26	29.63	29.99	30.35	30.71
1.047	44.01	42.80	41.62	40.47	39.34	38.25	37.18	36.13	35.10	34.10
1.048	27.89	28.29	28.69	29.08	29.47	29.85	30.23	30.60	30.97	31.33
1.048	44.97	43.73	42.52	41.35	40.20	39.08	37.98	36.91	35.86	34.84
1.049	28.44	28.85	29.26	29.66	30.05	30.44	30.83	31.21	31.58	31.95
1.049	45.93	44.66	43.43	42.23	41.05	39.91	38.79	37.69	36.62	35.58
1.050	28.99	29.41	29.83	30.23	30.64	31.03	31.43	31.81	32.20	32.57
1.050	46.88	45.59	44.33	43.11	41.91	40.74	39.59	38.48	37.38	36.32

RATE	PERCENT REACTION									
RATIO	70.00	69.00	68.00	67.00	66.00	65.00	64.00	63.00	62.00	61.00
1.001	0.52	0.53	0.54	0.55	0.56	0.57	0.58	0.59	0.60	0.61
1.001	1.21	1.18	1.15	1.11	1.08	1.06	1.03	1.00	0.97	0.95
1.002	1.03	1.06	1.08	1.09	1.11	1.13	1.15	1.17	1.19	1.21
1.002	2.42	2.35	2.29	2.22	2.16	2.11	2.05	2.00	1.94	1.89
1.003	1.55	1.58	1.61	1.64	1.67	1.70	1.72	1.75	1.78	1.81
1.003	3.62	3.52	3.43	3.34	3.25	3.16	3.07	2.99	2.91	2.83
1.004	2.06	2.10	2.14	2.18	2.22	2.26	2.29	2.33	2.37	2.40
1.004	4.83	4.70	4.57	4.45	4.33	4.21	4.10	3.99	3.88	3.78
1.005	2.57	2.62	2.67	2.72	2.77	2.82	2.86	2.91	2.95	3.00
1.005	6.04	5.88	5.72	5.56	5.41	5.27	5.13	4.99	4.85	4.72
1.006	3.08	3.14	3.20	3.26	3.32	3.37	3.43	3.49	3.54	3.59
1.006	7.25	7.06	6.86	6.68	6.50	6.32	6.15	5.99	5.83	5.67
1.007	3.59	3.66	3.73	3.80	3.87	3.93	4.00	4.06	4.13	4.19
1.007	8.47	8.24	8.01	7.80	7.59	7.38	7.18	6.99	6.80	6.62
1.008	4.10	4.18	4.26	4.34	4.41	4.49	4.56	4.64	4.71	4.78
1.008	9.68	9.42	9.16	8.91	8.67	8.44	8.21	7.99	7.78	7.57
1.009	4.60	4.69	4.78	4.87	4.96	5.04	5.13	5.21	5.29	5.37
1.009	10.90	10.60	10.31	10.03	9.76	9.50	9.24	8.99	8.75	8.52
1.010	5.11	5.21	5.31	5.41	5.50	5.60	5.69	5.78	5.87	5.96
1.010	12.12	11.79	11.46	11.15	10.85	10.56	10.27	10.00	9.73	9.47
1.011	5.61	5.72	5.83	5.94	6.05	6.15	6.25	6.35	6.45	6.55
1.011	13.34	12.97	12.62	12.27	11.94	11.62	11.31	11.00	10.71	10.42
1.012	6.11	6.24	6.36	6.47	6.59	6.70	6.81	6.92	7.03	7.14
1.012	14.56	14.16	13.77	13.40	13.03	12.68	12.34	12.01	11.68	11.37
1.013	6.62	6.75	6.88	7.00	7.13	7.25	7.37	7.49	7.61	7.72
1.013	15.78	15.35	14.93	14.52	14.13	13.75	13.37	13.01	12.66	12.32
1.014	7.12	7.26	7.40	7.53	7.67	7.80	7.93	8.06	8.18	8.31
1.014	17.00	16.54	16.08	15.65	15.22	14.81	14.41	14.02	13.64	13.27
1.015	7.62	7.77	7.92	8.06	8.21	8.35	8.49	8.62	8.76	8.89
1.015	18.23	17.73	17.24	16.77	16.32	15.88	15.45	15.03	14.62	14.23
1.016	8.12	8.28	8.43	8.59	8.74	8.89	9.04	9.19	9.33	9.47
1.016	19.46	18.92	18.40	17.90	17.42	16.94	16.49	16.04	15.61	15.18
1.017	8.61	8.78	8.95	9.12	9.28	9.44	9.60	9.75	9.91	10.06
1.017	20.68	20.11	19.56	19.03	18.51	18.01	17.52	17.05	16.59	16.14
1.018	9.11	9.29	9.47	9.64	9.81	9.98	10.15	10.31	10.48	10.64
1.018	21.91	21.31	20.73	20.16	19.61	19.08	18.56	18.06	17.57	17.10
1.019	9.60	9.80	9.98	10.17	10.35	10.53	10.70	10.88	11.05	11.21
1.019	23.14	22.51	21.89	21.29	20.71	20.15	19.61	19.08	18.56	18.06
1.020	10.10	10.30	10.50	10.69	10.88	11.07	11.25	11.44	11.62	11.79
1.020	24.38	23.70	23.06	22.43	21.82	21.22	20.65	20.09	19.54	19.02
1.021	10.59	10.80	11.01	11.21	11.41	11.61	11.80	11.99	12.18	12.37
1.021	25.61	24.90	24.22	23.56	22.92	22.30	21.69	21.10	20.53	19.98
1.022	11.08	11.30	11.52	11.73	11.94	12.15	12.35	12.55	12.75	12.94
1.022	26.85	26.11	25.39	24.70	24.02	23.37	22.74	22.12	21.52	20.94
1.023	11.57	11.80	12.03	12.25	12.47	12.69	12.90	13.11	13.31	13.52
1.023	28.08	27.31	26.56	25.83	25.13	24.44	23.78	23.14	22.51	21.90
1.024	12.06	12.30	12.54	12.77	13.00	13.23	13.45	13.66	13.88	14.09
1.024	29.32	28.51	27.73	26.97	26.23	25.52	24.83	24.15	23.50	22.86
1.025	12.55	12.80	13.05	13.29	13.53	13.76	13.99	14.22	14.44	14.66
1.025	30.56	29.72	28.90	28.11	27.34	26.60	25.87	25.17	24.49	23.82

RATE	PERCENT REACTION									
RATIO	70.00	69.00	68.00	67.00	66.00	65.00	64.00	63.00	62.00	61.00
1.026	13.04	13.30	13.56	13.81	14.05	14.30	14.54	14.77	15.00	15.23
1.026	31.80	30.92	30.07	29.25	28.45	27.68	26.92	26.19	25.48	24.79
1.027	13.53	13.80	14.06	14.32	14.58	14.83	15.08	15.32	15.56	15.80
1.027	33.05	32.13	31.25	30.39	29.56	28.76	27.97	27.21	26.47	25.75
1.028	14.01	14.29	14.57	14.84	15.10	15.36	15.62	15.87	16.12	16.37
1.028	34.29	33.34	32.42	31.53	30.67	29.84	29.02	28.24	27.47	26.72
1.029	14.50	14.79	15.07	15.35	15.62	15.89	16.16	16.42	16.68	16.94
1.029	35.54	34.55	33.60	32.68	31.78	30.92	30.08	29.26	28.46	27.69
1.030	14.98	15.28	15.57	15.86	16.15	16.43	16.70	16.97	17.24	17.50
1.030	36.78	35.76	34.78	33.82	32.90	32.00	31.13	30.28	29.46	28.66
1.031	15.46	15.77	16.07	16.37	16.67	16.95	17.24	17.52	17.79	18.07
1.031	38.03	36.98	35.96	34.97	34.01	33.08	32.18	31.31	30.45	29.62
1.032	15.94	16.26	16.58	16.88	17.19	17.48	17.78	18.06	18.35	18.63
1.032	39.28	38.19	37.14	36.12	35.13	34.17	33.24	32.33	31.45	30.59
1.033	16.42	16.75	17.07	17.39	17.70	18.01	18.31	18.61	18.90	19.19
1.033	40.54	39.41	38.32	37.27	36.25	35.26	34.29	33.36	32.45	31.57
1.034	16.90	17.24	17.57	17.90	18.22	18.54	18.85	19.15	19.45	19.75
1.034	41.79	40.63	39.51	38.42	37.37	36.34	35.35	34.39	33.45	32.54
1.035	17.38	17.73	18.07	18.41	18.74	19.06	19.38	19.70	20.01	20.31
1.035	43.04	41.85	40.69	39.57	38.49	37.43	36.41	35.42	34.45	33.51
1.036	17.86	18.22	18.57	18.91	19.25	19.58	19.91	20.24	20.56	20.87
1.036	44.30	43.07	41.88	40.72	39.61	38.52	37.47	36.45	35.45	34.48
1.037	18.34	18.70	19.06	19.42	19.76	20.11	20.44	20.78	21.10	21.43
1.037	45.56	44.29	43.07	41.88	40.73	39.61	38.53	37.48	36.45	35.46
1.038	18.81	19.19	19.56	19.92	20.28	20.63	20.98	21.32	21.65	21.98
1.038	46.82	45.51	44.25	43.03	41.85	40.70	39.59	38.51	37.46	36.43
1.039	19.28	19.67	20.05	20.42	20.79	21.15	21.50	21.85	22.20	22.54
1.039	48.08	46.74	45.44	44.19	42.98	41.80	40.65	39.54	38.46	37.41
1.040	19.76	20.15	20.54	20.92	21.30	21.67	22.03	22.39	22.74	23.09
1.040	49.34	47.97	46.64	45.35	44.10	42.89	41.72	40.58	39.47	38.39
1.041	20.23	20.63	21.03	21.42	21.81	22.19	22.56	22.93	23.29	23.64
1.041	50.61	49.19	47.83	46.51	45.23	43.99	42.78	41.61	40.47	39.37
1.042	20.70	21.11	21.52	21.92	22.32	22.70	23.09	23.46	23.83	24.20
1.042	51.87	50.42	49.02	47.67	46.36	45.08	43.85	42.65	41.48	40.34
1.043	21.17	21.59	22.01	22.42	22.82	23.22	23.61	23.99	24.37	24.75
1.043	53.14	51.66	50.22	48.83	47.49	46.18	44.92	43.68	42.49	41.32
1.044	21.64	22.07	22.50	22.92	23.33	23.74	24.13	24.53	24.91	25.30
1.044	54.41	52.89	51.42	50.00	48.62	47.28	45.98	44.72	43.50	42.31
1.045	22.11	22.55	22.99	23.41	23.83	24.25	24.66	25.06	25.45	25.84
1.045	55.68	54.12	52.62	51.16	49.75	48.38	47.05	45.76	44.51	43.29
1.046	22.57	23.03	23.47	23.91	24.34	24.76	25.18	25.59	25.99	26.39
1.046	56.95	55.36	53.82	52.33	50.88	49.48	48.12	46.80	45.52	44.27
1.047	23.04	23.50	23.96	24.40	24.84	25.27	25.70	26.12	26.53	26.94
1.047	58.22	56.59	55.02	53.49	52.02	50.58	49.19	47.84	46.53	45.25
1.048	23.50	23.98	24.44	24.90	25.34	25.78	26.22	26.65	27.07	27.48
1.048	59.50	57.83	56.22	54.66	53.15	51.69	50.27	48.89	47.54	46.24
1.049	23.97	24.45	24.92	25.39	25.84	26.29	26.74	27.17	27.60	28.03
1.049	60.77	59.07	57.42	55.83	54.29	52.79	51.34	49.93	48.56	47.22
1.050	24.43	24.92	25.40	25.88	26.34	26.80	27.25	27.70	28.14	28.57
1.050	62.05	60.31	58.63	57.00	55.43	53.90	52.41	50.97	49.57	48.21

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RATE            PERCENT   REACTION
RATIO     80.00     79.00     78.00     77.00     76.00     75.00     74.00     73.00     72.00     71.00

1.001      0.41      0.42      0.43      0.44      0.46      0.47      0.48      0.49      0.50      0.51
1.001      1.62      1.57      1.52      1.48      1.43      1.39      1.35      1.32      1.28      1.24
1.002      0.81      0.83      0.86      0.88      0.90      0.93      0.95      0.97      0.99      1.01
1.002      3.23      3.13      3.04      2.95      2.86      2.78      2.70      2.63      2.55      2.48
1.003      1.21      1.25      1.28      1.32      1.35      1.39      1.42      1.45      1.49      1.52
1.003      4.84      4.70      4.56      4.42      4.30      4.17      4.05      3.94      3.83      3.73
1.004      1.61      1.66      1.71      1.75      1.80      1.84      1.89      1.93      1.98      2.02
1.004      6.46      6.27      6.08      5.90      5.73      5.57      5.41      5.26      5.11      4.97
1.005      2.00      2.07      2.13      2.19      2.25      2.30      2.36      2.41      2.47      2.52
1.005      8.08      7.84      7.60      7.38      7.17      6.96      6.76      6.57      6.39      6.21
1.006      2.40      2.48      2.55      2.62      2.69      2.76      2.83      2.89      2.96      3.02
1.006      9.71      9.41      9.13      8.86      8.60      8.36      8.12      7.89      7.67      7.46
1.007      2.80      2.88      2.97      3.05      3.13      3.21      3.29      3.37      3.44      3.52
1.007     11.33     10.99     10.66     10.35     10.04      9.76      9.48      9.21      8.96      8.71
1.008      3.19      3.29      3.39      3.48      3.58      3.67      3.76      3.84      3.93      4.01
1.008     12.96     12.57     12.19     11.83     11.49     11.16     10.84     10.53     10.24      9.96
1.009      3.59      3.70      3.81      3.91      4.02      4.12      4.22      4.32      4.42      4.51
1.009     14.60     14.15     13.73     13.32     12.93     12.56     12.20     11.86     11.53     11.21
1.010      3.98      4.10      4.23      4.34      4.46      4.57      4.68      4.79      4.90      5.00
1.010     16.23     15.73     15.26     14.81     14.38     13.96     13.57     13.18     12.82     12.46
1.011      4.37      4.51      4.64      4.77      4.90      5.02      5.15      5.27      5.38      5.50
1.011     17.87     17.32     16.80     16.30     15.83     15.37     14.93     14.51     14.11     13.71
1.012      4.76      4.91      5.06      5.20      5.34      5.47      5.61      5.74      5.87      5.99
1.012     19.51     18.91     18.34     17.80     17.28     16.78     16.30     15.84     15.40     14.97
1.013      5.15      5.32      5.47      5.63      5.78      5.92      6.07      6.21      6.35      6.48
1.013     21.15     20.50     19.88     19.29     18.73     18.19     17.67     17.17     16.69     16.23
1.014      5.54      5.72      5.89      6.05      6.21      6.37      6.53      6.68      6.83      6.97
1.014     22.79     22.09     21.43     20.79     20.19     19.60     19.04     18.50     17.99     17.49
1.015      5.93      6.12      6.30      6.48      6.65      6.82      6.98      7.15      7.31      7.46
1.015     24.44     23.69     22.98     22.29     21.64     21.02     20.42     19.84     19.28     18.75
1.016      6.32      6.52      6.71      6.90      7.08      7.26      7.44      7.61      7.78      7.95
1.016     26.09     25.29     24.53     23.80     23.10     22.43     21.79     21.18     20.58     20.01
1.017      6.71      6.92      7.12      7.32      7.52      7.71      7.90      8.08      8.26      8.44
1.017     27.74     26.89     26.08     25.30     24.56     23.85     23.17     22.51     21.88     21.27
1.018      7.09      7.31      7.53      7.74      7.95      8.15      8.35      8.55      8.74      8.92
1.018     29.40     28.49     27.63     26.81     26.03     25.27     24.55     23.85     23.18     22.54
1.019      7.48      7.71      7.94      8.16      8.38      8.60      8.81      9.01      9.21      9.41
1.019     31.06     30.10     29.19     28.32     27.49     26.69     25.93     25.19     24.49     23.80
1.020      7.86      8.11      8.35      8.58      8.81      9.04      9.26      9.47      9.69      9.89
1.020     32.72     31.71     30.75     29.83     28.96     28.12     27.31     26.54     25.79     25.07
1.021      8.24      8.50      8.75      9.00      9.24      9.48      9.71      9.94     10.16     10.38
1.021     34.38     33.32     32.31     31.35     30.43     29.54     28.70     27.88     27.10     26.34
1.022      8.63      8.90      9.16      9.42      9.67      9.92     10.16     10.40     10.63     10.86
1.022     36.05     34.94     33.88     32.87     31.90     30.97     30.08     29.23     28.41     27.61
1.023      9.01      9.29      9.57      9.84     10.10     10.36     10.61     10.86     11.10     11.34
1.023     37.72     36.55     35.44     34.38     33.37     32.40     31.47     30.58     29.72     28.88
1.024      9.39      9.68      9.97     10.25     10.53     10.80     11.06     11.32     11.57     11.82
1.024     39.39     38.17     37.01     35.91     34.85     33.84     32.86     31.93     31.03     30.16
1.025      9.77     10.07     10.37     10.67     10.95     11.23     11.51     11.78     12.04     12.30
1.025     41.06     39.79     38.58     37.43     36.33     35.27     34.25     33.28     32.34     31.44
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RATE	PERCENT REACTION									
RATIO	80.00	79.00	78.00	77.00	76.00	75.00	74.00	73.00	72.00	71.00
1.026	10.15	10.46	10.78	11.08	11.38	11.67	11.95	12.23	12.51	12.78
1.026	42.74	41.42	40.16	38.96	37.81	36.71	35.65	34.63	33.66	32.71
1.027	10.52	10.85	11.18	11.49	11.80	12.10	12.40	12.69	12.97	13.25
1.027	44.42	43.04	41.73	40.48	39.29	38.14	37.05	35.99	34.97	33.99
1.028	10.90	11.24	11.58	11.90	12.22	12.54	12.84	13.14	13.44	13.73
1.028	46.10	44.67	43.31	42.01	40.77	39.58	38.44	37.35	36.29	35.27
1.029	11.28	11.63	11.98	12.31	12.65	12.97	13.29	13.60	13.90	14.20
1.029	47.78	46.30	44.89	43.55	42.26	41.03	39.84	38.71	37.61	36.56
1.030	11.65	12.02	12.38	12.72	13.07	13.40	13.73	14.05	14.37	14.68
1.030	49.47	47.94	46.48	45.08	43.75	42.47	41.24	40.07	38.93	37.84
1.031	12.03	12.40	12.77	13.13	13.49	13.83	14.17	14.50	14.83	15.15
1.031	51.16	49.57	48.06	46.62	45.24	43.92	42.65	41.43	40.26	39.12
1.032	12.40	12.79	13.17	13.54	13.91	14.26	14.61	14.95	15.29	15.62
1.032	52.86	51.21	49.65	48.16	46.73	45.36	44.05	42.79	41.58	40.41
1.033	12.77	13.17	13.57	13.95	14.32	14.69	15.05	15.40	15.75	16.09
1.033	54.55	52.86	51.24	49.70	48.23	46.82	45.46	44.16	42.91	41.70
1.034	13.14	13.56	13.96	14.36	14.74	15.12	15.49	15.85	16.21	16.56
1.034	56.25	54.50	52.83	51.24	49.72	48.27	46.87	45.53	44.24	42.99
1.035	13.51	13.94	14.35	14.76	15.16	15.55	15.93	16.30	16.67	17.03
1.035	57.95	56.15	54.43	52.79	51.22	49.72	48.28	46.90	45.57	44.28
1.036	13.88	14.32	14.75	15.16	15.57	15.97	16.36	16.75	17.13	17.50
1.036	59.66	57.80	56.03	54.34	52.72	51.18	49.69	48.27	46.90	45.58
1.037	14.25	14.70	15.14	15.57	15.99	16.40	16.80	17.20	17.58	17.96
1.037	61.36	59.45	57.63	55.89	54.23	52.64	51.11	49.64	48.23	46.87
1.038	14.62	15.08	15.53	15.97	16.40	16.82	17.24	17.64	18.04	18.43
1.038	63.07	61.10	59.23	57.44	55.73	54.10	52.53	51.02	49.57	48.17
1.039	14.99	15.46	15.92	16.37	16.81	17.25	17.67	18.08	18.49	18.89
1.039	64.78	62.76	60.83	59.00	57.24	55.56	53.95	52.39	50.90	49.47
1.040	15.35	15.84	16.31	16.77	17.23	17.67	18.10	18.53	18.95	19.35
1.040	66.50	64.42	62.44	60.55	58.75	57.02	55.37	53.77	52.24	50.77
1.041	15.72	16.21	16.70	17.17	17.64	18.09	18.53	18.97	19.40	19.82
1.041	68.22	66.08	64.05	62.11	60.26	58.49	56.79	55.15	53.58	52.07
1.042	16.08	16.59	17.09	17.57	18.05	18.51	18.97	19.41	19.85	20.28
1.042	69.94	67.75	65.66	63.68	61.78	59.96	58.21	56.54	54.92	53.37
1.043	16.45	16.97	17.47	17.97	18.45	18.93	19.40	19.85	20.30	20.74
1.043	71.66	69.42	67.28	65.24	63.29	61.43	59.64	57.92	56.27	54.68
1.044	16.81	17.34	17.86	18.37	18.86	19.35	19.82	20.29	20.75	21.20
1.044	73.39	71.09	68.90	66.81	64.81	62.90	61.07	59.31	57.61	55.98
1.045	17.17	17.71	18.24	18.76	19.27	19.77	20.25	20.73	21.20	21.66
1.045	75.12	72.76	70.52	68.38	66.33	64.37	62.50	60.70	58.96	57.29
1.046	17.53	18.09	18.63	19.16	19.68	20.18	20.68	21.17	21.64	22.11
1.046	76.85	74.43	72.14	69.95	67.85	65.85	63.93	62.08	60.31	58.60
1.047	17.89	18.46	19.01	19.55	20.08	20.60	21.11	21.60	22.09	22.57
1.047	78.58	76.11	73.76	71.52	69.38	67.33	65.36	63.48	61.66	59.91
1.048	18.25	18.83	19.39	19.94	20.48	21.01	21.53	22.04	22.54	23.02
1.048	80.32	77.79	75.39	73.10	70.91	68.81	66.80	64.87	63.01	61.22
1.049	18.61	19.20	19.77	20.34	20.89	21.43	21.95	22.47	22.98	23.48
1.049	82.06	79.48	77.02	74.68	72.44	70.29	68.24	66.26	64.37	62.54
1.050	18.97	19.57	20.16	20.73	21.29	21.84	22.38	22.91	23.42	23.93
1.050	83.80	81.16	78.65	76.26	73.97	71.78	69.68	67.66	65.72	63.85

RATE	PERCENT REACTION									
RATIO	90.00	89.00	88.00	87.00	86.00	85.00	84.00	83.00	82.00	81.00
1.001	0.26	0.28	0.29	0.31	0.32	0.34	0.35	0.37	0.38	0.39
1.001	2.31	2.21	2.13	2.05	1.97	1.90	1.84	1.78	1.72	1.67
1.002	0.52	0.55	0.58	0.61	0.64	0.67	0.70	0.73	0.76	0.78
1.002	4.62	4.43	4.25	4.09	3.94	3.81	3.68	3.56	3.44	3.33
1.003	0.77	0.82	0.87	0.92	0.96	1.01	1.05	1.09	1.13	1.17
1.003	6.94	6.65	6.39	6.14	5.92	5.71	5.52	5.33	5.16	5.00
1.004	1.02	1.09	1.16	1.22	1.28	1.34	1.39	1.45	1.50	1.56
1.004	9.26	8.87	8.52	8.20	7.90	7.62	7.36	7.12	6.89	6.67
1.005	1.28	1.36	1.44	1.52	1.59	1.67	1.74	1.81	1.88	1.94
1.005	11.58	11.10	10.66	10.26	9.88	9.54	9.21	8.90	8.62	8.34
1.006	1.53	1.63	1.73	1.82	1.91	2.00	2.08	2.17	2.25	2.33
1.006	13.92	13.34	12.81	12.32	11.87	11.45	11.06	10.69	10.35	10.02
1.007	1.78	1.90	2.01	2.12	2.23	2.33	2.43	2.52	2.62	2.71
1.007	16.25	15.58	14.96	14.39	13.86	13.37	12.92	12.49	12.08	11.70
1.008	2.03	2.16	2.29	2.42	2.54	2.66	2.77	2.88	2.99	3.09
1.008	18.60	17.82	17.11	16.46	15.86	15.30	14.77	14.28	13.82	13.38
1.009	2.28	2.43	2.58	2.72	2.85	2.98	3.11	3.23	3.36	3.47
1.009	20.94	20.07	19.27	18.54	17.86	17.23	16.63	16.08	15.56	15.06
1.010	2.53	2.70	2.86	3.01	3.16	3.31	3.45	3.59	3.72	3.85
1.010	23.30	22.32	21.43	20.62	19.86	19.16	18.50	17.88	17.30	16.75
1.011	2.78	2.96	3.14	3.31	3.48	3.64	3.79	3.94	4.09	4.23
1.011	25.66	24.58	23.60	22.70	21.87	21.09	20.37	19.69	19.05	18.44
1.012	3.02	3.23	3.42	3.61	3.79	3.96	4.13	4.30	4.46	4.61
1.012	28.02	26.85	25.77	24.79	23.88	23.03	22.24	21.50	20.80	20.13
1.013	3.27	3.49	3.70	3.90	4.10	4.29	4.47	4.65	4.82	4.99
1.013	30.39	29.11	27.95	26.88	25.89	24.97	24.11	23.31	22.55	21.83
1.014	3.52	3.75	3.98	4.19	4.41	4.61	4.81	5.00	5.19	5.37
1.014	32.77	31.39	30.13	28.98	27.91	26.92	25.99	25.12	24.30	23.53
1.015	3.76	4.01	4.26	4.49	4.71	4.93	5.14	5.35	5.55	5.74
1.015	35.15	33.67	32.32	31.08	29.94	28.87	27.87	26.94	26.06	25.23
1.016	4.01	4.28	4.53	4.78	5.02	5.25	5.48	5.70	5.91	6.12
1.016	37.53	35.95	34.51	33.19	31.96	30.82	29.76	28.76	27.82	26.93
1.017	4.25	4.54	4.81	5.07	5.33	5.57	5.81	6.05	6.27	6.49
1.017	39.92	38.24	36.71	35.30	33.99	32.78	31.65	30.59	29.59	28.64
1.018	4.50	4.80	5.09	5.36	5.63	5.89	6.15	6.39	6.63	6.87
1.018	42.32	40.54	38.91	37.41	36.03	34.74	33.54	32.41	31.35	30.35
1.019	4.74	5.06	5.36	5.65	5.94	6.21	6.48	6.74	6.99	7.24
1.019	44.72	42.83	41.11	39.53	38.07	36.71	35.44	34.24	33.12	32.06
1.020	4.98	5.31	5.63	5.94	6.24	6.53	6.81	7.09	7.35	7.61
1.020	47.13	45.14	43.32	41.65	40.11	38.68	37.34	36.08	34.90	33.78
1.021	5.22	5.57	5.91	6.23	6.55	6.85	7.14	7.43	7.71	7.98
1.021	49.55	47.45	45.54	43.78	42.16	40.65	39.24	37.92	36.67	35.50
1.022	5.46	5.83	6.18	6.52	6.85	7.17	7.48	7.77	8.07	8.35
1.022	51.97	49.76	47.76	45.91	44.21	42.62	41.15	39.76	38.45	37.22
1.023	5.70	6.09	6.45	6.81	7.15	7.48	7.81	8.12	8.42	8.72
1.023	54.39	52.08	49.98	48.05	46.26	44.60	43.05	41.60	40.23	38.94
1.024	5.94	6.34	6.72	7.09	7.45	7.80	8.13	8.46	8.78	9.09
1.024	56.82	54.41	52.21	50.19	48.32	46.59	44.97	43.45	42.02	40.67
1.025	6.18	6.60	7.00	7.38	7.75	8.11	8.46	8.80	9.13	9.45
1.025	59.26	56.74	54.44	52.33	50.39	48.58	46.88	45.30	43.81	42.40

RATE RATIO	PERCENT REACTION 90.00	89.00	88.00	87.00	86.00	85.00	84.00	83.00	82.00	81.00
1.026	6.42	6.85	7.27	7.67	8.05	8.43	8.79	9.14	9.49	9.82
1.026	61.70	59.07	56.68	54.48	52.45	50.57	48.81	47.15	45.60	44.13
1.027	6.66	7.10	7.54	7.95	8.35	8.74	9.12	9.48	9.84	10.19
1.027	64.15	61.41	58.92	56.64	54.52	52.56	50.73	49.01	47.39	45.87
1.028	6.89	7.36	7.80	8.23	8.65	9.05	9.44	9.82	10.19	10.55
1.028	66.60	63.76	61.17	58.79	56.60	54.56	52.66	50.87	49.19	47.60
1.029	7.13	7.61	8.07	8.52	8.95	9.36	9.77	10.16	10.54	10.91
1.029	69.06	66.11	63.42	60.96	58.68	56.56	54.59	52.73	50.99	49.34
1.030	7.37	7.86	8.34	8.80	9.24	9.67	10.09	10.50	10.89	11.28
1.030	71.52	68.46	65.68	63.12	60.76	58.57	56.52	54.60	52.80	51.09
1.031	7.60	8.11	8.61	9.08	9.54	9.98	10.41	10.83	11.24	11.64
1.031	73.99	70.83	67.94	65.29	62.85	60.58	58.46	56.47	54.60	52.84
1.032	7.84	8.36	8.87	9.36	9.83	10.29	10.74	11.17	11.59	12.00
1.032	76.47	73.19	70.21	67.47	64.94	62.59	60.40	58.35	56.41	54.59
1.033	8.07	8.61	9.14	9.64	10.13	10.60	11.06	11.50	11.94	12.36
1.033	78.95	75.56	72.48	69.65	67.04	64.61	62.35	60.22	58.22	56.34
1.034	8.30	8.86	9.40	9.92	10.42	10.91	11.38	11.84	12.28	12.72
1.034	81.44	77.94	74.76	71.83	69.14	66.63	64.29	62.10	60.04	58.09
1.035	8.53	9.11	9.66	10.20	10.71	11.21	11.70	12.17	12.63	13.08
1.035	83.93	80.32	77.04	74.02	71.24	68.66	66.25	63.99	61.86	59.85
1.036	8.77	9.36	9.93	10.48	11.01	11.52	12.02	12.50	12.98	13.44
1.036	86.43	82.71	79.32	76.22	73.35	70.69	68.20	65.87	63.68	61.61
1.037	9.00	9.60	10.19	10.75	11.30	11.83	12.34	12.84	13.32	13.79
1.037	88.93	85.10	81.61	78.42	75.46	72.72	70.16	67.76	65.51	63.38
1.038	9.23	9.85	10.45	11.03	11.59	12.13	12.66	13.17	13.66	14.15
1.038	91.44	87.50	83.91	80.62	77.58	74.76	72.12	69.66	67.34	65.15
1.039	9.46	10.10	10.71	11.30	11.88	12.43	12.97	13.50	14.01	14.50
1.039	93.96	89.90	86.21	82.82	79.70	76.80	74.09	71.55	69.17	66.92
1.040	9.69	10.34	10.97	11.58	12.17	12.74	13.29	13.83	14.35	14.86
1.040	96.48	92.31	88.52	85.04	81.82	78.84	76.06	73.46	71.00	68.69
1.041	9.92	10.59	11.23	11.85	12.46	13.04	13.60	14.15	14.69	15.21
1.041	99.01	94.72	90.83	87.25	83.95	80.89	78.04	75.36	72.84	70.47
1.042	10.14	10.83	11.49	12.13	12.74	13.34	13.92	14.48	15.03	15.56
1.042	101.54	97.14	93.14	89.47	86.09	82.94	80.01	77.27	74.68	72.25
1.043	10.37	11.07	11.75	12.40	13.03	13.64	14.23	14.81	15.37	15.91
1.043	104.08	99.57	95.46	91.70	88.22	85.00	81.99	79.18	76.53	74.03
1.044	10.60	11.31	12.01	12.67	13.32	13.94	14.55	15.13	15.71	16.27
1.044	106.63	102.00	97.79	93.93	90.37	87.06	83.98	81.09	78.38	75.81
1.045	10.82	11.56	12.26	12.94	13.60	14.24	14.86	15.46	16.05	16.62
1.045	109.18	104.43	100.12	96.16	92.51	89.12	85.97	83.01	80.23	77.60
1.046	11.05	11.80	12.52	13.21	13.89	14.54	15.17	15.78	16.38	16.96
1.046	111.74	106.87	102.45	98.40	94.66	91.19	87.96	84.93	82.08	79.39
1.047	11.27	12.04	12.77	13.48	14.17	14.84	15.48	16.11	16.72	17.31
1.047	114.30	109.32	104.79	100.64	96.82	93.27	89.95	86.85	83.94	81.19
1.048	11.50	12.28	13.03	13.75	14.45	15.13	15.79	16.43	17.05	17.66
1.048	116.87	111.77	107.14	102.89	98.97	95.34	91.95	88.78	85.80	82.98
1.049	11.72	12.52	13.28	14.02	14.74	15.43	16.10	16.75	17.39	18.01
1.049	119.44	114.23	109.49	105.14	101.14	97.42	93.96	90.71	87.66	84.78
1.050	11.94	12.75	13.54	14.29	15.02	15.72	16.41	17.07	17.72	18.35
1.050	122.02	116.69	111.84	107.40	103.30	99.50	95.96	92.65	89.53	86.59

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RATE              PERCENT  REACTION
RATIO    100.00     99.00     98.00     97.00     96.00     95.00     94.00     93.00     92.00     91.00

1.001      0.00      0.05      0.08      0.11      0.14      0.16      0.18      0.20      0.22      0.24
1.001   -999.99      4.62      3.92      3.52      3.23      3.01      2.82      2.67      2.53      2.42
1.002      0.00      0.10      0.16      0.22      0.27      0.32      0.36      0.40      0.44      0.48
1.002   -999.99      9.26      7.86      7.04      6.46      6.01      5.65      5.34      5.07      4.83
1.003      0.00      0.14      0.24      0.33      0.41      0.48      0.54      0.60      0.66      0.72
1.003   -999.99     13.92     11.81     10.58      9.71      9.03      8.48      8.01      7.61      7.25
1.004      0.00      0.19      0.32      0.44      0.54      0.63      0.72      0.80      0.88      0.95
1.004   -999.99     18.60     15.78     14.13     12.96     12.06     11.32     10.70     10.16      9.68
1.005      0.00      0.23      0.40      0.54      0.67      0.79      0.90      1.00      1.10      1.19
1.005   -999.99     23.30     19.76     17.69     16.23     15.10     14.17     13.39     12.71     12.12
1.006      0.00      0.28      0.48      0.65      0.80      0.94      1.07      1.19      1.31      1.42
1.006   -999.99     28.02     23.75     21.27     19.51     18.14     17.03     16.09     15.27     14.56
1.007      0.00      0.33      0.56      0.75      0.93      1.10      1.25      1.39      1.53      1.66
1.007   -999.99     32.77     27.77     24.85     22.79     21.20     19.89     18.79     17.84     17.00
1.008      0.00      0.37      0.63      0.86      1.06      1.25      1.42      1.59      1.74      1.89
1.008   -999.99     37.53     31.80     28.45     26.09     24.26     22.77     21.51     20.42     19.46
1.009      0.00      0.41      0.71      0.96      1.19      1.40      1.60      1.78      1.96      2.12
1.009   -999.99     42.32     35.84     32.07     29.40     27.33     25.65     24.23     23.00     21.91
1.010      0.00      0.46      0.79      1.07      1.32      1.56      1.77      1.98      2.17      2.35
1.010   -999.99     47.13     39.90     35.69     32.72     30.42     28.54     26.95     25.58     24.38
1.011      0.00      0.50      0.86      1.17      1.45      1.71      1.95      2.17      2.38      2.58
1.011   -999.99     51.97     43.98     39.33     36.05     33.51     31.44     29.69     28.18     26.85
1.012      0.00      0.55      0.94      1.28      1.58      1.86      2.12      2.36      2.59      2.81
1.012   -999.99     56.82     48.07     42.98     39.39     36.61     34.34     32.43     30.78     29.32
1.013      0.00      0.59      1.02      1.38      1.71      2.01      2.29      2.56      2.81      3.04
1.013   -999.99     61.70     52.18     46.64     42.74     39.72     37.26     35.18     33.38     31.80
1.014      0.00      0.64      1.09      1.48      1.84      2.16      2.46      2.75      3.02      3.27
1.014   -999.99     66.60     56.30     50.32     46.10     42.84     40.18     37.94     36.00     34.29
1.015      0.00      0.68      1.17      1.59      1.97      2.31      2.64      2.94      3.23      3.50
1.015   -999.99     71.52     60.44     54.01     49.47     45.97     43.11     40.70     38.62     36.78
1.016      0.00      0.72      1.24      1.69      2.09      2.46      2.81      3.13      3.44      3.73
1.016   -999.99     76.47     64.60     57.71     52.86     49.10     46.05     43.47     41.24     39.28
1.017      0.00      0.77      1.32      1.79      2.22      2.61      2.98      3.32      3.65      3.96
1.017   -999.99     81.44     68.77     61.43     56.25     52.25     48.99     46.25     43.88     41.79
1.018      0.00      0.81      1.39      1.89      2.35      2.76      3.15      3.51      3.85      4.18
1.018   -999.99     86.43     72.96     65.16     59.66     55.41     51.95     49.04     46.52     44.30
1.019      0.00      0.85      1.46      1.99      2.47      2.91      3.32      3.70      4.06      4.41
1.019   -999.99     91.44     77.16     68.90     63.07     58.57     54.91     51.83     49.16     46.82
1.020      0.00      0.89      1.54      2.10      2.60      3.06      3.49      3.89      4.27      4.63
1.020   -999.99     96.48     81.39     72.65     66.50     61.75     57.89     54.63     51.82     49.34
1.021      0.00      0.94      1.61      2.20      2.72      3.20      3.65      4.08      4.48      4.86
1.021   -999.99    101.54     85.63     76.42     69.94     64.94     60.87     57.44     54.48     51.87
1.022      0.00      0.98      1.69      2.30      2.85      3.35      3.82      4.26      4.68      5.08
1.022   -999.99    106.63     89.88     80.20     73.39     68.13     63.85     60.25     57.14     54.41
1.023      0.00      1.02      1.76      2.40      2.97      3.50      3.99      4.45      4.89      5.31
1.023   -999.99    111.74     94.15     84.00     76.85     71.34     66.85     63.08     59.82     56.95
1.024      0.00      1.06      1.83      2.50      3.09      3.64      4.16      4.64      5.09      5.53
1.024   -999.99    116.87     98.44     87.80     80.32     74.55     69.86     65.91     62.50     59.50
1.025      0.00      1.10      1.90      2.59      3.22      3.79      4.32      4.82      5.30      5.75
1.025   -999.99    122.02    102.75     91.63     83.80     77.77     72.87     68.75     65.18     62.05
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RATE            PERCENT  REACTION
RATIO   100.00    99.00    98.00    97.00    96.00    95.00    94.00    93.00    92.00    91.00

1.026     0.00     1.14     1.97     2.69     3.34     3.93     4.49     5.01     5.50     5.97
1.026  -999.99   127.20   107.07    95.46    87.30    81.01    75.90    71.59    67.88    64.61
1.027     0.00     1.18     2.05     2.79     3.46     4.08     4.65     5.19     5.70     6.19
1.027  -999.99   132.41   111.41    99.31    90.80    84.25    78.93    74.45    70.58    67.18
1.028     0.00     1.23     2.12     2.89     3.58     4.22     4.82     5.38     5.91     6.41
1.028  -999.99   137.63   115.77   103.17    94.32    87.50    81.97    77.31    73.29    69.75
1.029     0.00     1.27     2.19     2.99     3.70     4.37     4.98     5.56     6.11     6.63
1.029  -999.99   142.88   120.14   107.05    97.85    90.77    85.01    80.17    76.00    72.33
1.030     0.00     1.31     2.26     3.08     3.83     4.51     5.14     5.74     6.31     6.85
1.030  -999.99   148.16   124.53   110.93   101.39    94.04    88.07    83.05    78.72    74.92
1.031     0.00     1.35     2.33     3.18     3.95     4.65     5.31     5.93     6.51     7.07
1.031  -999.99   153.46   128.94   114.84   104.94    97.32    91.14    85.94    81.45    77.51
1.032     0.00     1.39     2.40     3.28     4.07     4.79     5.47     6.11     6.71     7.29
1.032  -999.99   158.78   133.36   118.75   108.50   100.61    94.21    88.83    84.18    80.11
1.033     0.00     1.43     2.47     3.37     4.19     4.93     5.63     6.29     6.91     7.50
1.033  -999.99   164.13   137.80   122.68   112.07   103.92    97.29    91.73    86.93    82.71
1.034     0.00     1.47     2.54     3.47     4.31     5.08     5.79     6.47     7.11     7.72
1.034  -999.99   169.50   142.26   126.63   115.66   107.23   100.39    94.63    89.67    85.32
1.035     0.00     1.51     2.61     3.56     4.42     5.22     5.96     6.65     7.31     7.94
1.035  -999.99   174.90   146.74   130.58   119.26   110.55   103.49    97.55    92.43    87.94
1.036     0.00     1.55     2.68     3.66     4.54     5.36     6.12     6.83     7.51     8.15
1.036  -999.99   180.32   151.24   134.55   122.87   113.88   106.59   100.47    95.19    90.56
1.037     0.00     1.58     2.75     3.75     4.66     5.50     6.28     7.01     7.70     8.36
1.037  -999.99   185.77   155.75   138.54   126.49   117.22   109.71   103.40    97.96    93.19
1.038     0.00     1.62     2.82     3.85     4.78     5.64     6.44     7.19     7.90     8.58
1.038  -999.99   191.25   160.28   142.54   130.12   120.57   112.84   106.34   100.74    95.82
1.039     0.00     1.66     2.88     3.94     4.90     5.78     6.59     7.37     8.10     8.79
1.039  -999.99   196.74   164.83   146.55   133.76   123.94   115.97   109.28   103.52    98.47
1.040     0.00     1.70     2.95     4.04     5.01     5.91     6.75     7.54     8.29     9.00
1.040  -999.99   202.27   169.39   150.58   137.42   127.31   119.12   112.24   106.31   101.11
1.041     0.00     1.74     3.02     4.13     5.13     6.05     6.91     7.72     8.49     9.22
1.041  -999.99   207.82   173.98   154.62   141.08   130.69   122.27   115.20   109.11   103.77
1.042     0.00     1.78     3.09     4.22     5.25     6.19     7.07     7.90     8.68     9.43
1.042  -999.99   213.39   178.58   158.68   144.76   134.08   125.43   118.17   111.92   106.43
1.043     0.00     1.82     3.15     4.32     5.36     6.33     7.23     8.07     8.87     9.64
1.043  -999.99   218.99   183.20   162.75   148.45   137.49   128.60   121.15   114.73   109.10
1.044     0.00     1.85     3.22     4.41     5.48     6.46     7.38     8.25     9.07     9.85
1.044  -999.99   224.62   187.83   166.83   152.15   140.90   131.78   124.13   117.55   111.77
1.045     0.00     1.89     3.29     4.50     5.59     6.60     7.54     8.42     9.26    10.06
1.045  -999.99   230.27   192.49   170.93   155.87   144.32   134.97   127.13   120.37   114.45
1.046     0.00     1.93     3.35     4.59     5.71     6.73     7.69     8.60     9.45    10.27
1.046  -999.99   235.95   197.16   175.04   159.60   147.75   138.17   130.13   123.21   117.14
1.047     0.00     1.97     3.42     4.68     5.82     6.87     7.85     8.77     9.64    10.48
1.047  -999.99   241.66   201.86   179.17   163.33   151.20   141.38   133.14   126.05   119.83
1.048     0.00     2.00     3.49     4.77     5.93     7.00     8.00     8.94     9.84    10.68
1.048  -999.99   247.39   206.57   183.31   167.09   154.65   144.59   136.15   128.89   122.53
1.049     0.00     2.04     3.55     4.86     6.05     7.14     8.16     9.12    10.03    10.89
1.049  -999.99   253.14   211.30   187.47   170.85   158.12   147.82   139.18   131.75   125.24
1.050     0.00     2.08     3.62     4.95     6.16     7.27     8.31     9.29    10.22    11.10
1.050  -999.99   258.93   216.05   191.64   174.62   161.59   151.05   142.21   134.61   127.95
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REFERENCES

1 Krouse, R. H., Thesis, McMaster University (1960)

2 Harrison, A. G., Thesis, McMaster University (1956)

3 Ford, R. G., Thesis, McMaster University (1957)

4 Voge, H. H., J. Am. Chem. Soc. 61, 1032 (1939)

5 Haissinsky, M. and Pappas, A., J. Chim. Phys. 47, 506 (1950)

6 Urey, H. C. and Greiff, L. J., J. Am. Chem. Soc. 57, 321 (1935)

7 Bigeleisen, J. and Mayer, M. G., J. Chem. Phys. 15, 261 (1947)

8 Tudge, A. P. and Thode, H. G., Can. J. Res. B28, 567 (1950)

9 Roginskii, S. Z., Theoretical Principles of Isotope Methods for Examining Chemical Reactions, A.E.C.-tr-2873

10 Cragg, C. B., Thesis, McMaster University (1961)

11 Herzberg, G., Infrared and Raman Spectra, Van Nostrand, N.Y. (1947)

12 Hulston, J. R., Thesis, McMaster University (1964)

13 Urey, H. C., J. Chem. Soc. 562 (1947)

14 Bailey, C. R. et al., J. Chem. Soc. 971 (1936)

15 Redlich, O., Z. Physik. Chem. B28, 371 (1935)

16 Tatevsky, V. M. and Frost, A. V., Bull. Moscow State Univ. 12, 113 (1947)

17 Kuznetsova, E. M., Gryaznova, Z. V. and Panchenkov, V., Doklady Phys. Chem. 148, 18 (1963)

18 Bigeleisen, J., J. Chem. Phys. 17, 675 (1949)

19 Eyring, H., J. Chem. Phys. 3, 107 (1935)

20 Evans, M. G. and Polanyi, M., Trans. Farad. Soc. 31, 875 (1935)

21 Glasstone, S., Laidler, K. J. and Eyring, H., The Theory of Rate Processes, McGraw Hill, N.Y. (1941)

22 Slater, N. B., Theory of Unimolecular Reactions, Cornell (1959)

23 Bigeleisen, J. and Wolfsberg, M., Advances in Chem. Phys. 1, 15 (1958)

24 Schulek, E. and Barcza, L., Talanta 3, 23 (1959)

25 Kolthoff, I. M. and Elving, P. J., Treatise on Analytical Chemistry, Pt. II Vol. 7, Interscience, N.Y. (1961)

26 Anal. Abstracts, 7, 1723

27 Brasted, R. C. and Sneed, M. C., Comprehensive Inorganic Chemistry, Van Nostrand, Toronto (1961)

28 Vogel, A. I., Textbook of Quantitative Inorganic Analysis, Wiley, N.Y., (1961)

29 Yost, D. M. and Russell, H., Systematic Inorganic Chemistry, Prentice Hall, N.Y. (1944)

30 Hildebrand, W. M. and Lundell, G. E. F., Applied Inorganic Analysis, Wiley, N.Y. (1929)

31 Benger, E. B., J. Am. Chem. Soc. 39, 2171 (1917)

32 Neptune, J. A. and King, E. L., J. Am. Chem. Soc. 75, 3069 (1953)

33 Caley, E. R. and Henderson, C. L., Anal. Chem. 32, 975 (1960)

34 de Salas, S. M., Rev. Obras. Sanit Nación (Buenes Aires) 20, 264 (1947)

35 Wanless, R. K. and Thode, H. G., J. Sci. Inst. 30, 395 (1953)

36 Wentink, T., J. Chem. Phys. 30, 105 (1959)

37 Jones, L. J. and McLaren, E., J. Chem. Phys. 28, 995 (1958)

38 Kujumzelis, T. G., Physik. Z. 39, 665 (1938)

39 Heath D. F. and Linnett, J. W., Trans. Farad. Soc. 44, 873 (1948)

40 Rocchiccioli, C., Comptes Rendus 247, 1108 (1958), and Annales de Chimie 5, 999 (1960)

41 Walrafen, G. E., J. Chem. Phys. 36, 90 (1962)

42 Wells, A. F. and Bailey, M., J. Chem. Soc. 1282 (1949)

43 Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds, Wiley, N.Y. (1963)

44 Pistorius, C. W. F. T., J. Chem. Phys 27, 965 (1957)

45 Walrafen, G. E., J. Chem. Phys. 39, 1479 (1963)

46 Thode, H. G., Shima, M., Krishnamurty, K. V. and Rees, C. E., Unpublished Work, McMaster University.

47 Latimer, W. M., The Oxidation States of the Elements and their Potentials, Prentice Hall, N.Y. (1952)

48 Tomlinson, R. H., Private Communication