The Thermodynamic Properties of Isotopic Substances.

LIVERSIDGE LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY IN THE ROYAL INSTITUTION ON DECEMBER 18TH, 1946.

By HAROLD C. UREY.

(Institute of Nuclear Studies, University of Chicago.)

THE discovery of the isotopes of the elements resulted from the careful study of the properties of radioactive substances during the first years of this century. The conclusion that certain species of atoms had identical chemical properties but different radioactive properties came from chemical studies which accompanied the study of radioactivity. Boltwood [1] noted that thorium and ionium were very similar in chemical properties, so similar, in fact, that he was unable to separate them if they were mixed. Marckwald and Keetman [2] investigated this problem with greater care, as did Auer v. Welsbach [3], and all these authors came to the conclusion that ionium and thorium are identical in chemical properties. Further, Marckwald [4] and Soddy [5] showed that radium and mesothorium constitute another such pair of substances. At present many such radio-elements which are chemically the same elements or are identical with non-radioactive elements are known. Soddy was able to conclude that this occurrence of two or more varieties of elements of identical chemical properties was probably of general occurrence, and that such identical elements differed in atomic weight as well as radioactive properties, and Sir J. J. Thompson proved that such isotopes existed in the case of stable atoms as well and detected them by the action of electric and magnetic fields on beams of ionized atoms which separated the atoms of different atomic weights. The outstanding work of Aston then gave us an extensive knowledge of the isotopes of the elements and their exact masses, and this has been followed by many researches which have completed or nearly completed our knowledge of this field.

Lindemann [6] first applied statistical mechanical methods to the problem of chemical differences of isotopes. He applied these calculations to the differences in vapour pressures of the lead isotopes and showed that considerable differences should exist if the half quantum of zero point energy were not present. Since experiments showed no difference in vapour pressure, he concluded that the half quantum of zero point energy must exist. Neither the method of calculation nor the conclusions have been changed by any work since this pioneer work of Lindemann, but it is unfortunate that this work was done on a heavy element, for all differences in chemical properties of isotopic compounds diminish rapidly with increasing atomic weight. Had these experiments been applied to water, using precision methods for determining density, positive results would have been secured.

Keesom and van Dijk [7] did demonstrate that differences in the vapour pressures of the neon isotopes exist by fractionally distilling liquid neon at − 248·4°, and partially separated the neon isotopes in considerable quantity by this method. Urey, Brickwedde, and Murphy [8] showed that a large difference in the vapour pressures of the isotopic molecules of hydrogen, H_2 and HD, was to be expected even though the zero point energy was assumed, and concentrated the heavy isotope of hydrogen sufficiently to make its detection possible. Also, Lewis and Cornish [9] demonstrated the existence of vapour-pressure differences between the isotopic molecules, H_2O^{16}, D_2O^{16}, and H_2O^{18}. Urey and Rittenberg [10] showed from theoretical calculations that marked differences in the equilibrium constants of exchange reactions between hydrogen and deuterium on the one hand, and the hydrogen and deuterium compounds of the halogens on the other should exist, and Farkas and Farkas [11] applied the same methods to exchanges with water. Urey and Greiff [12] then applied the same methods to exchange reactions involving other isotopes. These researches first established the existence of comparatively large differences in properties of the hydrogen and deuterium compounds and of smaller but definite differences in the chemical properties of other isotopic compounds of elements of low atomic weight.

The marked differences in chemical properties of protium and deuterium and their compounds stimulated many researches on these substances during the 'thirties, and a very considerable literature on them exists at the present time. It is not the purpose of this paper to review this literature in detail, but rather to review a limited amount of this interesting work in relation to similar work on the isotopic compounds of other elements where the effects observed are much smaller. Also, the present paper is limited to equilibrium properties and does not include work dealing with differences related to the kinetics of chemical reactions. These latter effects are largely unknown for isotopic compounds other than those of hydrogen except in so far as they relate to properties directly related by simple kinetic theory to molecular weights, as in the case of diffusion processes, or to molecular weights and forces between molecules, as in the case of the thermal diffusion method of separating isotopes, where the emphasis has largely been on the separation problem rather than on the fundamental properties of substances.

The theory of these differences in thermodynamic properties of isotopic compounds is well known in special cases and not in others. The physical properties of the elementary hydrogens, H_2, HD, and D_2, have been extensively studied [13] and the vapour pressure of protium tritide, HT, in its solution in natural hydrogen has been determined at one temperature.[14] The differences in vapour pressures are large and the heat capacity measurements on H_2, HD, and D_2 show that the Debye frequencies are so large that the heat capacities of the condensed phases are much less than those expected for high temperatures. This makes the differences in vapour pressures understandable in a qualitative way, though quantitative agreement is not secured since the Debye θ's are not inversely proportional to the molecular weights. Other attempts to correlate these properties have been made by Bijl and Hobbs [15] and better but not completely satisfactory agreement secured.

The differences in the vapour pressures of other compounds of protium and deuterium have been observed but no satisfactory theory with regard to these differences exists. With the exception of the hydrogens and the neons, none of these vapour pressure differences can be satisfactorily related to the translational or sound vibrations of the solids or liquids. The isotopic compounds of the hydrogens differ in heats of fusion, vaporisation, molar volumes, heats of solution and many other ways. These differences in the hydrogen compounds have prompted the study of similar differences between the isotopic compounds of other elements, and though the differences are very much smaller, they show similarities to the differences in the hydrogen compounds. These differences in the case of hydrogen as well as other of the lighter elements could not have been overlooked during the 19th century had there not been a sort of conspiracy in Nature which prevented their observation until other evidence indicated both the existence of isotopes and their chemical differences. Thus the hydrogen isotopes and their compounds are markedly different, but the extreme rarity of the heavy isotope prevented the observation of these differences. Similarly, carbon, nitrogen, and oxygen should show variations in their atomic weights, but the rarity of their isotopes makes observation difficult, though not at all impossible in the case of oxygen because of the great sensitivity with which the density of water may be determined. Variations in the properties of the compounds of lithium and boron are difficult to detect because of the general chemical character of their compounds, or failure to study them as quantitatively as the compounds of other elements have been covered. Only in the case of oxygen and chlorine should the variations of atomic weight have been noticed, and that they were overlooked in these cases was understandable in view of the size of the expected variations.

The Theory of the Equilibrium Constants of Exchange Reactions.

The differences in chemical properties of isotopic substances are mostly not exactly correlated in theoretical calculations with physical observations, but in the case of exchange reactions the observed phenomena are well correlated with the energy states of the molecules as secured from spectral data by the use of statistical mechanics. These correlations show the physical basis for the differences in these special cases, and throw light on the nature of other phenomena.

A typical exchange reaction may be written

$$a\mathrm{A}_1 + b\mathrm{B}_2 = a\mathrm{A}_2 + b\mathrm{B}_1$$

where A and B are molecules which have some one element as a common constituent and the subscripts 1 and 2 indicate that the molecule contains only the light or the heavy isotope respectively. (The case of molecules containing both isotopes simultaneously will be considered later.) Then the equilibrium constant for this reaction is given by

$$K = \left(\frac{Q'_{\mathrm{A}_2}}{Q'_{\mathrm{A}_1}}\right)^a \Bigg/ \left(\frac{Q'_{\mathrm{B}_2}}{Q'_{\mathrm{B}_1}}\right)^b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the Q's are the partition functions of the molecules. Only the ratios of partition functions enter into these equilibrium constants and this makes it necessary to consider only these simple ratios here.[16] The ratio Q'_2/Q'_1 for a chemical compound is given rigorously by the equation

$$\frac{Q'_2}{Q'_1} = \frac{\sigma_1}{\sigma_2}\left(\frac{M_2}{M_1}\right)^{3/2} \Sigma \mathrm{e}^{-E_2/kT} / \Sigma \mathrm{e}^{-E_1/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ_2, and σ_2 are the symmetry numbers of the two molecules (identical in the example given), M_1 and M_2 are their molecular weights, E_1 and E_2 are particular energy states of the molecules, and the summations are to be taken over all such energy states. These energies must be calculated relative to the hypothetical vibrationless state, *i.e.*, with no zero point energy, or relative to the completely dissociated molecules. Since it is not possible to determine the energies of isotopic molecules relative to the dissociated states, and since the zero point energies cannot be directly observed, it is necessary to assume that the potential functions are the same for isotopic molecules, and estimate the zero point energies from the empirical but theoretically justified formulæ of molecular energy levels. If the temperature is so high that $\boldsymbol{k}T$ is large compared with the separations of the rotational energy levels, as it is in most of the cases we shall consider, and if the vibrational energy levels are sufficiently nearly harmonic, equation (2) can be replaced by

$$\frac{Q'_2}{Q'_1} = \frac{\sigma_1}{\sigma_2}\frac{I_2}{I_1}\left(\frac{M_2}{M_1}\right)^{3/2}\frac{e^{-u_2/2}}{1-e^{-u_2}}\frac{1-e^{-u_1}}{e^{-u_1/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for diatomic molecules and

$$\frac{Q'_2}{Q'_1} = \frac{\sigma_1}{\sigma_2}\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2}\Pi_i\frac{e^{-u_{2i}/2}}{1-e^{-u_{2i}}}\frac{1-e^{-u_{1i}}}{e^{-u_{1i}/2}} \quad . \quad . \quad . \quad . \quad (4)$$

for polyatomic molecules where the I's and A's, B's, and C's are the moments of inertia of the diatomic molecules and the principle moments of inertia of the polyatomic molecules, respectively, and the u's are related to the corresponding frequencies of vibration by relations of the kind, $u_i = \boldsymbol{hc}\omega_i/\boldsymbol{k}T$, and the product extends over all frequencies of the polyatomic molecule. If the right and left sides of equations (3) and (4) are multiplied by $(m_1/m_2)^{3/2n}$, where m_1 and m_2 are the atomic weights of the isotopic atoms being considered and n is the number of isotopic atoms being exchanged, and if the right sides of (3) and (4) are multiplied and divided by the ratios u_1/u_2 and $\Pi_i\ u_{1i}/u_{2i}$ respectively, it is possible to simplify these expressions and define new partition functions which are in fact the equilibrium constants for exchange reactions between the compound considered and the separated atoms. Thus (3) and (4) became

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\frac{u_2}{u_1}\frac{e^{-u_2/2}}{1-e^{-u_2}}\frac{1-e^{-u_1}}{e^{-u_1/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3')$$

and

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\Pi_i\frac{u_{2i}}{u_{1i}}\frac{e^{-u_{2i}/2}}{1-e^{-u_{2i}}}\frac{1-e^{-u_{1i}}}{e^{-u_{1i}/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

since

$$\frac{I_2}{I_1}\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{m_1}{m_2}\right)^{3/2n}\frac{u_1}{u_2} = \left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{m_1}{m_2}\right)^{3/2n}\Pi_i\frac{u_{1i}}{u_{2i}} = 1$$

according to a theorem of Teller and Redlich.[17] This makes it possible to calculate these ratios without calculating the moments of inertia and, in fact, from a knowledge of the frequencies only. Of course, it is necessary to secure the frequencies for isotopic molecules either by direct observation or by calculation in the case of rarer isotopes, and in this latter case much information is often needed in order to make the necessary calculations. It is obvious that the equilibrium constant K is given by

$$\left(\frac{Q_{2A}}{Q_{1A}}\right)^a \Big/ \left(\frac{Q_{2B}}{Q_{1A}}\right)^b = K$$

for the general exchange reaction just as it is given by (1).

The equations (3′) and (4′) can be put into more convenient form for purposes of calculation. Defining

$$x_i = \frac{u_{1i}+u_{2i}}{4} \text{ and } \delta_i = \frac{u_{1i}-u_{2i}}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and expanding in terms of the δ_i's, we get [18]

$$\ln\frac{Q_2}{Q_1} = \ln\frac{\sigma_1}{\sigma_2} + \Sigma_i \ln\frac{u_{2i}}{u_{1i}} + \Sigma_i[\coth x_i\delta_i + \frac{1}{12}\coth x_i\,(\coth^2 x_i - 1)\,\delta_i^3 + - - -] \ . \quad (6)$$

This equation can be used without the term in δ_i^3 for all calculations reported in this paper except those of LiH, LiD; NaH, NaD; KH, KD; and H_2O, D_2O.

If the u's are small, *i.e.*, either the frequencies low or the temperature high, the right sides of equations (3′) and (4′) can be easily expanded to give

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\left(1 - \frac{1}{24}\,(u_2^{\,2} - u_1^{\,2})\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

and

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\,\pi_i\left[1 - \frac{1}{24}\,(u_{2i}^{\,2} - u_{1i}^{\,2})\right] . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

Since the u's contain the inverse of the temperature, the ratio of the Q's approaches the ratio of the symmetry numbers, and in this case no differences in chemical properties exist. The partition function ratio Q'_2/Q'_1 approaches the value $\frac{\sigma_1}{\sigma_2}\left(\frac{m_2}{m_1}\right)^{3/2n}$ instead of $\frac{\sigma_1}{\sigma_2}$ in the case of Q_2/Q_1.

Bigeleisen and Mayer have shown how this formula can be used without solving the equations of motion, and have applied these methods to the silicon and tin fluorides and the fluorosilicate and fluorostannate ions.

For precise calculations it is necessary to include the anharmonic terms in the vibrational energy. When the frequencies are small these terms may be neglected and when they are large coth x_i is nearly equal to unity. In the case of diatomic molecules a correction for the anharmonicity terms can be made by substituting the true difference in zero point energies in calculating δ [equation (5)] instead of using harmonic terms only. In the case of polyatomic molecules this cannot be done since the anharmonic terms are not uniquely related to the ω_i's, because of cross product terms. In this case a sufficiently good approximation can be made by adding to equation (6) a term $\Delta E'/kT$, where $\Delta E'$ is the contribution to the zero point energy difference from the anharmonic energy terms. If the coefficients of the anharmonic terms are negative (the usual case) $\Delta E'$ is negative and decreases the calculated value of Q_2/Q_1.

Equations (3) and (4), (3′) and (4′) and (6) must be further corrected when the rotational partition functions have not reached classical values. Such corrections can be neglected at the temperatures which we consider here in all cases except those of the hydrogen exchange reactions. The formulæ for these corrections were first derived by Mulholland,[19] Viney,[20] and Gordon [21] and are reviewed in detail by Kassel.[22] The formulæ for these corrections are given for all cases by the last author.

If the molecule of a chemical compound under consideration contains only one atom of the element for which exchange is considered, then the symmetry numbers of the two isotopic molecules are the same and σ_1/σ_2 is equal to unity. Also if a molecule contains more than one such atom but these atoms occupy indistinguishable positions in the molecule and if they are all exchanged in the reaction considered, the ratio of symmetry numbers is again unity. When these conditions are not met, the ratio of symmetry numbers is not unity and their values must be determined for each particular case.

In general, we are interested in the overall ratio of the isotopes of an element in one chemical compound as compared with a similar ratio in a second chemical compound. Thus the fractionation of the isotopes of oxygen between carbon dioxide and water is given by the ratio

$$\frac{2[\mathrm{CO_2}^{18}] + [\mathrm{CO^{16}O^{18}}]}{[\mathrm{CO^{16}O^{18}}] + 2[\mathrm{CO_2}^{16}]}\Big/\frac{[\mathrm{H_2O^{18}}]}{[\mathrm{H_2O^{16}}]} = \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

It can easily be shown that this reduces to

$$\frac{[\mathrm{CO_2}^{18}]^{1/2}}{[\mathrm{CO_2}^{16}]^{1/2}}\Big/\frac{[\mathrm{H_2O^{18}}]}{[\mathrm{H_2O^{16}}]} = \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

if the equilibrium constant for the reaction

$$\mathrm{CO_2}^{18} + \mathrm{CO_2}^{16} = 2\ \mathrm{CO^{16}O^{18}}$$

is 4, and this will be true providing the partition function for the molecule $\mathrm{CO^{16}O^{18}}$ is the geometric mean of those for $\mathrm{CO_2}^{16}$ and $\mathrm{CO_2}^{18}$ divided by their symmetry numbers so that the equilibrium constant is $\sigma_1\sigma_2/\sigma_{12}^{\,2}$, and since σ_1 and σ_2 are 2 and σ_{12} is 1, this equals 4. Similarly, the fractionation factor for the distribution of the oxygen isotopes between $\mathrm{CO_2}$ and $\mathrm{CO_2}^{=}$ will be

$$\frac{[\mathrm{CO_3}^{18=}]^{1/3}}{[\mathrm{CO_3}^{16=}]^{1/3}}\Big/\frac{[\mathrm{CO_2}^{18}]^{1/2}}{[\mathrm{CO_2}^{16}]^{1/2}}$$

if the proportion of the isotopic molecules is determined by the symmetry numbers alone. The generalisation of this rule is obvious, but it will not apply to molecules in which two or more atoms of the same element do not occupy equivalent positions, as for example the case of nitrogen in the unsymmetrical molecule, N_2O. Also this rule does not apply in the case of the hydrogen isotopes where the isotopic effect on vibration frequencies is very large.

The justification of the rules given in the preceding paragraph is difficult unless one calculates the vibration frequencies of all the molecules involved, and this is a very laborious task which has not been extensively undertaken. In the case of the exchange between CO_2^{16}, CO_2^{18}, and $CO^{16}O^{18}$, the equilibrium constant has been calculated [23] and found to be 3·9990 at 0°. α is decreased by $\left(1 - \frac{\Delta}{8}\right)$ at low concentrations of the heavy isotope and increased by $\left(1 + \frac{\Delta}{8}\right)$ at high concentrations of this isotope, where Δ is the difference between 4 and the actual constant. The equilibrium constants for the exchange between O_2^{16}, O_2^{18}, and $O^{16}O^{18}$ and N_2^{14}, N_2^{15}, and $N^{14}N^{15}$ are 3·9859 and 3·9918 respectively and the α's for reactions involving CO_2, O_2, and N_2 differ from those given by (6) by 1·000125, 1·0018, and 1·0010 respectively, all at 0° C. Errors of the same order of magnitude are probable in other cases. These are the largest deviations to be expected and are not important as compared to other probable errors. The special problem presented by the hydrogen isotopes will be considered again.

There is an electronic isotope effect for the H and D atoms of 30 cm.$^{-1}$, and isotope effects of this order of magnitude should be present for all compounds of protium and deuterium. It is improbable that they will always cancel completely, and since they are unknown, there are uncertainties in the calculations of the Q_2/Q_1 values for the protium and deuterium compounds. These uncertainties are greater in the case of the tritium compounds.

In the case of all polyatomic molecules except CO_2 and HCN and all ionic molecules only the observed fundamentals are known. In these cases the errors may be larger than estimated above because of errors in the calculation of the zero point energy, since anharmonic terms are unknown and because of errors in calculating the fundamentals of the rare isotopic mosecules from the observed fundamentals of the more abundant isotopic molecules. If the anharmonic terms are negative (the usual case) the neglect of this factor makes the calculated Q_2/Q_1 too small. In the case of CO_2 and HCN, positive and negative anharmonic terms occur and the total effect on the calculated ratio is small. We have no way of estimating the magnitude or even the sign of these uncertainties.

If equilibrium constants for exchanges between gaseous substances and substances in condensed phases are desired, calculations for such constants are readily made from the equilibrium constants for gaseous substances and the appropriate relative vapour pressures if they are known. Since ionic substances are always in solution or in a solid phase, it is to be expected that calculated constants neglecting such effects may be in error by as much as a factor of 1·01. Such differences must be due to the application of statistical mechanical formulæ applicable to ideal gaseous substances to condensed phases without considering the effects of interaction between internal vibrations of a molecule and the fields produced by the other molecules of the condensed phase.

In a number of cases equilibrium constants for exchange reactions change with temperature from a region in which K is greater than unity to one in which it is less than unity, or the reverse. This is not a general phenomenon but neither is it uncommon. By expanding ln u_{2i}/u_{1i} in equation (6) and neglecting the δ_i^3 terms, it is easy to show that in the region of large values for all u_i's

$$\ln K = \ln\left(\frac{f_{2A}}{f_{1A}}\right)^a \Big/ \left(\frac{f_{2B}}{f_{1B}}\right)^b = -a\Sigma\frac{\delta\omega_{iA}}{\omega_{iA}} + a\Sigma\delta_{iA} + b\Sigma\frac{\delta\omega_{iB}}{\omega_{iB}} - b\Sigma\delta_{iB}$$

or if $K = 1$ and we substitute the values of the δ_i's in terms of the $\delta\omega_i$'s and solve for T, we get

$$T_1 = \frac{a\Sigma\delta\omega_{iA} - b\Sigma\delta\omega_{iB}}{a\Sigma\left(\frac{\delta\omega}{\omega}\right)_{iA} - b\Sigma\left(\frac{\delta\omega}{\omega}\right)_{iB}} \cdot \frac{hc}{2k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

for the temperature at which K crosses the value unity as the temperature increases. Applying the equation to some of these exchange reactions, we get the results shown in Table I. These

TABLE I.

Reaction.	$T(K = 1)$.
$\frac{1}{2}H_2 + DI = \frac{1}{2}D_2 + HI$	114°
$D_2O^{16} + \frac{1}{2}O_2^{18} = D_2O^{18} + \frac{1}{2}O_2^{16}$	123
$H_2O^{16} + \frac{1}{2}O_2^{18} = H_2O^{18} + \frac{1}{2}O_2^{16}$	495
$CO^{16} + \frac{1}{2}CO_2^{18} = CO^{18} + \frac{1}{2}CO_2^{16}$	384

calculations are only approximate, since they neglect anharmonic effects and disagree in some cases with the more exact calculations of the other tables. This crossing will occur if the difference in the sums of differences of frequencies has the same sign as the differences in the sums of the fractional differences of frequencies.

Numerical Results.

The vibration frequencies available for such calculations are very numerous but vary considerably in reliability for these purposes. Table II contains a list of the frequencies of diatomic and polyatomic molecules used for the calculations presented here. Unless the anharmonic terms in the vibrational energy level formulæ are known, exact equilibrium constants

TABLE II.

Molecular Frequencies.

(a) *Diatomic molecules for which exact constants are known.*

Molecule.	ω_θ.	$-x_\theta\omega_\theta$.	Ref. (see p. 568).	Molecule.	ω_θ.	$-x_\theta\omega_\theta$.	Ref. (see p. 568).
HCl^{35}	2988·95	51·65	Herzberg, I, p. 488	NaH	1170·8	18·90	Herzberg, I, p. 490
DCl^{35}	2143·52	26·56	Calculated	NaD	845·3	9·84	Calculated
HCl^{37}	2987·5	51·57	Calculated	KH	983·3	14·40	Herzberg, I, p. 489
HBr^{79}	2649·67	45·21	Herzberg, I, p. 487	KD	704·2	7·38	Calculated
DBr^{79}	1885·95	22·90	Calculated	$C^{12}O^{16}$	2167·4	13·28	Herzberg, I, p. 486
HBr^{81}	2646·6	45·19	Calculated	$C^{13}O^{16}$	2119·2	12·69	Calculated
HI	2309·53	39·73	Herzberg, I, p. 488	CO^{18}	2115·2	12·65	Calculated
DI	1639·45	20·02	Calculated	${N_2}^{14}$	2359·6	14·45	Herzberg, I, p. 490
H_2	4405·3	125·32	Herzberg, I, p. 487	${N_2}^{15}$	2279·6	13·48	Calculated
HD	3817·09	94·02	Libby	$N^{14}O$	1906·54	14·50	Herzberg, I, p. 490
D_2	3118·8 }	64·15 }	Herzberg, I, p. 487	$N^{15}O$	1872·34	13·99	Calculated
	3117·07 }	62·72 }	Libby	${O_2}^{16}$	1580·4	12·07	Herzberg, I, p. 490
HT	3598·14	83·60	Libby	${O_2}^{18}$	1490·0	10·73	Calculated
DT	2845·64	52·28	Libby	${Cl_2}^{35}$	564·9	4·0	Herzberg, I, p. 485
T_2	2546·50	41·88	Libby	${Cl_2}^{37}$	549·4	3·8	Calculated
Li^6H	1420·32	23·69	Calculated	${Br_2}^{79}$	323·86	1·07	Herzberg, I, p. 484
Li^6D	1074·59	13·72	Calculated	${Br_2}^{81}$	319·84	1·04	Calculated
Li^7H	1405·65	23·20	Herzberg, I, p. 489	${I_2}^{127}$	214·36	0·59	Herzberg, I, p. 488
Li^7D	1055·12	13·23	Herzberg, I, p. 489	${I_2}^{129}$	212·69	0·58	Calculated

(b) *Diatomic molecules for which only the frequencies for the observed fundamentals are known.*

$C^{12}N^{14-}$	2080	Estimated from Hibben, p. 453	$C^{13}N^{14-}$	2036·47	Calculated
			$C^{12}N^{15-}$	2047·76	Calculated

(c) *Polyatomic molecules for which exact constants are known. The multiplicity of degenerate frequencies is indicated in parentheses.*

Molecules.	ω_i.	x_{ij}.		Ref. (see p. 568).	Molecules.	ω_i.	x_{ij}.		Ref. (see p. 568).
H_2O	3825·32	−43·89	−20·02	Herzberg, II, p. 282	D_2O^{18}	2744·2	−22·58	−10·44	Calc., Valence forces
	1653·91	−19·5	−155·06			1202·7	−10·31	−80·88	
	3935·59	−46·37	−19·81			2861·7	−24·52	−10·47	
HDO	2820·3	−42·27	−89·3	Libby	CO_2	1351·20	−0·3	+5·7	Herzberg, II, p. 276
	1449·4	4·1	−16·0			672·20(2)	−1·3	−21·9	
	3883·8	−77·39	−25·53			2396·40	−12·5	−11·0	
D_2O	2758·06	−22·81	−10·56	Herzberg, II, p. 282	$C^{13}O_2$	1351·20	−0·30	+5·54	Calc., Valence forces
	1210·25	−10·44	−81·92			653·12(2)	−1·23	−21·28	
	2883·79	−24·90	−10·62			2328·40	−11·80	−10·38	
HTO	2365·0	−29·43	−18·93	Libby	${CO_2}^{18}$	1273·92	−0·27	+5·29	Calc., Valence forces
	1374·5	−5·91	−11·63			661·94(2)	−1·26	−20·33	
	3882·6	−77·70	−26·95			2359·81	−12·12	−10·67	
DTO	2357·1	−27·84	−13·53	Libby	HCN	2000·6	+52·0	−4·2	Herzberg, II, p. 280
	1117·9	−13·7	−9·01			729·3(2)	−2·85	−14·40	
	2830·7	−41·77	−11·3			3451·5	−55·48	−19·53	
T_2O	2296·63	−15·71	−4·27	Libby	$HC^{13}N$	1966·63	+50·25	−4·09	Calc., Valence forces
	1017·89	−8·21	−56·79			722·96(2)	−2·80	−14·09	
	2436·12	−18·39	−6·21			3435·38	−54·96	−19·27	
H_2O^{18}	3815·5	−43·66	−19·89	Calc., valence forces	HCN^{15}	1968·63	+50·36	−4·13	Calc., Valence forces
	1647·8	−19·36	−154·03			728·22 (2)	−2·84	−14·17	
	3919·4	−45·99	−19·66			3450·86	−55·46	−19·50	

The frequencies are listed in the order ω_1, ω_2, and ω_3 and the x_{ij}'s in the order

$$\begin{array}{cc} x_{11} & x_{12} \\ x_{22} & x_{13} \\ x_{33} & x_{23} \end{array}$$

TABLE II.—*continued.*

Molecular Frequencies.

(d) *Polyatomic molecules for which only frequencies for the observed fundamentals are known.*

Molecule.	Frequencies.				Ref. (see below).
$B^{10}F_3$	888	719·5	1497(2)	482(2)	Anderson, Lassettre, and Yost
$B^{11}F_3$	888	691·3	1445·9(2)	480·4(2)	
$B^{10}Cl_3$ (l.)	471	471·5	989(2)	253(2)	
$B^{11}Cl_3$ (l.)	471	451	946(2)	253(2)	
$B^{10}Cl_3$ (g.)	471	483	996(2)	243(2)	
$B^{11}Cl_3$ (g.)	471	462	958(2)	243(2)	
$B^{10}Br_3$ (l.)	279	390	846(2)	151(2)	
$B^{11}Br_3$ (l.)	279	371·5	806(2)	151(2)	
$CO_3^{=}$	1087	878	1437(2)	714(2)	Urey and Greiff
$C^{13}O_3^{=}$	1087	850·56	1393·89(2)	712·81(2)	Calculated
$CO_3^{18=}$	1024·83	868·19	1415·87(2)	673·75(2)	Calculated, Hibben, p. 466
NH_4^+	3040	1725(2)	3142(3)	1411(3)	
$N^{15}H_4^+$	3040	1725(2)	3130·3(3)	1405·7(3)	Calculated, Rosenthal Herzberg, II, p. 164
NH_3	3337	950	3414(2)	1628(2)	
$N^{15}H_3$	3333·9	945·2	3403·9(2)	1625·1(2)	Calculated, Valence forces
$SO_4^{=}$	980	451·0(2)	1113·6(3)	618·9(3)	Urey and Greiff
$SO_4^{18=}$	924·0	425·2(2)	1081·9(3)	589·4(3)	Urey and Greiff
SO_2	1151	519	1361	—	Herzberg, II, p. 285
SO_2^{18}	1101·36	496·96	1317·07	—	Calculated
ClO_2	954	529	1105	—	Urey and Greiff
ClO_2^{18}	925·13	499·16	1070·18	—	Calculated, Valence forces
$Cl^{37}O_2$	949·29	524·72	1091·73	—	
ClO_4^-	935	462(2)	1102(3)	628(3)	Herzberg, II, p. 167
$Cl^{37}O_4^-$	935	462(2)	1085·31(3)	626·42(3)	Calculated, Valence forces
ClO_3^-	932	615	980(2)	480(2)	Kujemzelis
$Cl^{37}O_3^-$	917·80	614·67	971·20(2)	479·14(2)	Calculated, Valence forces
$Br^{79}O_3^-$	805	420	810(2)	358(2)	Kujemzelis
$Br^{81}O_3^-$	802·91	419·12	808·31(2)	357·75(2)	Calculated, Valence forces
$I^{127}O_3^-$	798	365	780(2)	323(2)	Kujemzelis
$I^{129}O_3^-$	797·20	364·58	779·33(2)	322·89(2)	Calculated, Valence forces

Herzberg, I; Herzberg, " Molecular Spectra and Molecular Structure," I, Diatomic Molecules, Prentice-Hall, Inc., New York, 1939.

Herzberg, II; Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co., Inc., New York, 1945.

Urey and Greiff, *loc. cit.*, ref. (12).

Libby, *J. Chem. Physics*, 1943, **11**, 101. The ϵ_1 and ϵ_2 are omitted in the anharmonicities of the waters.

Hibben, " The Raman Effect and Chemical Applications," Reinhold Publishing Corp., New York, 1939.

Anderson, Lassettre, and Yost, *J. Chem. Physics*, 1936, **4**, 703.

Rosenthal. *Physical Rev.*, 1934, **45**, 538.

Kujemzelis, *Z. Physik*, 1938, **109**, 586.

TABLE III.

*Ratios of Partition Functions for Hydrogen and Water Molecules.**

	Temp. ° K.				
Molecule pair.	273·1	298·1	400.	500.	600.
HD/H_2	7·6282	6·7366	4·7672	3·8941	3·4030
D_2/HD	2·4017	2·0704	1·3715	1·0752	0·9154
$(D_2/H_2)^{\frac{1}{2}}$	4·2803	3·7346	2·5570	2·0462	1·7650
HT/H_2	12·496	10·537	6·5542	4·9642	4·1258
T_2/HT	5·1548	4·1182	2·2041	1·5298	1·2003
$(T_2/H_2)^{\frac{1}{2}}$	8·0260	6·5873	3·8008	2·7558	2·2254
DT/D_2	3·6482	3·4426	2·9246	2·6652	2·5034
T^2/DT	0·9617	0·9020	0·7545	0·6799	0·6346
$(T^2/D_2)^{\frac{1}{2}}$	1·8731	1·7622	1·4855	1·3462	1·2605
HDO/H_2O	32·7400	24·9460	11·7240	7·5602	5·6614
D_2O/HDO	8·3185	6·3065	2·9282	1·8791	1·4044
$(D_2O/H_2O)^{\frac{1}{2}}$	16·503	12·543	5·8592	3·7689	2·8196
HTO/H_2O	95·507	65·266	22·681	12·281	8·2027
T_2O/HTO	28·575	19·085	6·2523	3·2871	2·1593
$(T_2O/H_2O)^{\frac{1}{2}}$	52·241	35·293	11·908	6·3535	4·1603
DTO/D_2O	5·9628	5·3294	3·9068	3·2674	2·9088
T_2O/DTO	1·6805	1·4857	1·0573	0·8696	0·7658
$(T_2O/D_2O)^{\frac{1}{2}}$	3·1656	2·8138	2·0324	1·6857	1·4925

* Rotation corrections were not made for any of the values for water listed in this table because the rotation constants for the mixed molecules are now known, and better values of the ratios are obtained if no corrections are made than if they are made for only some of the molecules.

TABLE IV.

Equilibrium Constants for Hydrogen and Water Exchange.

Equilibrium.	Temp., ° K.					
	0.	273·1.	298·1.	400.	500.	600.
$[HD]^2/[H_2][D_2]$	0	3·18	3·25	3·48	3·62	3·72
$[HDO]^2/[H_2O][D_2O]$	0	3·94	3·96	4·00	4·02	4·03
$[HDO][H_2]/[H_2O][HD]$	∞	4·29	3·70	2·46	1·94	1·66
$[D_2O][HD]/[HDO][D_2]$	∞	3·46	3·05	2·14	1·75	1·53
$[HT]^2/[H_2][T_2]$	0	2·42	2·56	2·97	3·24	3·44
$[HTO]^2/[H_2O][T_2O]$	0	3·34	3·42	3·63	3·74	3·80
$[HTO][H_2]/[H_2O][HT]$	∞	7·64	6·19	3·46	2·47	1·99
$[T_2O][HT]/HTO][T_2]$	∞	5·54	4·63	2·84	2·15	1·80
$[DT]^2/[D_2][T_2]$	0	3·79	3·82	3·88	3·92	3·94
$[DTO]^2/[D_2O][T_2O]$	0	3·55	3·59	3·70	3·76	3·80
$[DTO][D_2]/[D_2O][DT]$	∞	1·63	1·55	1·34	1·23	1·16
$[T_2O][DT]/[DTO][T_2]$	∞	1·75	1·65	1·40	1·28	1·21

TABLE V.

Hydrogen Exchange.

	$\left(\frac{D_2O}{H_2O}\right)^{\frac{1}{2}}$.	$\frac{DCl}{HCl}$.	$\frac{DBr}{HBr}$.	$\left(\frac{D_2}{H_2}\right)^{\frac{1}{2}}$.	$\frac{DI}{HI}$.	$\frac{LiD}{LiH}$.	$\frac{NaD}{NaH}$.	$\frac{KD}{KH}$.	T, ° K.
$\frac{Q_2}{Q_1}$	16·467	6·3726	5·1278	4·2803	4·0172	1·8604	1·6908	1·5047	273·1
	12·518	5·3059	4·3454	3·7346	3·4744	1·7287	1·5819	1·4248	298·1
	5·8504	3·1881	2·7445	2·5570	2·3236	1·4151	1·3271	1·2377	400
	3·7648	2·3695	2·1013	2·0462	1·8434	1·2700	1·2105	1·1524	500
	2·8222	1·9493	1·7652	1·7650	1·5873	1·1891	1·1463	1·1055	600
$\left(\frac{D_2O}{H_2O}\right)^{\frac{1}{2}}$		∞	∞	∞	∞	∞	∞	∞	0
	1·000	2·584	3·211	3·847	4·099	8·851	9·739	10·944	273·1
		2·359	2·881	3·352	3·603	7·241	7·913	8·786	298·1
		1·835	2·132	2·288	2·518	4·134	4·408	4·727	400
		1·589	1·792	1·840	2·042	2·964	3·110	3·267	500
		1·448	1·599	1·599	1·778	2·373	2·462	2·533	600
$\frac{DCl}{HCl}$			∞	∞	∞	∞	∞	∞	0
		1·000	1·243	1·489	1·586	3·425	3·769	4·235	273·1
			1·221	1·421	1·527	3·069	3·354	3·724	298·1
			1·162	1·247	1·372	2·253	2·403	2·576	400
			1·128	1·158	1·285	1·866	1·957	2·056	500
			1·104	1·104	1·228	1·639	1·701	1·763	600
$\frac{DBr}{HBr}$				∞	∞	∞	∞	∞	0
			1·000	1·198	1·276	2·756	3·033	3·408	273·1
				1·164	1·251	2·514	2·747	3·050	298·1
				1·073	1·181	1·939	2·068	2·217	400
				1·027	1·140	1·655	1·736	1·823	500
				1·000	1·112	1·484	1·540	1·597	600
$\left(\frac{D_2}{H_2}\right)^{\frac{1}{2}}$					0	∞	∞	∞	0
				1·000	1·065	2·301	2·532	2·845	273·1
					1·075	2·160	2·361	2·621	298·1
					1·100	1·807	1·927	2·066	400
					1·110	1·611	1·690	1·776	500
					1·112	1·484	1·540	1·597	600
$\frac{DI}{HI}$						∞	∞	∞	0
					1·000	2·159	2·376	2·670	273·1
						2·010	2·196	2·439	298·1
						1·642	1·751	1·877	400
						1·451	1·523	1·600	500
						1·335	1·385	1·436	600
$\frac{LiD}{LiH}$							∞	∞	0
						1·000	1·100	1·236	273·1
							1·093	1·213	298·
							1·066	1·143	400
							1·049	1·102	500
							1·038	1·076	600
$\frac{NaD}{NaH}$								∞	0
							1·000	1·124	273·1
								1·110	298·1
								1·072	400
								1·050	500
								1·038	600

cannot be calculated. For this reason such compounds as H_2CO, H_2S, H_2Se, H_2O_2, and C_2H_2 have not been included although calculations of such constants have been reported in the literature.

In Table II the substances are classified into two groups, those for which the spectroscopic data are very reliable and detailed, and those for which only more approximate data are known. The equilibrium constants which depend on this second class of data are less reliable than those which depend on the first class only. Formulæ used for the calculations of frequencies of the rarer and unobserved isotopic molecule can be made by well-known methods for diatomic molecules, but a choice of formula must be made in the case of polyatomic molecules. Footnotes to the table indicate the type of formula used in these calculations.

In Tables III—XIII are recorded the values of the ratios of partition functions and equilibrium constants for exchange reactions involving the isotopes of H, Li, B, C, N, O, Cl, Br, and I. At the top under a symbol for the substance are given the values for Q_2/Q_1, at five temperatures, and then the equilibrium constants for all possible exchanges between these substances with respect to a particular isotope. A value in the body of the table is the

TABLE VI.

Lithium Exchange.

	$\frac{\mathrm{Li^7D}}{\mathrm{Li^6D}}$.	$\frac{\mathrm{Li^7H}}{\mathrm{Li^6H}}$.	$\frac{\mathrm{Li^7}}{\mathrm{Li^6}}$.	T, ° K.
$\frac{Q_2}{Q_1}$	1·0334	1·0281	1·0000	273·1
	1·0292	1·0249	1·0000	298·1
	1·0181	1·0161	1·0000	400
	1·0123	1·0113	1·0000	500
	1·0089	1·0083	1·0000	600
		∞	∞	0
$\frac{\mathrm{Li^7D}}{\mathrm{Li^6D}}$	1·000	1·005	1·033	273·1
		1·004	1·029	298·1
		1·002	1·018	400
		1·001	1·012	500
		1·000$_5$	1·009	600
			∞	0
$\frac{\mathrm{Li^7H}}{\mathrm{Li^6H}}$		1·000	1·028	273·1
			1·025	298·1
			1·016	400
			1·011	500
			1·008	600

TABLE VII.

Boron Exchange.

	$\frac{\mathrm{B^{11}F_3}}{\mathrm{B^{10}F_3}}$.	$\frac{\mathrm{B^{11}Cl_3}\ (\mathrm{l.})}{\mathrm{B^{10}Cl_3}\ (\mathrm{l.})}$.	$\frac{\mathrm{B^{11}Cl_3}\ (\mathrm{g.})}{\mathrm{B^{10}Cl_3}\ (\mathrm{g.})}$.	$\frac{\mathrm{B^{11}Br_3}\ (\mathrm{l.})}{\mathrm{B^{10}Br_3}\ (\mathrm{l.})}$.	T, ° K.
$\frac{Q_2}{Q_1}$	1·2727	1·1739	1·1567	1·1441	273·1
	1·2374	1·1497	1·1350	1·1234	298·1
	1·1471	1·0891	1·0805	1·0724	400
	1·1005	1·0591	1·0536	1·0477	500
	1·0728	1·0420	1·0380	1·0336	600
		∞	∞	∞	0
$\frac{\mathrm{B^{11}F_3}}{\mathrm{B^{10}F_3}}$	1·000	1·084	1·100	1·112	273·1
		1·076	1·090	1·101	298·1
		1·053	1·062	1·076	400
		1·039	1·044	1·050	500
		1·030	1·033	1·038	600
			∞	∞	0
$\frac{\mathrm{B^{11}Cl_3}\ (\mathrm{l.})}{\mathrm{B^{10}Cl_3}\ (\mathrm{l.})}$		1·000	1·015	1·026	273·1
			1·013	1·023	298·1
			1·008	1·016	400
			1·005	1·011	500
			1·004	1·008	600
				0	0
$\frac{\mathrm{B^{11}Cl_3}\ (\mathrm{g.})}{\mathrm{B^{10}Cl_3}\ (\mathrm{g.})}$			1·000	1·011	273·1
				1·010	298·1
				1·008	400
				1·006	500
				1·004	600

TABLE VIII.

Carbon Exchange.

	$\frac{C^{13}O_3^{=}}{C^{12}O_3^{=}}$.	$\frac{C^{13}O_2}{C^{12}O_2}$.	$\frac{C^{13}}{C^{12}}$.*	$\frac{HC^{13}N}{HC^{12}N}$.	$\frac{C^{13}O}{C^{12}O}$.	$\frac{C^{13}N^-}{C^{12}N^-}$.	*T*, ° K.
$\frac{Q_2}{Q_1}$	1·2358	1·2169	1·2081	1·1358	1·1086	1·0980	273·1
	1·2057	1·1909	1·1786	1·1206	1·0970	1·0875	298·1
	1·1274	1·1233	1·1077	1·0802	1·0659	1·0589	400
	1·0870	1·0877	1·0722	1·0581	1·0479	1·0427	500
	1·0629	1·0656	1·0516	1·0441	1·0360	1·0323	600
		∞		∞	∞	∞	0
$\frac{C^{13}O_3^{=}}{C^{12}O_3^{=}}$	1·000	1·016	1·023	1·088	1·115	1·126	273·1
		1·012	1·023	1·076	1·099	1·109	298·1
		1·004	1·018	1·045	1·058	1·066	400
		$0{\cdot}999_4$	1·014	1·027	1·037	1·042	500
		$0{\cdot}997_5$	1·011	1·018	1·026	1·030	600
			0	∞	∞	∞	0
$\frac{C^{13}O_2}{C^{12}O_2}$		1·000	1·007	1·071	1·098	1·108	273·1
			1·010	1·063	1·086	1·095	298·1
			1·014	1·040	1·055	1·061	400
			1·014	1·028	1·038	1·043	500
			1·013	1·021	1·029	1·032	600
				∞	∞	∞	0
$\frac{C^{13}}{C^{12}}$			1·000	1·064	1·090	1·100	273·1
				1·052	1·074	1·084	298·1
				1·025	1·039	1·046	400
				1·013	1·023	1·028	500
				1·007	1·015	1·017	600
					∞	∞	0
$\frac{HC^{13}N}{HC^{12}N}$				1·000	1·025	1·034	273·1
					1·022	1·030	298·1
					1·013	1·020	400
					1·010	1·015	500
					1·008	1·011	600
						∞	0
$\frac{C^{13}O}{C^{12}O}$					1·000	1·010	273·1
						1·009	298·1
						1·007	400
						1·005	500
						1·004	600

* The partition function recorded here is for diamond. The Debye θ's have been taken as 1860 and 1787 for C^{12} and C^{13} respectively. The partition functions have been calculated using the equations given by Mayer and Mayer, "Statistical Mechanics," John Wiley and Sons, New York, 1940.

equilibrium constant at the temperature shown in the far right column between the molecules listed at the top of the column and at the left. If these constants are greater than unity the heavier isotope will concentrate preferentially in the compound listed at the left. The blank part of the table could be filled with the reciprocals of the numbers listed.

In the case of the hydrogen exchange reactions as listed in Table V, the constants recorded are only approximate when H_2, D_2, T_2, and H_2O, D_2O, and T_2O are involved, since the equilibrium constants involving the mixed molecules are not approximately equal to 4. It is necessary to calculate the partition functions for the mixed molecules. The ratios of these partition functions and equilibrium constants are listed in Tables III and IV. The symbol Q_{12} refers to the mixed molecules, and the values of Q_1 and Q_2 for the homogeneous molecules are the squares of those listed in the main tables.

The constants listed in Table IV in which either H_2, D_2 or H_2O, D_2O are involved will give the exact ratio of isotopes when the concentrations of H_2 and D_2 in the hydrogen gas are equal or when the concentrations of H_2O and D_2O are equal in the water vapour.

The equilibrium constants listed in Table VI for lithium are few in number and do not deviate from unity as much as one might expect for this light element. The maximum deviation from unity in the case of boron is 0·112 whereas for lithium this is 0·033. It seems probable that considerable fractionation would occur between the very stable compounds of lithium such as the oxide and fluoride and, say, the metal vapour, but these compounds do not lend themselves either to spectroscopic investigations or to experimental exchange reaction studies.

The boron exchanges are limited to the boron halides. Of particular interest is the predicted difference in vapour pressures of the isotopic boron chlorides. In other cases in which Raman

TABLE IX.

Nitrogen Exchange.

	$\frac{N^{15}H_4^+}{N^{14}H_4^+}$.	$\left(\frac{N_2^{15}}{N_2^{14}}\right)^{\frac{1}{2}}$.	$\frac{N^{15}H_3}{N^{14}H_3}$.	$\frac{N^{15}O}{N^{14}O}$.	$\frac{HCN^{15}}{HCN^{14}}$.	$\frac{CN^{-15}}{CN^{-14}}$.	T, ° K.
$\frac{Q_2}{Q_1}$	1·1184	1·0908	1·0768	$1{\cdot}073_8$	1·0736	1·0718	273·1
	1·1059	1·0814	1·0688	$1{\cdot}065_9$	1·0655	1·0641	298·1
	1·0721	1·0558	1·0472	$1{\cdot}044_0$	1·0439	1·0433	400
	1·0530	1·0410	1·0350	$1{\cdot}031_6$	1·0316	1·0315	500
	1·0409	1·0311	1·0271	$1{\cdot}023_8$	1·0238	1·0239	600
$\frac{N^{15}H_4^+}{N^{14}H_4^+}$		∞	∞	∞	∞	∞	0
	1·000	1·025	1·039	1·042	1·042	1·043	273·1
		1·023	1·035	1·038	1·038	1·039	298·1
		1·015	1·024	1·027	1·027	1·028	400
		1·012	1·017	1·021	1·021	1·021	500
		1·010	1·013	1·017	1·017	1·017	600
$\left(\frac{N_2^{15}}{N_2^{14}}\right)^{\frac{1}{2}}$			∞	∞	∞	∞	0
		1·000	1·013	1·016	1·016	1·018	273·1
			1·012	1·015	1·015	1·016	298·1
			1·008	1·011	1·011	1·012	400
			1·006	1·009	1·009	1·009	500
			1·004	1·007	1·007	1·007	600
$\frac{N^{15}H_3}{N^{14}H_3}$				∞	∞	∞	0
			1·000	1·003	1·003	1·005	273·1
				1·003	1·003	1·004	298·1
				1·003	1·003	1·004	400
				1·003	1·003	1·003	500
				1·003	1·003	1·003	600
$\frac{N^{15}O}{N^{14}O}$					∞	∞	0
				1·000	$1{\cdot}000_2$	1·002	273·1
					$1{\cdot}000_4$	1·002	298·1
					$1{\cdot}000_1$	1·001	400
					$1{\cdot}000_0$	1·000	500
					$1{\cdot}000_0$	1·000	600
$\frac{HCN^{15}}{HCN^{14}}$						∞	0
					1·000	1·002	273·1
						1·001	298·1
						1·001	400
						1·000	500
						1·000	600

frequencies for the liquid and gaseous states have been observed as well as in this, the frequencies are usually lower for the liquid state and this should result in a preferential concentration of the heavier isotope in the gas phase. This is not true in this case because of the larger observed isotopic shift of the ω_3 frequency in the liquid as compared with the gas. If this is in error for some reason not evident from the paper by Anderson, Lassettre, and Yost, the predicted difference in vapour pressures will be incorrect, and in fact may be so because of the application of gaseous partition functions to the liquid state.

The equilibrium constants for chlorine exchange reactions are surprisingly large. This is due to the increased number of vibrational degrees of freedom as the number of oxygen atoms combined with the chlorine atom increases, and the approximate constancy of the vibrational frequencies of all the oxygen compounds of chlorine. Similar effects should occur in the case of the sulphur isotopes, and in fact the experimental values for their fractionation between sulphur dioxide and bisulphite ion are close to the corresponding value for the chlorine isotopes.*

The tables for chlorine, bromine, and iodine show the trend of these equilibrium constants with atomic weight for constant difference of atomic weight. The exchange constants for ClO_3^-, BrO_3^-, and IO_3^- and their corresponding elements at 298·1° are 1·040, 1·007, and 1·003, respectively. It is evident that these chemical differences decrease rapidly with atomic weight though there is considerable irregularity in many cases, as for example in the calculated values for lithium and those for chlorine. The iodine example using I^{129} has been included for the purpose of comparison.

The values of the equilibrium constants at 0° K. are either 0 or ∞ and depend on the zero point energies only. When the equilibrium constants are nearly unity at higher temperatures

---

* That such large fractionation factors should exist was first called to my attention by Dr. Duane Vier, who made the calculation for the chlorine dioxide–chlorine exchange.

TABLE X.

Oxygen Exchange.

	$\left(\frac{CO_2^{18}}{CO_2^{16}}\right)^{\frac{1}{2}}$	$\frac{CO^{18}}{CO^{16}}$	$\left(\frac{CO_3^{18=}}{CO_3^{16=}}\right)^{\frac{1}{3}}$	$\left(\frac{SO_4^{18=}}{SO_4^{16=}}\right)^{\frac{1}{4}}$	$\left(\frac{SO_2^{18}}{SO_2^{16}}\right)^{\frac{1}{2}}$	$\frac{D_2O^{18}}{D_2O^{16}}$	$\left(\frac{O_2^{18}}{O_2^{16}}\right)^{\frac{1}{2}}$	$\frac{H_2O^{18}}{H_2O^{16}}$	$\left(\frac{ClO_2^{18}}{ClO_2^{16}}\right)^{\frac{1}{2}}$	T, ° K.
$\frac{Q_2}{Q_1}$	1·1331	1·1181	1·1090	1·1073	1·1017	1·0974	1·0923	1·0741	1·0717	273·1
	1·1172	1·1053	1·0945	1·0924	1·0888	1·0872	1·0818	1·0667	1·0621	298·1
	1·0750	1·0714	1·0576	1·0557	1·0551	1·0594	1·0533	1·0465	1·0375	400
	1·0525	1·0518	1·0388	1·0370	1·0376	1·0437	1·0374	1·0350	1·0251	500
	1·0387	1·0390	1·0279	1·0261	1·0271	1·0336	1·0274	1·0275	1·0179	600
		∞	∞	0	∞	∞	∞	∞	∞	0
$\left(\frac{CO_2^{18}}{CO_2^{16}}\right)^{\frac{1}{2}}$	1·000	1·013	1·022	1·023	1·029	1·033	1·037	1·055	1·057	273·1
		1·011	1·021	1·023	1·026	1·028	1·033	1·047	1·052	298·1
		1·003	1·016	1·018	1·020	1·015	1·021	1·027	1·036	400
		1·000$_7$	1·013	1·015	1·014	1·008	1·016	1·017	1·027	500
		0·999$_7$	1·011	1·012	1·011	1·005	1·011	1·011	1·020	600
			0	0	0	∞	∞	∞	∞	0
$\frac{CO^{18}}{CO^{16}}$		1·000	1·008	1·010	1·015	1·019	1·024	1·041	1·043	273·1
			1·010	1·012	1·015	1·017	1·022	1·036	1·041	298·1
			1·013	1·015	1·015	1·011	1·017	1·024	1·033	400
			1·014	1·014	1·014	1·008	1·014	1·016	1·026	500
			1·011	1·013	1·012	1·005	1·011	1·011	1·021	600
				0	∞	∞	∞	∞	∞	0
$\left(\frac{CO_3^{18=}}{CO_3^{16=}}\right)^{\frac{1}{3}}$			1·000	1·002	1·007	1·011	1·015	1·033	1·035	273·1
				1·002	1·005	1·007	1·012	1·026	1·031	298·1
				1·002	1·002	0·998	1·004	1·011	1·019	400
				1·002	1·001	0·995	1·001	1·004	1·013	500
				1·002	1·001	0·994	1·000	1·000$_4$	1·010	600
					∞	∞	∞	∞	∞	0
$\left(\frac{SO_4^{18=}}{SO_4^{16=}}\right)^{\frac{1}{4}}$				1·000	1·005	1·009	1·014	1·031	1·033	273·1
					1·003	1·005	1·010	1·024	1·029	298·1
					1·001	0·997	1·002	1·009	1·018	400
					0·999	0·994	0·999$_6$	1·003	1·012	500
					0·999	0·993	0·999	0·999	1·008	600
						∞	∞	∞	∞	0
$\left(\frac{SO_2^{18}}{SO_2^{16}}\right)^{\frac{1}{2}}$					1·000	1·004	1·007	1·026	1·028	273·1
						1·001	1·006	1·021	1·025	298·1
						0·996	1·003	1·008	1·017	400
						0·994	1·000	1·003	1·012	500
						0·994	0·999$_7$	0·999$_6$	1·009	600
							0	∞	∞	0
$\frac{D_2O^{18}}{D_2O^{16}}$						1·000	1·005	1·022	1·024	273·1
							1·005	1·019	1·024	298·1
							1·006	1·013	1·021	400
							1·006	1·008	1·018	500
							1·006	1·006	1·015	600
								∞	∞	0
$\left(\frac{O_2^{18}}{O_2^{16}}\right)^{\frac{1}{2}}$							1·000	1·017	1·019	273·1
								1·014	1·019	298·1
								1·006	1·015	400
								1·002	1·012	500
								0·999$_9$	1·009	600
									0	0
$\frac{H_2O^{18}}{H_2O^{16}}$								1·000	1·002	273·1
									1·004	298·1
									1·009	400
									1·010	500
									1·009	600

these values for 0° K. may easily be in error since a small error in estimating the zero point energy could change these from 0 to ∞ or the reverse.

Experimental Confirmation of the Calculations.

Of the many equilibrium constants calculated, only a few have been checked by experiment. Most of these cannot be confirmed because no method of establishing equilibrium is possible owing to the slowness with which equilibrium is established or because chemical reactions occur between the chemical compounds involved. The equilibrium between H_2, I_2, and HI was compared by Urey and Rittenberg[24] with that between D_2, I_2, and DI and the ratio of

Table XI.

Chlorine Exchange.

	$\frac{Cl^{37}O_4^-}{Cl^{35}O_4^-}$.	$\frac{Cl^{37}O_3^-}{Cl^{35}O_3^-}$.	$\frac{Cl^{37}O_2}{Cl^{35}O_2}$.	$\left(\frac{Cl_2^{37}}{Cl_2^{35}}\right)^{\frac{1}{2}}$.	$\frac{HCl^{37}}{HCl^{35}}$.	T, ° K.
$\frac{Q_2}{Q_1}$	1·0972	1·0551	1·0360	1·0086	1·0050	273·1
	1·0847	1·0478	1·0313	1·0074	1·0046	298·1
	1·0521	1·0291	1·0185	1·0043	1·0032	400
	1·0353	1·0196	1·0130	1·0028	1·0024	500
	1·0253	1·0140	1·0094	1·0019	1·0019	600
		∞	∞	∞	∞	0
$\frac{Cl^{37}O_4^-}{Cl^{35}O_4^-}$	1·000	1·040	1·059	1·088	1·092	273·1
		1·035	1·052	1·077	1·080	298·1
		1·022	1·033	1·048	1·049	400
		1·015	1·022	1·032	1·033	500
		1·011	1·016	1·023	1·023	600
			∞	∞	∞	0
$\frac{Cl^{37}O_3^-}{Cl^{35}O_3^-}$		1·000	1·018	1·046	1·050	273·1
			1·016	1·040	1·043	298·1
			1·010	1·025	1·026	400
			1·007	1·017	1·017	500
			1·005	1·012	1·012	600
				∞	∞	0
$\frac{Cl^{37}O_2}{Cl^{35}O_2}$			1·000	1·027	1·031	273·1
				1·024	1·027	298·1
				1·014	1·015	400
				1·010	1·010	500
				1·007	1·007	600
					∞	0
$\left(\frac{Cl_2^{37}}{Cl_2^{35}}\right)^{\frac{1}{2}}$				1·000	1·004	273·1
					1·003	298·1
					1·001	400
					$1{\cdot}000_4$	500
					$1{\cdot}000_0$	600

Table XII.

Bromine Exchange.

	$\frac{Br^{81}O_3^-}{Br^{79}O_3^-}$.	$\left(\frac{Br_2^{81}}{Br_2^{79}}\right)^{\frac{1}{2}}$.	$\frac{HBr^{81}}{HBr^{79}}$.	T, ° K.
$\frac{Q_2}{Q_1}$	1·0093	1·0014	1·0009	273·1
	1·0080	1·0012	1·0008	298·1
	1·0048	1·0007	1·0006	400
	1·0032	1·0004	1·0004	500
	1·0022	1·0003	1·0003	600
		∞	∞	0
$\frac{Br^{81}O_3^-}{Br^{79}O_3^-}$	1·000	1·008	1·008	273·1
		1·007	1·007	298·1
		1·004	1·003	400
		1·003	1·003	500
		1·002	1·002	600
			∞	0
$\left(\frac{Br_2^{81}}{Br_2^{79}}\right)^{\frac{1}{2}}$		1·000	$1{\cdot}000_5$	273·1
			$1{\cdot}000_4$	298·1
			$1{\cdot}000_1$	400
			$1{\cdot}000_0$	500
			$1{\cdot}000_0$	600

Table XIII.

Iodine Exchange.

	$\frac{I^{129}O_3^-}{I^{127}O_3^-}$.	$\left(\frac{I_2^{129}}{I_2^{127}}\right)^{\frac{1}{2}}$.	T, ° K.
$\frac{Q_2}{Q_1}$	1·0031	1·0003	298·1
		∞	0
$\frac{I^{129}O_3^-}{I^{127}O_3^-}$	1·0000	$1{\cdot}002_8$	298·1

equilibrium constants agreed with those calculated for the exchange reaction. Several authors [25] have investigated the equilibrium between H_2, HD, H_2O, and HDO and given several values which are in rough agreement with the calculated results. Libby [26] has calculated the equilibrium constants for the hydrogen–water exchanges with respect to protium, deuterium, and tritium, and he and Taylor and Black have checked these calculations for the protium–tritium exchange with excellent agreement. The equilibrium constants given here differ slightly from Libby's owing to the inclusion of rotational corrections in some cases and to small errors made by Libby (see corrections in forthcoming issue of the *J. Chem. Physics*). The present calculations still do not include the rotational corrections for the water molecules and they also neglect small corrections for the anharmonicities. They agree better with experiment than do Libby's. Calculations were made by using anharmonic terms calculated by the Dennison and Darling rule and slightly better agreement with experiment was secured. Since there is a consistent difference between calculated and the experimental values, there is probably a systematic error present. On the theoretical side, this may be due to errors in the anharmonic terms or to electronic isotope effects, though both of these should lead to a constant percentage error with temperature and not a constant difference which appears to be the case. Since the equilibrium constants for the hydrogen exchange reactions must include all corrections discussed in this paper, exact calculations cannot be made without a full knowledge of the structure of the molecules, and for this reason exact agreement between calculated and observed values cannot be expected for many feasible reactions.

These reactions, as well as others that have been studied, are listed in Table XIV. All the reactions involving other isotopes than those of hydrogen are two-phase reactions and, except for the first for which the relative vapour pressures are known, exact agreement cannot be expected. Reasonably satisfactory agreement is secured, and in the case of those reactions for which spectroscopic data are lacking, fractionation of the isotopes of the correct order of magnitude is observed. Some of the observed values are derived from isotope separation

TABLE XIV.

Reaction.	T, ° K.	α (exp.).	α (calc.).	Ref.
$\frac{1}{2}CO_2^{16} + H_2O^{18}$ (liq.) $= \frac{1}{2}CO_2^{18} + H_2O^{16}$ (liq.)	273·1	1·046	1·044	(1)
$N^{15}H_3 + N^{14}H_4^+ = N^{14}H_3 + N^{15}H_4^+$	298·1	1·034 ± 0·002	1·035	(2)
$N^{15}H_3 + N^{14}H_3$ (aq.) $= N^{14}H_3 + N^{15}H_3$ (aq.)	298·1	1·006 ± 0·002	—	(2)
$HC^{12}N + C^{13}N^- = HC^{13}N + C^{12}N^-$	295*	Near 1·026	1·030	(3)
$HCN^{14} + CN^{15-} = HCN^{15} + CN^{14-}$	295 *	Slightly < 1	1·002	(4)
$C^{12}O_3^{=} + C^{13}O_2 = C^{13}O_3^{=} + C^{12}O_2$	273·1 ?	1·017	1·016	(5)
$\frac{1}{3}CO_3^{16=} + H_2O^{18} = \frac{1}{3}CO_3^{18=} + H_2O^{16}$	273·1 ?	1·036	1·033	(6)
$HC^{12}O_3^- + C^{13}O_2 = HC^{13}O_3^- + C^{12}O_2$	298 *	> 1·014	—	(7)
$S^{34}O_2 + HS^{32}O_3^- = S^{32}O_2 + HS^{34}O_3^-$	298·1	1·019 ± 0·002	—	(2)
$S^{36}O_2 + HS^{32}O_3^- = S^{32}O_2 + HS^{36}O_3^-$	298·1	1·043 ± 0·004	—	(2)
$Li^7Z + Li^{6+} = Li^6Z + Li^{7+}$	295 *	1·022	—	(8)
Li^7 (amal.) $+ Li^6Cl = Li^6$ (amal.) $+ Li^7Cl$	295 *	1·025	—	(9)
$HD + H_2O = HDO + H_2$	293	3·2	3·81	(10)
$HD + H_2O = HDO + H_2$	800	1·28	1·36	(11)
$HT + H_2O = HTO + H_2$	273·1	7·74	7·64	(12)
,, ,,	298·1	6·26	6·19	(12)
,, ,,	400	3·52	3·46	(12)
,, ,,	500	2·55	2·47	(12)
,, ,,	600	2·08	1·99	(12)

* These temperatures are assumed to be 72° F., *i.e.*, the usual room temperature in the U.S.

(1) Weber, Wahl, and Urey, *J. Chem. Physics*, 1935, **3**, 129.
(2) Thode, Graham, and Ziegler, *Canadian J. Res.*, 1945, **23** *B*, 40; Kirschenbaum and others, in the press. The latter authors have extrapolated the values of Thode *et al.* to zero concentration of NH_3 in the solution. The constant 1·006 is the average of those reported by these authors.
(3) Cohen, *J. Chem. Physics*, 1940, **8**, 588.
(4) Hutchison, Stewart, and Urey, *ibid.*, p. 532.
(5) Nier and Gulbransen, *J. Amer. Chem. Soc.*, 1939, **61**, 697; Murphey and Nier, *Physical Rev.*, 1941, **59**, 771.
(6) Dole and Slobod, *J. Amer. Chem. Soc.*, 1940, **62**, 471.
(7) Urey, Aten, junr., and Keston, *J. Chem. Physics*, 1936, **4**, 622.
(8) Taylor and Urey, *ibid.*, 1938, **6**, 429.
(9) Lewis and MacDonald, *J. Amer. Chem. Soc.*, 1936, **58**, 2519.
(10) Bonhoeffer, *Z. Elektrochem.*, 1934, **40**, 469.
(11) Crist and Dalin, *J. Chem. Physics*, 1934, **3**, 735.
(12) Black and Taylor (*loc. cit.*) give a formula covering data between 16° C. and 302·9° C. from which the "experimental" data of the table have been calculated. They estimate their probable errors as ±0·02 to ±0·12 and thus theory and experiment are in agreement within these limits.

experiments under conditions which must give results lower than the true values. It is seen that good agreement is secured. The results of Thode and his co-workers are based on very careful work.

Vapour Pressures of Isotopic Compounds.

The ratios of vapour pressures of hydrogen and deuterium and their compounds have been extensively studied.[27] Similar differences in vapour pressures in the case of isotopic molecules of other elements exist, though the differences are much smaller than in the case of protium and deuterium compounds. Such differences have been determined in only a few cases and are recorded in Table XV together with those for protium and deuterium oxide and the protium and deuterium ammonias for comparison. In the last column are given the temperatures at which the vapour pressures are equal. These are calculated from the formulæ in all cases except for H_2O and D_2O. This " crossing-over phenomenon " seems to be a regular feature of all such ratios of vapour pressures. Bernal and Tamm [28] have assumed that a frequency of libration of the water molecule in ice of 477 cm.$^{-1}$ exists and that this accounts for the differences in vapour pressures of H_2O and D_2O. However, it does not account for the " crossing-over phenomenon " and it seems clear that much more extensive theories to account for the ratio of vapour-pressure curve are required. It is interesting to note that this same " crossing-over phenomenon " exists for some exchange reactions as mentioned before, and that it can be calculated in these cases though no obvious similar method can be applied to the vapour pressures.

The vapour pressures of N_2^{14} and N_2^{15} suggest the possibility of an excellent separation method for the oxygen isotopes. Since carbon monoxide and nitrogen have such similar physical properties, similar differences in vapour pressure might be expected between $C^{12}O^{16}$ and $C^{12}O^{18}$ for which a difference of two atomic weight units exists as in the case of the nitrogens. If a difference of 1% in vapour pressures exists, distillation of carbon monoxide should furnish the most effective method for the separation of these isotopes and at the same time increase the concentration of the carbon isotope to some extent.

Also, if the predicted difference in vapour pressures of $B^{10}Cl_3$ and $B^{11}Cl_3$ can be confirmed, the distillation of boron chloride should be a most effective method for separating the isotopes of boron.

TABLE XV.

$$\log_{10}\frac{p_1}{p_2} = \frac{a}{T} + b.$$

Compounds.	a.	b.	Δ^2H.	$\Delta T.P.$	$\frac{p_1}{p_2}$ (b.p.).	$T(p_1 = p_2)$.	Ref.
N_2^{14},N_2^{15} (liq.)	0·7230	−0·005822	3·33	0·058	1·0081	124°	(1)
$N^{14}H_3,N^{15}H_3$ (liq.) ...	1·3665	−0·004622	6·25	0·188	1·00246	298	(2)
NH_3,ND_3 (liq.)	46·25	−0·14003	216	3·11	1·110	330·3	(1)
NH_3,ND_3 (sol.)	49·69	−0·1305	227·5	3·11	—	—	(1)
H_2O^{16},H_2O^{18} (liq.) ...	2·74	−0·0056	13	—	1·0046	490	(3)
H_2O,D_2O (liq.)	†	†	406 *	3·8	1·051	497 (obs.)	(4)

* Value at the triple point according to Riesenfeld and Chang.

† Miles and Menzies give the following equation for the ratio of vapour pressures :

$$\log\frac{p_1}{p_2} = \frac{268·8426}{T} - 16·998671 + 7·49716 \log T - 9·7611 \times 10^{-3}T + 4·4288 \times 10^{-6}T^2.$$

(1) Kirschenbaum and Urey, *J. Chem. Physics*, 1942, **10**, 706.
(2) Thode, *J. Amer. Chem. Soc.*, 1940, **62**, 1581.
(3) Riesenfeld and Chang, *Z. physikal Chem.*, 1936, *B*, **33**, 127.
(4) *Idem, ibid.*, p. 120; Miles and Menzies, *J. Amer. Chem. Soc.*, 1936, **58**, 1068.

In many cases the equilibrium constants of exchange reactions involving liquid water rather than gaseous water are desired. The equilibrium constants of Table V and Table X involving water must be increased in the horizonal rows and decreased in the vertical columns in the ratio of the vapour pressures of H_2O^{16} and H_2O^{18} or the square root of the ratio of H_2O and D_2O in order to secure the constants for liquid water. These ratios at temperatures (K.) 273·1°, 298·1°, and 400° are for H_2O^{16} and H_2O^{18}, 1·011, 1·008 and 1·003, and for H_2O and D_2O, 1·102, 1·074, and 1·017, respectively.

The Geological Abundances of the Carbon and Oxygen Isotopes.

Dole and Nier and their co-workers have determined the ratio of the oxygen and carbon isotopes in various geological deposits. The carbonates are of particular interest in connection with the calculations presented here. It is not possible to calculate the Q_2/Q_1 values for the carbon and oxygen isotopes in the carbonates with certainty, for the formulæ for the vibration frequencies using a quadratic formula for the potential energy[29] require five constants for the determination of four frequencies and none of the central force or valence force formulæ gives satisfactory results since the force constants calculated from the observed frequencies are complex. Even if satisfactory agreement were secured, there would be no certainty that the isotopic shifts in frequencies calculated would be correct, as is also true in other cases. In view of this difficulty, another approach to the problem has been used.[30]

The experimental facts are briefly that O^{18} is more abundant in limestones than in water by a factor of 1·035, and C^{13} is also more abundant in carbonates of all geological ages including the present than in atmospheric carbon dioxide, by a factor of 1·013 to 1·022, as shown by Nier. There is a slight disagreement between the results of Nier and Gulbransen and of Murphy and Nier.[31]

No satisfactory calculation of the constants for the exchange constants for the reactions

$$\tfrac{1}{2}C^{13}O_2 + \tfrac{1}{3}C^{12}O_3^{=} = \tfrac{1}{2}C^{12}O_2 + \tfrac{1}{3}C^{13}O_3^{=} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$H_2O^{18} + \tfrac{1}{3}CO_3{}^{16=} = H_2O^{16} + \tfrac{1}{3}CO_3{}^{18=} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

can be made, but it is possible to ask whether the two observed values are consistent with each other. There is no difficulty in calculating the isotopic shifts for frequencies ν_1 (symmetrical vibrations of the oxygen atoms in the plane of the molecule) and ν_2 (vibration perpendicular to the plane of the molecule), but the doubly degenerate frequencies ν_3 and ν_4 cannot be calculated since three constants are required in the potential-energy functions.

Rosenthal shows that the formula for the frequencies ν_3 and ν_4 is

$$m^2\lambda^2 - m\lambda\,(\tfrac{1}{3}\,A/\mu + D) + (1/\mu)\,(AD - E^2) = 0 \quad . \quad . \quad . \quad . \quad (16)$$

where the roots of this equation, λ_3 and λ_4, are $4\pi^2\nu_3{}^2$ and $4\pi^2\nu_4{}^2$; m is the mass of the oxygen atom and $\mu = M/(M + 3m)$, M being the mass of the carbon atom. Solving for λ_3 and λ_4 and forming

$$\frac{\partial \ln \lambda_3}{\partial M},\ \frac{\partial \ln \lambda_4}{\partial M},\ \frac{\partial \ln \lambda_3}{\partial m}\ \text{and}\ \frac{\partial \ln \lambda_4}{\partial m},$$

it is easily possible to eliminate all force constants between the expressions

$$\frac{\partial \ln \lambda_3}{\partial M}\ \text{and}\ \frac{\partial \ln \lambda_4}{\partial m}\ \text{and between}\ \frac{\partial \ln \lambda_4}{\partial M}\ \text{and}\ \frac{\partial \ln \lambda_4}{\partial m}.$$

Then, replacing $\dfrac{\partial \ln \lambda_3}{\partial M}$, etc., by the approximate values $\dfrac{\Delta\lambda_3}{\Delta M\lambda_3}$, etc., the following relations are secured :

$$-\left(\frac{\Delta\nu_3}{\nu_3}\right)_0 = \frac{\Delta m}{2m} + \frac{M\Delta m}{m\Delta M}\left(\frac{\Delta\nu_3}{\nu_3}\right)_C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and

$$-\left(\frac{\Delta\nu_4}{\nu_4}\right)_0 = \frac{\Delta m}{2m} + \frac{M\Delta m}{m\Delta M}\left(\frac{\Delta\nu_4}{\nu_4}\right)_C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where the $\Delta\nu$'s are negative quantities when the Δm and ΔM are positive.[31a] By using the last term of equation (16) and noting that it is $m^2\lambda_3\lambda_4$, we get,

$$\ln \lambda_3\lambda_4 = -\,2 \ln m + \ln (M + 3m) - \ln M + \ln (AD - E^2)$$

By expanding the right-hand side of this equation in terms of Δm or ΔM and substituting numerical values for m and M, we secure

$$\left(\frac{\Delta\nu_3}{\nu_3}\right)_0 + \left(\frac{\Delta\nu_4}{\nu_4}\right)_0 = -\,0{\cdot}0703 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and

$$\left(\frac{\Delta\nu_3}{\nu_3}\right)_C + \left(\frac{\Delta\nu_4}{\nu_4}\right)_C = -\,0{\cdot}031667 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Urey and Greiff used frequencies calculated by Dr. Rosenthal for $C^{13}O_3^{=}$ and these frequencies agree with the requirement of equation (20). It is possible to choose values for $\left(\dfrac{\Delta\nu_3}{\nu_3}\right)_C$ and $\left(\dfrac{\Delta\nu_4}{\nu_4}\right)_C$ consistent with equation (20) and then calculate values for $\left(\dfrac{\Delta\nu_3}{\nu_3}\right)_0$ and $\left(\dfrac{\Delta\nu_4}{\nu_4}\right)_0$. From these quantities we can now calculate the Q_2/Q_1 values and from them and the values of Q_2/Q_1

for H_2O^{18}–H_2O^{16}, and CO_2^{18}–CO_2^{18} the equilibrium constants for the reactions (14) and (15). Table XVI gives the results of such a calculation for three arbitrary choices of $\left(\frac{\Delta\nu_3}{\nu_3}\right)_C$, the one choice 0·03109 being that secured by Rosenthal, and for two temperatures 273·1° K. and 298·1° K.

TABLE XVI.

$\left(\frac{\Delta\nu_3}{\nu_3}\right)_C$	0·03107	0·030	0·0285	$\left(\frac{Q_2}{Q_1}\right)_C$ (273·1)	1·2406	1·2358	1·2291
$\left(\frac{\Delta\nu_4}{\nu_4}\right)_C$	0·000576	0·001667	0·003167	$\left(\frac{Q_2}{Q_1}\right)_0$ (273·1)	1·1068	1·1090	1·1120
$\left(\frac{\Delta\nu_3}{\nu_3}\right)_0$	0·013103	0·014707	0·016912	$\left(\frac{Q_2}{Q_1}\right)_C$ (298·1)	1·2097	1·2057	1·1997
$\left(\frac{\Delta\nu_4}{\nu_4}\right)_C$	0·057976	0·056374	0·054168	$\left(\frac{Q_2}{Q_1}\right)_0$ (298·1)	1·0928	1·0947	1·0979
$(\Delta\nu_3)_C$	44·68	43·11	40·95	K_C (273·1) ...	1·0195	1·0156	1·0101
$(\Delta\nu_4)_C$	0·41	1·19	2·26	K_C (298·1) ...	1·0158	1·0123	1·0073
$(\Delta\nu_3)_0$	18·83	21·13	24·30	K_0 (273·1) ...	1·0304	1·0325	1·0353
$(\Delta\nu_4)_0$	41·40	40·25	38·68	K_0 (298·1) ...	1·0245	1·0261	1·0288

Dole's value for the difference in density of water from the tap at Northwestern University and water prepared from carbon dioxide from Grenville limestone is 7·9 p.p.m. or a ratio of isotopes of 1·0356 greater than his standard water. If we assume that fresh water has the same composition as water vapour from the oceans, then this is directly the ratio which we have calculated. This assumption seems to be in as close accord with experimental determination of the differences in density between ocean water and fresh water as any other. Nier's values for the enrichment of C^{13} in carbonates range from 1·013 to 1·021. We will take 1·0175 as a reasonable value. Then the calculations of Table XVI for 0° C. indicate that the values for $(\Delta\nu_3/\nu_3)_C = 0·030$ are best, but both are lower than the experimental values. Also, the values calculated at 25° C. are lower, but also $(\Delta\nu_3/\nu_3)_C = 0·030$ gives the best fit to the data. Hence this value is chosen as the best fit with experiment and all Q_2/Q_1 ratios of Tables VIII and X are made on this basis.

The discrepancy between the calculated and the observed values is not surprising in view of the neglect of anharmonic terms, and the application of partition functions for gaseous substances to the solid state. It seems unnecessary at present to suggest other explanations for the disagreement. It may be noted that the organisms which lay down carbonate use oxygen for their metabolic processes which contains more O^{18} than would be in equilibrium with water, but according to present beliefs in regard to biological oxidation the oxygen of the carbon dioxide produced comes from the water and, hence, no increase in O^{18} content should come from this source.

These calculations suggest investigations of particular interest to geology. A change from 0° C. to 25° C. should change the O^{18} content of carbonate by 1·004 relative to liquid water and the C^{13} content by 1·003. Accurate determinations of the O^{18} content of carbonate rocks could be used to determine the temperature at which they were formed. Since the relative abundances of isotopes have been determined by Dole with a probable error of less than 0·002 and Thode has made mass-spectrometric measurements with the same probable error, it is possible to determine such a temperature within 12° C. Nier has developed a mass spectrometer which will determine these ratios with an error of ± 0·001 and very probably less, and thus an error in temperature of only 6° C. or less is possible. This would be a very satisfactory error in temperature considering the times to which they may refer. At higher temperatures the coefficient becomes smaller, but still it may be possible to determine temperatures with sufficient precision to supply valuable data on a very difficult problem.

There are many questions which arise in regard to this suggestion in addition to whether animals lay down carbonates in equilibrium with water. It is not certain that the carbonates once deposited do not exchange their oxygen with ground water at a temperature different from the original or of isotopic composition different from that of sea water. Diffusion processes in carbonate rocks must be slow but the carbonates may be porous and finely divided. Such questions are all subject to experimental investigation, as is also the experimental determination of the true temperature coefficient. Even the present calculation and experimental observations indicate that the earth's temperature has not changed greatly in the last odd billion years. Also, the O^{18} content of carbonates deposited in fresh water should be less than that deposited in sea water and might be used to distinguish fresh and salt-water deposits.[32] The use of the C^{13} content of rocks would be more difficult because of the smaller enrichment and also because the geological history of carbon must be far more complex than that of oxygen. While the oxygen of the oceans constitutes a very large reservoir for the deposition of carbonate and hence has not changed its isotopic composition with time, carbon is a much rarer element and the carbon dioxide of the air and the ocean is part of the complex biochemical carbon cycle of Nature. However, the abundance of C^{13} in the rocks, if sufficiently accurately determined, might give additional data on the amount of carbon dioxide in the air during past epochs, particularly if combined with accurate temperature determinations by the use of the O^{18} content of the carbonates.

The oxygen isotopic abundances seem to be best suited for the determination of temperatures. First, there is the large reservoir of oxygen in the oceans which cannot have changed in isotopic concentrations during geological times. Secondly, the ideal isotopic solutions both solid and liquid make possible continuous variations of composition with temperatures. Thirdly, it is possible to determine deviations in isotopic abundances with considerable precision. Fourthly, oxygen forms relatively stable compounds which might be expected to remain unchanged for long periods of time. Ordinary chemical equilibria do not meet these conditions. The hydrogen compounds fail with respect to the third and the fourth point. Other elements fail with respect to the first and, hence, are not suitable. Calcium is widely distributed in Nature but fails with respect to the first point.

Dole has studied the relative abundances of the oxygen isotopes in iron ores and finds but a slight difference between them and the abundances in fresh water. A determination of the relative abundances in freshly deposited iron oxide and a comparison of these with geological deposits might give information in regard to the conditions under which such deposits were laid down.

Other oxygen compounds besides carbonates and iron oxides are available for similar studies. The exchange between sulphate and water shows a similar temperature coefficient to that between carbonate and water, and similar coefficients for the phosphate and water and the silica and water exchanges are to be expected. These last two are particularly interesting because animals and plants deposit both of these substances and also since silica has been deposited inorganically from solutions. In some cases connate water has been preserved, thus supplying both phases for investigation.

Nier and his co-workers have found that C^{13} is rarer in carbon derived from plants than it is in carbon dioxide of the air or carbon from the carbonate rocks. Such variations must result from biochemical processes which are far more complex than those considered here, and it seems that they are probably not due to thermodynamic equilibria alone but rather to differences in the kinetics of such processes. Nevertheless, the variation of kinetic processes with temperature may also result in different abundances of the isotopes. It seems probable that plant carbon compounds synthesised at different temperatures may contain varying amounts of C^{13}. Again, this possibility is subject to experimental investigation. It would be interesting indeed to know not only the mean temperature but also the variations of temperature on an ancient beach or in the forests where coal was deposited and whether a prehistoric animal had warm blood or not. However, too much optimism is not justified, for all the thermometers may be destroyed.

The values of $(\Delta\nu_3 + \Delta\nu_4)$ for the carbon isotopes can vary from 45·5 to 22·6, and for the oxygen isotopes from 59·6 to 93·3, and hence wide variations of equilibrium constants may be secured all consistent with the general equation, and since our choice of $(\Delta\nu_3/\nu_3)_C$ is near the maximum and $(\Delta\nu_4/\nu_4)_C$ is near the minimum value, it may be that similar extreme cases may occur in the case of other molecules. Hence, all calculations of this kind in which less independent force constants are used to calculate the frequencies than the number required for the potential-energy function using all quadratic terms may be in error by substantial amounts. This statement applies to all polyatomic molecules considered except CO_2, HCN, NH_4^+, and H_2O, for which all constants are known.

The Relative Abundances of the Oxygen Isotopes in Air and Water.

Extensive studies in regard to the relative abundances of the oxygen isotopes in the oxygen of the air and natural waters of the earth have been reported. Dole [33] first reported that water made from oxygen of the air was more dense than fresh water by 6·6 parts per million. This difference has been confirmed by other workers.[34] There is some disagreement in regard to the difference in density of fresh water and sea water due to the O^{18} content, but the values reported indicate about 2 parts per million, which is in reasonable agreement with the relative vapour pressures of H_2O^{16} and H_2O^{18}, assuming that fresh water is less dense because it results from evaporation of sea water. Again, assuming that fresh water has the composition of water vapour in equilibrium with ocean water, Dole's observed difference should agree with that calculated here. The equilibrium constants for exchange between oxygen and gaseous water from Table X at 273·1° K. and 298·1° K. are 1·017 and 1·014 respectively, while Dole's observed value corresponds to 1·030, and hence agreement with the assumption of equilibrium between air oxygen and ocean water is not secured. If equilibrium with fresh water is assumed, the disagreement is even greater. These calculated values are considerably less than those calculated by Urey and Greiff, the change being due to new values for the frequencies of the water molecule. Since the constants for H_2O and O_2 are known in complete detail, it does not seem probable that the calculated values will be altered much by future changes in these constants. Other explanations for this effect have been proposed and are reviewed by Kamen [35] and since the calculations here contribute nothing new to the previous discussion, no review of the problem will be made here.

The Atomic Weights of the Elements.

The variations in relative abundances of the isotopes of the elements cause corresponding variations in the chemical atomic weights. These are small in all cases but have been observed in the case of hydrogen and oxygen and should be observable in the case of chlorine. The observed constancy of the atomic weights in the case of these elements must be due to the selection of the same source for the element and the careful duplication of purification procedures. The largest changes in atomic weights to be expected from the equilibrium constants given in the tables for the various elements are given in Table XVII. Since the standard of chemical atomic weights varies, the same uncertainty enters into all the atomic weights. Fortunately the variability is low and in fact so low that no important error in chemical work will occur. The calculated change in the atomic weight of chlorine is surprisingly large.

TABLE XVII.

Calculated Maximum Variations in Atomic Weights.

Hydrogen *	0·00047	Nitrogen	0·00016
Lithium	0·0022	Oxygen	0·0023
Boron	0·016	Chlorine	0·031
Carbon	0·0014	Bromine	0·004

* In this case the water–hydrogen equilibrium at 0° C. is used rather than the water–potassium hydride equilibrium.

Application to the Separation of Isotopes.

During the past twenty-five years several interesting methods for the separation of isotopes have been devised, including the centrifugal, electromagnetic, and thermal and pressure diffusion of gases, and the electrolytic mobility method. These differences in chemical properties furnish another method for effecting such separations. Like all chemical methods, they are very specific, so that each element presents a separate and distinct research problem. Counter-current methods are necessary in order to secure large changes in concentration. These require two-phase systems and necessitate some convenient reflux reaction at the end of the apparatus where the desired isotope concentrates. When these conditions can be met, these chemical methods constitute very effective means for separating isotopes in quantity. Exchange reactions have been used for the concentration of D, Li, C^{13}, N^{15}, and S^{34} by reactions listed in Table XIV.[36] Also the differences in vapour pressures of isotopic compounds have been utilised for the concentration of D and O^{18}.[37] Unless the fractionation factors are about 1·01 or greater, these methods are difficult to use both because of the large size of the apparatus required and the expense of operation and because the times required for the apparatus to reach the steady state appropriate for continuous production become very large.

Conclusion.

Before the discovery of isotopes, it was generally assumed that all atoms of an element were identical in all respects. With their discovery it was evident that such atoms may differ in atomic weights, but it was believed that their chemical and physical properties were identical except for those properties directly related to mass such as densities of gases and condensed phases, rates of diffusion and evaporation, and others of this kind. As a result of the theoretical and experimental studies reviewed in this paper, we now know that isotopes and isotopic compounds differ in their thermodynamic properties. These differences are small except in the case of the hydrogens and they generally decrease with increasing atomic weight. These small differences make possible the concentration and separation of the isotopes of some of the elements and may have important applications as a means of determining the temperatures at which geological formations were laid down.

My best thanks are due to Mr. L. S. Myers for his help in making the many calculations recorded in the tables of this paper.

[1] *Amer. J. Sci.*, 1906, **22**, 537; 1907, **24**, 370.

[2] Keetman, *Jahrb. Radioaktivität*, 1909, **6**, 265; Marckwald and Keetman, *Ber.*, 1908, **41**, 49; see also Hahn, *Ber.*, 1907, **40**, 4415.

[3] *Wien. Ber.*, 1910, ii*a*, **119**, 1011.

[4] *Ber.*, 1910, **43**, 3420.

[5] *J.*, 1911, **99**, 72.

[6] *Phil. Mag.*, 1919, **37**, 523; **38**, 173.

[7] *Proc. Roy. Acad. Amsterdam*, 1931, **34**, 42; 1934, **37**, 615; 1935, **38**, 809.

[8] *Physical Rev.*, 1931, **39**, 164; 1932, **40**, 1.

[9] *J. Amer. Chem. Soc.*, 1933, **55**, 2616.

[10] *J. Chem. Physics*, 1933, **1**, 137.

[11] *Proc. Roy. Soc.*, 1934, *A.*, **144**, 467.

[12] *J. Amer. Chem. Soc.*, 1935, **57**, 321.

[13] Scott, Brickwedde, Urey, and Wahl, *J. Chem. Physics*, 1934, **2**, 454; Clusius and Bartholomé, *Z. physikal. Chem.*, 1935, *B*, **30**, 237; Scott and Brickwedde, *Bull. Amer. Physical Soc.*, 1935, **10**, 9.

[14] Libby and Barter, *J. Chem. Physics*, 1942, **10**, 184.

[15] Bijl, *Physica*, 1937, **4**, 329; Hobbs, *J. Chem. Physics*, 1939, **7**, 318.

[16] See, for example, Mayer and Mayer, " Statistical Mechanics," John Wiley and Company, New York (1940), for a complete discussion of these functions and their derivation.

[17] Redlich, *Z. physikal. Chem.*, 1935, *B*, **28**, 371; see also W. R. Angus *et al.*, *J.*, 1936, 971. This theorem holds for each symmetry type as well as for all vibrations as stated here.

[18] Waldman (*Naturwiss.*, 1943, **31**, 205) has made a similar expansion of this function. Bigeleisen and Mayer (*J. Chem. Physics*, in the press) have expanded the function to secure

$$\ln \frac{Q_2}{Q_1} = \ln \frac{\sigma_1}{\sigma_2} + \Sigma_i \left(-\frac{1}{u_i} + \frac{1}{2} + \frac{1}{1 - e^{-u_i}}\right) \Delta u_i$$

and they have calculated tables giving values of the function in the parenthesis for values of u usually encountered. I am indebted to them for the use of these tables for many of these calculations.

[19] *Proc. Camb. Phil. Soc.*, 1928, **24**, 280.

[20] *Ibid.*, 1933, **29**, 142, 407.

[21] *J. Chem. Physics*, 1934, **2**, 65.

[22] *Chem. Reviews*, 1936, **18**, 277.

[23] Urey and Greiff, *loc. cit.*, ref. (12).

[24] *Loc. cit.*, ref. (10).

[25] Farkas and Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1076; Bonhoeffer and Rummel, *Naturwiss.*, 1934, **22**, 45; Bonhoeffer, *Z. Elektrochem.*, 1934, **40**, 469.

[26] *J. Chem. Physics*, 1943, **11**, 101; Black and Taylor, *ibid.*, p. 395.

[27] See " Chemie der Deuteriumverbindungen," Tagungshefte der Deutschen Bunsen-Gesellschaft, p. 21 ff. (1938), for a review of these data.

[28] *Nature*, 1935, **135**, 229.

[29] Rosenthal, *Physical Rev.*, 1935, **47**, 236.

[30] I am indebted to Dr. Edward Teller and Dr. Maria G. Mayer for calling this method to my attention.

[31] The former authors report values of the C^{13}/C^{12} ratio from 1·013 to 1·022 above that for the carbon dioxide of the air for limestones, clam-shell, and sodium carbonate, while the latter authors report an average of 1·021 with no trend which they believe to be significant. The variation is probably not significant but, as we shall see, it is more difficult to account for the larger values. The variation is probably due to variations in the C^{13} content of air carbon dioxide, this variation being due to the low C^{13} content of coal and the presence of carbon dioxide from coal in the samples of air investigated.

[31a] In using equations (17) and (18) it is best to use average values for m and M, that is, 17 and 12·5 for oxygen and carbon respectively. It is possible to secure exact values for the frequencies of the isotopic oxygen molecule from assumed self-consistent values for the isotopic carbon molecule. Also, the frequencies of the $C^{12}O_2{}^{16}O^{18=}$ molecule can be calculated in a similar way. Because of the errors due to unknown anharmonic terms, such calculations are hardly justified.

[32] This possibility was discussed by Professor Paul Niggli of Zürich when the author discussed this subject at the University of Zurich.

[33] *J. Amer. Chem. Soc.*, 1935, **57**, 2731; *J. Chem. Physics*, 1935, **4**, 268.

[34] Greene and Voskuyl, *J. Amer. Chem. Soc.*, 1936, **58**, 693; Hall and Johnson, *ibid.*, p. 1920; Jones and Hall, *ibid.*, 1937, **59**, 259; Smith and Matheson, *J. Res. Nat. Bur. Stand.*, 1936, **17**, 625.

[35] *Bull. Amer. Mus. Nat. Hist., New York*, 1946, **87**.

[36] See references given in the table. Also Smyth, " Atomic Energy for Military Purposes," Princeton University Press (1945).

[37] Pegram, Huffman, and Urey, *Ind. Eng. Chem.*, 1937, **29**, 531; Thode, Smith, and Walking, *Canadian J. Res.*, 1944, **22***B*, 127. Also, Dr. Merle Randall has used this method for concentrating these isotopes.