believe, within the limit of error in method, heats of fusion and heat capacities.

Summary

1. The freezing point–composition diagram for the system biphenyl–bibenzyl shows a simple eutectic at 44.3 mole per cent. biphenyl and at 29.5°; biphenyl–naphthalene a simple eutectic at 55.6 mole per cent. biphenyl and at 39.4°; bibenzyl–naphthalene a simple eutectic at 38.6 mole per cent. naphthalene and at 32.7°.

2. Solubilities, eutectic temperatures and eutectic compositions in each of the three binary systems are within the limits of error equal to those calculated for ideal solutions.

3. The freezing point–composition diagram for the ternary system biphenyl–bibenzyl–naphthalene shows a simple ternary eutectic at 33.8 mole per cent. biphenyl, 39.2 mole per cent. bibenzyl, and at 17.4°.

4. The ternary eutectic temperature and composition are in good agreement with the values calculated for ideal solution behavior by two methods.

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Isotopic Exchange Equilibria

BY HAROLD C. UREY AND LOTTI J. GREIFF

Equilibrium constants involving hydrogen and deuterium have been calculated from statistical theory in recent years and these constants have been beautifully confirmed by experiment. Two such instances are the equilibrium constants of the reactions

$$H_2 + 2DI \rightleftharpoons 2HI + D_2, \text{ and} \qquad (1)$$
$$H_2 + D_2 \rightleftharpoons 2HD \qquad (2)$$

which have been calculated and experimentally confirmed by Urey and Rittenberg,[1] and in the case of the second reaction particularly nicely observed by Gould, Bleakney and Taylor.[2] The values of the constants obtained in these cases by calculation are exact, since the energy levels of the molecules involved are well known. In addition, the equilibrium constants of the reactions

$$D_2O + H_2 \rightleftharpoons H_2O + D_2 \qquad (3)$$
$$H_2 + HDO \rightleftharpoons HD + H_2O \qquad (4)$$

have been calculated and experimentally confirmed by others,[3] who used approximate formulas valid at ordinary temperatures and higher. These have been found to agree very satisfactorily with experimental values.

Equilibria in exchange reactions involving isotopes of other elements therefore become of interest and can be made with confidence. In this paper we shall present calculations of the equilibrium constants for exchange reactions involving isotopes of some of the lighter elements. These equilibrium constants differ by small factors from the values expected if the isotopes were distributed by chance between the molecules. It is predicted from an evaluation of the effect of such exchange that appreciable variations in the determinations of the atomic weights of elements are to be expected. Moreover, it seems possible that some concentration of the less abundant isotopes may be accomplished through the use of such exchange reactions.

Theoretical

The equilibrium constant, K, of a reaction

$$aA + bB + \ldots \rightleftharpoons mM + nN + \ldots$$

is given by the relation

$$-RT \ln K = \Delta F^\circ = -RT \ln \frac{f_N^m f_N^n}{f_A^a f_B^b} \qquad (5)$$

where $K = p_A^a p_B^b / p_M^m p_N^n$, and f_M is the distribution function of molecule M. This distribution function, f, of a diatomic or polyatomic molecule is given by the relation

$$f = M^{3/2} T^{5/2} Q \frac{(2\pi)^{3/2} k^{5/2}}{h^3 N^{3/2}} \qquad (6)$$

Here Q is the summation of state and the remaining symbols have their usual meaning. For diatomic molecules the summation of state is

$$Q = \sum_{v,j} p_j \exp - \frac{E(J, v)}{kT} \qquad (7)$$

and the energy of a diatomic molecule is given by the formula

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[1] Urey and Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933); THIS JOURNAL, **56**, 1885 (1934); Rittenberg, Bleakney and Urey, *J. Chem. Phys.*, **2**, 48 (1934).

[2] Gould, Bleakney and Taylor, *ibid.*, **2**, 362 (1934).

[3] Crist and Dalin, *ibid.*, **2**, 735 (1934); Farkas and Farkas, *Nature*, **132**, 894 (1933); *Proc. Roy. Soc.* (London), **A144**, 467 (1934).

$$E/hc = \tilde{\omega}_e\left(v+\frac{1}{2}\right) - x\tilde{\omega}_e\left(v+\frac{1}{2}\right)^2 + \ldots + \left[B_e - \alpha\left(v+\frac{1}{2}\right) + \gamma\left(v+\frac{1}{2}\right)^2 - \delta\left(v+\frac{1}{2}\right)^3 + \ldots\right] J(J+1) + \left[D_e + \beta\left(v+\frac{1}{2}\right) + \ldots\right] J^2(J+1)^2 + F_eJ^3(J+1)^3 \quad (8)$$

An approximate value of Q for calculations at ordinary temperatures and above may be used. For diatomic molecules this[4] is

$$Q = \frac{8\pi^2IkT}{\sigma h^2}\left(1 - \exp\frac{hc\tilde{\omega}_e}{kT}\right)^{-1}\exp\left(-\frac{hc\tilde{\omega}_e}{2kT} + \frac{B_ehc}{4kT}\right) \quad (9)$$

Here σ is the symmetry number and corrects the expression for the alternation in *a priori* probabilities of the rotational levels if the atoms are identical. The formula does not include the effect of nuclear spin on the free energy but this is unnecessary since the nuclear spin does not affect equilibrium constants above ordinary temperatures in any case. The term exp $(B_ehc/4kT)$ can be neglected for such calculations except in the case of H_2, HD, and D_2 where the moments of inertia are small. The summation of state for polyatomic molecules, derived in a similar way, is found to be

$$Q = \frac{8\pi^2(8\pi^3ABC)^{1/2}}{\sigma h^3}(kT)^{3/2}\Pi_i\frac{\exp - \dfrac{h\tilde{\omega}_ic}{2kT}}{1 - \exp - \dfrac{h\tilde{\omega}_ic}{kT}} \quad (10)$$

where A, B and C are the moments of inertia of the molecule and the product Π_i is taken over all frequencies of vibration of the molecule, $\tilde{\omega}_i$, one for each vibrational degree of freedom. This again neglects all effects of the nuclear spin and all cross product and higher power terms in the energy other than those dependent on the first power of the vibrational quantum numbers and the square of the rotational quantum numbers. This simplification is valid only in those cases in which the moments of inertia are large and the temperatures are high.

In this paper we shall consider equilibria of the type

$$O_2^{16} + 2H_2O^{18} \rightleftharpoons O_2^{18} + 2H_2O^{16}$$

for which

$$K = \frac{f_{(O_2^{18})}}{f_{(O_2^{16})}} \times \frac{f^2_{(H_2O^{16})}}{f^2_{(H_2O^{18})}} \quad (11)$$

It is obvious that the equilibrium constant, K, depends upon the ratios of the distribution functions of like isotopic molecules. For diatomic molecules this ratio is, in accordance with equations (6) and (9)

$$f_1/f_2 = (M_1/M_2)^{3/2}I_1/I_2\exp\left[-hc/2kT\,(\tilde{\omega}_1 - \tilde{\omega}_2)\right]\frac{1 - e^{-hc\tilde{\omega}_2/kT}}{1 - e^{-hc\tilde{\omega}_1/kT}} \quad (12)$$

A similar expression easily deduced from equations (6) and (10) holds for polyatomic molecules, namely

$$f_1/f_2 = \left(\frac{A_1B_1C_1}{A_2B_2C_2}\right)^{1/2}\left(\frac{M_1}{M_2}\right)^{3/2}\exp\left[-\frac{hc}{2kT}(\Sigma\tilde{\omega}_{1i} - \Sigma\tilde{\omega}_{2i})\right]\Pi_i\frac{1 - e^{-hc\tilde{\omega}_{2i}/kT}}{1 - e^{-hc\tilde{\omega}_{1i}/kT}} \quad (13)$$

The molecular constants of the rarer isotopic molecules are in most cases calculated from the known spectral data of the more abundant molecules. For this purpose we have employed, for diatomic molecules, the theory of the isotope effect which is well known and experimentally confirmed. In the case of polyatomic molecules we have used the best theoretical relationships available. For the calculation of the required ratios between moments of inertia it is necessary to know the angle between the bonds joining dissimilar atoms. This angle, determined from spectral data, has already been calculated for a number of molecules. Fortunately, interatomic distances are not needed.

In Table I we list the molecular constants which we have used in these calculations, and refer to the sources of the experimental data and theoretical relationships employed. Our choice of molecules was determined in part by the availability of the spectral data on the molecule and in part by the promise afforded by its reactions for experimental verification. The degree of degeneracy of the frequency is indicated in the table by the number in parentheses following the value of the frequency. In the cases where the values of the frequencies for the abundant molecule do not agree with the published experimental values, force constants were secured by putting the observed frequencies into the theoretical equations and solving by successive approximations. When a good agreement between observed and calculated values was secured, the approximations were carried no further but frequencies for both the abundant and rarer molecules were calculated by means of these theoretical equations containing the chosen force constants. This procedure yields accurate frequency differences, which are of greater importance here than are the values of the frequencies themselves.

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(4) Mulholland, *Proc. Cambridge Phil. Soc.*, **24**, 280 (1928); Southerland, *ibid.*, **26**, 402 (1930); Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

TABLE I

MOLECULAR CONSTANTS

Monatomic Molecules

Molecule	θ (Debye)
C^{12} (diamond)	1860[a,b]
C^{13} (diamond)	1787

Diatomic Molecules

Molecule	$\tilde{\omega}$	I_2/I_1	Molecule	$\tilde{\omega}$	I_2/I_1
N_2^{14}	2359.6[c]	1.0714	HCl^{35}	2989.7[g]	1.0015
N_2^{15}	2279.6		HCl^{37}	2987.5	
O_2^{16}	1584.9[d]	1.1250	HBr^{79}	2647.0[g]	1.0003
O_2^{18}	1494.3		HBr^{81}	2646.6	
Cl_2^{35}	564.9[e]	1.0571	CO^{16}	2167.4[h]	1.0500
Cl_2^{37}	549.4		CO^{18}	2115.2	
Br_2^{79}	323.86[e]	1.0253	$C^{12}O$	2167.4[h]	1.0460
Br_2^{81}	319.84		$C^{13}O$	2119.2	
Li^6H	1420.7	1.0208	$N^{14}O$	1906.54[i]	1.0369
Li^7H	1406.1[f]		$N^{15}O$	1872.34	

Polyatomic Molecules

Molecule	$\tilde{\omega}_1$	$\tilde{\omega}_2$	$\tilde{\omega}_3$	$\tilde{\omega}_4$	α[j]	A_2/A_1	B_2/B_1	C_2/C_1
H_2O^{16}	3517.0[k]	3562.8	1658.4	....	50°	1.0048	1.0125	1.0000
H_2O^{18}	3503.6	3553.1	1652.6	....	50°			
CO_2^{16}	1361[l]	673.0(2)	2378	....	90°	1.1250	1.1250	....
CO_2^{18}	1283.2	662.7(2)	2341.7	....	90°			
$C^{16}O^{18}$	1321.7[m]	667.9(2)	2360.4	....	90°	(See footnote [n])		
$C^{12}O_2$	1361[l]	673.0(2)	2378	....	90°	1.0000	1.0000	....
$C^{13}O_2$	1361	653.9(2)	2310.5	....	90°			
SO_2^{16}	1361[o,p]	1150.3	605.9	....	61°45′	1.1250	1.0588	1.1167
SO_2^{18}	1317.7	1100.9	580.0	....	61°45′			
ClO_2^{16}	954[q]	1105	529	....	60°40′	1.1160	1.0620	1.1125
ClO_2^{18}	913	1068	505.7	....	60°40′			
ClO_2^{16}	529[q]	1105	954	....	32°30′	1.0895	1.0620	1.125
ClO_2^{18}	500.3	1068.9	911	....	32°30′			
$C^{12}O_3$	1087[r]	1437(2)	714(2)	878	60°	1.0000	1.0000	1.0000
$C^{13}O_3$	1087	1393(2)	713.5(2)	850.6	60°			
SO_4^{16}	980[s]	451.0(2)	1113.6(3)	618.9(3)	54°45′	1.1250	1.1250	1.1250
SO_4^{18}	924.0	425.2(2)	1081.9(3)	589.4(3)				

[a] θ^{12} from Eucken, "Lehrbuch der chemischen Physik," Leipzig, 1930, p. 128.

[b] F/T from θ/T, "Handbuch der Physik," Berlin, 1926, Vol. 10, p. 369.

[c] Jevons, "Report on Band Spectra of Diatomic Molecules," University Press (Camb.), 1932, p. 284.

[d] Jevons, *loc. cit.*, p. 290.

[e] Jevons, *loc. cit.*, p. 280.

[f] Jevons, *loc. cit.*, p. 272.

[g] Jevons, *loc. cit.*, p. 276.

[h] Jevons, *loc. cit.*, p. 86.

[i] Jevons, *loc. cit.*, p. 288.

[j] α is the half angle $X - Y - X$.

[k] For equations employed see Van Vleck and Cross, "A Calculation of Vibration Frequencies and other Constants of the H_2O Molecules," *J. Chem. Phys.*, **1**, 357 (1933).

[l] Values of fundamental frequencies for CO_2^{16} from Adel and Dennison, "Infra Red Spectrum of Carbon Dioxide," *Phys. Rev.*, **44**, 99 (1933).

[m] Frequencies for $CO^{16}O^{18}$ calculated from equations derived for us by Dr. Jennie Rosenthal.

[n] Ratios of moments of inertia of the mixed molecule to those of each of the symmetrical molecules needed. $A_{CO^{16}O^{18}}/A_{CO_2^{16}} = B_{CO^{16}O^{18}}/B_{CO_2^{16}} = 1.0598$; $A_{CO^{16}O^{18}}/A_{CO_2^{18}} = B_{CO^{16}O^{18}}/B_{CO_2^{18}} = 0.9420$.

[o] For equations employed see "Absorption Spectrum of Chlorine Dioxide," Z. W. Ku, *Phys. Rev.*, **44**, 376 (1933).

[p] Experimental values from infra red data by Duncan (private communication).

[q] Constants and equations, Z. W. Ku, *Phys. Rev.*, *loc. cit.* Both sets of constants given by Ku were employed, *i. e.*, $\alpha = 32°30'$ and $\alpha = 60°40'$.

[r] Fundamental frequencies $C^{12}O_3$ estimated for us by Dr. Jennie Rosenthal. Frequencies of isotopic $C^{13}O_3$ calculated in accordance with relationships which she has derived.

[s] For equations and fundamental frequencies employed see Urey and Bradley, "The Vibrations of Pentatomic Tetrahedral Molecules," *Phys. Rev.*, **38**, 1969 (1931).

In Table II we list the values of the ratios of distribution functions for pairs of isotopic molecules and in Table III the equilibrium constants for the reactions given.

The enrichment factor is defined as $\frac{N_1}{N_2}\Big/\frac{n_1}{n_2}$ where N_1 and N_2 are the numbers of light and heavy atoms in the one compound and n_1 and n_2 the corresponding numbers for the other compound. The enrichment factors are calculated on the assumption that two isotopes are distributed in molecules containing two or more atoms of the element in a random manner. Thus it is assumed that

$$[O_2^{16}]:[O^{16}O^{18}]:[O_2^{18}] = \alpha^2:2\alpha(1-\alpha):(1-\alpha)^2$$

and

$$[SO_4^{16}]:[SO_3^{16}O^{18}]:[SO_2^{16}O_2^{18}]:[SO^{16}O_3^{18}]:[SO_4^{18}] = \alpha^4:4\alpha^3(1-\alpha):6\alpha^2(1-\alpha)^2:4\alpha(1-\alpha)^3:(1-\alpha)^4$$

TABLE II

RATIOS OF DISTRIBUTION FUNCTIONS

Molecule (1)	Molecule (2)		f_2/f_1 273.1°A.	f_2/f_1 298.1°A.	f_2/f_1 600°A.
Li^6	Li^{7a}		1.2601	1.2601	1.2601
C^{12}	C^{13b}		....	1.3289	1.2033
N_2^{14}	N_2^{15}		1.4655	1.4399	1.3083
O_2^{16}	O_2^{18}		1.7025	1.6691	1.5041
Cl_2^{35}	Cl_2^{37}		1.2022	1.1992	1.1862
Br_2^{79}	Br_2^{81}		1.08093	1.08046	1.07853
Li^6H	Li^7H		1.2959	1.2918	1.2707
HCl^{35}	HCl^{37}		1.0924	1.0919	1.0890
HBr^{79}	HBr^{81}		1.03914	1.03905	1.03855
CO^{16}	CO^{18}		1.3352	1.3200	1.2403
$C^{12}O$	$C^{13}O$		1.2510	1.2378	1.1686
H_2O^{16}	H_2O^{18}		1.2743	1.2663	1.2231
CO_2^{16}	CO_2^{18}		1.8315	1.7800	1.5375
$C^{12}O_2$	$C^{13}O_2$		1.3732	1.3437	1.2020
ClO_2^{16}	ClO_2^{18}	(a)	1.6720	1.6375	
		(b)	1.6599	1.6274	
SO_2^{16}	SO_2^{18}		1.7362	1.6946	1.5038
$C^{12}O_3$	$C^{13}O_3$		1.3936	1.3594	1.1987
SO_4^{16}	SO_4^{18}		3.0476	2.8875	2.2470

[a] $f_{Li^7}/f_{Li^6} = (M_{Li^7}/M_{Li^6})^{3/2}$

[b] $f_{C^{13}}/f_{C^{12}} = e^{-(F^0_{13}-F^0_{12})/RT}$

where α is the total mole fraction of O^{16} atoms in all varieties of the molecule. This assumption is very closely true for diatomic molecules such as chlorine where exact calculations have been made;[4] it is also approximately true for the reaction

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

as is shown in Table III where $K(273°\text{A.}) = 3.999$ instead of 4 as would be required by this assumption. The deviation from the value 4, as can be seen from the table, decreases with increased temperature to 600° A., and hence we may assume that simple statistical distribution of the atoms among the various molecules holds equally well for other cases including molecules with more than two oxygen atoms. Taking the water–carbon dioxide reaction as an example, the enrichment factor is

$$\frac{2[CO^{18}_2] + [CO^{16}O^{18}]}{2[CO^{18}_2] + [CO^{16}O^{18}]}\Big/\frac{[H_2O^{18}]}{[H_2O^{16}]} = \frac{[CO_2^{18}]^{1/2}}{[CO_2^{16}]^{1/2}}\Big/\frac{[H_2O^{18}]}{[H_2O^{16}]}$$

This follows from the use of 4 for the equilibrium constant for the exchange reaction between the three varieties of carbon dioxide molecules, and it should be noted that this is the square root of the equilibrium constant. In general the enrichment factor will be the equilibrium constant raised to a power equal to the reciprocal of the number of oxygen atoms in the compounds containing more than one such atom.

These calculations cannot be regarded as precise in all cases nor can we determine the limits of error. However, the calculations for gaseous neutral molecules, as sulfur dioxide and oxygen, can be regarded as fairly accurate. To estimate the probable error due to choice of constants we have repeated the entire calculation for the equilibrium between water and carbon dioxide using for the fundamental frequencies of CO_2^{16}: $\tilde{\omega}_1 = 1285.8$, $\tilde{\omega}_2 = 667.5$ and $\tilde{\omega}_3 = 2350$. This we believe is about as bad a choice for these constants as could be made. For the reaction

$$CO_2^{16} + 2H_2O^{18}(g) \rightleftharpoons CO_2^{18} + 2H_2O^{16}(g)$$

at 273.1°A., the value of the equilibrium constant is 1.114 as compared with 1.128 as given in Table III, where the correct values of the frequencies have been used. This difference decreases slightly with increase in temperature. In addition, in the case of chlorine dioxide we used both possible sets of constants given by Ku and listed in Table I. In this case the equilibrium constants for the reaction

$$ClO_2^{16} + H_2O^{18} \rightleftharpoons ClO_2^{18} + H_2O^{16}$$

at 273.1°A., for $\alpha_{(ClO_2)} = 32°30'$ and $\alpha_{(ClO_2)} = 60°40'$ with the other constants corresponding, are 1.030 and 1.022, respectively, *i. e.*, they differ by about eight parts in one thousand. This difference also decreases with increase in temperature. It is most probable that these differences greatly exceed errors due to uncertainties in the constants chosen.

Where water is one of the reactants it is possible to calculate the enrichment factor for equilibrium between liquid water and the gaseous

TABLE III

EQUILIBRIUM CONSTANTS AND ENRICHMENT FACTORS

Reaction	K Temp., °A. 273.1	K 298.1	K 600	Enrichment factors Temp., °A. 273.1	Enrichment factors 298.1	Enrichment factors 600
$SO_2^{16} + 2H_2O^{18}(g) \rightleftharpoons SO_2^{18} + 2H_2O^{18}(g)$	1.069	1.057	1.005	1.034	1.028	1.003
$SO_2^{16} + 2H_2O^{18}(l) \rightleftharpoons SO_2^{18} + 2H_2O^{16}(l)$	1.040	1.028		1.020	1.014	
$CO_2^{16} + 2H_2O^{18}(g) \rightleftharpoons CO_2^{18} + 2H_2O^{16}(g)$	1.128	1.110	1.028	1.064	1.054	1.014
$CO_2^{16} + 2H_2O^{18}(l) \rightleftharpoons CO_2^{18} + 2H_2O^{16}(l)$	1.097	1.080		1.047	1.039	
$SO_4^{16} + 4H_2O^{18}(g) \rightleftharpoons SO_4^{18} + 4H_2O^{16}(g)$	1.156	1.123	1.004	1.037	1.029	1.001
$SO_4^{16} + 4H_2O^{18}(l) \rightleftharpoons SO_4^{18} + 4H_2O^{16}(l)$	1.093	1.062		1.023	1.015	
$CO^{16} + H_2O^{18}(g) \rightleftharpoons CO^{18} + H_2O^{16}(g)$	1.048	1.042	1.014	1.048	1.042	1.014
$CO^{16} + H_2O^{18}(l) \rightleftharpoons CO^{18} + H_2O^{16}(l)$	1.033	1.028		1.033	1.028	
$O_2^{16} + 2H_2O^{18}(g) \rightleftharpoons O_2^{18} + 2H_2O^{16}(g)$	1.048	1.041	1.005	1.024	1.020	1.003
$O_2^{16} + 2H_2O^{18}(l) \rightleftharpoons O_2^{18} + 2H_2O^{16}(l)$	1.020	1.012		1.010	1.006	
$ClO_2^{16} + 2H_2O^{18}(g) \rightleftharpoons ClO_2^{18} + 2H_2O^{16}(g)$	1.030^a	1.021		1.015	1.010	
	1.022^b	1.015		1.011	1.007	
$ClO_2^{16} + 2H_2O^{18}(l) \rightleftharpoons ClO_2^{18} + 2H_2O(l)$	1.002^a	0.993		1.001	0.996	
$SO_2^{16} + O_2^{18} \rightleftharpoons SO_2^{18} + O_2^{16}$	1.020	1.015	0.9998	1.010	1.008	1.000
$2CO^{16} + O_2^{18} \leftrightarrows 2CO^{18} + O_2^{16}$	1.047	1.044	1.023	1.023	1.022	1.011
$SO_4^{16} + 2O_2^{18} \leftrightarrows SO_4^{18} + 2O_2^{16}$	1.051	1.036	0.993	1.013	1.009	0.998
$CO_2^{16} + CO_2^{18} \leftrightarrows 2CO^{18}O^{18}$	3.9990	3.9993	4.0000	0.9997	0.9998	1.000
$C^{13}O + C^{12}O_2 \leftrightarrows C^{12}O + C^{13}O_2$	1.098	1.086	1.029	1.098	1.086	1.029
$C^{13}O_2 + C^{12}O_3 \leftrightarrows C^{12}O_2 + C^{13}O_3$	1.015	1.012	0.997	1.015	1.012	0.997
$C^{12} + C^{13}O \rightleftharpoons C^{13} + C^{12}O$		1.074	1.030		1.074	1.030
$C^{12} + C^{13}O_2 \rightleftharpoons C^{13} + C^{12}O_2$		0.989	1.002		0.989	1.002
$Cl_2^{35} + 2HCl^{37} \rightleftharpoons Cl_2^{37} + 2HCl^{35}$	1.007	1.006	1.0003	1.004	1.003	1.00015
$Br_2^{79} + 2HBr^{81} \rightleftharpoons Br_2^{81} + 2HBr^{79}$	1.001	1.0008	0.99994	1.0005	1.0004	0.99997
$Li^6H + Li^7 \rightleftharpoons Li^7H + Li^6$	1.028	1.025	1.008	1.028	1.025	1.008
$N_2^{14} + 2N^{15}O \rightleftharpoons N_2^{15} + 2N^{14}O$	1.033	1.030	1.015	1.016	1.015	1.007

[a] Molecular constants used assuming =32°30′. [b] Molecular constants used assuming =60°40′. Constants not calculated for 600°A. because of nature of reaction.

TABLE IV

CALCULATED EFFECT OF ISOTOPIC EXCHANGE ON ATOMIC WEIGHT DETERMINATIONS

Element	Reaction	Enrichment factor (298.1°A.)	Atomic weight	Change in atomic weight due to isotopic exchange
Li	$Li^6H + Li^7 \rightleftharpoons Li^7H + Li^6$	1.0251	6.940	0.001
C	$C^{12} + C^{13}O \rightleftharpoons C^{13} + C^{12}O$	1.074	12.00	.0007
N	$N_2^{14} + 2N^{15}O \rightleftharpoons N_2^{15} + 2N^{14}O$	1.015	14.008	.00005
O	$CO_2^{16} + 2H_2O^{18} \rightleftharpoons CO_2^{18} + 2H_2O^{16}(g)$	1.054	16.0000	.0002
	$CO_2^{16} + 2H_2O^{18} \rightleftharpoons CO_2^{18} + 2H_2O^{16}(l)$	1.039	16.0000	.00014
Cl	$Cl_2^{35} + 2HCl^{37} \rightleftharpoons Cl_2^{37} + 2HCl^{35}$	1.003	35.457	.0010
Br	$Br_2^{79} + 2HBr^{81} \rightleftharpoons Br_2^{81} + 2HBr^{79}$	1.0004	79.916	.0002

substance (if its solubility is small) by dividing the enrichment factors for gaseous water by 1.014, the ratio of the vapor pressure of H_2O^{16} to that of H_2O^{18} at 284.1°A. as determined by Urey and Wahl.[5] Considering this ratio as valid also at 273.1 and 298.1°A. we obtained the equilibrium constants and the enrichment factors recorded in Table III for reactions involving liquid water [$H_2O(l)$]. The constants calculated for the equilibrium between water and sulfate ion or between a gas and an ion dissolved in water must be regarded as unreliable, for we really cannot assume that the theory for a gas applies to a condensed phase. They show, in a general way, what the order of magnitude of the enrichment factor might be in such cases.

Variations in Atomic Weights.—The deviation of these enrichment factors from unity is sufficient to predict detectable variations in the atomic weight of the lighter elements, dependent upon the reaction employed in the determination of such atomic weights. As indicated in Table IV, the atomic weight of oxygen in carbon dioxide which is in equilibrium with gaseous water differs from that of the oxygen in the water by about one

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(5) The different vapor pressures of H_2O^{16} and H_2O^{18} were first reported by Lewis and Cornish [THIS JOURNAL, 55, 2616 (1933)]. The ratio given here and the method of determination will be published soon.

part in one hundred thousand, so that the standard of atomic weights certainly cannot be regarded as constant within this limit. The possible variations in the atomic weights of lithium and chlorine are shown to be approximately one (1) in the last accepted figure of these atomic weights. Our calculations indicate that more precise determinations of these atomic weights are futile. Atomic weights given to more significant figures will be meaningless unless the isotopic composition is specified. Many of the methods of determination of the isotopic composition apparently would give false results because of fractionation in the processes involved. If these difficulties were overcome, and the exact value for the atomic weight of a given sample of an element were secured, it could not be used with certainty for some other sample unless its isotopic composition were known. Thus we must conclude that the atomic weights of many common elements, as determined by known chemical methods, are not fundamental constants of nature to more than a limited precision. This limit of precision has been reached in the case of lithium, oxygen, chlorine and, perhaps, other elements.

Separation Methods.—The enrichment factors suggest, in addition, that the isotopes of the lighter elements might be separated by these chemical exchange reactions; and that the equilibria might be established in two-phase systems by the use of countercurrent methods. The most practicable two-phase system is, obviously, a liquid and a gas. A rapid establishment of equilibrium is desirable and it is necessary to be able to convert the gaseous compound into the liquid and the reverse without increasing nor decreasing the quantity of the element being separated.

Distilling columns have been designed having 100 theoretical plates. Table V shows the over-all enrichment factors for such a column in comparison with the enrichment factors for the simple process. For fifty theoretical plates, the over-all enrichment factor would be the square root of these. Even in this case, many of the reactions which we have considered might be adapted to countercurrent scrubbing processes and effective fractionation secured.

TABLE V

ENRICHMENT IN A SCRUBBING TOWER, EFFICIENCY CORRESPONDING TO 100 THEORETICAL PLATES

Simple process factor	Over-all factor[a]
1.010	2.705
1.014	4.016
1.020	7.245
1.025	11.86
1.030	19.22
1.040	50.50
1.070	867.7

[a] Over-all factor = (simple process factor)^n where n = no. of theoretical plates.

Of the reactions which we have considered, that between carbonate ion and carbon dioxide is the most interesting from the standpoint of manipulation. Although the theoretical calculations indicate only a small separation of the carbon isotope, and these calculations are, moreover, very doubtful because of an inadequate theory of the vibrational frequencies, the general indications of enrichment factors differing from unity and the evident possibility of using a distilling column as a countercurrent scrubbing apparatus make this reaction one worthy of study for the separation of C^{13} and C^{12}. For this separation of the carbon isotopes the exchange reaction between $C^{13}O_2$ and $C^{12}O$ would be particularly successful according to the equilibrium constant (1.086 at 298.1°A.). Experimental difficulties connected with the separation of the carbon dioxide after equilibrium had been obtained, by condensation with liquid air or absorption in alkaline solution or by other means, tend to discourage experiments with these compounds. The enrichment factor between solid carbon and carbon monoxide is favorable, but the effect decreases rapidly with increasing temperature. At temperatures where the diffusion would be sufficiently rapid to maintain equilibrium concentrations throughout the solid carbon, the enrichment factor would be nearly unity. Further, the calculations have been made with diamond since a theory for a polyatomic solid such as graphite is not known. It seems probable that the fractionation will be less in the latter case since the heat capacity of graphite rises more rapidly to the value $3R$ than does that of diamond. The great simplicity of manipulation for the reaction

$$HC^{13}O_3^- + C^{12}O_2 = HC^{12}O_3^- + C^{13}O_2$$

makes this the most promising of these reactions to use experimentally. Although no calculations have been made for this reaction because of the uncertainty of the molecular constants for the bicarbonate ion, the small enrichment factor calculated for the reaction

$$C^{13}O_3^- + C^{12}O_2 = C^{13}O_3^- + C^{12}O_2$$

does indicate the possibility of some separation by means of the reaction involving the bicarbonate ion. Work on exchange reaction between bicarbonate and carbon dioxide is in progress in this Laboratory.

Of the reactions involving the fractionation of oxygen, the equilibrium between water and carbon dioxide seems to be the most encouraging. The factor here is 1.039 for the equilibrium between liquid water and gaseous carbon dioxide and favors the concentration of O^{18} in the carbon dioxide.[6] A fractionating column could be used for this reaction. At the top carbon dioxide can be converted to water by the reaction

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

and the water refluxed.[7] At the bottom water can be converted to hydrogen and oxygen by electrolysis and the oxygen allowed to react with carbon to form carbon dioxide which could be passed up the column. In this way a countercurrent process could be constructed operating in much the same way as a fractionating column. Experimental work on this method of separation is also in progress in our laboratories.

In the case of nitrogen, the one reaction considered has a small enrichment factor. Moreover, it would probably be impossible to establish the equilibrium at ordinary temperatures. Other reactions involving the nitrogen isotopes may be suggested, such as

$$N^{14}O + N^{15}O_2 \rightleftharpoons N^{15}O + N^{14}O_2$$

This equilibrium could be established through the reaction

$$NO_2 + NO \rightleftharpoons N_2O_3$$

This reaction seems unfavorable from an experimental standpoint because of the low temperatures necessary and the corrosive character of these oxides. Moreover, it seems impossible to make any calculations on the enrichment factor. Slight fractionation might be reasonably expected. Again the reaction

$$N^{14}H_3 + N^{15}H_4^+ \rightleftharpoons N^{14}H_4^+ + N^{15}H_3$$

might be considered. Here the nitrogen isotope effect would be small and consequently little fractionation could be expected. This expectation might be false, however, for the 1.4% difference in the vapor pressures of H_2O^{16} and H_2O^{18} shows that slight enrichment can be secured in simple physical changes.

Though exact calculations can be made only for the gaseous state, we may expect that the isotopes of the lighter elements may be fractionated in many chemical reactions in condensed phases taking place near ordinary temperatures to about the extent that such fractionation occurs in the gaseous state.

Summary

In this paper we have calculated, by the use of spectroscopic data, the equilibrium constants and enrichment factors of several exchange reactions involving isotopes of the lighter elements. We have shown that as a result of the magnitude of these enrichment factors, there is a theoretical limit to the precision with which atomic weights may be determined, and that this limit has already been reached for several of the lighter elements. We have suggested reactions which might be used for the practical separation of the isotopes of some of the elements and have outlined a countercurrent scrubbing method for securing equilibrium in a few such reactions.

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(6) Reference to Table III will show that almost all of the reactions which we have considered involving water show a tendency to decrease the O^{18} content of the water at the temperatures which we have used.

(7) The solubility of carbon dioxide in water is slight even at 273.1°A. at ordinary pressures, so that loss of the heavy isotope due to this solubility would be insignificant.