

## ON THE RELATIVE ABUNDANCES OF ISOTOPES

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## ABSTRACT

The relative abundances of nuclei are often supposed to be related to nuclear stability. We may consider stability in two ways: on the one hand stability may refer to a mixture in thermodynamic equilibrium; or, on the other it is often used when referring to a system characterized by a slow rate of change to a thermodynamically stable state. It appears possible to test the hypothesis of equilibrium by a number of transmutation reactions. We restrict ourselves to those reactions in which the same elements, differing only in mass, occur on each side of the equation, and find that the thermodynamic calculations become very simple. The calculations are in agreement with the assumption that the atomic nuclei on earth do not represent an equilibrium mixture at any temperature.

THE relative abundances of isotopes have often been used in discussing nuclear stability. We may consider two types of stability. In the first place stability may represent thermodynamic equilibrium which existed under some certain set of physical conditions. That is the relative abundances of nuclear types on earth may represent a mixture which came to equilibrium at some previous time. Or the composition of the earth may be determined by the relative velocities of change of one atomic type into another, or into radiation. Here, slow rate of change would indicate "stability." The radioactive elements are examples of this latter type of stability since the more abundant radioactive nuclei disintegrate more slowly than the less abundant. We would not be justified in assuming that there is any simple relation between the relative abundances of radioactive nuclei and their relative abundances under equilibrium conditions. We have made this study utilizing the relative abundances of isotopes, to see if it is possible to decide between these two senses of stability as applied to nuclear types.

The type of calculations which seem best suited to the reactions we are considering are those which Debye and Hückel applied to the theory of dilute solutions where the ions of the solute are singly charged, the solvent possesses a high dielectric constant, and the concentrations of solute are 0.01 molar or less. However, in the reactions under discussion, we are concerned with ions from which many, perhaps all, electrons have been removed, the dielectric constant of the medium is probably of the order of magnitude unity, and the pressures may represent a nuclear concentration of considerably more than 0.01 molar. Thus, the application of calculations of the Debye-Hückel type to conditions under which transmutation reactions might be taking place presents enormous mathematical difficulties. If any progress is to be

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made on the problem it seems necessary to find a much simpler special case than that presented by the general problem.

Before making our calculations it is necessary to decide if possible under what conditions the material of the earth might have been in equilibrium. These conditions might have been those existing in the sun at the time the planets were formed and which were probably similar to those existing in the sun at the present time. In this case the question is whether or not the atomic nuclei of the sun are in equilibrium. If they are, those of the earth may be an equilibrium mixture and any calculations for the temperature of equilibrium should come out near  $10^7$  degrees.

On the other hand if the nuclei of the sun are not in equilibrium, they can hardly represent a mixture which would be in equilibrium at a higher temperature. If the composition of the sun is the same now as at some previous higher temperature, its atoms must have been converted into radiation at such relative rates that the composition remained unchanged. This would mean that the probability of the disappearance of a nucleus is the same for all nuclei. We regard this as improbable and expect that if the distribution of nuclei is one of equilibrium at any temperature, then that temperature is the temperature of the sun's interior.

The transmutation reactions which present the fewest difficulties for the thermodynamic calculations are those in which different isotopes of the same element appear on each side of the equation. We may take as an example,



The equilibrium constant of this reaction is given by the usual thermodynamic equation:

$$\ln K = \ln \frac{a_{13}a_{16}}{a_{12}a_{17}} = - \frac{\Delta E}{RT} + \frac{\Delta S}{R} \quad (2)$$

where  $K$  is the equilibrium constant,  $a_{13}$ ,  $a_{16}$ ,  $a_{12}$ , and  $a_{17}$  are the activities of  $\text{C}^{13}$ ,  $\text{O}^{16}$ ,  $\text{C}^{12}$ , and  $\text{O}^{17}$  respectively,  $\Delta E$  and  $\Delta S$  are the energy and entropy changes for the reaction. By substituting the products of concentrations and activity coefficients for the activities we secure for the equilibrium constant

$$K = \frac{a_{13}a_{16}}{a_{12}a_{17}} = \frac{C_{13}C_{16}}{C_{12}C_{17}} \frac{\gamma_{13}\gamma_{16}}{\gamma_{12}\gamma_{17}}, \quad (3)$$

where  $C_{13}$ , etc. and  $\gamma_{13}$ , etc. are the concentrations and activity coefficients respectively. The activity coefficients correct for deviations from ideal solution laws. However, in this case, such deviations will be the same for two isotopes since the electron shells are identical except for very small differences. Thus the ratios  $\gamma_{13}/\gamma_{12}$  and  $\gamma_{16}/\gamma_{17}$  equal unity, and the term containing them becomes merely  $C_{13}C_{16}/C_{12}C_{17}$ . This is justified as long as the densities are so low that the deviations are determined only by the net nuclear charge. Deviations due to the differences in nuclear structure can only be important if the mean

distances between nuclei are small as compared to "nuclear" diameters. Taking nuclear diameters as about  $10^{-12}$  cm and the distances between nuclei as about  $10^{-8}$  cm or greater, we obtain the ratio of  $10^4$ . This is about 100 times as great as the ratio between distances between atoms and atomic diameters in a gas at atmospheric pressure. Thus we would not expect specific deviations from ideal gas or solution laws if the densities are not much greater than unity.

The energy change,  $\Delta E$ , may be written as

$$\Delta E = E_{13} + E_{16} - E_{12} - E_{17}, \quad (4)$$

where  $E_{13}$ , etc are the energies of the atoms entering into the reaction. The energy of one of these atoms may be divided into three parts,

$$E = E_0 + E_n + F(T), \quad (5)$$

where  $E_0 = Mc^2$ ,  $M$  being the atomic weight at absolute zero, and  $E_n$  is the mean energy of excitation of the nuclear energy levels. The term,  $F(T)$ , includes all energy supplied in bringing one isotope from absolute zero to the temperature and pressure of the arbitrarily chosen standard state. It includes heat capacity, energy of ionization, energy of solution in the star, etc. and it has the same value for isotopes of the same element. Thus

$$\Delta E = \Delta E_0 + \Delta E_n. \quad (6)$$

The entropy difference may be written

$$\Delta S = S_{13} + S_{16} - S_{12} - S_{17}$$

and each of these entropies is given by the expression

$$S = S_0 + R \ln (T^{5/2}/P) + (3/2)R \ln M + R \ln (g) + f(T) + S_n \quad (7)$$

where  $S_0$  is the Sakur-Tetrode constant,  $M$  is the atomic weight, and  $g$  is the *a priori* probability of the nucleus and is equal to  $2i+1$  ( $i$  = nuclear spin);  $f(T)$  is a function which is the same for two isotopes. If we think of our gas as passing from a monatomic gas at absolute zero to one at the temperature,  $T$ , and pressure,  $P$ , there will be a contribution to the entropy equal to  $\int_0^T (C/T) dT$ , where  $C$  is the heat capacity over and above the  $5R/2$  for an ideal gas. This will include the entropy of ionization of the atom. Then if this gas is condensed into the body of a star there will be a further contribution to the entropy equal to the partial molal heat of condensation divided by the temperature. These additional contributions to the entropy, (the same for both isotopes) are included in  $f(T)$ .  $S_n$  is an additional entropy arising from the excitation of the nuclear energy levels. Thus the entropy change becomes

$$\Delta S = (3/2)R \ln \frac{M_{13}M_{16}}{M_{12}M_{17}} + R \ln \frac{g_{13}g_{16}}{g_{12}g_{17}} + \Delta S_n. \quad (9)$$

Now it is known from statistical mechanics that

$$\frac{\Delta E_n}{RT} - \frac{\Delta S_n}{T} = \ln \frac{f_{13}f_{16}}{f_{12}f_{17}}, \quad (10)$$

where  $f$  is the partition function for the nuclear energy levels.

Substituting these values of  $\Delta S$  and  $\Delta E$  in Eq. (2), we obtain

$$\ln \frac{C_{13}C_{16}}{C_{12}C_{17}} = -\frac{\Delta E_0}{RT} + (3/2) \ln \frac{M_{13}M_{16}}{M_{12}M_{17}} + \ln \frac{g_{13}g_{16}}{g_{12}g_{17}} + \ln \frac{f_{13}f_{16}}{f_{12}f_{17}}. \quad (11)$$

In this equation, the  $f$ 's and  $T$  are unknown; the ratio of the concentrations of two isotopes is known within about a factor of two;  $\Delta E_0$  is known from the exact atomic weights; the  $g$ 's can be guessed fairly well where they are not known; however, the term containing the  $g$ 's is relatively unimportant.

In order to estimate the possible error that may be introduced by the last term of Eq. (11), we shall make the assumptions that only one of these nuclei has energy levels and that these levels are equally spaced about one million volts apart. We assume that they are equally spaced for ease of computation and that they are a million volts apart because experimental evidence indicates that this is about the correct order of magnitude.<sup>1</sup> On the basis of these assumptions,  $f = (1 - e^{-h\nu/kT})^{-1}$ . Substituting the numerical values, we find that  $f$  for different temperatures is as follows:

$T$	$f$
$10^9$	$1-4.54 \times 10^{-5}$
$10^{10}$	0.233

Even if the levels are considerably closer together,  $\ln f$  is very small at  $10^9$  degrees. Moreover,  $f_{13}$  and  $f_{16}$  act in the opposite direction to  $f_{12}$  and  $f_{17}$  so that a partial cancellation of their contributions is probable. Thus we see that the term containing the  $f$ 's will hardly be important below temperatures of  $10^9$  degrees, and may be neglected.

We shall calculate the temperature assuming that the mixture of isotopes on earth is one representing equilibrium, and therefore solve Eq. (11) for the temperature, omitting the term containing the  $f$ 's. Then

$$T = -\frac{c^2\Delta M}{R \ln \left( \frac{M_{12}M_{17}}{M_{13}M_{16}} \right)^{3/2} \frac{g_{12}g_{17}}{g_{13}g_{16}} \frac{C_{13}C_{16}}{C_{12}C_{17}}}. \quad (12)$$

<sup>1</sup> E. Rutherford, *Phil. Mag.* **4**, 580 (1927); E. Rutherford, and J. Chadwick, *Proc. Camb. Phil. Soc.* **25**, 186 (1929); C. D. Ellis, and H. W. B. Skinner, *Proc. Roy. Soc.* **A105**, 185 (1924); C. D. Ellis, and W. A. Wooster, *Proc. Camb. Phil. Soc.* **22**, 844 (1925); W. Bothe, and H. Fränzl, *Zeits. f. Physik* **49**, 1 (1928); W. Bothe, *Zeits. f. Physik* **51**, 613 (1928); **63**, 38 (1930); H. Fränzl, *Zeits. f. Physik* **63**, 370 (1930); *Phys. Zeits.* **30**, 381 (1930); W. Bothe, and H. Becker, *Die Naturwiss.* **18**, 705 (1930); H. Pose, *Zeits. f. Physik* **60**, 156 (1930); **64**, 1 (1930); J. Chadwick, J. E. R. Constable, and E. C. Pollard, *Proc. Roy. Soc.* **A130**, 463 (1931); F. G. Houtermans, *Ergeb. d. Exat. Naturwiss.* (1930).

For reactions other than the special one considered, (1), an obvious substitution must be made for the atomic masses, statistical weights, and concentrations.

The values for the atomic masses, the relative abundances of the elements used, and the spins assumed are given in Table I. The notes give sources of

TABLE I.

Atom	$M$	$i$	$g$	Relative abundances	Note
Li <sup>6</sup>	6.012	1	3	1:12.9	1
Li <sup>7</sup>	7.012	3/2	4		2
B <sup>10</sup>	10.0135	1	3	1:4.1	3
B <sup>11</sup>	11.0110	3/2	4		4
C <sup>12</sup>	12.0036	0	1	400:1	5
C <sup>13</sup>	13.0037	1/2	2		6
N <sup>14</sup>	14.0083	1	3	700:1 (N)	7
N <sup>15</sup>	15.0032	3/2	4	410:1 (M & C)	8
O <sup>16</sup>	16.0000	0	1	1075:0.125:1 (N)	9
O <sup>17</sup>	17.0029	1/2	2		10
	(17.00135)				
O <sup>18</sup>	18.0065	0 or 1	1 or 3	630:0.2:1 (M & C)	11

<sup>1</sup> For atomic mass; Aston, Proc. Roy. Soc. **A115**, 487 (1927); spin, assumed; relative abundances for Li<sup>6</sup> and Li<sup>7</sup>, calculated from chemical atomic weight.

<sup>2</sup> For atomic mass; Aston, note 1; spin; A. Harvey and F. A. Jenkins, Phys. Rev. **35**, 789 (1930); L. P. Granath, Phys. Rev. **36**, 1018 (1930).

<sup>3</sup> For atomic mass; Aston, note 1; spin, assumed; relative abundances for B<sup>10</sup>:B<sup>11</sup> calculated from chemical atomic weight.

<sup>4</sup> For atomic mass; Aston, note 1; spin, assumed.

<sup>5</sup> For atomic mass; Aston, note 1; spin; A. S. King and R. T. Birge, Astrophys. J. **72**, 19 (1930).

<sup>6</sup> For atomic mass; R. T. Birge, Phys. Rev. **37**, 841 (1931); spin, assumed.

<sup>7</sup> For atomic mass; R. T. Birge, Phys. Rev. Suppl. **1**, 1 (1929); spin; L. S. Ornstein and W. R. van Wijk, Zeits. f. Physik **49**, 315 (1928); Rasetti, Nature **123**, 757 (1929), Proc. Nat. Acad. Sci. **15**, 515 (1929); relative abundances N<sup>14</sup>:N<sup>15</sup>; Naudé, Phys. Rev. **36**, 333 (1930), and calculated on basis of Mecke and Childs relative abundances for oxygen.

<sup>8</sup> For atomic mass; R. T. Birge, notes 6 and 7; spin, assumed.

<sup>9</sup> Spin; Mulliken, Phys. Rev. **32**, 880 (1928); relative abundances O<sup>16</sup>:O<sup>17</sup>:O<sup>18</sup>; S. M. Naudé, Phys. Rev. **36**, 333 (1930); R. Mecke and W. H. J. Childs, Zeits. f. Physik **68**, 362 (1931).

<sup>10</sup> For atomic mass; W. F. Giauque, Nature **124**, 265 (1929); J. Chadwick, J. E. R. Constable, and E. C. Pollard, Proc. Roy. Soc. **A130**, 463 (1931); H. C. Urey, Phys. Rev. **37**, 923 (1931); spin, assumed.

<sup>11</sup> For atomic mass; R. T. Birge, notes 6 and 7; H. D. Babcock and R. T. Birge, Phys. Rev. **37**, 233 (1931); spin, assumed.

the constants used. It is difficult to understand why there should be a discrepancy in the values for O<sup>17</sup>, but the weight of evidence appears to the writers to be in favor of the larger value and it is therefore given preference in the calculations.

The results calculated are given in Table II.

The successive columns give an arbitrary number for reference to be used in the discussion, the transmutation reaction, the change in mass for the reaction, the calculated temperatures using Naudé, Mecke and Child's relative abundances, and the change in mass calculated by assuming equilibrium at 10<sup>9</sup> degrees.

TABLE II.

No.	Reaction	$\Delta M$	$*T \times 10^{-9}$	$**T \times 10^{-9}$	$\Delta M$ calculated for $T = 10^9$ <sup>o</sup> (Naudé) (M and C)	
1	$\text{Li}^7 + \text{B}^{10} \rightarrow \text{B}^{11} + \text{Li}^6$	-0.0025	-25.6		0.0001	0.0001
2	$\text{Li}^7 + \text{C}^{12} \rightarrow \text{C}^{13} + \text{Li}^6$	+0.0001	+ 0.1		0.0008	0.0008
3	$\text{Li}^7 + \text{N}^{14} \rightarrow \text{N}^{15} + \text{Li}^6$	-0.0051	- 6.1	- 6.5	+0.0008	+0.0008
4	$\text{Li}^7 + \text{O}^{16} \rightarrow \text{O}^{17} + \text{Li}^6$	+0.0029 (+0.00135)	+ 2.6 (+ 1.2)	+ 2.9 (+ 1.3)	+0.0011	+0.0010
5	$2\text{Li}^7 + \text{O}^{16} \rightarrow \text{O}^{18} + 2\text{Li}^6$	+0.0065	+ 6.0	+ 6.2	+0.0011	+0.0011
6	$\text{B}^{11} + \text{C}^{12} \rightarrow \text{C}^{13} + \text{B}^{10}$	+0.0026	+ 3.6		-0.0007	-0.0007
7	$\text{B}^{11} + \text{N}^{14} \rightarrow \text{N}^{15} + \text{B}^{10}$	-0.0026	- 3.6	- 3.8	+0.0007	+0.0007
8	$\text{B}^{11} + \text{O}^{16} \rightarrow \text{O}^{17} + \text{B}^{10}$	+0.0054 (+0.00385)	+ 5.4 (3.8)	+ 6.0 (4.3)	+0.0010	+0.0008
9	$2\text{B}^{11} + \text{O}^{16} \rightarrow \text{O}^{18} + 2\text{B}^{10}$	+0.0115	+12.9	+13.8	+0.0009	+0.0008
10	$\text{C}^{13} + \text{N}^{14} \rightarrow \text{N}^{15} + \text{C}^{12}$	-0.0052	-350.2	+150.3	+0.0000	-0.0003
11	$\text{C}^{13} + \text{O}^{16} \rightarrow \text{O}^{17} + \text{C}^{12}$	+0.0028 (+0.00125)	+10.0 (+ 5.7)	+14.9 (+ 8.4)	+0.0003	+0.0002
12	$2\text{C}^{13} + \text{O}^{16} \rightarrow \text{O}^{18} + 2\text{C}^{12}$	+0.0063	-12.1	-11.0	-0.0005	-0.0006
13	$\text{N}^{15} + \text{O}^{16} \rightarrow \text{O}^{17} + \text{N}^{14}$	+0.0080 (+0.00645)	+29.8 (+24.1)	+35.6 (+28.7)	+0.0002	+0.0002
14	$2\text{N}^{15} + \text{O}^{16} \rightarrow \text{O}^{18} + 2\text{N}^{14}$	+0.0167	-28.5	-31.1	-0.0006	-0.0005
15	$2\text{O}^{17} \rightarrow \text{O}^{18} + \text{O}^{16}$	+0.0007 (+0.0038)	- 0.6 (- 3.5)	- 0.7 (- 4.0)	-0.0011	-0.0009

Temperatures given in parentheses are calculated on basis of mass of  $\text{O}^{17} = 17.00135$ .

\* Temperatures calculated using relative abundances of oxygen and nitrogen according to Naudé.

\*\* Temperatures calculated using relative abundances of oxygen (and nitrogen) according to Mecke and Childs.

The calculated temperature using either Naudé's ratios or Mecke and Child's ratios for the oxygen and nitrogen isotopes is not constant. The possible errors may be in (1) the relative abundances of the isotopes, (2) the atomic weights. The first of these can be excluded immediately for it would require very large changes in the relative abundances to bring most of these calculated temperatures to  $10^9$  degrees or less. The second source of error is very much more important but difficult to estimate, when the results are given in this way. It will be noticed that the two values assumed for the mass of  $\text{O}^{17}$  give quite large differences in calculated temperatures.

A better way to estimate the effects of uncertainties in the masses is to calculate the mass differences for the reactions assuming that the mixture is an equilibrium one at some temperature. We have taken this as  $10^9$  degrees because at that temperature known nuclear processes appear to be sufficiently rapid to permit the establishing of an equilibrium mixture.

Taking the values of  $\Delta M$  calculated as listed in Table II and taking Birge's value for the mass of  $\text{O}^{18}$  in terms of  $\text{O}^{16}$  as  $18.0065 \pm 0.0002$  we can calculate the mass differences of other pairs of isotopes and thus compare these with the mass differences determined from molecular spectra or by the mass spectrograph. For most of the reactions of Table II the masses are so badly known that it is possible to explain the whole variation as due to error in the masses. In Table III we list only those reactions for which the mass differences are sufficiently well known to indicate significant agreement or disagreement between calculated and observed values. In securing the calculated values from

TABLE III. Mass differences of pairs of isotopes assuming that the mixture is in equilibrium at  $10^9$  degrees.

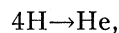
No.	Isotopes	Mass difference calc.	Mass difference observed
	$O^{18} - O^{16}$	(2.0065)	2.0065
9	$B^{11} - B^{10}$	1.0027	$0.9975 \pm 0.002$
8	$O^{17} - O^{16}$	1.0036	$1.0029 \pm ?$
11	$C^{13} - C^{12}$	1.0033	$1.0003 \pm 0.0013$
12	$C^{13} - C^{12}$	1.0035	$1.0003 \pm 0.0013$
13	$N^{15} - N^{14}$	1.0034	$0.9949 \pm 0.0033$
14	$N^{15} - N^{14}$	1.0036	$0.9949 \pm 0.0033$
10	$N^{15} - N^{14}$	1.0003	$0.9949 \pm 0.0033$
	or $C^{13} - C^{12}$	0.9949	$1.0003 \pm 0.0013$

these reactions we have used the mass difference of  $O^{18}$  and  $O^{16}$  as 2.0065 and then deduced the mass differences for two isotopes by assuming that the preceding calculated values are correct, except in the case of the last reaction. In this case we first took the experimental value of the  $C^{13} - C^{12}$  mass difference and calculated the  $N^{15} - N^{14}$  mass difference and second we took the  $N^{15} - N^{14}$  experimental value and calculated the  $C^{13} - C^{12}$  value. The number in the first column indicates the reaction of Table II used in the calculation.

Only in the case of the  $O^{17} - O^{16}$  mass difference is agreement indicated. Assuming other temperatures than  $10^9$ , we found equally bad agreement. We conclude that the observed relative abundances of nuclei are not in agreement with the hypothesis of a thermodynamic equilibrium at any temperature.

In conclusion we may say that we recognize that the extrapolation from the secure ground of thermodynamic experiment is very great and that unknown effects may be important, such as the effect of large radiation density at these temperatures. We feel also that the current theories in regard to the history of the sun with its probable large loss of mass favor the hypothesis that the relative abundances of nuclei are determined by their rates of conversion into radiation rather than the hypothesis that they represent a thermodynamic equilibrium mixture.

*Note added in proof:* Tolman<sup>2</sup> has made a similar calculation for the transmutation reaction,



and comes to the same conclusion as we do in this paper. Because of the very large discrepancy between the calculated and the observed values for the hydrogen in equilibrium with helium, his calculation is probably more conclusive than ours. The particular reactions which we discuss in this paper are particularly nice, however, because it is unnecessary to make any assumptions in regard to the absolute concentrations and because deviations from ideal solution laws do not enter into the calculations.

<sup>2</sup> R. C. Tolman, J. Am. Chem. Soc. **44**, 1902 (1922).