EQUILIBRIUM ABUNDANCES OF ISOTOPES.

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ABSTRACT.

The relative abundances of isotopes are used to determine the temperature and neutron concentration for an assembly (in thermodynamic equilibrium) in which the isotopes in their observed proportions would constitute an equilibrium mixture. The temperature of the assembly can be readily estimated graphically from figure 1 and the neutron concentration is also easily obtained. Different combinations of isotope-pairs give widely different values for the temperature and neutron concentration. Section 2 deals with a simplified assembly composed of electrons, positrons, nucleons and alpha-particles. The effect of electron-degeneracy is briefly discussed.

A study of the relative abundances of the elements and their isotopes is of great astrophysical interest, and to account theoretically for the observed abundances is an attractive cosmological problem though its solution for the present seems to be far off. When we examine the relative abundances of the elements and their isotopes we notice a few striking facts. The heavier elements are much more rare than the lighter ones and also that, whereas in the case of a light element there is one isotope which is more abundant than the others, in the case of a heavy element there are several isotopes which have approximately the same abundance. These are a few important facts which any satisfactory theory of the evolution of elements must explain. As a first attempt it was suggested by Weizsäcker (1938) that the elements were formed at some pre-stellar stage as a result of thermal equilibrium between nuclei of all sorts, neutrons, protons, electrons and positrons. The properties of a nuclear assembly in thermal equilibrium have been discussed in a recent paper by Chandrasekhar and Henrich (1942). Urey and Bradley (1931) in an earlier discussion concluded that the present abundances do not represent an equilibrium mixture at any temperature. There seems little doubt that non-equilibrium reactions must have played a dominating rôle in determining the present abundances. All the same, a detailed study of a nuclear assembly in thermal equilibrium is of interest not only *per-se*, but also as a prelude to the study of non-equilibrium processes. The present paper is confined to an equilibrium assembly, and the discussion of this problem has been carried further than has been done previously.

1. Let us consider an assembly in thermodynamic equilibrium at temperature T containing isotopes of elements X, $\overline{X}$, etc. If X_1 and X_{r+1} denote the isotopes of the element X *differing in mass number by r units*, then (representing neutrons by O),

$$X_1+rO \rightleftarrows X_{r+1}+U, \qquad \ldots \quad (1)$$

and we have

$$\frac{y_1}{y_{r+1}}=\left\{\frac{1}{n_0/q_0}\left(\frac{2\pi M_0RT}{h^2A^2}\right)^{\frac{3}{2}}\right\}^r e^{-U/RT}, \qquad \ldots \quad (2)$$

$$y_1=\frac{x_1}{q_1M_1^{3/2}}, \qquad y_{r+1}=\frac{x_{r+1}}{q_{r+1}M_{r+1}^{3/2}}$$

where R denotes the gas constant, A the Avogadro number, h the Planck constant, and x_1, x_{r+1} and n_0 denote the concentrations (number of particles per unit volume) of the isotopes X_1, X_{r+1} and neutrons respectively. M_1, M_{r+1} and M_0 represent their (exact) masses and q_1, q_{r+1} and q_0 their weight factors ($q_0 = 2$). When the reaction proceeds in the direction $X_1+rO \rightarrow X_{r+1}$ the energy liberated is

$$U = [(M_1+rM_0)-M_{r+1}]c^2, \qquad \text{(3)}$$

c being the velocity of light.

If the element X possesses (besides X_1 and X_{r+1}) another isotope X_{s+1}, then, using equation (2) for the pairs (X_1, X_{r+1}) and (X_1, X_{s+1}), and eliminating n_0 between them, we have

$$T = \frac{-\Delta c^2}{2{\cdot}3R\left\{\frac{1}{r}\,\mathrm{Log}\left(\frac{y_1}{y_{r+1}}\right)-\frac{1}{s}\,\mathrm{Log}\left(\frac{y_1}{y_{s+1}}\right)\right\}}, \qquad \text{(4)}$$

where

$$\Delta = \frac{M_1-M_{r+1}}{r}-\frac{M_1-M_{s+1}}{s}. \qquad \text{(5)}$$

In the case of $r = 1$, $s = 2$ we have

$$T = \frac{-\Delta_1 c^2}{2{\cdot}3R\,\mathrm{Log}\left(\frac{y_1 y_3}{y_2{}^2}\right)}, \qquad \text{(6)}$$

$$\Delta_1 = M_1+M_3-2M_2.$$

The special feature of equation (4) is that only isotopes of one element are used, but it is applicable only when the element has three (or more) isotopes. It cannot, therefore, be applied to an element of *odd atomic number* as such elements possess only two isotopes. However, we can always determine the temperature of the assembly by using any two elements, each of which has at least two isotopes. Let X_1, X_{r+1} be two isotopes of an element X and $\overline{X}_1$, $\overline{X}_{s+1}$ be two isotopes of $\overline{X}$, then using (2) for the pairs (X_1, X_{r+1}) and ($\overline{X}_1$, $\overline{X}_{s+1}$), we have

$$T = \frac{-\Delta c^2}{2{\cdot}3R\left\{\frac{1}{r}\,\mathrm{Log}\,\frac{y_1}{y_{r+1}}-\frac{1}{s}\,\mathrm{Log}\,\frac{\bar{y}_1}{\bar{y}_{s+1}}\right\}}, \qquad \text{(7)}$$

$$\Delta = \frac{M_1-M_{r+1}}{r}-\frac{\overline{M}_1-\overline{M}_{s+1}}{s},$$

and for the special case of $r = s = 1$, it reduces to

$$T = \frac{-\Delta_1 c^2}{2{\cdot}3R\,\mathrm{Log}\left(\frac{y_1}{y_2}.\frac{\bar{y}_2}{\bar{y}_1}\right)}, \qquad \text{(8)}$$

$$\Delta_1 = (M_1-M_2)-(\overline{M}_1-\overline{M}_2).$$

The neutron concentration of the assembly can be determined by substituting the value of the temperature in equation (2). This is as far as we can go without recourse to further knowledge about the chemical composition of the assembly.

Equation (7) was first used by Urey and Bradley to calculate the equilibrium temperatures using the relative abundances of the isotopes of lithium, boron, carbon, nitrogen and oxygen. The calculated values were both positive and negative and ranged from 3×10^{10} ° to -3×10^{11} °. They, therefore, concluded that the terrestrial abundances of isotopes do not represent an equilibrium mixture at any temperature.

For the case of two isotopes differing in mass numbers by unity we write equation (2) in the form

$$\text{Log}\,\frac{y_1}{y_2} = \left(\text{Log}\,.\frac{q_0}{n_0}+\frac{3}{2}\,\text{Log}\,\frac{2\pi M_0RT}{h^2A^2}-\frac{M_0c^2}{2{\cdot}3RT}\right)+\frac{(M_2-M_1)c^2}{2{\cdot}3RT}, \quad \ldots \quad (9)$$

$$= \frac{M_2-M_1}{T^1}+b,$$

where

$$T^1 = \frac{2\cdot3RT}{c^2} \sim 2{\cdot}13\times10^{-13}T, \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

and

$$b = \text{Log}\,.\frac{q_0}{n_0}+\frac{3}{2}\,\text{Log}\,\frac{2\pi M_0RT}{h^2A^2}-\frac{M_0c^2}{2{\cdot}3RT}. \quad \ldots \quad \ldots \quad (11)$$

For two isotopes which differ in mass number by r, we have instead of (9)

$$\frac{1}{r}\,\text{Log}\,.\frac{y_1}{y_{r+1}} = \frac{M_{r+1}-M_r}{rT^1}+b. \quad \ldots \quad \ldots \quad \ldots \quad (9')$$

In figure 1 we represent the isotope-pairs for the various elements from Li to Kr by plotting $(M_{r+1}-M_1)/r$ as abscissa and $y = \frac{1}{r}\,\text{Log}\left(\frac{y_1}{y_{r+1}}\right)$ as ordinate. For elements heavier than Kr the masses are not known with an accuracy necessary for the purpose. The tangent of the angle with the Y-axis by the line joining any two points (whether referring to different elements or to two isotope-pairs of the same element) in the figure gives the equilibrium temperature for the two pairs of isotopes.

The neutron concentration corresponding to any two isotope-mixtures is obtained by noting on the Y-axis the intercept b made by the line joining the two points representing the isotope-pairs. If T be the temperature determined by the slope of the lines mentioned above, the neutron concentration is given by

$$n_0 = q_0\left(\frac{2\pi M_0RT}{h^2A^2}\right)^{\frac{3}{2}}\cdot10^{-\left(b+\frac{M_0c^2}{2\cdot3RT}\right)}. \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

In the figure the origin has been taken at $(M_{r+1}-M_1)/r = 1$ and hence if b^1 be the intercept on the Y-axis in the figure, we have

$$n_0 = q_0\left(\frac{2\pi M_0RT}{h^2A^2}\right)^{\frac{3}{2}}\cdot10^{-\left(b^1+\frac{(M_0-1)c^2}{2\cdot3RT}\right)}. \quad \ldots \quad \ldots \quad (12')$$

When T is negative n_0 is imaginary. As an illustration of the use of (14), we have from the figure $b^1 = 0{\cdot}86$ for the carbon (12, 13)-boron (10, 11) pairs and $n_0{\sim}2\times10^{31}$, and hence the *lower limit* to the density of the assembly becomes $\frac{M_0n_0}{A}{\sim}3{\cdot}3\times10^7$ gm./c.c.

It may be noted that, even in the case of an element possessing more than three isotopes, the equilibrium temperatures determined by combining the isotope-pairs in different ways among themselves do not come out to be the same. In particular in the case of Ti one calculated temperature is lower than the other temperatures by a factor of 100. Above all, we get absurd results in the case of argon

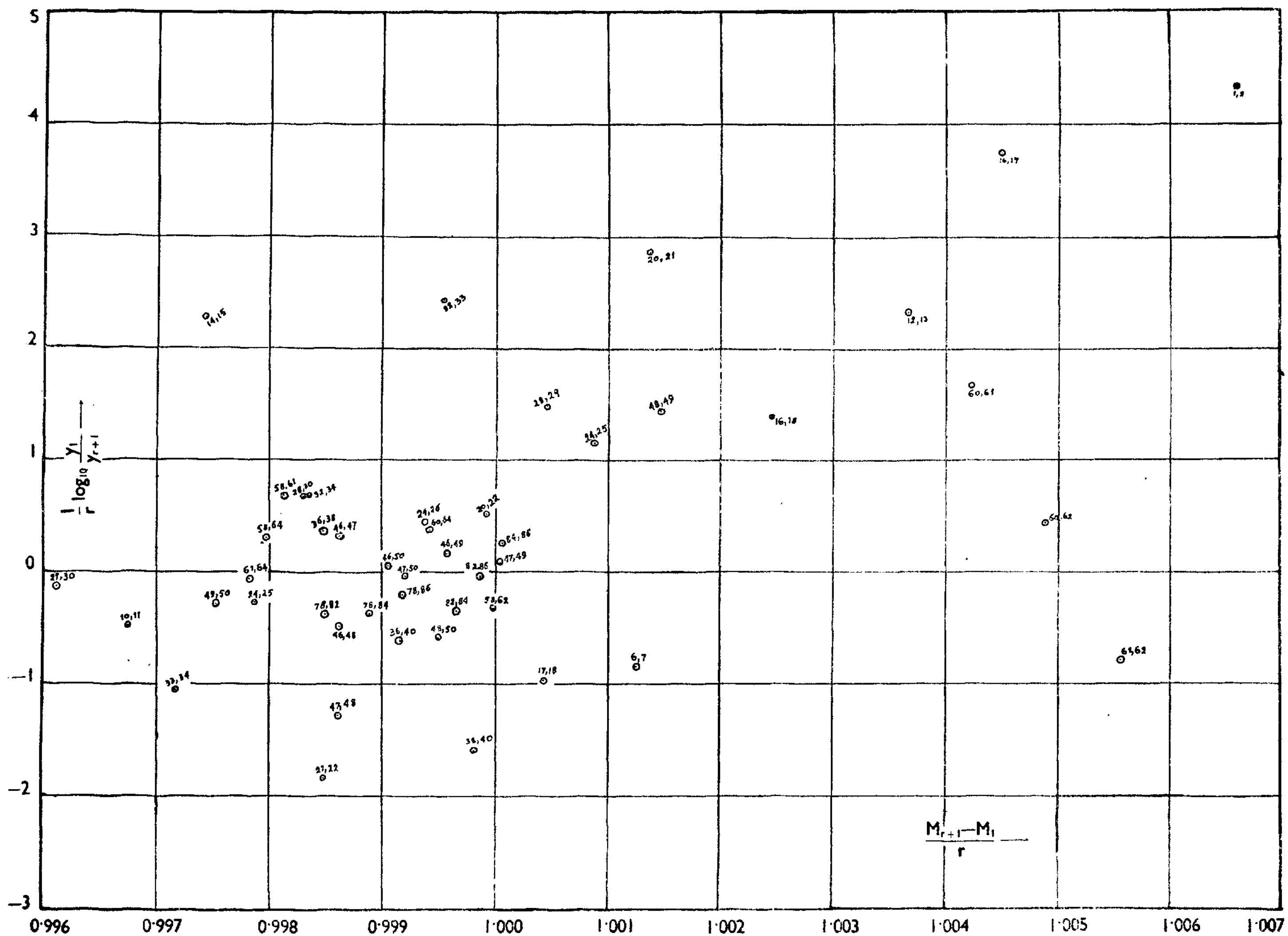

Fig. 1.

The abscissa represents $\left(\frac{M_{r+1}-M_1}{r}\right)$ gm. and the ordinate $\frac{1}{r}\log_{10}\frac{y_1}{y_{r+1}}$. Each point in the figure is labelled by the mass numbers of the pair representing it.

and nickel. Also the calculated equilibrium temperatures are not always higher for the heavier elements than for the lighter ones. The relative abundances of even the isotopes of the same element do not represent an equilibrium ratio.

As mentioned above for any two isotope-pairs the temperature of the hypothetical assembly can be determined and also the relevant neutron concentration. Fig. 3 shows Log n_0 and T obtained for the various combinations of the isotope-pairs extending to S^{32}. (Log n_0, T)-values are shown in the figure by 'circles' and 'crosses'. The circles represent the values obtained by taking the two isotope-pairs of the same element (O, Ne, Mg, Si and S) whereas in the case of crosses the two isotope-pairs belong to different elements. The curve in Fig. 3 is theoretical and has been obtained in a manner to be described later.

2. We now introduce a somewhat drastic simplification, in that we suppose the assembly to consist of elementary particles (viz. electrons, positrons, neutrons and protons) and α-particles, all other nuclei are ignored. Such an assembly is of some interest as in the actual universe (it appears) helium is far more abundant than any other element with the possible exception of hydrogen. However, the above simplification imposes restrictions on the densities and temperatures possible for the assembly. Consider the reaction

$$4\alpha \rightleftarrows O_8^{16} + U \quad \ldots \quad (13)$$

which gives

$$\frac{n_\alpha}{n} = \frac{64}{n_\alpha{}^3}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{9}{2}} e^{-U/kT} \quad \ldots \quad (14)$$

where M is the mass of the proton and n the concentration of oxygen. For the concentration of oxygen to be small compared to that of helium it follows that for any temperature T

$n_\alpha \ll n_\alpha{}^0$, where $n_\alpha{}^0$ is given by

$$\text{Log } n_\alpha{}^0 = \frac{3}{2}\text{ Log}\left(\frac{2\pi Mk}{h^2}\right) + \text{Log } 4 + \frac{3}{2}\text{ Log } T - \frac{U}{2{\cdot}3\times 3\times kT}$$

or

$$\text{Log } n_\alpha{}^0 = 37{\cdot}38 + \frac{3}{2}\text{ Log } T - \frac{24{\cdot}37}{T}, \quad \ldots \quad (15)$$

where T is in the units of 10^9 degrees.

In the following table the values of Log $n_\alpha{}^0$ and Log $(4Mn_\alpha{}^0)$ are given for three different temperatures :—

TABLE I.

Temperature $\times 10^9$	Log $n_\alpha{}^0$	Log $(4Mn_\alpha{}^0)$ or Log ρ . (ρ in gm./c.c.)	Log n_0*
5	33·55	10·37	28·99
8	35·69	12·51	33·47
10	36·44	13·26	35·01

The above limitation on the concentration of α-particles leads to a restriction on the neutron concentration of the assembly. We readily find with the help of equation (33) described in the sequel that $n_\alpha \ll n_\alpha^0$ implies $n_0 \ll n_0^*$ (n_0 is the neutron concentration) where n_0^* is given by

$$\text{Log } n_0{}^* = \frac{3}{4}\left[52{\cdot}10+2 \text{ Log } T - \frac{74{\cdot}23}{T}\right] \quad \ldots \quad \ldots \quad \ldots \quad (16)$$

We now revert to the discussion of the simplified assembly. *Let the concentrations of neutrons, protons, α-particles, electrons and positrons be n_0, n_p, n_2, n^- and n^+ respectively. The reactions that occur are:

$$e^- + e^+ \rightleftarrows \text{radiation}, \quad \ldots \quad (17)$$

$$P + e^- \rightleftarrows 0, \quad \ldots \quad (18)$$

$$2P + 20 \rightleftarrows \alpha. \quad \ldots \quad (19)$$

Since the assembly as a whole is electrically neutral

$$n^- = n^+ + n_p + 2n_2. \quad \ldots \quad (20)$$

The equation governing the concentrations of electrons and positrons is

$$n^+ n^- = 4\cdot\left(\frac{2\pi m_e kT}{h^2}\right)^3 \cdot e^{-2m_e c^2/kT}. \quad \ldots \quad (21)$$

And similarly for protons, electrons and neutrons we have

$$\frac{n_p n^-}{n_0} = 2\cdot\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} e^{-c^2(M_1 - M_0)/kT}, \quad \ldots \quad (22)$$

where m_e, M_1 and M_0 are the masses of electron, hydrogen atom and neutron respectively.

Finally the equation governing the concentration of α-particles in terms of the proton and the neutron concentrations is

$$\frac{n_p{}^2 n_0{}^2}{n_2} = 2\,.\left(\frac{1}{4}\right)^{\frac{3}{2}}.\left[2\,.\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}\right]^3 e^{-D_2/kT}, \quad \ldots \quad (23)$$

where $D_2 = c^2(2M_p + 2M_0 - M_2)$.

From equations (20), (21), (22) and (23) the relation between n_p and n_0 is

$$\frac{1}{n_p^3} - \frac{1}{{}_p n}\left(\frac{A}{B^2}\cdot\frac{1}{n_0^2} + \frac{1}{Bn_0}\right) - \frac{2n_0}{BC} = 0\,, \quad \ldots \quad (24)$$

where

$$\left.\begin{aligned} A &= 4\cdot\left(\frac{2\pi m_e kT}{h^2}\right)^3 \cdot e^{-2m_e c^2/kT} \\ B &= 2\cdot\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} e^{-c^2(M_1 - M_0)/kT} \\ C &= 2\cdot\left(\frac{1}{4}\right)^{\frac{3}{2}}\cdot\left[2\cdot\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}\right]^3 e^{-D_2/kT} \end{aligned}\right\} \quad \ldots \quad (25)$$

* This case has been considered by Chandrasekhar and Henrich. We have stated here the temperature-density limitations of such an assembly. Explicit expressions for the various limiting cases are given later.

We have calculated the proton concentration n_p for various neutron concentrations at three different temperatures, 5, 6·5, and 8×10^9°K. The relation between n_p and n_0 as given by (24) is represented in Fig. 2 for three different temperatures. In

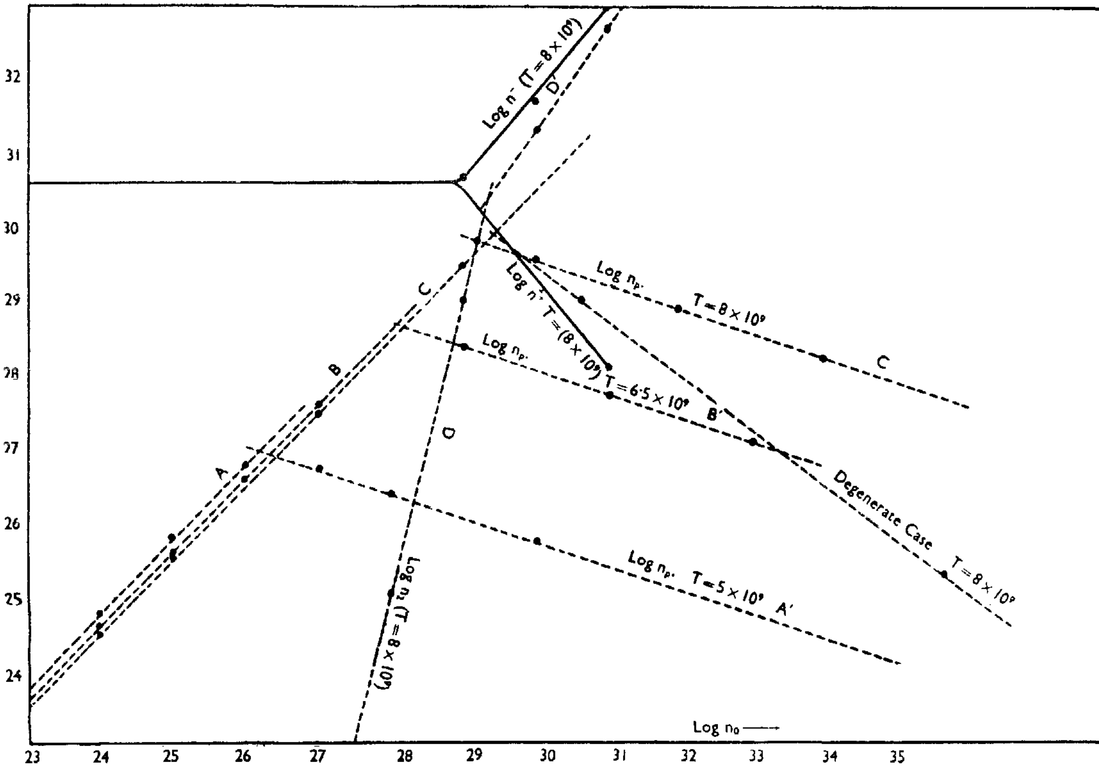

Fig. 2

the same figure we have also plotted Log n^-, Log n^+ and Log n_2 against Log n_0 for temperature 8×10^9°K. For a fixed temperature, the proton concentration increases, as the neutron concentration increases, reaches a maximum value and then decreases. Thus for any temperature T there is a maximum permissible value $\bar{n}_p$ for the proton concentration.

Assuming for a moment that the assembly contains only electrons and positrons (and radiation), the electron and positron concentration will be given by

$$n^- = n^+ = 2\cdot\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}}\cdot e^{-m_e c^2/kT}. \quad \ldots \quad \ldots \quad (26)$$

The electron concentration will stay at practically the above value so long as the proton and the α-particle concentrations are small compared to it. Under these conditions from equation (22) it follows that n_p will be directly proportional to n_0. Substituting the value of n^- from (26) we have

$$\text{Log } n_p = \text{Log } n_0 + \frac{c^2(M_0 - M_p)}{2{\cdot}3kT}, \quad \ldots \quad \ldots \quad \ldots \quad (27)$$

$$= \text{Log } n_0 + \frac{3{\cdot}76}{T}$$

where T is in units of 10^9 degrees.

From equations (23) and (27) we find that the α-particle concentration is determined by

$$n_2 = n_0^4 \cdot \frac{1}{2}\left[\frac{h2}{2\pi MkT}\right]^{\frac{9}{2}} \cdot e^{(4M_0-M_2)c^2/kT}, \quad \ldots \quad \ldots \quad (28)$$

or

$$\text{Log } n_2 = 4 \text{ Log } n_0 + \overline{102}\cdot 36 - \frac{9}{2}\text{ Log } T + \frac{149\cdot 60}{T} \quad \ldots \quad \ldots \quad (29)$$

The validity of the above equations depends on the electron concentration being very much greater than the proton and the α-particle concentrations. Under the condition (29) shows that the α-particle concentration is smaller than the proton concentration. The dotted lines A, B and C represent Log n_p against Log n_0 according to (27) for temperatures 5, 6·5 and 8×10^9°K. respectively. The dotted line D in Fig. 2 represents Log n_2 according to equation (29) for the temperature 8×10^9°K.

At the other extreme we consider the case when the electron concentration instead of being very large compared to the α-particle concentration is practically twice the α-particle concentration ($n^- \sim 2n_2$). Substituting $n_2 = \frac{n^-}{2}$ in equation (23) and replacing n^- in terms of n_0 and n_p with the help of (22) we have

$$3 \text{ Log } n_p = -\text{Log } n_0 + \text{Log } 2 + 6 \text{ Log } T + 6 \text{ Log } \left(\frac{2\pi k}{h^2}\right) + \frac{9}{2}\text{ Log } M$$
$$+\frac{3}{2}\text{ Log } m_e - \frac{c^2(3M_p+M_0-M_2)}{2\cdot 3kT}, \quad \ldots \quad \ldots \quad (30)$$

or $$3 \text{ Log } n_p = 130{\cdot}52 + 6 \text{ Log } T - \text{Log } n_0 - \frac{138\cdot 20}{T} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (31)$$

Dotted lines A', B' and C' in Fig. 2 represent Log n_p against Log n_0 as given by the above equation for temperatures 5, 6·5 and 8×10^9°K. respectively. Under the condition $n^- \sim 2n_2$ assumed above the proton concentration for a fixed temperature varies as $n_0^{-\frac{1}{3}}$ and again it is very small compared to the α-particle concentration. The positron concentration is no longer nearly equal to the electron concentration but n^+ is much smaller than n^- the ratio being given by

$$\frac{n^+}{n^-} = n_0^{-\frac{8}{3}} \cdot 2^{\frac{2}{3}} \cdot \left(\frac{2\pi kT}{h^2}\right)^4 \cdot m_e M^3 \cdot e^{-2c^2(4M_0-M_2+3m_e)/3kT} \quad \ldots \quad \ldots \quad (32)$$

The α-particle concentration in terms of the neutron concentration with the help of (22) and (23) is given by

$$n_2 = 2^{-\frac{1}{3}} n_0^{\frac{4}{3}} \cdot \frac{hm_e}{(2\pi RT)^{\frac{1}{2}}.M^{\frac{3}{2}}} \cdot e^{c^2(4M_0-M_2)/3kT}, \quad \ldots \quad \ldots \quad (33)$$

or $$\text{Log } n_2 = \frac{4}{3}\text{ Log } n_0 + \overline{15}{\cdot}28 - \frac{1}{2}\text{ Log } T + \frac{49{\cdot}86}{T} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (34)$$

The dotted line D' in Fig. 2 represents Log n_2 against Log n_0 for $T = 8\times10^9$°K. for the case $n^- \sim 2n_2$. The co-ordinates of the point of intersection of equations (27) and (31) give for any temperature T the maximum proton concentration $\bar{n}_p$ and the corresponding neutron concentration $\bar{n}_0$. We have

$$\text{Log } \bar{n}_p = 32{\cdot}63 + \frac{3}{2}\text{ Log } T - \frac{33{\cdot}65}{T}, \quad \ldots \quad \ldots \quad \ldots \quad (35)$$

and

$$\text{Log } \bar{n}_0 = 32 \cdot 63 + \frac{3}{2} \text{ Log } T - \frac{37 \cdot 40}{T} \quad \ldots \quad \ldots \quad \ldots \quad (36)$$

It follows, therefore, that the first limiting case, when the electron concentration is very large compared to the proton and the α-particle concentrations, corresponds to $n_0 \ll \bar{n}_0$. The other limiting case for which $n^- \sim 2n_2$ corresponds to $n_0 \gg \bar{n}_0$.

In the foregoing discussion we have assumed the electron gas to be non-degenerate. However, it is easy to show that when $n_0 \gg \bar{n}_0$ the electrons constitute a degenerate gas. This introduces some modification in the above results, for instance, the fall of the proton concentration with increasing neutron concentration becomes more rapid. The modified curve for a temperature 8×10^9°K. is shown in Fig. 2.

We have noticed in Section 1 that we can calculate (n_0, T) values by (1) utilising, as has been done by Chandrasekhar and Henrich, the observed relative abundances of three isotopes of an element (examples of such elements are provided by O, Ne, Mg, Si and S) and (2) by using the relative abundance of two isotopes for each of any two elements. For brevity of description we shall call these (n_0, T) values as 'observed values', as an observational element enters in their calculation. These values are shown in Fig. 3, already referred to in Section 1. The continuous curve

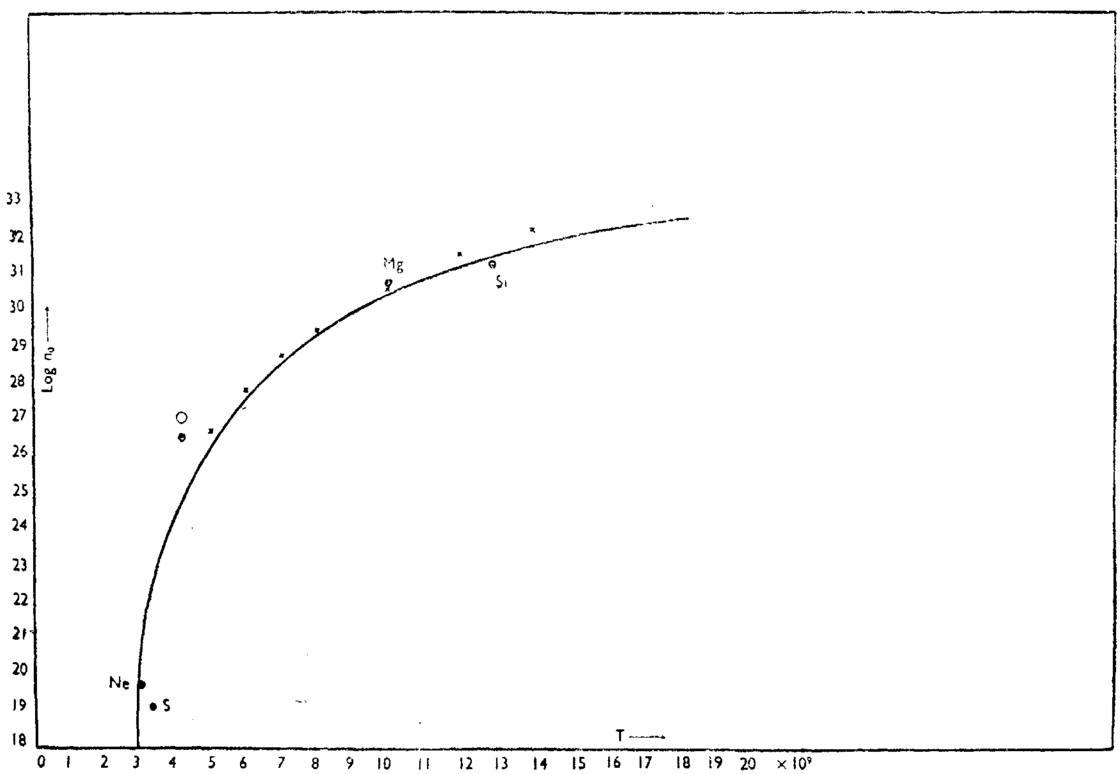

FIG. 3. The abscissa represents temperature and the ordinate Log n_0. The circles correspond to the two isotope-pairs of the same element (O, Ne, Mg, Si and S) and the crosses to the two isotope-pairs belonging to different elements. The continuous curve is theoretical and represents equation (36).

represents the relation between temperature and the neutron concentration when the proton concentration has its maximum permissible value: the curve is represented by equation (36). The run of the observed values follows the theoretical curve and as already remarked by Chandrasekhar and Henrich that this is a result whose significance appears worth inquiring into. We hope to take this up in a subsequent paper.

The writers take this opportunity to express their thanks to Prof. D. S. Kothari for suggesting the problem and his continued guidance throughout the course of this work and to Sir K. S. Krishnan, Kt., for valuable discussions.

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