

volume expansion from room temperature to just below the transition point is about 10.2 per cent, which is comparable with the density decrease of 9 per cent suggested by Robertson and Brockway as likely to occur if the triclinic crystal had taken a monoclinic structure by a slight rearrangement. The abrupt volume change at the transition point is 3.65 c.c./mole, corresponding to about 2.4 per cent of the volume at room temperatures. After passing through the transition point, the volume still increases to a conspicuous maximum value (178.5 c.c./mole) at about 130° C. and then decreases to a minimum value (160.5 c.c./mole), showing negative thermal expansion, melting finally at 165.5° C. The volume change at the melting point is about 30 c.c./mole, corresponding to 8 per cent of the volume at room temperatures.

The ratio of entropy changes at the transition and melting points measured by Parks and others is nearly equal to the ratio of the corresponding volume changes given above. Examples of similar unusual negative thermal expansion are known in the cases of ammonium iodide⁴ (− 60° C. ∼ − 40° C.), deuterioammonium bromide (ND₄Br)⁵ (− 70° C. ∼ − 58° C.), ice⁶ under the pressures of about 1,500 kgm./cm.² (− 10° C. ∼ − 2° C.), and a few other substances in the neighbourhood of their transition points. We are now making an X-ray analysis of the structure in the region between the transition and the melting points. The examination of the effect of substitution of the methyl groups by chlorine atoms will also be interesting in connexion with the dielectric study by White and Bishop⁷.

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¹ Brockway and Robertson, *J. Chem. Soc.*, 1324 (1939).

² Pauling, *Phys. Rev.*, **36**, 430 (1930).

³ Spaght, Thomas and Parks, *J. Amer. Chem. Soc.*, **55**, 882 (1932).

⁴ Smits and Müller, *Z. phys. Chem.*, B, **36**, 140 (1938).

⁵ Smits, Pollender and Kröger, *Z. phys. Chem.*, B, **41**, 215 (1938).

⁶ Bridgman, "Physics of High Pressure".

⁷ White and Bishop, *J. Amer. Chem. Soc.*, **62**, 16 (1940).

Nitrogen Afterglow

IN a recent communication in *Nature*, L. Herman and R. Herman¹ have given an account of their spectroscopic study of the complex afterglow in nitrogen immediately after the discharge is stopped. These short-lived afterglows have also been extensively studied by Kaplan². In this connexion, Herman and Herman remark that it seems difficult to explain the characteristics of the complex afterglow as recorded by them with the help of the theory of active nitrogen proposed by me³. It appears, however, that these authors have missed the very important point that my theory was developed for the long-lived Lewis-Rayleigh afterglow, and not for the short-lived Kaplan afterglow, which is quite a distinct phenomenon. According to my hypothesis, the Lewis-Rayleigh afterglow phenomena, for example, the long life, the rate of decay, ionization, the characteristic spectrum (selected bands from the first positive group), etc., can be very satisfactorily explained if it is assumed that the active substance in the glow is N₂⁺(X') ions. The Kaplan afterglows, however, contain besides N₂⁺(X') ions other particles

such as N₂⁺(A'), N, N' which are responsible for the complex nature of the short-lived spectrum. It may, however, be mentioned in this connexion that in some of his experiments Kaplan has observed the persistence of the first negative bands for several seconds after the discharge is stopped. This provides a direct proof of the presence of N₂⁺ ions, at least in the first stage of the afterglow. According to my hypothesis, the N₂⁺ ions continue their existence even after the short-lived afterglows have died out and produce the phenomena associated with the Lewis-Rayleigh afterglow.

For explaining the afterglow characteristics M. and Mme. Herman prefer the Cario-Kaplan mechanism⁴. This necessitates the presence of atomic nitrogen. There is no doubt that nitrogen molecules (N₂) are dissociated in the strong discharge and excited nitrogen atoms are produced. This, indeed, is proved by some of Kaplan's spectrograms⁵. But the presence of such atoms when the discharge is on, or for a very short time thereafter, is a different matter from their persistence for several hours producing the Lewis-Rayleigh afterglow, remembering that atomic nitrogen is known to have very short life.

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¹ Herman, L., and Herman, R., *Nature*, **161**, 1018 (1948).

² Kaplan, J., papers published in the *Physical Review* from 1932 onwards.

³ Mitra, S. K., "Active Nitrogen—A New Theory" (Monograph), Indian Association for the Cultivation of Science, Calcutta (1945). See also *Nature*, **154**, 212 and 576, 831 (1944).

⁴ Cario, G., and Kaplan, J., *Z. Phys.*, **58**, 769 (1929).

⁵ Kaplan, J., *Nature*, **149**, 273 (1942).

Evolution of the Universe

IN checking the results presented by Gamow in his recent article on "The Evolution of the Universe" [*Nature* of October 30, p. 680], we found that his expression for matter-density suffers from the following errors: (1) an error of not taking into account the magnetic moments in Eq. (7) for the capture cross-section, (2) an error in estimating the value of α by integrating the equations for deuteron formation (the use of an electronic analogue computer leads to $\alpha = 1$), and (3) an arithmetical error in evaluating ρ_0 from Eq. (9). In addition, the coefficient in Eq. (3) is 1.52 rather than 2.14. Correcting for these errors, we find

$$\rho_{\text{mat.}} = \frac{4.83 \times 10^{-4}}{t^{3/2}}.$$

The condensation-mass obtained from this corrected density comes out not much different from Gamow's original estimate. However, the intersection point $\rho_{\text{mat.}} = \rho_{\text{rad.}}$ occurs at $t = 8.6 \times 10^{17}$ sec. $\approx 3 \times 10^{10}$ years (that is, about ten times the present age of the universe). This indicates that, in finding the intersection, one should not neglect the curvature term in the general equation of the expanding universe. In other words, the formation of condensations must have taken place when the expansion was becoming linear with time.

Accordingly, we have integrated analytically the exact expression¹:

$$\frac{dl}{dt} = \left[\frac{8\pi G}{3} \left(\frac{aT^4}{c^2} + \rho_{\text{mat.}} \right) l^2 - \frac{c^2 l_0^2}{R_0^2} \right]^{1/2},$$

with $T \propto 1/l$ and $R_0 = 1.9 \times 10^9 \sqrt{-1}$ light-years. The integrated values of ρ_{mat} and ρ_{rad} intersect at a reasonable time, namely, 3.5×10^{14} sec. $\cong 10^7$ years, and the masses and radii of condensations at this time become, according to the Jeans' criterion, $M_c = 3.8 \times 10^7$ sun masses, and $R_c = 1.1 \times 10^8$ light-years. The temperature of the gas at the time of condensation was 600°K ., and the temperature in the universe at the present time is found to be about 5°K .

We hope to publish the details of these calculations in the near future.

Our thanks are due to Dr. G. Gamow for the proposal of the topic and his constant encouragement during the process of error-hunting. We wish also to thank Dr. J. W. Follin, jun., for his kindness in performing the integrations required for the determination of α , on a Reeves Analogue Computer. The work described in this letter was supported by the United States Navy, Bureau of Ordnance, under Contract NOrd-7386.

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¹ Gamow, G., *Phys. Rev.*, **70**, 572 (1946).

Relative Abundances of Potassium and Argon in the Earth's Surface Materials

E. Bleuler and M. Gabriel¹ have recently shown that potassium-40 decays radioactively in two different ways. Apparently a potassium-40 nucleus can decay either by emitting a beta-ray, or by capturing one of its own *K*-electrons and emitting a gamma-ray. In the first case the resulting product is calcium-40, and the latter argon-40. 1.9 capture processes occur for every beta-ray emission.

The beta-ray emission of potassium-40 has been known for many years, and the accepted half-life of the reaction is $(7 \pm 1) \times 10^8$ yr. The effect of the *K*-electron capture process is to reduce the total half-life of potassium-40 to about 2.4×10^9 yr. E. Gleditsch and T. Graf² have pointed out the importance of this fact in geophysical theory, and have shown, for example, that the heating effect of potassium-40 in the earth's crust 2.4×10^9 years ago must have been about two hundred times greater than the total radioactive heating at the present day. So far as I am aware, however, the problem of the amount of argon-40 which would have been produced by the reaction in the life-time of the earth has not been considered.

Potassium is an abundant element in the earth's surface materials. If, following F. W. Clarke³, we consider an outer spherical shell of the earth 10 miles deep, its composition is: atmosphere, 0.03 per cent; ocean, 7.08 per cent; solid crust, 92.80 per cent. The total percentage of potassium is about 2.4, and since the relative abundance of potassium-40 in natural potassium⁴ is 0.012 per cent, the present percentage of potassium-40 in the shell is $1.2 \times 10^{-4} \times 2.4 = 2.9 \times 10^{-4}$ per cent. Argon constitutes about 1.44 per cent of the atmosphere by mass; hence its percentage in the total shell is $0.03 \times 1.44 \times 10^{-2} = 4.3 \times 10^{-4}$ per cent, or 1.5 the present amount of potassium-40.

If we take a figure of 2.4×10^9 years as a reasonable estimate of the age of the crust, it follows that the original amount of potassium-40 would have been 2^{10} , or about 1,000 times greater than the present amount. Of this quantity, approximately two-thirds would have been transformed to argon; that is, the total quantity of argon present in the surface materials of the earth should be about 430 times the known amount of argon in the atmosphere.

It might be assumed that the bulk of the argon generated in the solid crust was retained in the crust, but even this assumption will only reduce the discrepancy. From the quantity of sodium retained in the ocean, F. W. Clarke⁵ estimates that an amount of solid material equal to about 5 per cent of the postulated shell has undergone erosion. It is hard to imagine that, if during this process the sodium was extracted from the rock, the argon would not also escape, and this process would supply a quantity of argon more than twenty times that of atmospheric argon. If, on the other hand, we assume that the argon of the atmosphere⁶, which is 99.6 per cent A^{40} , is derived from the eroded layer only, we easily arrive at an age of the crust of about 1.3×10^9 years, which differs by a factor of about 2 from the accepted estimates of geological ages. A correction to these results should be applied for the amount of argon in solution in the ocean; but it can easily be shown that this correction is of no importance.

Two other possibilities may be considered: (1) that argon-40 is itself unstable and changes to some other element; or (2) that argon escapes from the atmosphere into space. Both processes seem to be highly improbable. At the lower end of the periodic table, the mass defect of the stable elements increases with atomic number, and this consideration alone seems to rule out the decay of argon-40 to any other stable element. Apart from this, argon is very commonly used in Wilson cloud chambers, and it is highly unlikely that its hypothetical decay would have escaped detection. The escape of argon from the atmosphere would seem also to involve the escape of nitrogen, oxygen and probably carbon dioxide. This seems very unlikely.

It is known, however, that cosmic rays produce atomic disintegrations; but again it can be shown that the amount of argon which could be destroyed by this process is probably exceedingly small. It is estimated by Powell and his co-workers that, at a height of 3,000 m., fifteen explosive atomic disintegrations occur per c.c. per diem in a nuclear photographic emulsion. This means that in 2.4×10^9 years, 1.3×10^{13} atoms per c.c. would have been disintegrated, assuming, of course, that the cosmic ray intensity remained constant. There are, however, nearly 10^{23} atoms per c.c. of the emulsion; hence about one atom in 10^{10} of the emulsion would disintegrate. The effect on the average chemical composition of the emulsion is obviously insignificant. Argon, owing to its distribution throughout the atmosphere, may behave in a different manner; but it seems improbable that a factor of at least 10^9 could be introduced. Also we are faced with the problem of disposing of the large quantities of helium and hydrogen which would result from the destruction of the argon. These, of course, might escape from the atmosphere.

We are accordingly forced to conclude that either the assumed data for the breakdown of potassium-40 and its abundance in the surface materials are incorrect, or that the present estimates of the age of