

Next, the values of p_c/t_c for the substances in each group were plotted against the number

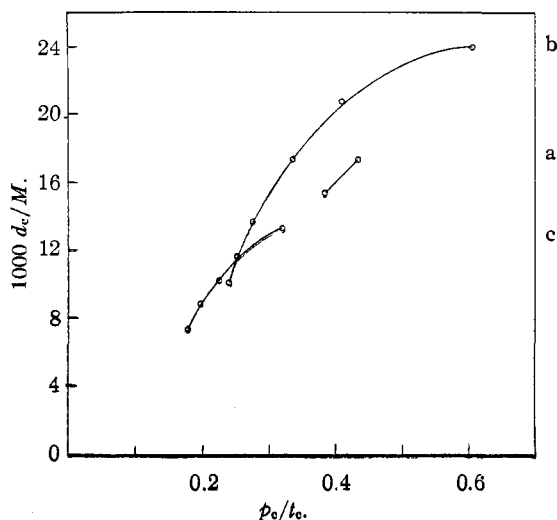


Fig. 1.—Groups: a, helium; b, neon; c, argon.

of hydrogen atoms, and all known values but that of hydrogen sulfide fall into a consistent series of curves.

This seems to indicate that the reported value for hydrogen sulfide is incorrect. In order to place it on the curve it is necessary to assume that its critical pressure is 84 atmospheres instead of the reported 88.9 atmospheres, critical temperature being assumed correct. Using these curves the unknown value for hydrogen fluoride is interpolated.

From these estimates values of n were computed and then the critical molecular densities were plotted against p_c/t_c in Fig. 1.

It will be noticed that the neon and argon groups each begin with an inert gas (non-polar), then include three polar substances, and are completed with a non-polar substance. From the relationships just discussed it would seem safe to assume that the critical molecular density is but little affected by the polarity of any substance. The effect of polarity is seen in the reduction of the values of p_c/t_c (atmospheres per degree) for polar substances with the resultant increase in the value of n .

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COMMUNICATIONS TO THE EDITOR

THE ISOTOPES OF POTASSIUM AND LITHIUM IN SARATOGA MINERAL WATER AND CRYPTOZOON

Sir:

The abundance ratio for the isotopes of potassium in ocean water and in most minerals has been shown to be $K^{39}/K^{41} = 14.20$ to 14.25 [Brewer, THIS JOURNAL, 58, 365-370 (1936)]. Kelp and agar, in comparison to ocean water, possess an appreciably higher concentration of K^{41} . Since no significant deviation from the average has been detected in the large number of rocks and minerals investigated, it was felt that it would be of interest to test the isotope ratio in old mineral formations of presumably marine plant origin.

The most prevalent organism of the Ozarkian period (upper Cambrian time) was calcareous (lime secreting) algae or seaweed grown half a billion years ago, known as Cryptozoon [H. P. Cushing and R. Ruedemann, New York State

Museum Bull. 169 (1914); R. T. Colony, Legislative Document No. 70 (1930); Oskar Baudisch, "Comparative Spectroscopic Studies of *Cryptozoon proliferum* and the Mineral Springs of Saratoga Springs, N. Y."]. These very striking and spectacular fossils are exposed as reef beds in the Saratoga area in New York. What we see here today is a portion of the old sea-bottom elevated into land area. In the shallow warm water of the Cambrian sea grew the multitudinous colonies of Cryptozoon and seaweed. Accordingly, tests have been made of the abundance ratio of isotopes of potassium, lithium and rubidium in these formations as well as the overlying shale and the Saratoga Springs mineral waters.

The K^{39}/K^{41} abundance ratios from the rocks and waters tested are given in Table I.

The results just presented show an appreciable concentration for K^{41} in the mineral water and

a small concentration for the cryptozoon formations. The overlying shale, however, does not differ appreciably from that normally present in rocks of this type.

TABLE I

| Source | Per cent. total K | Abundance ratio | Per cent. K^{41} |
|-------------------|-------------------|-----------------|--------------------|
| Mineral Water | | | |
| Geyser | 3.40 | 13.85 \pm 0.1 | 6.76 |
| Coesa | 3.73 | 13.85 \pm .1 | 6.76 |
| Hathorn | 6.03 | 13.85 \pm .1 | 6.76 |
| Cryptozoon | | | |
| <i>Undulatum</i> | Small | 13.95 \pm 0.1 | 6.69 |
| <i>Proliferum</i> | | 13.95 \pm .1 | 6.69 |
| Trenton limestone | Trace | 14.00 \pm .1 | 6.67 |
| Shale overlying | ? | 14.20 \pm .03 | 6.58 |

The abundance ratio for the isotopes of lithium in the Saratoga mineral waters and cryptozoon was $Li^7/Li^6 = 11.8 \pm 0.1$. In comparison the abundance ratio for the majority of other lithium sources tested ranged between 11.6 and 11.8. The lithium isotope ratio in Saratoga water, therefore, does not differ appreciably from normal. The amount of rubidium present was so small that an accurate abundance ratio could not be obtained, although the results showed that the ratio did not differ appreciably from normal, which is $Rb^{85}/Rb^{87} = 2.6$.

The results just described are of interest in that they represent the only inorganic source so far discovered in which the K^{41} content is appreciably higher than normal. It is significant that the lithium isotope ratio does not deviate correspondingly. It would appear, in consequence, that the process which concentrated K^{41} does not concentrate Li^7 ; this precludes most physical mechanisms [Brewer, *J. Chem. Phys.*, 4, 350 (1936)] for the isotope effect since they would be expected to result in larger deviations for lithium than for potassium. The simplest interpretation for these results is, therefore, that the salt deposits from which the water arises are of marine plant origin rather than that any isotope effect is occurring at the present time which would result in an abnormal abundance ratio for potassium.

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RECEIVED JUNE 14, 1937

POLAR GROUP ORIENTATION IN LINEAR POLYMERIC MOLECULES. THE OMEGA-HYDROXYDECANOIC ACIDS

Sir:

From dielectric constant-frequency data obtained with dilute solutions the average times of relaxation and molecular weights of zein, gliadin, lignin, hemoglobin, etc., have been determined. In these cases the molecular weight values so obtained agree with figures which have been obtained by the application of the classical diffusion, sedimentation and osmotic pressure methods, and the identity of the electrical and molecular kinetic units is established.

However, there is a class of high molecular weight polymeric substances which at least in dilute solutions did not give a measurable dispersion of dielectric constant in a frequency interval where an effect of this kind would be expected if electrical and kinetic or chemical units are assumed to be equivalent, but the data do show a definite and constant orientation contribution of the solute molecules to the dielectric constant of the solution over a considerable range of frequency.

The ω -hydroxydecanoic acid polymers are typical of substances of this class. Their dielectric behavior in dilute solution can be explained if it is assumed that in the long molecules there are polar groups at regularly recurring intervals which can orient in the applied field. Since there are nine C-C bonds between each pair of polar ester groups, free rotation of the latter seems probable. In this event the mean square sum of n group moments is approximately equal to the sum of the squares of the several individual moments; thus

$$\mu^2 = \mu_{OH}^2 + \mu_{COOH}^2 + (n - 1) \mu_{COOC}^2$$

In this equation, μ is the average dipole moment of the polymeric molecules. Since, in Debye units, $\mu_{OH} \cong 1.7$; $\mu_{COOH} \cong 1.4$; $\mu_{COOC} \cong 1.8$, this equation reduces to $\mu^2 = 4.85 + (n - 1) 3.24$. We give in tabular form below electric moment data for six polymeric ω -hydroxydecanoic acids. The observed moments have been calculated from dielectric constant, density and refractive index data for dilute benzene solutions obtained in this Laboratory. Dielectric constant measurements were made at wave lengths $\lambda = 79$ m. and $\lambda = 180$ m.

It appears that the individual polar ester groups spaced in regular fashion along the length