On the Chemical Differences Between Nitrogen Isotopes

We wish to report on some preliminary experiments concerning the possibility of a chemical separation of the nitrogen isotopes. Although our work in this field has not yet been completed, a publication by E. Ogawa[1] causes us to publish a short summary of our conclusions at this time.

The analyses were performed with a mass spectrometer in the laboratory of Professor Bleakney in Princeton University as described by Wahl, Huffman and Hipple.[2] As these authors found indications of a small difference in vapor pressure between $N^{14}H_3$ and $N^{15}H_3$ and because distillation, if effective, would be by far the easiest way to obtain a change in the isotope rates, we first experimented on this possibility. We used the method by which Wahl and Urey investigated the vapor pressure ratios in water.[3] Distillations were carried out without boiling at different temperatures, the final residue varying between 1/15 and 1/70 of the amount of starting material. No definite trend of the vapor pressure ratio with temperature could be distinguished. As an average value for the pressure ratio $P(N^{14}H_3) : P(N^{15}H_3)$ we obtained 1.0025 in six experiments, with an average error of 0.003. It may be mentioned that Wahl, Huffman and Hipple give 1.0052 as their best figure for this proportion. It is probable that $N^{14}H_3$ is slightly more volatile than is $N^{15}H_3$, but we feel convinced that the vapor pressure ratio differs from unity only a few tenths of a percent at most. Therefore the nitrogen separation by the distillation of ammonia does not seem promising. Next we investigated the reaction of $N^{15}H_3 + N^{14}H_4OH \rightleftharpoons N^{14}H_3 + N^{15}H_4OH$ for which Wahl, Huffman and Hipple had reported a possible but uncertain concentration of the heavy isotope in the NH_4OH. Purified air was passed through a bottle containing concentrated ammonia till only a small fraction of the original amount of ammonia was left in the solution. From the isotopic composition of the original material and the final sample we calculated the equilibrium constant from the Rayleigh formula. We found that the N^{15} possibly concentrates slightly in the liquid but the effect is so small at any rate, that it could not be recognized with certainty.

Then we turned to the exchange reaction $N^{15}H_3 + N^{14}H_4{}^+ \rightleftharpoons N^{14}H_3 + N^{15}H_4{}^+$, already considered by Urey and Greiff.[4] We started from a concentrated solution of ammonium chloride, to which at intervals we added small amounts of sodium hydroxide solution. A current of purified air removed the NH_3 formed after each addition. At the moment we have the analysis of only one run in which we started with 0.61 mole NH_4Cl and finished with 0.052 mole. During this process the ratio of $N^{14}N^{15}$ decreased from 250.2 to 233.8. (These numbers are not corrected for diffuse background and hence the analysis of the original material does not agree with the generally accepted value). This gives for the fractionation factor the value 1.027. We hope to check this value soon with other samples we have prepared, but we have been forced to abandon this matter temporarily because it will not be possible to obtain analyses by the mass spectrometer for some time.

The last experiment described seems to be the same as one performed by Ogawa, an extract of which publication is printed in *Nature*.[5] From the figures given fractionation factors ranging from 1.7 to 1.8 can be calculated which are very much higher than ours. We feel quite certain that as large an increase in concentration of N^{15} could not remain undetected by the mass spectrometer and that Ogawa's values, which are obtained from atomic weight determinations, are too high.

The importance of finding the most favorable reaction is clearly seen from the calculations by Urey and Greiff on the efficiency of a column as depending on the separating factor of the process used.

Finally, it may be mentioned that a preliminary experiment on the exchange $HCN^{15} + CN^{14-} \rightleftharpoons HCN^{14} + CN^{15-}$ indicated that N^{15} was concentrated in the HCN gas to quite an appreciable extent.

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Effect of Hydrocarbons at Low Temperatures on Slow Neutrons

Investigations of the properties of slow neutrons passed through paraffin at various temperatures have established the fact that temperature equilibrium must be attained at least partially.[1-5] The somewhat remarkable character of this fact, considering the size of the energy losses and the probable mechanisms involved led the authors to investigate the phenomenon in more detail, first with paraffin and later with pure normal heptane.

The apparatus used is shown in Fig. 1. It consists of a metal Dewar (brass and monel metal walls 1 mm thick) surrounded by a large cylindrical block of paraffin in which the radon-beryllium neutron source (100–220 millicuries) was imbedded. The inside diameter of the Dewar was 14 cm and the height one meter. A soft glass Dewar (3 cm outside diameter) was mounted along the axis of the metal Dewar, to allow irradiation of the cylindrical silver targets without alteration of the temperature of the hydrocarbon. The cylindrical copper container shown was used for the heptane only, and was the same length as the silver targets (11 cm), and 4.5 cm thick, with a wall thickness of 0.3 mm. Copper-constantan thermocouples were

TABLE I.

Thickness of paraffin cylinder	Temperature (°K)	Activity (% 300°K activity)
1.5	300°–200°	100 ±2
	100°– 11°	113 ±2
2.5	70°	94 ±2
	21°	86 ±2
3.5	90°	103 ±2
	55°	71 ±2

soldered to the top and bottom of the container to measure the temperature of the hydrocarbon. The targets were silver cylinders 13 mm in diameter, 11 cm long, and 0.25 mm thick, which could be slipped tightly over the thin wall tube counter used for measuring the activities. In the work with paraffin, the copper container for the heptane was removed and replaced by cylinders of paraffin of different thicknesses.

The procedure was to cool the contents of the Dewar to 20°K by keeping liquid hydrogen around the container for approximately 20 minutes. The hydrogen was then allowed to boil away and readings were taken when the temperature of the hydrocarbon had risen to 25°K, thus insuring the absence of any liquid hydrogen in the Dewar. Readings of the silver activities were taken continuously, as the Dewar warmed, over a period of eighteen hours. The results for normal heptane are shown in Fig. 2 in which the circles show the measured activity (140 seconds period). The solid curve was calculated from the equation

$$A = \delta e^{-\gamma T^{-\frac{1}{2}}}(1 - e^{-\eta T^{-\frac{1}{2}}}),$$

in which A is the silver activity, δ, γ and η are constants, and T is the absolute temperature of the hydrocarbon. The assumptions on which the equation is based are (a) that the neutrons are at the temperature of the hydrocarbon, (b) that the proton capture cross section is proportional to the reciprocal of the neutron velocity, and (c) that the silver capture cross section obeys the same law. The constant η is evaluated from the thickness of the silver targets and the cross section, 36×10^{-24} cm², from the data of Amaldi and Fermi[6] for the capture by silver of the neutrons
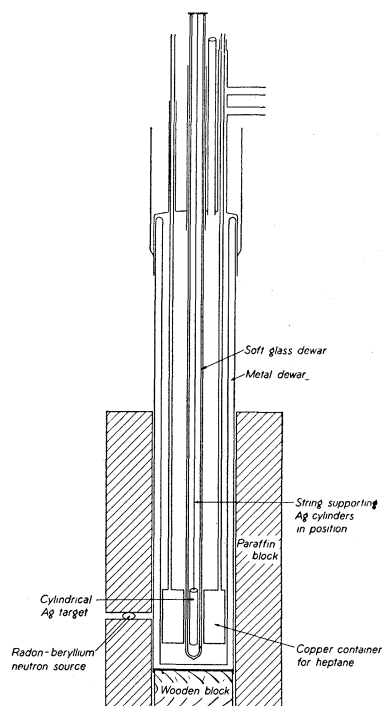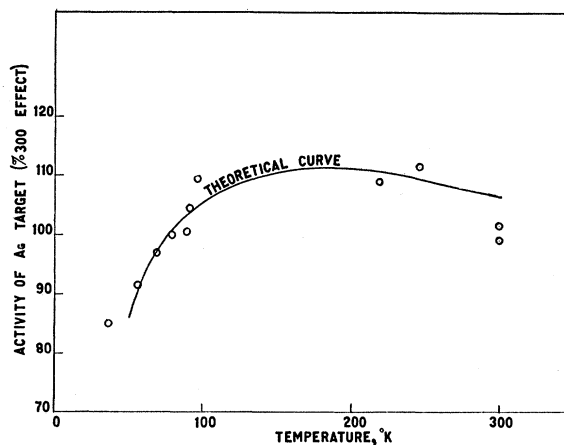

FIG. 1.

FIG. 2.

exciting the 140 seconds silver activity. The data seem to be in essential agreement with these assumptions.

The data obtained in some preliminary work with paraffin cylinders, are presented in Table I.

The 1.5 cm cylinder caused an increase in the activity, which appeared between 200° and 100°, and was relatively constant from 100° down to liquid helium temperatures (4°K); the 2.5 cm cylinder showed a small decrease, slightly dependent on temperature at 70° and below; and the 3.5 cm cylinder showed a rapid decrease between 90° and 60°. Though none of these results were obtained over as wide a range of temperatures as those for the heptane, they are all in agreement with the heptane results, and the assumptions listed above.

All of the above results apply to the thermal neutrons (those absorbed by 0.3 mm Cd) which excite the 140 seconds silver activity. A series of experiments with a 0.3 mm thick cadmium shield around the silver targets showed that at least 92 percent of the activity disappeared on interposition of the cadmium shield, roughly independent of the temperature (20°–300°K) of the surrounding hydrocarbon cylinder. The activity with the cadmium shield interposed was too small to measure accurately. This large cadmium absorption effect may be connected with the fact that the majority of the neutrons pass through approximately 2 mm of soft glass and 2 mm of brass and monel metal before striking the target.

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