would fall within this range. If it can be shown that the mobility of the Cl ion is the same in all 0.1 *N* solutions of the rare earth chlorides, the low transference number of gadolinium is indicative of a lower ion mobility. Conductivity measurements are necessary for exact conclusions.

It does not seem possible under any circumstances that the mobility of the gadolinium ion at 0.1 *N* is greater than that of either the samarium or the neodymium ions. These results thus seem to contradict both Kendall and Hopkins, who found gadolinium concentrating at the cathode end of their migration tubes when in a mixture with samarium. They were working with 0.5 *N* solutions, however, and at such widely different concentrations results are hardly comparable. Hopkins could get no evidence of separation of samarium from neodymium, which is as might be expected from the identical values of their transference numbers.

If the relatively small differences in mobility as indicated by the transference numbers of the three rare earth ions investigated is characteristic of all the rare earth ions, it is obvious that material separation of rare earth compounds can hardly be achieved through an ionic migration method.

Summary

The transference numbers of the neodymium, samarium and the gadolinium ions, measured in 0.1 *N* solutions of their chlorides at 25° by the moving boundary method, are 0.442, 0.442 and 0.433, respectively.

The significance of the transference numbers is discussed from the point of view of mobility and ionic hydration.

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Further Studies in the Rare Gases. II. The Diffusion of Helium through Crystalline Substances and the Molecular Flow through Rock Masses[1]

BY WILLIAM D. URRY

In the determination of geologic time by the helium–uranium–thorium ratio, it is important to ascertain a factor expressing the possibilities of migration of helium in the substance under investigation. Thus, Paneth and Urry[2] have shown that the loss of helium from the iron meteorites on heating at 1000° for several hours corresponds to the surface helium only. In corroboration of this fact the following experiments on iron and steel

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(1) "Further Studies of the Rare Gases. I. The Permeability of Various Glasses to Helium," appeared in THIS JOURNAL, **54**, 3887 (1932). This second paper presents the negative results obtained with metals and the mechanism and rate of flow through rock masses. A mathematical term is derived expressing the fineness of grain of a rock.

(2) Heliumuntersuchungen IX, *Z. physik. Chem.*, **A152**, 127 (1931).

have now been made. On account of the reported possibility of the formation of a bismuth helide[3] the diffusion of helium through bismuth was also investigated with the same negative result as holds for iron and palladium at all temperatures, the last metal having been investigated by Paneth and Peters.[4] In the case of bismuth the effect of excitation of the helium was determined.

The Non-Passage of Helium through Metals

The analytical methods employed in the purification and determination of helium with a limit of detection of 10^{-10} cc. have been referred to in Part I of this series and are described in a series of papers by Paneth and co-workers.[5] The purification and storage of helium was described in Part I, the apparatus here employed being identical except for the replacement of the glass-test device by the metal-test apparatus.

In Fig. 1 A is a glass container about 6 cm. in diameter and 18 cm. long closed at one end by a ground glass joint B, the male being closed with a tight fitting rubber bung C, picein being used to obtain vacuum tightness. The metal tube D under investigation, closed at the one end, is soldered or brazed at E to the copper tube H which is cooled down to the joint E by the metal water jacket I. This water jacket serves the double purpose of maintaining the solder joint cold and preventing any portion of the tube H from direct contact with the helium in A. A small porcelain tube F fits loosely around D and is wound with the heating element. The leads are sufficient support and pass through the mercury contact seals G. The tube H ends in a metal to glass ground joint K and the glass cap so formed carries the thermocouple leads and a connection through a stopcock to the analysis apparatus. Such a metal to glass joint can be made as completely vacuum tight as the usual glass to glass. The high vacuum side thus consists of only a solder joint and ground joints. L is an aluminum electrode, the tube under investigation forming the second electrode in the discharge experiments. The whole is immersed in water to a level M.

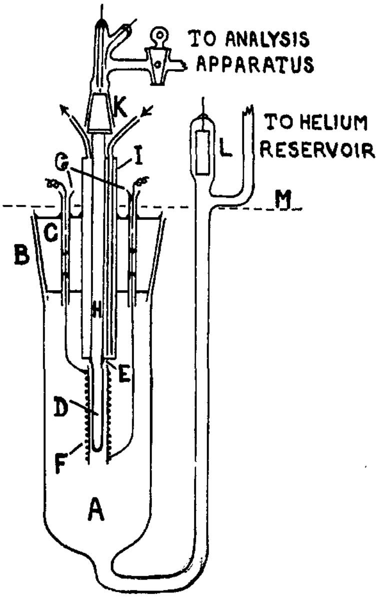

Fig. 1.

The reservoir side was evacuated and the analysis side kept on the pump while the tube was heated (120° for bismuth and 700° for iron) for two days. To test for tightness the container A was filled with air and twenty-hour runs made at the above temperatures, the vacuum in D being maintained by immersing one of the charcoal tubes on the analysis apparatus in liquid air. By an analysis of the transpired air for helium and neon the order of 10^{-7} cc. air per hour could

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[3] Morrison, *Nature*, **120**, 224 (1927).

[4] Heliumuntersuchungen III, *Z. Physik. Chem.*, **B1**, 253 (1928).

[5] See references, THIS JOURNAL, **54**, 3888 (1932).

have been detected in the event of a leak. The limit of detection of helium was 10^{-9} cc. by spectroscopic observation of the residual gas in a 0.1 mm. McLeod capillary.

Table I records the experimental results for both iron and bismuth tubes of 1 mm. wall and 6 mm. outside diameter, 60 mm. long. Appended also are the results of passing a discharge through the helium from the tube to the electrode L, the supply being a 60 cycle, 2 kw., 20,000 volt transformer arranged to supply about 500 watts at 15,000 volts.

TABLE I

BISMUTH TUBE NO. 1

Expt.	Description	He press., mm.	Time, hrs.	Temp., °C.	Result
1	After initial control experiment	35	2	120	$<10^{-9}$ He
	Time for establishment of equilibrium	35	15	120	
2	Experiment	35	3	120	$<10^{-9}$ He
3	Increase of helium pressure	125	5	120	About 10^{-9} He
	Evacuated both sides (two runs)	0	4	120	$<10^{-9}$ He
	Establishment of equilibrium	134	8	120	
4	Experiment	134	4	120	$<10^{-9}$ He
5	With 500 watt, 15,000 v. discharge	23	4	120	1.9×10^{-7} He
6	With above discharge in 63 mm. of hydrogen. After "clean up" of hydrogen pure helium was left	...	4	110	About 4×10^{-6} hydrogen, and 2.9×10^{-7} He
7	Heating only in 63 mm. of hydrogen After "clean up" of hydrogen pure helium was again left	...	4	110	About 10^{-6} hydrogen and 2.9×10^{-7} He
	Evacuated and heated	0	10	120	
8	Control experiment	0	4	120	9×10^{-8} He, no hydrogen

IRON TUBE NO. 3

Expt.	Description	He press., mm.	Time, hrs.	Temp., °C.	Result
	Establishment of equilibrium	100	10	620	
1	Experiment	100	4	650	$<10^{-9}$ He
	Establishment of equilibrium	100	10	640	
2	Experiment	120	5	700	$<10^{-9}$ He
3	Experiment	200	3	700	$<10^{-9}$ He

With bismuth and iron there is no diffusion of helium within our present limits of detection under normal conditions and a considerable range of temperature. It is interesting to note, however, that helium passes through bismuth in the excited state. The existence of a volatile bismuth hydride having been definitely established,[6] it was thought of interest to determine the passage of hydrogen through bismuth during discharge. This experiment happened to follow on the excited helium experiment. A quite conclusive amount of hydrogen passed through but of especial interest is the fact that after the "Clean-up effect" of the hydrogen in the McLeod capillary of the analysis apparatus even more helium was found to have been freed from the bismuth than passed through during the

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(6) Paneth and Winternitz, *Ber.*, **51**, 1728 (1918).

discharge in helium. Such a result may have an explanation in that during excitation helium may pass into the mass of the tube owing to the formation of an excited bismuth-helium compound. At the conclusion of the discharge such helium remained in the bismuth and was swept out by the passage of hydrogen through the bismuth in the following experiment. Such a procedure has been found to occur with glasses.[7] After the first experiment in the discharge it was found impossible to remove completely the helium from a bismuth tube.

The Adsorption of Helium on Steel.—Three specimens of ground tool steel of approximately the same surface extent but of different volumes were sealed up in 247.0 mm. of helium for three months at room temperature. They were then separately analyzed by solution in hydrochloric acid according to the method of Paneth and Urry.[2] Within the limit of detection of 10^{-9} cc. of helium all three gave negative results. The specimens had a total surface of about 27 sq. cm. and volumes of 3.7, 2.8 and 0.95 cc. Even assuming a true surface for steel and a unit cell length of 2.8 Å. units, with one atom of helium to each unit cell, the adsorption alone would be of the order of 10^{-3} cc. per specimen. Such a result is significant in that it excludes the possibility of the adsorption or absorption of helium by the iron meteorites when they might come into a helium-rich atmosphere and substantiates on one more point the reliability of the age determinations of the iron meteorites.[8]

The Leakage of Radioactive Helium from Rocks and Minerals.—Whereas the fact that highly radioactive material tends to lose its helium, even on grinding, is not attacked here, it has been a mistake in the past to carry over such a statement to the case of the ordinary rocks and minerals. Thus, that a loss should occur on grinding or heating such material as uraninites, etc., which may contain up to 10 cc. of helium per gram is to be expected. Such material certainly does not retain all its radioactive helium during geologic time. Since preliminary work has shown that the helium method applied to ordinary rocks yields age results comparable with other methods, it is important to investigate the retaining power of such specimens for helium. The results appear to be diametrically opposed to the findings with the radioactive material referred to above, but it must be remembered that the total helium content of ordinary rocks rarely exceeds 10^{-4} cc. per gram. Two fine-grained specimens of basalt and felsite on removal from the copper mines in the Upper Peninsula, Michigan, were immediately sealed up in air-free oxygen.[9] 'After three months, the specimen tubes were opened under mercury and the gas con-

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(7) Further Studies in the Rare Gases. I.

(8) *Z. Elektrochem.*, **36**, 727 (1930).

(9) I wish to express my thanks to Professor C. M. Carson, Director of the Chemistry Department, Michigan College of Mining and Technology, Houghton, Mich., for placing at my disposal the necessary facilities for this part of the experiment. The preparation of air-free oxygen has been described by Paneth and Peters, *Z. physik. Chem.*, **134**, 353 (1928).

tent analyzed for helium. Upon analysis small traces of neon and helium in the ratio found in the air were obtained, probably from traces of air left in the rock. This does not invalidate the conclusions, however, for an excess of 10% of helium over that in the neon–helium mixture obtained from pure air can be spectroscopically detected. Of the 10^{-8} cc. of the mixture found, 2.5×10^{-9} cc. is helium (neon to helium, 3 to 1 in the atmosphere). An excess of 2.5×10^{-10} cc. of helium over this quantity could be detected and hence the loss per three months per specimen is $<2.5 \times 10^{-10}$ cc. The complete data are given in Table II together with the helium content of a Keweenawan basalt analyzed by the flux method described by Paneth and Urry.[2] It will be noted that whether the sample is taken in one piece, several small pieces, or finely powdered, the analysis yields the same helium content, and hence there was no loss of helium during the twenty-four hours between the time of grinding and the time of fluxing, during one hour of which the powder was *in vacuo*.

TABLE II

Specimen	Type	Weight and surface	Helium loss per year per gram, cc.	Loss per 100 years as % of total content
11	Keweenawan basalt	8 g., about 13 sq. cm.	$<1.1 \times 10^{-10}$	0.05
25	Keweenawan felsite	8 g., about 12 sq. cm.	$<1.1 \times 10^{-10}$	0.03

ANALYSIS OF PIECE AND POWDERED SPECIMENS OF A KEWEENAWAN BASALT

Specimen	Remarks	Specimen		Total helium content per gram, cc.
23	Highest helium content of 20 Keweenawan basalts	1	1.96 g. in one piece	38.98×10^{-5}
		2	1.96 g. in 19 pieces	38.90
		3	1.96 g. finely powdered	39.34

The Passage of Helium through Rocks.—The following experiments show that a rock mass acts as a porous membrane of widely differing porosity according to the type of rock or mineral. A single crystal, at least of quartz, however, does not permit the passage of helium and since the radioactive points may be considered as existing throughout the crystal lattices of many crystals which go to make up the rock mass, the measurement of the rate of flow of helium, *per se*, through the rock specimens will not yield much information as to possible losses of radioactive helium. There is some evidence that in special cases the radioactivity is to some extent concentrated on the crystal surfaces and hence in the fine capillaries. Leaching experiments have shown that such may be the case particularly with highly radioactive material, but such material has been shown definitely to be unsuitable for helium ratio determinations. The measurement of the rate of gas flow as treated here, however, does give us very definite evidence as to the structure of rock masses, the size and number of fine capillaries and hence the state of division of a mineral. Any loss of helium from the rock itself is most likely to occur through these fine capillaries and hence a knowledge of their dimensions is valuable.

Figure 2 illustrates the apparatus employed to determine the rate of flow of helium through ground slices of material and again merely replaces the apparatus previously used for the passage of helium through metals. The use of helium allows the measurement of very small gas flows. A is the same container that was used for the apparatus in Fig. 1, this having been converted for the present use. The glass tube B joined to the analysis apparatus through the stopcock C ends in a plane ground flange D. The sliced and flat ground specimen E is affixed to this plate with stopcock grease and to ensure a high degree of tightness, mercury can be run up into the container A until it stands level with the top of the specimen, forming a mercury seal to the already well-fitting joint between D and E. Care was taken that in fixing the specimen to the plate no grease covered the portion of the specimen E exposed to the tube B. The whole was immersed in water up to the stopcock C. In order to establish equilibrium, several days were allowed to elapse after creating a new pressure of helium in A before making a run, the tube B being open to the pumping system. During the run the pressure in B was, for the purposes of calculation, negligible compared to the pressure on the helium side A. The usual control experiment was made with each specimen by filling A with air at atmospheric pressure and determining whether any residual neon and helium was present on analysis. The time of a run was varied considerably but the rate of flow was found to be constant.

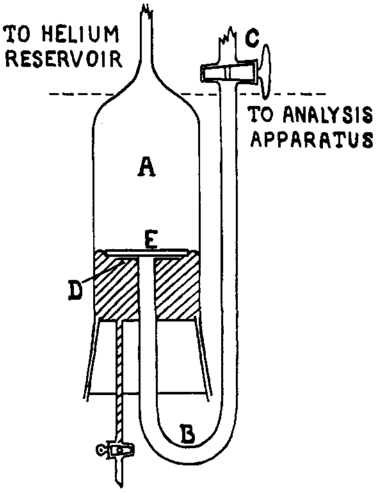

Fig. 2

The first specimen designated Keweenawan No. 5 was a close-grained basalt. If Q represents the quantity of gas flowing in cc. per sec. (the product of the volume V and the pressure at which it is measured P), then $Q/(p_1 - p_2)$ should be a constant independent of p_1 and p_2, the reservoir and vacuum side pressures, respectively, provided the flow is strictly molecular. Such is the case with both specimens used. Table III gives the values for the above specimen. Since p_2 is negligible, $(p_1 - p_2) = p$, the pressure in the container A.

TABLE III

p_1, mm	8.5	26.0	64.0	102.0	150.0	177.0	
V, cc. per sec. at $P = 760$, mm., $\times 10^{10}$	6.96	21.56	53.02	83.04	127.94	149.32	
$Q/p \times 10^8$	6.22	6.30	6.30	6.19	6.48	6.41	Mean 6.32

The full equation for each capillary is given by

$$Q = \frac{\sqrt{2\pi}}{6l} d^3 \sqrt{\frac{RT}{M}} \cdot (p_1 - p_2) \tag{1}$$

If n is the number of capillaries per sq. cm., the total number is given by nS, where S is the effective cross section of the flow. Rearranging (1) we have

$$nd^3 = \frac{Q}{(p_1 - p_2)} \left[\frac{6l}{\sqrt{2\pi}\, S} \cdot \sqrt{\frac{M}{RT}} \right] \tag{2}$$

The bracketed portion is a constant φ which is dependent upon the gas transpiring, the temperature of the gas and the dimensions of the specimen. The term nd^3 is independent of the experimental conditions and dependent only upon the structure of the specimen. In the evaluation of φ, M has the value of the molecular weight of the diffusing gas, T being the absolute temperature and R having a value 83.15×10^6 ergs°C. The length of the capillaries l is given a value equal to the thickness of the specimen in cm. Since such capillaries are tortuous it might be more correct to evaluate a term nd^3/l, but since the assumption that the capillaries are round is also hypothetical it is simpler to include tortuousness in the factor nd^3. For purposes of comparison of different specimens it is unimportant. S is the area in sq. cm. exposed for diffusion and in evaluating this term care has been taken of the variation of this effective area with depth in the slab. When such units are taken, the value of nd^3 is obtained as the product of a number and the cube of a diameter measured in cm. This term may be regarded as a structure constant for a given rock formation considered as an aggregate of crystals. The value of Q/p is determined as shown in Table III and a mean value taken if constant over the range of pressure investigated. The product of this value and the term φ gives the structure constant nd^3. In order to compare several rocks it would be advantageous to use the same gas since many investigators have found that variations occur in the inverse square root of the molecular weight law. The second specimen was a single quartz crystal which was fortunately flawless. The result was completely negative even after runs of twenty-six days' duration. This is important, for if it is true of all single crystals it is the probable explanation of the high degree of retention of radioactive helium in ordinary rocks, except, as has been mentioned, in the cases where the radioactive material has crystallized in the capillaries themselves rather than in the separate lattice structures. A quartz mass of fine crystals was studied as a comparison. The structure constant is approximately ten times greater than that of the basalt with a correspondingly greater molecular flow. Although the work on the determination of the ages of rocks by the helium method is only in the preliminary stage, there are indications that the granites, which are of similar structure to the quartz mass, yield ages which are low compared with the geological horizon in which they are found. This is in accord with the above result. Wells and Stevens[10] have determined the rate of flow of hydrogen and air through a material known as Swedish Kolm, an oil shale-like material. From their data the structure constant has been calculated and included in Table IV. The deviation from the inverse square root of the molecular weight relation can be noted by the difference in the constant determined with the two gases. This deviation is probably due, in part, to the independent diffusion

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(10) Wells and Stevens, *J. Washington Acad. Sciences*, **21**, 17, 413 (1931).

of each of the gas components in the case of air. Moreover, the nature of the material is such that solution processes may also occur as in the case of glasses. From the recent data of Warrick and Mack[11] on artificially prepared copper membranes, the structure constant for such gas-molecule sieves was evaluated and forms an interesting comparison with naturally occurring material.

TABLE IV

Specimen	Gas	φ	Mean Q/p	Structure constant nd^3
Single crystal of quartz	Helium	....	0	....
Fine-grain basalt	Helium	1.021×10^{-5}	6.32×10^{-8}	6.45×10^{-13}
Quartz mass	Helium	1.066×10^{-5}	6.29×10^{-7}	6.71×10^{-12}
Kolm shale	Hydrogen	7.478×10^{-7}	1.45×10^{-4}	1.08×10^{-10}
	Air	2.827×10^{-6}	4.82×10^{-5}	1.36×10^{-10}
Copper membrane	Air	4.61×10^{-7}	5.06×10^{-8}	2.33×10^{-9}

An upper limit for the value of d may be fixed roughly by determining the pressure and hence the mean free path at which a deviation from the molecular flow equation first occurs. With the basalt and quartz specimens this gives a value of the order of 500 Å. units, the lower limit being presumably a few molecular diameters. Without narrowing down such limits it is impossible to obtain any significant data by the separation of the terms n and d^3.

Summary

1. Helium fails to pass through various metals and such a negative effect persists over a range of temperature and pressure. The diffusion of a small quantity of helium through bismuth was first detected on excitation of that gas.

2. The adsorption of helium on steel was found to be zero.

3. It has been shown that the loss of helium from rocks cannot be compared to the loss from the usual radioactive minerals.

4. From the measurement of the rate of flow of gases (helium) through naturally occurring rock material it is possible to express the structure (fine, medium or coarse grain) by a mathematical term. The rate of flow of helium through a single quartz crystal was found to be zero.

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[11] Warrick and Mack, THIS JOURNAL, **55**, 1324 (1933).