

untold ages. What about these idle fellows who spend their nights, not in honest sleep, but in peering through great telescopes into the starry heavens, or instead of reading the story of creation, so beautifully told in the book of Genesis, go reading the riddle of the rocks in a vain effort to controvert Moses' account of the beginning of things?

This revolutionary evolution theory is gaining alarming headway, and unless something is done about it right away there is no telling what may happen. And popular education¹ is doing it. Woodrow Wilson, the greatest educator of his time, when asked his opinion of evolution said: "I take it no educated man questions the established fact of organic evolution." The schools and universities are to blame for the spread of this dangerous doctrine, and if statesman Hobbs would insure the rising generation against this corrupting teaching he should introduce a bill abolishing all public and private schools. The uneducated man accepts what he has been told by mother and the preacher; asking no questions. But as soon as the child appears in school, he begins to ask a reason for things. Oh, for a return of the simple faith in witches and ghosts and horse shoes and rabbit feet, a flat earth and a revolving sun, etc., and no questions asked. Lawmaker Hobbs is Kentucky's hope for this happy return of the good old days, but, alas! it is to be feared that he is casting his pearl before swine in that sceptic bunch at Frankfort.—*Kentucky Republican*.

SEPARATIONS BY THE IONIC MIGRATION METHOD

THE development of the ionic migration method for effecting difficult separations has been described in a number of articles appearing in the *Proceedings of the National Academy of Sciences*¹ and in the *Journal of the American Chemical Society*.² This series of investigations, carried out at Columbia University between 1920 and 1926 and continued at New York University since the latter date, has now given results of interest in several quite diverse fields. The presentation of an informal summary and the correlation of the results obtained are the purposes of this paper.

The work was started as an attempt to devise a practicable method for the separation of isotopes. Other investigators had succeeded in obtaining, at best, only a very slight degree of separation of isotopic elements into their various atomic species after heroic expenditures of time and labor by other meth-

ods, and it appeared that there did exist the possibility here of obtaining a quick and decisive result. The situation with regard to ionic mobility may be explained very briefly. A long-standing controversy has been waged on this property; one school insisting that ionic mobility is fundamentally dependent upon ionic volume, another being equally confident that it is fundamentally dependent upon ionic mass. The results available in the literature for homologous series of organic anions and cations have been utilized by both parties to give their respective points; but, since we have no definite knowledge as to what amount of solvent accompanies any ion in its journey towards an electrode and since it is the *total mass* or *total volume* of the ion and of its accompanying solvent envelope which must be taken into account, such data obviously offer us no means for definitely determining the problem.

The discovery that isotopes possess *equal atomic volumes*, made by Soddy and Richards in 1914,³ first put us in a position to impose a crucial test, for isotopic ions necessarily *differ in mass*. If mass is influential, therefore, it should be possible to obtain a separation of isotopes by taking advantage of the fact that the lighter ion will migrate more rapidly than the heavier. This idea of an "isotopic race," however, can not be carried out experimentally as simply as it might seem at first sight. Ions do not compete under the influence of the electric current in the manner of a track meet, unless we extend our experiences to include a continuous relay race. We can not start all of our ions at one point and obtain a separation by noting when those of a certain species have passed a given goal, for there must be maintained a steady supply all the way from one electrode to another in order for the current to pass, and it will not help us much if a faster ion hurries ahead of its slower neighbor, since it will merely find itself in the company of other slower ions which happened to start a little in advance. By a modification of the experimental procedure, nevertheless, our "isotopic race" may be converted into a "parade" which can be suitably regulated.

The apparatus used is shown in the accompanying diagram, and its applicability may be illustrated by a condensed description of the technique employed in the case of chlorine.

An agar-agar gel A containing sodium chloride is inserted as a short middle section in a long horizontal tube of pyrex glass, one and a half inches in internal diameter. On one side of the chloride gel is added a gel B containing sodium hydroxide; on the other side a gel C containing sodium acetate. The ends of the tube

¹ *Proc. Nat. Acad. Sci.*, 9, 75, 1923; 10, 458, 1924; 11, 393, 1925.

² *Jour. Amer. Chem. Soc.*, 48, 2619 and 3114, 1926.

³ Aston, "Isotopes," 17, 1922 (Arnold and Co.).

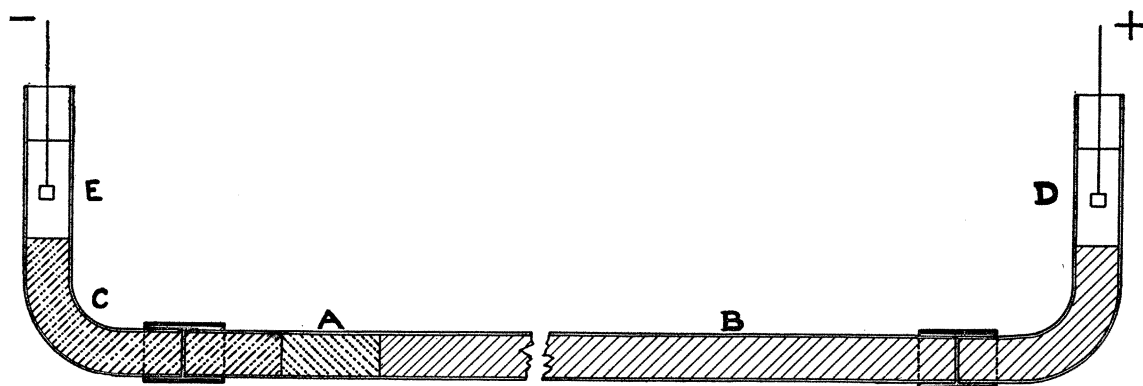


Fig. 1

are connected with right-angled pyrex bends of the same diameter, and the gels continue well up into these bends, as in the diagram. Above the hydroxide gel, after it has set, is poured concentrated sodium hydroxide solution D, and above the acetate gel a solution E of sodium acetate in concentrated acetic acid. Platinum electrodes are placed in these two solutions, and a current is passed through the tube, the electrode in D being made the anode and the electrode in E the cathode. The heating effect of the current upon the gel may be minimized by submerging the tube in a long trough filled with running tap-water.

At the beginning of the run, the boundary surfaces between the various sections of the gel are perfectly sharp. When the current is turned on, the boundaries move toward the anode. Inasmuch as there is a faster-moving ion in front of the chloride ion, and a slower-moving ion behind it, admixture of the salts is absolutely prohibited and the boundaries remain distinct throughout the whole experiment. In order to maintain the width of the chloride section approximately constant, it is well to arrange the concentrations of the various salts in their respective gels in accordance with the transference numbers of their anions. Even if this is not done, however, the boundary concentrations soon automatically adjust themselves to the required ratios. Care must be taken that the solution around the cathode always contains sufficient excess of acetic acid to neutralize the sodium hydroxide that is there formed.

The rate at which the boundaries move depends upon the potential drop between the electrodes, the length of the tube, and the concentrations of the solutions. In actual practice, the horizontal tube is made up of three three-foot sections, connected by rubber bands, and the current is regulated (100 to 500 volts) so that the boundaries advance about 12 to 18 inches a day. When the front chloride boundary has almost reached the end of the tube, the apparatus is taken apart. The two rear sections are discarded, two new sections filled with hydroxide gel are inserted in front of the chloride, and new bends are fitted on as before. The chloride ions are now forced to migrate into these two new sections, and the whole procedure is repeated until they have pro-

gressed through about 100 feet of the gel. The chloride gel is then removed from the tube and immediately cut up into strips about 1 cm. in width.

If, now, the isotopic chloride ions with atomic masses 35 and 37, respectively, possess significantly different mobilities, the front segments of the gel will contain only the faster-moving and the rear segments only the slower-moving isotope. Preliminary experiments in which a mixture of two sodium salts with anions of known mobilities was substituted for the middle sodium chloride section fully demonstrated this point. Thus when a mixture of sodium iodide and sodium thiocyanate was employed and the boundary was moved only a few feet, the front segments were found to contain only sodium iodide and the rear segments only sodium thiocyanate. The observed lag of the slower ion was almost exactly equal to that calculated from the difference in mobilities. In this particular case, the difference is approximately 16 per cent. In subsequent experiments this difference was narrowed by choosing other suitable pairs of ions; *e.g.*, barium and calcium, barium and strontium, and iodide and chloride. The differences in mobilities are here reduced to 8 per cent., 5 per cent., and 1 per cent., respectively, and the results obtained showed that the method could be depended upon to provide a very considerable degree of separation even at the lowest limit tested.

It was highly disappointing, therefore, to be forced to admit from the results of all our experiments with isotopic ions that no significant separation could ever be detected. The only conclusion that can logically be drawn is that the mobilities of isotopic ions are well within 1 per cent. of equality and that those workers are substantially justified who contend that volume is the decisive factor in determining ionic mobilities. More recent theoretical advances, it must be added, support this view, although the matter is still not absolutely settled.⁴

Experimental difficulties encountered in connection with this work on isotopes can not be discussed in full

⁴ Jette, *Phil. Mag.*, 3, 58 (1927).

detail here, but mention may be made in passing, of two points. One was the impossibility of determining whether any separation was proceeding within a section except by interrupting its progress irretrievably through segmentation and analysis. In other words, there was no way of telling in advance if a run of 100 feet was any more advantageous than a run of 10 feet, or whether a run of 500 feet should be preferred. It was proposed by one assistant to solve this difficulty by incorporating with the material under examination a small amount of a substance containing a colored ion with a mobility *intermediate* between those of the two isotopes. The end of an experiment would then be automatically announced by the appearance of a thin colored strip in the center of the section, the gel in front of this strip containing only the faster isotope and the gel in the rear of it only the slower. Unfortunately, no colored ion with the properties required has yet been discovered. A second difficulty consisted in fixing the exact position of the boundaries during a run. Slight changes in the color of the agar-agar gel induced by the different salts present, or slight differences in the refractive index of the various sections were sometimes sufficiently good indications, but the much larger variations in their electrical resistance offered, in general, more dependable assistance. The approximate position of a boundary could frequently be determined merely by lifting the apparatus from the water trough for a few minutes, running the hand along the tube and noting the place at which a temperature gradient became evident. Finally, more exact information was obtained by fusing two short platinum wires through the glass at suitable points on the tubes and establishing the passage of a boundary past these points by noting when an abrupt change occurred in the electrical resistance of the gel between them.

Although all the work on isotopes, as has been stated, led to no successful separations, yet the positive results obtained in the test experiments on known mixtures did inspire the hope that the ionic migration method might, after all, prove of practical service in the separation of more familiar materials which are ordinarily obtained by the chemist in a pure state only with extreme difficulty. The most important instance of this type is furnished by the family of the rare earth metals. The group of elements known as the rare earths comprises the elements of atomic number 57 to 71 inclusive, and yttrium with atomic number 39. These elements are distinguished by such extraordinary likeness in chemical and most physical properties, due to the identical arrangements of their two outer shells of electrons, that they actually approach isotopes in similarity. It is necessary, in

practice, to take advantage of slight differences in solubility observed for corresponding salts and to resolve a given mixture into its components by a long series of fractional crystallizations or precipitations, ranging in number from several hundred to many thousand according to the elements present and the degree of purity desired. These operations are so laborious and time-consuming that chemically pure samples of individual rare earth compounds are practically unknown, save on the shelves of a few skilled workers in the field of atomic weights. The "rareness" of the rare earths is due not so much to the lack of abundance of their ores in nature as to the lack of a simple method for their separation.

Little is known of the relative mobilities of the rare earth cations in aqueous solution, but ionic volume and hydration variations within the group may be expected to cause differences in ionic mobilities which will, in most cases, exceed one per cent., so that a ready analysis of a given mixture into its pure components should be, in general, feasible. The experiments described below furnish, in fact, two instances of the successful separation of typical binary rare earth mixtures by the ionic migration method.

The first separation attempted was upon a mixture of yttrium and erbium, kindly furnished by Professor James, of the University of New Hampshire. Potassium was used as a preceding faster ion and trivalent chromium as a following slower ion. Not only could the position of the rear boundary be more conveniently followed in this particular case because of the color of the chromic solution, but it was also found possible to observe the actual progress of the separation within the rare earth section in a very simple way by means of a small direct-vision hand spectroscope. The majority of the rare earths give solutions with characteristic absorption spectra and, by noting the increase or decrease in intensity of the most prominent lines in various parts of a section, the experimenter could immediately detect any change in composition in the whole length of the section without interrupting the run. Here yttrium rapidly accumulated in the front half of the section and erbium was relegated to the rear. After a run of fourteen days, during which the boundaries moved two meters, an almost perfect separation had been effected.

The next mixture tested consisted of neodymium and praseodymium, two elements which are so nearly alike that their first differentiation by Otto von Welsbach still forms one of the triumphs of technique in this difficult field. Neodymium salts exhibit a purple solution in water, however, while praseodymium salts give a green solution. A beautiful crystal of neodymium nitrate and an equally fine specimen of praseodymium sulphate were secured from the

Chandler chemical museum of Columbia University and the careful work of several years was deranged in a few minutes by mixing these two salts to obtain a solution with an intermediate neutral tint. With this solution as a central section and with the same arrangement as in the preceding experiment, it required only a few days' migration to disclose the fact that the front portion of the section was becoming distinctly green and the rear portion purplish. Observation by means of the spectroscope simultaneously showed that the characteristic absorption lines of praseodymium were becoming more pronounced in the front section and fading out in the rear, with the opposite behavior for the neodymium. At the end of ten days, substantially complete separation had been accomplished.

Experiments with other mixtures of rare earths showed that, while complete separation could not be secured in every case, yet in most mixtures the mobilities of the ions were sufficiently divergent to compel a very rapid concentration of one particular component in the front or in the rear section. The method may, therefore, be considered as a general new method for obtaining pure samples of the rare earth elements with the expenditure of much less time and trouble than is required by the classical method of fractional crystallization. Professor Hopkins, of the University of Illinois, is, it may be mentioned, at present attempting to utilize the ionic migration method for the more rapid concentration of illinium (the last member of the rare earth family, discovered by him in 1925) from the neodymium and samarium residues in which minute traces of it exist.

Important industrial uses for the rare earth elements will undoubtedly be discovered as soon as more convenient means for their isolation are developed. Aluminum remained a chemical curiosity until this same end was achieved, and while the later members of the aluminum family may not duplicate the successful career of their brilliant brother, yet it would indeed be strange if nature had omitted to endow them, alone of all the elements, with no properties of service to mankind.

The success of the experiments with rare earths suggested that the method might be applicable to the separation of radium from barium. The concentration of radium from the barium residues of carnotite ores at present involves a very tedious series of fractional crystallizations, and, since it had already been found that barium could be separated from the other elements of the alkaline earth family by the method here under discussion, it appeared very probable that a similar separation from radium, the last member of this same family, could also be accomplished. Samples of barium residues containing known

amounts of radium and of mesothorium (an isotope of radium) were obtained and, after a few days' migration, the sections were segmented and their radioactivity examined. It was found that the radioactive components of each mixture tested accumulated very rapidly in the front part of the section. The ease of the separation in this case is so striking as to suggest that the ionic migration method may come into technical use for the concentration of radium in barium residues.

An attempt to separate hafnium and zirconium did not lead to such conclusive results. Hafnium exists to the extent of several per cent. in all zirconium ores, and the similarity in properties is so pronounced that the actual discovery of hafnium was not definitely established until 1923. A sample of hafnium-rich zirconium oxide was kindly furnished us by Professor Hevesy. The elements were not amenable to separation by the ionic migration method in the form of positive ions, owing to hydrolysis, and only after considerable search was a suitable negative complex ion discovered in the form of a complex oxalate. After long migration, analysis showed a very slight accumulation of hafnium in the rear of the section, the mobilities of the complex anions being evidently so close together as to render a complete separation impracticable.

The results in an entirely different field have been of better promise. Many of the alkaloids particularly useful for medicinal purposes are derived from natural sources as mixtures of several individual members which can be separated by the ordinary methods of organic chemistry only with great difficulty. The alkaloids, however, are weak bases which form soluble hydrochlorides, and the mobilities of the cations of these salts are not identical. It should, consequently, be possible to obtain a pure sample of an especially valuable alkaloid from the mixture of similar materials with which it naturally occurs by use of the ionic migration method, and several preliminary experiments indicate that the method is indeed applicable in a majority of cases. Details will appear in a forthcoming communication.

Several other lines of research are also being followed. A very interesting case is the search for the missing element number 87. This element, from its position in the periodic system, should be a highly radioactive alkali metal. Just as radium is found associated with barium, so this missing element might be expected to occur in nature with other members of the alkali metal group. Now it is a very significant fact that the only elements of low atomic weight which exhibit radioactivity are potassium and rubidium. Two alternative explanations have been advanced, the first being the obvious suggestion that the radio-

activity is due to an infinitesimal trace of the missing alkali element, the second being that it is due to some unstable isotope of the commoner alkali metal. Without going into details, it may be stated that each alternative has, at present, more experimental facts in its disfavor than in its favor, and a third entirely novel explanation is by no means excluded. The present method appears to furnish some hope of advancing our solution of this question for if, by migration of a potassium or rubidium salt, it should be found that the radioactivity was concentrating in the very front or in the very rear of the section, then the isotopic explanation would presumably fall into the discard and further investigation might very conceivably justify the announcement of the discovery of the missing element.

The experiments thus far completed on potassium have not given any final results. It is true that no noticeable concentration of the radio-activity in either the front or the rear has been obtained, but this can quite plausibly be ascribed to the fact that the mobility of the unknown alkali metal ion is substantially the same in aqueous solution as that of potassium ion. The heavier members of the alkali metal group, indeed, all have ionic mobilities in water which are substantially identical within the limits of experimental error. In methyl alcohol solution, however, it has been shown that the mobilities differ very markedly and consequently it may be expected that the addition of some methyl alcohol to the aqueous gel will stagger the values sufficiently to enable a separation to be secured if any unknown alkali metal is present. This point is being tested experimentally at the present time.

Finally, the possibility is being investigated of the applicability of the method to the separation of organic isomers of various types. More complex biochemical problems, such as the concentration or isolation of specific proteins or even of vitamins from natural sources, are probably also open to attack by the ionic migration method, but the experimental technique in such cases has not yet been worked out in detail.

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SCIENTIFIC APPARATUS AND LABORATORY METHODS

DETERMINING SOIL MOISTURE RAPIDLY AND ACCURATELY BY METHYL ALCOHOL

In a former communication (this Journal, April 5, 1927) the use of alcohol was proposed as a basis for

a very rapid means of determining the moisture content of soils and possibly of other materials. The form of alcohol that was then suggested was ethyl alcohol. In order to ascertain whether there are other liquids that would be more satisfactory than ethyl alcohol, an investigation has been conducted in which a large number of liquids have been examined. It has been discovered that of all the liquids studied, methyl alcohol seems to be the most satisfactory, as it is the most powerful dehydrating agent. Indeed, this form of alcohol seems to be able to replace or reduce the moisture content of soils down to practically the absolutely dry basis, as will be readily seen from the data below.

Percentage of water recovered
from water added to
oven dry soils.
Per cent.

Sand	100.05
Loam	100.03
Clay	99.99
Muck	99.01
Silica gel	99.30

The directions for executing a moisture determination by methyl alcohol are the same as those already published (this Journal, April 15, 1927) for ethyl alcohol. There are five points in the procedure, however, that one must always pay special attention to. These are first, the soil must be stirred with a strong rod and reduced to the particle state so the alcohol can come into intimate contact with the entire soil mass. Second, the liquid must be always filtered. Third, great care must be taken to prevent evaporation. The latter can be mainly accomplished by keeping the funnel covered during filtering. Fourth, the temperature of the liquids should always be recorded and reduced to the same basis. And fifth, in calibrating the hydrometer, the specific gravity of the absolute alcohol should be taken under controlled temperature. Allowing the alcohol to stand in running tap-water, to attain the temperature of the latter is sufficient.

It is advisable to use absolute methyl alcohol.

In case of soils containing more than 50 per cent. of moisture, such as muck and peats, only about 10 grams of soil should be used to 50 cc of alcohol.

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A CONVENIENT METHOD OF MEASURING QUANTITIES OF CHLOROPLAST PIGMENTS

ALTHOUGH the photosynthetic mechanism in the leaves of plants has long attracted the attention of