AN INVESTIGATION OF A NEW METHOD
FOR
POTASSIUM-ARGON AGE DETERMINATION

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By

Ira Lynus Barnes, Jr.

Thesis Committee:

John J. Naughton, Chairman
Gordon A. Macdonald
Richard G. Inskeep
Michael M. Frodyma
Harry Zeitlin

To Nelle, whose patient understanding made it possible

"And some rin up hill and down dale
knapping the chucky stanes to pieces
wi' hammers, like sae many
road makers run daft. They say
it is to see how the world was made."

-Sir Walter Scott

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I. Introduction

A. Historical

It is interesting to note that throughout all of recorded history, man has sought a system of recording happenings which were eventful to himself and his family or community and of relating these happenings to each other through some time scale. Each such time scale, of course, had to have a beginning and the logical, although by no means universally used, beginning became the time of "creation" of the world. We still know very little about this beginning unless we accept the absolute time scale established by the ancient Hindus who decided, by a somewhat obscure method, that the year 1963 is 1,988,148,964 years since the earth came into existence.

John Lightfoot settled the question for all time, he thought, when he stated in his treatise "A Few and New Observations on the Book of Genesis: Most of Them Certain, the Rest Probable, All Harmless, Strange and Rarely Heard-of Before," that the moment of creation was, indeed, 9:00 o'clock in the morning on September 17, 3928 B.C. No one has been quite so definite since, although the subject has interested many persons including such eminent scientists as James Hutton and John Joly, Edmund Halley, Charles Darwin, Lord Kelvin, Lord Rayleigh, Arthur Holmes and Admiral Perry. Among the proposals for the establishment of a system of determining the age of the earth, two which were given the most serious consideration were:

1. A calculation of the saltiness of the sea, since it was believed that the rate of increase of salt content was constant and that the oceans started out as fresh water.

2. A calculation of the rate of the cooling of the earth, since it was believed that the earth was cooling at a constant rate and that there was no heat input.

Geologists and others have been able to build up, over the years, what must be referred to as a geologic time scale from the evidence found in layered sedimentary rocks of the successive evolution of plants and animals, the rates of weathering, and other geologic processes. This scale, although useful, suffers from two serious deficiencies:

1. It can only be a relative scale, i.e., "this period of geologic time occurred some time after that one," and
2. It covers perhaps only one-sixth of the earth's history.

In 1907, however, the American chemist Boltwood(1) made a suggestion which, much later, was to lead to a method -- in fact, to many methods which enabled geologists to start putting absolute dates on the various geological formations of the earth. Boltwood observed that uranium and thorium minerals invariably contained lead and helium. He concluded that these were the stable end-products of the radioactive disintegration of uranium and thorium. He suggested that since the rate of disintegration was known, the time since the mineral crystallized could be calculated. This method was applied as an approximation, at first, but after the work of A. O. Nier(2) on the isotopic composition of lead, this became an accurate method for "dating" and the three well known lead methods have been used extensively.

For any dating system that depends upon radioactive decay it is necessary to make at least the following four assumptions:

1. It must be assumed that the decay scheme of the parent element is known accurately.
2. It must be assumed that the concentration of the parent element has been changed only by radioactive decay.
3. It must be assumed that all of the decay products have been retained.
4. It must be further assumed that no daughter elements were retained at the time of formation.

In many cases where it is known that one or more of the above cannot be safely assumed, suitable corrections may be made and the method may still be useful. As an example, it is known that many uranium and thorium bearing minerals contain a significant amount of primordial lead at the time of formation. However, since lead has an isotope (Pb^{204}) which is known not to be a product of radioactive decay, a correction for the amount of lead present at the time of formation may be made, based on the measured content of this isotope.

A much more serious limitation of the lead methods comes about because of the magnitude and uncertainty of the experimental quantities determined, and the form in which they appear in the mathematical expression. Due to this, the whole system becomes insensitive to time at about 500 million years(3) and thus cannot usually be used for rocks and minerals younger than this.

Fortunately, at about the same time that workers were fully realizing the shortcomings of the various lead methods, Thompson and Rowlands in 1942(4) proved that the radioactive disintegration of potassium-40 involved the production of argon-40, which had been predicted by Von Weiszacher in 1937(5). A number of geologists and physicists tried to show a relation between the ratio of argon-40 to potassium-40 in rocks and minerals and their time of formation. This was done successfully five years later (1948) by Aldrich and Nier(6).

As will be shown in a later section, this method of geochronological measurement, or dating based on the decay of potassium-40 to argon-40 does not contain the experimental and mathematical difficulties inherent in the various lead methods and could, in theory, be used for determining the ages of minerals from those as old as the earth itself, to those formed a few years ago.

That the potential usefulness of this method was quickly realized may be seen from even a cursory review of the literature of the past 15 years. The potassium-argon method has been used to date a large number of minerals and rocks ranging in age from 4500 million years (my)(7) to approximately 10 my(8). Very good reviews of these and other datings and their geological significance have been written by Kulp(9) and Tilton and Davis(10). One cannot read these above mentioned reports without coming to the conclusion that we are rapidly reaching a position where we shall be able to develop the absolute scheme sought by man ever since he first started to look philosophically on his environment. Indeed, from the dating of meteorites, done by the potassium-argon method,(11) it is perhaps not too presumptious to suggest that we might even be starting on a scale of absolute dating of our whole solar system.

B. Background of Problem

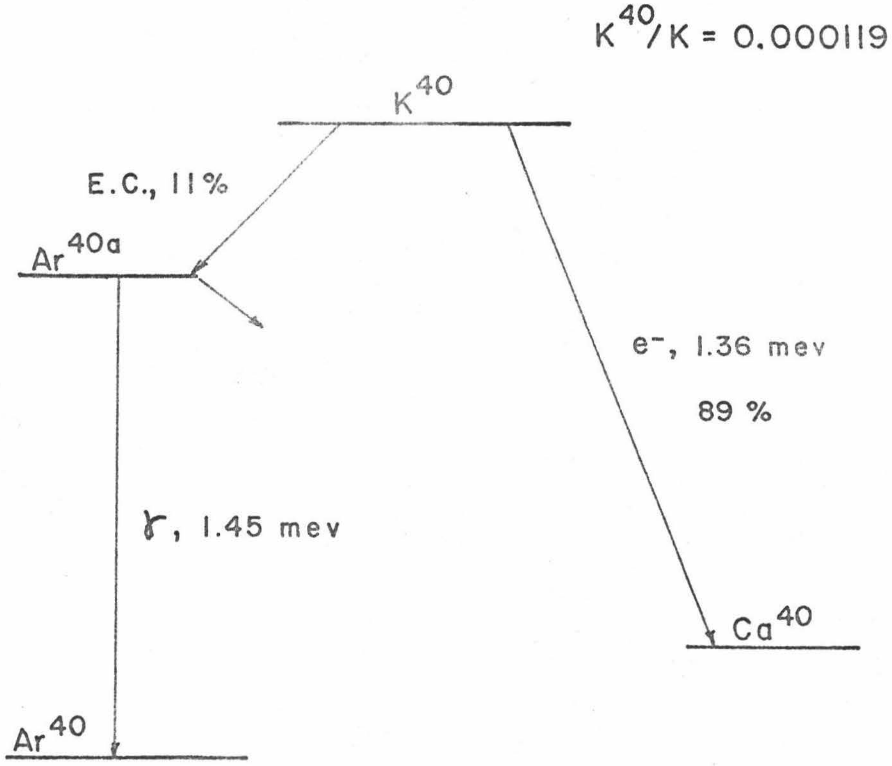
While, as noted above, the potassium-argon method has yielded some ages of unquestionable value to geologists, it should be pointed out that the accuracy of many of these values is only to within ± 50%, and probably few, if any, of the results obtained before 1958 are better than ± 20%. In rocks and minerals older than 100 my, inaccuracies of this magnitude may be relatively insignificant, but in those much younger than this, and particularly rocks in the age range of .5 to 20 my which are of present interest to geologists and volcanologists studying the Hawaiian Island chain and its growth, uncertainties of as much as ± 5% become important in the interpretation of the sequence of the various phenomena involved. As an aid to understanding the cause of these uncertainties and the source of the many remaining problems, consider the decay scheme of potassium-40; Figure 1.

From Figure 1, it may be seen that potassium-40 constitutes only 0.0118% of natural potassium, and in addition, only 11% of this decays to argon-40. The small quantities involved have made the determination of the various decay constants difficult. While there still remains some uncertainty in the values of these constants, a great deal of work has been done on them and it now appears that further work will result in little change.

Using the above decay scheme, the following formula may be derived for the amount of argon-40 formed in some time, t:

$$Ar^{40} = K^{40} \frac{R}{1+R} \; e \; (\lambda\gamma - \lambda B) \; t - 1$$

where:



$$T_{1/2} = 1.26 \times 10^{9} \text{ yr.}$$

$$\lambda_{\gamma} = 0.603 \times 10^{-10} \text{ yr}^{-1}$$

$$\lambda_{e^-} = 4.88 \times 10^{-10} \text{ yr}^{-1}$$

$$\frac{\lambda_{\gamma}}{\lambda_{e^-}} = 0.123$$

FIGURE 1

Decay Scheme of Potassium-40

Ar^{40} = number of atoms of Ar^{40} at time t

K^{40} = number of atoms of K^{40} at time t

R = $\lambda \gamma / \lambda B$

Rearranging the above, solving for t and using the latest values for the various constants as given by Glendenin(12), the following expression is obtained: (See Appendix 1)

$$t = 0.1825 \ln (1 + 9.130 Ar^{40} / K^{40}) \times 10^4 \text{ my}$$

A sample calculation, using the above and assuming a rock or mineral with a potassium concentration of 2% and an age of 10 my, indicates that we may expect 8.2×10^{-7} Std. cc/gm of argon-40. This argon must be extracted from the sample, carefully purified, since very many times this quantity of other gases are also obtained, and then measured.

Just a few years ago, these three steps would have represented an almost impossible task for this very small quantity of gas. The only alternative left would be to work with unmanageably large rock samples in order to obtain gas quantities within the limits of accurate measurement by the available equipment. While the handling, purifying, and measuring of amounts of various gases of this order of magnitude is still not an easy matter, by borrowing heavily from the techniques developed in the field of ultra-high vacuum (i.e. pressures less than 10^{-8} Torr) and with the advent of a very sensitive, completely bakeable mass spectrometer, it is now well within the realm of experimentation.

Unfortunately, however, both of the above fields are still in the developmental stage and many phenomena connected with these operations are still not well understood. Therefore a necessary corollary to the researches which are reported here was the study of the extraction and purification process as well as ultra-high vacuum techniques. In addition, because of the very high cost of a mass spectrometer, it seemed desirable to attempt the development of a procedure for the potassium-argon method in which the use of the instrument was not absolutely necessary.

A scheme which might accomplish this purpose would involve preparing an artificial material of the approximate composition of the rocks or minerals to be dated, producing within this artificial material a radioactive isotope of argon (i.e. Ar^{39}, half-life= 325 years(13)) and determining the quantity of the isotope contained in the material.

This material could be mixed with the rock or mineral to be dated and the mixture placed within an ultra-high vacuum system. After placing the sample under vacuum, contaminating air argon might be removed by a drastic baking schedule. This is not possible with present methods since no means of correction for the simultaneous losses of radiogenic argon-40 is possible.

The use of the radioactive isotope does allow this correction to be made, although information about the diffusion of argon in the artificial mineral is required for the correction. By determining the total argon extracted ($Ar^{40} + Ar^{39}$) by volume measurements and the amount of argon-39 by radioactive counting and knowing the amount of argon-39 added as an isotopic diluent, the amount of radiogenic argon-40 can be determined thus:

$$Ar^{40}\ \text{(total radiogenic)} = Ar^{39}\ \text{(added)} \times \frac{Ar^{40}}{Ar^{39}}\ \text{(found)}$$

C. Survey of the pertinent literature

The discussion of the potassium-argon method of geochronological measurement may, for purposes of discussion, be divided into four separate parts. These are:

a. Theoretical aspects including the decay constants.
b. Selection and treatment of suitable rocks or minerals.
c. Potassium determination.
d. Argon determination.

Most of the theoretical considerations have already been mentioned. However, it was pointed out that one of the basic assumptions was that the decay constants themselves were well known.

In some of the earlier work, a reverse approach to the determination of the constants was used. Because the results obtained with the then accepted values of the decay and branching constants did not seem to be correct, Wasserburg et al.(14),(15), Follinsbee et al.(16), Shillibeer and Burwash(17) and Goldich(18) all proposed values for this constant based on the results of their age determinations. Most of these workers, however, recognized that these values might be artificial and incorrect if the minerals had lost some of their radiogenic argon. Aldrich and Wetherill(19) presented a review of the various constants (for other methods, as well) and Glendenin(12) reported the results of the most recent physical determinations. He suggests that these values are probably the true ones to within a few percent, and these are the values used in

Figure 1 and throughout the present work.

The question of sample selection is not a vitally important one in this work. However, it should be noted that the criteria of no argon being retained at the time of mineral formation, and of no argon being lost after formation as already implied above, are difficult to meet. As early as 1948, Aldrich and Nier(20) reported that an almost potassium free beryl seemed to contain about 10^{-3} Std. cc/gm of radiogenic argon and in 1956 Wasserberg and his co-workers(21) and Jeffery(22) showed that while micas retain most of their argon, feldspars do not. Since then, these results have been confirmed many times, indicating that great care must be exercised in the selection of the rock or mineral to be dated. It is always tacitly assumed that the sample has been carefully considered for its geological significance. Further discussion of the samples used in this study is deferred until later.

The problem of potassium analysis was probably best summed up by W. H. Pinson, Jr. in 1961(23). Opening this report, he said, "I have always thought that it is one of the great curiosities of modern analytical chemistry that it is possible to analyze for argon, which occurs to the extent of about 0.01 to 0.001 cc of gas/gm in a sample to a much greater accuracy and with more confidence than it is possible to analyze for one of the major elements, namely potassium."

Because of the interest in this determination, created by the potassium-argon method, a number of workers have tried to improve the analysis. Wilson and co-workers(24) tried a radioactive counting method but did not check for other radioactive materials present, which could lead to very large errors. Beukenkamp and Rieman(25) and later, Sweet, Rieman and Beukenkamp(26) developed a method which first separated the potassium by ion exchange chromatography and then determined the potassium by flame photometry. They claim an accuracy of ± 5% but reported major difficulties with the method which they ascribed to differences in the ion exchange material used, (Dowex 50). Dean(27) reports the results of many workers who tried flame photometry without the prior separation by ion exchange and their attempts to avoid the many interferences. Edwards and Urey(28) separate the potassium by vacuum furnace distillation and then determine the element with a flame photometer using a lithium internal standard. Ishimori and Takashima(29) tried a novel method of precipitating the potassium as a potassium sodium cobaltinitrite where the cobalt used was radioactive, and then counting the precipitate. They report very good precision but poor accuracy. Yankov(30) precipitated potassium with tetraphenylboron, and several groups have tried to improve the classical Lawrence-Smith chloroplatinate precipitation(23). In addition, methods using isotope dilution - mass spectroscopy(23) and neutron activation(23) have been used. None of these seem to give results to better than ± 6%(23). Adams(31), however, in 1961 reported a procedure using a Beckman D.U. Spectrophotometer and a set of very carefully prepared standards with which he was able to get good results on certain silicate glasses. The most commonly used methods by persons involved with potassium-argon dating seem to be the Lawrence-Smith precipitation, mass spectroscopy, and flame photometry using a Perkin-Elmer instrument with provisions for constantly monitoring the lithium line. Unfortunately, this instrument is no longer available commercially.

Although the amount of argon extracted from the rock or mineral sample could, in theory, be measured volumetrically after carefully removing all other gases (except the other rare gases which are present in sufficiently small amounts as to be negligible), in practice this is never done. Aside from the very small quantities involved which make volumetric measurement extremely difficult, some of the argon may be lost in the process of extraction and subsequent handling. To determine this amount of "lost" argon, an isotope dilution technique is often utilized, making the use of a mass spectrometer manditory for the measuring process. The mass spectrometric measurement also allows corrections to be made for the contamination of the sample by atmospheric air, probably one of the most troublesome problems facing workers using the potassium-argon method. This problem arises because air contains 0.93% argon(32) which has the following isotopic composition:(33)

Ar^{36} - 0.33%
Ar^{38} - 0.063%
Ar^{40} - 99.600%

Thus any air contamination introduces a relatively large amount of argon-40 which cannot be distinguished from that due to the radioactive disintegration of potassium-40. It is possible to make corrections for this air argon by the measurement of the amounts of the argon-36 present, and then to calculate and subtract the air argon-40 determined in this manner. This has not been, and probably never will be, a completely satisfactory method for making this correction because any error in measuring the amount of argon-36 is multiplied by a factor of about 300 in making the final correction.

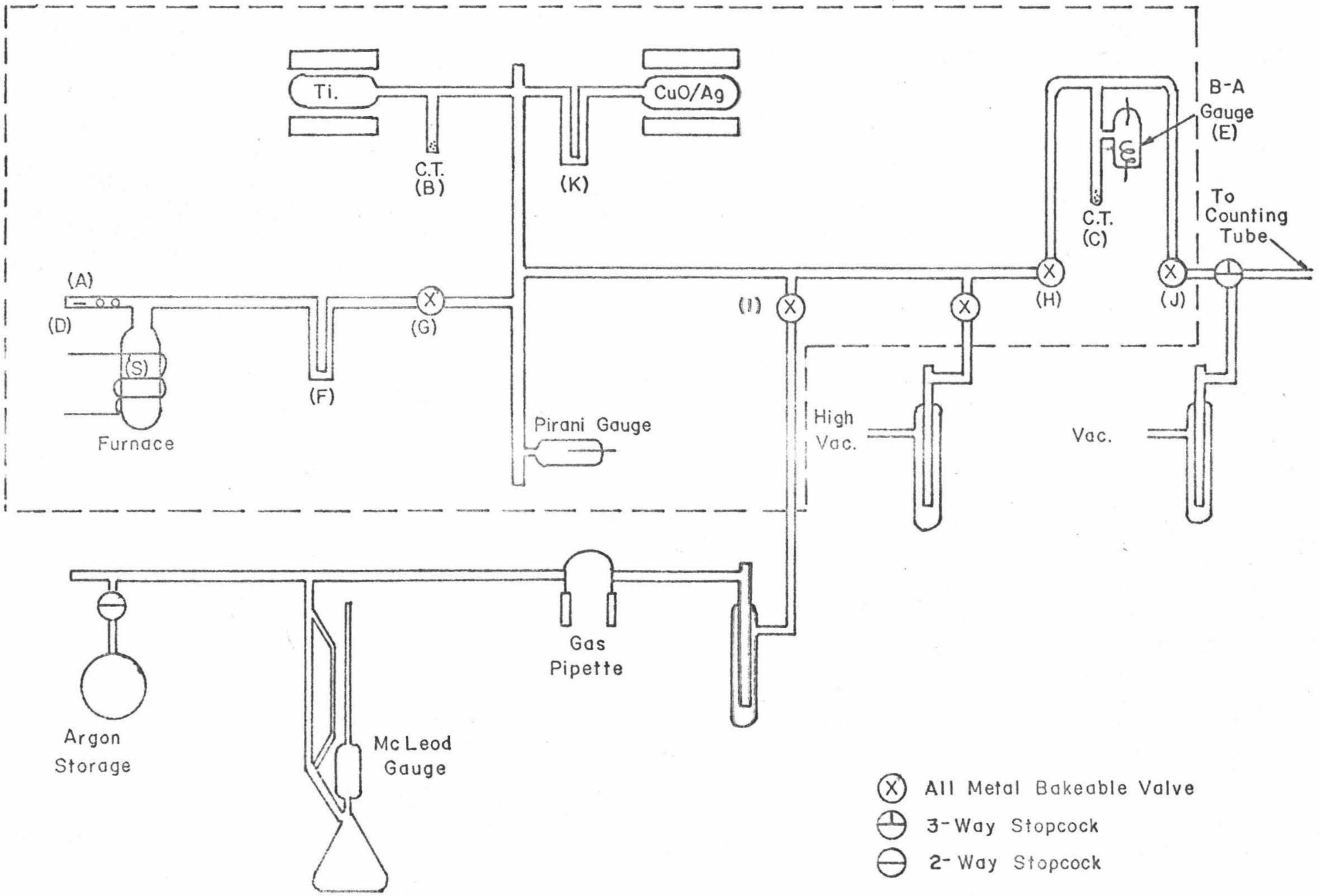
There are almost as many different techniques of dealing with the above problems as there are workers in this field since no system has been proven to be wholly satisfactory. The publications of a few groups, however, may be cited as representative examples of the various techniques used. Carr and Kulp(34), Curtis and Reynolds(35), Lipson(36), Folinsbee et al.(16), and Hurley and co-workers(37) have all given good descriptions of the methods in use at their respective laboratories. These various methods may be summarized by referring to Figure 2. Figure 2 is a diagram of a typical system showing the various parts. It may be seen that the system can be divided into three essential parts:

1. The sample melting system
2. The ultra-high vacuum system
3. The mass spectrometer

Fundamental investigations of various parts have been made by Carr and Kulp(34) who examined the procedures used in the sample melting portion and gettering system. They found that the sample could be satisfactorily melted without a flux and that neither the melting system nor the gettering system held up any of the gas, although their gettering system did not remove hydrogen.

In the last few years there has been a large amount of work done on various basic techniques and components of the ultra-high

FIGURE 2 - Schematic Diagram of Early Ultra-High Vacuum System



vacuum system by researchers in the electronics and space industries. Most of this work has been based on the original, classic papers of Bayard and Alpert(38), Alpert(39), and Alpert and Buritz(40). In these papers are described the Bayard-Alpert gauge, the all metal bakeable valve, and the small simple ovens which might be used to bake the whole vacuum system. They also contain a good, theoretical discussion of the operation of these components. Alpert recognized that the Bayard-Alpert gauge acted as a pump and indeed used this effect as a means of obtaining high vacuum. He did not, apparently, investigate the effect of re-emission of gas from the walls of the tube.

More recently, McGowan and Kerwin(41) measured the sensitivities of various Bayard-Alpert gauges for different gases. Carter and Leck(42) proposed a mechanism for the pumping action and showed that argon was removed from the walls by heating, but was not removed at room temperature. Blodgett and Vanderslice(43), however, suggest that argon was re-released during normal operation, but Baker(44) found that argon was re-emitted at a much slower rate and in lesser quantity. Nottingham(45),(46) suggested an improved design of the Bayard-Alpert gauge and examined the design parameters influencing sensitivity. Winters et al.(47) examined the operating parameters of this type of gauge and suggested the operation of the gauge at low emission currents, and Denison(48) examined the bakeout procedures giving optimum performance as a pump.

Biondi(49), investigating material for a trap to be used with oil diffusion pumps, reported that Linde molecular sieve materials seemed to be good adsorbents for water and hydrocarbons.

Although it has been known for some time that various materials could be heated or sputtered in an enclosed space to produce a vacuum or to reduce further the pressure in an existing vacuum system, very little work has been done on the mechanism of this "gettering" and the composition of the remaining gases. Dushman(50) gave a very good discussion of the information available up to 1961 for various materials used either as chemical getters or as bulk getters.

Porta and his group(51) investigated the bulk gettering properties of titanium, zirconium, hafnium, and thorium and these metals alloyed with aluminum. Unfortunately they limited their investigation to temperatures below 400°C. Most workers doing age work by the potassium-argon method empirically use either calcium metal or titanium at temperatures ranging from 800°C. to 1100°C.

In an attempt to resolve the discrepancy occurring where cogenic minerals give varying ages, the diffusion constants of argon in a number of different minerals have been determined. Reynolds(52) apparently first examined the diffusion constants for lepidolite and potash feldspar. He found that more argon was released from the feldspars at all temperatures, and that the room temperature coefficient was large enough to account for the feldspar-mica age discrepancy. There were some inconsistancies in his data, however, which he suggested might be caused by argon situated in several different kinds of crystallographic sites with different activation energies for diffusion from each site. Evernden(53) and associates measured argon diffusion in a number of different minerals and found, as Reynolds did, that the plots of diffusion coefficients vs. reciprocal temperature showed curves with changes in slope although they placed a different interpretation on the reason for this. Hart(54) has also reported similar effects for several minerals, as have Gentner and his group,(55),(13). M. B. Reynolds(56) has measured the diffusion of argon in a potassium - lime - silica glass. Reynolds(57), in measuring rare gases in tektites, discovered that when glasses were exposed to air, argon seemed to be the first gas to enter the glass. He reported also that the diffusion constant in glass was much larger than in crystalline materials. Gerling et al.(58) showed that different values were found for diffusion from ground micas than from cut micas. Amirkhanoff et al.(59) have recently studied the migration of argon from micas, and while, again, they found results similar to the above workers, they ascribed the phenomena observed to an entirely new mechanism in order to explain the results.

While the method proposed in this research has never been described in the literature, Naughton(60) has suggested the possible use of argon-39 as a tracer in age work and it should be noted that one other method avoiding the use of a mass spectrometer has been reported. Moivk, Drever and Curran(61) have used a neutron activation procedure using the reaction:

$$Ar^{40}\ (n, \gamma)\ Ar^{41}$$

However, it was necessary to seperate the argon before bombardment because of the interfering reaction:

$$K^{41}\ (n, p)\ Ar^{41}$$

D. Object of this research

It was the object of this research to investigate the possibility of a new method for potassium-argon age determination based on isotope dilution with a radioactive isotope which would not necessarily require the use of a mass spectrometer. The diffusion of argon through artificial glasses was to be determined. Also a number of the assumptions regarding the operation of an ultra-high vacuum system when used statically as a part of the general apparatus for argon determination were to be investigated.

II. Experimental

A. Description of samples

A description of the samples used in the various parts of this work is tabulated below.

1. (K. S.) Artificial potassium silicate

This material was prepared by Professor J. J. Naughton by melting in vacuo 19% potassium carbonate and 81% optical grade silica glass. The sample was remelted several times and crushed between each melting. The sample was finally crushed to -80 + 200 mesh, placed in an optical grade quartz tube, sealed, and irradiated in the pile at Brookhaven National Laboratories. After irradiation (and "cooling") the tubes were opened under water and a quantity removed for analysis by mass spectrometry. The tubes were reopened under water at this laboratory and a quantity of approximately 30 grams removed. This sample was placed in a vacuum dessicator and kept under vacuum and was withdrawn only shortly before use.

2. (K. A. S.) Potassium aluminum silicate

This sample was prepared from 71.3% optical grade silica glass, 16.5% potassium carbonate and 12.2% aluminum oxide. (Note: this resulted in a material approximately of the composition of the mineral leucite, $KAlSi_2O_6$) The melting, crushing, and irradiation procedures were the same as those for the potassium silicate. Both of these samples were annealed for 4½ hours at 250°C. after irradiation.

3. Mica sample

A sample of muscovite of unknown origin: Potassium analysis run at Brookhaven gave 9.06% potassium. Samples gave a potassium-argon age of 2490 million years and a Rb-Sr age of 2520 million years.

4. Diabase

A sample of Palisades diabase, whole rock at contact, as reported by Erickson and Kulp(62), kindly supplied us by Professor Kulp. The reported age is 202 ± 10 million years and the potassium analysis shows 0.52% potassium. The material was reported to show 100% argon retentivity.

5. NBS-1

National Bureau of Standards, Sample number 1: an argillaceous limestone: analysis reported as $K_2O = 1.15\%$.

6. S.S. 4984

National Bureau of Standards, Standard Sample #4984, a triassic diabase from Centerville, Virginia. Analysis reported as $K_2O = 0.58\%$.

7. Trachyte

A glassy trachyte specimen collected by the writer from the

Mauna Kuwale area, Oahu. The sample was crushed, sieved and the -20 +50 fraction used for analysis. This sample has not been analyzed in another laboratory; however, Macdonald and Katsura(63) reported on a sample from the same area. Their analysis shows K_2O = 3.60%.

B. Potassium analysis

One of the most useful methods of potassium analysis is the flame photometer. In this device, a solution of the element or elements is atomized into a flame which provides sufficient energy to excite the element to a level at which it emits characteristic radiation. This characteristic radiation may be analyzed by means of a spectrophotometer and the intensity of the radiation measured. The intensity of the radiation is proportional to the concentration, and thus with suitable calibration and comparison with standards, may be used for analytical determinations. Flame excitation sources can be reproduced accurately with relative ease and thus offer an analytical precision which is difficult to match by other methods. In addition, the spectra as developed by flame sources are relatively simple and interference by the spectral lines of other, similar elements is usually totally absent or, at least, small.

Unfortunately, in the case of potassium, each spectral line has a neighboring sodium line with which interference may occur. Since almost all rocks and minerals contain sodium in quantities equal to or greater than the potassium concentration, the problem of compensating for the sodium interference is always present. The most commonly used approach is to add a sodium buffer and thus produce a constant amount of interference. This method, while successful with materials containing large amounts of potassium, leads to errors and loss of sensitivity when the sample contains relatively small amounts of this element. The procedure and pitfalls have been well described by Dean(27).

It seemed that a more desirable method would be to eliminate the interference completely. Beukenkamp and co-workers(25),(26) attempted to develop a method based on this idea by separating the potassium on an ion-exchange column using Dowex 50 resin in the column. They reported partial success but stated that they were troubled with varying results when using different batches of the resin. This writer experienced the same difficulty when using this same resin.

Amphlett et al.(64) described an inorganic ion-exchange material which may be used for the separation of the alkali metals. The use of inorganic materials as cationic exchange agents is a relatively new development but seems to offer several advantages in inherently greater thermal and chemical stability. One of these, zirconium phosphate, is available commercially. This material is supplied in the form of a micro-crystalline gel and while the exact structure is not known, it has been shown that the ratio of zirconium ions to phosphate ions may be varied over a wide range with little effect to the ion-exchange properties.

Recently Adams(31) reported a rapid technique of potassium analysis which, surprisingly, did not require the prior separation of potassium. He reported results indicating an accuracy of 2% or better. Again, this writer has not been able to duplicate these results. Accordingly, a method based somewhat on both of the above procedures has been developed. This procedure is reported here, but the analytical results and a discussion of the method is given in the following sections.

1. Reagents and apparatus

a. Reagents

Reagent grade hydrofluoric acid and reagent grade nitric acid were used. Reagent grade sulfuric acid was mixed 1:5 with distilled, deionized water. Reagent grade hydrochloric acid was used to make solutions 0.05N, 0.1N, 0.3N and 1N in HCl. A stock solution of 1000 p.p.m. K was prepared by dissolving reagent grade KCl with a small quantity of water and then diluting to the appropriate volume with 0.1N HCl. This stock solution was used to make a series of standard solutions containing 0.5 to 10 p.p.m. by pipeting aliquots and dilution to volume with 0.1N HCl. The series was made to intervals of 0.5 p.p.m. within the above range.

b. Apparatus

A Beckman DU spectrophotometer equipped with a flame photometer attachment, an oxy-hydrogen burner, and a spectral energy recording attachment was used.

A Varian G-10, 10 mv, 1 second recorder was used to record the output from the spectrometer. This unit was equipped with a scale expansion accessory manufactured by the Wilkens Instrument Company, Walnut Creek, California, which made it possible to change the recorder sensitivity from 1 mv to 10 mv full scale. The most sensitive scale, 1 mv, was used where possible.

2. Procedure

a. Sample preparation

A representative sample was ground and passed through a 325 mesh U.S. standard size sieve. Of this, 0.25 gms. was weighed into a platinum crucible and heated to redness to destroy organic matter. The crucible was cooled and 1 ml. of sulfuric acid (1:5) was added and stirred with a platinum wire. Five ml. of concentrated HF was added and then the solution was evaporated on a hot plate to fumes of SO_3. This procedure was repeated, when necessary, to put the sample into solution. The residue was transferred to a beaker with 100 ml. of water and 5-10 ml. of HNO_3 and evaporated to dryness. The residue was taken up with not more than 25 ml. of 0.05NHCl and placed on the column.

b. Column

Columns 25 cm by 1.5 cm diameter were prepared with Bio-Rad ZP-1 exchange material of 50 to 100 mesh (Zirconium Phosphate microcrystalline gel manufactured by Bio-Rad Laboratories, Richmond, California) using standard methods. It was found necessary to pretreat the material by stirring with water, allowing it to settle for a few minutes and decanting off the liquid to remove "fines." This was repeated 2 to 3 times and then the material slurryied into the column. After treating the column with approximately 100 ml. of 0.05N HCl, the sample solution was placed on the column. Elution was started with 0.1N HCl until 50 ml had been used, then 0.3N HCl until 100 ml of this had been used and finally 1 N HCl. The first 120 ml was discarded, the next 400 ml was saved, diluted to 500 ml and an aliquota used for flame photometry using the procedure given below. A diagram comparing sodium and potassium concentration found vs. elution volume is shown in Figure 3.

c. Instrumental technique

The hydrogen pressure was set to 5 p.s.i., the oxygen pressure to 14 p.s.i. and the flame lighted. The DU sensitivity control was set to the counter-clockwise limit and the slit set to 0.15. Aliquots of the samples and standards were transferred to 5 ml. cups with care taken to fill each cup to the same level. One of the standards was placed under the burner capillary and the wave length dial moved carefully until it was ascertained that the instrument was set exactly on the 767 mu. potassium line.

The 10 p.p.m. standard was placed in position under the burner and the 100% potentiometer, photomultiplier sensitivity control and the recorder sensitivity control set. The

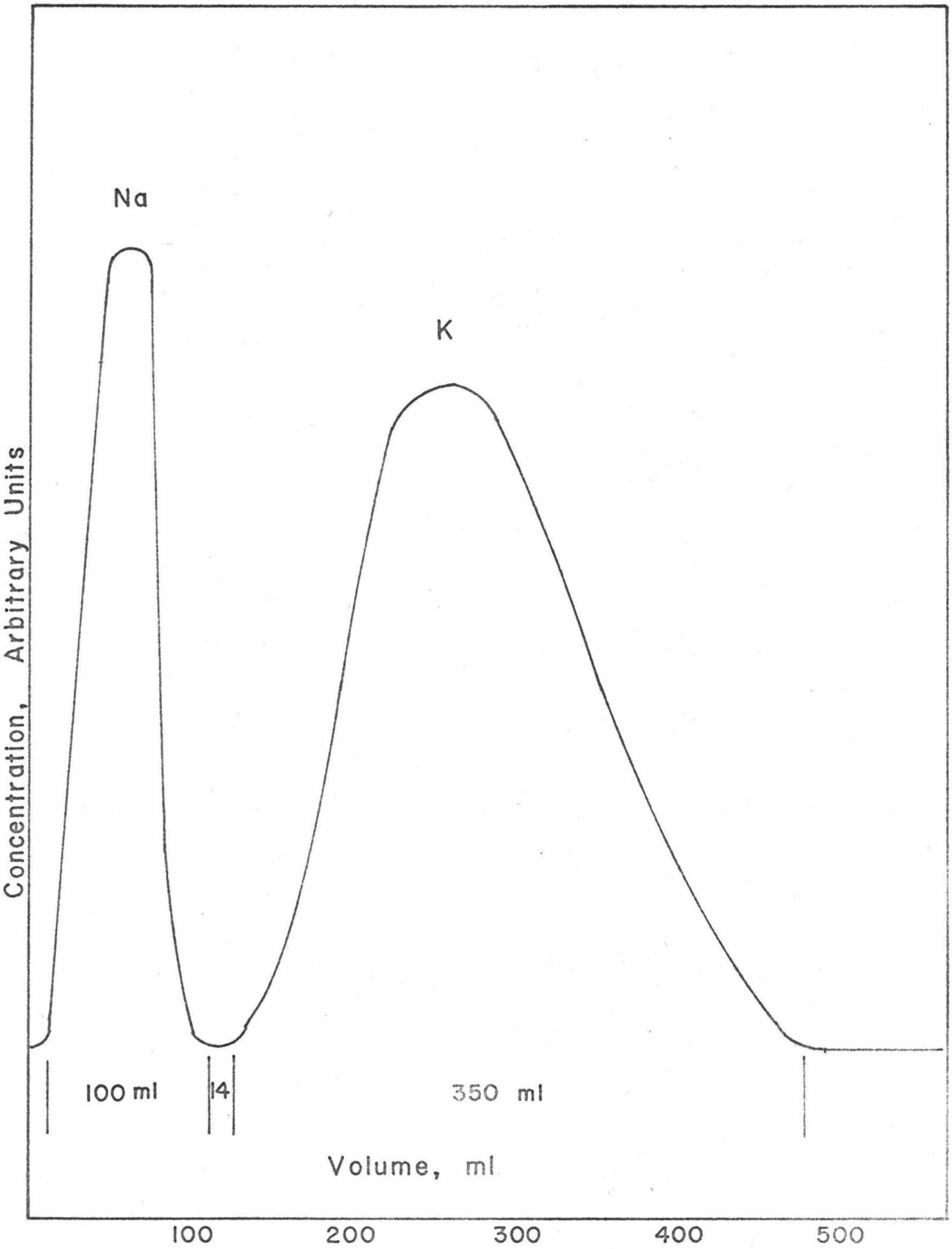


FIGURE 3 - Diagram Showing Sodium-Potassium Separation of Bio-rad ZP-1 Column

recorder response was near full scale. Each sample was then aspirated into the flame and each response recorded. This first check gave an approximate value of the potassium concentration so that the appropriate standard could be selected. At this time, any sample showing a concentration of greater than 10 p.p.m. was diluted to within this limit since a check had revealed that the determination followed a linear law only up to this point. See Figure 4.

After selecting the appropriate recorder range, adjusting it, and selecting the proper standard, the samples were run in the following manner, performing each change of solution as rapidly as possible. The standard was placed under the burner for a few seconds, withdrawn until the capillary emptied and then replaced for 5 - 10 seconds. The first response was discarded and only subsequent ones used. This was repeated with the sample and then again with the standard, and the whole procedure repeated at least twice more. A portion of a typical chart record obtained is shown in Figure 5.

The value of the base line and the value obtained from a blank determination was subtracted from the average recorder response and the results calculated according to the formula:

$$K\ (\%) = \frac{X}{A} \times \frac{B \times V}{W} \times 10^{-4}$$

where:

K = % potassium in the sample

X = net recorder response for sample

A = net recorder response for standard

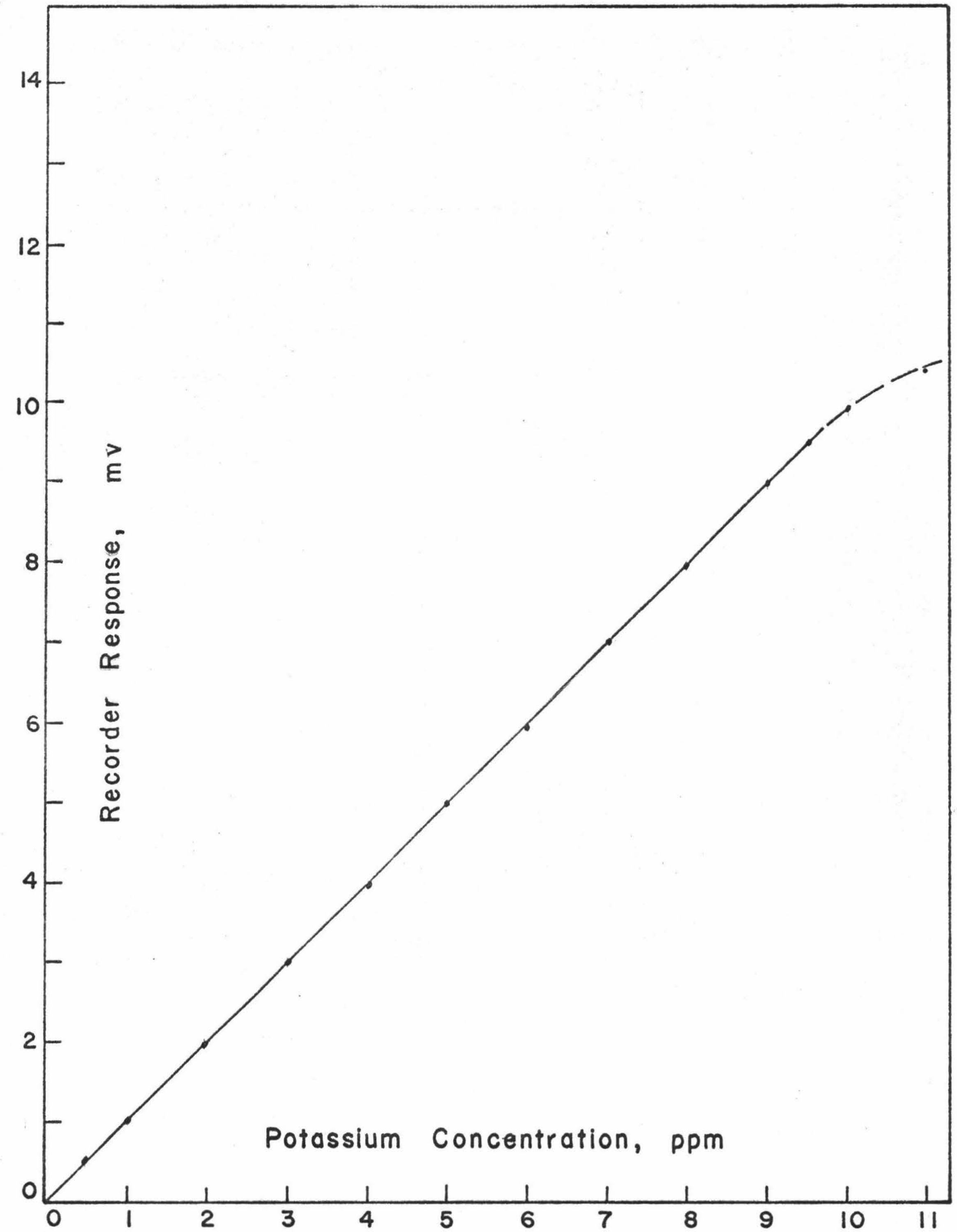


FIGURE 4 - Graph of Concentration vs Recorder Response for Potassium Analysis

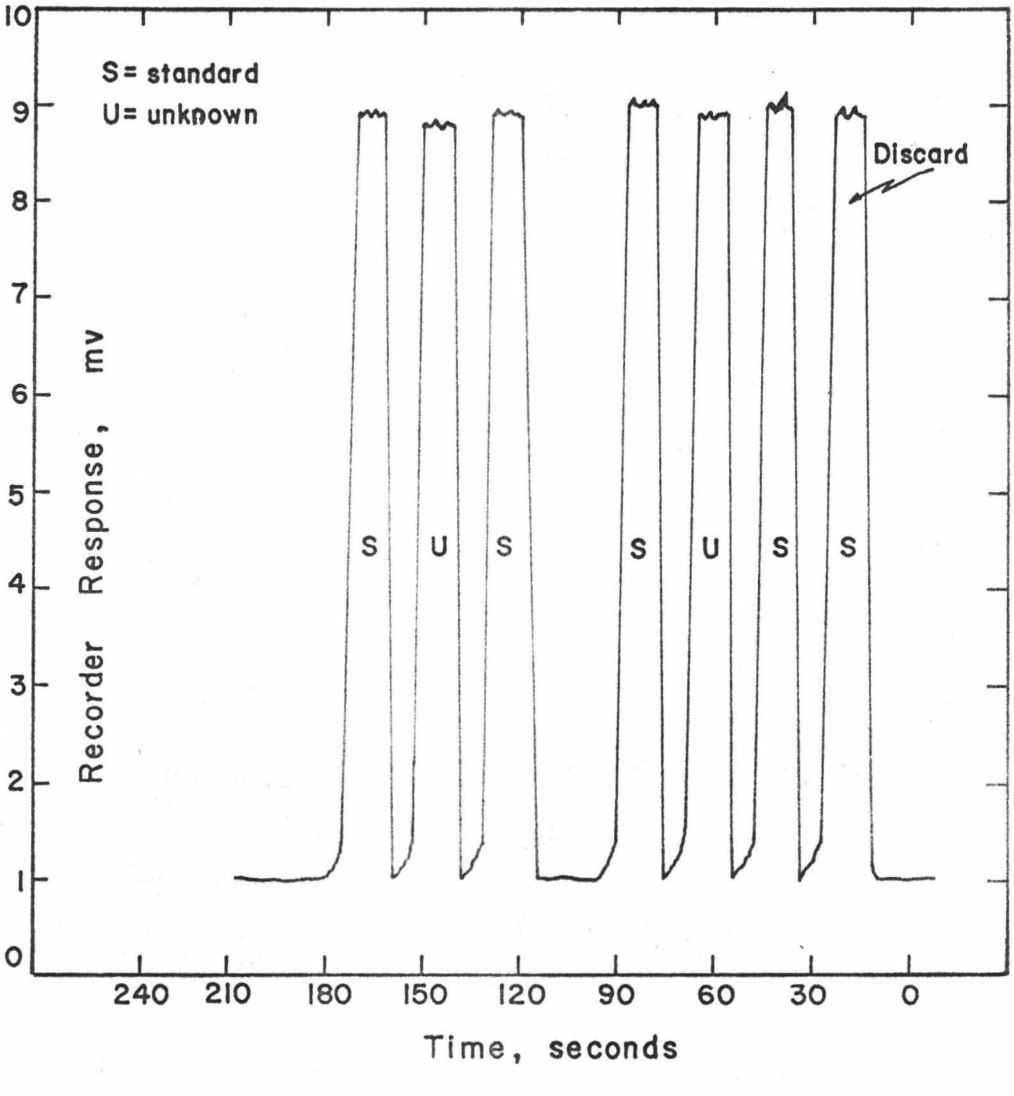


FIGURE 5

Typical Chart Record from Flame Photometer

S = concentration of standard, p.p.m. potassium

V = sample volume

W = sample weight

C. Diffusion studies

1. Vacuum system

To study the diffusion of argon in the artificial minerals, an ultra-high vacuum system was constructed as shown schematically in Figure 2. While the construction followed the general form as given by Alpert(39), modifications were made and the essential details are explained here. The system was mounted on a bench approximately 2 ft. wide x 3 ft. high x 5 ft. long constructed of Equipto angles. The top was covered with a piece of ½" thick transite with the underside lined with 2" of glass wool insulation.

The glass section was supported within a frame constructed of ½ in. round, type 302 stainless steel rods. The portion to be baked, shown in Figure 2 within the dashed box, was constructed on top of the bench while the remainder of the system was built under or to the side of the bench. Ovens to fit the top section of the system were constructed in two sections. Each section (approximately 17" high x 24" wide and 30" long, outside dimensions) was fabricated of 18 gauge aluminum sheet with an outer shell and an inner shell 4" smaller on all sides than the outer shell. These were put together with 4" of glass wool insulation separating the two. Four heater assemblies were prefabricated by bolting three 24 in., 500 watt chromalux heating bars to a piece of 1/8" x 12" x

2¼" type 302 stainless steel plate for each assembly. Two of these assemblies were bolted to the inside of each oven section parallel with the 30" side. The three heater bars were wired in series, with each section controlled with a 12 amp. Variac. With 11 amps passing through each heater assembly, the temperature inside the ovens could be raised to 350°C. in one hour.

The valves shown within the dotted line section in Figure 2 are all metal, bakeable, ultra-high vacuum valves (Granville-Phillips Type C.) One of the sections, marked "getter," was made from quartz tubing 20 mm. in diameter, closed on one end and connected through a quartz-to-Pyrex graded seal to the remainder of the system. This tube contained 30 gms. of copper wire clippings mixed with 2 gms. of silver moss, both of which had been carefully cleaned and solvent degreased before adding to the tube.

The other "getter" section was assembled from a nickel tube of 20 mm. outside diameter, 14 mm. inside diameter, closed at one end. A 20 mm. Kovar-to-Pyrex graded seal was soldered to one end of this nickel tube and 3 turns of 1/4" copper tubing coiled around and soldered to the Kovar-nickel joint. During use, water was circulated through the tubing to protect the joint. The nickel tube was fitted with a molybdenum "boat" containing 100 gms. of -20 +50 mesh titanium sponge. Each getter tube was fitted with a resistance wire wound furnace. The copper getter was operated at a temperature of 450°C. The titanium getter was heated to 950-1000°C., and then cooled to room temperature in contact with the gases to be purified. Between the getters was placed a 10 mm. quartz tube with approximately 0.1 gm. of -20 +50 mesh wood charcoal to act as an adsorbant for argon.

The sample compartment, also of quartz, was constructed from 20 mm. tubing constricted at the top to 10 mm. and attached to the system through a quartz-to-Pyrex graded seal. The unit marked "gauge" in Figure 2 was a Veeco, Bayard-Alpert ionization gauge (Vacuum Electronics No. RP-75). This gauge was controlled by a Veeco ionization gauge control which supplied the operating voltages to the gauge and also contained an electrometer for reading the plate current on a microammeter. This meter was calibrated to read the pressure directly as mm. of mercury (equivalent nitrogen pressure). The operating voltages used were as follows:

Plate potential	0 volts
Grid potential	+150 volts
Filament potential	+30 volts
Filament voltage	3 - 5 volts A.C.
Emission current, 10^{-4} scale	1 ma.
Emission current, 10^{-5} - 10^{-9} scales	10 ma.

The section under the bench consisted of three parts. These were:

1. The rough vacuum system
2. The calibrating and "spike" system
3. The transfer system used to transfer argon to a gas counting tube. These are shown in Figure 2 as the parts outside of the dashed lines and were the unbaked portions.

The vacuum system consisted of a mechanical pump attached to a two stage mercury diffusion pump. A 20 mm. bore trap was attached between the diffusion pump and the remainder of the system and the trap was kept cooled with liquid nitrogen at all times. The calibrating and "spike" system had a gas pipet modified by Professor J. J. Naughton after a Brookhaven design, which was connected to a one liter bulb of argon (Airco, analyzed, reagent grade). The pipet was made with a capillary section extending on either side to mercury in a reservoir, the level of which could be controlled by raising or lowering small side arms. One side of the capillary could be closed by a ¼" steel ball forced against an end of the capillary which had been ground previously to fit the steel ball.

In this manner, the cut-off point at the end of the capillary was accurately determined. This section also contained a Mc Leod gauge used to read and set the argon pressure.

The transfer section led to a 3-way stopcock. One side of this was attached to a vacuum pump (Welch 1400). The other two arms led to a counting tube and to the ultra-high vacuum system.

2. Counting system

a. Internal-fill gas counting tubes

The counting tubes used both for the diffusion studies and, later, for the age studies were patterned after those described by Bernstein and Ballentine(65). Some modifications were found necessary, however, to adapt this type of tube for this work. Ground glass joints were added to the filling tube so that the tubes could be easily and quickly added to or removed from the vacuum system. It was found more convenient to fill the tubes with counting gas on an auxillary system, and the glass joints facilitated this operation. A small "finger" was added to each tube (at point A in Figure 6) containing approximately 0.1 gm. of -20, +50 mesh wood charcoal so that the argon could be adsorbed and thereby moved into the tube. In addition, the tubes were manufactured with a 0.001 inch tungsten wire anode in place of the 0.003 inch wire used by Bernstein and Ballentine, since it was found by Glascock$^{(66)}$ that the plateau voltage for these tubes was a direct function of the anode diameter. The 0.001 inch wire lowered the plateau voltage to a more convenient range. A diagram of these tubes is included as Figure 6.

As mentioned above, an auxillary vacuum was constructed for evacuating and filling the tubes. This system consisted of a manifold to which was attached a container of a 90% argon - 10% methane proportional counting gas (Nuclear Chicago P-10) and a small mercury manometer, (A, Figure 7) used to measure the pressure of the gas in the system and tube. The system also contained a vacuum pump (Welch #1390), and a small thermocouple gauge (Consolidated Vacuum Corp.) as well as the necessary cold traps, (B, C) a schematic diagram of which is given in Figure 7.

The counting tubes, after filling to a pressure of 758-768 mm. of mercury with the filling gas, were connected through a preamplifier (Tracerlab P-30) to a scaler (Tracerlab Versamatic II)

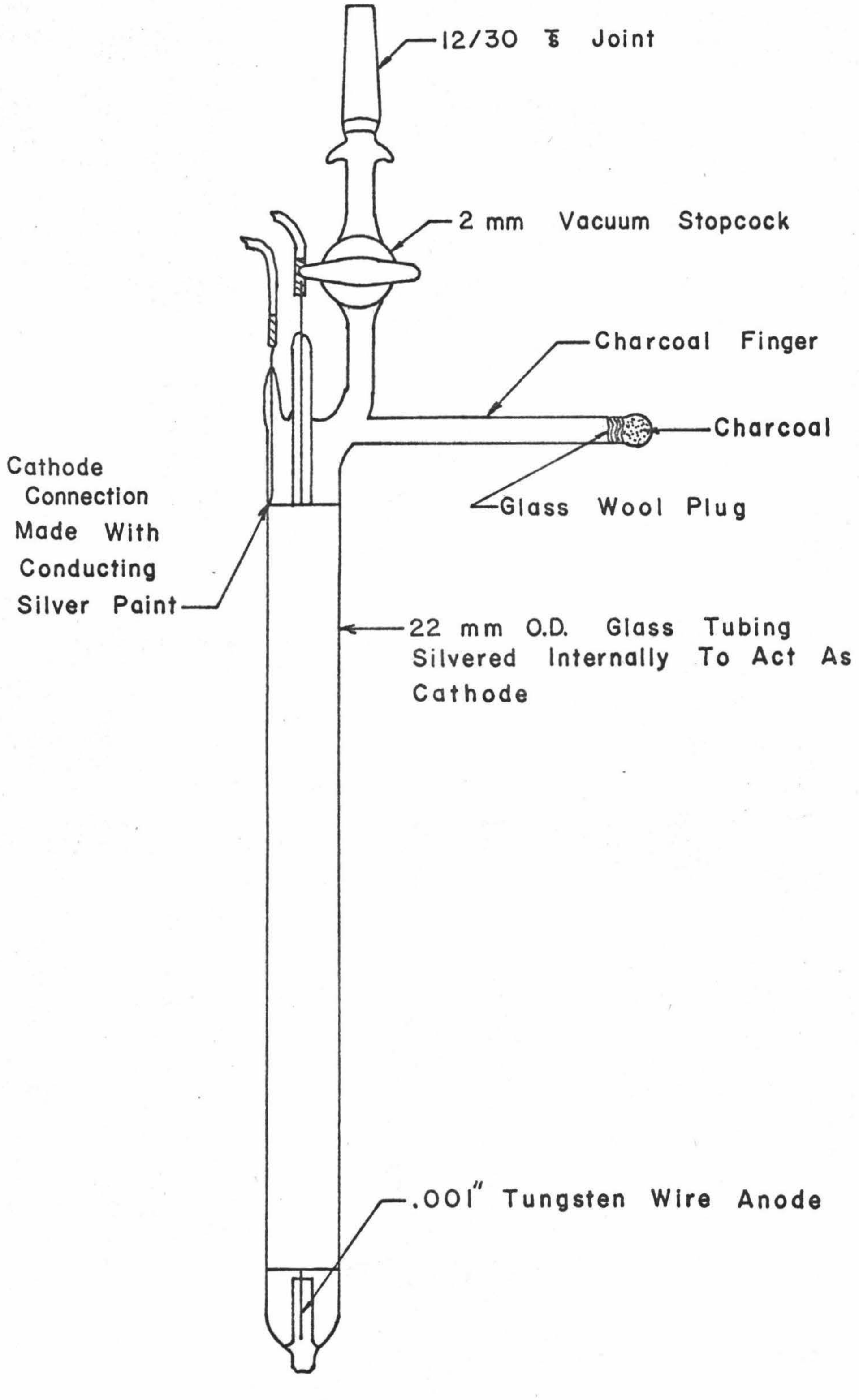


FIGURE 6 - Modified Bernstein-Ballentine Internal Fill Counting Tube

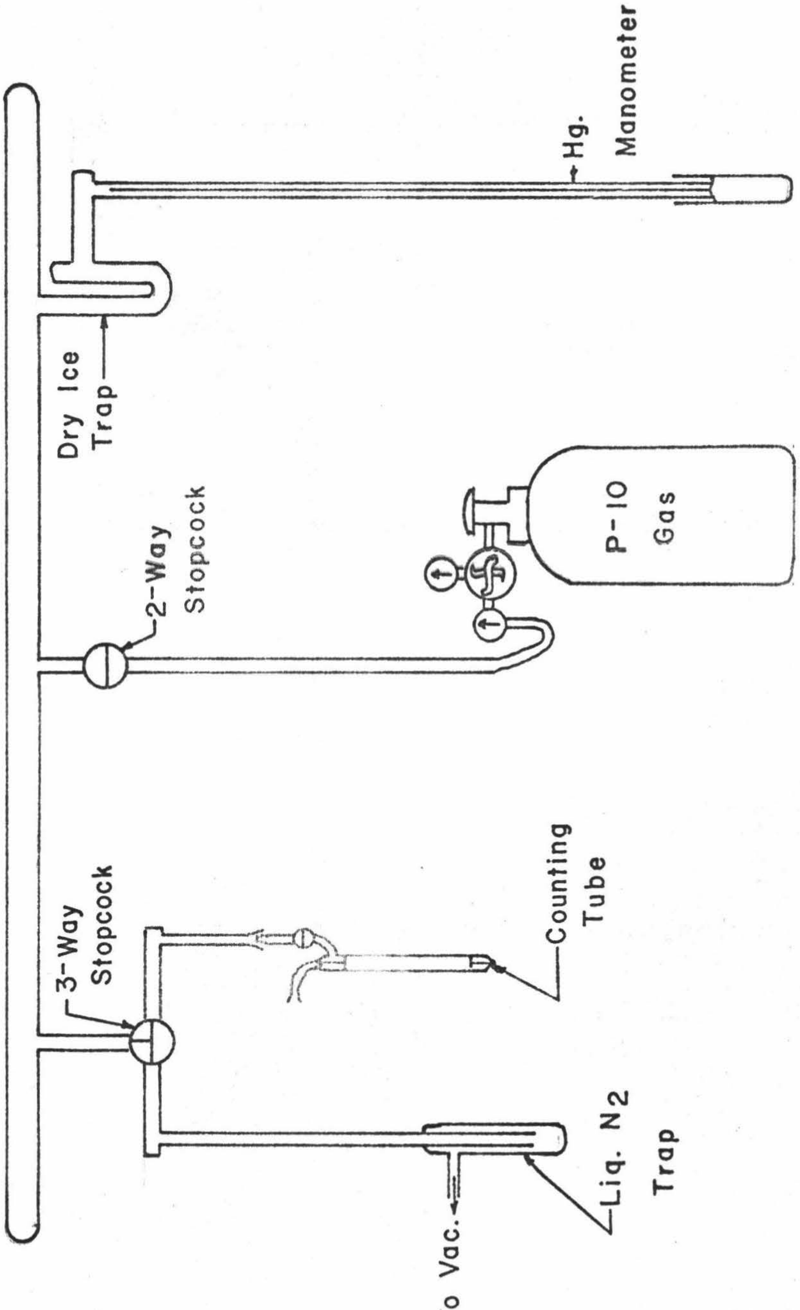


FIGURE 7 - Schematic Diagram of Filling System for Counting Tube

which contained an integral 0-3000 volt high voltage power supply. It was found that the counting tubes as supplied gave a rather high background count. To improve this, a cylindrical well or shield was constructed from a section of 6" diameter x ¼" wall pipe 14" long and a section of 1½" diameter x ¼" wall x 14" long tubing. These were welded together to make a hollow cylinder with approximately 2" space between the walls which was filled with mercury. The counting tube, when within the well, gave a background which was reduced by a factor of 3 to 4 times that of the unprotected tube.

3. Procedure

a. Calibration of tubes

Before each tube was put into service, the small charcoal "finger" was added and the active volume of the tube determined. This was necessary since the silvered area used as the cathode covered only a portion of the tube. The volume enclosed by the cathode was ascertained by adding redistilled toluene from a buret until it reached the lower edge of the silvered area and this value recorded. More toluene was added until the top edge of the silvered area was reached and this value recorded. The tube was then filled until the toluene had reached the bottom edge of the stopcock. The ratio of the total volume, obtained from the above values, to the volume enclosed by the cathode was used as a correction and all counting rates multiplied by this figure. After the above calibration, the tube was emptied, evacuated with a water pump, and then connected to the filling system. The tube was evacuated on this system while a small oven was put on the charcoal trap and the tube itself wrapped with a heating tape. Evacuation was continued while the trap was heated to 300°C. and the tube heated to 100°C. Heating was continued for 4 to 6 hours after which the tube was cooled to room temperature and filled with the counting gas mixture to a pressure of 758 to 760 mm. of mercury. The tube was then removed to the counting room, connected to the scaler and allowed to equilibrate for 4 to 8 hours after which the high voltage was adjusted and counting started in the usual manner. A curve of counts per minute vs. applied voltage was made, and from this the operating voltage determined.

It should be noted that in this particular design of the Bernstein-Balentine tube the electrode leads are only 8 mm. apart and under conditions of high humidity a leakage path developed between the electrodes. It was found that this could be corrected by coating the electrode end of the tube with Desicote (Beckman Instruments) and allowing the 4 to 8 hour equilibration period mentioned above. It was also found that the counting characteristics were changed drastically with the slightest contamination by mercury vapor. Even though all sources of mercury were kept well trapped with dry ice - acetone or liquid nitrogen traps, there always remained the possibility of contamination. For this reason the counting tubes in use were checked for operating voltages and background at least three times each week although it soon became evident that the actual background was constant and, in fact, the background of no tube changed by more than 2% during the period covered by this work. The various operating parameters of the tubes used are given in Table I.

b. Operation

(1) Vacuum system (Figure 2)

The following procedure was used whenever the vacuum system was started after a shut-down or whenever it became necessary to bake the entire system. This procedure varies slightly from the one ordinarily used but accomplishes the same result in slightly less time.

After the weighed sample was added to the side arm (A) above the sample tube along with a small magnetic "pusher" the vacuum system was sealed and the mechanical pump started. When the entire system was at a pressure of about 10^{-2} mm. of mercury, all glass parts were checked for leaks with a Tesla coil. At this point the diffusion pump was started and liquid nitrogen added to the trap on this pump. After a pressure of 10^{-3} -10^{-4} mm. of mercury was obtained, the various charcoal traps (B, C) were flamed to red heat with a hand torch and the ionization gauge degassed (E) by passing a current of 10 amps through the grid for 10 to 15 minutes.

Table 1

Operating Data for Counting Tubes

Tube	Plateau Length Volts	Slope Change Per 100 Volts	Operating Voltage Volts	Ave. Background CPM	Volume Factor
B	200	4.7%	2150	60.94	1.2139
D	150	5%	2150	58.27	1.2206
F	200	4%	2225	40.90	1.2292
J	250	4%	2100	57.64	1.1709
L	275	4%	2200	63.28	1.2151

After this the valve bodies were removed from the metal valves, bake-out clamps installed, the ovens placed over the system and the whole system was baked at 350°C. for 8 to 12 hours. The ovens were then allowed to cool to approximately 100°C. and then reheated to 350°C. for a second period of 8 to 12 hours. Leads were affixed to the small furnace covering the titanium getter and this furnace operated at a temperature of 900°C. to 950°C. during the second baking period. During the last three hours of this second baking period the liquid nitrogen level was lowered to cover only the lower 2 to 3 inches of the trap to remove condensed material to a lower part of the trap, thereby preventing re-evaporation when the liquid nitrogen level varied.

At the completion of the baking period the trap was covered with liquid nitrogen and the ovens turned off but allowed to cool in place until the temperature had dropped to approximately 100°C. The ovens were removed, the valve bodies replaced and the ionization gauge turned on. After a few minutes of pumping with this gauge, the pressure in the system was commonly around 10^{-9} mm. of mercury.

(2) Diffusion studies.

After the vacuum system pressure had reached approximately 5×10^{-9} mm. of mercury, a small resistance wire furnace was placed around the quartz sample tube (S) and this tube was heated to a temperature of 950°C. for 10 hours.

This temperature was at least 150°C. above the maximum to be used in the diffusion studies. This step was deemed necessary since it had been found by Naughton(67) in earlier work that fresh quartz tubing gives up large quantities of argon. When the sample tube had been thoroughly degassed, a small magnet was used to actuate the magnetic bar (D) inside the system and thus push the sample down into the sample tube. The copper getter was heated to its operating temperature, the titanium getter heated to 950°C. and the sample furnace preheated to 50-75 degrees above the temperature to be used. The pumps and gauge were then closed off from the sample and getter portions of the system. Liquid nitrogen was placed around the charcoal trap (B) and U-tube traps (K, F) and the sample furnace placed around the sample tube (S).

By preheating the furnace, the drop in temperature of the furnace when placed around the sample was held to about 50°C. below the temperature desired. The furnace reached the operating level within 10 minutes after being placed around the sample. After the selected time for the diffusion anneal had elapsed, the sample furnace was removed as quickly as possible and the sample allowed to cool to room temperature. The valve (G) connecting the sample and gettering sections was closed and the argon collected in the charcoal trap was released. After contact with the hot titanium for 20 minutes the sample was refrozen for 10 minutes and then released a second time.

When a second 20 minute period of contact with the hot titanium had passed, the getter furnace was removed and the titanium allowed to cool to room temperature. This took approximately 45 minutes. At this point, liquid nitrogen was placed around the charcoal trap (C) connected to the gauge section of the system and then the valve (H) connecting this section was opened and the purified argon allowed to distill into this trap. After 20 minutes, argon carrier gas was added from the storage bulb. This was added through the pipet whose volume had been determined by filling with mercury and then weighing the mercury used. The volume was calculated to be 0.12 ml. and with the pressure of argon carrier gas set at 350 microns, this meant that about 7×10^{-5} cc S.T.P. of argon carrier gas was added.

When the carrier gas had been added, the valves (H, I) were closed to isolate this mixture in the gauge section and the gases mixed by releasing and refreezing several times. When the gases had been thoroughly mixed, the valve (J) was manipulated to move the argon into a counting tube which had been connected to the system and evacuated during the above procedure. The charcoal trap on the tube cooled with liquid nitrogen was used for this transfer. A number of blank runs determined that 20 minutes was sufficient to effect this transfer but the process was always continued for one hour as a precautionary measure. The tube was moved to the auxiliary filling system, the line connecting the tube to the system was evacuated and the tube was filled with the counting mixture by expansion of the mixture into the tube. The tube was removed from the filling system and the electrode sections washed with acetone to remove traces of oil and grease, moved to the counting room, attached to the scaler, and counted as outlined above.

These operations may be summarized as follows:

1. Sample tube preheated
2. Getters heated, liquid nitrogen placed around collecting charcoal trap and sample heated
3. Collected gases released to getters
4. Background pressure in gauge determined
5. Purified argon moved to gauge and pressure determined
6. Carrier gas added and gases mixed
7. Gases transferred to counting tube
8. Counting tube filled with proportional counting gas
9. Argon-39 counted

(3) Age studies

(a) Apparatus

The apparatus for the first series of age studies was essentially the same as that for the diffusion studies as shown above with the exception of the sample heating section. Since the samples were to be heated to a temperature above their melting points, the simple quartz tube was replaced with a water jacketed apparatus containing a molybdenum funnel leading into a ½" diameter x 3/4" deep molybdenum crucible (A, Figure 8). This apparatus also contained several side arms for storage and manipulation of a number of samples and was equipped with a small 90° prism above the crucible so that the temperature in the crucible might be determined by sighting through the prism with a Leeds and Northrup optical pyrometer. This container was heated through an induction coil made from 10 turns of ¼" copper tubing attached to a 4 KW Lepel spark gap converter induction heater. A diagram of this sample container is shown in Figure 8.

(b) Procedure

Weighed portions of the rock or mineral to be used and the artificial potassium-aluminum-silicate were wrapped in small pieces of 0.001 inch thick copper metal foil and placed in one of the side arms in the sample system. As many as 10 to 12 samples could be introduced at one time but usually only 3 to 5 were added. The system was closed and a portable vacuum pump attached through a dry ice - acetone trap to the sample section. The sample section was evacuated, carefully flamed with a hand torch and then the portable pump disconnected by sealing off the glass connecting tube with the torch. The sample section was opened to the pumping section of the regular system and a small furnace placed around those samples

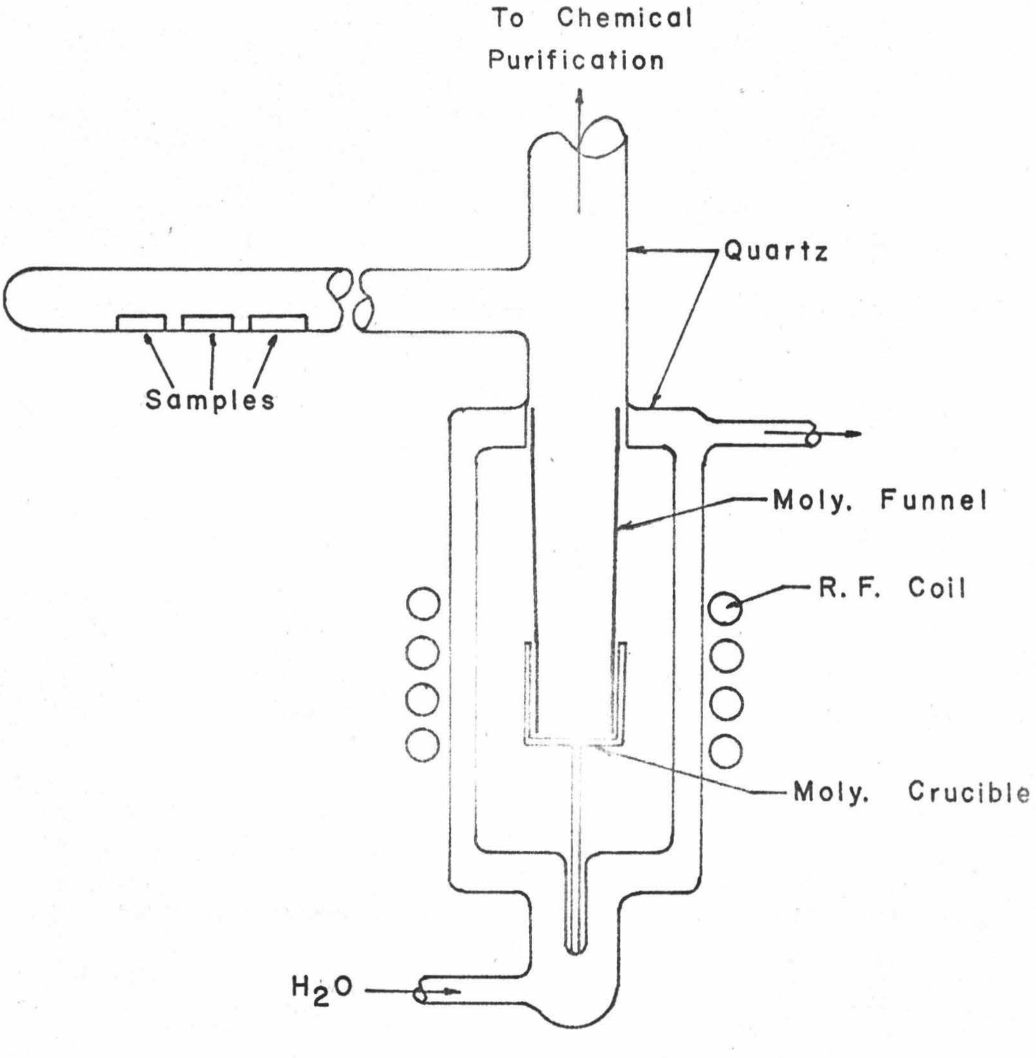


FIGURE 8

Drawing of Water Jacketed Sample Container Used for Original Age Determination Trials heated to 300°C. for 8 hours.

At the end of this time the funnel and crucible were preheated with the Lepel machine and then the section pumped until a pressure of approximately 5×10^{-8} mm. of mercury had been reached. The sample to be melted was then pushed into the crucible with a magnet. The samples were heated until a temperature of 1550°C. was reached (2 - 3 minutes) and then the heating continued for an additional 20 minutes. This heating was repeated for a second period of 20 minutes after which the sample section was closed off and the gettering process started. This process was the same as that already described above for the diffusion study.

The gauge and control as received from the manufacturer were calibrated with nitrogen and were therefore recalibrated with argon from the carrier gas section. For this calibration, various measured pressures of argon were added in increments of 0.12 ml. from the gas pipet and the pressure measured in the gauge after each increment. The results of the calibration and their significance are discussed in a later section.

Just prior to transferring the purified argon to the gauge, the background pressure in the gauge section was carefully measured and then the argon was moved to the gauge charcoal trap with liquid nitrogen. After the transfer the gauge section was closed, the liquid nitrogen removed and the pressure measured in the gauge section. Because of the known pumping action of the gauge, pressure readings were taken at a number of time intervals and a plot of pressure vs. time was extrapolated back to $t = 0$ to give the initial pressure. The liquid nitrogen was again placed on the charcoal and the gauge degassed for a period of time identical with the measuring period after which carrier gas was added and the gas mixed and transferred as described above. The measuring process, sketched here, became the subject of much study and is discussed in greater detail below.

An outline of this procedure is given here:

1. Samples weighed, wrapped and introduced into the system.
2. Sample section evacuated and samples baked.
3. Sample pushed into crucible and melted.
4. Collected gases released to getters.
5. Gases moved to gauge section and pressure measured.
6. Carrier gas added and gases mixed.
7. Gases transferred to counting tube.
8. Counting tube filled with proportional counting gas.
9. Argon-39 counted.

(4) Age studies - new system

After a careful study of the various parts and components of the vacuum system, it became apparent that gases were being adsorbed or trapped and later readmitted to the system causing large errors in the process. There was also some evidence at this point that the original gauge calibration curves might be in error due to some contaminating material in the trap separating the gas pipet and the gauge, and this was being transferred into the gauge along with the measured volumes of argon. To eliminate as many of these sources of error as possible, the system was redesigned and rebuilt, and the procedure was changed where necessary.

(a) Vacuum system changes

Since it was expected that the various rocks and minerals used would release a very large quantity of water by comparison with the other gases released, simple U-tube traps were added to the system. These traps were kept cool with liquid nitrogen during the runs and then were warmed and pumped out between runs. In the studies of the various parts of the system, it was found that these traps were also holding a quantity of argon and it was deemed necessary to try a different method of eliminating the water from the gases in the system. It was decided that one of the molecular sieve materials might be suitable for this purpose. These are artificial zeolite-like materials manufactured by the Linde Company and have structures consisting of three dimensional networks of silica tetrahedrons with "tunnels" within the network.

These "tunnels" or openings are of such size that water molecules should be trapped while the smaller argon molecules should move freely through the openings. There have been a few studies which confirm this and which have been reviewed and discussed by Cook(68). One of these materials, Linde molecular sieve No. 5A was available and the U-tube traps were replaced by 30 mm. tubes containing 50 gms. of this material in the form of 1/8" round by 1/4" long pellets.

In the original system, the same Bayard-Alpert type ionization gauge was used alternately as an ion pump and as a measuring device. This proved to be unsatisfactory because of re-emission of argon from the gauge when used in this manner. To correct this condition a second gauge was added, connected to the system through an additional all metal, bakeable valve. By this means, this new gauge, which was used only as a pump, could be isolated from the system during processing. This is shown schematically in Figure 9 at A, along with the other changes described.

It also proved to be desirable to operate the second gauge, which was now used only as a measuring device, at lower emission currents than were readily available with the Veeco ionization gauge control. Professor D. D. Denison of the Physics Department, Washington State University, very generously supplied a schematic drawing

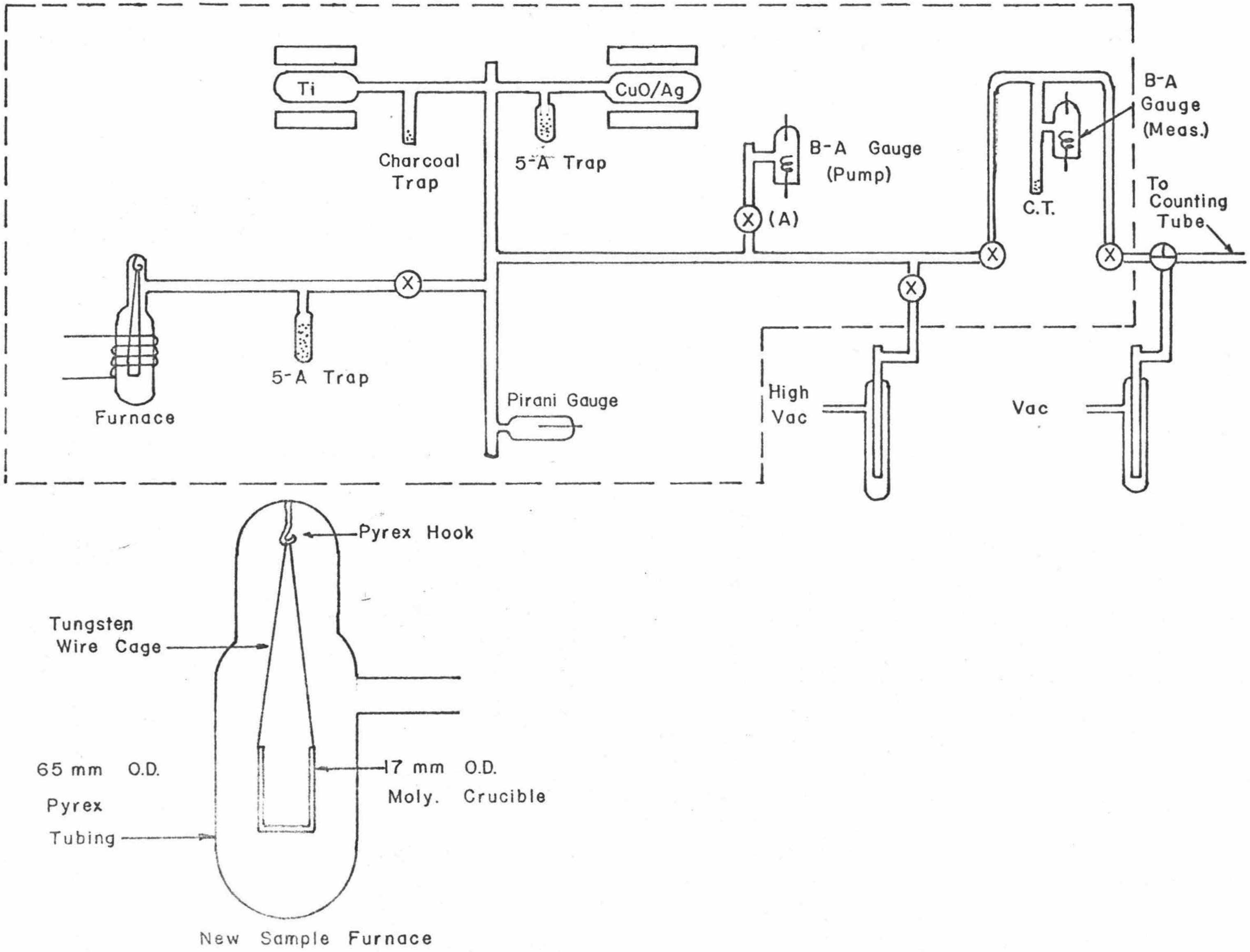


FIGURE 9 - Diagram of Redesigned Vacuum System with New Sample Container

of an ionization gauge control developed at Washington State which contained provisions for varying the emission current over a wide range. A unit (hereafter referred to as the Denison gauge control) based on this design was constructed and proved to operate in a very satisfactory manner. This unit was used to supply the operating voltages for the gauge used as a measuring device as follows:

plate potential	0 volts
grid potential	+150 volts
filament potential	+45 volts
filament voltage	3 to 5 volts A.C.
emission current	10 microamperes

A General Radio D.C. Amplifier and Electrometer was used to measure the plate current which was the parameter directly proportional to pressure.

In addition, this particular unit was designed to perform the function of degassing the gauge in a different manner than the Veeco control unit. The Veeco unit performs the degassing operation by passing a current of 10 amps through the grid which then heats the other elements by radiant heat. The Denison unit degasses by connecting the grid and collector together at the potential of 700 volts and passing a current of 10 amps through the filament. This heats the elements by ion bombardment. This latter method proved to be more satisfactory since the glass envelope was heated to a higher temperature which resulted in a lower ultimate pressure.

(b) Sample container

As will be shown in section III, the method of wrapping the samples in copper foil resulted in large losses of argon due to adsorption on the vaporized copper surface. It was decided that a system using a new sample container for each run, and thus eliminating the use of the copper foil, would remove this source of error. Accordingly a sample container of Pyrex glass was designed with a hook from which was suspended a cage made of 0.060 inch tungsten wire. A molybdenum crucible ½" in diameter by 1½ inches long was held within the tungsten cage. This sample container is shown in Figure 9. This design eliminated the outer water jacket used previously as it was found that, by cooling the walls with forced air from a small compressor and several small blowers, the container could be kept cool enough to prevent collapsing of the walls. The inner container was heated by the Lepel induction heater in the regular manner.

(c) Carrier gas system

The entire carrier gas system was removed from the ultra-high vacuum system and rebuilt as a separate independent unit. This unit is diagrammed in Figure 10.

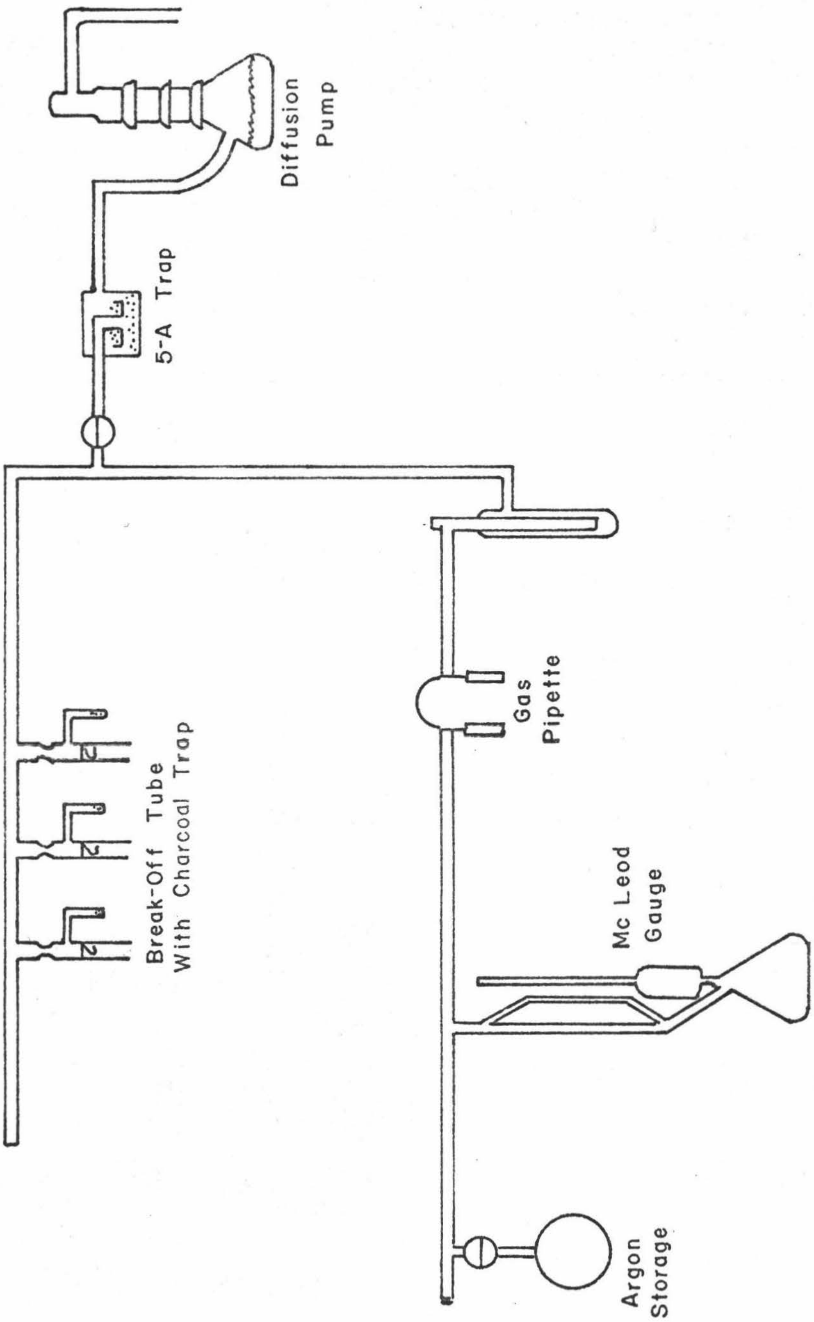


FIGURE 10 - Carrier Gas System for Redesigned Vacuum System

The operation of this system was essentially the same as before except that the dry ice - acetone trap needed to keep mercury vapor from the carrier gas could be removed and cleaned after preparing each set of calibration or carrier gas volumes. To transfer this argon to the regular system, small break-off sealed tubes were prepared with a small side tube containing a few pieces of wood charcoal. After fastening 10 to 12 of these tubes to the manifold by glass blowing, the charcoal tubes were heated to 300°C. for 2 hours. Argon was measured into these tubes through the gas pipet at a known pressure as measured with the Mc Leod gauge as before.

These tubes were then pulled off from the system with a torch while the charcoal was still cooled with liquid nitrogen. The tubes, now sealed and containing a known volume of argon, could be inverted, a small magnetic bar added and sealed to the ultra-high vacuum system, to be opened when needed.

(d) Procedure changes

The sample container was prepared by assembling the unit with the crucible in place, attaching it to an auxiliary vacuum system, evacuating to a pressure of 10^{-6} mm. of mercury and heating with the induction heater for 40 minutes. A temperature of 1680°C. as measured with an optical pyrometer was reached within four minutes. After cooling, the container was removed, opened, and the previously weighed mixture of sample and artificial silicate added to the crucible, the container resealed and the whole assembled on the ultra-high vacuum system as quickly as possible. This was done after some experience in 15 minutes but in no case did it take longer than 45 minutes. A sealed break-off tube containing 7-8 x 10^{-5} cc S.T.P. of argon carrier gas had been added to this section earlier.

The sample section was evacuated with the portable pump and trap system while a small oven was placed around the molecular sieve trap and a larger oven around the entire sample container. The sieve material was heated at 300°C. for four hours while the sample compartment was baked at 400°C. for 12 hours. At the end of this period the portable pump was sealed off, the sample section opened to the remainder of the ultra-high vacuum system and the whole system pumped with the pumping Bayard-Alpert gauge until a pressure of 5-8 x 10^{-8} mm. of mercury was reached.

At this point the pumping gauge was isolated from the system by closing the valve, the sample melted for 20 minutes with the Lepel machine and then the argon purified by gettering in the usual manner. After gettering, the gas was moved to the gauge section as before and measured, except that measurements were taken with an emission current of 10 microamps and readings were taken for no more than 15 seconds. These readings were plotted vs. time, and the plate current at time equal to zero obtained by extrapolation. This reading was translated into a pressure measurement from a previously prepared calibration curve.

Carrier gas was added from the break-off tube by breaking the small seal with a small magnetic bar actuated externally by a magnet, the gas mixed, transferred to a counting tube and counted in the previously described manner.

(5) Calculations

For reference, it is repeated here that the process for age determination that was investigated in this study involved the following:

1. Extraction of an amount of mixed argon-39 and argon-40* (The * hereafter refers to argon-40 that is the product of the radiogenic disintegration of potassium-40) from the sample plus the diluting artificial mineral.
2. Removal by gettering of all other gases.
3. Measuring by means of an ionization gauge of the total volume of gas remaining.
4. Measuring by radioactive counting the amount of argon-39 in the above volume.

Assuming for the moment that the above steps could be performed with adequate accuracy and that the concentration of potassium was known, the age of a rock or mineral could be determined by the sets of calculations as shown below. Since the calculations leading to the determination of an "age" for the sample involve a number of steps, these are discussed here in some detail.

1. Amount of argon-39 recovered.

$$Ar^{39} = \frac{(C - B) \times F}{K \times W}$$

Where:

Ar^{39} = amount of argon-39 recovered Std. cc/gm.

C = counting rate, counts per minute

B = background, counts per minute

F = tube factor, ratio of total to active volumes

K = number of counts per minute expected for 1 S.T.P. cc

$Ar^{39} = 7.87 \times 10^{10}$

Ar^{39}, $t_{\frac{1}{2}}$ = 325 years = 1.7082×10^{8} minutes

$$\text{dpm/Std. cc} = \frac{1}{2} \times \frac{6.023 \times 10^{23}}{2.24 \times 10^{4} \times 1.7082 \times 10^{8}}$$

$$\frac{\text{atoms/gm. at. wt.}}{\text{Std.cc/gm.at.wt.x min}}$$

$= 7.87 \times 10^{10}$

W = Weight of argon-39 containing material used

2. Fraction of argon-39 retained through baking and processing

$$f = \frac{Ar^{39}\ (r)}{Ar^{39}\ (a)}$$

Where:

f = fraction of argon-39 retained through process.

Ar^{39} (r) = amount of argon-39 recovered, Std. cc/gm

Ar^{39} (a) = amount of argon-39 added in diluting material Std. cc./gm.

3. Fraction of argon-39 lost in processing only.

$A = (1-f) - Y$

Where:

A = Fraction of argon-39 lost in processing

(1-f) = Fraction of argon-39 lost in processing and baking

Y = Fraction of argon-39 lost in baking only

This fraction Y is obtained either from direct independent measurement or from Figure 11.

4. Amount of argon-40* measured

As noted earlier, the gauge was calibrated in terms of argon measured by adding known amounts of argon and obtaining a corresponding reading of the gauge. This calibration is shown in Figure 12. From the calibration, the number of cc. S.T.P. of argon in the gauge volume could be read directly.

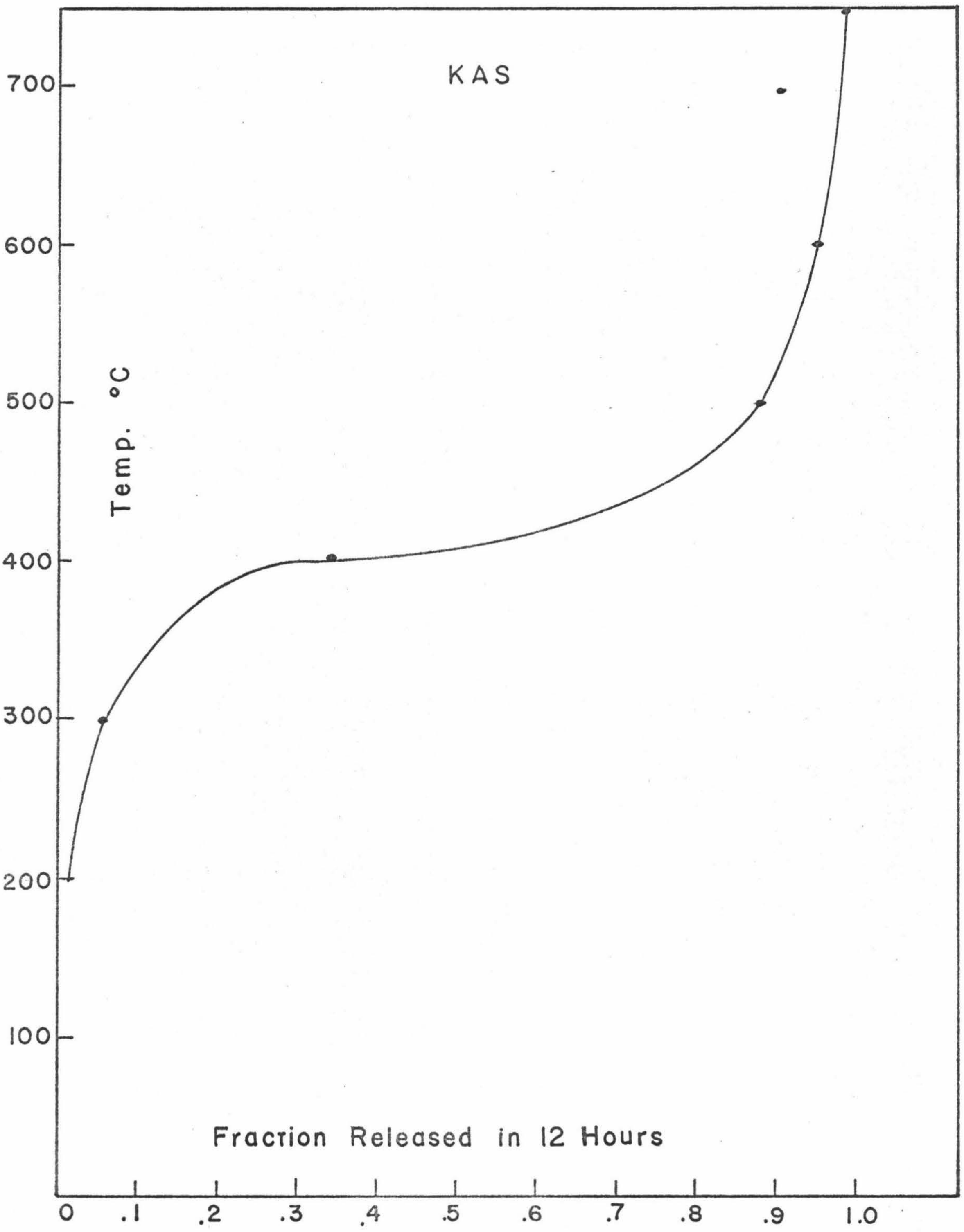


FIGURE 11 - Graph Showing Fraction of Argon Released from the Artificial Potassium Aluminum Silicate During a 12 Hour Bake at Various Temperatures

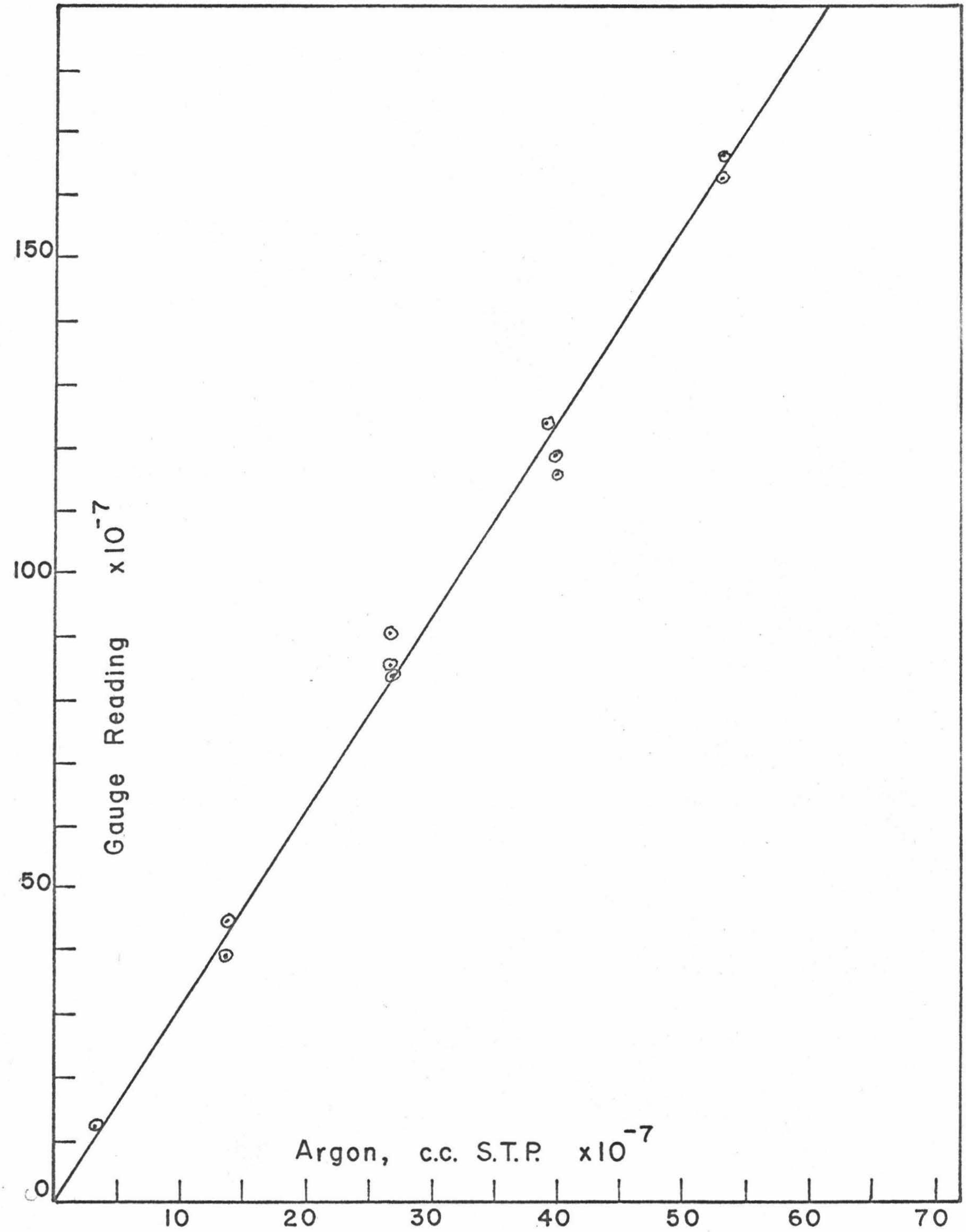


FIGURE 12 - Original Bayard-Alpert Gauge Calibration at 10 ma. Emission Current

5. Argon-40* lost in baking.

In this study of the amount of radiogenic argon which was lost in the baking could easily be calculated since this information was available from previously published results of other workers for a variety of rocks and minerals. The values used were 2% argon lost for the mica, from the data published by Reynolds(52), and 3% argon lost from the diabase, from data published by Hart(69). If samples had been used where diffusion properties were not known, the amount of argon lost in the baking process would have had to be determined in a separate study. This step could be avoided if the material containing the diluting isotope was exactly the same as the natural sample, both chemically and structurally. This condition would be difficult to meet experimentally. It should be possible, however, to generate the diluting isotope (argon-39) within the sample itself by neutron bombardment and then measure the diffusion characteristics as was done with the artificial samples used in this work. The chemical composition of the sample in some cases would make further handling difficult due to other long lived isotopes produced by the bombardment, but this problem could be anticipated for any particular sample by careful examination of the composition.

6. Total radiogenic argon-40* obtained from the sample before processing - $Ar^{40*}(t)$

$$Ar^{40*}_{(t)} = (Ar^{40*}_{(m)} \times X) + Ar^{40*}_{(m)}$$

Where:

$Ar^{40*}_{(t)}$ = Ar^{40*} obtained from the sample before processing, Std. cc.

$Ar^{40*}_{(m)}$ = Ar^{40*} as measured, Std. cc.

X = fraction lost in baking process

7. Total argon-40* obtained from sample

$$Ar^{40*}_{(T)} = Ar^{40*}_{(t)} + (Ar^{40*}_{(t)} \times A)$$

Where:

$Ar^{40*}_{(T)}$ = Total argon-40* obtained from the sample corrected for losses in baking and processing, Std. cc.

A = fraction of argon-39 lost in processing

8. Total weight of argon-40* in sample

From the above calculations of the total amount of argon-40* obtained from the sample corrected for losses from baking and from the processing procedure, the weight of Ar^{40*} in the sample can be determined:

$$\text{Weight of } Ar^{40*} = \frac{Ar^{40*}_{(T)} \times 40}{22.4 \times 10^{3} \times W}$$

Where:

$Ar^{40*}_{(T)}$ = total corrected volume of argon-40* from sample, Std. cc.

W = Weight of sample taken, grams

9. Total potassium-40 in sample

Natural potassium contains 0.0122 weight per cent of potassium-40 and therefore the weight of potassium-40 in the sample may be calculated:

$K^{40} = \% K \times 0.0122 \times 10^{-4}$

10. Ratio of argon-40* to potassium-40 in the sample

$$\frac{Ar^{40*}}{K^{40}} = \frac{Ar^{40*}_{(T)}}{K^{40}} \quad \begin{array}{l} \text{(As determined in 8 above)} \\ \text{(As determined in 9 above)} \end{array}$$

11. Age of sample

When the above ten steps have been completed, the necessary information is available for the calculation of the age of the sample by substitution in the formula:

$t = 0.1825 \ln (1 + 9.130\ Ar^{40*}/K^{40}) \times 10^4$ my

See appendix I.

12. Example

To illustrate how the above steps lead to the calculation of an age for the sample, an actual sample calculation is included here. In the run involving the mica, the following data were obtained:

a. Sample weight taken = 0.00659 gms.

b. K.A.S. weight taken = 0.45299 gms.

c. Counting rate obtained = 5248.40 cpm.

d. Tube background = 63.28 cpm.

e. Tube factor = 1.2151

f. Bayard-Alpert gauge plate current = 0.500×10^{-8} amps

g. Gauge background plate current = 0.045×10^{-8} amps

Then repeating the above steps:

1. Amount of argon-39 recovered

$$Ar^{39} = \frac{(5248.40 - 63.28) \times 1.2151}{7.87 \times 10^{10} \times 0.45299}$$

$$= 1.77 \times 10^{-7} \text{ Std. cc/gm}$$

2. Fraction of argon-39 retained through baking and processing

Note: From previous blank runs and from mass spectrometric measurements, this sample is known to contain 3.55×10^{-7} Std. cc/gm. argon-39.

$$f = \frac{1.77 \times 10^{-7}}{3.55 \times 10^{-7}} = 50\%$$

3. Fraction of argon-39 lost in processing only

Note: Previously determined that this sample would lose 35% of its argon-39 in baking.

$$A = (1 - .50) - .35$$

$$= .15 \text{ or } 15\% \text{ lost in processing}$$

4. Amount of argon-40* measured

Gauge current = 0.500×10^{-8} amps - background =

(less) $\underline{-0.045 \times 10^{-8} \text{ amps}}$

Net current 0.455×10^{-8} amps

From Figure 13, gauge calibration, this current represents 9.3×10^{-6} Std. cc. argon = $Ar^{40*}_{(m)}$

5. Argon-40* lost in baking

   As mentioned above, a figure of 2% lost in baking was obtained from diffusion data published by Reynolds.

6. Total argon-40* obtained from sample before processing - $Ar^{40*}_{(t)}$

   $Ar^{40*}_{(t)} = 9.3 \times 10^{-6} \times 0.02 + 9.3 \times 10^{-6}$

   $= 9.49 \times 10^{-6}$ Std. cc.

7. Total argon-40* obtained from sample - $Ar^{40*}_{(T)}$

   $Ar^{40*}_{(T)} = 9.49 \times 10^{-6} + 9.49 \times 10^{-6} \times 0.15$

   $= 10.91 \times 10^{-6}$ Std. cc.

8. Total weight of argon-40* in sample

   $$\text{Wt. of } Ar^{40*} = \frac{10.91 \times 10^{-6} \times 40}{22.4 \times 10^{3} \times .00659}$$

   $= 0.2956 \times 10^{-5}$ gms/gm

9. Total potassium-40 in sample

   Sample contained 9.06% natural potassium, therefore

   $K^{40} = 9.06 \times 0.0122 \times 10^{-4}$

   $= 0.1105 \times 10^{-4}$ gms/gm

10. Ratio of argon-40* to potassium-40

    $$R = \frac{0.2956 \times 10^{-5}}{0.1105 \times 10^{-4}}$$

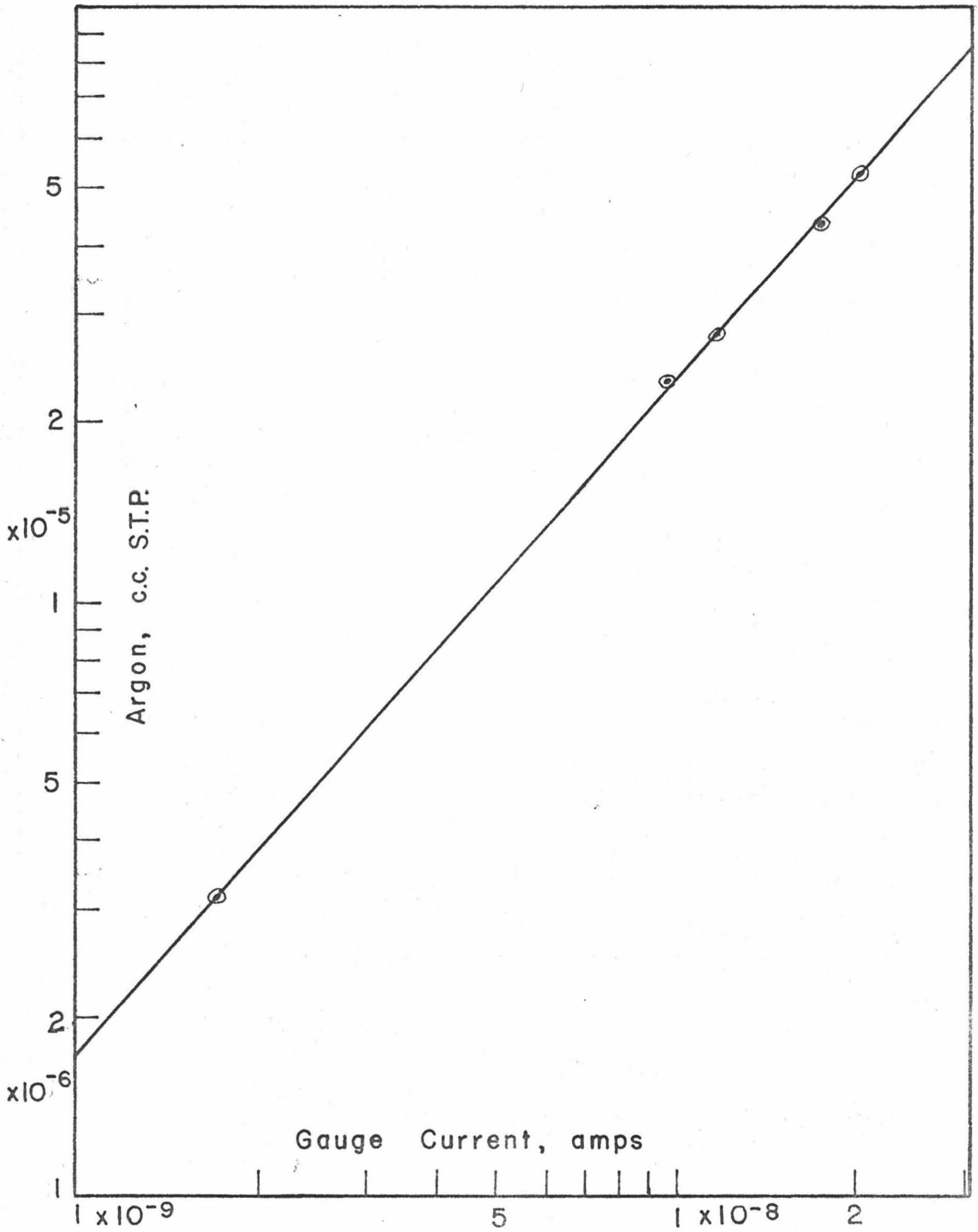


FIGURE 13 - Calibration Plot for Bayard-Alpert Gauge at 10 ua. Emission Current

$= 0.2675$

11. Substituting this value in the equation:

$t = 0.1825 \ln (1+9.130 \times Ar^{40*}/K^{40}) \times 10^4$ my

Results in $t = 0.2304 \times 10^4$ my

$t = 2304$ my

III. Results and discussion

A. Potassium analysis

The results of the potassium analysis of the various rocks and minerals are given in Table 2.

In addition to the samples shown, the mica sample was also analyzed and while the precision was excellent, the accuracy when compared with the results of a professional analyst was very poor (ie. 14%). It may be that the results of the other analyst are in error, but also it is believed that this sample may have been inadequately or improperly dried.

It should be noted that in each of the cases cited in Table 2, the analytical results are within approximately 1% of the accepted value and it is to be anticipated that other types of rocks and minerals would give results around this level of accuracy. This expectation is based partially on the fact that the two analysts mentioned were relatively inexperienced undergraduate assistants, and in spite of this they experienced few difficulties. Persons familiar with the use of the ion-exchange columns and flame photometry will immediately be aware that nothing in the above procedure is aimed towards a rapid analysis. It is unfortunate that this is so, although it is believed that the consistent accuracy obtainable with this method will more than offset the comparatively long periods of time involved, particularly when dealing with the problem of determining ages of young rocks with low potassium concentrations.

B. Diffusion studies

Table 2

Results of Potassium Analysis of Various Rock and Mineral Samples

Sample	Accepted Value % K	Results (1) Analyst 1	Results (1) Analyst 2	Standard Deviation	Accuracy (2)
NBS - 1	0.95	.95	.94	.009	0.5%
SS - 4984	0.48	.47	.48	.006	1.04%
Diabase	0.52	.52	.52	.000	0.0%
Trachyte	(3)	---	3.34	.002	---

(1) Average of 3 - 4 determinations by each analyst

(2) % deviation of average from accepted value

(3) No value, see remarks in Section II

In the age studies reported here, the only information required concerning the diffusion of argon in the artificial silicates was the value of F, the fraction of argon diffusing in a particular time at various temperatures. As will be shown below, however, this value of F may be used with certain mathematical manipulations to yield the diffusion constant for the diffusion of argon through, and out of, the samples. In fact, the value of F is the only measurement that is needed if suitable assumptions may be made about the structure and grain size of the particles. It was felt that in addition to this use, the information might be of particular importance in deciding the suitability of various basalts or rocks of this type for age studies since very little is known about the retentivity for radiogenic argon-40 in these materials.

The diffusion constant, of course, coupled with some idea of the thermal history of the rocks, will allow an estimate of the retentivity. Thus the extension of the experiments was made to temperatures higher than absolutely necessary. The results of these studies, the information deduced from them, and the possible significance are reported here.

The basis of most descriptions of the various diffusion phenomena is the statement:

$$J = -D \frac{\partial C}{\partial x}$$

first postulated in 1855 by Adolf Fick. This equation states that the flow, J, is proportional to the concentration gradient, $\partial C/\partial x$. The proportionality constant, D, is the diffusion co-efficient.

Although Fick's law may be applied in the solution of a very large number of physical chemical problems, the present interest is only in the solution and numerical evaluation for a relatively few geometric and boundary conditions which apply to the diffusion of the rare gases from rocks and minerals under natural conditions. If a homogeneous phase with a uniform gas concentration is assumed, and the concentration of the gas at the surface is taken as zero, then the solution of Fick's law for a number of simple particle geometries is easily obtained. Under the experimental conditions ordinarily used where the diffused gas is expanded into a vacuum system with a large volume and, in addition, is being constantly adsorbed on activated charcoal, the assumption of zero surface concentration is considered valid.

In this particular study, the samples involved were all assumed to have spherical geometry, and a solution valid for a sphere was used and converted into an equation in terms of F, the fraction of argon released in any time, t, and is given by Jost(70) and by Crank(71). This equation is:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \frac{-n^2 \pi^2 Dt}{a^2}$$

where a is the radius of the sphere. Reichenberg(72) arrived at an approximation of the above which is accurate for conditions where F is less than 0.85 at which time this approximation is particularly convenient. The equation is:

$$F = \frac{6}{\pi^{3/2}} \sqrt{Bt} - \frac{3}{\pi^2} (B\ t)$$

where $B = \pi^2 D/a^2$

Reichenberg further gives a table of values of Bt for various values of F.

As was described in Section II, measurements of the amount of argon released at different time intervals at a fixed temperature were made. The total argon contained in the sample was measured by fully melting the sample and thus the fraction F released by diffusion was determined. From the Reichenberg tables, a value of Bt is found for each value of F and this value is plotted vs. the corresponding time. These data for the two samples of artificial silicate are given in Tables 3 and 4 and the plots of Bt vs. t are given in Figures 14 - 18.

If no process except pure volume diffusion is taking place, the plots of Bt vs. t should give a straight line passing through the origin. In fact, this condition is rarely if ever found, and it may be seen that these sample plots were not exceptions. An examination of the plots shows that in all cases the points may be represented by two or more straight line segments. This effect has been interpreted by other workers (see, for example, Hart(69)) as implying that the diffusion of argon takes place for two or more structural positions and this interpretation seems reasonable and is accepted here.

The slope, B, of the lines in the above graphs, is related to the diffusion coefficient by $B = \pi^2 D/a^2$. By finding the value of the slope and measuring a, the effective radius of the particle, conversion can be made to the diffusion coefficient D, although there is always some uncertainty about the actual value of a. For

Table 3

Data for Argon Released from Samples

Sample	Temp. °C.	Time (sec)	Ar^{39} Released Std. cc x 10^{-7}	Ar^{39} Cumulative Total x 10^{-7}	F Fraction Released x 10^{-2}	Bt x 10^{-3}
K.S.	300	3600	.0054	.0054	.186	.0029 *
	500	3600	.062	.062	2.13	.30 *
	600-1	3600 60	.112	.112	3.8	1.20
	600-2	7200 120	.008	.120	4.1	1.42
	600-3	10,800 180	.023	.143	4.9	2.10
	600-4	14,400 240	.036	.179	6.1	3.30
	750-1	3,600 300	.087	.266	9.1	7.30
	750-2	7,200 360	.033	.299	10.27	9.40
	750-3	10,800 420 180	.008	.307	10.55	10.10
K.A.S.	300	3600	.021	.021	1.78	0.27 *
	500	3600	.061	.061	5.19	2.29
	600-1	3600	.055	.117	9.82	8.70
	600-2	7200	.017	.132	11.13	11.40
	600-3	10,800	.023	.155	13.05	15.70
	600-4	16,200	.019	.175	14.70	20.20
	600-5	19,800 5½ hrs	.017	.192	16.14	24.60
	700-1	3,600	.014	.206	17.33	28.70
	700-2	7,200	.008	.214	18.03	31.10
	700-3	10,800	.004	.219	18.41	32.50
	700-4	14,400	.002	.221	18.60	33.20
	800-1	3,600	.0016	.222	18.74	33.80
	800-2	7,200	.00058	.223	18.79	33.91
	800-3	10,800	.00039	.224	18.82	34.10
	800-4	14,800	.000426	.225	18.86	34.22

Items marked with an * indicate separate samples

Table 4

Data for Diffusion Curves

Sample	Temp. °C	$\frac{1000}{T(^{\circ}K)}$	D/a^2	$\mathrm{Log}_{10}\, D/a^2$
K.S.	300	1.75	8.39×10^{-11}	-10.07598
	500	1.294	8.4×10^{-9}	- 8.07572
	600	1.145	3.4×10^{-8}	- 7.46852
	750	0.978	2.05×10^{-7}	- 6.68825
K.A.S.	300	1.75	7.69×10^{-9}	- 8.11460
	500	1.294	6.44×10^{-7}	- 6.19111
	600	1.145	2.45×10^{-6}	- 5.61083
	700	1.028	8.05×10^{-4}	- 3.0942
	800	0.932	9.51×10^{-4}	- 3.02182

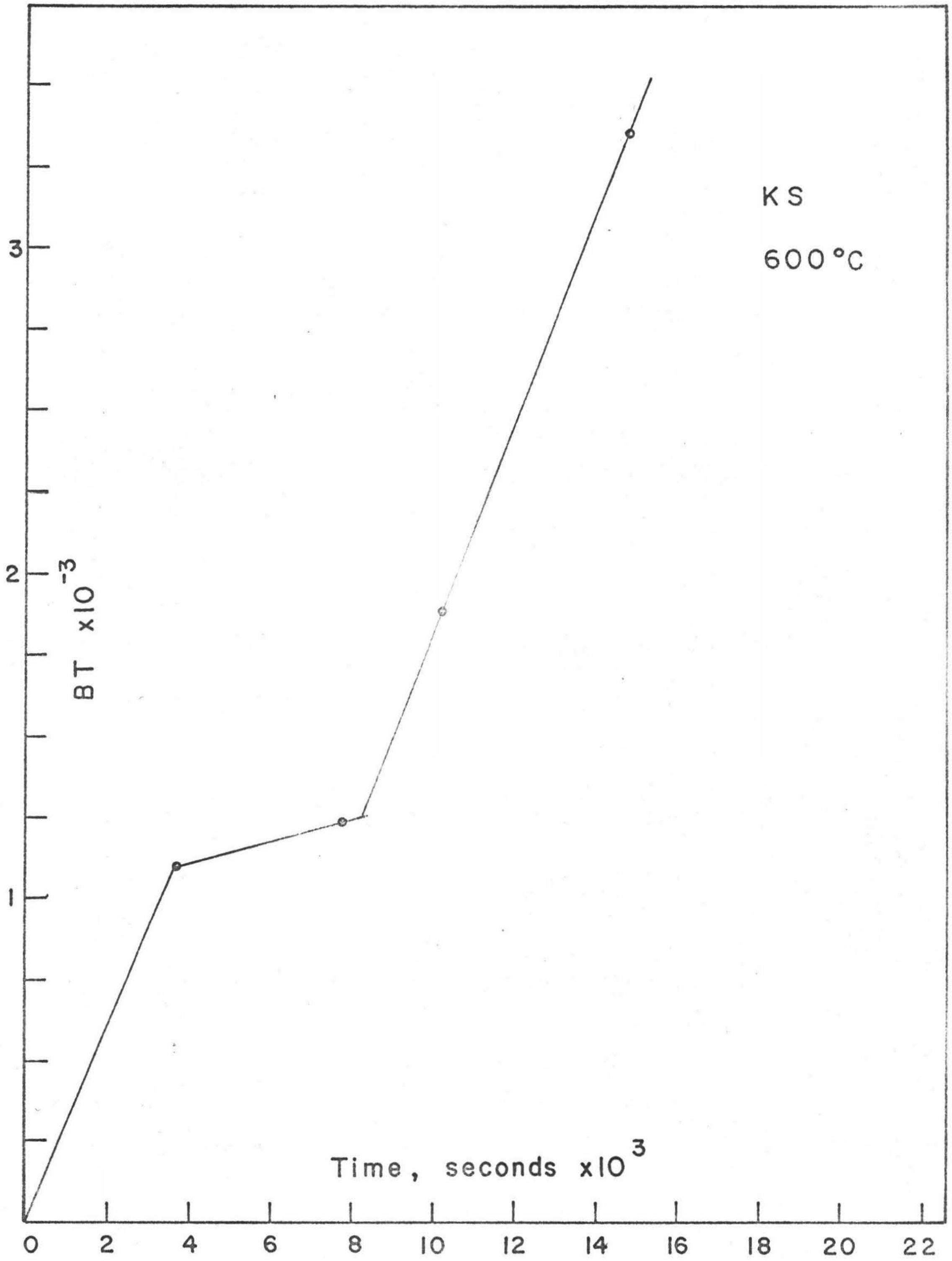


FIGURE 14 - Plot of Bt vs Time for Potassium Silicate at 600°C

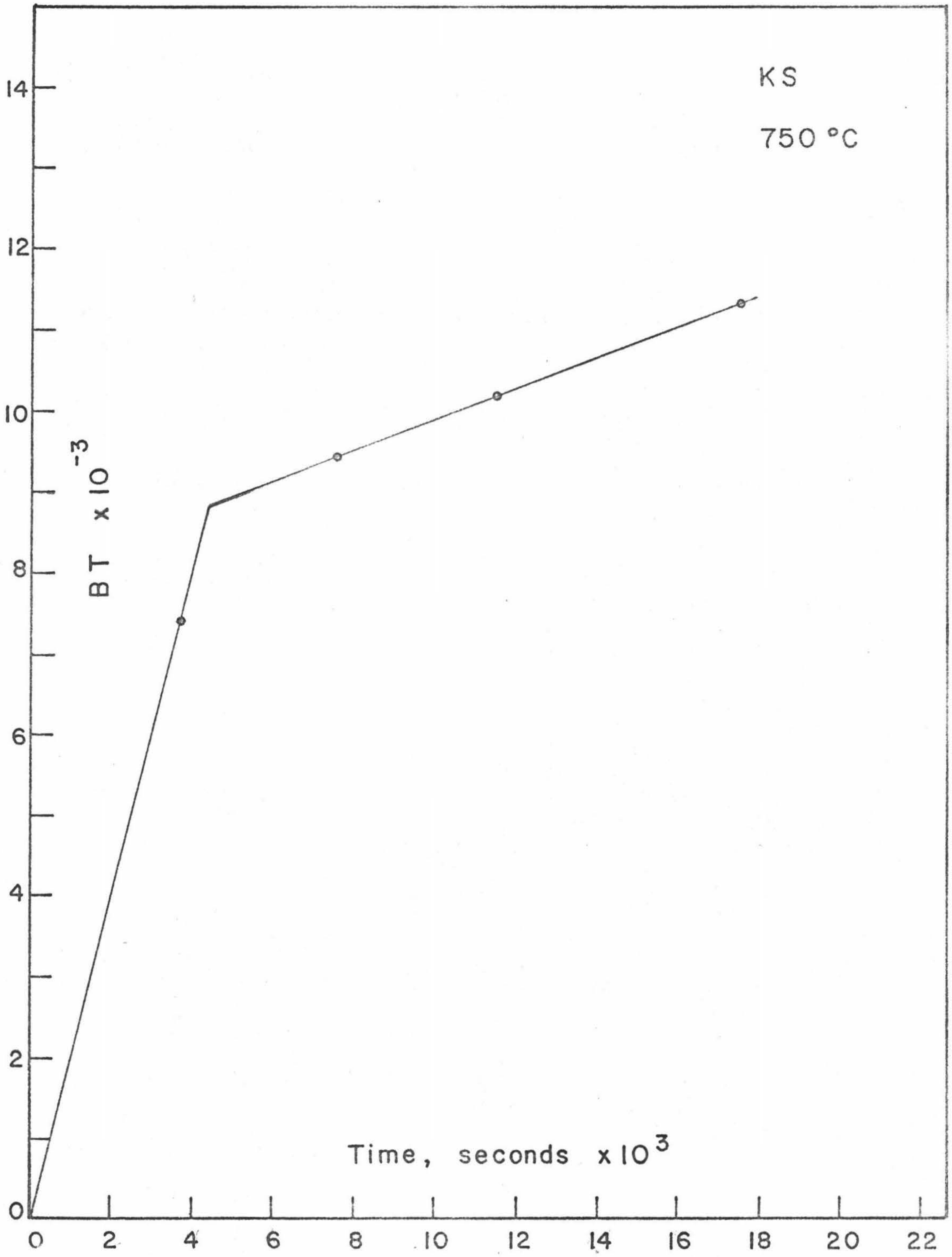


FIGURE 15 - Plot of Bt vs Time for Potassium Silicate at 750°C

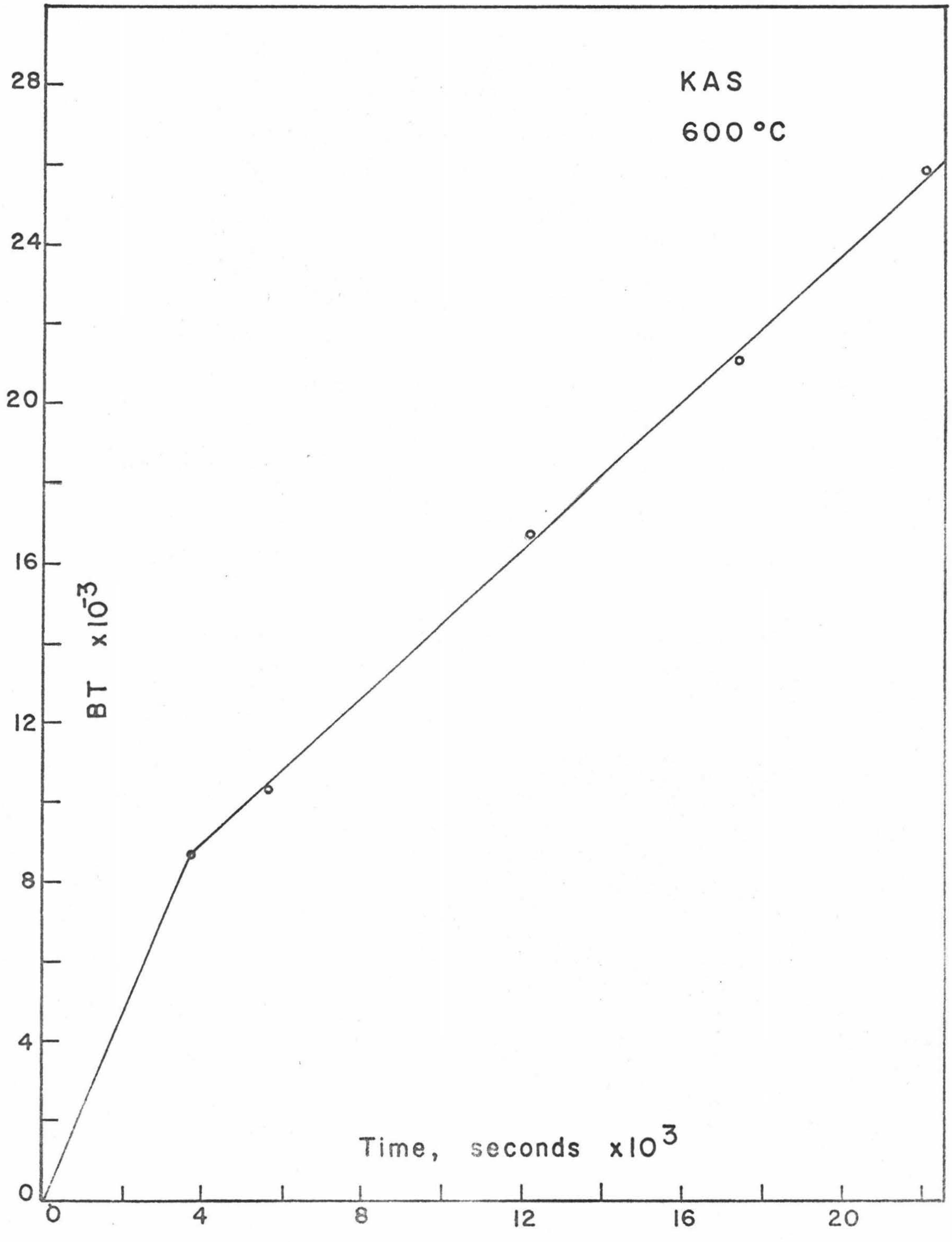


FIGURE 16 - Plot of Bt vs Time for Potassium Aluminum Silicate at 600°C

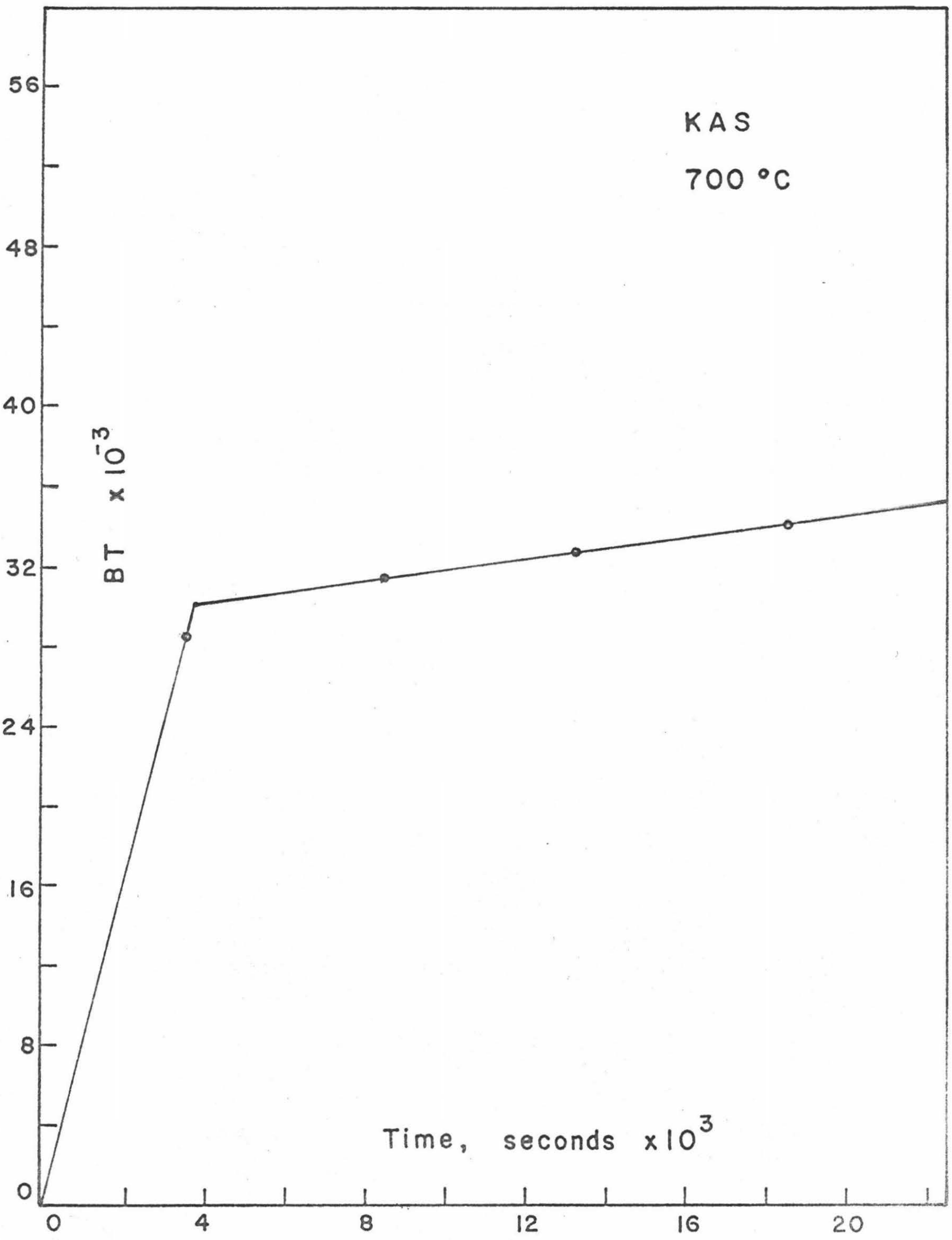


FIGURE 17 - Plot of Bt vs Time for Potassium Aluminum Silicate at 700°C

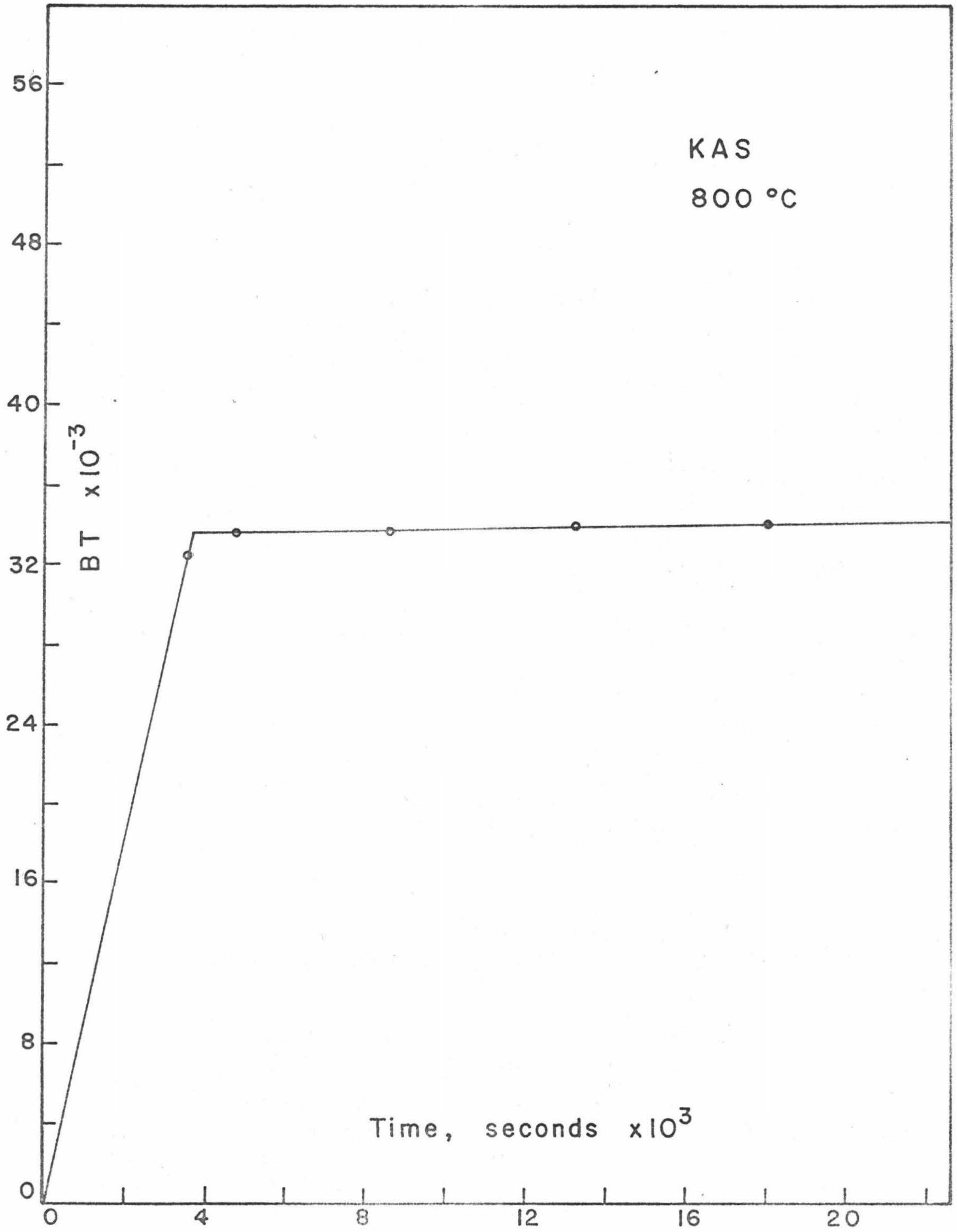


FIGURE 18 - Plot of Bt vs Time for Potassium Aluminum Silicate at 800°C

this reason, values of D/a^2 are usually used. In this study, values of D/a^2 for the early segments of each plot (representing the argon most easily lost) were calculated and plotted vs. 1000/T. In this form, values of the "energy of activation" for argon diffusion may be obtained through the equation:

$$D = Do \exp \frac{Q}{RT}$$

The graphs of D/a^2 vs. 1000/T are shown in Figures 19 and 20.

The plot in Figure 19 for the potassium silicate material is a straight line as would be expected if argon was released by simple diffusion from any particular region within the individual particles. The activation energy of 20 KCal/mole is in good agreement with values found for glasses of this general type.

The graph of Figure 20, however, is not a simple straight line but is composed of two straight line segments. This has been noted for other materials by a number of workers and the explanation of this has been the subject of some controversy. Hart(69) and Evernden et al.(53) noted this effect for feldspars and offered the explanation that some kind of change of phase within the sample during heating was responsible for the change in slope. Gentner and co-workers(13) however postulated that the second or middle segment represented argon diffusing from areas of crystal imperfections and defects and was not the result of a phase change.

To attempt to resolve this controversy, at least for the artificial potassium-aluminum silicate used here, x-ray diffraction powder photographs were made of this material both before and after

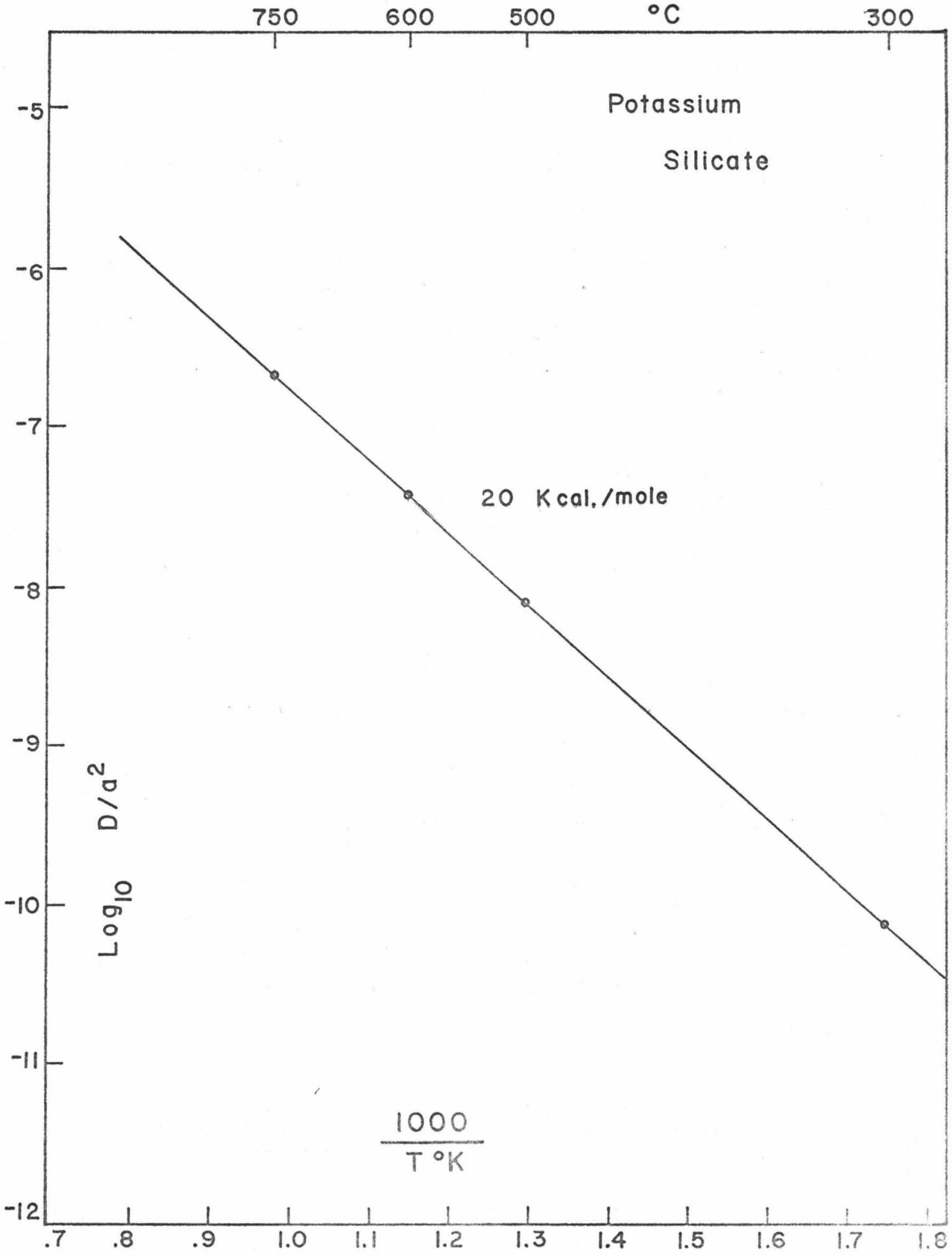


FIGURE 19 - Plot of Log D/A^2 vs 1000/T for Artificial Potassium Silicate

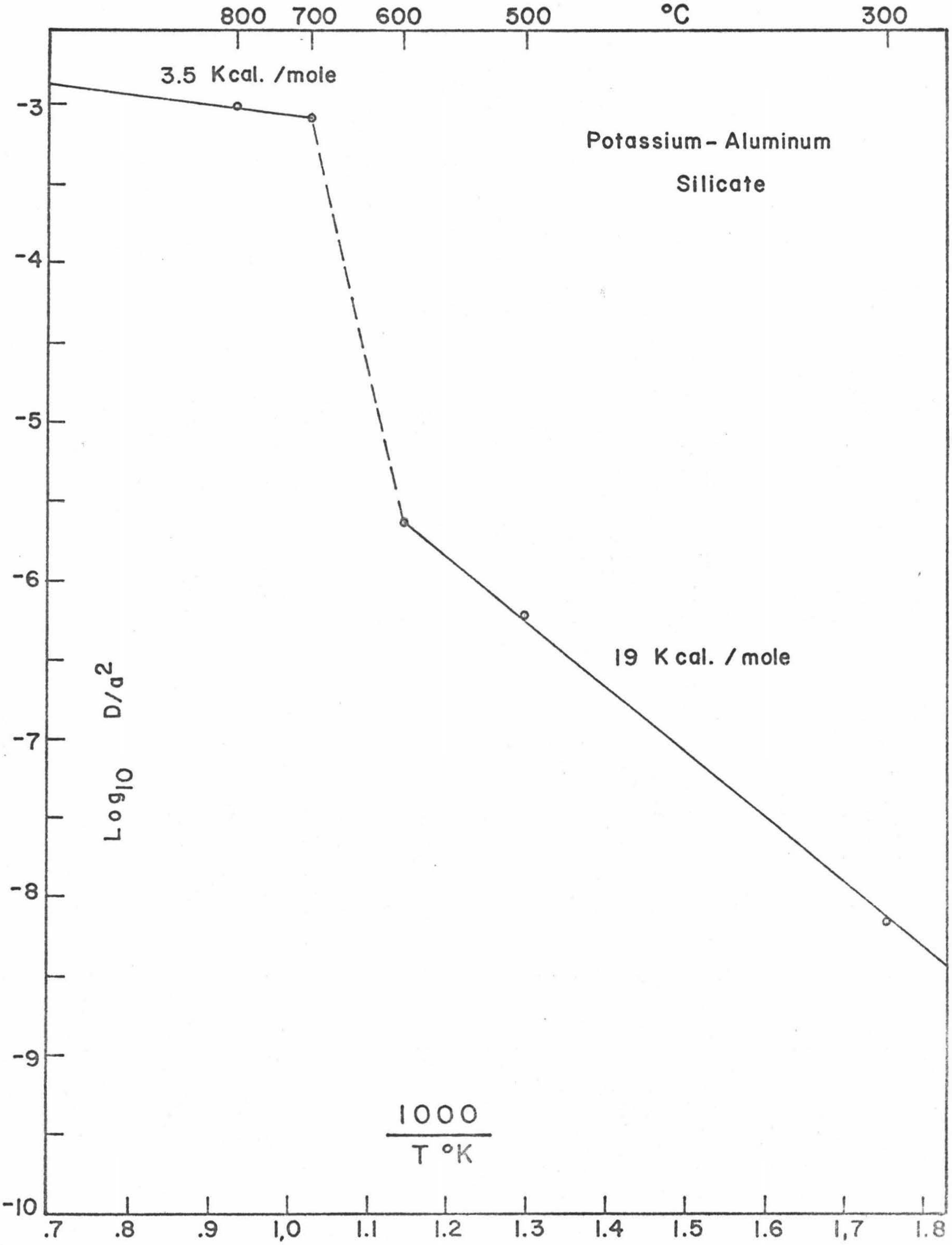


FIGURE 20 - Plot of Log D/A^2 vs 1000/T for Potassium Aluminum Silicate

the heating process. The photograph of the material before heating showed no diffraction lines at all but only the very diffuse pattern expected of a completely amorphous glass. The photograph of the material which had been used for the diffusion determination, however, gave a definite diffraction pattern. The "d" spacings of these lines were measured and corresponded to spacings of 3.44, 3.28, 2.76, and 1.949 angstroms which correspond quite well with those expected from crystalline leucite. This data would indicate that the change of slope found in the diffusion curve was definitely due to a change of phase within the material when heated in the range of 600 - 700°C. As indicated earlier, however, the data needed for other parts of this work was the fraction of argon released as a function of the baking time and this data was calculated from the above for a baking period of 12 hours and in shown in Figure 11.

C. Initial age studies

The vacuum system as originally constructed, including all of its various components was a standard type used by a number of groups doing age determinations and no difficulty was anticipated with the operation of these components. The only detail in which this system varied was in the counting system. This system was thoroughly checked with a sealed Co^{60} source which was taped to the outside of the tube and then counted. From the known disintegration rate of the source, geometry of the source and of the thickness of the tube wall, calculations indicated that these tubes were not only counting satisfactorily but were counting with almost 100%

efficiency. This same result had been found for tubes of a similar design by Glascock(66) when counting carbon-14 (for which an internal standard is available). He reported that these tubes counted with at least 99% efficiency within the active volume. In addition, studies by Carr and Kulp(34), using radioactive argon-37, indicated that argon could be moved through a vacuum system with no losses, and Hurley(37) has reported that argon may be quantitatively adsorbed on activated charcoal at liquid nitrogen temperatures in 10 minutes at room temperatures.

It was, therefore, somewhat disappointing when early experiments indicated that large quantities of a contaminating gas, probably argon, were present. In addition, experiments with the artificial silicate alone (using only the argon-39 component) indicated that argon was being lost in the system and in variable quantities. Results of a few of the early experiments, both with argon-39 alone and with mixtures of argon-39 and argon-40, are shown in Table 5. Because of the variable results found as shown in this table, it was decided to investigate each component part of the vacuum system and, in particular, the Bayard-Alpert gauge and its operation in a static system.

It was determined early in the history of the development of this gauge that in addition to its great sensitivity as a measuring device and its low limit of useful operation, that it was an effective ultra-high vacuum pump. Alpert(39) devised equations for the chemical and electrical pumping speeds of this gauge. His equations predict that this pumping speed is a function of the pressure, and

Table 5

Results of Some Representative Early Experiments

Sample No.	Material	Pretreatment	Ar^{39} (Std.cc/gm) $\times 10^{-7}$	Ar^{40*} (gms/gm) $\times 10^{-7}$	Age (my)
34	KAS	Bake 12 hrs. at 300°C.	1.51	--	
35	KAS + Mica	"	2.21	25.28	2101
36	KAS + Mica	"	1.10	19.48	1786
37	KAS	None	4.71	--	
38	KAS	None	2.97	--	
39	KAS	Bake 12 hrs. at 300°C.	4.31	--	
40	KAS	"	3.69	--	
41	KAS	"	4.40	--	
42	KAS + Mica	"	1.30	--	
43	KAS + Mica	"	1.78	30.62	2348
44	KAS + Mica	"	1.02	31.19	2372
45	KAS + Diabase	"	0.45	0.101	1000 +
46	KAS + Diabase	"	0.19	0.025	1000 +
47	KAS + Diabase	"	1.87	0.127	313

Note: Age of Mica, 2490 my.

Age of Diabase, 202 my.

his experimental work demonstrated the validity of his equations. It was also found that the total volume pumped by any gauge was dependent upon the past history of that gauge. A large amount of work has been done in the past few years on the mechanism of this pumping action, and while the mechanism is still not completely understood, there is increasing evidence for a mechanism involving ions striking and being buried in the glass walls of the gauge. The walls of the tube have been shown to reach the potential of the cathode by Blodgett and Vanderslice(73) and without question, the potentials in an operating gauge are such that positive ions formed outside the grid will be attracted to the walls which are the most negative area.

Because of this pumping action, all measurements made with the gauge during this work were made at several successive times, but as quickly as possible (in most cases within 15 seconds after turning on the gauge) and the logarithm of these readings was plotted vs. time. These points invariably fell on a straight line which could be extrapolated back to time equal to zero. The pressure found by this method was taken as the initial pressure in the gauge. A plot of pressure vs. time for readings taken over a relatively long time is shown in Figure 21 to show this logarithmic decrease in pressure.

It was suspected that, for some reason, the pressure was increasing to a large degree in the gauge during the period that the gauge was turned off and that this increase was the cause of the large variations in the amount of argon measured. Blodgett and Vanderslice(73) had reported this effect and showed that the increase was due to argon re-emitted from the walls of the gauge.

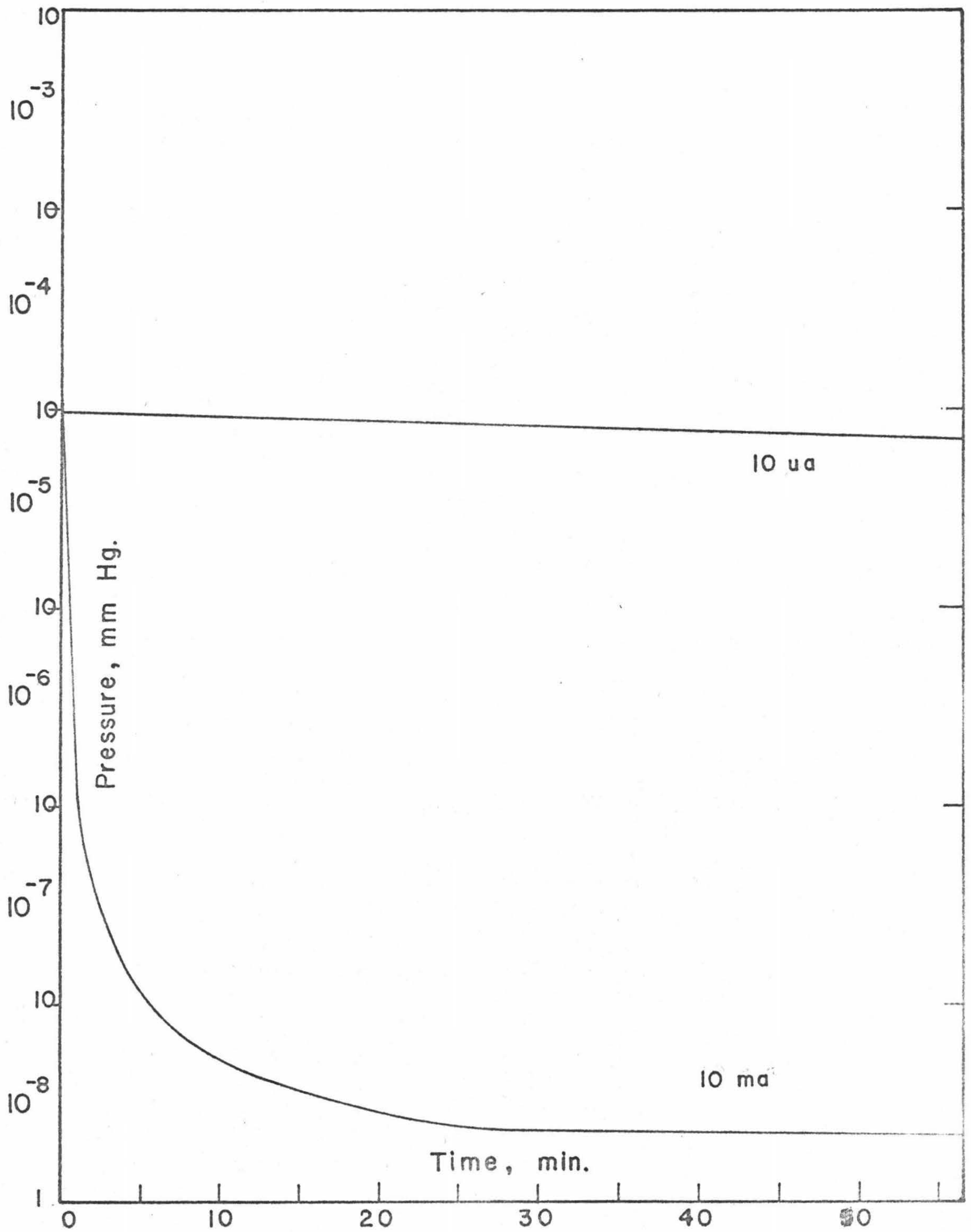


FIGURE 21 - Diagram Comparing Pressure Decrease in System as a Result of Pumping by Bayard-Alpert Gauge

They reported that the fraction of argon recovered was of the order of 10% but might be as high as 22% under some conditions. When these results became known, experimental runs of a carefully degassed and flamed gauge were attempted. Argon was admitted to make the system pressure around 8 x 10^{-5} mm. of mercury, the gauge sealed off from the system, and a Leeds and Northrup, model H recorder with a response time of ½ second was attached to the gauge control. The gauge was then operated for 5 minutes, turned off for 5 to 10 minutes, the gauges operated for 5 more minutes and turned off for 5 to 10 minutes and this cycle repeated several more times. The results of this experiment are shown in Figure 22.

These results show that the same general trend as noted by Blodgett and Vanderslice except that the recovery time is many fold less than their data indicated and the amount recovered was of the orderof 80% rather than 20%. Blodgett and Vanderslice have explained the re-emission of argon as due to a diffusion process but postulate the existence of a "bombarded layer" in which the activation energy for diffusion is much lower than in the main portion of the glass. It is difficult to see that any simple diffusion mechanism could be responsible for the large quantities of argon re-emitted in these experiments and it is believed that perhaps the mechanism of pumping and subsequent re-emission depends much more on the actual gauge geometry than has been believed.

In Blodgett and Vanderslice's experiments, the glass walls of the gauge were protected during processing by a metal can or shield which prevented any metal evaporated from the tube elements from

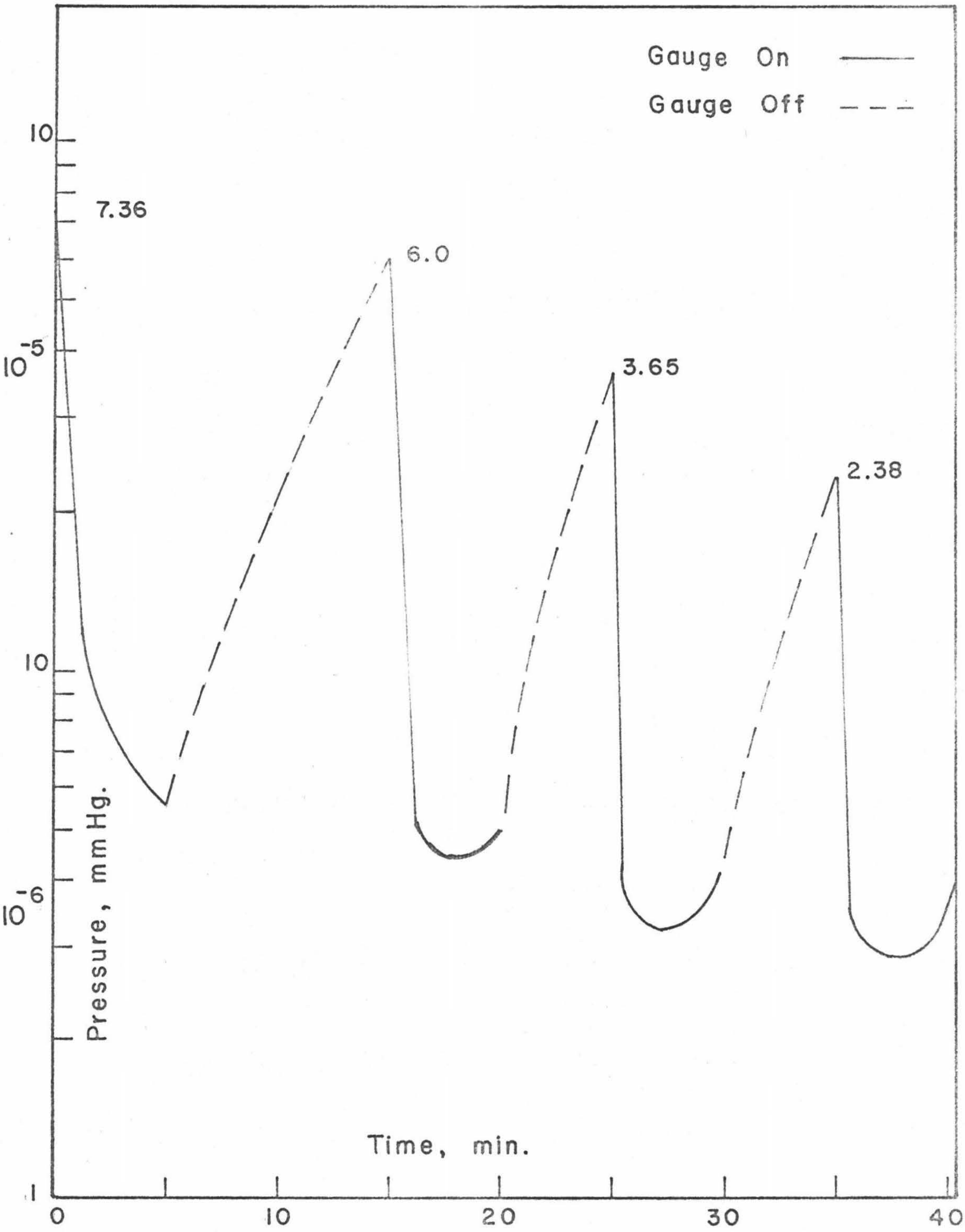


FIGURE 22 - Diagram of Pressure Changes Caused by Pumping and Re-emission of Gas in Gauge

reaching and coating the walls. In the present study, a new gauge was used but the walls were not protected. Thus it is probable that there was a thin coating of molybdenum on the walls from the grid of the tube. It is postulated here that this coating would limit the penetration of ions into the glass walls. However, in order to account for the ready re-emission of pumped gas, it still becomes necessary to assume, in the manner of Blodgett and Vanderslice, a lower than normal energy of activation in the metal layer since it is well known that diffusion of gases through metals is many times slower than through glass.

The thickness of the molybdenum coating on the walls of the tube in any given time will, of course, depend upon the gauge geometry. In addition, Young(74) has shown that various molybdenum oxides on the walls can contribute to the total pressure in the gauge since the vapor pressure of some of these oxides is of the order of the pressure ranges with which these gauges are normally used. The amount of oxide coating would, again, be a function of the gauge geometry and also its past history.

However, Denison and his co-workers(47) published the results of a series of experiments showing that the pumping rate of a Bayard-Alpert gauge could be reduced some 10,000 fold to a negligible amount by reducing the emission current from 10 ma to 10 ua and, as mentioned earlier, Dr. Denison very generously supplied wiring diagrams for a suitable gauge control unit which would supply the needed voltages with suitable regulation. This unit was constructed and tests of the finished unit demonstrated that pumping was reduced to an almost undetectable amount and re-emission of argon was also undetectable. This unit was used in all subsequent work, throughout the period of this research. In addition, the original gauge was used as a pump in the redesigned system and for this purpose operated at a higher emission current. It was connected to the system through a valve in order that it could be isolated to prevent re-emission of argon into the system after completion of a pumping cycle.

A further set of experiments was designed to determine in what part, or parts, of the system argon was being lost or "held-up." This involved carefully cleaning and degreasing the system and then running one sample of the potassium-aluminum silicate in the normal manner. When this sample had been counted it was found that instead of the expected 3.55×10^{-7} S.T.D. cc/gm of argon-39, only 1.57×10^{-7} S.T.D. cc/gm was recovered. Argon carrier gas was then added to the system and the liquid nitrogen on the U-tube water traps removed for 15 to 20 minutes and then replaced. This was repeated several times and then the argon moved to a counting tube and counted.

The titanium sponge getter was heated and put through its normal cycle with liquid nitrogen on the charcoal trap to adsorb the argon. Carrier gas was added and the argon moved to a counting tube and counted. The copper metal deposit on the walls of the quartz sample tube resulting from the vaporization of the copper foil in which the sample was wrapped was heated to redness with a torch, again with liquid nitrogen on the charcoal trap, carrier gas was added and the gas moved to a counting tube and counted. Following the same procedure the copper oxide-silver getter was heated and cooled several times and the collected gas counted. Also the Bayard-Alpert gauge was lagged with 2" glass wool and degassed. With this procedure the walls of the tube were baked for 2 hours reaching a temperature of 450°C. The gas collected was counted. The equivalent amounts of gas recovered from each of these sections are shown in Table 6. It may be seen from this table that while by far the largest amount of argon is trapped by the freshly deposited copper film, significant amounts are held by the titanium sponge and by the U-tube water traps.

In a recent personal communication, Drs. Curtis and Evernden of the University of California Geology Department reported that they had switched to titanium metal foil as a gettering material and that this material was apparently working satisfactorily without the hold-up as found in this study. They also reported the use of a zeolite material as a water trap on their system, and while they had not specifically examined the mass spectrometer background for hydrogen (indicating that water was passing through the trap) this material was not holding a significant amount of argon.

D. Corrected system

As a result of this information and this series of experiments, the system was redesigned and rebuilt to eliminate the above sources of error, as described in section II. These changes, in brief, involved replacing the freeze-out traps with traps of molecular

Table 6

Equivalent Amounts of Ar^{39} Collected from Sections of the Ultra-high Vacuum System

Section	Ar^{39} Count/minute	Ar^{39} Std. cc/gm. $\times 10^{-7}$	Per cent Recovered Argon
Bayard-Alpert Gauge	401	0.051	4.2%
Titanium Getter	1904	0.242	19.8%
Copper Oxide Getter	None	--	
Deposited Copper	5761	0.732	60.0%
U-Tube Traps	1535	0.195	16.0%
Total Recovered from System		1.22	
Total Lost		1.98	

Note: 0.76×10^{-7} Std. cc/gm still held in system.

sieve material, replacing the sample melting section so that a fresh container and crucible were used for each determination. This, of course, eliminated the use of copper foil. The mode of operation of the getter was changed so that the argon was held on charcoal while the getter cooled. This resulted in some hydrogen being carried with the argon to the gauge but chemical gettering with the filament of the gauge held at 1550°C. during transfer removed this hydrogen. When these changes had been made the Bayard-Alpert gauge was recalibrated to give conversion from plate current to standard cc. of argon in the gauge volume.

The calibration was performed by sealing a number of small break-off tubes containing known amounts of spectroscopically pure argon to the system and releasing these to the gauge section. The gauge plate current was then measured with an electrometer and a plot of gauge current vs. argon contained in this volume was made. This calibration plot is shown in Figure 13. When this calibration was completed a series of samples of mica and of the Palisades diabase were run. These samples were mixed with the artificial potassium-aluminum silicate in the usual manner but samples of this material alone were run as a check of the complete recovery of argon-39 (and thus of argon-40). The results of the series are shown in Table 7.

In the series shown in Table 7, two rather wide extremes are represented: In one case a 2000 my old mica with 9% potassium and in another a 200 my diabase with approximately 0.5% potassium. In both cases, suitable sized samples had been chosen in order to give

Table 7

Results of Age Determinations With Redesigned System

Sample	Pretreatment	Ar^{39} Std. cc/gm. $\times 10^{-7}$	Ar^{40*} Std. c.c.	Ar^{40*} Corr. Std. c.c.	Ar^{40*} gms/gm	Age (my)	Age Previously Determined (my)
KAS	None	3.53	--	--	--	--	
KAS	None	3.54	--	--	--	--	
KAS + Mica	Bake 12 hrs. at 400°C.	1.77×10^{-7}	9.3×10^{-6}	1.09×10^{-5}	$.295 \times 10^{-5}$	2304	2490 ± 250
KAS + Mica	"	2.14×10^{-7}	10.3×10^{-6}	1.11×10^{-5}	$.308 \times 10^{-5}$	2312	2490 ± 250
KAS + Diabase	"	2.30×10^{-7}	4.40×10^{-6}	4.53×10^{-6}	$.81 \times 10^{-8}$	206	202 ± 10

approximately equal quantities of radiogenic argon-40. Noting that the amount of argon-40 to be expected must be a function of both the age and the potassium concentration, it is thought that this later material constitutes the approximate lower limit of this method. An attempt to lower this limit would, at present, result in samples that would be of an unmanageable size. Using smaller sizes would result in plate currents which would be in the range of the inherent electrical background of the measuring system and these could not be measured with sufficient accuracy to be of practical use. The lower limit of useful measurement of the gauge and gauge control is now approximately 5×10^{-10} amps but it is thought that the gauge control might be reconstructed using components with the best available electrical insulation. This should decrease the background noise of the equipment and would probably lower the useful limit by one to two orders of magnitude.

Of course, as mentioned, younger samples with higher potassium concentrations (by at least an order of magnitude larger) could be successfully run at the present time. It was originally intended to investigate the possibility of using this new method for the dating of rocks and minerals in the age range which might be expected from samples of various formations in the Hawaiian Islands, but it is regretfully concluded that these materials are below the useful limit of the present equipment.

E. General discussion and remarks

In addition to the points discussed above, there are several areas of significance to the general field of the age determination of young materials for which these researches give some pertinent information, and which might be considered here. As was shown in the Introduction, perhaps the largest source of error and the most troublesome problem to workers in this field is the contamination of radiogenic argon-40 by argon-40 from the atmosphere. Because of the inherent difficulty of measuring the very small argon-36 peak in the mass spectrometer and the very large multiplication of this error in the final correction for air argon-40 (ie. by a factor of approximately 300) it is essential that this air contamination be reduced as much as possible. It is, however, also essential that in doing so, no radiogenic argon-40 be lost since there is no means of correcting for this loss at present.

Thus most workers strive for some kind of a compromise to insure that there is no loss of radiogenic argon-40 but accept the error which necessarily results. It is felt that this work clearly shows that the addition of argon-39 in the form of a solid material before baking offers an effective means of correcting for the loss of radiogenic argon-40 if a higher baking schedule is used to lower the contamination by air argon-40.

Schaeffer, Stoenner and Bassett(75) have suggested that glasses or rocks with a glassy matrix might be materials particularly suitable for the dating of young rocks. This suggestion was based on the results of dating of lavas of the Marysville, Utah area. They state, however, that in a number of cases discordant ages were obtained and suggest that this might be due to devitrification of the glass. Most of the samples which were suspect were those in which the glass was present in extremely fine particles.

As a result of the work reported here, it is suggested that while devitrification of the glass should certainly make the material unsuitable for age work, a major concern should be a consideration of the possible thermal history of the glass. It is shown in these diffusion studies that the diffusion coefficient of a glass may be many orders of magnitude larger than that of the crystalline material of the same general composition. For example, the value of D/a^2 for leucite at 310°C. found by Evernden et al.(53) is of the order of 10^{-14} while that of the glass of the same composition is around 10^{-6} at the same temperature. The values of D/a^2 at room temperature for the glass investigated here is of the order of 10^{-15}. This would indicate that this material would be suitable for study in very young rocks where the diffusion of argon from the sample due to time alone would be very small. However, since the rate of diffusion of gas increases greatly with even a slight elevation in temperature, one would have to be certain that the sample had not been heated for any appreciable time above perhaps 50°C. Reynolds(57) in his work on glassy tektites has also shown this, and the work of M. B. Reynolds(56), Norton(76) and others on rates of diffusion in glasses gives further substantiation. In fact, it must be concluded that nothing found in this work indicates that glasses are, per se, particularly suitable materials for age studies.

This work does clearly show that, in any isotope dilution method, where the diluting isotope is used to correct for losses of argon in the purification system, it is absolutely essential that the diluting isotope be added at the earliest possible step in the procedure since the various parts of the system may "hold-up" a significant amount of the argon.

A fourth point relevant to the operation of mass spectrometers is shown in the study of the Bayard-Alpert gauge. Since the source region of a mass spectrometer tube is essentially the same as an ionization gauge, there seems to be no reason to believe that the spectrometer should not suffer from the same errors as the Bayard-Alpert gauge with improper operation. In addition, the possibility of mass discrimination inherent in a mass spectrometer tube should multiply these errors. It is common practice to operate these tubes at approximately the same emission currents (ie. 3 to 10 ma) as used in the Bayard-Alpert gauge. This should lead to the same pumping action and indeed, this effect has been noted. However, this pumping is commonly ignored during its early stages and instead a series of measurements taken when the tube has "settled down" (corresponding to the lower section of the curve in Figure 21) and then the measurements extrapolated back to zero time to give the initial peak height.

It has been shown in this work that the "settling down" is actually an equilibrium between re-emitted gas from previous pumping and present pumping action, and thus cannot be safely ignored. It should, however, be equally possible to reduce this pumping action by reducing the emission current. It appears that no work has been done on the re-emission of gas from the walls of a spectrometer tube and it is suggested that the possibility of error from this source should be a suitable field for investigation. This work points to one method of reducing the effect.

In the past, work in the potassium-argon field has been concentrated on samples of older rocks and minerals where small errors were not of great importance. Surely the tremendous potentialities of this method for young rocks and minerals as shown by recent work of Leakey, Evernden and Curtis(77) and by Mc Dougall(78) justify the effort necessary to eliminate or reduce these sources of error.

IV. Summary

An investigation has been made of a method for potassium-argon age determination utilizing isotope dilution techniques. This approach differs from the usual methods in that a mass spectrometer would not be necessary for the determination. The diluting isotope is introduced in a solid, artificial mineral which can be intimately mixed with the sample before extraction of the argon. These artificial minerals had been bombarded previously by neutrons to produce argon-39 by the reaction:

$$K^{39}\ (n,\ p)\ Ar^{39}.$$

The extracted and purified argon is measured in a calibrated volume with a Bayard-Alpert type ionization gauge and the proportion of radioactive argon-39 determined by counting in an internal-fill counting tube. The results of these measurements are then used to calculate the radiogenic argon-40 present in the rock or mineral. The determination of potassium in the rock is necessary, and an investigation of a technique suitable for minerals was undertaken and perfected. From the data obtained from these measurements, the age of the rock or mineral can be determined.

It was hoped that, by the use of this isotopic dilution method, the problem of contamination of the radiogenic argon-40 by air argon-40 could be eliminated since the loosely held atmospheric argon could be removed by baking the samples at a relatively high temperature. From the measurements made with the diluting isotope (argon-39), corrections could be made for the amount of radiogenic argon-40 lost in the baking process. To make these corrections, the diffusion constants for argon in the artificial minerals were determined.

Becaused of the great sensitivity of the radioactive technique it was possible to do a critical evaluation of the method of gas extraction and purification which is usually used in age determinations, and also to investigate some of the errors and limitations of pressure measurements in static systems in the ultra-high vacuum range (10^{-6} - 10^{-9} Torr) with the use of a Bayard-Alpert gauge. Thus the amounts of argon held in each part of the system were determined. It was found that assumptions made by previous workers regarding the loss or trapping of rare gases in the various parts of an ultra-high vacuum system were not valid.

Also the usual method of operation of a Bayard-Alpert gauge was found to be completely unsatisfactory due to the pumping action and subsequent re-emission of the pumped gas. A method of operation which would give more correct values of the true pressure was developed. Based on the information gained in these studies, a redesigned vacuum system was built. This allowed the determination of ages of old rocks with an accuracy equal to that of slower, more expensive conventional methods. For young rocks and minerals, results show that it is possible to make satisfactory use of this procedure for samples of ages of about 100 million years or perhaps even younger. For very young rocks (circa. 1 million years) it is not thought that this would be a satisfactory replacement for the method using the mass spectrometer.

In addition, the results of this research have the following important implications with regard to the more accurate operation of mass spectrometers.

(1) The technique of isotope dilution with argon-39 would be applicable in mass spectrometry and has the advantage of making possible independent check measurements.

(2) The mechanism of pumping and re-emission of gas found in the Bayard-Alpert gauge applies equally to the source region of the mass spectrometer and techniques developed to minimize this effect can be applied.

Appendix I - Derivation of the age equation

Let:

Ar^{40} = number of atoms of argon-40 (radiogenic) at time t.

K^{40} = number of atoms of potassium-40 at time t.

K_o^{40} = number of atoms of potassium-40 at time t = 0.

k_1 = decay constant for branch of potassium-40 decay scheme going to argon-40 by electron capture.

k_2 = decay constant for branch of potassium-40 decay scheme going to calcium-40 by beta emission.

R = ratio of k_1 to k_2

From the basic equation for radioactive decay:

$$\frac{-dN}{dt} = kN$$

$$\frac{-dK^{40}}{dt} = (k_1 + k_2)\, K^{40}$$

$$\frac{-dK^{40}}{K^{40}} = (k_1 + k_2)dt$$

Which yields,

$$-\ln K^{40} = (k_1 + k_2)\, t + C$$

Since,

$$\text{at } t = 0,\ K^{40} = K_o^{40}$$

$$C = -\ln K_o^{40}$$

Then,

$$-\ln K^{40} = (k_1 + k_2)\, t - \ln K_o^{40}$$

Or $$K^{40} = K_o^{40} \exp -(k_1 + k_2)t \qquad (I)$$

Also,

$$\frac{dAr^{40}}{dT} = k_1\, K^{40} \qquad (II)$$

Sub. (I) into (II) and,

$$dAr^{40} = k_1 K_o^{40} (\exp - (k_1 + k_2) t)\, dt$$

Which yields

$$Ar^{40} = (K_o^{40}) \left(- \frac{k1}{k1+k2}\right) (\exp - (k_1 + k_2) t) + C$$

$$= K_o^{40} \left(- \frac{R}{1+R} \right) (\exp - (k_1 + k_2) t) + C$$

But the assumption is made that

at $t = 0$, $Ar^{40} = 0$

Therefore

$$C = K_o^{40} \frac{R}{1+R}$$

And

$$Ar^{40} = (K_o^{40}) \left(- \frac{R}{1+R} \right) (\exp - (k_1 + k_2) t) + K_o^{40} \frac{R}{1+R}$$

Rearranging

$$Ar^{40} = \left(\frac{R}{1+R} \right) K_o^{40} \frac{\exp (k1 + k_2) t - 1}{\exp (k_1 + k_2) t} \qquad (III)$$

From equation (I)

$$K_o^{40} = K^{40} \exp (k_1 + k_2) t$$

Sub. into (III) and,

$$Ar^{40} = \frac{R}{R+1} K^{40} (\exp (1 + R) (k_2 t)) - 1$$

Divide by K^{40} and solve for t,

$$t = \frac{1}{(1+R)\, k_2 t} \ln \left(\frac{1+R}{R} \frac{Ar^{40}}{K^{40}} + 1\right)$$

Sub. values of k_2 and R as follows,

$$k_2 = 0.488 \times 10^{-9}$$

$$R = 0.123$$

And: $t = 0.1825 \ln (1 + 9.130\, Ar^{40}/K^{40}) \times 10^4$ my

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