

The Relationship between Balancing Reactions and Reaction Lifetimes: A Consideration of the Potassium–Argon Radiometric Method for Dating Minerals

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Science educators share a common objective: to familiarize students with critical thinking. An instructor may select a topic of current interest from the scientific literature or from the popular media and ask students to write critical essays concerning some aspect of this topic. For instance, students may criticize bond stretch isomerism (1), gallium–gallium triple bonds (2), the nature of carbon compounds in an alleged Martian meteorite found in Antarctica (3), or some other fun and controversial topic. Participation in such projects allows students to practice the scientific method firsthand. The students must gather facts concerning what is known, intelligently criticize published explanations of the facts, create imaginative and alternative explanations, and formulate experiments that could potentially falsify the explanations. Such an experience is a very important part of a thorough education in science.

The radiometric dating of minerals is an interesting topic to many students because such dating provides support for the modern evolutionary view of natural history. This view features an earth that is 4.5 billion years old (4) and emphasizes that earth's biological diversity results from evolution by natural selection from common ancestors. If earth's age were actually much younger than 4.5 billion years, perhaps on the order of thousands or tens of thousands of years, for instance, then Darwinian evolution clearly fails as an explanation for major speciation in life on earth. Hence, some students may feel impassioned to criticize the radiometric dating procedures, and, interestingly, other students seem equally impassioned to defend the procedures. Emotional drive tempered with a respectful tolerance for the diverse views of others can lead to a highly productive and educational debate among students.

This paper presents some critical thoughts concerning the potassium–argon procedure for dating minerals. These thoughts and ideas originated in an introductory inorganic chemistry course taught at the University of Alaska Fairbanks. The purpose of this writing is simply to stimulate critical thinking in the minds of chemistry students by posing uncommon questions concerning radiometric dating.

Background: The Radioactive Decay of ^{40}K in Minerals

There are three natural isotopes of potassium, namely ^{39}K , ^{40}K , and ^{41}K ; their abundances¹ are $93.258 \pm 0.003\%$, $0.01167 \pm 0.00004\%$, and $6.730 \pm 0.003\%$, respectively (5). Only ^{40}K is radioactive, decaying by either β^- -emission to produce ^{40}Ca or by nuclear electron capture to produce ^{40}Ar , as illustrated in Scheme 1. None of the natural isotopes of calcium or argon are radioactive.

Of every 100 decay events involving ^{40}K , 89 will lead to ^{40}Ca atoms by emitting a β^- -particle and an anti-neutrino from the ^{40}K nucleus. The nuclear binding energy for the ^{40}Ca nucleus is 1.31 MeV lower than that for the ^{40}K nucleus, and this energy is liberated upon β^- -decay. Usually, the anti-neu-

trino absorbs most of the energy, while the β^- -particle absorbs less and the ^{40}Ca atom absorbs the least amount of energy. Nevertheless, this “recoil” energy absorbed by the ^{40}Ca nucleus may be comparable with many chemical bond energies.

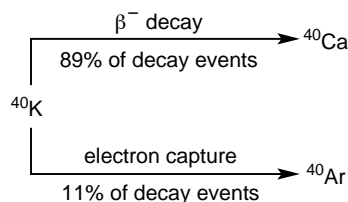
If 89 of 100 ^{40}K atoms have undergone β^- -decay, the remaining 11 atoms will undergo nuclear electron capture, which involves combining an orbital electron with the nucleus in order to convert a proton to a neutron. Electron capture results in the formation of ^{40}Ar and the emission of X-rays, γ -rays, and a neutrino that absorbs most of the liberated nuclear binding energy (1.50 MeV). The total half-life for the radioactive decay of ^{40}K , comprising both β^- -decay and electron capture, is 1.250 ± 0.002 billion years.²

There are three dating methods based on the radioactive decay of ^{40}K , namely the ^{40}K – ^{40}Ar method (6), the ^{40}K – ^{40}Ca method (7), and the ^{40}Ar – ^{39}Ar method (8). These dating methods have been used to support ideas concerning the biological evolution of humans. For instance, the older ^{40}K – ^{40}Ar method was employed in dating the fossilized remains of “Lucy”, the *Australopethicus afarensis* ancestor to modern *Homo sapiens* (9).

While some have questioned the accuracy of the dating methods based on the radioactive decay of ^{40}K , the ^{40}Ar – ^{39}Ar method has been demonstrated to be highly accurate in at least one case: a sanidine (KAlSi_3O_8) mineral, formed in the eruption of Mt. Vesuvius in 79 A. D., was dated by the ^{40}Ar – ^{39}Ar method in 1997, and the age was determined to be 1925 years old, differing by only seven years from the historically accepted age of 1918 years old (10). This amazing degree of accuracy may effectively counter arguments to the contrary.

The Unknown Chemistry of the K–Ar Reaction

A few examples of potassium-bearing minerals that have been dated include sanidine (KAlSi_3O_8) (10, 11) and leucite (KAlSi_2O_6) (12). If the potassium atom in KAlSi_3O_8 suddenly changed into a calcium atom or an argon atom, what would happen to the remaining atoms in the formula (AlSi_3O_8)? Nuclear decay reactions are generally not influenced by the chemical environment of the unstable nucleus (13), but the chemical environment is certainly influenced by the nuclear decay. In fact, any radioactive decay that occurs



Scheme 1. Radioactive decay of ^{40}K .

in nature *must* be accompanied by some sort of chemical change when the chemical properties of the parent and daughter atoms are profoundly different. In this case, a group 1 metal atom with an oxidation state of +1 can change into either a noble gas, which does not bond to anything, or a group 2 metal atom that usually adopts an oxidation state of +2.

An inorganic chemistry student may well ask, "What is the complete reaction involving the radioactive decay of potassium that actually occurs in rocks and minerals?" In other words, can the radioactive decay of ^{40}K in KAlSi_3O_8 be expressed as a balanced equation? Has anyone ever tried to identify and quantify all of the side products from the decay of ^{40}K in any mineral? Very interestingly, it appears that such questions have never been addressed in the scientific literature. Thus, nobody knows what the actual, complete potassium–argon reaction is!

A Chemist's Skepticism and the Importance of Balancing Reactions

Undergraduate chemistry students learn that there exists an intimate connection between reaction lifetimes and balancing chemical reactions. This connection is implicit in the reaction mechanism, which completely specifies a chemical reaction. For obvious reasons, a reaction mechanism cannot be known if the chemist does not know what all of the products are. Thus, when a chemist discovers a new reaction and wishes to decipher the mechanism for that reaction, the chemist *must* identify and quantify all products from the reaction, in addition to carrying out kinetics studies. Such experiments are absolutely necessary. If a chemist does not know what the products are or how much of each product is formed, then it is impossible to understand the reaction fully and to make trustworthy predictions based on that reaction.

The grocery store problem, described below, may be used to teach the connection between balancing chemical reactions and reaction lifetimes.

The Grocery Store Problem: Reactions and Their Lifetimes

A stocker at a local grocery store is given the task of stocking store shelves with cans of corn. The stocker removes 10 cans of corn from each carton, places the cans on the shelf, and discards the empty carton in a nearby waste bin. The stocker works for awhile and then breaks for lunch. A store manager inspects the work after the stocker has left and wishes to know how long the stocker had worked. She finds that there are 100 cans stacked on the shelf, and 10 empty cartons in the waste bin. She knows that the stocker works at a constant rate of emptying 1 carton per minute and concludes that the stockman must have worked for 10 minutes. Although her conclusion may or may not be correct, her logic is certainly reasonable.

Now, imagine that the manager finds that there are 100 cans stacked on the shelf, but only 8 empty cartons in the waste bin. Can she draw a reasonable conclusion concerning how long the stocker had worked? Perhaps the stocker worked for 10 minutes and discarded 10 empty cartons. Then, someone else removed 2 empty cartons from the waste bin. Or, perhaps the stocker had worked for only 8 minutes, and someone else placed 20 extra cans of corn on the shelf. From the data given, the manager cannot know whether the stocker worked 8 or 10 minutes. The number of cans on the shelf

must correlate with the number of discarded cartons in order for the manager to draw a reasonable conclusion concerning how long the stocker had worked.

Now, imagine another case, in which the manager counts 100 cans of corn on the shelf, but she does not bother to count how many empty cartons are in the waste bin. She concludes that the stocker must have worked for 10 minutes. Is the manager's conclusion reasonable? One may argue that her conclusion is not reasonable because she does not have all of the facts. Although there may be 100 cans of corn on the shelf, perhaps there may be found 20 empty cartons in the waste bin. The stocker actually worked for 20 minutes and stacked 200 cans of corn on the shelf. Then a mad rush of customers removed and purchased 100 cans of corn. If this were the case, then the manager's conclusion is incorrect. The manager should have counted the discarded cartons as well as the cans of corn in order to avoid the false conclusion that the stocker worked for 10 minutes.

The grocery store problem nicely illustrates, in non-scientific language, the relationship between balancing reactions and reaction lifetimes. Just as the manager must count cans of corn *and* discarded cartons in order to judge how long the stocker had been working, so must the chemist identify and quantify all products from a reaction in order to determine how long the reaction has been going.

This same logic should apply to nuclear reactions occurring in minerals as well. Yet, a geochronologist typically identifies and quantifies only one product from the potassium–argon reaction, namely argon. Scientists know that ^{40}Ca also forms from the radioactive decay of ^{40}K , although the chemical identities and quantities of the ^{40}Ca products are unknown.

Geochronologists recognize that ^{40}Ar can get inside a mineral through a variety of ways (14), such as:

1. Contamination with air
2. Contamination with bits of older minerals (inherited ^{40}Ar)
3. From the ^{40}Ar dissolved in the molten rock before cooling and hardening
4. Radioactive decay of ^{40}K atoms within the mineral after the mineral has hardened

There may be even more ways in which ^{40}Ar can get inside a mineral! Each of these processes by which ^{40}Ar can get inside the mineral is a separate mechanism, and the process in which ^{40}Ar comes from the radioactive decay of ^{40}K within the hardened mineral is the radiogenic mechanism. The geochronologist subtracts out all ^{40}Ar from air and from any other known non-radiogenic sources and assumes the remainder to be radiogenic ^{40}Ar . The mineral's age is then calculated based on the amounts of ^{40}K and ^{40}Ar from the radiogenic mechanism. But how can the geochronologist know that all of the ^{40}Ar that he or she thinks is radiogenic really is radiogenic? In other words, how can the geochronologist know the mechanism by which this ^{40}Ar came to be inside the mineral when no one has ever bothered to look for the other products that must form, and so no one even knows what the other products are? Based on an incomplete understanding of the potassium–argon reaction, the mineral's age is calculated.

In order to build confidence in their work, geochronologists will occasionally determine mineral ages by more than one radiometric dating method (15). Many times, the inde-

pendent dating methods yield very similar ages, usually within experimental error,³ and so one may think that such results verify the accuracy of the age determination. Nevertheless, as is the case with the potassium–argon system, the complete chemistries associated with alternative dating procedures, such as uranium–lead and rubidium–strontium, are also unknown. In order to understand how these unknown chemistries still present a problem, consider the following modification to the grocery store analogy.

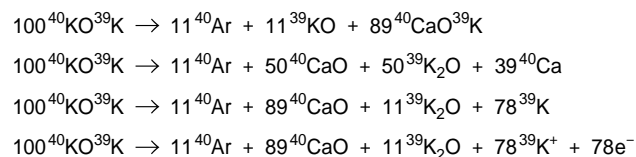
The Grocery Store Problem Revisited

Three different stockers are now stocking the store shelf with canned vegetables, and each works independently. The first stocks cans of corn at a rate of 10 cans per minute; the second stocks cans of carrots at a rate of 20 cans per minute; and the third stocks cans of beans at a rate of 5 cans per minute. Again, each carton of canned vegetables holds 10 cans, and each stocker discards the empty carton in a waste bin after stocking all the cans. All three stockers begin work at the same time, and all three break for lunch at the same time.

The store manager inspects the work after the three stockers have left for lunch. She finds that there are 118 cans of corn, 243 cans of carrots, and 61 cans of beans on the shelf. Moreover, she counts 21 empty cartons in the waste bin. Based on her observations, can the manager conclusively determine exactly how long the stockers had been working? Obviously, the answer is no. The fact that there are three independent stockers working at different rates instead of only one improves the precision of the manager's time calculation, but not the accuracy. Likewise, the similarities in mineral ages determined by three independent dating methods (K–Ar, U–Pb, and Rb–Sr) will surely improve the precision of the age calculation, but nothing can be said of the accuracies of the ages.

It should be emphasized here that the discussion in the previous paragraphs has absolutely nothing to do with questioning the rate of radioactive decay of ⁴⁰K atoms. The first-order kinetics and the half-life (1.250 ± 0.002 billion years) of the radioactive decay of ⁴⁰K are very well known and are not in doubt.

It should also be stressed that the purpose of this paper is *not* to suggest that mineral ages determined by the potassium–argon method are erroneous. It is entirely possible that ages calculated from the potassium–argon procedure may be highly accurate. Rather, the argument here is that one cannot *know* a mineral's age from the potassium–argon dating procedure unless the chemistry of the potassium–argon reaction is also known. (It may be necessary to stress with students that knowing something and merely thinking that one knows something are two very different circumstances.) If a geochronologist truly knows a mineral's age, then that geochronologist should be able to describe the chemistry behind



Scheme 2. Four possible balanced equations for the radioactive decay of ⁴⁰K in a crystal of K₂O.

the radioactive decay of ⁴⁰K in that mineral in great detail. If the geochronologist is not able to do so, then the mineral's age is not really known. Any argument against this logic is an argument against some fundamental and well-established principles of the science of chemistry.

Speculations Concerning the Chemistry behind the Potassium–Argon Reaction

Since the chemistry of the potassium–argon reaction in minerals is unknown, chemists (and their students) may speculate on what that chemistry might be. Imagine a crystal of absolutely pure potassium oxide (K₂O).⁴ Sites in this crystalline lattice are occupied by O²⁻ ions and K⁺ ions, and only $0.01167 \pm 0.00004\%$ of the K⁺ ions are radioactive. If this crystal is a perfectly closed system (i.e., a system in which no matter enters or exits) (16), what will be the chemical composition of this crystal after aging for a great period of time?

Since the concentration of ⁴⁰K⁺ ions is so relatively small within the crystal of K₂O and the concentration of ³⁹K⁺ ions is so relatively large, the form of K₂O that is of interest to the present discussion will be written as ⁴⁰KO³⁹K. Four hypothetical, balanced equations describing the radioactive decay of ⁴⁰K in the K₂O crystal are shown in Scheme 2. Each equation has been constructed with the understanding that ⁴⁰K converts to ⁴⁰Ar 11% of the time and to ⁴⁰Ca 89% of the time. These balanced reactions are also constructed with the understanding that mass and charge *must* be conserved in nuclear decay reactions, as is the case with normal chemical reactions. Each of the four possible balanced reactions reveals two very important facts concerning the chemistry of the potassium–argon reaction:

1. In addition to ⁴⁰Ar and ubiquitous compounds like CaO and K₂O, there must form product(s) with very unusual oxidation states—such as ³⁹KO (17, 18), or ³⁹K⁴⁰CaO (19), or elemental ⁴⁰Ca, or elemental ⁴⁰K, or bare electrons.
2. The quantities of the unusual products must be significantly greater than the quantity of radiogenic ⁴⁰Ar. In fact, ⁴⁰Ar is only a *minor* product in the potassium–argon reaction!

Theory versus Reality

Although chemical reactions and nuclear reactions are similar in many ways, they are also different in some aspects. For instance, nuclear decays result in the release of highly significant quantities of energy. Who knows how this energy release will affect the chemical composition of a mineral? Is it realistic to expect geochronologists to find all of the products from the radioactive decay of ⁴⁰K, or is this an idea that is far too impractical?

Suppose that, in any given mineral, it is impossible to determine all of the products from the potassium–argon reaction. In no way does this inability to characterize the potassium–argon reaction undermine the conclusions drawn in this paper. It is still true that one must know the complete chemistry in order to know the mineral's age. If the full potassium–argon chemistry cannot be known, that calls into question the usefulness of the potassium–argon dating procedure.

A credible argument favoring the notion that the potassium–argon chemistry can be known is constructed below. Problems associated with determining the chemistry are given, with a counterargument following the problem.

Validity of the ^{40}K – ^{40}Ar Method: Problem 1

Nuclear decay reactions liberate tremendous quantities of energy that can produce sequences of ionization events within the mineral. Geochronologists will not be able to find any of the unusual by-products shown in Scheme 2 because these entities will likely be decomposed by the ionizations or by the electron and recoil tracks. Only stable, ubiquitous compounds like CaO and K_2O will remain.

Validity of the ^{40}K – ^{40}Ar Method: Counterargument 1

The energy release from the radioactivity of ^{40}K may indeed destroy some of the unusual chemical products that must be formed, but not all. In support of this statement, consider the fact that the noble gas compounds XeCl_4 and XeCl_2 can be formed as intact molecules from the β -decay of $[\text{}^{129}\text{ICl}_4]^-$ and $[\text{}^{129}\text{ICl}_2]^-$, respectively (20). In general, noble gas compounds tend to be highly fragile and to decompose very easily. Since such fragile compounds can exist in the presence of highly energetic β -decay reactions, it is certainly reasonable to think that some of the unusual chemical products from the potassium–argon reaction will survive the energy release from the ^{40}K nuclear reactions.

Validity of the ^{40}K – ^{40}Ar Method: Problem 2

One may also argue that cosmic ray bombardment over millions of years is likely to convert any of the unusual products shown in Scheme 2 into K_2O or CaO eventually.

Validity of the ^{40}K – ^{40}Ar Method: Counterargument 2

Trapped charges are known to persist in minerals for ca. 10^5 years or more; in fact, such trapped charges are the basis for dating minerals by electron spin resonance spectroscopy (21) and thermoluminescence (22). Obviously, cosmic ray bombardment over 10^5 years does not annihilate trapped charges in some natural minerals. Also, as mentioned previously, minerals as young as 2000 years have been dated based on the potassium–argon reaction (10). Therefore, it is reasonable to think that cosmic rays will not annihilate the unusual chemical products from the radioactive decay of ^{40}K in minerals 10^5 years old and younger.

Validity of the ^{40}K – ^{40}Ar Method: Problem 3

Another argument against the possibility of characterizing the unusual products from the potassium–argon reaction involves the migration of f centers (electrons occupying anionic sites in the lattice). If f centers are formed, they may migrate throughout the solid lattice (23), eventually reaching the surface of the mineral. At the surface, the charge is quenched by contact with atmospheric oxygen or with some other reactive environmental substance.

Validity of the ^{40}K – ^{40}Ar Method: Counterargument 3

It is not known, however, whether f centers are even formed from the potassium–argon reaction. If f centers do not form, then the argument based on migrating f centers is obviously of no concern. If f centers do form, then it is reasonable to think that they will persist for at least 10^5 years because it is known that trapped charges in natural minerals do have such lifetimes. Thus, if f centers are produced from the potassium–argon reaction, they should be detectable in minerals 10^5 years old and younger.

Validity of the ^{40}K – ^{40}Ar Method: Problem 4

A much more substantial reason for the failure to characterize the potassium–argon reaction may be the fact that minerals are often contaminated with redox-active impurities such as air, water, and transition metal ions. Such impurities can absorb or supply electrons within the mineral and easily convert any chemically unusual products to very stable and ordinary compounds. Ideally, geochronologists could date a sanidine mineral that was absolutely pure KAlSi_3O_8 in the beginning. Provided that cosmic ray bombardment and quenching by environmentally reactive substances are not significant, all of the products from the radioactive decay of ^{40}K atoms could be identified and quantified in such an ideal mineral.

So, why has the chemistry of the potassium–argon reaction never been completely characterized? A very likely answer is that geochronologists often do not consider the complete chemistry and assume that the only by-products will be ubiquitous ^{40}CaO and K_2O . With so much ^{40}CaO already in the mineral, geochronologists are unable to distinguish the radiogenic ^{40}CaO from that which was present in the mineral in the beginning; they may then conclude that identifying and quantifying the by-products is not worthwhile (24).

Final Remarks

The premise developed here—that knowing all of the products from the potassium–argon reaction is necessary in order to know the age of the mineral—is hardly debatable. While characterizing the chemistry may be very difficult or impossible in some cases, this work should be done in order to determine the mineral's age with certainty. The more knowledge scientists have concerning the decay of ^{40}K within a mineral, the better they can understand and distinguish the various mechanisms by which ^{40}Ar can get inside a mineral.

The significance of this discussion is twofold. First, many of those involved with teaching biological evolution in public schools erroneously believe that scientists understand radioactive decay reactions very well—enough, at least, to predict the ages of minerals accurately (25). The reality is that no one understands these reactions entirely; the present exercise in critical thinking underscores this truth.

Second, the implications of this exercise in critical thinking have great educational significance. Undergraduate chemistry students should be taught to think critically about ideas and common practices in science and to question claims in order to determine their underpinning principles that may then be accepted or rejected based on the scientific rigor of the claims. This exercise raises some interesting questions:

- How can one know the age of a mineral based on the potassium–argon reaction, when nobody knows what the potassium–argon reaction is?
- What might the potassium–argon reaction be in a simple ionic compound, such as K_2O , for instance?
- Is it at all possible to know the potassium–argon chemistry in any given mineral?

This paper provides a detailed examination of a commonly accepted practice in geology, offers an example of how to stimulate critical thinking, teaches students how to “read” reactions, and challenges students to formulate better experiments for determining mineral ages more accurately. In an-

ecdotal feedback from undergraduate chemistry students at the University of Alaska Fairbanks they have commented favorably on such exercises in critical thinking.

Acknowledgments

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Notes

1. Different values for the abundances of the potassium isotopes can be obtained from different sources. The abundances listed here were obtained from ref *8b*.

2. This half-life value was also obtained from ref *8b*.

3. Occasionally, the ages determined by different radiometric methods are *not* within experimental error. For instance, see ref *15b*.

4. K_2O , a strong base according to both the Brønsted and Lux–Flood definitions, is too reactive to be found in nature and is usually combined with Lux–Flood acids like SiO_2 or Al_2O_3 . Nevertheless, minerals such as sanidine and leucite are actually reducible to $K_2O + SiO_2 + Al_2O_3$, and so this discussion concerning K_2O is relevant to natural geology.

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- Such reasoning is expounded upon in Shillibeer, H. A.; Russell, R. D. *Can. J. Phys.* **1954**, *32*, 681–693.
- For example, the National Center for Science Education (NCSE) is devoted to protecting the teaching of biological evolution in public schools. At the Web site for the NCSE, George S. Bakken has stated that “radioactive decay [is] well understood”. See: Bakken, G. S. Creation or Evolution? http://www.ncseweb.org/resources/articles/6733_creation_or_evolution_12_7_2000.asp (accessed Mar 2005).