

Chemical Properties of Radon*

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Radon is frequently regarded as a totally inert element. It is, however, a "metalloid" -- an element which lies on the diagonal of the Periodic Table between the true metals and nonmetals and which exhibits some of the characteristics of both. It reacts with fluorine, halogen fluorides, dioxygenyl salts, fluoronitrogen salts, and halogen fluoride-metal fluoride complexes to form ionic compounds. Several of the solid reagents can be used to collect radon from air but must be protected from moisture, since they hydrolyze readily. Recently, solutions of nonvolatile, cationic radon have been produced in nonaqueous solvents. Ion-exchange studies have shown that the radon can be quantitatively collected on columns packed with either Nafion resins or complex salts. In its ionic state, radon is able to displace H^+ , Na^+ , K^+ , Cs^+ , Ca^{2+} , and Ba^{2+} ions from a number of solid materials.

Since the discovery of the first noble gas compound, $Xe^+PtF_6^-$ (Bartlett, 1962), a number of compounds of krypton, xenon, and radon have been prepared. Xenon has been shown to have a very rich chemistry, encompassing simple fluorides, XeF_2 , XeF_4 , and XeF_6 ; oxides, XeO_3 and XeO_4 ; oxyfluorides, $XeOF_2$, $XeOF_4$, and XeO_2F_2 ; perxenates; perchlorates; fluorosulfates; and many adducts with Lewis acids and bases (Bartlett and Sladky, 1973). Krypton compounds are less stable than xenon compounds, hence only about a dozen have been prepared: KrF_2 and derivatives of KrF_2 , such as $KrF^+SbF_6^-$, $KrF^+VF_6^-$, and $KrF^+Ta_2F_{11}$. The chemistry of radon has been studied by radioactive tracer methods, since there are no stable isotopes of this element, and it has been deduced that radon also forms a difluoride and several complex salts. In this paper, some

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of the methods of preparation and properties of radon compounds are described. For further information concerning the chemistry, the reader is referred to a recent review (Stein, 1983).

Clathrate Compounds

Radon forms a series of clathrate compounds (inclusion compounds) similar to those of argon, krypton, and xenon. These can be prepared by mixing trace amounts of radon with macro amounts of host substances and allowing the mixtures to crystallize. No chemical bonds are formed; the radon is merely trapped in the lattice of surrounding atoms; it therefore escapes when the host crystal melts or dissolves. Compounds prepared in this manner include radon hydrate, $\text{Rn} \cdot 6\text{H}_2\text{O}$ (Nikitin, 1936); radon-phenol clathrate, $\text{Rn} \cdot 3\text{C}_6\text{H}_5\text{OH}$ (Nikitin and Kovalskaya, 1952); radon-p-chlorophenol clathrate, $\text{Rn} \cdot 3\text{p-ClC}_6\text{H}_4\text{OH}$ (Nikitin and Ioffe, 1952); and radon-p-cresol clathrate, $\text{Rn} \cdot 6\text{p-CH}_3\text{C}_6\text{H}_4\text{OH}$ (Trofimov and Kazankin, 1966). Radon has also been reported to co-crystallize with sulfur dioxide, carbon dioxide, hydrogen chloride, and hydrogen sulfide (Nikitin, 1939).

Radon Difluoride

Most chemical experiments with radon have been carried out with isotope ^{222}Rn (half-life 3.82 days), which decays by α -emission as shown in Figure 1. The β - and γ -emitting daughters ^{214}Pb and ^{214}Bi , as well as the α -emitting daughters ^{218}Po and ^{214}Po , grow into radioactive equilibrium with the parent within four hours. We have used the 1.8 MeV γ -ray of ^{214}Bi , which can be measured conveniently through the walls of glass or metal apparatus, to determine the position of radon in tracer experiments, since the bismuth follows the radon as it moves from one location to another.

Figure 2 shows a Monel vacuum line, constructed with Autoclave Engineers Type 30 VM6071 valves and a 0-1000 torr Helicoid pressure gauge, which is currently used for the preparation of radon compounds. The radon is obtained from a Pyrex bulb containing an aqueous solution of radium chloride (approximately 30 mCi of $^{226}\text{RaCl}_2$ in dilute HCl). The bulb is suspended in a plastic cup surrounded by lead bricks and is attached to the line by a Kovar-Pyrex seal. In a typical experiment, approximately 0.1 to 1.0 mCi of ^{222}Rn is pumped from the bulb through a bed of Drierite, condensed in a cold trap at -195°C , distilled in vacuum from the trap at 23°C to the reaction vessel at -195°C , mixed with a fluorinating agent, and allowed to react at either room temperature or an elevated temperature. The reaction vessel may be a closed-end Monel tube, as shown, or a Kel-F plastic test tube.

When radon is heated to 400°C with fluorine, a nonvolatile fluoride is formed (Fields *et al.*, 1962, 1963). It has been deduced from the chemical behavior that the product is radon difluoride, RnF_2 . (Products of the tracer experiments have not been analyzed because of their small mass and intense radioactivity.)



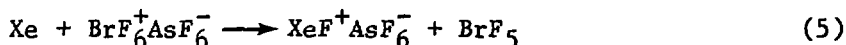
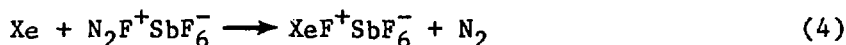
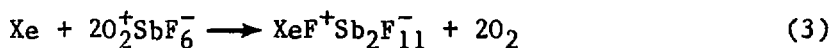
The compound can be reduced with hydrogen at 500°C to quantitatively recover elemental radon.



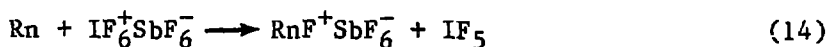
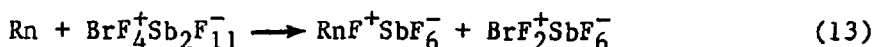
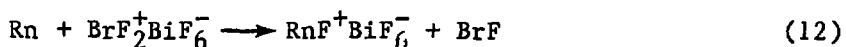
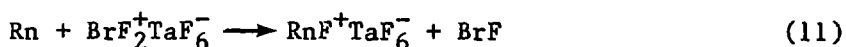
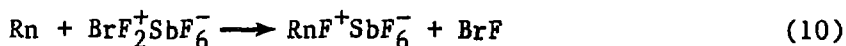
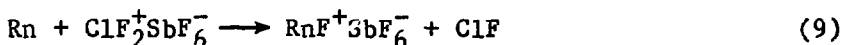
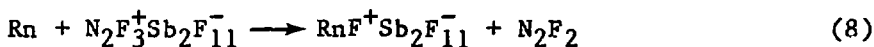
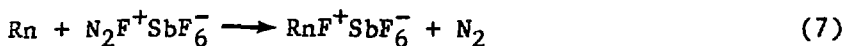
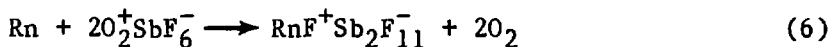
If a large amount of radon, such as 10 mCi, is mixed with fluorine in a small vessel (e.g., a 30 ml Kel-F test tube), the fluorination occurs spontaneously in the gas phase at room temperature or in liquid fluorine at -195°C. The activation is provided by the intense α radiation, which produces large numbers of ions and excited atoms.

Complex Fluorides

Radon reacts spontaneously at room temperature with many solid compounds that contain oxidizing cations, such as BrF_2^+ , IF_6^+ , O_2^+ , and N_2F^+ (Stein, 1972, 1973, 1974; Stein and Hohorst, 1982). Xenon also reacts with a few compounds of this type which have very high oxidation potentials (Stein, 1973, 1974). The xenon products have been analyzed by Raman and mass spectrometric methods and shown to consist of xenon (II) complex fluorides.

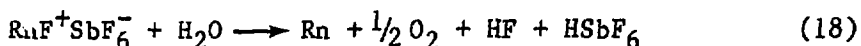
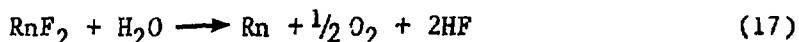
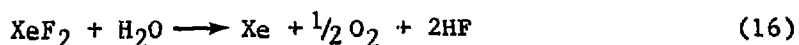
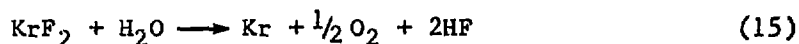


By analogy, radon is believed to form the following products.



Hydrolytic Reactions of Radon Compounds

Radon difluoride is quantitatively reduced to elemental radon by water in a reaction which is analogous to the reactions of krypton difluoride and xenon difluoride with water. Complex salts of radon also hydrolyze in this fashion.

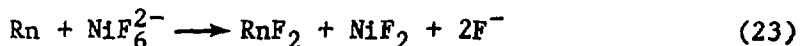
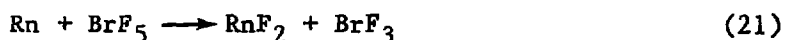
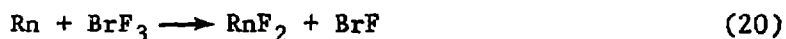


This behavior provides evidence that in each of the compounds, radon is in the +2 oxidation state. When higher-valent xenon compounds, such as XeF_4 and XeF_6 , are hydrolyzed, water-soluble xenon species (XeO_3 and XeO_6^{4-}) are produced (Malm and Appelman, 1969). We have observed no radon species corresponding to these xenon species in hydrolysis experiments.

Russian scientists (Avrorin *et al.*, 1981, 1985) have reported that reactions of complex mixtures of radon, xenon, metal fluorides, bromine pentafluoride, and fluorine yield a higher fluoride of radon which hydrolyzes to form RnO_3 . However, efforts to confirm these findings have been unsuccessful. In similar experiments which have been carried out at Argonne National Laboratory (Stein, 1984), it has been found that radon in the hydrolysate is merely trapped in undissolved solids; centrifugation removes the radon from the liquid phase completely. This is in marked contrast to the behavior of a solution of XeO_3 , which can be filtered or centrifuged without loss of the xenon compound. Hence there is no reliable evidence at present for the existence of a higher oxidation state of radon or for radon compounds or ions in aqueous solutions. Earlier reports of the preparation of oxidized radon species in aqueous solutions (Haseltine and Moser, 1967; Haseltine, 1967) have also been shown to be erroneous (Flohr and Appelman, 1968; Gusev and Kirin, 1971).

Solutions of Ionic Radon

Stable solutions of radon difluoride can be prepared in nonaqueous solvents, such as halogen fluorides and hydrogen fluoride (Stein, 1969, 1970). Radon reacts spontaneously at 25°C or at lower temperatures with each of the halogen fluorides except IF_5 . It also reacts with mixed solvent-oxidant pairs, such as $\text{HF}-\text{BrF}_3$, $\text{HF}-\text{BrF}_5$, and IF_5-BrF_3 , and solutions of K_2NiF_6 in HF.



Electromigration studies, which have been carried out with a Kel-F plastic cell (Figure 3), have shown that radon is present in many of these solutions as a cation (Stein, 1970, 1974). When the cell

is filled with inactive solvent and a solution of radon difluoride is added to the center leg, the application of a D.C. voltage to the nickel electrodes causes the radon to move to the cathode. In a pure conducting solvent, such as bromine trifluoride, the following ionization occurs:



In a solution containing added electrolyte, however, dissociation may be suppressed, and the radon may form anionic complexes.

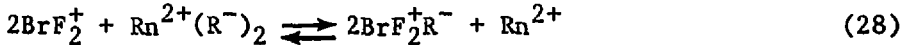
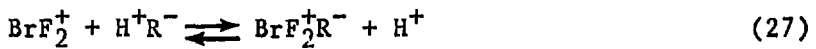
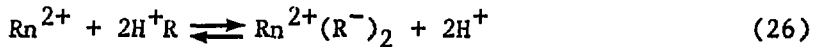
Recently, a search has been conducted for solvents which are less hazardous to handle than halogen fluorides and hydrogen fluoride and which can be used to prepare solutions of the cationic species. Two have been found that are highly oxidation-resistant and suitable for this purpose: 1,1,2-trichlorotrifluoroethane and sulfonyl chloride. Solutions of cationic radon prepared by oxidizing ^{222}Rn with halogen fluorides in these solvents have been shown to be stable when stored in capped FEP Teflon bottles at room temperature for several weeks (Stein, 1985). Because of their ease of preparation and relative safety, solutions of this type can be used most readily to study reactions of radon.

Ion-Exchange Reactions of Cationic Radon

Figure 4 shows the behavior that is observed when a solution of cationic radon in 1,1,2-trichlorotrifluoroethane is passed through a column packed with KPF_6 . The radon displaces potassium ion and adheres in a narrow band at the top of the column. It can be washed repeatedly with dilute BrF_3 in the halocarbon solvent, then eluted rapidly with 1.0 M BrF_3 in sulfonyl chloride. The radon daughters remain on the column during elution and decay in situ; new daughters are generated in the radon-containing eluant fractions.

We have found that similar behavior occurs when the column is packed with other salts of Group I elements, such as NaSbF_6 , Na_3AlF_6 , or K_2NiF_6 , or with Nafion ion-exchange resins (H^+ or K^+ forms). In batch equilibration experiments, using 1 g amounts of solids stirred with 5-15 ml volumes of solutions, we have found that the radon ions can also be collected on the compounds CsBrF_4 , $\text{Ca}(\text{BrF}_4)_2$, and $\text{Ba}(\text{BrF}_4)_2$. Thus it is apparent that, in its oxidized state, radon can displace H^+ , Na^+ , K^+ , Cs^+ , Ca^{2+} , and Ba^{2+} ions from a number of solid materials.

By measuring the distribution coefficient, K_d , of cationic radon on Nafion resin (H^+ form) in BrF_3 -trichlorotrifluoroethane solutions as a function of the concentration of BrF_3 , we have been able to show that the charge on the radon cation is +2 and that the parent molecule is RnF_2 . This physico-chemical method makes use of the fact that BrF_3 produces the univalent cation BrF_2^+ , which competes with Rn^{2+} for sites on the resin. The following equilibria occur in this system (R^- represents the anion of the resin):



Many finely divided solids will partly remove trace amounts of radon from solution by physical adsorption, but we have found that removal by ion-exchange is much more efficient. The distribution coefficient, K_d , of cationic radon ranges from about 90 to 4000 ml/g on ion-exchange materials that have been tested thus far in dilute BrF_3 -trichlorotrifluoroethane solutions. In contrast, the coefficient is less than 10 ml/g on materials which do not undergo ion-exchange with the radon species, such as LiF , MgF_2 , PbF_2 , Al_2O_3 , and CeO_2 .

These studies show that radon can be classified as a metalloid element, together with boron, silicon, germanium, arsenic, antimony, tellurium, polonium, and astatine. Like these elements, radon lies on the diagonal of the Periodic Table between the true metals and nonmetals (Figure 5) and exhibits some of the characteristics of both (Stein, 1985).

Possible Applications of Radon Chemistry

Tests in the laboratory with radon-air mixtures have shown that two reagents, dioxygenyl hexafluoroantimonate ($\text{O}_2^+\text{SbF}_6^-$) and hexafluoroiodine hexafluoroantimonate ($\text{IF}_6^+\text{SbF}_6^-$) are particularly well suited for trapping radon (Stein *et al.*, 1977; Stein and Hohorst, 1982). In the form of powders or pellets, both compounds remove more than 99% of the radon from air at low or moderate flow rates. The air must first be dried by passage through a bed of desiccant, however, since the compounds are decomposed by moisture. Figure 6 shows one type of metal and plastic cartridge containing 1.0-1.5 g of $\text{O}_2^+\text{SbF}_6^-$ powder that has been tested as a device for analyzing ^{222}Rn . To perform an analysis with this system, a measured volume of air is drawn by a battery-operated pump through a drying tube and the cartridge, which captures the radon as a nonvolatile compound. After radioactive equilibrium has been established between radon and its short-lived daughters (approximately 4 hours), the γ -emission of the cartridge is measured with a well-type scintillation counter. The amount of radon is then calculated from the γ -emission rate. In tests conducted with samples of air containing 3.5 to 11,700 pCi/l of ^{222}Rn (simulating the wide range of radon concentrations that can occur in a uranium mine), this type has been found to have a count rate of 2.74 counts/min/pCi of ^{222}Rn (all γ -ray energies).

An advantage of this method over the collection of radon with charcoal is that no refrigerant is required; both $\text{O}_2^+\text{SbF}_6^-$ and $\text{IF}_6^+\text{SbF}_6^-$ have been shown to operate efficiently at temperatures ranging from 10° to 40°C and probably can also be used at higher or lower temperatures. An advantage over the grab sampling technique is that only the radon is collected; a large volume of air (10-50 liters, for example) can be sampled, all of the radon retained, and the air discarded. This reduces the volume of sample that must be transported to a laboratory for analysis. A disadvantage of the

method is that the background count rate of a γ -scintillation counter is usually higher than that of a Lucas flask-photomultiplier combination, a very sensitive α counter. However, the background count rate can be reduced by using lead shielding, several scintillators, and anti-coincidence circuitry.

Chemical methods have been proposed for purifying radon-laden air in uranium mines (Stein, 1975, 1983). The cost of operating a full-scale air purification system using $O_2^+SbF_6^-$ reagent in a mine has been estimated at 0.245 U.S. dollars per 1000 standard cubic ft of treated air (1975 dollars) (Lindsay et al., 1975). This includes the cost of drying the air beforehand with a refrigerant-desiccant system. Comparable costs for removing the radon by physical methods have been estimated as follows: cryogenic condensation, \$0.117; adsorption on charcoal at $-80^\circ C$, \$0.170; adsorption on Molecular Sieve at $-80^\circ C$, \$0.376; and membrane permeation, \$0.402 per 1000 standard cubic ft of treated air. All of these methods are considered to be too expensive, in comparison to ventilation, to be used at present.

Some mixtures of noble gases can be separated by chemical methods. A mixture of radon and xenon, for example, can be separated by selectively oxidizing the radon with $ClF_2^+SbF_6^-$, $BrF_2^+SbF_6^-$, or $IF_6^+SbF_6^-$. Xenon can be trapped with stronger oxidants, such as $O_2^+SbF_6^-$, $O_2^+PtF_6^-$, or $N_2F^+SbF_6^-$, and thus separated from krypton and lighter noble gases. Ternary mixtures of krypton, xenon, and radon can be separated by successive oxidation of the radon and xenon.

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Figure 1. The decay scheme of radon-222.

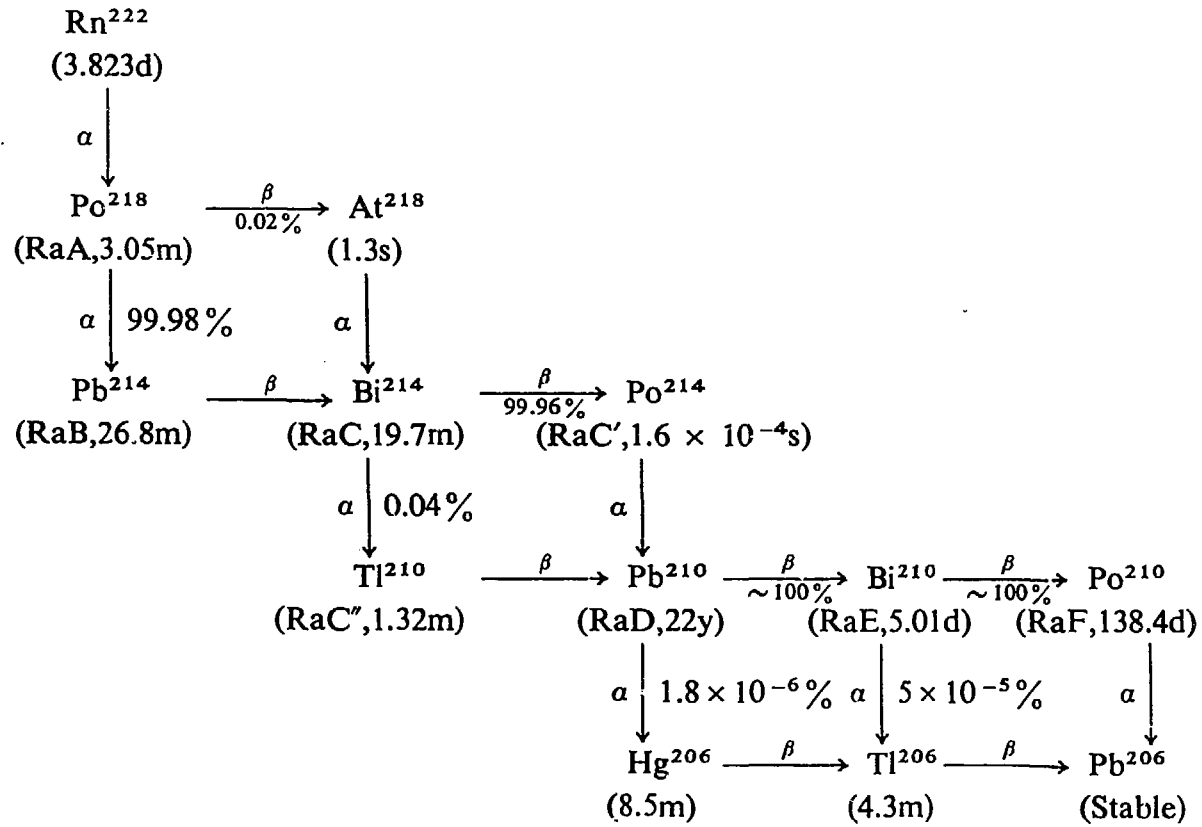
Figure 2. Monel vacuum line for the preparation of radon compounds.

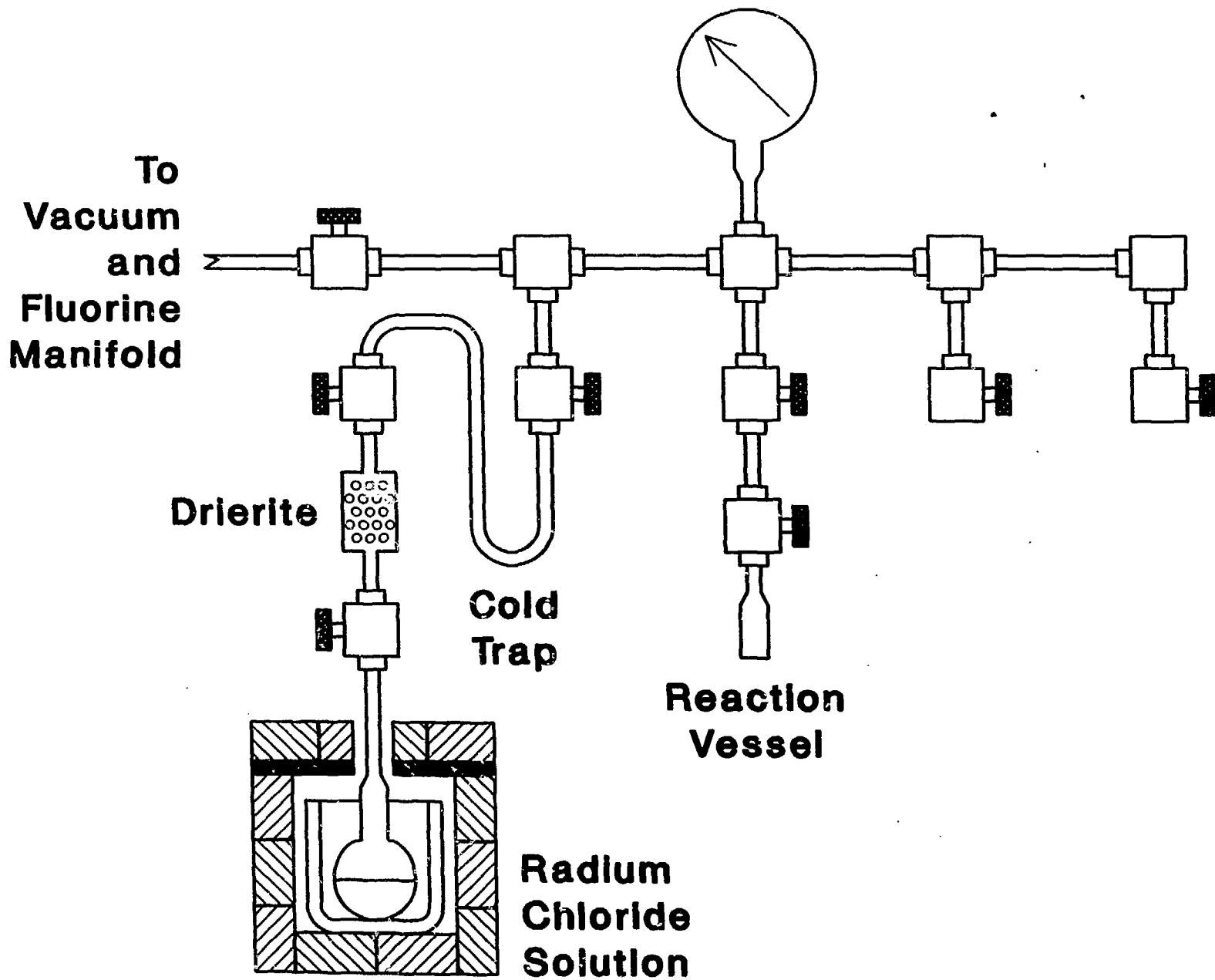
Figure 3. Kel-F plastic electrolysis cell.

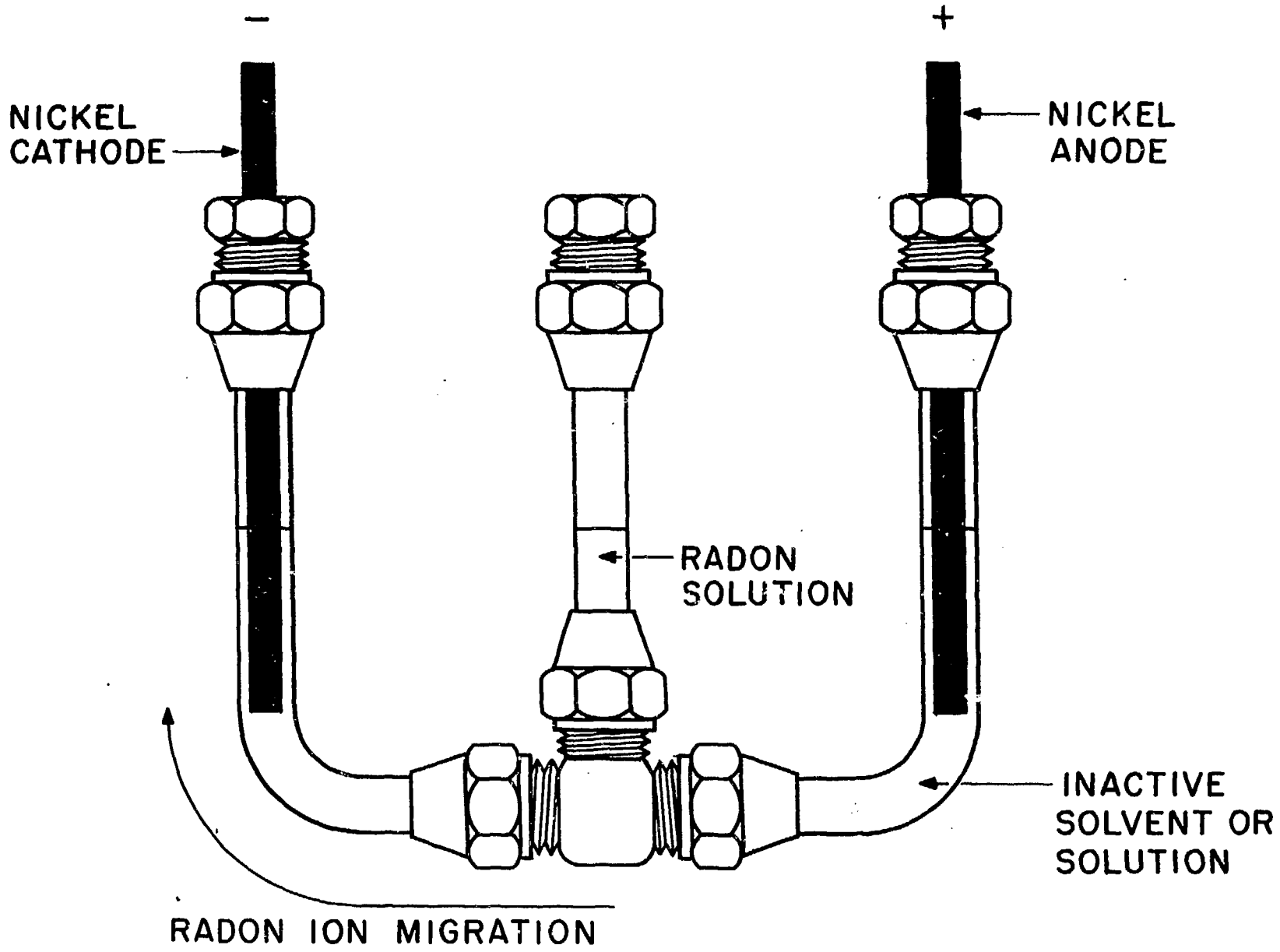
Figure 4. The ion-exchange behavior of cationic radon on a column packed with $K^+PF_6^-$.

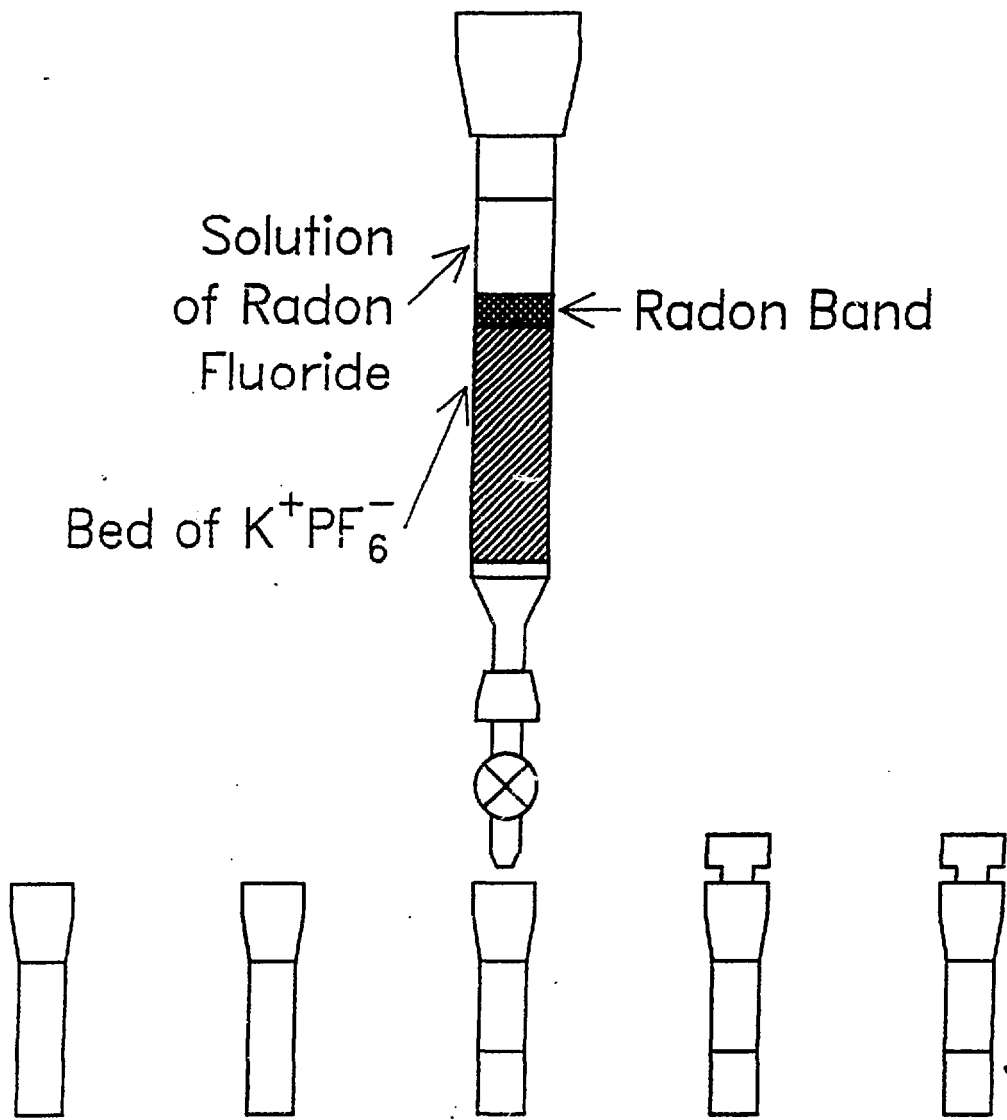
Figure 5. The arrangement of the metalloïd elements (dark shading) in the Periodic Table.

Figure 6. Kel-F plastic cartridge containing $O_2SbF_6^+$ reagent for the analysis of radon gas (from Stein et al., 1977).









Solution
of Radon
Fluoride

Radon Band

Bed of $K^+PF_6^-$

Effluent Fractions

