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RADON

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RADON

Element.[1] Radon, symbol Rn, is a chemical element of the Helium Group. All isotopes are radioactive. The naturally occurring isotopes are ^{222}Rn (which is the longest lived isotope, of half life 3.82 days), ^{220}Rn (also called thoron) and ^{219}Rn (also called actinon). All decay by α particle emission. Twenty two other isotopes have been synthesized in nuclear reactions in particle accelerators. The ground-state electronic configuration is KLMN $5s^2 5p^6 5d^{10} 6s^2 6p^6$ and the atomic number (Z) = 86. As with other elements of the He group, radon is placed between a halogen (At) and an alkali metal (Fr). Like the lighter gases Xe and Kr, radon exhibits some chemical acitvity.

Discovery.[2] Owens and Rutherford were the first, in 1899, to show that some of the radioactivity of thorium preparations could be removed in a stream of gas but it was Soddy and Rutherford, in 1906, who first showed that the emanation from Radium could be condensed by liquid air and behaved as an element of the He group. In 1910, Ramsay and Whytlaw-Gray confirmed its membership of this group by a gas density determination. Because of the family relationship to xenon, krypton and argon and because of the derivation of the most stable isotope from radium the element was named radon.

Origin.[1] All natural radon is derived from radioactive primordial precursors. Thus ^{222}Rn occurs in the sequence: $^{238}U(\alpha, 4.51 \times 10^{9}y) \rightarrow {}^{226}Ra(\alpha, 1620y) \rightarrow {}^{222}Rn(, 3.82d) \rightarrow$ in several steps ^{206}Pb. ^{220}Rn is produced in the sequence: $^{232}Th(\alpha, 1.41 \times 10^{10}y) \rightarrow {}^{224}Ra(\alpha, 3.64d) \rightarrow {}^{220}Rn(\alpha, 0.93m) \rightarrow$ in several steps ^{208}Pb. Polonium (which is radioactive) is a usual intermediate decay product. The final stable product is usually a lead isotope. The most stable of the isotopes made in nuclear transformations in particle accelerators is ^{211}Rn which has a half life of 16 hrs.

Occurrence.[1,3] Radon is widely distributed, but usually in very low concentration, in the atmosphere, the oceans and the lithosphere. Since the element is a gas it plays an important part in contributing radioactivity to the biosphere. In areas with large uranium or thorium deposits the radon concentrations are proprotionately large, but for average concentrations of these elements in rocks and soil the radon generation amounts to 1 pico-curie (pC) of radon radioactivity per gram (1 pC = 10^{-12} curie). Much of the radon is trapped in the mineral in which it is produced and further decays there. Some escapes to the air and usually amounts to 0.2 pC per litre although there is variation with location and climatic factors.[4] It has been estimated that ^{222}Rn enters the atmosphere at the rate of about 0.5 pC per second per square meter of ground surface. Its vertical distribution depends greatly on the turbulence of the air. ^{220}Rn has about the same concentration as ^{222}Rn at the air-earth interface, but the shorter life of ^{220}Rn generally results in a lower concentration at higher altitudes. Radon is present in steady-state concentration throughout the ocean waters. ^{222}Rn derives from dissolved ^{226}Ra and from 1 to 5 k, below the surface the concentration of each increases steadily from 0.06 to 0.08 pC per litre in the Atlantic and approximately twice these values in the Pacific. Nearer the surface ^{222}Rn is at 0.04 pC per litre

in both oceans. Drinking water can contain large ^{222}Rn concentrations. Values varying from 30 - 300 pC per litre have been reported in an Illinois, U.S.A. survey, but values as high as 240,000 pC per litre have been reported in New England, U.S.A. A survey in Sweden revealed levels of ^{222}Rn activity of 100 - 300 pC per litre and the same survey revealed that milk samples contained up to 1500 pC per litre. The radioactivity of many mineral springs is usually attributable to ^{222}Rn which can occur to the extent of 1,000,000 pC per litre. In uranium mines and other mines in the region of heavy element deposits, the radon concentration in the air can be high. A 1950 survey showed the ^{222}Rn content in Colorado mines to range from 135 to 22,300 pC per litre. Ventilation now usually maintains the level at 100 - 1,000 pC per litre. The decay of $^{222}Rn(\alpha, 3.82d) \rightarrow {}^{218}Po(\alpha, 3.05m) \rightarrow {}^{214}Pb(26.8m) \rightarrow {}^{214}Bi(\beta, \alpha, 19.7m) \rightarrow {}^{210}Pb(\beta, 22y) \rightarrow {}^{210}Po(\alpha, 138d) \rightarrow {}^{206}Pb$. Results in contamination, mainly with the daughters ^{210}Pb and ^{210}Po. These isotopes are deposited on vegetation, enter the food chain and are responsible for most of the radioactivity normally present in humans. By breathing air with presently permissible levels of radon (100 pC per litre, including daughters, for an industrial 40 hr. week) a human would accumulate a steady-state body content of about 5,000 pC, which is less than the radon ingested from a single drink of water containing the maximum "permissible" concentration for drinking water of 200,000 pC per litre.

Physical Properties.[1] Radon is colorless and odorless. The principal physical properties are given in Table 1. The radon atom is the largest and most polarizable of those of the helium group (see Kr). The large polarizability of the atoms of Rn give rise to a marked departure of the gas from ideal gas behavior and to its greater solubility in liquids and its more ready adsorption, enclathration and encapsulation when compared with the lighter gases of the He family. Thus radon

has more than twice the solubility (in cc per litre) in water than Xe and more than twenty times that of helium. The difficulties associated with handling even the largest lived of the isotopes (^{222}Rn) are responsible for the paucity of data. The higher molar solubility of radon in water compared with the lighter noble gases indicates that the trend of increasing polarizability with increasing mass down the noble-gas group is maintained. The ready adsorption of radon on activated charcoal and on a variety of surfaces is in harmony with high atomic polarizability. The structure of the solid is not known but it is likely to have the face-centered-cubic close packed structure adopted by all of the lighter gases except He. The first ionization potential is the lowest of the noble-gases and is consistent with Rn being the most easily oxidized of these elements.

Adsorption and Enclathration.[1,3] (see Argon for a historical note on clathrates). All evidence points to radon being more readily adsorbed and enclathrated than the lighter gases. The water clathrate 8 Rn .46 H_2O has the lowest dissociation pressure of the noble-gas hydrates. A phenol clathrate has been described in which hydrogen sulfide is also incorporated. Adsorption of Rn by activated charcoal has been recommended[5] as a means of removing radon from the air in uranium mines. Air containing Rn was passed through a carbon bed (the carbon had a surface area of 1,400 m^2/g) at ambient temperature until the bed was exhausted. The bed was then heated to $\sim$ 120°C, in a much smaller volume of air, to desorb the Rn and was then used again. It is estimated that one litre of carbon will purify in excess of 10 litres of Rn-contaminated air per minute. The ready adsorption and the characteristic radioactivity of the Rn isotopes has led to their application in surface labeling.

Chemical Properties. Radon is readily oxidized by fluorine and certain halogen fluorides (see below).

Laboratory Preparation.[1] Because of the ease of adsorption and encapsulation of Rn generated from a solid radium containing sample it is usual for Rn to be 'milked' from an aqueous solution of a radium salt. Since the radioactivity itself splits up the water into hydrogen and oxygen and since helium is also a decay product the Rn must be separated from these gases which are usually present in 500,000 excess by volume. The gaseous mixture is 'sparked', to induce H_2O formation, then dried. Radon is condensed with liquid oxygen refrigerent and the He and other gases pumped off. The Rn gas is stored in sealed gold or glass tubes which may also contain activated charcoal.

Analysis.[1] Although Rn may be detected and quantitatively estimated by emission spectrometry or mass spectrometry, it is usual to use the characteristic half-life and energy, associated with the radioactive decay ofeach isotope, in its analysis. It is essential to discriminate between the Rn activity and that of its daughters. Alternatively the Rn can be analyzed by counting the daughters specifically. Millicurie amounts may be determined by comparing the strength of the γ radiation from short-lived daughters with similar radiation from a calibrated radium standard.

Physiological Effects.[1] The high polarizability of radon leads to its high solubility in water, oils and fats. No doubt Rn would be a superior ansthetic to xenon, but the radioactive properties rule out such applications. Inhibition (90%) of the respiration of nucleated avian red cells has been observed. Physiological effects are, of course, those of Rn and its radioactive and non-volatile daughters. Tissue cultures in the presence of radon show damage to the nuclear proteins and later to

the cytoplasmic components. It also has a germicidal action on Brucella and other microorganisms. Small doses in animals cause increased excretion of water and experiments with A-strain mice have established that radon shortens the life span even more than an equivalent X-radiation, presumably because of α radiation. Primary radiation injury to the respiratory tract in animals is attributable, however, to the daughters not to Rn itself. Exposure of plants to small doses of Rn produced sterile mature barley plants; stimulated on short exposure, the growth of vetch, beans and corn; decreased the keeping time of potatoes; and caused premature flowering in onions and decreased their yield.

Uses.[1] In all uses of radon either the α or the γ activity of radon or its daughters is exploited. The gaseous nature of radon provides for easy control of the amount of α or γ radiation desired. For more than 50 years radon has been used chemically as a source of γ radiation, but has largely been superceded by other high energy sources. The capsules of radon prepared as described under 'Preparation' and commonly referred to as 'seeds' are placed in tissue to destroy it; the tissue is usually cancerous, but lymphatic tissue, causing certain kinds of deafness, has also been destroyed in this way. Seeds may be left in situ because the radiation decays rapidly. Radon has been used as a source in gamma radiography and can be used for the radiography of steel in thicknesses of 4 in. or more. The radiation from radon has been used to initiate the oxidation of 2,7 dimethyl octane by oxygen and could no doubt be used to initiate many other reactions. The half-life of ^{222}Rn makes it an excellent species by which atmospheric diffusion and turbulence can be studied.

Radon Compounds.[1(b), 6] Very soon after the preparation of the first true compounds of Xenon in 1962, Stein and his coworkers demonstrated that radon formed a fluoride. The great experimental difficulties associated with the handling of macroscopic quantities of radon have hindered the research into its chemistry. Efforts to make other compounds than the fluoride have failed so far. Radon is oxidized at ordinary temperatures and pressure by gaseous fluorine and the following liquids, ClF_3, ClF_5, BrF_3, BrF_5 and IF_7. The following solid complexes have also proved to be effective[6,8] (% Rn retention is given in parentheses): $KBrF_4$(28), $CsBrF_6$(7), $KClF_4$(19), $RbClF_4$(16), ClF_2SbF_6(100), BrF_2SbF_6(100), $BrF_4Sb_2F_{11}$(100), $IF_6Sb_3F_{16}$(100), BrF_2BiF_6(100), BrF_2TaF_6(27), IF_4SbF_6(76), O_2SbF_6(100), $O_2Sb_2F_{11}$(100). The latter, O_2^+ salts, are potentially valuable as reagents for the chemical scrubbing of Rn contaminated air (see below).

Radon (I) Compounds. Pitzer has pointed out[9] that because of relativistic effects, which are important for the large many-electron atoms, the preferred first oxidation state for radon may be +1 and he has suggested that the reported involatile fluoride (see below) could be RnF. This suggestion springs from the finding that relativistic s orbitals of Rn are suitable for bonding but that relativistic $p_{1/2}$ and $p_{3/2}$ orbitals are not. For example, a detailed consideration of a diatomic molecular orbital based on $p_{1/2}$ relativistic atomic orbitals indicates 1/3 σ-bonding and 2/3 π-antibonding character on the basis of the angular factors of the large components. Full σ-bonding character is obtained with the combination $1/3p_{1/2} + 2/3p_{3/2}$. In the case of the positive ion Rn^+ the lowest energy state ($6p^2_{1/2}\ 6p_{3/2}$, $2P_{3/2}$) is not effective in bonding. The valence state for bonding is at the energy 1/3 ($2P_{1/2}$) + 2/3 ($P_{3/2}$) i.e. higher by one third of the $p_{1/2} - p_{3/2}$

energy difference. This promotion energy is 1.42 eV for Rn and is comparable with the energy of an electron pair bond such as that to be expected in $(Rn-F)^+$. On the basis of an ionic lattice energy of 10.76 eV for crystalline Rn^+F^-, and assuming the same bonding energy for the molecule RnF_2 (from $Rn^+ + F^- + F$) as for the XeF_2 case, the enthalpy of formation of RnF_2 is calculated to be 1.92 eV. This is 0.37 eV less favorable than the enthalpy of formation calculated for the salt Rn^+F^- (i.e. -2.29 eV). Ionic RnF should be of low volability and should also show migration as a cation in electrolysis -- both properties have been observed for radon fluoride (see below).

Fluorination of Radon, RnF_2?[1(b),6,7] Radon interacts at ordinary temperature and pressures with fluorine and several halogen fluorides to yield an involatile fluoride (or fluorides). This has been assumed to be RnF_2 but its composition has not in fact been established. The interaction of Ru with liquid bromine trifluoride proceeds spontaneously at 23-25°C to form a solution of radon fluoride

$$(Rn + BrF_3 \text{ (large excess)} \longrightarrow \text{solution of } RnF_2(?) + BrF)$$

and in a D.C. field the radon migrates to the cathode. The solution can be exposed to the atmosphere, poured from one container to another and the solvent removed by vacuum distillation without any loss of radon. A deposit of solid radon fluoride remains. On the basis of the observation that Rn is oxidized by bromine trifluoride but is not oxidized by arsenic pentafluoride, Stein has estimated the enthalpy of formation of RnF_2 to be between -29 and -51 kcal $mole^{-1}$. The sublimation energy must be greater than 13 kcal $mole^{-1}$ (the value for XeF_2[1(b)]) hence the average bond energy must be in excess of 40 kcal $mole^{-1}$. The fluoride decomposes above 250°C in a vacuum and no radon fluoride has been detected as a vapor species.

Addition of water to the white solid fluoride leaves little radon in the aqueous phase, the reaction appears to be $RnF_2 + H_2O \rightarrow Rn + 1/2\ O_2 + 2\ HF$.

Rn (I or II) Complex Fluorides.[6,8] Radon interacts with a number of complexes of halogen fluorides with fluoride ion acceptors e.g. $Rn + BrF_2^+SbF_6^- \rightarrow RnF^+SbF_6^-(?) + BrF$; $Rn + ClF_2^+SbF_6^- \rightarrow RnF^+SbF_6^-(?) + ClF$; $Rn + BrF_4^+Sb_2F_{11}^- \rightarrow Rn^+SbF_6^-(?) + BrF_2^+SbF_6^-$; $Rn + IF_6^+Sb_3F_{16}^- \rightarrow RnF^+SbF_6^-(?) + IF_4^+Sb_2F_{11}^-$. Since XeF^+ and KrF^+ salts are known[1(b)] it is reasonable to assume that the radon analogue is formed in these reaction, but there is no analytical data to support these formulations. RnF^+ salts are also assumed to be produced when Rn is oxidized by O_2^+ salts: $Rn + 2\ O_2^+SbF_6^- \rightarrow RnF^+Sb_2F_{11}^- + 2\ O_2$ (see below).

Removing Radon from Air by Oxidation.[6] Radon can be collected by halogen fluoride complexes such as ClF_2SbF_6, BrF_2SbF_6, $BrF_4Sb_2F_{11}$ and $IF_6Sb_3F_{16}$; with the dioxygenyl salt O_2SbF_6; and with the fluoronitrogen salts N_2FSbF_6 and $N_2F_3Sb_2F_{11}$. It is recommended that air to be scrubbed by such reagents should be passed successively to a dust filter, blower, air drier, radon absorbtion tower, vapor trap and liquid circulating pump. For application to a uranium mine it is estimated that a flow capacity of at least 5,000 cfm would be needed to appreciably lower the radon concentration in a single stope.

References

(1)(a) "Argon, Helium and The Rare Gases," Two Volumes, G. A. Cook, ed., Interscience Publishers, New York, London, 1961, is the most comprehensive single work on radon.

(b) "The Chemistry of The Monatomic Gases," A. H. Cockett, F. C. Smith, N. Bartlett, and F. O. Sladky, Pergamon Press, Oxford, 1975.

(2) "Discovery of the Elements," M. E. Weeks, and H. M. Leicester, Journal of Chemical Education, 7th Edition, Easton, Pa., 1968, pp. 785-787.

(3) "Noble Gases," R. E. Stanley and A. A. Moghissi, eds., U. S. Environmental Protection Agency; Report of Symposium held Sept. 24-28, 1973 Las Vegas, Nevada, U. S. A.

(4) J. H. Harley in (3) pp. 109-114

(5) J. W. Thomas in (3) pp. 637-646

(6) L. Stein in (3) pp. 376-385

(7) L. Stein, Science 168, 362 (1970).

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(9) K. S. Pitzer, J. C. S. Chem. Comm., 760 (1975).

Table 1. Physical Properties of Radon[a]

Isotope half life (d = day, h = hour, m = minute, s = second) and emission

isotope	204	206	207	208	209	210	211	212	215
half life	3 m	5.3-7 m	10 m	22 m	30 m	2.4 h	16 h	23 m	10^{-6} s
emission	α	α	α	α	α	α	α	α	α
isotope	216	217	218	219	220	221	221	222	
half life	10^{-4} s	10^{-3} s	0.019 s	3.92 s	54.5	25	---	3.82_3 d	
emission	α	α	α	α	α	α	β	α	

Density of gas, at 0°C, at 1.01325 bars, g liter^{-1}	9.73
Triple point, °C	-71
Pressure at triple point, mm Hg	∿ 509
Boiling point (normal, 1 atemsphere) °C	-62
Critical temperature, °C	105
Critical pressure, atmospheres	62
Density of liquid at normal boiling point, g cm^{-3}	4.4
Pressure-temperature relationship from critical point to triple point: $\log_{10} P(atm) = 4.0915 - (862.8/T)$	
Heat capacity of gas, C_p, at 25°C and 1 atmosphere, cal(°K g-mole)	4.968
Ratio, C_p/C_v,	----
Heat of vaporization of liquid at normal boiling point Cal g-mole^{-1}	4325
Viscosity at 0°C, 1 atmosphere, μ poises	212
Wavelengths of emission lines for identifying gas (relative intensity in parentheses) in Å units:	7450.0(600) 7055.42(400)
Covalent radius[b]:	1.4-1.5 Å
Ionization potential, eV: 1st	10.748

Electronegativity coefficient (after Pauling)[c]	2.3-2.5
Solubility (cm^3 of gas (STP) per 1000 g water, at 1 atmosphere partial pressure, at 20°C	230

(a) The physical properties, except where otherwise indicated, are those of ^{222}Rn. Most of the data is drawn from "Argon, Helium and the Rare Gases," G. A. Cook, ed., Vols. I and II, Interscience Publishers, New York and London, 1961.

(b) From estimates given by R. G. Gillespie, in "Noble Gas Compounds," H. H. Hyman, ed., The University of Chicago Press, Chicago and London, 1963, p. 333 and by B.-M Fung (d).

(c) Value derived by B.-M. Fung, J. Phys. Chem., 64, 596 (1965).

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