# 64. *The Structure of Molecular Compounds. Part VIII. The Compound of Krypton and Quinol.*

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By crystallisation of an aqueous solution of quinol under 20 atmospheres pressure of krypton the clathrate compound of composition $3C_6H_4(OH)_2,0{\cdot}74Kr$ [ideally $3C_6H_4(OH)_2,Kr$] is obtained in a form similar to that of the corresponding argon compound.

The general series of clathrate compounds of ideal formula $3C_6H_4(OH)_2,M$ formed by quinol with a variety of substances M, which in their ordinary states at room temperature may be volatile liquids or gases, owe their existence to the formation by quinol, in the presence of the second component, of a special cage-like structure which imprisons single molecules M each in its own cavity. No ordinary chemical bonds are needed between quinol and the other molecule.

From the general properties and modes of formation it was suggested (Part IV, *J.*, 1948, 61) that the inert gases would form such compounds if a solution of quinol under high pressure of the inert gas were allowed to crystallise. The argon compound has already been prepared (Powell and Guter, *Nature*, 1949, **164**, 240; Powell, Part VII, preceding paper), but the helium compound appears not to exist. As discussed in Part IV, the enclosed molecule must satisfy certain requirements of size and shape. It must not be too large for the space available in the cavity although minor modifications in the shape of the enclosing quinol framework may be made to accommodate different molecules (Palin and Powell, Part VI, *J.*, 1948, 815). For a small effectively spherical molecule such as hydrogen chloride which does not completely fill the cavity, the two interpenetrating hydrogen-bonded quinol frameworks, which together form the walls of the enclosing cavities, adjust themselves to the equilibrium positions that they would occupy in the absence of any enclosed component, but for non-spherical molecules such as methyl cyanide the quinol structure distends in the manner of a piece of trellis. For enclosure of the inert-gas atoms the undistended form is to be expected and has been found for the argon compound. The absence of a helium compound is attributed to the small effective size of the atom, which could escape through a hole in the cage walls provided by six oxygen atoms linked through hydrogen bonds of length 2·75 A. along the sides of a plane hexagon. As shown in Part VI, a very slight distension of the quinol structure occurs when the methanol molecule is enclosed, and a molecule considerably larger than that of methanol, *e.g.*, methyl cyanide, will fit into the cavity by arranging its length in a way that fits the surrounding structure. The van der Waals radius for a $CH_3$ group in crystals is about 2 A., and it is therefore expected that spherical atoms of this size and somewhat larger will be enclosed and retained by the cages. From crystal-structure examinations the radii of the inert-gas atoms (for temperatures at which these substances solidify) are Ne 1·61, A 1·9, Kr 2·0, Xe 2·2 A. The radii for room temperature will be somewhat greater. The krypton atom, intermediate in size between argon and the methyl group, should therefore form a compound, and it seems probable that the xenon atom which is not much larger than a methyl group will be capable of enclosure in the same way. The solubilities in water of the inert gases increase with increasing atomic number, and since the higher solubility increases the chance of an inert-gas atom being available in the right place for enclosure, it may be expected that the compound will form more readily the higher the atomic number.

The krypton compound has now been prepared. 60 C.c. of a solution of quinol in water saturated at room temperature were contained in a pressure vessel with a further 2 g. of quinol. A pressure of 20 atm. of krypton was applied from a cylinder of the gas. The temperature was raised to 95° in order to dissolve the additional quinol, and the solution allowed to cool during 12 hours. The product consisted of crystals, some several mm. in thickness, similar in appearance to those of the argon compound, and distinguishable from a small amount of fine needles of α-quinol which also came out. A complete separation could not be made, and an analysed sample probably contained a small proportion of α-quinol. When heated to 120° with precautions to prevent loss of quinol by volatilisation, it lost 14·3% by weight. This corresponds to a composition $3C_6H_4(OH)_2$,0·67Kr. As was expected, a somewhat higher krypton content was calculated from the density of a single selected crystal of the compound. This gave by flotation $d$ = 1·51 g./c.c., and for a unit cell of the same size as the argon compound this corresponds to 15·8% krypton content, *i.e.*, a composition $3C_6H_4(OH)_2$,0·74Kr. Thus about three-quarters of the available cavities are occupied by krypton atoms. This may be compared with the 80% occupancy in the argon compound made in similar conditions but under 40 atmospheres' pressure. The procedure of the preparation excludes all possibility of anything but krypton being available for enclosure, and the high density cannot be explained except by the presence of these heavy atoms. Addition of methanol to the crystals causes dissolution with vigorous effervescence owing to liberation of krypton.

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