CLATHRATE COMPOUNDS OF QUINOL

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A clathrate may be described as a single-phased solid consisting of two distinct components, the host and the guest; the guest is retained in closed cavities or cages provided by the crystalline structure of the host. Generally, a cage and its enclosed molecule or molecules are taken as a unit cell.

As early as 1849 and 1859, Wohler[1] and Clemm[2] described the preparation of hydrogen sulphide and sulphur dioxide complexes of hydroquinone. Mylius[3] made careful observation on complex compounds formed by quinol with certain volatile compounds, such as hydrogen sulphide, sulphur dioxide, and hydrogen chloride. He found that these compounds do contain three or four molecules of quinol to each molecule of the other component. He suggested that no ordinary combination occurred between the two types of compounds but that during crystallization the quinol molecules were in some way able to lock the volatile compounds into position without chemical bonding. The other compounds of quinol, with HCl and HBr, were prepared by Schmidlin and Lang[4] and Gomberg and Cone[5] respectively.

Heydrich[6] determined the relation between the density and index of refraction in crystalline solids and placed quinol in the ditrigonal scalenohedral or calcite class. The crystal structure of quinol has been examined by Becker and Jancke[7] and Caspari[8,9] Caspari prepared the quinol crystals by slow evaporation at room temperature, of aqueous solutions to which a little potassium bisulphite had been added. Prisms of all thicknesses up to 1·5 mm. were obtained and he showed that quinone belongs to the trigonal rhombohedral or dioptase class. This conclusion was based on X-ray photographs taken by the Laue and rotation methods. By the latter, the cell dimensions were evaluated as $c = 5 \cdot 62$ A°, normal to the (0001) plane, and $a = 22 \cdot 07$ A°, normal to the (1120) plane. The unit cell is hexagonal not rhombehodral and contains 18 molecules. The space group requires only 6, so an association in group of 3 was suggested.

In 1927, Caspari found that when quinol is deposited from methyl alcoholic solution at the ordinary temperature, it crystallizes in hexagonal prisms resembling those of α—quinol at first sight, but belonging to a different subdivision of the trigonal system. This modification he termed β—quinol. The crystals consisted of prisms capped, not by rhombohedra, but by trigonal pyramids both of the first order, with a well marked hemimorphism along the c-axis. Laue and rotation X-ray photographs showed it to belong to the trigonal polar class, the unit cell dimensions being $a = 16 \cdot 24$ A°, $c = 5 \cdot 53$ A°. There are 9 molecules per unit cell, with 3 lattice units per unit cell, each containing 3 molecules. The 3 molecules per unit have no symmetry either separately or as a group. The space group appears to be C_3.

The trigonal modification of quinol which crystallizes from aqueous solutions, is called α—quinol. γ—Quinone, formed by sublimation has a density of 1·35, melting point of 169° while β—quinone has a density of 1·31 and melting point of 166°. Rotation

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photographs gave the dimensions of γ—quinone, $a=13\cdot24$ A°, $b=5\cdot20$A° and $c=8\cdot11$ A°. The space group appears to be C^5_{2h}. γ—Quinone is less stable than the other forms.

Palin and Powell[10] determined the structure of addition complexes of quinol with certain volatile compounds. The basic principle of the structure is the hydrogen bond between three quinol OH groups giving rise to a structure like a cup; this cup is the unit from which the lattice is built up. Two cups—one upside down—form one cage. Crystals were prepared by slow crystallization from a solution of quinol in water which was saturated with sulphur dioxide. This component (SO_2) was taken as a basis for discussion of the general type of compounds $3C_6H_4(OH)_2$ M in which M is H_2S, SO_2, HCO_2H, HCN, HCL, HB_1, CH_2OH_3 or CH_3CN. In some instances of larger molecules such as CH_3CN, the lattice is somewhat stretched in one direction. Apparently almost any substance may occupy the cavities, provided its molecules are neither too large (CCl_4) nor too small (H_2) and do not react with quinol in the ordinary sense. If quinol is denoted by Q and the second component by A, the geometry of the lattice entails a limiting composition 3Q:1A of the crystals, but a considerably smaller amount of A may be sufficient to produce a thermodynamically stable crystal. The two components in the crystal are not joined by ordinary chemical bonds and the Q–A distances following the X-ray analysis are non-bonded distances. Thus, the interaction of the encaged molecules A with the surrounding quinol network will be very similar to that found between adjacent molecules in a liquid, but it nevertheless gives an essential contribution to the stability of the complex crystal.

Powell and his coworkers[10–21] remarkably developed the subject and studied the crystal structure of other quinol clathrates.

Dryden and Meakins[22] measured the low-frequency dielectric absorption and direct-current conductivity in quinol. Hydrogen-bonded hydroxyl groups are present in the dihydric phenol quinol, according to a structure proposed from X-ray crystallographic data[10], but in this case the hydrogen bonds form regular hexagons. With such a structure the resultant dipole moment should be zero and the compound should give no dielectric absorption. However, they[22] observed considerable low-frequency absorption in three samples of quinol crystallized from water, ethanol and methanol. The absorption and conductivity decreased with time, and were contributed to partial breakdown of the crystalline structure during grinding, resulting in the formation of H-bond chains, which have a large dipole moment. The dielectric properties of some other clathrate compounds of quinol were measured by Dryden and Meakings[23].

Wynne—Jones and Anderson[24] studied the thermodynamic conditions for the formation and existence of clathrate compounds. The complexes of hydroquinone with MeOH and SO_2 were prepared and their vapour pressure was measured as a function of temperature. The heat of evaporation of CH_3OH and SO_2 which followed from these measurements were the same as for the pure substances. This indicated that the heat of formation of these clathrate compounds is zero. The difference in free energy between the compounds and the pure components therefore must be due to a difference in entropy.

A new twin microcalorimeter in which differential or direct heats of solution can be measured accurately was described by Evans and Richards[25]. The calorimeter was vacuum and pressure tight, and the solutions came into contact with glass surfaces only. Since β—quinol is less stable thermochemically than α—quinol, the latter will be the stable modification at low temperatures if the two forms are entantiotropic[26]. However, α—quinol also seems to be stable up to its melting point, since samples of β—quinol go over rapidly into α—quinol at higher temperatures, and hence the system α—β—quinol is probably monotropic. The very small energy difference between the two forms of quinol may be explained by the more extensive hydrogen bonding in the β—form, which almost compensates for the energy lost by the fewer van der Waals contacts.

The methods for preparing clathrate compounds of quinol and oxygen, and of quinol and nitric oxide were devised by Evans and Richards [27]. The specific susceptibilities of the compounds have been measured, and the values of χ for the enclosed molecules calculated. For O_2 in the clathrate compound, $\chi = 108 \cdot 8 \times 10^{-6}$, which agrees within experimental error with measurements in the gas phase.[30], [31] For NO in its compound, $\chi = 51 \cdot 6 \times 10^{-3}$. This value was higher than the recorded results; for gaseous NO; $47 \cdot 7 \times 10^{-6}$, $49 \cdot 2 \times 10^{-6}$, $49 \cdot 3 \times 10^{-6}$ and $47 \cdot 7 \times 10^{-6}$.

Dryden [32] investigated the dielectric properties of clathrate compounds of quinol containing C_2H_2, H_2S, CH_3OH_2, HCN and SO_2. With the exception of the CH_3CN compound, the clathrate compounds containing polar molecules possess dielectric absorption at ultra high radio frequencies.

Evans and Richards[33] showed calorimetrically that apart from the crystalline lattice forces, the only significant forces that are involved in hydroquinone clathrate are those due to the interaction of a guest molecule with its enclosing cage. Such clathrates are, in some ways, thermodynamically analogous to the dilute solutions.

Cooke and others[34] measured the magnetic susceptibility of oxygen enclosed in a β—quinol clathrate at temperatures from 1 to 20°K; and Cooke and Duffus [35] of NO at temperatures 10° K to 300°K. Above 2°K, the susceptibility of the oxygen in the clathrate compound agreed within the experimental error with the calculated susceptibility. Below 2°K, however, they did not agree, nor was any difference observed between oxygen of normal isotopic constitution and oxygen enriched at 11 per cent in ^{16}O ^{18}O, whereas the magnetic susceptibility calculated for an enriched specimen of the free gas would differ appreciably from that of the normal gas at temperatures below 2°K. The NO magnetic susceptibility, which obeyed Curie's law at room temperature, approached a temperature independent value at low temperatures.

The statistical mechanical formulation of the crystalline compounds formed between quinol and non-polar gases has been given by van der Waals [36]. The thermodynamic model is a system in equilibrium consisting of three phases: clathrate, nonclathrate modification of the host component (α—hydroquinone), and pure nonpolar gas. The theoretical treatment of the problem requires that no more than one guest molecule be present in a cavity. The method of Lennard—Jones and Devonshire [37], [38] was used to calculate the potential field in which a gas molecule moves within its cavity, and the corresponding contribution to one partition function was constructed. The energy of formation and dissociation pressure of the clathrate could thus be expressed in terms of the Lennard—Jones force constants of the gaseous component, which could be derived from measurements of the second virial co-efficient of the gas. van der Waals and Platteeuw[39] also showed that it is possible to derive the free energy function of a clathrate crystal by a statistical mechanical technique analogous to that used for describing ideal localized adsorption [40]. van der Waals [36] obtained the following equation for the vapour pressure of a non-polar gas clathrate of hydroquinone,

$$P = kT \frac{\varphi(T)}{h(T)} \frac{y}{1-y}$$

where P is the pressure of the non-polar gas, ϕ (T) is the partition function of the free gas, h(T) is the contribution to the partition function of the clathrate assembly that is due to the interaction of a gas molecule with its enclosing cage, and y is the fraction of cages in the clathrate that are occupied by the gas molecules. The fraction y is a function of the difference in chemical potentials of the clathrate and non-clathrate crystalline modification of hydroquinone according to the reaction:

$$\alpha - C_6H_4\,(OH)_2 = \beta - C_6H_4\,(OH)_2$$

The absorption and differential potassium bromide pellet spectra, covering the range 1·5—15 μ, of hydroquinone clathrate with small molecules such as HCl, H_2S, SO_2 and CO_2 were described by Hexter and Goldfarb[41]. The reported spectra were in good agreement with the difference in crystal structure between α—hydroquinone and its β—allomorph. In addition, some results were presented which indicated the extent of rotational motion of the small molecules included in the clathrate, and the extent of the binding of the small molecules to the clathrate lattice.

Meyer and others[42] stated that it was possible to deduce the size of the potential barrier of oxygen in a clathrate compound from the magnetic data. It was assumed that the molecule was not free. Additional evidence for this assumption was furnished by the absence of ordinary resonance of oxygen in the clathrate compound.

Some new clathrates of hydroquinone with the maximum composition formula x. A. 3 $C_6H_4\,(OH)_2$ in solution of ethanol were investigated by Peyronel and Barbieri[43]. A study of the influence of the pressure (between 30° and 22°) on the clathrability of different molecules (CH_4, CH_3Cl, N_2O and C_3H_8) etc. has shown that the clathration of smaller molecules like N_2 and CH_4 increases regularly with increasing pressures, up to the maximum value of one molecule per cage [1A. $3C_6H_4(OH)_2$] at about 100 atmospheres. For bigger molecules like nitrogen protoxide and carbon dioxide the clathration increases upto a maximum value of about 0·75 molecules per cage, at about 20—30 atmosphere; and then lowers progressively to very smaller values at greater pressures.

Ferroni and Cocchi[44] studied the epitaxy on muscovite mica of clathrates of quinol with H_2S, SO_2, MeOH and HCO_2H. Oriented overgrowths were obtained in each case, the crystals being identified and orientation determined by X-ray examination after fixing in a polyvinyl adhesive. In each case $10\overline{1}0$ face of clathrate was in contact with 001 of muscovite mica; the (0001) axis of clathrate may be oriented parallel to (010) are (100) of muscovite mica or at 30° or 60° to (010). The results confirmed that H–bonds were formed between quinol and muscovite mica and that the symmetry of the interphasal plane must be a maximum[45].

The equilibrium clathrate—gas for the quinol—argon compound at 60°C has been studied by Platteeuw[46]. He found that the argon pressure was related to the composition of the clathrate according to a Langmuir isotherm, as predicted on theoretical grounds.

Lahr and Williams[47] prepared the clathrate compound of argon—hydroquinone, argon—phenol, krypton—phenol and xenon—phenol by a direct reaction of the rare gas with the solid organic compound. Heats of formation of the phenol clathrates were found to be—9·85, — 8·98 and —8·8 kcal., respectively, per gram mole of argon, krypton and xenon. Heats of formation of some other quinol clathrates are given in Table I.

TABLE I

HEATS OF FORMATION OF SOME QUINOL CLATHRATES

Gas	△ H in k cal/mole	
	Theoretical	Observed[33].
A	—5·5	—6·0
N_2	—5·2	—5·8
O_2	—5·6	—5·52
HCl	—9·3	—9·2

Parsonage and Staveley [48,49] and Grey and coworkers [50] measured the heat capacity of various clathrates between ∿13°K to 300°K. The agreement between theoretical and practical studies was satisfactory. The rotation of the methane molecules was almost unrestricted [49] and C_p was found to be a linear function of composition [50].

A new technique for the preparation of quinol—krypton^{85} clathrate compounds was developed by Chleck, and Ziegler [51,52]. They placed a sample of quinol in a pressure vessel eliminated atmospheric gases and filled the apparatus with carrier-free krypton containing 5% Kr^{85}, the form commonly available from Oak Ridge. The quinol was heated to slightly above its melting point (185°C) and then slowly cooled over a long time. High gas pressure and controlled cooling to prevent rapid crystal formation fulfilled the requirements that they stated for good clathration. Their maximum clathrating efficiency was obtained at 60 atmospheres and a growth period of 72 hours.

Meyer and Scott [53] observed the pure quadrupole resonance of 14_{N_2}' molecules trapped in β—quinol clathrates at temperatures below 25°K. The resonance occurred at about 3·6 Mc/S and there was an extensive fine structure of at least seven lines. Foner and others[54] studied the low temperature paramagnetism of trapped O_2 molecules. Staveley [55] put forward the thermodynamic studies of molecular rotation in solids and pointed out that it was possible for molecules to rotate in crystal lattices with almost complete freedom, examples being the oxygen and methane molecules in the quinol clathrates. Bowlinson [56,57] pointed out that recent analysis of the configurational heat capacities of the liquids has shown that this difference persists into the liquid state. Liquid methane has no observable configurational heat capacity of rotation either at constant volume or at constant pressure. Diatomic molecules have observable heat capacities which increase in the order oxygen, nitrogen, carbon monoxide.

Puig and Sandier [58] reported work on solid sources of Kr^{85} at the Copenhagen Conference on the use of Radioisotopes in the Physical Sciences and Industry. They described a method of Kr fixation in a macromolecular matrix formed by mass polymerization of a liquid monomer containing Kr. They also gave an account of the preparation of two types of source produced in this way; one enclosed in polystyrene, the other in polyvinyl acetate. Such sources lose Kr, the activity of the first decreases by 8 percent daily, that of the second by 3 per cent daily. These apparent decays enabled the diffusion coefficients of Kr. in these polymers to be calculated. Diffusion appeared to be prevented by the cross-linkages which exist in the polymers.

Mock and others [59,60] described several convenient methods for preparing rare-gas clathrate compounds. Data showed that the clathrates were stable to a gamma dose of

$1\cdot14 \times 10^{8}$ rads. They also investigated methods of forming these unique compounds of quinol in aqueous and non-aqueous solutions, from the quinol melt, and directly from the vapour phase. Both xenon and krypton are considerably more soluble in most common solvents than argon. Since solubility plays such an important role in rare-gas clathrate formation, xenon and krypton would be expected to fill more clathrate vacancies than argon under identical operating conditions of pressure, quinol concentration and cooling rate. The calculated results, given in Table 2, verified this assumption.

TABLE 2

COMPARISON OF CLATHRATES

Solvent	Concn. g./c.c.	Weight %			% Cavities filled		
		A	Kr	Xe	A	Kr	Xe
		p= 200 p.s.i.g.					
Ethyl ether	0·18	7·0	18·1	—	65·2	89·5	—
Ethyl alcohol	0·50	7·4	15·1	—	68·8	74·8	—
Butyl acetate	0·18	6·8	17·5	—	63·5	86·5	—
Water	0·10	3·3	8·6	—	30·5	42·3	—
		p = 175		p.s.i.g.			
Ethyl ether	0·18	6·3	..	27·1	58·2	—	96·0
Ethyl alcohol	0·50	5·3	..	15·5	49·0	—	54·7
Butyl acetate	0·18	5·8	..	17·0	53·8	—	60·0
Water	0·10	3·0	..	11·9	27·7	—	42·0

van der Waals [61] remarked that it was not strictly possible to write the potential energy of the encaged molecule as a sum of two terms, depending on the potential and orientational coordinates, respectively. In fact, the rotational contribution to the free energy would depend on the vibrational state corresponding to the "rattling" of the molecule in its cage. The loss of orientational freedom of polyatmoc molecules in a clathrate is clearly borne out by their smaller entropy of clathration relative to that of monatomic gases.

Describing the potential binding, it was found—

$Vo = 0\cdot06$ kcal/mole for O_2

$Vo = 0\cdot44$ kcal/mole for N_2;

the former value was in good agreement with that following from the susceptibility measurements[42].

van Vleck [62] and Meyer [63] studied the magnetic properties and susceptibility, respectively, of the nitric oxide clathrate. Foner and others [64] described the low temperature paramagnetic resonance experiments of oxygen molecules trapped in single crystal of β—quinol clathrate. Rotariu and others [65,67] formulated a novel "chain reaction" concept for the determination of substances which can clathrate with hydroquinone. They stated that ferric chloride, dissolved in benzene, toluene, xylene, nitrile silicone, FC-43 fluorocarbon, and trifluorotoluene, reacts directly with suspended solid hydroquinone—sulphur dioxide clathrate, slowly at room temperature and more rapidly at elevated temperatures. Ferric nitrate under the same conditions reacts faster than the chloride with the clathrate.

Some of the important hydroquinone and hydroquinone-krypton clathrate properties are given in Table 3.

TABLE 3

PROPERTIES OF HYDROQUINONE [68] AND HYDROQUINONE-KRYPTON CLATHRATE [69]

Property		Hydroquinone	Hydroquinone-Kr clathrate
Melting point		172·3°C	approx. 172°C
Vapour pressure,	25°C		0·4 atm. (or, 302 mm. Hg. equil.)
	155°C	5·9 mm. Hg.	—
	173·7°C	18·2 mm. Hg.	—
Heat of melting		58·85 cal./g.	—
Energy of formation		—	—6·1 kcal.

The Mossbauer effect in Kr^{83} trapped in a clathrate compound has been studied by Hazoni and co-workers[70]. The striking points of investigation were: 1. the large value and small temperature dependence of the Mossbauer efficiency above 125°K, 2. the sharp break to a higher efficiency below the temperature and 3. the large line width at 102°K. The large value of f, came from the small size of the box, which was comparable with the gamma wavelength, so that the vibrational level separations were comparable with the recoil energy. The line width came from the dynamics or from a quadrupole interaction with the cavity, which was substantially non-spherical.

Hommel and others[71] describeda radioactive method for the detection of parts per million concentration of gaseous fluorine utilizing the interaction with $Kr.^{85}$—quinol clathrate. Coulter and co-workers[72] studied the nature of motion of nitrogen, carbon monoxide and methane in β—quinol clathrates.

USES

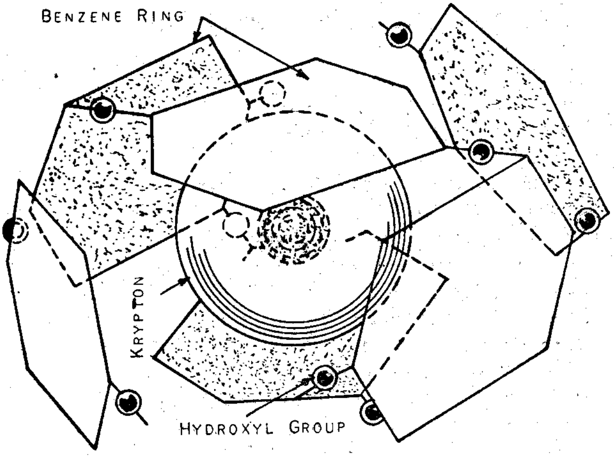
The rare-gas clathrates offer the nuclear scientist and engineer a new material possessing unique properties. Kr^{85} offers the advantage of useful 10·3 years half-life and an uncomplicated beta emission. Its chemical inertness is both an advantage and a disadvantage. Since it does not combine, it does not enter a metabolic system and is very safe from a biological standpoint. At the same time, since it does not combine, it is hard to handle. Heavy cylinders that are usually used to store and compress the gas also suppress the beta particles from it. Kr^{85} clathrate overcomes the difficulty and provides a safe and useful source of beta radiation [51,52].

The hydroquinone-inert gas clathrates present some more possibilities for the useful employment of clathrates. These compounds are granular materials whose gaseous constituents may be about 10 per cent of the total weight. Taking the solid volume into account, this concentration of gas would exert a pressure of 90 atmospheres in a similar free volume space. Since the rare-gas is immediately recoverable, either by heating or dissolution, the clathrates could be used as temporary but convenient storage media in certain flow processes; such as in the processing of spent fuel elements.

Some of the dangers inherent in the industrial use of radioactive isotopes may be sharply reduced by the method of utilizing Kr^{85}, the radioactive isotope produced by the fission of uranium in unclear reactors. The technique for trapping Kr atoms in the crystal lattice of hydroquinone has been very useful in this regard.

Kr^{85} is an ideal source of ionizing radiation for many industrial purposes. Heretofore, however, the usefulness of the isotope has been limited by the fact that Kr is a gas at ordinary temperatures. In order to use Kr^{85} as a reasonably compact source of beta rays, the gas must be compressed in thick-walled containers that absorb much of its radiation. Quinol-Kr^{85} clathrate forms a stable and almost leakproof container for the Kr trapped within the crystals. The clathrate crystals produce radiation more than 25 times as intense as that from an equal volume of Kr gas at atmospheric pressure. Chleck and Ziegler[51,52] suggested that these radioactive clathrates will lead to measure the thickness of light materials such as paper. For gauging heavier materials requiring more penetrating radiation, they suggested mixing the crystals with substances that emit X-rays when irradiated by Kr^{85}. An experimental air-pollution monitor based on this principle can detect concentrations of sulphur dioxide of ozone as low as a few parts per billion.

Robinson and Krause[73] have shown that the yield of xenon and krypton in the thermal neutron fission of U-235 can be as high as 24 atoms of xenon per 100 atoms fissioned, and 11 atoms of krypton per 100 atoms fissioned. As has been pointed out by Steinberg and Manowitz[74] and Adams and others[75], the danger of atmospheric pollution by the accumulation of fission product xenon and krypton is constantly increasing due to expanding reactor operations. The problem arises as to the best method for permanently retaining these radioisotopes so that they will not become a health or genetic hazard. To avoid the expense of high pressure storage equipment or low temperature facilities, it is feasible to use the clathrates as a means of permanently holding these gases. The clathrates also present a convenient form for handling, processing, and shipping rare-gas radioisotopes.



Swift[76] has shown that the use of Kr^{85} in industrial thickness gages substantially improves the signal-to noise ratio of these instruments. Use of the Kr^{85} clathrate could increase the specific activity by a factor of 70, thus permitting a reduction in size of the gaging source.

Xe^{133}, which emits gamma rays of 81 kev, has proved to be of value for specific applications where conventional X-ray machines are inconvenient or not applicable[77]. Use of clathrates could reduce considerably the size of the radiographic source.

Kr^{85} with its relatively long half-life of 10·3 years could prove to be a convenient and compact source of energy for a small atomic battery, when used in the clathrate form, and could be used as a phosphor exciter [59,60] Rotariu and coworkers [67], using the quinol clathrates, reported the tests that ferric ion can be determined to at least parts-per-million. The radioactive method for the detection of parts per million concentrations of gaseous fluorine utilizing the interaction with Kr^{85} quinol clathrate has been described by Hommel and others[71]. Because molecular fluorine is so reactive that its existence is relatively transient, except when properly stored determination is generally of interest only to manufacturers and uses of the gas, and then only in those processes in which its generation may occur as a side product. Neon can be separated from a mixture with argon, krypton and xenon, because it is the only one that does not give a clathrate with hydroquinone.

The use of these clathrates can provide a very good way of examining magnetic susceptibilities of free molecules below the temperature at which they will normally condense, to a liquid [35].

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