CLATHRATES

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Received June 10, 1959

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I. INTRODUCTION

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.

Since a given crystalline structure cannot be easily deformed, a particular cage retains only molecules or atoms that are within a definite range of size and shape. The lower limit of size of the guest component is determined by the openings in the cage walls through which escape can occur. There may be two series of clathrates which have a common host component, but which have different cage structures and contain physically different guest components. There are also clathrates whose unit cells contain cages of two different sizes. A single clathrate of this type may have two different guest components.

The two components of a clathrate do not react chemically with each other. Indeed, chemical reactivity precludes clathrate formation. Moreover, a chemical equation implying bonds and chemical stoichiometry is inapplicable here. Instead, a simple clathrate may be designated by a maximum-composition formula of $n\mathrm{C}\cdot m\mathrm{M}$, where C and M are host and guest components, respectively, n is the number of C molecules per unit cage cell, and m is the maximum number of M molecules that could be accommodated in a single cage. Occasionally, it is more convenient to use the formula $\frac{n}{m}\,\mathrm{C}\cdot\mathrm{M}$.

There are other classes of substances that have been referred to as clathrates. These include the urea adducts and the zeolite complexes, whose structures are in the form of channels which are open at both ends, and the graphite and silica complexes, in which the second component is sandwiched between layers of the host component. The term "clathrate" has also been used to designate the dextrin–iodine type of solution complexes. The present discussion deals only with three-dimensionally closed structures and does not include similar but open structures.

II. HISTORICAL

Powell (39) was the first to describe the clathrate structure from x-ray structural analyses. He and his associates are responsible for most of the basic work done hitherto on these unique substances. Their discovery of the clathrate structure is a landmark among the successes of the x-ray technique. In fact, there is no other method known by which unequivocal identification of clathrates can be made. The sulfur dioxide clathrate of hydroquinone was the first clathrate to be so resolved (33, 34, 39).

Since it is presently impossible in most instances to predict molecular crystalline structure *a priori*, the discovery of a clathrate has been and still is a matter of chance. Powell's efforts were directed to the resolution of certain relatively stable chemical complexes known as molecular compounds. A molecular compound is unusual, since its composition cannot be accounted for on the basis of chemical bonding. Hexamethylisocyanidoferrous chloride trihydrate and the sulfur dioxide and methanol complexes of β-hydroquinone are such compounds which were resolved as clathrates. Powell's initial success stimulated a lively interest in clathrates, as can be seen from the growing number of publications on various aspects of the subject. Other known molecular compounds have since been the subject of x-ray structural analyses which revealed the clathrate structure for some. These results have been the basis for synthesis of new clathrates. Furthermore, a fair amount of work has been devoted to the study of the physical properties of clathrates, both because of an interest in them per se and because of the growing number of practical and academic applications.

III. PREPARATION AND STRUCTURE OF CLATHRATES

A clathrate is generally prepared by recrystallization from solution. The composition of the clathrate depends on the availability of the guest component at the site of crystal growth. If the host is soluble in the guest component the preparation is simple, and maximum clathrate composition is realized. Otherwise, it is necessary to use a common solvent which cannot be clathrated by the host. In the preparation of a gas clathrate, the gas must often be kept at a high pressure. Furthermore, in crystallizing solutions where the concentration of the guest component is low, stirring and slow crystallization are necessary to avoid depletion of the guest component at the site of crystallization after initial clathrate formation.

A. β-Hydroquinone

The hydroquinone series of clathrates has been most extensively studied. Three crystalline forms of hydroquinone have been known for a long time (6, 7). The α-form is obtained by recrystallization from all common solvents except methanol. Recrystallization from methanol yields β-hydroquinone containing one mole of methanol for every three moles of hydroquinone. γ-Hydroquinone is formed by sublimation.

Powell and his associates (35, 39) showed that the methanol complex of hydroquinone belongs to a series of clathrates of β-hydroquinone with a maximum-composition formula of $3C_6H_4(OH)_2 \cdot M$. The hydroquinone molecules of β-hydroquinone crystals are arranged in the form of extremely large cage networks with 1.5 molecules per unit cage cell. Each network interpenetrates one other in such a manner as to form a smaller cage capable of enclosing molecules of the size of methanol, hydrogen sulfide, and sulfur dioxide. These cages are slightly flexible and are able to contain molecules of various shapes (36). Three molecules of hydroquinone are associated with each small cage, whence comes the maximum-composition formula $3\beta\text{-}C_6H_4(OH)_2 \cdot M$.

The following have been incorporated into the β-hydroquinone clathrate structure: sulfur dioxide, hydrogen sulfide, hydrogen cyanide, hydrogen chloride, acetylene, hydrogen bromide, formic acid, methanol, carbon monoxide (34, 39), argon (40), krypton (41), xenon (42), nitrogen (22), and oxygen (19). The rare gas clathrates are very striking because of their apparent stability under ordinary conditions. Other condensed systems involving such composition of rare gases are stable only at high external pressures of the gases.

B. α-Hydroquinone

The structure of α-hydroquinone is more compact than that of β-hydroquinone. However, evidence resulting from some preliminary x-ray data led Powell to suggest that α-hydroquinone may also possess a clathrate structure with six hydroquinone molecules per unit cage cell (maximum-composition formula, $6\alpha\text{-}C_6H_4(OH)_2 \cdot M$ (39)). This speculation was also based on the observation that crystals of the α-form were obtained on recrystallization from a benzene solution which was subjected to a very high pressure of carbon dioxide, while the β-modification was obtained at a lower pressure. The high-pressure product contained less carbon dioxide than the product obtained at a relatively lower pressure. To account for this pressure effect, Powell proposed that the hydroquinone crystals, growing in benzene (which cannot enter into the interior of the lattice), were subjected to an inward force resulting from the external gas pressure. At a sufficiently high pressure this inward force would be so great as to permit formation of only the more compact α-structure. Under these conditions, the amount of gas, carbon dioxide, included in the clathrate structure is limited by the corresponding maximum-composition formula.

C. Water

The series of clathrates in which water is the host are more commonly known as "gas hydrates." Gas hydrates of small molecules (such as chlorine, sulfur dioxide, methyl mercaptan, hydrogen sulfide, methyl bromide, methyl chloride, bromine, methane, ethene, and ethane) and of larger molecules (such as chloroform, methyl iodide, ethyl chloride, and isobutane) have been known for a long time. Some of these solids melt and decompose at temperatures above the melting point of ice (14). The mole fraction of the guest component at maximum composition varies from 0.15 for small molecules to 0.05 for larger molecules. Double hydrates, containing two guest components, have also been prepared (57, 58, 60).

The structures of these unique water complexes have been elucidated by von Stackelberg and his associates (30, 54, 57, 60, 61). Their conclusions, based on data from x-ray analysis, were corroborated by Claussen, who constructed physical models of gas hydrates (9, 10), and by Pauling and Marsh (37).

There are two cubic crystalline forms of gas hydrates. One form has a cubic cell constant of 12 A. and contains forty-six molecules of water per unit cell. In this cell there are eight completely bounded cavities. Two of these are small, and each can retain one guest molecule such as argon, hydrogen sulfide, and methane. Each of the other six is larger and can also contain such molecules as ethane, sulfur dioxide, and chlorine. The other crystalline form of gas hydrates is essentially similar. Its cubic cell constant is 17 A., the unit cell having one hundred thirty-six water molecules associated with it. There are sixteen small and eight large cavities in each cell. The double hydrates are of this second crystalline modification (57, 58, 60) as well as of the first (5), in which the small cavities are occupied by small molecules, and large cavities by large molecules. Thus, there are the following five maximum-composition formulas for this form:

$5.7H_2O \cdot M_1$, where M_1 is a molecule of the size of methane or hydrogen sulfide (12 A.)
$7.7H_2O \cdot M_2$, where M_2 is a molecule of the size of bromine, sulfur dioxide, or chlorine (12 A.)
$46H_2O \cdot 2M_1 \cdot 6M_2$, the double hydrate (12 A.)
$17H_2O \cdot M_3$, where M_3 is a molecule of the size of propane, methyl iodide, or ethyl chloride (17 A.)
$17H_2O \cdot 2M_1 \cdot M_3$, the double hydrate (17 A.)

D. Phenol

Clathrates of phenol and the following (as guest components) have been prepared: xenon, hydrogen chloride, hydrogen bromide, hydrogen iodide, hydrogen sulfide, hydrogen selenide, sulfur dioxide, carbon dioxide, carbonyl sulfide, carbon disulfide, methyl bromide, methylene chloride, fluoroethylene, 1,1-difluoroethane, and carbon disulfide + air (32, 57, 59, 64). The detailed structure of these clathrates appeared recently in a paper by von Stackelberg, Hoverath, and Scheringer (59).

Every phenol molecule in the clathrate is associated with a planar hexagon which is composed of hydrogen-bonded O—O linkages formed from the hydroxyl groups of six phenol molecules. The associated phenyl nuclei are located alternately above and below the hexagon. These six-membered groups are arranged in pairs whose hexagons are opposite and parallel to one another. Each pair constitutes a cage which can retain one molecule such as sulfur dioxide. The unit cell is a rhombohedron, each of whose corners is occupied by such an arrangement of twelve phenol molecules. The rhombohedron itself is an elongated cage which is three times the size of the other cages. To summarize: there are twelve phenol molecules, one large cavity, and one small cavity per unit cell in a phenol clathrate. The maximum-composition formulas are:

$12C_6H_5OH \cdot 5M_1$, where M_1 is a molecule of the size of hydrogen chloride or hydrogen bromide (four such molecules can be located in the large cavity)
$12C_6H_5OH \cdot 4M_2$, where M_2 is a molecule of the size of sulfur dioxide
$12C_6H_5OH \cdot 2M_3$, where M_3 is a molecule of the size of carbon disulfide (only two carbon disulfide molecules can be located in the large cavity and none in the small cavity)
$12C_6H_5OH \cdot 2M_3 \cdot M_1$, for the double clathrate

E. Monoamminenickel(II) cyanide

The maximum-composition formula for a series of monoamminenickel(II) cyanide clathrates is $[Ni(NH_3)]^{++}$, $2CN^- \cdot M$, where M may be benzene, thiophene, furan, pyrrole, aniline, or phenol (46, 49). In the presence of the guest component, the complex crystallizes in planar arrays of nickel cyanide and the ammonia molecules, bonded to nickel atoms, project above and below each plane. Each guest molecule is located in a cavity bound by two planes of nickel cyanide and by vertically aligned pairs of ammonia molecules.

Certain biphenyls (biphenyl, 4-aminobiphenyl, and 4-hydroxybiphenyl) cocrystallize with monoamminenickel(II) cyanide as solids with a characteristic composition formula of $2[Ni(NH_3)]^{++}$, $2CN^- \cdot M$ (28). The structure of these solids has not been determined. It may be similar to that of the mononuclear clathrates, each dinuclear molecule being apportioned between two adjacent cages.

F. Tetra(4-methylpyridine) nickel(II) dithiocyanate and analogous Werner complexes

A series of these Werner complexes have been claimed to function as hosts in clathrate systems similarly to monoamminenickel(II) cyanide (52, 65). They are a potential source for many different clathrates.

G. Hexamethylisocyanidoferrous chloride

This complex crystallizes as a trihydrate, the water being present as the guest component in a clathrate structure whose formula is $[Fe(CNCH_3)_6]^{++},2Cl^- \cdot 3H_2O$. Powell and Bartindale (39, 45) showed that the unit cell is formed by packing two hexagonal layers of iron ions, the $CNCH_3$ groups projecting octahedrally about each iron ion. This structure has four adjacent voids, three of the voids being similar. Two chloride ions are so located in the three similar voids that two dissimilar but closed cavities result. Two water molecules are held in one cavity and one in the other. No other clathrates of this complex have been reported.

H. Tri-o-thymotide

Tri-*o*-thymotide ($C_{33}H_{36}O_6$) is a twelve-membered-ring compound formed by the condensation of thymotic acid. It was isolated by Baker, Gilbert, and Ollis (3), who found it to be very versatile in the formation of crystalline complexes with a number of solvents. Some of these complexes may be clathrates of the type defined here (44). The maximum-composition formula for one possible clathrate series of tri-*o*-thymotide is $2C_{33}H_{36} \cdot M$, where M is benzene or chloroform.

I. Dianin's compound

Dianin's compound ($C_{18}H_{20}O_2$) is the product of the condensation of phenol and mesityl oxide. It was originally synthesized by Dianin (15), who found that it possesses the unique property of retaining fixed amounts of several solvents from which it was recrystallized. Baker and his associates (2, 4) extended the investigation of this property and found that even an inert gas such as argon is retained by Dianin's compound.

Some preliminary x-ray data obtained by Powell and Wetters (48) indicate that these solid complexes are clathrates. Each molecule of Dianin's compound possesses one hydroxyl group which constitutes part of a hexagonal series of six hydrogen-bonded O—O linkages. The six molecules so bounded together into one giant molecule are located alternately above and below the plane of the hexagon. Each of these groups of three small molecules is arranged in a cuplike structure which stands on the hexagon. The giant molecules are stacked linearly with their hydrogen-bonded hexagons parallel to and above each other. Two such neighbors are held together by strong van der Waals bonds or by entanglement at their extremities. Thus, a single cavity is completely bounded by two cuplike structures and has six molecules of Dianin's compound associated with it. The number of molecules that can be accommodated in the cavity is determined by their size. Methanol is apparently the smallest molecule that can be retained by Dianin's compound, each cavity holding three such molecules. Hence, there are three maximum-composition formulas for clathrates of Dianin's compound:

$6C_{18}H_{20}O_2 \cdot 3M_1$, where M_1 is a molecule of the size of methanol
$6C_{18}H_{20}O_2 \cdot 2M_2$, where M_2 is a molecule of the size of carbon tetrachloride (two molecules per cavity)
$6C_{18}H_{20}O_2 \cdot M_3$, where M_3 is a molecule of the size of ethylene dichloride (one molecule per cavity)

Molecular ratios of some fifty clathrates of Dianin's compounds support these three maximum-composition formulas (2).

J. α-Cyclodextrin

Cramer and Henglein (13) found that α-cyclodextrin retains significant quantities of gas when recrystallized in the presence of various gases (chlorine, krypton, xenon, oxygen, carbon dioxide, ethylene, methane, ethane, propane, and butane) at high pressure. The α-cyclodextrin–gas complexes may well be clathrates. It is possible that the α-cyclodextrin ring forms part of the structure that retains an inert gas, the gas atom or molecule being located within the molecular ring. An appropriately staggered arrangement of these rings could seal off the remaining route of escape of the inert gas.

K. p-Cresol novolac tetramer

Hunter and his associates (25, 26) found that the tetranuclear condensation polymer of *p*-cresol and formaldehyde retains ethylene dichloride in a 1:1 mole ratio when recrystallized from that solvent. By means of a molecular model, they showed that this complex is a clathrate.

IV. PROPERTIES OF CLATHRATES

A. Molecular properties

The host component of a clathrate is characterized by one or more permanent molecular dipoles and/or an awkward molecular shape. Molecules not possessing such characteristics are usually arranged, in the crystalline state, as closely packed aggregates in which the intermolecular distances are so small that the empty crystalline spaces cannot accommodate molecules larger than those of hydrogen. These molecular properties of the clathrate host cause intermolecular interactions and orientations in the crystalline state that lead to the formation of open molecular arrangements which are essential for a clathrate structure. The conditions for unpacked structures apply even to clathrates whose total assembly is closely packed (note the benzene clathrate of monoamminenickel (II) cyanide), since the structural stability of a clathrate is mainly dependent on the host component. The clathrate structure of Dianin's compound is an example of the effects of both a permanent dipole and an awkward molecular shape (48). Dianin's compound is a trinuclear molecule which possesses a hydroxyl group. The six molecules constituting two halves of adjacent cages are held together by hydrogen bonding of the hydroxyl groups, which are arranged in the form of a closed ring. The bulky trinuclear groups emanating from the hydroxyl groups project alternately above and below the ring and form two cuplike lattices for which the ring serves as a common base. In the cage structure, the intermolecular distances across the interior are large, whereas those along the periphery are relatively small. Such known molecular dispositions in the solid state are accounted for by molecular properties. However, the present state of knowledge does not permit the prediction of crystalline structure from molecular properties.

The molecular size and shape of the guest component are determined by the cage structure. There are certain weak interactions between a guest molecule and its surrounding cage. These interactions are similar to those found in physical adsorption and range from very weak van der Waals intermolecular attractions to highly oriented dipole contacts. The resultant forces of these interactions contribute in a positive fashion to the stability of a clathrate. However, clathrate formation is excluded for molecules whose interactions with the host are sufficiently great as to create new molecular species. Hydrogen sulfide interacts very weakly with water, and it therefore forms a clathrate with water because of its appropriate molecular size. However, hydrogen chloride will react chemically with water to form hydronium and chloride ions rather than remain undissociated in a water clathrate structure which accommodates molecules of that size.

B. Thermodynamics

Van der Waals (62) presented a very successful statistical mechanical interpretation of the thermodynamics of hydroquinone clathrates of nonpolar gases. The thermodynamic model is a system in equilibrium consisting of three phases: clathrate, nonclathrate modification of the host component (α-hydroquinone), and free nonpolar gas. The theoretical treatment of the problem requires that no more than one guest molecule be present in a cavity. Evans and Richards (22) showed calorimetrically that apart from the crystalline lattice forces, the only significant forces that are involved in hydroquinone clathrates 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.

From the above considerations, van der Waals obtained the following equation for the vapor pressure of a nonpolar gas clathrate of hydroquinone:

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

where P is the pressure of the nonpolar gas, $\phi(T)$ 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 nonclathrate crystalline modifications of hydroquinone according to the reaction:

$$\alpha\text{-}C_6H_4(OH)_2 = \beta\text{-}C_6H_4(OH)_2$$

Evans and Richards determined ΔH for this reaction both directly, using guest-free β-hydroquinone (21), and indirectly from the zero intercepts of heat of for-

TABLE 1

Heats of formation of various clathrates

Reaction	$-\Delta H$	References
	kcal.	
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{A} \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{A}$	5.9	(22)
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{O}_2 \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{O}_2$	5.5	(22)
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{N}_2 \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{N}_2$	5.8	(22)
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{HCl} \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{HCl}$	9.2	(22)
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{HBr} \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{HBr}$	10.2	(22)
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{CH}_3\text{OH} \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{CH}_3\text{OH}$	11.0	(22)
$3\beta\text{-C}_6\text{H}_4(\text{OH})_2 + \text{CH}_2\text{O}_2 \rightarrow 3\beta\text{-C}_6\text{H}_4(\text{OH})_2 \cdot \text{CH}_2\text{O}_2$	12.2	(22)
$n\text{H}_2\text{O (ice)} + \text{M} \rightarrow n\text{H}_2\text{O} \cdot \text{M}^*$	5–8	(5, 55)
$[\text{Ni}(\text{NH}_3)^{++}, 2\text{CN}^-] + \text{C}_6\text{H}_6 \rightarrow [\text{Ni}(\text{NH}_3)^{++}, 2\text{CN}^-] \cdot \text{C}_6\text{H}_6$	10	(1)
$n\text{C}_6\text{H}_5\text{OH} + \text{M} \rightarrow n\text{C}_6\text{H}_5\text{OH} \cdot \text{M}^\dagger$	8	(32)

* n = 6, 8, and 17.

† n = 2.5–3; M = carbon dioxide, xenon, hydrogen chloride, hydrogen sulfide, hydrogen bromide, and sulfur dioxide.

mation vs. clathrate composition lines (22). Experimental values for P and y of the hydroquinone–argon clathrate at 25°C. were subsequently obtained by van der Waals and Platteeuw (63) and agreed with those calculated theoretically. Platteeuw (38) also confirmed the P–y relationship at 60°C.

The thermodynamics of more complex clathrates are more difficult to handle unless simplifying assumptions are made. Barrer and Stuart (5) applied for the gas hydrates the same theoretical procedure as did van der Waals. One significant simplifying assumption made here is that the heat of the reaction,

$$\text{Empty clathrate crystal} = \text{ice}$$

is approximately zero (55). Their results support those obtained by von Stackelberg (55, 56, 60), whose calculations are based on the use of physical adsorption model, this simplifying assumption, and on judicious application of Trouton's rule. Barrer and Stuart's treatment of the thermodynamics of gas hydrates is generally quite complete and appears to explain satisfactorily many of the pressure–temperature–composition relationships observed experimentally for gas hydrates.

Table 1 summarizes the heats of formation of various clathrates according to the reaction:

$$n\text{C(s)} + \text{M(g)} \rightarrow n\text{C} \cdot \text{M}$$

These heats are quite low, the higher values reflecting strong interactions of the guest molecule with its enclosing cage.

C. Interaction of the guest molecule with its cage

A molecule enclosed in a cage has lost not only its translational energy but also some of its free rotational and vibrational energies because of interaction with the cage. Evans and Richards (22) showed that the ΔH's for hydroquinone clathrates are the energies of interaction of the guest molecules with their surrounding cages. They concluded that, where nonpolar molecules are involved, these energies depend mainly on the polarizability of the enclosed molecules. It is obvious then that unsymmetrical nonpolar and polar molecules assume some definite orientations in their enclosing cages. Indeed, Palin and Powell (36) have illustrated the actual dispositions of some polar molecules in hydroquinone clathrates.

Dryden and Meakins (16, 17) investigated the high-frequency dielectric characteristics of several hydroquinone clathrates of polar molecules. Enhancements in relative permittivity, due to the enclosed polar molecules, were found to be related to the dipole moments of these molecules. However, activation energies, relaxation times, amd measurements made perpendicular and parallel to the *c*-axis of single crystals showed orientation effects for methyl cyanide but not for methanol in their respective clathrates. It is possible that the experimental sensitivity was not sufficient to permit detection of the weaker orientation of the methanol molecules in the hydroquinone cages. Meyer and associates (12, 29) extended previous low-temperature measurements of the magnetic susceptibility of oxygen in the hydroquinone clathrate (11, 19) to still lower temperatures (0.25°K.). They showed that the observed measurements are consistent with the assumption that at very low temperatures the rotation of an oxygen molecule is hindered by its enclosing cage. Similarly, part of the infrared spectrum of the hydroquinone–carbon dioxide clathrate was interpreted in terms of restricted rotation of a carbon dioxide molecule (24).

Variations in these energies of interaction may be the basis for a method for the separation of mixtures of physically similar molecules. Benzene of very high purity has been separated from thiophene by successive clathration with monoamminenickel(II) cyanide (18). The complex forms clathrates of benzene and of thiophene, but benzene is probably more strongly bound in the cage structure and, therefore, it is clathrated preferentially.

D. Thermal decomposition

The thermal decomposition of a clathrate into its free host and guest constituents, at temperatures below its melting point, may involve one or more of the following processes: (*a*) sublimation of the host, (*b*) change of the clathrate structure to the nonclathrate form of the host, (*c*) diffusion of guest molecules through the lattice structure of the clathrate, and (*d*) desorption of the guest component from the surface of the solid clathrate. All of these processes, except (*b*), are characterized by kinetic expressions that include the geometry of the clathrate particles that are being decomposed. The activation energies of processes (*a*) and (*b*) are determined by the crystalline lattice energies of the clathrate, (*c*) by the lattice energy and guest molecule–cage interaction energy, and (*d*) by the forces of attraction of the guest molecule to the surface of the solid clathrate. It is obvious that a kinetic interpretation of decomposition data can be extremely difficult when more than one of these processes is occurring.

Aynsely, Campbell, and Dodd (1) investigated the thermal decomposition of the benzene clathrate of monoamminenickel(II) cyanide and suggested that the rate-determining step is escape of benzene from the surface, and that diffusion within the lattice is comparatively easy.

It is reasonable to assume that a measure of stability can be imposed on a clathrate by decreasing its surface-to-volume ratio. Moreover, extensive lattice changes may be involved in the decomposition of certain clathrates. Such changes require high activation energies, thereby accounting for the apparent stability of clathrates, such as the hydroquinone–rare gas clathrates, under conditions in which they are thermodynamically unstable.

V. USES OF CLATHRATES

The discovery of clathrates as a distinct class of materials opened up a wide area for research which embraces further synthesis of these unique substances, studies of their properties, and consequent practical and academic applications. Presently, the usefulness of clathrates is considerably restricted because of the small number of materials that are available to serve as host components. However, several useful potentialities of clathrates can be presented as consequences of their known properties. In fact, a number of interesting applications have already been realized.

The hydroquinone–inert gas clathrates present some possibilities for the useful employment of clathrates. These clathrates 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 atm. in a similar free-volume space. The gas can be released by heating or dissolving the clathrate. Thus, clathrates may be used for convenient storage of inert gases or to introduce such gases into fairly inaccessible locations. A predetermined amount of clathrate may be sealed into a container, which, on application of heat, is filled with a desired amount of gas.

It was mentioned earlier that the separation of mixtures of substances can be achieved by the appropriate use of a clathrate host component. First of all, molecules that are dissimilar may be easily separated because a clathrate cage will contain only such molecules as are within a certain range of sizes and shapes. Also, the ease with which a molecule is accommodated in a given cage varies with different molecular species, thus widening the separation potentiality of a clathrate host. Even before the establishment of the clathrate structure there appeared a patent on the fractionation of hydrocarbons by means of gas-hydrate formation (23, 27). Very recently, a series of processes was outlined for the separation of hydrocarbons using metal–nitrogen based Werner complexes as clathrate host reagents (8, 50, 51, 53). Benzene was essentially freed of thiophene impurity because of its greater affinity for clathrate formation with monoamminenickel(II) cyanide (18). A very noteworthy separation has been achieved in the optical resolution of *sec*-butyl bromide, using tri-*o*-thymotide (31, 43). This came as a result of the discovery of enantiomorphism in the cage structures of tri-*o*-thymotide.

A clathrate of a molecular gas affords a convenient opportunity for studying the free molecular properties of the gas in the absence of superimposed effects of intermolecular interactions. The magnetic susceptibilities of molecular oxygen and of nitric oxide, in hydroquinone clathrates, were determined at temperatures close to absolute zero (11, 12, 19, 29). At such low temperatures, oxygen and nitric oxide are solids which exhibit strong coupling effects. As clathrates, however, the molecules of these gases are effectively separated by the enclosing cage structure.

It is obvious that clathrates are in their infancy and that their potentialities have hardly been realized. The number of new clathrates that emerge with the discovery of a single clathrate structure is large. No stretch of the imagination is necessary to think of the possibilities that are offered from the assumption that only a small fraction of the known chemical compounds are capable of forming the clathrate host structure. Indeed, with further understanding of the factors that determine molecular arrangement in crystalline structures it would ultimately be possible to synthesize such structures possessing predesigned characteristics.

VI. SUMMARY

A clathrate is a solid consisting generally of two molecular components which are chemically inert toward each other. One of the components may be a solid, liquid, or gas, the molecules of which are retained ("clathrated") within closed cages provided by the crystalline structure of the other component. In this manner, significant quantities of volatile or reactive substances can be easily handled as solids. The clathrated component is released by simple means such as heating, dissolving, or even grinding the clathrate.

This review summarizes the literature pertaining to the synthesis, classification, structure, properties, and applications of clathrates. The problems encountered in the determination of the thermodynamics of clathrate systems and in the analysis of thermal decomposition data are discussed.

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