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# QUARTERLY REVIEWS

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## MOLECULAR INTERACTIONS IN CLATHRATES: A COMPARISON WITH OTHER CONDENSED PHASES

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### Introduction

**General Characteristics of Clathrates.**—As implied by their name, the principal novelty of clathrates lies in their geometrical structure. The *X*-ray studies of Powell and his co-workers<sup>1</sup> provided the details for a number of typical examples in which “guest” molecules (A) are entrapped within cavities, often pseudo-spherical in form, which appear in the “host” lattice (B). Two aspects are immediately noteworthy: first, the lattice structure of B in the clathrate is not its normal crystalline state, and the form with unoccupied cavities is usually less stable; secondly, the composition of the clathrate,  $A_nB$ , can vary over a range, often large, in which the clathrate is stable with respect to decomposition into guest and normal host. Accordingly, the clathrates are not stoicheiometric compounds: minimum values of  $n$  and the restrictions on the possible A components are dictated largely by geometric considerations. The best known examples have  $B = H_2O$  (ice), forming the so-called gas hydrates of *approximate* compositions  $n = 6$  when  $A = Cl_2, SO_2, CH_4, Ar, Kr, Xe$ , etc., or  $n = 17$  when  $A = CH_3I, C_3H_8$ , etc.; and  $B = p\text{-HO}\cdot C_6H_4\cdot OH$  (quinol),  $A = CO, N_2, H_2S, CH_3OH, Ar, Kr, Xe$ , etc. with  $n = 3.0$  ideally (*i.e.*, all cavities filled), but usually  $n \sim 3.5$  to 8 or more, depending on the conditions under which the clathrate is formed.

Powell's and von Stackelberg's researches have brought out very clearly the structural features of these cage-like complexes, while J. H. van der Waals has evaluated the thermodynamic aspects leading to their formation. In many respects they provide an interesting model of solution equilibria in that the “solute” molecules (A) are placed in cavities within the “solvent” (B). As van der Waals and other assessors have concluded, the energy of interaction (A)–(B) is normally small in the clathrates, and the entropy term is similar in magnitude to the entropy of vaporisation of a solute from a solution in which the solvent obeys Raoult's law. Further, the A component may be said to obey Henry's law in the sense that (A)–(A) interactions are negligible compared with (A)–(B) interactions. Because the

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<sup>1</sup> (a) D. E. Palin and H. M. Powell, *J.*, 1947, 208; (b) H. M. Powell, *ibid.*, 1948, 61; (c) D. E. Palin and H. M. Powell, *ibid.*, 1948, 571; (d) D. E. Palin and H. M. Powell, *ibid.*, 1948, 815; (e) J. H. Rayner and H. M. Powell, *ibid.*, 1952, 319; (f) S. C. Wallwork and H. M. Powell, *ibid.*, 1956, 4855; (g) D. Lawton and H. M. Powell, *ibid.*, 1958, 471.

environment of the guest molecule can be described fairly precisely, calculation of the interaction energy is more straightforward than it is for liquid solutions, and the cell model, sometimes employed in theoretical treatments of the liquid phase, can be applied realistically to clathrates.

Not surprisingly, therefore, both theoretical and practical interest in clathrates appears to be increasing. Diverse uses for clathrates have become apparent and more will certainly be developed: the purification of sea water,<sup>2</sup> the separation of aromatic mixtures,<sup>3</sup> and the introduction of clathrates as carriers<sup>4</sup> for radioactive <sup>85</sup>Kr and for free radicals<sup>5</sup> are a few examples.

The major purpose of this Review is to summarise the information revealed by thermodynamic data on the interaction energies of guest molecules with their encaging structures and that on the motion of the guest molecules provided by dielectric and infrared studies. Most of the discussion will relate to the quinol clathrates and the gas hydrates, because it is for these that the largest body of physicochemical data has accumulated. While a number of clear descriptive surveys of clathrates is available,<sup>6-10</sup> a brief reminder of the relevant structural aspects is first presented.

**Structures of Host Lattices.**—As a first approximation, the cavities in which the guest molecules are held can be regarded as spherically symmetric. Refinements to this approximation, which are required by a number of experimental results, will be discussed later. The structures of the cavities in the quinol clathrates and the gas hydrates revealed by X-ray diffraction studies are the chief basis for the assumption of spherical symmetry. In quinol clathrates the principal forces which hold the lattice together are hydrogen bonds between hydroxyl groups. Groups of six oxygen atoms are linked together to form hexagonal rings, which are parallel to one another and constitute the “top” and “bottom” of each cage (see Fig. 1).<sup>10</sup> The sides of the cage consist of portions of six benzene rings which are inclined at angles of 45° with respect to the plane of the hydroxyl hexagons. Since each hexagon participates in two cages, and since six quinol molecules are linked together in each hexagon, there are, on the average, three molecules of quinol per cage. The “free diameter” of the cage, or the distance from the boundary of an atom on the wall to the

<sup>2</sup> A. J. Barduhn, H. E. Towlson, and Yee-Chien Hu, U.S. Dept., Office Tech. Ser., P.B. Rept. 171,031 (1960); *Chem. Abs.*, 1962, **57**, 4477f.

<sup>3</sup> P. de Radzitsky and J. Hanotier, *Ind. Eng. Chem., Process Design Develop.*, 1962, **1**, 10.

<sup>4</sup> G. J. Rotariu, E. L. Hoskins, and D. M. Hatori, *U.S. Atomic Energy Comm.*, TI D-17223.

<sup>5</sup> P. Goldberg, *J. Chem. Phys.*, 1964, **40**, 427.

<sup>6</sup> Martinette Hagan, *J. Chem. Educ.*, 1963, **40**, 643.

<sup>7</sup> Martinette Hagan, “Clathrate Inclusion Compounds”, Reinhold, New York, 1962.

<sup>8</sup> R. M. Barrer in “Non-Stoichiometric Compounds”, ed. L. Mandelcorn, Academic Press, Inc., New York, 1964, chap. 6.

<sup>9</sup> L. Mandelcorn, *Chem. Rev.*, 1959, **59**, 827.

<sup>10</sup> H. M. Powell in “Non-Stoichiometric Compounds”, ed. L. Mandelcorn, Academic Press, Inc., New York, 1964, ch. 7.

boundary of an atom directly opposite, is approximately 4.2 Å when van der Waals radii are used. The geometry of the cage reveals that the force field within it is not precisely spherical. In fact, guest molecules such as sulphur dioxide and carbon dioxide have preferred orientations with their long dimension parallel to a line joining the centres of the hexagons.<sup>14</sup>

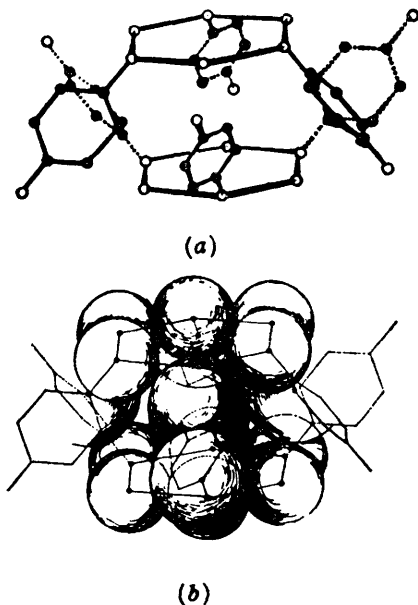


FIG. 1. (a) The positions of the six quinol molecules that form the immediate surroundings of an argon atom are shown in a perspective drawing. This is deceptive because the centres of the atoms are shown, and the space occupied by the atoms cannot be shown at the same time. (b) The spaces occupied by the atoms are indicated in a drawing on the same scale as that above. A few only of the atoms surrounding the central argon atom are shown. They are distinguished from those which have been omitted by small circles drawn around their centres. Broken lines are used to indicate that a part of the structure so represented lies behind some portion drawn with full lines. (Reproduced, with permission, from H. M. Powell, "Non-Stoichiometric Compounds," ed. L. Mandelcorn, Academic Press, Inc., New York, 1964, ch. 7.)

A closer approximation to spherical symmetry is found in the crystal structures of the gas hydrates.<sup>8,11,12</sup> Two common, cubic crystal structures, termed Structure I and Structure II, have been found for this class of clathrate. Recently several more novel structures have been discovered.<sup>13</sup> The unit cell of Structure I has forty-six water molecules, two small cavities, and six larger cavities. The small cavities are bounded by twenty water molecules, the oxygen atoms of which are nearly equidistant from the centre, so that the cavity has a free diameter of about 5.1 Å. Twenty-four

<sup>11</sup> M. von Stackelberg and H. R. Müller, *Z. Electrochem.*, 1954, **58**, 25.

<sup>12</sup> J. H. van der Waals and J. C. Platteeuw, *Adv. Chem. Phys.*, 1959, **2**, 1.

<sup>13</sup> P. T. Beurskens and G. A. Jeffrey, *J. Chem. Phys.*, 1964, **40**, 906, and earlier papers.

water molecules surround the larger cavities, which have an average free diameter of 5.8 Å with a variation of  $\pm 0.3$  Å. From the ratio of water molecules to cavities it can be seen that if each cavity contains one guest molecule, the composition of the hydrate is 5.75 molecules of water per molecule of guest.

Structure II hydrates contain cavities which are more disparate in size, and so these hydrates usually form when the guest molecules are too large to fit into the cavities of Structure I. The unit cell of 136 water molecules contains sixteen small and eight large cavities. Co-ordination numbers and free diameters are 20 and 28, and 5.0 Å and 6.7 Å, respectively. Distances from centre to wall are nearly constant for the two kinds of cavity. If only the large cavities are singly occupied by guest molecules, the composition of the hydrate is seventeen water molecules per guest molecule, e.g.,  $C_3H_8 \cdot 17H_2O$ .

### Thermodynamic Analysis of Clathrate Stability

**Phase Relationships.**—When compared with the vapour pressures of the pure guest liquids, the dissociation pressures of clathrates are surprisingly small. For example, at the boiling point of argon,  $-186^\circ C$ , the equilibrium dissociation pressure of the argon-quinol clathrate is  $2 \times 10^{-8}$  atm. The hydrogen sulphide hydrate has a dissociation pressure of 0.9 atm. at  $0^\circ$ , compared with a vapour pressure of 10 atm. for liquid hydrogen sulphide at this temperature. Thus it is apparent that the difficulty of escape of the guest molecule from the cage, that is, a high activation energy for decomposition, is not the only factor relating to clathrate stability. The thermodynamic driving force for the formation of many of these clathrates is relatively large.

Yet, it is also evident that these complexes have neither fixed compositions nor chemical bonds between host and guest. They are best regarded as solid solutions of the guest molecule in the host lattice, which, when empty, has a chemical potential slightly larger than that of the stable form of the host lattice ( $\alpha$ -form).<sup>12,14</sup> If one were to start with the empty metastable lattice of quinol ( $\beta$ -form) and slowly increase the pressure of a suitable foreign gas in contact with it, the cages would gradually become occupied, with a consequent stabilisation of the host lattice and lowering of its chemical potential. At a certain pressure, called the dissociation pressure, the degree of cavity occupation is such that the chemical potential of the clathrate host becomes equal to that of the  $\alpha$ -form. Under this condition the three phases, clathrate,  $\alpha$ -form, and gas can be in equilibrium. As the pressure is raised above the minimum value needed to make the clathrate stable, an increasing fraction of the cages is filled, and the chemical potential of the host in the clathrate falls below that of the  $\alpha$ -form. This is the region of stable solid solutions of varying composition.

These considerations can be illustrated by reference to data for the

<sup>14</sup> L. A. K. Staveley, *Adv. in Chem.*, 1963, No. 39, 218.

argon-quinol clathrate at 25°. The molar free energy of  $\beta$ -quinol is 82 cal./mole greater than that of  $\alpha$ -quinol. When a fraction equal to 0.34 of the cavities is filled, which occurs at an argon pressure of 3.4 atm., the chemical potential of the  $\beta$ -quinol has been reduced by 82 cal./mole and the chemical potentials of the  $\alpha$ - and  $\beta$ -forms are equal. At higher pressures larger fractions of the cavities are filled, the relationship between the two quantities being given by an equation identical in form to the Langmuir adsorption isotherm. The latter fact suggests that there is no interaction between the guest molecules in neighbouring cages, *i.e.*, that the "solution" is ideal. This conclusion is confirmed by the observation that the equilibrium clathrates of both argon-quinol and krypton-quinol have 34% of the cages filled at 25°. Thus, this fraction appears to be independent of the identity of the guest, as long as the lattice is not distorted by the guest molecules, and the solvent ( $\beta$ -quinol) then obeys Raoult's law.

A portion of the phase diagram at constant temperature (25°) of the argon-quinol system is given in Fig. 2. The solid curve represents equilibrium pressures of stable clathrate systems, while the broken curve corresponds to metastable clathrates. Point I is the invariant point (triple point), clathrate- $\alpha$ -quinol-argon gas.

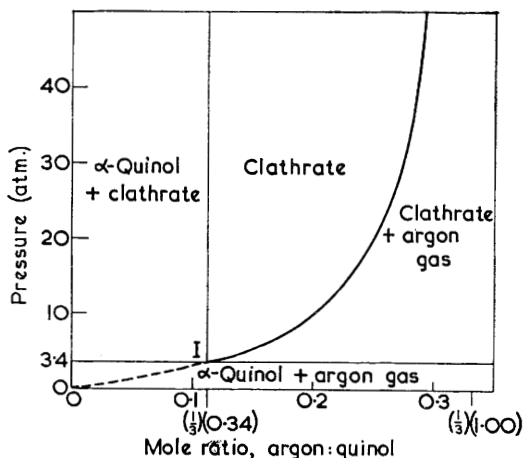


FIG. 2. Phase diagram for argon-quinol at 25°.

**Enthalpies and Entropies of Dissociation.**—Theoretical calculations of dissociation pressures and interaction energies of quinol clathrates and/or gas hydrates have been made by several authors.<sup>12,15-17</sup> The cell model has been employed in all treatments. It is assumed that the potential energy of interaction between a guest molecule and an atom in the wall of its cage is given by an equation such as the Lennard-Jones 6-12 potential function.

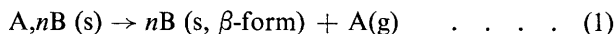
<sup>15</sup> R. M. Barrer and W. I. Stuart, *Proc. Roy. Soc.*, 1957, *A*, **243**, 172.

<sup>16</sup> R. M. Barrer and D. J. Ruzicka, *Trans. Faraday Soc.*, 1962, **58**, 2253.

<sup>17</sup> V. McKoy and O. Sinanoğlu, *J. Chem. Phys.*, 1963, **38**, 2946.

After summation over all atoms in the wall of the cage, the potential curve for the interaction between the guest molecule and its cage is found to have a broad minimum and steep sides. Therefore, it would not be far wrong to visualise the guest molecule as moving about in its cage in somewhat the same manner as a molecule in the gas phase moves in its container, with the very important difference that the volume of the cage is approximately 1/600th of the volume of a gas at S.T.P. divided by the number of molecules in the gas. Rather than speak of the translational motion of the guest molecule in the cage, the more realistic term, "rattling motion", is used. The theoretical treatments have also employed the assumption that the internal degrees of freedom of the guest molecule are the same as for the molecule in the gas phase. With the use of one or no adjustable parameters, depending on the particular treatment, the agreement between calculated and observed energies of interaction and dissociation pressures is fairly good for a considerable number of systems. Hence the assumption of spherically symmetric cavities is adequate to allow the prediction of some of the thermodynamic properties of clathrates with non-polar or slightly polar guest molecules.

By use of some of the theoretical results in a qualitative or semi-qualitative fashion, it is possible to ascertain whether clathrate stability is related primarily to enthalpy or to entropy factors. Before proceeding further, we must be precise about the dissociation process whose equilibrium position determines the stability. From the theoretical point of view it is convenient to discuss dissociation of the clathrate into the metastable host lattice and gaseous guest according to the equation,



Here A and B stand for guest and host, respectively, and  $n$  has the value corresponding to the invariant point on the phase diagram, for example, point I in Fig. 2. If this change occurs in a system showing no specific interaction energy beyond dispersion and repulsion terms for (A)-(B), then the appropriate concentration and statistical factors lead to an entropy change,  $\Delta S^\circ_\beta$ , given by the equation<sup>18</sup>

$$\Delta S^\circ_\beta = R \ln \frac{V}{V_f} - RT \left( \frac{\partial \ln V_f}{\partial T} \right)_V + R - S_c \quad \dots \quad (2)$$

where  $V$  is the molar volume of the gaseous guest in the standard state,  $V_f$  is the "free" volume per mole in the clathrate and is a measure of the empty space in the cavities, and  $S_c$  is the configurational entropy of the clathrate. The first term on the right-hand side of equation (2) is simply the increase in entropy which occurs on expanding a gas from volume  $V_f$  to volume  $V$ . The second term is related to the departure of the potential function for the interaction between guest and cage from the square-well potential function. There is a contribution of  $R$  to the  $\Delta S$  because the gas-

<sup>18</sup> W. C. Child, jun., *J. Phys. Chem.*, 1964, **68**, 1834.

eous guest has communal entropy, while the guest molecules in the clathrate do not. Finally,  $S_c$ , the configurational entropy, appears because some of the cavities are vacant, and there are a number of ways in which  $N$  guest molecules can be arranged in a larger number of cavities. Equation (2), it is important to emphasise, is valid provided that the internal degrees of freedom of the guest molecule are the same as in the gas phase and there is no distortion of the host lattice by the guest.

The change in internal energy,  $\Delta U^\circ_\beta$ , accompanying the process specified by equation (1) also has a simple interpretation: it is equal to the average potential energy of interaction between guest and host, to a fair approximation (<15% error).

Before we consider experimental values of  $\Delta S^\circ_\beta$  and  $\Delta H^\circ_\beta$  and their significance, it may be informative to examine the way in which these two thermodynamic quantities depend on cavity size. Three cases will be considered: (1) cavity diameter much larger than the diameter of the guest molecule, (2) cavity slightly larger than guest, and (3) cavity slightly smaller than the size of the guest, as measured by van der Waals radii. The qualitative features of the potential functions for these three situations are given in Fig. 3.

(1) When the cage is considerably larger than the guest molecule, for example, 20 Å *versus* 4Å for the respective diameters, then the internal energy of the gaseous guest is not very different from that of the guest in the clathrate, because the guest molecule spends a large proportion of the time near the centre of the cavity, where the potential energy of the system is zero relative to the separated guest and host. Therefore,  $\Delta U^\circ_\beta \cong 0$ , and  $\Delta H^\circ_\beta \cong RT \cong 600$  cal./mole at 298°K.  $\Delta S^\circ_\beta + S_c$  can readily be calculated from equation (2), with the assumption that the second term on the right is zero. To obtain  $V_f$  for the calculation, the approximate relationship<sup>12</sup>

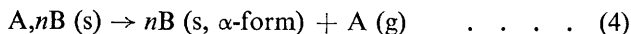
$$V_f = \frac{4}{3} \pi (a - \sigma)^3 N \dots \dots \dots (3)$$

can be used. In this equation,  $a$  is the average distance between the centre of the cage and the nuclei of the atoms in the wall of the cage,  $\sigma$  is the distance of closest approach between a guest molecule and an atom in the wall (*i.e.*, zero-energy collision diameter), and  $N$  is Avogadro's number. Equation (3) is valid in the square-well approximation. Using 10 Å and 3 Å for  $a$  and  $\sigma$  respectively, we find  $V_f$  to be 860 cm.<sup>3</sup>/mole, thirty times smaller than the molar volume of the gaseous guest. Substitution of this value into equation (2) yields, when the second term is neglected,  $\Delta S^\circ_\beta + S_c = 8.6$  e.u. at 298°K. Combining this quantity with the  $\Delta H^\circ_\beta$  estimated earlier, we obtain

$$\begin{aligned} \Delta G^\circ_\beta - TS_c &= \Delta H^\circ_\beta - T(\Delta S^\circ_\beta + S_c) \\ &= 600 - (298)(8.6) \\ &= -2000 \text{ cal. at } 298^\circ\text{K} \end{aligned}$$

It will be seen later that  $\Delta G_{\beta}^{\circ} - TS_c$  for the argon-quinol clathrate, for which  $a = 4 \text{ \AA}$ , is equal to  $-1200 \text{ cal.}$  at  $298^{\circ}\text{K}$ . Thus, there is only a slightly greater tendency for a clathrate having the relatively large cavities assumed in this example to decompose into the *metastable* host lattice plus guest than there is for the argon-quinol clathrate to undergo a similar decomposition, provided that in each clathrate the cavities are completely occupied so that  $S_c = 0$ .

Now, the stability usually observed in the laboratory is related not to  $\Delta G_{\beta}^{\circ}$  but rather to  $\Delta G_{\alpha}^{\circ}$ , which corresponds to the process,



Comparison of equations (1) and (4) shows that  $\Delta G_{\beta}^{\circ} - \Delta G_{\alpha}^{\circ} = n (G_{\beta} - G_{\alpha})$ , where  $G_{\beta} - G_{\alpha}$  is the difference between the molar free energies of metastable and stable host. Therefore, clathrate stability depends, in addition to the factors already mentioned, upon the value of  $G_{\beta} - G_{\alpha}$ . This quantity is only  $82 \text{ cal./mole}$  for the  $\alpha$ -quinol- $\beta$ -quinol system, as discussed earlier. It could be expected to be much larger, however, for a lattice with larger cavities, because the sum of the van der Waals attractions in such a lattice would be much less than in a more compact form. If the fraction of the cavities occupied in this host were small when the clathrate was in equilibrium with stable host and gaseous guest, additional stability would arise from the configurational entropy. This is unlikely, however, because a small fraction occupied implies a small value of  $G_{\beta} - G_{\alpha}$ , contrary to the statement just made. Therefore, the relative instability of the host lattice probably accounts for the fact that such clathrates are not commonly found, unless there is more than one guest molecule per cavity. It should be noted also that clathrates with large cavities generally have fairly large escape holes.<sup>8</sup> An additional characteristic, therefore, is a small activation energy for decomposition. It is undoubtedly this reason in addition to low thermodynamic stability which accounts for the non-existence of clathrates with the very small guest molecules  $\text{H}_2$ , He,  $\text{H}_2\text{O}$ , HF, and Ne. (The last molecule, however, is found in some double gas hydrates.<sup>19</sup>)

(2) When the "free diameter" of the cavity is, say,  $1 \text{ \AA}$  greater than the van der Waals diameter of the guest molecule, the average interaction energy can be appreciable, as shown qualitatively by curve (b) of Fig. 3. Since the free volume is of the order of  $1 \text{ cm.}^3/\text{mole}$ ,  $\Delta S_{\beta}^{\circ} + S_c$  is much larger than it is for (hypothetical) clathrates with relatively large cages. That is, the partial molar entropy of the guest in this second type of clathrate is relatively small, reflecting the reduced freedom of motion of the guest molecule within the cage. Again using as an example the argon-quinol clathrate, we have the experimental values  $\Delta H_{\beta}^{\circ} = 6.0 \text{ kcal./mole}$  and  $\Delta S_{\beta}^{\circ} + S_c = 24.0 \text{ e.u.}$ , which when combined as before give  $\Delta G_{\beta}^{\circ} - TS_c = -1150 \text{ cal.}$  at  $298^{\circ}\text{K}$ . This quantity is related to  $\Delta G_{\alpha}^{\circ}$  as follows:

<sup>19</sup> R. M. Barrer and D. J. Ruzicka, *Trans. Faraday Soc.*, 1962, **58**, 2239.



$$\begin{array}{r}
 \Delta G^\circ_\beta - TS_c = -1150 \text{ cal.} \\
 + TS_c = 1130 \\
 \hline
 -n(G_\beta - G_\alpha) = -720 \\
 \hline
 \Delta G^\circ_\alpha = -740 \text{ cal at } 298^\circ\text{K}
 \end{array}$$

$\Delta G^\circ_\alpha$  is actually less negative than  $\Delta G^\circ_\beta - TS_c$ , showing the important contribution of configurational entropy to clathrate stability in this example. In general, clathrates of this type are among the most stable found. Typical values of  $\Delta H^\circ_\beta$  and  $\Delta S^\circ_\beta + S_c$  will be compared with heats and entropies of vaporisation of the pure liquid guest substances in a later section.

(3) Coming now to those clathrates in which the guest molecule is so large that it can barely be squeezed into the cavity, we find that the trend in stability is easily predicted. In the first place, the average interaction energy is small compared with that of clathrates in the second group, because repulsive forces are more significant (see curve (c) of Fig. 3).

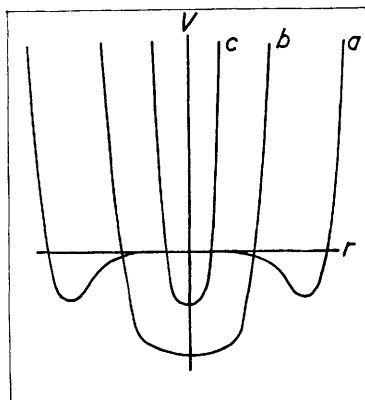


FIG. 3. Potential functions for three cage sizes, showing only the qualitative features.  $V$  = potential energy;  $r$  = distance from the centre of the cage. Curve (a), cage much larger than guest molecule; curve (b), cage slightly larger than guest; curve (c), cage slightly smaller than guest.

Secondly,  $\Delta S^\circ_\beta + S_c$  is larger than before because of a smaller free volume. Thirdly,  $\Delta S^\circ_\beta + S_c$  may be larger still because of a restriction on the rotation of the guest molecule in the cavity. Finally,  $G_\beta - G_\alpha$  may be anomalously large because of lattice distortion. All four factors operate in the direction of reducing clathrate stability. While quantitative data for clathrates of this sort are sparse, methanol-quinol and especially methyl cyanide-quinol are examples of this category. van der Waals and Platteeuw<sup>12</sup> have found that the fraction of the cavities occupied in the equilibrium methanol-quinol clathrate at  $298^\circ\text{K}$  is 0.474, compared with 0.34 for both the argon- and krypton-quinol clathrates. This difference is to be attributed to a larger value of  $G_\beta - G_\alpha$  in the methanol-quinol clath-

rate.  $\Delta H^\circ_\beta$  for the methyl cyanide–quinol clathrate is smaller than expected when compared with  $\Delta H_{\text{vap}}$  of liquid methyl cyanide (see later discussion).

Experimental enthalpies and entropies of dissociation of quinol clathrates, gas hydrates, and a few others are given in Table 1. Only for the quinol clathrates are  $\Delta H^\circ_\beta$  and  $\Delta S^\circ_\beta$  known with any accuracy. These quantities have been estimated for the gas hydrates by the application of several assumptions.<sup>18</sup>

**Comparison of  $\Delta H^\circ_\alpha$  and  $\Delta H^\circ_\beta$  with  $\Delta H_{\text{vap}}$  of the Pure Liquid Guest.**— Examination of the data in Table 1 reveals that  $\Delta H^\circ_\beta$  is larger than  $\Delta H_{\text{vap}}$  of the liquid guest at its boiling point by a factor of 2–3 in most cases. The ratio  $\Delta H^\circ_\beta/\Delta H_{\text{vap}}$  appears to be systematically larger for the quinol clathrates than for the gas hydrates, but this observation may not be significant, because the values of  $\Delta H^\circ_\beta$  for the latter clathrates are based on an estimate of  $H_\beta - H_\alpha$ , which has not been determined experimentally. In any case, it is evident that  $\Delta H^\circ_\alpha$  is also considerably larger than  $\Delta H_{\text{vap}}$ . Therefore, one can conclude that one reason why the dissociation pressures of clathrates are smaller than the vapour pressures of the pure guest liquids is that  $\Delta H^\circ_\alpha > \Delta H_{\text{vap}}$ .

An explanation for the large ratios,  $\Delta H^\circ_\beta/\Delta H_{\text{vap}}$ , can be sought among three factors: (1) the removal of a guest molecule from the clathrate leaves an empty cavity, whereas the removal of a molecule from the liquid does not leave a hole in the liquid; (2) the energy of interaction between a guest molecule and an element in the wall of its cage may be larger than the energy of interaction between a pair of molecules in the liquid; (3) the co-ordination number of the guest molecule may be larger than the co-ordination number of a molecule in the liquid.

(1) The removal of one mole of guest from a clathrate requires an energy,  $\Delta U^\circ_\beta$ , equal to  $Nz\epsilon$ , where  $N$  is Avogadro's number,  $z$  is the co-ordination number of a guest molecule, and  $\epsilon$  is the energy of interaction between the guest molecule and a molecule or small group of atoms in the cavity wall. By contrast, the energy of vaporisation of a liquid,  $\Delta U_{\text{vap}}$ , should be computed as  $\frac{1}{2}Nz\epsilon$ . The factor  $\frac{1}{2}$  is present to avoid counting interacting pairs twice. If we ignore for the moment any differences in  $z$  or  $\epsilon$ , it becomes apparent that  $\Delta U^\circ_\beta$  should more properly be compared with  $2\Delta U_{\text{vap}}$ , which represents the energy required to vaporise one mole from a large amount of liquid in such a way as to leave behind one mole of holes in the remaining liquid. Examination of Table 1 shows that  $2\Delta H_{\text{vap}}$  comes fairly close to  $\Delta H^\circ_\beta$ , although the latter is frequently larger than the former.

(2) This observation that  $\Delta H^\circ_\beta$  often exceeds  $2\Delta H_{\text{vap}}$  must, in this simple approach, be related to differences in  $z$  and/or  $\epsilon$ . The second of these factors, the average energy of interaction between a molecule and one of its neighbours, depends on the Lennard-Jones constants for the molecule and its neighbour and the free volume of the system. Inspection of typical

TABLE 1. Experimentally determined and estimated molar enthalpies and entropies of dissociation of clathrates.

Guest	$\Delta H_z^{ca}$ (kcal./mole)	$\Delta H_\beta^b$ (kcal./mole)	$\Delta H_{vap}^c$ (kcal./mole)	$\Delta H_\beta^c/2\Delta H_{vap}$ Quinol clathrates, A <sub>8</sub> -83C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> , T = 298°K.	$\Delta S_z^{ca}$ (e.u./mole)	$\Delta S_\beta^b$ (e.u./mole)	$\Delta S_\beta^c + S_e^d$ (e.u./mole)
Ar	4.6 <sup>e</sup>	6.0 <sup>f</sup>	1.56	1.9	17.8 <sup>l</sup>	20.1 <sup>m</sup>	23.9 <sup>n</sup>
Kr	4.9	6.3 <sup>g</sup>	2.16	1.5	18.1 <sup>k</sup>	20.4 <sup>aa</sup>	24.2 <sup>j</sup>
N <sub>2</sub>	4.4	5.8 <sup>f</sup>	1.33	2.2	14.6 <sup>l</sup>	16.9 <sup>m</sup>	20.7 <sup>n</sup>
O <sub>2</sub>	4.1	5.5 <sup>f</sup>	1.63	1.7	20.0 <sup>k</sup>	22.3 <sup>aa</sup>	26.1 <sup>o</sup>
CO					18.3 <sup>l</sup>	20.6 <sup>m</sup>	24.4 <sup>n</sup>
					18.6 <sup>k</sup>	20.9 <sup>aa</sup>	24.7 <sup>bb</sup>
CH <sub>4</sub>	5.8	7.2 <sup>h</sup>	1.96		21.4 <sup>k</sup>	23.7 <sup>aa</sup>	27.5 <sup>bb</sup>
HCl	7.8	9.2 <sup>f</sup>	3.86	1.8	20.3 <sup>k</sup>	22.6 <sup>aa</sup>	26.4 <sup>bb</sup>
HBr	8.8	10.2 <sup>f</sup>	4.21	1.2	20.2 <sup>k</sup>	22.5 <sup>aa</sup>	26.3 <sup>cc</sup>
H <sub>2</sub> CO <sub>3</sub> H	10.8	12.2 <sup>f</sup>	5.32	1.2	21.0 <sup>k</sup>	23.3 <sup>aa</sup>	27.1 <sup>h</sup>
CH <sub>3</sub> OH	~10.0	~11.0 <sup>f</sup>	8.43		~17.0 <sup>l</sup>	~19.0 <sup>m</sup>	~23.0 <sup>n</sup>
	9.2 <sup>z</sup>				22.5 <sup>k</sup>	24.8 <sup>aa</sup>	28.6 <sup>cc</sup>
	14.2 <sup>z</sup>						
SO <sub>2</sub>		7.5 <sup>i</sup>	6.1	0.5	21.7 <sup>z</sup>		
CH <sub>3</sub> CN			7.83		37.4 <sup>z</sup>		
H <sub>2</sub> S	5.6 <sup>o</sup>	6.7 <sup>r</sup>	4.46	0.8	22.3 <sup>s</sup>	20.2 <sup>t</sup>	v
CH <sub>4</sub>	4.55	5.6	1.96	1.4	22.6	20.5	
C <sub>2</sub> H <sub>6</sub>	5.8	6.9	3.52	1.0	26.2	24.1	
SO <sub>2</sub>	7.7	8.8	5.96	0.7	26.5	24.4	

TABLE 1.—continued

Guest	$\Delta H_a^a$ (kcal./mole)	$\Delta H_{\beta}^b$ (kcal./mole)	$\Delta H_{\text{vap}}^c$ (kcal./mole)	$\Delta H_{\beta}^d/2\Delta H_{\text{vap}}$	$\Delta_2^e S_a$ (e.u./mole)	$\Delta S_{\beta}^b$ (e.u./mole)	$\Delta S_{\beta}^b + S_c^e$ (e.u./mole)
			Structure I gas hydrates, A, 7·7H <sub>2</sub> O, T = 273°K				
Cl <sub>2</sub>	6·5 <sup>o</sup>	7·9 <sup>r</sup>	4·88	0·8	23·7 <sup>s</sup>	20·5 <sup>t</sup>	<sup>v</sup>
CH <sub>3</sub> Br	8·1	9·5	5·72	0·8	27·0	24·0	
			Structure II gas hydrates, A, 17H <sub>2</sub> O, T = 273°K				
CH <sub>3</sub> I	7·3 <sup>o</sup>	10·7 <sup>r</sup>	6·7	0·8	22·1 <sup>s</sup>	23·0 <sup>t</sup>	<sup>v</sup>
C <sub>2</sub> H <sub>5</sub> ·Cl	8·7	12·1	5·9	1·0	29·2	30·1	
C <sub>3</sub> H <sub>8</sub>	6·3	9·7	4·49	1·1	25·3	26·2	
CHCl <sub>2</sub> F	8·5 <sup>p</sup>	11·9	6·4	0·9	27·3 <sup>p</sup>	28·2	
CBrClF <sub>2</sub>	8·25 <sup>q</sup>	11·6	5·34	1·1	26·8	27·7	
			Miscellaneous, T = 298°K				
C <sub>6</sub> H <sub>6</sub> , X <sup>u</sup>	~10·0 <sup>w</sup>		7·35				
p-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> , Y <sup>v</sup>		17·8 <sup>x</sup>	10·1	0·9			
p-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> , Y <sup>v</sup>		21·3 <sup>x</sup>	11·0	1·0			

<sup>a</sup>Refers to the process, A, nB (s) → nB (s, stable) + A (g), where n has the value given in the various formulae in the Table. <sup>b</sup>Refers to the process, A, nB (s) → nB (s, metastable) + A (g), where n is the same as in (a). <sup>c</sup>Enthalpy of vaporisation of the pure liquid guest at its normal boiling point. Most of the values were taken from National Bureau of Standards, Circular 500. <sup>d</sup>S<sub>c</sub> = configurational entropy. <sup>e</sup>Unless noted otherwise,  $\Delta H_{\beta}^b$  for the quinol clathrates was calculated from  $\Delta H_{\beta}^b$  and  $H_{\beta} - H_g$ , the latter from D. F. Evans and R. E. Richards, *Proc. Roy. Soc.*, 1954, **4**, 223, 238. <sup>f</sup>Evans and Richards, *ref. e.* <sup>g</sup>Ref. 26c. <sup>h</sup>Ref. 26b. <sup>i</sup>H. G. McAldie, *Canad. J. Chem.*, 1963, **41**, 2137. <sup>j</sup>Ref. 26a. <sup>k</sup>Calc. from  $\Delta S_{\beta}^b$  and  $S_{\beta} - S_g$ , the latter from ref. 12. <sup>l</sup>Calc. from  $\Delta H_{\beta}^b$  and dissociation pressure, the latter from ref. 12. <sup>m</sup>Calc. from  $\Delta S_{\beta}^b$  and  $S_{\beta} - S_g$ , the latter from ref. 12. <sup>n</sup>Calc. from  $\Delta S_{\beta}^b$  and  $S_c = 3·8$  e.u. <sup>o</sup>Except where noted otherwise,  $\Delta H_{\beta}^b$  for the gas hydrates is taken from D. N. Glew, *J. Phys. Chem.*, 1960, **38**, 208. <sup>p</sup>All values of  $\Delta H_{\beta}^b$  for the gas hydrates are estimates, obtained from  $\Delta H_{\beta}^b$  and an estimated value of  $H_{\beta} - H_g$ , ref. 18. <sup>q</sup>Unless noted otherwise,  $\Delta S_{\beta}^b$  for the gas hydrates is taken from D. N. Glew, *ref. q.* <sup>r</sup>All values of  $\Delta S_{\beta}^b$  for the gas hydrates are estimates, obtained from  $\Delta S_{\beta}^b$  and an estimated value of  $S_{\beta} - S_g$ , ref. 18. <sup>s</sup>X = Ni(CN)<sub>2</sub>NH<sub>3</sub>. <sup>t</sup>Y = Ni(CNS)<sub>2</sub>(CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>N). <sup>u</sup>E. E. Aynsley, W. A. Campbell, and R. E. Dodd, *Proc. Chem. Soc.*, 1957, 210. <sup>v</sup>M. I. Hart, jun. and N. O. Smith, *J. Amer. Chem. Soc.*, 1962, **84**, 1816. <sup>w</sup>Within experimental error,  $S_c = 0$  for the gas hydrates. <sup>x</sup>W. F. K. Wynne-Jones and A. R. Jones, *Compt. rend. de la 2<sup>e</sup> Réunion de Chimie Physique (2-7 juin 1952, Paris)*. <sup>y</sup>Calc. from  $\Delta S_{\beta}^b + S_c$  and  $S_c = 3·8$  e.u. <sup>z</sup>Calc. from experimental heat capacities given in ref. 26d. <sup>aa</sup>G. L. Stepakoff, *Diss. Abs.*, 1963, **24**, 1424.

values<sup>12,18,20</sup> of these quantities for both clathrates and the pure guest liquids shows that the pair-wise interaction energies are not appreciably different.

(3) In a close-packed liquid the co-ordination number is 12, while in a more random and perhaps more realistic molecular arrangement, the most probable co-ordination number<sup>21</sup> is 8. On the other hand, the number of nearest elements about a guest molecule is about 24. Here, "element" refers to a water molecule in the case of the gas hydrates and to a C-H, O-H, or C group or atom in the case of the quinol clathrates. Hence, an element is not always comparable in size to the guest molecule. Nevertheless, it is felt that the larger co-ordination numbers in the clathrates probably account for some of the difference between  $\Delta H^\circ_\beta$  and  $2\Delta H_{\text{vap}}$ , at least for the smaller guest molecules.

To summarise this discussion of enthalpies, we can visualise the vaporisation of a liquid and the dissociation of a clathrate into stable products as each occurring in two hypothetical steps. Regarding the liquid, we imagine that first one mole of vapour is removed from a liquid with the simultaneous creation of one mole of holes, a process which is accompanied by an enthalpy increase of  $2\Delta H_{\text{vap}}$ . The second step is the collapse of the remaining liquid to produce a normal liquid; the enthalpy change for the process is  $-\Delta H_{\text{vap}}$ . In an analogous fashion, the sequence of steps for the clathrate is: first, the removal of one mole of guest from the lattice, for which the enthalpy change is  $\Delta H^\circ_\beta$ , and second, the collapse of the  $\beta$ -lattice to give to the  $\alpha$ -form, for which  $\Delta H = -n(H_\beta - H_\alpha)$ . By comparison first of the second steps, our discussion has shown that an important enthalpy factor which makes clathrates more stable than the pure guest liquids is that  $n(H_\beta - H_\alpha)$  is often considerably less than  $\Delta H_{\text{vap}}$ . We return, therefore, to the notion, stressed by other authors, that the metastable host lattice must have a structure which, although open, is particularly stable, usually because of hydrogen bonding, and that this is most readily attained when the cavities are small. A second factor which is apparent in much of the data is that  $\Delta H^\circ_\beta > 2\Delta H_{\text{vap}}$ , probably because  $z$ , the co-ordination number, is larger in the clathrates.

As a final remark on enthalpies, it should be noted that for the methyl cyanide-quinol clathrate  $\Delta H^\circ_\beta$  is no larger than  $\Delta H_{\text{vap}}$  (Table 1). This unusually small  $\Delta H^\circ_\beta$  is undoubtedly related to the tight fit of the methyl cyanide molecule in the  $\beta$ -quinol cavities, as mentioned earlier.

**Comparison of  $\Delta S^\circ_\alpha$  and  $\Delta S^\circ_\beta$  with  $\Delta S_{\text{vap}}$  of the Pure Liquid Guest.**—According to Table 1,  $\Delta S^\circ_\alpha$  of the quinol clathrates is close to  $\Delta S_{\text{vap}}$  of the pure liquid guests (18–20 e.u./mole.) This fact, of course, means that the extra stabilities of these clathrates relative to the pure liquid guests are not related to entropy considerations. One would expect  $\Delta S^\circ_\beta$  to be approxi-

<sup>20</sup> D. H. Everett, *J.*, 1960, 2566.

<sup>21</sup> J. D. Bernal, paper presented at the 1964 Anniversary Meeting of the Chemical Society at Birmingham.

mately equal to  $\Delta S_{\text{vap}}$ , because the theoretical entropy of vaporisation of a liquid with spherical molecules is given by an equation<sup>20</sup> similar to equation (2) and the free volumes of the two systems are the same order of magnitude ( $\sim 1 \text{ cm}^3/\text{mole}$ ). It happens that for the quinol clathrates the term  $[-n(S_\beta - S_\alpha)]$ , which must be added to  $\Delta S_\beta^\circ$  to give  $\Delta S_\alpha^\circ$ , is small.

The values of  $\Delta S_\alpha^\circ$  for the gas hydrates are significantly larger than  $\Delta S_{\text{vap}}$  of the pure guest liquids. Therefore these clathrates have lower entropies and would be less stable than the liquids if the entropy of the system were the only consideration. Only because  $\Delta H_\alpha^\circ > \Delta H_{\text{vap}}$  do the clathrates have the greater stabilities. The reasons for the fairly large values of  $\Delta S_\alpha^\circ$  cannot be discussed with precision because the values of  $S_\beta - S_\alpha$  for these systems are known only approximately. One factor, however, is known with certainty and must be significantly responsible for the reduced stabilities of the gas hydrates relative to the quinol clathrates. Since the fraction of the cavities occupied in the gas hydrates is found experimentally to be nearly 100%,  $S_c = 0$ , while for the quinol clathrates  $S_c = 3.8 \text{ e.u.}$  This difference is related ultimately to the fact that the empty  $\beta$ -type ice lattices are considerably less stable than ordinary ice (cf.  $\alpha$ - and  $\beta$ -quinol), and hence the degree of occupation of the former structures by guest molecules must be high in order that these structures be stabilised. Thus one finds in the enthalpy and entropy data for these two types of clathrate detailed explanations for the not unexpected conclusion that the clathrate with the least stable host lattice turns out to be the least stable clathrate.

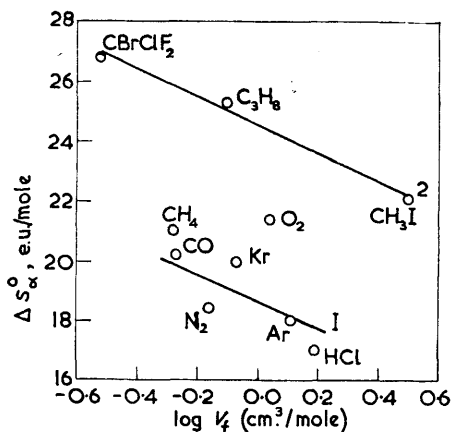


FIG. 4.  $\Delta S_\alpha^\circ$  v.  $\log V_f$  for the quinol clathrates (curve 1) and several structure II gas hydrates (curve 2). The lines have been given slopes of  $-2.3R$ , valid in the square-well approximation.

Within a group of clathrates in which  $S_\beta - S_\alpha$  and  $S_c$  are constant for the series,  $\Delta S_\alpha^\circ$  varies approximately linearly with  $\log V_f$  as predicted by equation (2), even when the approximate equation (3) is used for the calcu-

lation of the free volumes. This relationship is illustrated in Fig. 4 with data for the quinol clathrates and the structure II gas hydrates.

### Heat Capacities of Quinol Clathrates

**Deduction of Barriers to Rotation from Heat-capacity Data.**—Although the assumption of spherically symmetric cavities does not introduce appreciable error into the theoretical prediction of clathrate stabilities, several other kinds of experimental data demonstrate the existence of small potential barriers to the rotation of guest molecules, showing that the force-field within the cavities is not strictly isotropic. Three kinds of experiment which bear on this question will be discussed: heat capacity, dielectric, and infrared measurements. These and others have recently been discussed by Staveley.<sup>14,22</sup>

The effect on thermodynamic properties produced by a barrier to free *internal* rotation in molecules has been known for more than twenty years, and, in fact, a discrepancy between the "Third Law" entropy of ethane and the entropy calculated from statistical thermodynamics with the assumption of free internal rotation first led Kemp and Pitzer<sup>23,24</sup> to postulate a potential barrier hindering internal rotation of about 3 kcal./mole in ethane. Pitzer and Gwinn<sup>25</sup> later developed quantitative relationships between barrier height and thermodynamic properties such as heat capacity. These relationships apply not only to internal rotations but also to any molecular rotation which experiences a resisting force, and in the last few years workers at two laboratories<sup>26,27</sup> have calculated barriers to rotation in clathrates from heat capacity measurements over a range of temperatures.

When  $RT \ll V_0$ , the latter quantity being the barrier to rotation, then the guest molecule undergoes a librational motion which is approximated very closely by the equation of motion for a harmonic oscillator. The contribution to the heat capacity,  $C_{rot}$ , from the two-dimensional librational motion of a diatomic molecule is, therefore,  $2R$ . On the other hand, when  $RT \gg V_0$ , the molecule undergoes nearly free rotation, and  $C_{rot}$  becomes approximately  $R$ . The corresponding values of  $C_{rot}$  for a polyatomic guest molecule are  $3R$  and  $3/2R$ . In either case,  $C_{rot}$  starts out at very nearly zero for temperatures close to  $0^\circ\text{K}$ , because the librational motion is not excited, rises to a maximum at higher temperatures as the librational motion is excited, and then falls off slowly toward the limiting

<sup>22</sup> L. A. K. Staveley in "Non-Stoichiometric Compounds", ed. L. Mandelcorn, Academic Press, Inc., New York, 1964, ch. 10.

<sup>23</sup> J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, 1936, **4**, 749.

<sup>24</sup> J. D. Kemp and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 276.

<sup>25</sup> K. S. Pitzer and W. S. Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.

<sup>26</sup> (a) N. G. Parsonage and L. A. K. Staveley, *Mol. Phys.*, 1959, **2**, 212; (b) *ibid.*, 1960, **3**, 59; (c) N. R. Grey, N. G. Parsonage, and L. A. K. Staveley, *ibid.*, 1961, **4**, 153; (d) N. R. Grey and L. A. K. Staveley, *ibid.*, 1963, **7**, 83.

<sup>27</sup> L. V. Coulter, G. L. Stepakoff, and C. G. Roper, *J. Phys., Chem. Solids*, 1963, **24**, 711.

value for the free rotator at still higher temperatures. From the exact shape of the curve for  $C_{\text{rot}}$  against  $T$  one can evaluate the barrier to rotation. The problem then is to deduce  $C_{\text{rot}}$  from the total measured heat capacity,  $C$ , of a clathrate, and this is discussed in the next Section.

**Analysis of Heat-capacity Data for Clathrates.**—The total heat capacity of the clathrate per three moles of quinol is first subdivided<sup>26</sup> into contributions from the  $\beta$ -quinol lattice and the guest molecule as expressed in the equation,

$$C = 3C_{\text{Q}} + XC_{\text{G}} \quad . . . . . (5)$$

where  $C_{\text{Q}}$  is the molar heat capacity of  $\beta$ -quinol,  $X$  is the fraction of the cavities occupied, and  $C_{\text{G}}$  is the molar heat capacity of the guest in the clathrate. Since there are three molecules of quinol per cavity,  $X$  is numerically equal to the number of moles of guest per three moles of quinol. If both  $C_{\text{Q}}$  and  $C_{\text{G}}$  are truly independent of the degree of filling of the cavities, then  $C$  at a given temperature should vary linearly with  $X$  as expressed by equation (5). Nearly all the experimental results for six quinol clathrates have verified the linear relationship,<sup>26</sup> and  $C_{\text{G}}$  at a number of temperatures has been evaluated from the slopes of plots of  $C$  against  $X$ .

Next,  $C_{\text{rot}}$  is obtained by subtracting  $C_{\text{vib}}$ , the contribution to the heat capacity from the rattling of the guest molecule in the cage, from  $C_{\text{G}}$ .  $C_{\text{vib}}$  can be calculated from the theory of van der Waals and Platteeuw,<sup>12</sup> which has been confirmed by the experimental results for argon- and krypton-quinol clathrates,<sup>26a,b</sup> where the question of rotation does not arise. Finally, the barrier to rotation of the guest molecule can be determined by comparison of the experimental  $C_{\text{rot}}$  with  $C_{\text{rot}}$  calculated from various barrier heights (see Fig. 5). It is evident that the accumulation of errors in the final result is rather unfavourable because  $C_{\text{rot}}$  is only a small fraction of  $C$ .

The barrier heights determined by Staveley for the quinol clathrates of methane, oxygen, nitrogen, and carbon monoxide are  $\sim 0$ , 200–250,  $\sim 1100$ , and  $\sim 1200$  cal./mole respectively. In no case is the barrier height large enough to cause an appreciable discrepancy between the true  $\Delta S_{\beta}^{\circ}$  for these clathrates and the values predicted by equation (2), which is based on the assumption of free rotation. The virtually free rotation of methane in the clathrate at temperatures above  $\sim 150^{\circ}\text{K}$  is reminiscent of the similar behaviour in solid methane slightly below the melting point<sup>28</sup> and is undoubtedly related to the high symmetry of this molecule. Finite barriers are found in the other clathrates, however, even though the guest molecules are non-polar or only slightly polar. It has been suggested<sup>26d</sup> that an interaction between the quadrupole moment of the guest molecule and the cavity wall, which is electrically more negative in the regions of the two hydrogen-bonded hexagons than in the neighbourhood of the benzene rings, could give rise to preferred orientations of the guest molecule in the

<sup>28</sup> J. G. Aston, *Record Chem. Progr.*, 1959, 20, 41.



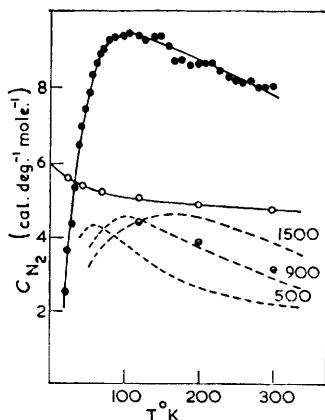


FIG. 5. Heat capacity-temperature plots for the nitrogen-quinol clathrate. Full circles,  $C_{N_2}$  = total heat capacity contribution per mole of  $N_2$  in  $\text{cal. deg}^{-1} \text{mole}^{-1}$ . Open circles, calculated values of  $C_{\text{vib}}$ . Half-shaded circles, derived values of  $C_{\text{rot}}$ . Dotted curves, calculated values of  $C_{\text{rot}}$  for hindering energy barriers of 500, 900, and 1500  $\text{cal. mole}^{-1}$ . (Reproduced, with permission, from N. R. Grey and L. A. K. Staveley, *Mol. Phys.*, 1963, 7, 83).

cavity. The observed barrier heights do in fact correlate qualitatively with quadrupole moments of the three guest molecules.

One anomaly appears in the heat capacity studies:  $C_0$ , which is obtained as the intercept in a plot of  $C$  against  $X$  (see equation 5), is not constant for all clathrates at the same temperature. Some of the differences are outside experimental error, particularly at the lowest temperatures. Furthermore, the entropy of the guest at 298°K, obtained from the equation

$$S_G = \int_0^{298} \frac{C_G}{T} dT \quad \dots \dots \dots (6)$$

differs by 2–3 e.u. from the entropy calculated from the theory of van der Waals and Platteuw<sup>12</sup> for the argon, methane, and krypton clathrates. The difference is 1 e.u. larger for krypton than for argon. These discrepancies suggest that the low frequency vibrations of the quinol lattice may be perturbed by the guest molecules.<sup>26</sup> For example, the entropy contributions from one-dimensional lattice vibrations of 120 and 150  $\text{cm}^{-1}$  differ by 0.43 e.u. at 298°K. Several other lines of evidence, however, argue against perturbations of appreciable magnitude. First, the theory, which neglects lattice distortion, correctly predicts the dissociation pressures of a number of quinol clathrates. Secondly, the experimentally determined fraction of the cavities occupied in both the argon and the krypton clathrates is 0.34 when the clathrate is in equilibrium with  $\alpha$ -quinol and gaseous guest at 298°K. If appreciable lattice perturbations occur in these two clathrates, they would have to be of similar magnitudes for such a result to be observed. Perhaps careful comparison of the infrared spectra of  $\beta$ -quinol and the clathrates would help to resolve this question.

In a study of heat capacities similar to that described above, Coulter, Stepakoff, and Roper<sup>27</sup> found barriers of 511 and 691 cal./mole restricting the rotation of N<sub>2</sub> and CO respectively in the quinol clathrates. They also found that the data of Parsonage and Staveley<sup>26b</sup> for methane-quinol in the range 15–50°K, are consistent with a barrier of 193 cal./mole. These results seem to be in satisfactory agreement with those of Staveley when the unfavourable propagation of error is recalled. The barriers found for a number of guests in the quinol lattice are summarised in Table 2. Results of measurements other than heat capacity are included for completeness.

TABLE 2. *Barriers hindering rotation in quinol clathrates*

Guest	Temp. Range (°K)	Barrier height (cal./mole.)	Method	Ref.
O <sub>2</sub>	0.25–4	128	A	a
	1.5–4.2	~250	B	b
	100–300	~200	C	26d
N <sub>2</sub>	1.5–25	940	D	c
	120–300	~1100	C	26d
	15–100	511	C	27
CO	100–300	~1200	C	26d
	15–100	691	C	27
CH <sub>4</sub>	150–300	~0	D	26b
	15–50	193	C	27

A, Magnetic susceptibility; B, Paramagnetic resonance; C, Heat capacity; D, Nuclear quadrupole resonance.

<sup>a</sup>H. Meyer, M. C. M. O'Brien, and J. H. van Vleck, *Proc. Roy. Soc.*, 1957, A, 243, 414.

<sup>b</sup>S. Foner, H. Meyer, and W. H. Kleiner, *J. Phys. Chem. Solids*, 1961, 18, 273. <sup>c</sup>H. Meyer and T. A. Scott, *ibid.*, 1959, 11, 215.

### Measurements of Dielectric Loss

**Results for Rotator-phase Solids and Solutions.**—Typical dielectric data which show the loss region are given for solid D-camphor in Fig. 6. At temperatures between –38° and its melting point, 178°, D-camphor is similar to a liquid in that its nearly spherical molecules experience very little resistance to rotation. For this reason, the dielectric constant or permittivity,  $\epsilon'$ , is nearly constant from 0 to ~500 Mc./sec., showing that in this frequency range the dipoles are able to reorient in phase with the applied field. At higher frequencies  $\epsilon'$  drops off because of the inability of the dipoles to rotate in phase with the field, and at sufficiently high frequencies  $\epsilon'$  reaches a small limiting value arising from atomic and electronic induced dipoles, all concerted rotation of permanent dipoles having ceased. In the "loss" region or region of decreasing  $\epsilon'$ , a conductance, which is proportional to  $\epsilon''$  (the loss factor), appears. This existence of a high-frequency conductance in a material with a high D.C. resistance can be traced to the existence of a component of (A.C.) current in phase with

the applied e.m.f. when the rotation of the molecular dipoles lags behind this e.m.f. Outside the loss region the A.C. current produced by the in-phase orientations of the dipoles with the field turns out to be precisely  $90^\circ$  out-of-phase with the field, and there is then no loss of energy or joule heating, *i.e.*, the medium is an ideal dielectric.

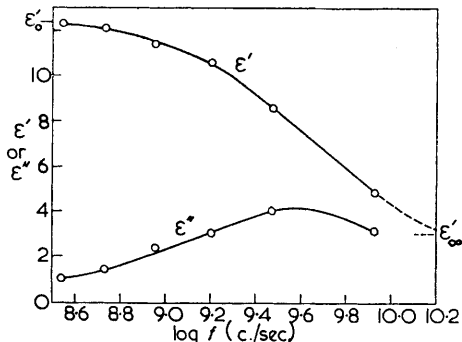


FIG. 6. Dielectric data for solid D-camphor at  $-20^\circ\text{C}$ . (Reproduced, with permission, from C. Clemett and M. Davies, *Trans. Faraday Soc.*, 1962, **58**, 1718.)

The particular frequencies at which an appreciable loss occurs are related to the relaxation time or spectrum of relaxation times for the system. In the simplest case, the single relaxation time is defined by the first-order rate equation

$$\frac{dp}{dt} = -kp = -\frac{p}{\tau} \quad \dots \dots \dots (7)$$

in which  $p$  stands for specific polarisation,  $k$  the first-order rate constant and  $\tau = 1/k$ , the relaxation time. Equation (7) describes the manner in which the specific polarisation of the sample decays with time after the instantaneous removal of a static electric field. The relaxation time,  $\tau$ , is the time required for  $p$  to fall to  $1/e$  of its original value. In the more complicated physical situation consisting of the application of an alternating field to the sample, dielectric theory shows that the maximum value of  $\epsilon''$  occurs at an angular frequency,  $\omega = 2\pi f$ , equal to  $1/\tau = k$ . Inspection of Fig. 6 shows that for D-camphor at  $-20^\circ$   $\epsilon''_{\text{max}}$  occurs at  $\sim 3700$  Mc./sec., which implies a relaxation time of  $4.3 \times 10^{-11}$  sec. This macroscopic relaxation time is very nearly equal to the relaxation time for individual dipole reorientations.

Since  $k$  is a first-order rate constant, its temperature dependence (and that of  $1/\tau$ ) might be expected to follow the Arrhenius or Eyring equations. That this is approximately so has been verified by a variety of experiments and a large number of energies or heats of activation have been evaluated. From the values of  $\tau$  for D-camphor at a number of temperatures,  $\Delta H_a$  of the Eyring equation has been found to be  $1.8 \pm 0.7$  kcal./mole.<sup>29b</sup> Both the small  $\Delta H_a$  and the small  $\tau$  point to the existence of fairly free

rotation in solid D-camphor down to  $-38^{\circ}\text{C}$ . For a number of other rotator-phase solids activation enthalpies of 1—2 kcal./mole have also been found.<sup>29a,b</sup>

Dielectric studies of polar solutes in non-polar solvents have shown behaviour similar to that of the rotator-phase solids. Typical values of  $\tau$  and  $\Delta H_a$  are  $10^{-12}$ — $10^{-11}$  sec. at room temperature and 1—2 kcal./mole. When the polar solute molecules are approximately spherical in shape, the rotations in solution may be even freer. For example,  $\Delta H_a$  is 1.5 and 0.3 kcal./mole for camphor and fluorobenzene respectively in carbon tetrachloride solution.<sup>30</sup> Apparently the fluorobenzene molecule rotates quite freely about the axis perpendicular to the plane of the molecule.

**Quinol Clathrates.**—In view of their structures and thermodynamic properties, one would expect to find for clathrates the very short relaxation times and small enthalpies of activation characteristic of rotator-phase solids and solutions. This expectation is borne out by the available data, although there is at least one interesting exception in the methyl cyanide-quinol clathrate.

The most significant published dielectric study of quinol clathrates is that of Dryden and Meakins,<sup>31a,b</sup> who measured the permittivities and losses of the methanol and methyl cyanide clathrates over a range of frequency and temperature. In addition, measurements of permittivity at one low frequency (50 kc./sec.) and room temperature were made for the  $\text{H}_2\text{S}$ ,  $\text{HCN}$ ,  $\text{SO}_2$ , and  $\text{C}_2\text{H}_2$  clathrates. These measurements showed that at 50 kc./sec. the permittivity values are larger than  $\epsilon'$  of quinol, the differences being approximately proportional to  $\mu^2$  of the guest molecule. Hence the loss regions must occur at frequencies higher than 50 kc./sec., and the barriers to rotation in these clathrates are probably small ( $< 5$  kcal./mole).

In the more extensive study<sup>31b</sup> of the methanol clathrate, however, an absorption peak, which had a shape corresponding to a single relaxation time, was revealed at  $\sim 10^{11}$  c./sec. at room temperature. The existence of a single relaxation time at a given temperature means that each methanol molecule has the same environment and that co-operative motions involving several methanol molecules are not significant in the reorientations of these molecules in an oscillating electric field. Neither conclusion is surprising in view of the structure of the clathrate. An Arrhenius activation energy of 2.3 kcal./mole was calculated from the temperature dependence of the relaxation time. For comparison with the activation energies quoted in the preceding section, this value should be reduced somewhat, as the Eyring activation energy is smaller than the Arrhenius value by the factor  $RT$ . Thus it is apparent that the barrier hindering the rotation of the

<sup>29</sup> (a) C. Clemett and M. Davies, *Trans Faraday Soc.*, 1962, **58**, 1705; (b) *ibid.*, p. 1718.

<sup>30</sup> Calculated from data given by W. E. Vaughan, W. P. Purcell, and C. P. Smyth, *J. Amer. Chem. Soc.*, 1961, **83**, 571.

<sup>31</sup> (a) J. S. Dryden and R. J. Meakins, *Nature*, 1952, **169**, 324; (b) J. S. Dryden, *Trans. Faraday Soc.*, 1953, **49**, 1333.

methanol molecules in the quinol clathrate is about the same as the barriers found in rotator-phase solids and in solutions. Measurements with single crystals of the clathrate and a detailed consideration of the values of  $(\epsilon'_0 - \epsilon'_\infty)$  (Fig. 6) at different temperatures indicated a lack of preferred orientations for the methanol molecule in the cage, contrary to the finding of Palin and Powell,<sup>1c</sup> whose X-ray diffraction measurements suggested that on the average the (C-O) axis of the methanol molecule points towards the hexagons of the hydrogen bonded (O-H) groups in the cage. The activation energy deduced from the dielectric absorption must probably be regarded as an average value for the overall rotation of the molecule within its cage. Owing to its small value and the inevitable uncertainties in it, unless the hindering potential were distinctly anisotropic it is not surprising that the dielectric study failed to show preferred directions for rotation.

An appropriately marked contrast is provided by the data for the methyl cyanide-quinol clathrate.<sup>31b</sup> Dielectric loss occurs at much lower frequencies (3 kc./sec. at room temperature), and the activation energy is 18 kcal./mole. Furthermore, anisotropic properties are revealed by experiments with single crystals of the clathrate. When the field is parallel to the *c* axis (the axis perpendicular to the hydroxyl hexagons), a region of strong dielectric loss appears, and the permittivity is 27 at 50 c./s. When the field is perpendicular to the *c* axis there is no absorption peak, and the permittivity is only 3. Both observations are consistent with the hypothesis that the equilibrium orientation for the methyl cyanide molecule is along the *c* axis of the crystal: owing to the  $C_{3v}$  symmetry of the molecule, the dipole moment is precisely along the (C-C-N) line. Introducing a field parallel to this axis causes the molecules to rotate through  $180^\circ$  by passing over a high barrier, reversing the whole of the dipole moment, while a perpendicular field encounters, at most, a very small component of the dipole moment. Accordingly, to such a field the crystal behaves like a non-polar medium. All these data fall in neatly with the observations of lattice distortion and a relatively small  $\Delta H^\circ_p$  for this clathrate.

**Gas Hydrates.**—The relaxation of the water molecules in the host lattice has been studied by Wilson and Davidson<sup>32</sup> for acetone hydrate and Brey and Legg<sup>33</sup> for trichlorofluoromethane hydrate. Both systems exhibit loss regions which are broader than would correspond to a single relaxation time, in contrast with the single relaxation time found for ordinary ice.<sup>34</sup> If the relaxation mechanism in both ice and the clathrates is assumed to be the diffusion of rotational defects through the lattice, then the existence of several diffusion paths in the gas hydrate lattices is implied. The activation energy for dipole reorientation was found to be smaller for the gas hydrates than for ice (6.3 and 9.2 versus 13.2 kcal./mole.). This lower hindrance to

<sup>32</sup> G. J. Wilson and D. W. Davidson, *Canad. J. Chem.*, 1963, **41**, 264.

<sup>33</sup> W. S. Brey, jun., and J. W. Legg, *J. Phys. Chem.*, 1963, **67**, 1737.

<sup>34</sup> R. P. Auty and R. H. Cole, *J. Chem. Phys.*, 1952, **20**, 1309.

reorientation is consistent with slightly weaker hydrogen bonds in the lattices of the gas hydrates.<sup>32</sup>

Motions of the guest molecules themselves have recently been examined in ethylene oxide hydrate (Structure I) and tetrahydrofuran hydrate (Structure II) by Davidson, Davies, and Williams.<sup>35</sup> Very short relaxation times ( $\sim 10^{-11}$  sec.) were found even down to liquid-nitrogen temperature, and the estimated (Eyring) enthalpies of activation are  $0.5 \pm 0.1$  and  $0.3 \pm 0.1$  kcal./mole for ethylene oxide and tetrahydrofuran hydrates respectively. These are extraordinarily small values for polar (oxygenated) molecules in an ice lattice. It appears that departures from spherical symmetry in the cavities are very slight indeed and that atoms in the wall of a cavity need not be pushed out of the way when the guest molecule rotates. Striking confirmation of this remarkable freedom is found in the permittivity values ( $\epsilon'$ ) of these ice-hydrates: the dielectric increment [ $\epsilon'$  (clathrate) —  $\epsilon'$  (ice)] measured even at  $3 \times 10^8$  c./sec. and  $-180^\circ\text{C}$  shows the guest molecules to be rotating as completely as in benzene solutions at room temperatures. The dipole moments deduced from the dielectric increments are practically identical despite the great difference in the media.

### Infrared Spectra

**Molecular Rotation revealed by Solution-phase Spectra.**—The large widths and peculiar contours of the vibration-rotational bands observed in the spectra of small molecules in the gas phase are familiar aspects of infrared spectroscopy. Less well understood are the often appreciable band widths and occasional multiple peaks found in the vibrational spectra of molecules in solution. If all the solute molecules were unable to rotate and had identical environments which did not vary with time, their infrared spectra would consist of sharp bands, whose finite widths would be determined mainly by instrumental parameters, because rotational transitions would be absent and the set of force constants would be the same for all molecules. Obviously this simple situation does not exist in solution, and the separation of all the factors influencing band shape has proved to be a difficult problem. Nevertheless, a substantial body of evidence, recently reviewed by Jones and Sheppard,<sup>36</sup> shows that when at least one moment of inertia of the solute molecule is small, some of the absorption bands have wings attributable to vibration-rotation transitions. For example, the perpendicular bands of the methyl halides in a variety of solvents have wings whose shapes approach the contours of the *P* and *R* branches of the gas-phase spectra. The half-widths of these bands are 20–50  $\text{cm.}^{-1}$ . There seems little doubt that at least some of the solute molecules are able to rotate freely and to undergo rotational transitions, although the rotational energy levels are blurred by interactions with the solvent.

<sup>35</sup> D. W. Davidson, M. Davies, and K. Williams, *J. Chem. Phys.* 1964, **40**, 3449.

<sup>36</sup> W. J. Jones and N. Sheppard, Spectroscopy Report, Conf. Organic Hydrocarbon Research Group Inst. Petrol., London, 1962, p. 181.

Analysis of the shapes of infrared bands to give barrier heights for rotation in solution has been attempted in only a few studies, and even in these, interpretations differ. For example, Bulanin and Orlova<sup>37</sup> have interpreted the spectra of solutions of carbon monoxide in thirteen solvents at room temperature to indicate potential barriers of 300—1000 cal./mole hindering the rotation of the carbon monoxide molecule. From the spectrum of CO dissolved in liquid oxygen at 90°K they concluded that nearly all rotational excitation is inhibited in this solution. On the other hand, Ewing<sup>38</sup> deduced from the spectrum of liquid CO at 80°K a barrier to rotation of ~120 cal./mole. According to the Boltzmann law, 55% of the molecules would be rotating freely in this liquid. A very similar condition was found for CO dissolved in liquid argon or nitrogen.

While the spectra of solute molecules in inactive solvents might be expected to have features in common with the spectra of the guest molecules in clathrates, an even greater similarity can be anticipated between the spectra of clathrates and those of small molecules trapped in solid rare-gas matrices. The infrared spectra of dilute solid solutions of HCl in argon,<sup>39</sup> CH<sub>4</sub> and CD<sub>4</sub> in argon, krypton, and xenon,<sup>40</sup> and H<sub>2</sub>O in argon, krypton, and xenon<sup>41</sup> do in fact have multiple peaks which have been attributed to free or slightly hindered rotation of the trapped molecules. In the case of H<sub>2</sub>O in rare-gas matrices, fine structure similar to that found in the spectrum of water vapour has been observed. It is only for the smallest solute molecules, however, that evidence for rotation has been noted. The infrared spectra of all other systems of this kind consist of purely vibrational bands.

It is noteworthy that the free diameter of a cavity in  $\beta$ -quinol is midway between the diameters of the cavities produced by the removal of rare gas atoms from the crystal lattices of krypton and xenon. The cavities in ice of Structures I and II are even larger than those in xenon. Thus one can predict the probable occurrence of complex features in the infrared bands of at least some of the clathrates.

**Quinol Clathrates.**—As is true for other physical properties, most of the infrared spectra reported for clathrates are for the quinols. The earliest study was that of Hexter and Goldfarb,<sup>42</sup> who investigated the HCl, H<sub>2</sub>S, SO<sub>2</sub>, and CO<sub>2</sub> clathrates. The spectra of the first three are dominated by quinol absorptions so that only for the SO<sub>2</sub> clathrate could a few weak bands of the guest be seen. On the other hand, the spectrum of the CO<sub>2</sub> clathrate shows peaks at 650 and 2340 cm.<sup>-1</sup>, which are 2% and 0.4%

<sup>37</sup> M. O. Bulanin and N. D. Orlova, *Optics and Spectroscopy*, 1963, **15**, 112.

<sup>38</sup> G. E. Ewing, *J. Chem. Phys.*, 1962, **37**, 2250.

<sup>39</sup> L. J. Schoen, D. E. Mann, C. Knobler, and D. White, *J. Chem. Phys.*, 1962, **37**, 1146.

<sup>40</sup> A. Cabana, G. B. Savitsky, and D. F. Hornig, *J. Chem. Phys.*, 1963, **39**, 2942.

<sup>41</sup> R. L. Redington and D. E. Milligan, *J. Chem. Phys.*, 1963, **39**, 1276, and references therein.

<sup>42</sup> R. M. Hexter and T. D. Goldfarb, *J. Inorg. Nuclear Chem.*, 1957, **4**, 171.

lower in frequency than the corresponding band centres in the spectrum of gaseous  $\text{CO}_2$ . Similar "solvent shifts" are found in solution spectra and reflect interactions between solute and solvent. The band at  $2340\text{ cm}^{-1}$  has two maxima, each of which has a half-width of about  $5\text{ cm}^{-1}$ . Because of the narrowness of this band, it was considered to be a  $Q$  branch; therefore the rotation of the  $\text{CO}_2$  molecule in the cage appears to be considerably hindered, a finding consistent with the known distortion of the  $\beta$ -quinol lattice by the  $\text{CO}_2$  molecule.<sup>1d</sup> It should be noted that only if the barrier hindering rotation is less than  $\sim 2\text{ kcal./mole}$  will a significant fraction of the molecules have rotational energies lying above the barrier at room temperature. At lower temperatures, this figure, of course, becomes smaller. Therefore, the absence of appreciable width or  $P$  and  $R$  contours in an infrared band only sets a fairly small lower limit to the barrier.

A detailed study of the  $\text{CO}$ -quinol clathrate over a range of temperatures was made by Ball and McKean.<sup>43</sup> This clathrate is particularly suitable for the study of rotational motion in the infrared, because the  $\text{CO}$  molecule has a small moment of inertia and its vibrational frequency occurs in a part of the spectrum where quinol absorbs only weakly. The band due to  $\text{CO}$  is shown in Fig. 7 for the clathrate in an  $\text{NaBr}$  disc at several

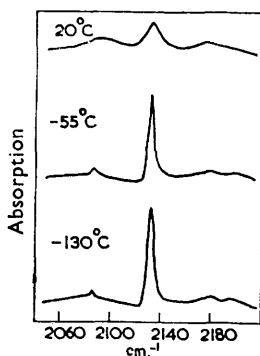


FIG. 7. Infrared spectrum of  $\text{CO}$ -quinol clathrate at  $20^\circ$ ,  $-55^\circ$ , and  $-130^\circ\text{C}$ . (Reproduced, with permission, from D. F. Ball and D. C. McKean, *Spectrochim. Acta*, 1962, **18**, 933.)

temperatures. An  $\text{NaBr}$  disc containing the krypton or nitrogen clathrates was used in the reference beam of the spectrometer to cancel out the quinol absorption.

The appearance of a strong  $Q$  branch at  $2133\text{ cm}^{-1}$  demonstrates that a considerable fraction of the molecules are in rotational energy states lying below the barrier, for if there were free rotation, the  $Q$  branch would be forbidden. Wings of weaker intensity, displaced about  $40\text{ cm}^{-1}$  from the  $Q$  branch, are also evident. Although the entire band is similar in some ways to the spectra of  $\text{CO}$  in solution, the half-widths of the  $Q$  branches

<sup>43</sup> D. F. Ball and D. C. McKean, *Spectrochim. Acta*, 1962, **18**, 933.



are significantly different in the two cases. They are 15–20 and  $\sim 30$   $\text{cm}^{-1}$  for clathrate and hydrocarbon and halogenated hydrocarbon solutions,<sup>37</sup> respectively, at room temperatures. Similarly, at 140°K the half-width of the clathrate  $Q$  branch is  $\sim 5$   $\text{cm}^{-1}$ , while at 80–90°K half-widths are 22, 18, 26, and  $\sim 30$   $\text{cm}^{-1}$  in the pure liquid, liquid argon, liquid nitrogen, and liquid oxygen, respectively.<sup>37,38</sup> Whether these differences imply greater rotational freedom for CO in solution, or whether the broadening of the  $Q$  branch in solution should be attributed to a diffusion of the rotational process, as claimed by Bulanin and Orlova,<sup>37</sup> is a question which cannot be answered at present.

A decision regarding the source(s) of the several satellites appearing in the clathrate spectra is made difficult by the existence of a number of possibilities, including combination bands with rattling and librational frequencies, and  $P$  and  $R$  branches arising from vibration-rotational transitions between states above the barrier. Ball and McKean ascribe the high-frequency satellites appearing at low temperature to rattling and librational combinations; the high temperature bands on either side of the  $Q$  branch are likely to be  $P$  and  $R$  branches, although the other possibilities cannot be ruled out. By use of the  $P$ - $R$  separation in a calculation similar to that employed by Bulanin and Orlova, the height of the barrier hindering rotation was estimated to be 720 cal./mole, in reasonable agreement with other determinations of this barrier height (see Table 2).

A solvent shift of 0.5% to lower frequency was observed for the clathrate. This is larger than most of the solvent shifts found for CO in solution and may be related to a possible quadrupole interaction in the clathrate as discussed by Staveley.<sup>26d</sup>

Quinol clathrates with HCl, DCl, SO<sub>2</sub>, CH<sub>3</sub>·OH, CH<sub>3</sub>·CN, H·CO<sub>2</sub>H, CH<sub>3</sub>F, and CH<sub>2</sub>Cl as guests and eight clathrates of Dianin's compound have recently been investigated.<sup>44</sup> In general, very few manifestations of the rotational motions of the guest molecules can be seen in the infrared spectra. Several features of the spectrum of the methanol clathrate are interesting in light of the dielectric evidence already obtained for this clathrate.<sup>31b</sup> A band at 3620  $\text{cm}^{-1}$  is clearly evident and belongs to the O-H stretching mode of monomeric CH<sub>3</sub>·OH. Comparison of the ratio of the heights of this peak and a methanol absorption at 1024  $\text{cm}^{-1}$  with the corresponding ratio for monomeric methanol in solution shows that probably all the CH<sub>3</sub>·OH molecules in the clathrate are in a non-hydrogen-bonded condition, even though the cavity presents twelve oxygen atoms each of which uses only one lone pair in hydrogen bonding.

The (O-H) monomer stretching absorption of methanol is shifted downward from  $\nu_{\text{gas}}$  by 1.8% in the clathrate and 1.3% in carbon tetrachloride solution; the respective half-widths are 41 and  $\sim 24$   $\text{cm}^{-1}$ . Since O-H stretching frequencies are known to be particularly sensitive to changes in environment, the appreciable solvent shift in the clathrate is not

<sup>44</sup> M. Davies and W. C. Child, jun., to be published.

surprising and is indicative of interactions between the O-H dipole and the atoms in the wall of the cavity. At least two causes for the considerably larger half-width in the clathrate band can be found. A greater freedom of rotation of the  $\text{CH}_3\cdot\text{OH}$  molecule in the clathrate is consistent with this observation. A second possibility relates to the variation in the force field for the molecule as it undergoes librational and rattling motions. Such motions produce varying perturbations on the O-H bond and a spread of frequencies in the observed  $\nu_{\text{O-H}}$ . This kind of explanation is supported by the findings from dielectric measurements that the activation energy for rotation is over 2 kcal./mole and that there are probably a number of equilibrium positions for the  $\text{CH}_3\cdot\text{OH}$  molecule.

The spectra of some samples of  $\text{CH}_3\text{F}$ -quinol are anomalous in that several weak bands which do not belong either to methyl fluoride or to  $\alpha$ - or  $\beta$ -quinol are evident. As the fraction of cavities occupied decreases, the intensities of these bands increase. Partially occupied  $\text{CH}_3\cdot\text{OH}$ -quinol exhibits a similar but less pronounced behaviour. The most probable explanation is that these samples suffer lattice distortions or have a crystal form different from that of  $\beta$ -quinol. A similar observation was made by Hexter and Goldfarb<sup>42</sup> for the  $\text{CO}_2$ -quinol clathrate.

**Other Clathrates.**—Only a few additional spectra have been reported, and in these instances the guest spectra are similar to the spectra of the guest in the liquid phase. Aynsley, Campbell, and Dodd<sup>45</sup> and Drago, Kwon, and Archer<sup>46</sup> have studied some clathrates of the type,  $\text{Ni}(\text{CN})_2\text{NH}_3\cdot\text{M}$ , where M, the guest, is benzene, aniline, pyrrole, or thiophen. Hart and Smith<sup>47</sup> have noted the spectra of the *p*-xylene and *p*-dichlorobenzene clathrates of tetra-(4-methyl pyridine)nickel(II) thiocyanate. Mandelcorn, Goldberg, and Hoff<sup>48</sup> observed one band of sulphur hexafluoride in the spectrum of the clathrate of this compound and Dianin's compound.

In conclusion, it appears that a complete interpretation of the infrared spectra of clathrates is not yet possible, even though the forces acting on the guest molecules are more easily predicted and analysed than are the forces operating in the liquid phase. It is to be hoped that an elucidation of the spectra of clathrates will help to disentangle the various factors affecting spectra in solution.

The author is grateful to Dr. Mansel Davies for his many helpful suggestions regarding this Review.

<sup>45</sup> E. E. Aynsley, W. A. Campbell, and R. E. Dodd, *Proc. Chem. Soc.*, 1957, 210.

<sup>46</sup> R. S. Drago, J. T. Kwon, and R. D. Archer, *J. Amer. Chem. Soc.*, 1958, **80**, 2667.

<sup>47</sup> M. I. Hart, jun., and N. O. Smith, *J. Amer. Chem. Soc.*, 1962, **84**, 1816.

<sup>48</sup> L. Mandelcorn, N. N. Goldberg, and R. E. Hoff, *J. Amer. Chem. Soc.*, 1960, **82**, 3297.