

# Hydroquinone Clathrates and the Theory of Clathrate Formation★

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**Abstract.** The model of a clathrate solid solution, taking into account directed and nondirected guest-guest interactions, has been obtained using statistical thermodynamic methods in the approximation of the mean-field type for the general case (the formation of cavities of several types and the inclusion of different kinds of guest molecules by the host). Consideration of this interaction has been shown to improve the quantitative agreement between theory and experiment. When the guest-guest interaction is considerable in the case of guest molecules of the same type a phase transition (of a gas-liquid type) of the guest component may occur in the clathrate matrix. In the case of guests of two different types, the phase transition of the guest subsystem of the liquid-liquid type may also occur within one framework at the expense of a preferable interaction among guest molecules of the same type.

We present the isothermal (20°C) section of the phase diagram of a hydroquinone – formic acid – acetonitrile system. Clathrates, forming in the binary systems (with hydroquinone) produce restricted solid solutions (of type IV, according to Roozeboom). These and other experimental data are discussed in terms of the proposed theory.

**Key words:** Clathrate, theory of clathrate formation, hydroquinone clathrate, the role of the guest-guest interaction, statistical thermodynamics.

## 1. Introduction

In 1947–1948 Powell [1, 2] opened the first page of a most fascinating branch of chemistry – that of clathrate compounds – where coordinatively saturated molecules combine in some way without forming any specific chemical bonds. Hydroquinone (Q) and its compounds have played a major part in the development of clathrate chemistry: it was on the basis of its compounds that a new principle of the organization of chemical matter was discovered [1] and that a new term ‘clathrate’ and the basic concepts of clathrate chemistry [2, 3], were introduced. The first quantitative theory of clathrate formation, suggested by van der Waals [4, 5], is based on data on the phase equilibria in hydroquinone-guest systems (mainly noble gases and their analogues).

It was the study of phase equilibria in hydroquinone – methanol – solute systems [8, 9] that gave impetus to the development of the van der Waals theory which has been undertaken by the authors of the present communication [6, 7].

★ Dedicated to Professor H. M. Powell.

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While creating his theory, van der Waals [4,5] made four assumptions:

- (a) 'The contribution of the Q molecules to the free energy is independent of the mode of occupation of the cavities.'
- (b) 'The encaged molecules are localized in the cavities and a cavity can never hold more than one solute molecule.'
- (c) 'The mutual interaction of the solute molecules is neglected.'
- (d) 'Classical statistics are valid.'

Even if assumption (b) for hydroquinone clathrates (and for a number of others as well) is strictly fulfilled, and assumption (d) holds for the cases where temperatures are not very low, then assumption (a) should not be taken for granted. However, assumption (c) seems to be the most vulnerable, considering the distances between the guest-molecule centres. For instance, in  $\beta$ -hydroquinone, the distances between guests is only a little larger than their dimensions. It is not difficult to state the value of the guest-guest interaction, which is of the order of  $1200 \text{ J mol}^{-1}$  for the clathrate with xenon. This value is greater than  $\Delta\mu = -343 \text{ J mol}^{-1}$  [5] and, evidently, must measurably affect the process of clathrate formation.

Attempts have already been made to take the guest-guest interaction into account while explaining the low temperature phase transition in hydroquinone clathrates, which has to do with a disorder of the guest molecule dipoles [10, 12]. It is shown in [13] that the introduction of a nondirected guest-guest interaction results in the alteration of the chemical potential expressions for guest molecules and the sorption isotherms, as introduced in [5]. This interaction effect on the clathrate stoichiometry has not been discussed. We [6, 7, 14] have tried to take into account the guest-guest interaction effect on the stoichiometry and have shown that it considerably influences the degree of cavity filling and, under certain conditions, it can cause the guest component to stratify within one cage structure, even at room temperature.

In this paper we discuss the general case where the clathrate framework, having  $K$  types of cavities, can include  $M$  types of guest molecules, the guest-guest interaction being taken into account, and the rest of the van der Waals assumptions being confirmed. Theoretical conclusions are compared with experimental data.

## 2. Phase Equilibria in the Hydroquinone (Q)-Acetonitrile-Formic Acid System

In his first papers Powell [1, 2] showed that, due to the existence of a rather flexible hydrogen bond system, the  $\beta$ -hydroquinone framework can make its dimensions and shape fit those of the guest molecule which is included. We do not know of any investigations of a joint inclusion of guest molecules of different types into the  $\beta$ -hydroquinone framework (except for the  $20^\circ\text{C}$  isotherm fragment for Q-CH<sub>3</sub>OH-HCl [8, 9] and the synthesis of the mixed CH<sub>3</sub>OH and SO<sub>2</sub> clathrate [2]). Investigations of such systems are interesting from the point of view of revealing the combined mutual influence of the system components.

### 2.1. EXPERIMENTAL

Hydroquinone was purified by recrystallization from degassed water solutions acidified by sulfuric acid [15]. 'Chromatographically-pure' acetonitrile was not additionally purified. After freezing out and distillation, 'pure for analysis' formic acid had m.p. =  $8.50^\circ\text{C}$ .

Hydroquinone was analyzed by titration with cerium (IV) sulfate solution in 3 M sulfuric acid using phenylanthranilic acid as indicator. Formic acid was analyzed by titration with a 0.07 M solution of NaOH.

The solubility isotherm (20°C) was studied using Schreinemakers' method [16] and preparative techniques. Special attention was paid to obtaining data corresponding to the equilibrium state of the system. When mixtures consisting of three components (in different ratios, in the presence of the solid phase) were stirred (at  $20 \pm 0.1^\circ\text{C}$ ), equilibrium was established in 5–15 days (in regions rich in acetonitrile, equilibrium is established much quicker). Analysis of the saturated solution and 'moist residue' was carried out for hydroquinone and formic acid.

Compositions of the solid phases were determined in the following way: the phase (produced during a period of 15 days) was separated and washed with small portions of ether on a glass filter, dried until the first signs of dimness were observed through a microscope, and analyzed. Using the technique described the equilibrium composition of the solid phase during its separation from the equilibrium liquid phase did not change: the figurative point of the solid solution fell on the corresponding Schreinemakers' ray.

## 2.2. RESULTS

In Table I, we summarize the data on the solubility isotherm of the Q–CH<sub>3</sub>CN–HCOOH system. The diagram of the distribution between liquid and solid phases is given in Figure 1. These data are indicative of the presence of two crystallization regions in the system: a solid solution with an acetonitrile clathrate base, and a solid solution having a clathrate with a formic acid base. Three equilibrium phases occur at the eutectic point: the saturated solution (10.79% weight Q, 70.80% weight HCOOH) and two types of crystals, belonging to different regions of the solid solutions.

To check whether the systems are in equilibrium, the following experiment was carried out: individual clathrates, obtained by saturation of the host by the gas-phase guest [30, 31], were

Table I. Solubility isotherm (20°C) in a hydroquinone-acetonitrile-formic acid system

No.	Liquid phase (weight %)			Solid phase (weight %)			Degree of filling	
	Q	HCOOH	HCOOH <sup>a</sup>	Q	HCOOH	HCOOH <sup>a</sup>	$y_1$	$y_2$
1	11.79	–	–	89.14	–	–	0.99	–
2 <sup>b</sup>	11.55	4.85	5.48	89.29	0.08	0.75	0.96	0.01
3	11.20	28.26	31.82	89.50	0.29	2.76	0.92	0.02
4	10.91	32.98	37.02	89.29	0.27	2.52	0.94	0.02
5	11.03	38.03	42.74	89.42	0.28	2.65	0.93	0.02
6	10.37	50.59	56.44	89.53	0.63	6.02	0.88	0.05
7	10.22	65.55	73.01	89.49	1.85	17.60	0.78	0.15
8	10.98	70.68	79.40	90.05	6.12	61.51	0.34	0.49
9	10.60	70.91	79.32	90.50	8.08	85.05	0.13	0.64
10	10.16	74.11	82.49	91.04	8.44	94.20	0.05	0.66
11 <sup>b</sup>	8.98	85.60	94.05	91.10	8.71	97.86	0.01	0.69
12	8.95	90.00	98.85	90.43	9.47	98.95	0.01	0.75
13	8.40	91.60	100	90.89	9.11	100	–	0.72

<sup>a</sup> Formic acid content in guest subsystem (without consideration of hydroquinone).

<sup>b</sup> Mixtures were prepared from individual clathrates (see the text).

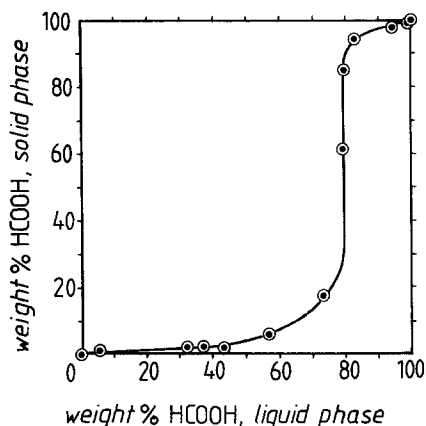


Fig. 1. The distribution diagram in the hydroquinone-acetonitrile-formic acid system (20°C).

deliberately placed under nonequilibrium conditions – a clathrate with acetonitrile (with composition  $0.99 \text{ CH}_3\text{CN} \cdot 3\text{Q}$ ) was placed in formic acid and a clathrate with formic acid  $0.73 \text{ HCOOH} \cdot 3\text{Q}$  was placed in acetonitrile. Mixtures (with the solid phase being present) were thermostated and stirred. Recurrent analyses of the liquid phase and the 'moist residue' for hydroquinone and HCOOH showed a change in the solid phase composition. Equilibrium in the mixture, rich in acetonitrile, was established in 8 days; in the other mixture it was established in 20 days. No further changes in the liquid phase compositions were observed. Analysis of the solid phases, followed by determination of the figurative points on the

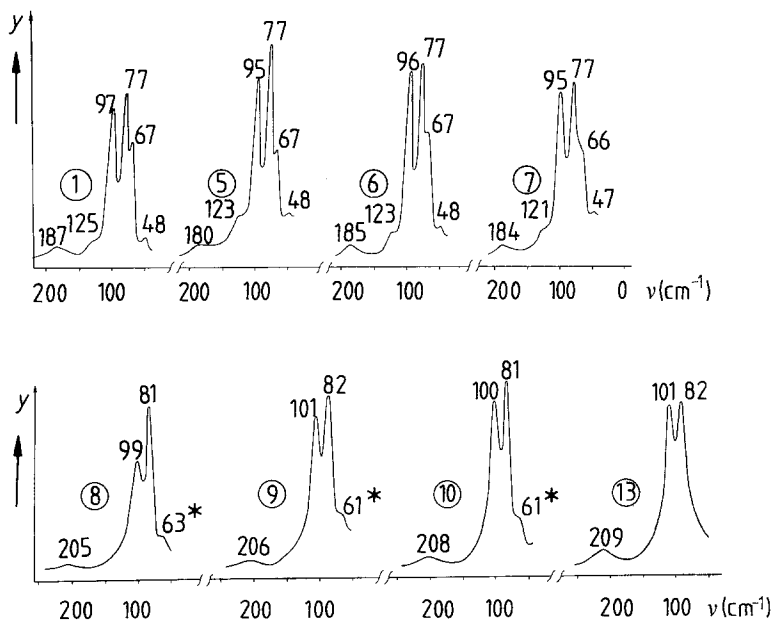


Fig. 2. The Raman spectra of individual and mixed clathrates in the hydroquinone-acetonitrile-formic acid system: the upper line is the spectra obtained on a formic acid clathrate basis (figures correspond to those in column 7 of Table I). The spectra were taken at room temperature with the exciting line 632.8 nm of a He-Ne laser.

distribution diagram, confirmed the equilibrium state of the data obtained (Nos. 2 and 11, Table I). The same procedures, using clathrates in a coarse-crystal state, delayed the establishment of equilibrium for an indefinite period.

In Figure 2, Raman spectra of the individual and mixed acetonitrile and formic acid clathrate samples are presented, and can easily be seen to divide into two types: an acetonitrile clathrate base (upper traces), and the spectra of the solid solutions having a clathrate with a formic acid base.

Thus, the solid solutions, having a  $\beta$ -hydroquinone base with the break of a continuity belonging to type IV, according to Roozeboom's classification, are observed in the Q-CH<sub>3</sub>CN-HCOOH system.

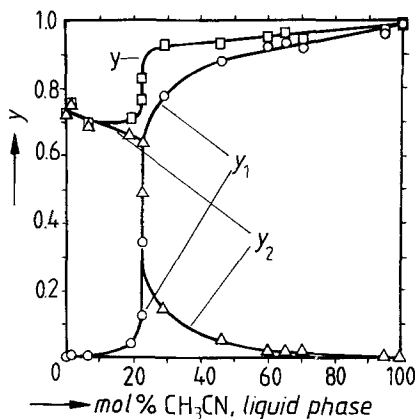


Fig. 3. The change of the total ( $y$ ) and component degrees of filling ( $y_1$  – for acetonitrile,  $y_2$  – for formic acid) in the hydroquinone-acetonitrile-formic acid system at 20°C.

Figure 3 shows the values of the degrees of filling the cavities of a  $\beta$ -hydroquinone framework for mixed clathrates in the systems concerned. When the ratio in the liquid phase is 3.4 (HCOOH: CH<sub>3</sub>CN), the degree of filling the cavities in  $\beta$ -hydroquinone is interrupted, resulting in the formation of the solid phases.

Thus, within one structural type of  $\beta$ -hydroquinone different types of solid solutions (even systems with eutectics) can be found depending on the guest molecule types. In the case of inert gases and small guest molecules uninterrupted sets of solid solutions with bigger or smaller deviations from ideality, depending on the mutual influence of the enclosure and encirclement, are most likely.

### 3. Statistical Thermodynamics of a Clathrate Phase with Guest-Guest Interaction Taken into Account and Phase Equilibria

Let us consider a system consisting of  $N_Q$  host molecules, forming a structure with  $K$ -cavity types, each of which includes one of the  $M$  guest molecule types. Guest molecules have a dipole moment which can take two opposite directions, when the molecules are in the  $t$  ( $t = 1, 2, \dots, K$ ) – type cavity. (For simplicity, we shall consider two dipole orientations, which is enough to show the characteristic feature of the directed interactions. A summary of the case where there are more than two orientations is given in [18–19].)

The free energy  $F$  of the system involved is described by [17]:

$$F = -kT \ln \sum_{\{n\}} \exp\left(\frac{-E_n}{kT}\right), \quad (1)$$

where  $E_n$  is the  $n$ -level energy (index  $n$  represents the total quantum numbers defining the state of the system).

To determine  $F$  from (1), we shall write down  $E_n$  using a number of assumptions, including van der Waals' assumptions (a), (b) and (d) above, which reflect the main properties of clathrate compounds.

### 3.1. A DESCRIPTION OF THE MODEL

Let us assume, as in [5], that the guest molecules influence only slightly the set of quantum numbers of the host framework, and corrections for the free energy, connected with this influence, are small. This means that  $E_n$  can be presented as the sum of two numbers:

$$E_n = E_m^Q + E_b \quad (2)$$

where  $E_m^Q$  is the  $m$ -level energy of the host molecule systems,  $E_b$  is the  $b$ -level energy of the guest molecule system and  $m$  and  $b$  are the totality of the quantum numbers, describing the host framework and guest molecule system, respectively.

We shall single out the part of the  $E_b$ -energy describing the guest molecule state as a whole

$$E_b = E_a + E(p, q), \quad (3)$$

where  $E_a$  can be described as the energy sum  $\varepsilon_{a_i}^t$  of individual guest molecules situated in the cavities:

$$E_a = \sum_{l=1}^M \sum_{t=1}^K \sum_{i=1}^{N_{lt}} \varepsilon_{a_i}^t \quad (4)$$

where  $N_{lt}$  is the number of  $l$ -type guest molecules situated in the  $t$ -type cavities, index  $a_i$  includes the set of quantum numbers describing the state of the  $i$ th molecule in the cavity; the host-structure effect on the  $i$ th molecule being taken into account (the kinetic energy of the molecule's progressive movement as a whole is excluded). Expression (3) is true only in the case where the surrounding guest molecules do not affect (or negligibly affect) the  $\varepsilon_{a_i}^t$  molecule internal levels.

If we assume that classical statistics can be used for describing the guest molecule state as a whole, we can determine the  $E(p, q)$  energy, where  $p$  and  $q$  stand for the set of impulses and coordinates of the guest molecules, respectively. Then  $E(p, q)$  is likely to look as follows:

$$E(p, q) = \sum_{i=1}^M \sum_{t=1}^K \sum_{i=1}^{N_{lt}} \left[ \frac{\mathbf{p}_{lit}^2}{2m_l} + W_{lt}(\mathbf{r}_{lit}) \right] + U(q), \quad (5)$$

where  $m_l$  stands for the  $l$ -type guest molecules mass;  $\mathbf{p}_{lit}$ ,  $\mathbf{r}_{lit}$ ,  $W_{lt}$  stand for the impulse, coordinate and potential energy of the interaction of the  $i$  guest molecule with the host structure respectively; and  $U(q)$  stands for the potential energy of the guest molecule interaction. Since guest molecules are restricted in motion and orientation by cavity dimensions, the change of the potential  $U(q)$  with a change of the position of the guest molecules within the cavities is insignificant, and we shall neglect it. This will allow us to replace the atom coordinates in  $U(q)$  by the coordinates of the  $q^0$  cavities' centres, which is where the

guest molecules are situated. Let us represent  $U(q^0)$  as a sum of the pair interactions of the molecules with one another:

$$U(q) \simeq U(q^0) = \sum_{li; l'j} U_{li; l'j}, \quad (6)$$

where  $U_{li; l'j}$  is the energy of the interaction of the  $l$ -type  $i$ th guest molecule situated in the  $l$ -type cavity with the  $l'$ -type  $j$ th guest molecule situated in the  $l'$  cavity. In Equation (6) it is convenient to pass from the summation of all the pairs of guest molecules to the summation of all the pairs of cavities and to single out the members connected with the dipole interaction. To do this we shall add variable  $\sigma_{li}$ , acquiring a value of 1, to each cavity if it is occupied by a guest molecule, and we shall add 0 if it is empty. We shall add variable  $S_{li}$  to each guest molecule acquiring the value 1, if the dipole is oriented in the chosen direction along the axis, common for  $l$ -type cavities and acquiring the value  $-1$  in the opposite direction. For these variables the expression looks as follows:

$$\begin{aligned} U(q^0) &\equiv U(\sigma, S) \\ &= \sum_{li; l'j} [U_{li; l'j}^{\delta} + S_{li} S_{l'j} U_{li; l'j}^D] \sigma_{li} \sigma_{l'j}, \end{aligned} \quad (7)$$

where  $U_{li; l'j}^{\delta}$  is the dispersion interaction energy;  $U_{li; l'j}^D$  is the energy of the dipole-dipole guest-guest interaction, when the  $i$ th dipole is oriented along the axis, common for all the  $l$ -type cavities and the  $j$ th dipole is oriented along the axis common for the  $l'$ -type cavities. Using expressions (3)–(5), (7), we shall substitute (2) into (1) and obtain the following expression for the free energy:

$$F = F_Q + F_1 + F_2, \quad (8)$$

where

$$F_Q = -kT \ln \sum_{\{m\}} \exp\left(\frac{-E_m^Q}{kT}\right) \quad (9)$$

is a contribution to the free energy connected with the 'empty' host framework. The part of the free energy  $F_1$  connected with the interaction between guest molecules and the host framework is expressed in the following way:

$$\begin{aligned} F_1 &= -kT \ln \prod_{l=1}^M \prod_{l'=1}^K \prod_{i=1}^{N_l} \left( \int d^3 \mathbf{p}_{li} d^3 \mathbf{r}_{li} (2\pi\hbar)^{-3} \times \right. \\ &\quad \left. \times \sum_{\{a_i\}} \exp\{[\varepsilon_{a_i}^l + p_{li}^2/2m_l + W_{li}(\mathbf{r}_{li})]/kT\} \right) \\ &\equiv kT \sum_{l=1}^M \sum_{l'=1}^K N_l \ln h_{li} = -kT \sum_{l=1}^M \sum_{l'=1}^K \sum_{i=1}^{N_l} \sigma_{li} \ln h_{li}, \end{aligned} \quad (10)$$

where the designations of [5] are used, i.e.,

$$h_{li} = 2\pi a_i^3 g_{li} \phi_{li}(T) \exp[-W_{li}(0)/kT], \quad (11)$$

$$\phi_{li} = (2\pi\hbar)^{-3} \int d^3 \mathbf{p} \sum_{\{a\}} \exp[-(\varepsilon_a^l + p^2/2m_l)/kT], \quad (12)$$

$$g_{li} = (2\pi a_i^3)^{-1} \int d^3 \mathbf{r} \exp\{-[W_{li}(\mathbf{r}) - W_{li}(0)]/kT\}, \quad (13)$$

When obtaining (8)–(13) we did not think of  $\varepsilon_a^H$ ,  $W_{it}(0)$  as depending on the orientation of the molecule dipole moment, but we consider  $W_{it}(\mathbf{r})$  to be symmetrical to the dipole moment orientation and the integration in (13) is carried out for half a cavity, in which one of the symmetrical parts of the potential is determined.  $F_1$  does not contain an entropy term, connected with the arrangement of the guest molecules in the cavities and their orientation, and which is present in  $F_2$ . In (8),  $F_2$  is a part of the free energy connected with the interaction of the guest molecules on each other, and  $F_\Gamma = F_1 + F_2$  is the contribution connected only with the guest molecules. In terms of the variables  $\sigma$  and  $S$ ,  $F_\Gamma$  can be expressed in the following way:

$$F_\Gamma = -kT \ln \sum_{\{\sigma, S\}} \exp \left\{ \sum_{it} \sigma_{it} \ln h_{it} - U(\sigma, S)/kT \right\}, \quad (14)$$

In (14) we take the sum over all the configurations  $\{\sigma, S\}$ , which are determined by giving variables  $\sigma_{it}$ ,  $S_{it}$  concrete values.

### 3.2. THE CLATHRATE FREE ENERGY IN A MEAN-FIELD APPROXIMATION

The free energy of the system consists of the  $F_Q$  part (connected with the host framework) and the  $F_\Gamma$ -part (connected with the guest molecules). Assuming that  $F_Q$  is known, we shall determine  $F_\Gamma$ . To calculate  $F_\Gamma$ , it is necessary to carry out a summation over all the configurations in (14). The way of accurately finding such a solution is known for a small number of simple models [20]. However, various approximate ways of finding such solutions have recently been developed. We employed the mean-field approximation. Although this method is the most approximate, it gives a qualitatively correct picture. The whole point is that, when we sum over the configurations  $\{\sigma, S\}$  in (14), variables  $\sigma_{it}$ ,  $S_{it}$  are substituted by the mean values  $\langle \sigma_{it} \rangle$ ,  $\langle S_{it} \rangle$ , which do not depend on the index  $i$  and are determined according to the following formulae:

$$\langle \sigma_{it} \rangle \equiv y_{it} = N_{it}/N_t, \quad (15)$$

$$\langle S_{it} \rangle \equiv S_{it} = (N_{it}^+ - N_{it}^-)/N_{it}, \quad N_{it} = N_{it}^+ + N_{it}^-, \quad (16)$$

where  $N_t$  stands for the number of  $t$ -type cavities:  $N_{it}^+$  – for the number of dipoles of the  $l$ -type molecules which are situated in the  $t$ -type cavities, directed along the axis common for these cavities and  $N_{it}^-$  stands for the number of the dipoles, oriented in the opposite direction. The variable  $y_{it}$  describes the degree of filling of the  $t$ -type cavities by the  $l$ -type guest molecules; the variable  $S_{it}$  is the order parameter of the  $t$ -type guest molecule dipoles, situated in the  $t$ -type cavities.

After the substitution in (15) and (16) is performed in the usual way, the number of states with given values  $N_{it}$  and  $N_{it}^+$ , i.e., with given values  $y_{it}$ ,  $S_{it}$ , are calculated. Summing over all the configurations  $\{\sigma, S\}$  amounts to summing over all the possible values  $N_{it}^+$ . The expression for  $F_\Gamma$  looks as follows:

$$F_\Gamma = -kT \ln \prod_t \frac{N_t!}{(N_t - \sum_l N_{lt})!} \times \\ \times \prod_l \left\{ \sum_{N_{lt}^+=0}^{N_{lt}} [(N_{lt}^+)! (N_{lt} - N_{lt}^+)!]^{-1} \times \right. \\ \left. \times \exp \left[ N_{lt} y_{lt} \left( \ln h_{lt} - \frac{1}{2kT} \sum_{l' t'} y_{l' t'} U_{l' t'}'' \right) \right] \right\}, \quad (17)$$



where

$$U_{ll'}^{u'} = U_{ll'; u'}^{\delta} + S_u S_{l't'} U_{ll'; l't'}^D,$$

$$U_{ll'; l't'}^{\delta(D)} = N_t^{-1} \sum_j U_{ll'; l't'j}^{\delta(D)} \tag{18}$$

is the energy of the dispersion (dipole-dipole) interaction of the *l*-type guest molecule situated in the *t*-type cavity, with the *l'*-type guest molecules situated in the *t'*-type cavity, in the case where their orientation along the axis is common for *t'*-type cavities, and where all *t'*-type cavities are filled by *l'*-type guest molecules.

Since the major contribution to (17) is provided by the members with big  $N_{ll}$  and  $N_{ll}^+$ , it is possible to make use of the Sterling formula and to find the maximum term in the sums over  $N_{ll}^+$ , which will define the free energy of the clathrate. With the given  $N_{ll}$  (or  $y_{ll}$ ) the values  $N_{ll}^+$  (or  $S_{ll}$ ), corresponding to this maximum term, are determined by solving the systems of nonlinear equations that are written down in the following way:

$$\ln \frac{1 + S_{ll}}{1 - S_{ll}} = - \frac{2}{kT} \sum_{l't'} y_{l't'} S_{l't'} U_{ll'; l't'}^D. \tag{19}$$

The free energy associated with the given  $y_{ll}$  is described by the expression:

$$\begin{aligned} F = F_Q - kT \sum_t N_t \sum_l y_{ll} \ln h_{ll} + \frac{1}{2} \sum_{u, l', t'} N_t y_{ll} y_{l't'} U_{ll'}^{u'} + \\ + kT \sum_t N_t \left\{ \left( 1 - \sum_l y_{ll} \right) \ln \left( 1 - \sum_l y_{ll} \right) + \right. \\ \left. + \sum_l y_{ll} \left[ \ln y_{ll} + \frac{1}{2} (1 + S_{ll}) \ln [(1 + S_{ll})/2] + \frac{1}{2} (1 - S_{ll}) \ln [(1 - S_{ll})/2] \right] \right\}, \tag{20} \end{aligned}$$

where it is necessary to substitute  $S_{ll}$  found from the system of Equations (19). The chemical potentials of the host and guest components  $\mu_Q, \mu_l^{(Q)}$  are determined by the corresponding differentiation:

$$\mu_Q = \mu_Q^0 + kT \sum_t v_t \ln \left( 1 - \sum_l y_{ll} \right) - \frac{1}{2} \sum_{u, l', t'} v_t y_{ll} y_{l't'} U_{ll'}^{u'}, \tag{21}$$

$$\mu_l^{(Q)} = -kT \ln h_{ll} + \sum_{l't'} y_{l't'} \bar{U}_{ll'}^{u'} + kT \ln \left[ y_{ll} (1 + S_{ll}) / 2 \left( 1 - \sum_{l'} y_{l't'} \right) \right], \tag{22}$$

where

$$\bar{U}_{ll'}^{u'} = U_{ll'; l't'}^{\delta} + S_{l't'} U_{ll'; l't'}^D. \tag{23}$$

and  $v_t = N_t/N_Q$  is the number of cavities of type *t* per molecule Q. Expressions (19)–(23) are the solutions of the raised problem.

3.3. CLATHRATES WITH ONE TYPE OF CAVITY AND ONE TYPE OF GUEST MOLECULE ( $K = 1$ ,  $M = 1$ ): MONOARIANT EQUILIBRIA

This particular case was discussed in [6]. In the present paper it results from general formulae (19)–(23), if indices  $l, t$  are omitted. We are concerned with the equilibrium:

$$\Gamma_{\text{gas}} + nQ_{\text{solid}}^{\alpha} \rightleftharpoons \Gamma nQ_{\text{solid}}^{\beta} \tag{24}$$

Equations describing this equilibrium (obtained by van der Waals and Platteeuw without the guest-guest interaction being taken into account) are changed and assume the following appearance:

$$\Delta\mu/vkT = \ln(1 - y) - y^2 U/2kT \equiv f(y), \tag{25}$$

$$p_{\Gamma} = \frac{kTy(1 + S)}{4\pi a^3 g(1 - y)} \frac{\phi_{\Gamma}(T)}{\phi(T)} \exp\{[W(0) + y\bar{U}]/kT\}, \tag{26}$$

where  $\Delta\mu = \mu_{Q^{\alpha}}^0 - \mu_{Q^{\beta}}^0$  ( $\mu_{Q^{\alpha}}^0, \mu_{Q^{\beta}}^0$  stands for the chemical potentials of the host component which are in the stable ( $Q^{\alpha}$ ) and the metastable clathrate ( $Q^{\beta}$ ) modifications);  $\phi(T), g, U, \bar{U}$  are described by formulae (12), (13), (18), and (23) respectively, where the indices  $l$  and  $t$  should be omitted;  $\phi_{\Gamma}(T)$  is described by formula (12), where values  $\varepsilon_a$  are the energy levels of the guest molecule which is in the gas phase;  $n = (vy)^{-1}$  stands for the stoichiometry coefficient; the order parameter of  $S$  is determined according to Equation (19) which, in this case, is, as follows:

$$\ln[(1 + S)/(1 - S)] = -2ySU^D/kT. \tag{27}$$

At constant temperature,  $S$  and  $y$  are determined by solving the nonlinear equation system (25) and (27). The values obtained for  $y$  and  $S$  allow us to determine the pressure  $p_{\Gamma}$ , under which equilibrium (24) is achieved, from Equation (26).

3.4. STOICHIOMETRY

An analysis of the solution of Equations (25) and (27) is given in detail in [7]. In the present paper, we have only quoted the major results. The dependence  $S(y)$  for various values of  $B = -U^D/kT$ , obtained by the numerical solution of Equation (27) is summarized in Figure 4. The order parameter of  $S(y)$  is identically equal to zero when  $y < y_c = B^{-1}$  and increases

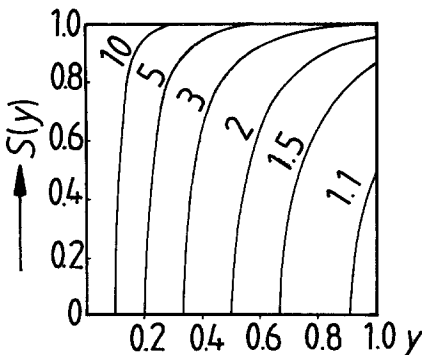


Fig. 4. The diagram of the  $S(y)$  function, when  $B$  has the values given on the curves.

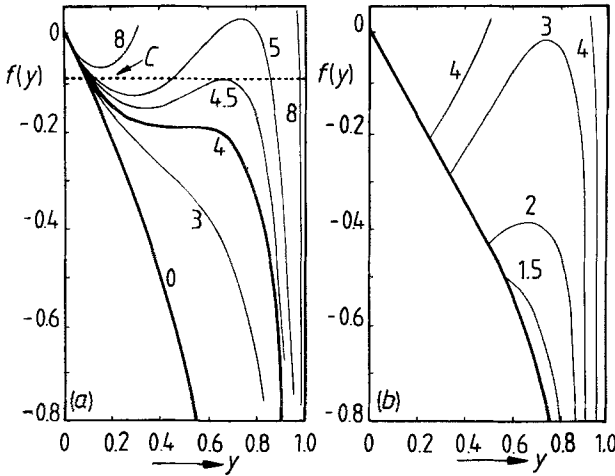


Fig. 5. The diagrams of the  $f(y)$  function: (a)  $B = 0$ , the corresponding values of  $A$  are given on the curves; (b)  $A = 2$ , the corresponding values of  $B$  are given on the curves ( $A \equiv -U^\delta/kT$ ).

sharply in the range  $y > y_C$ . The solution of Equation (25) was found as the crossing point of the function  $f(y)$ , which is the right-hand part of Equation (25), with a horizontal straight line  $C = \Delta\mu/vkT$ , as shown in Figure 5a. The function  $f(y)$  has a maximum and a minimum when  $A > 4$  and  $B = 0$ . When  $B \neq 0$  an additional maximum can appear, and a minimum value of  $f(y)$  can appear at a breakpoint, as shown in Figure 5b. If such behaviour of  $f(y)$  is observed after the maximum (related to  $A$ ), this can cause the straight line  $C$  to cross the curve  $f(y)$  three or even five times, i.e., Equation (25) can have three or five solutions, describing stable, metastable, and unstable solutions. We shall not discuss unstable solutions any further. The ranges of the values of  $A$  and  $B$ , for which only one (range I), two (II, III) and three (IV) 'physical' solutions are possible, are shown in Figure 6. In the majority of these cases, it is possible to choose temperatures which are sufficiently high, but at which the clathrate is still stable, so that  $A$  and  $B$  should be situated in range I. When temperature decreases,  $A$  and  $B$  increase and lie on the straight line  $B = AU^D/U^\delta$ . This straight line can both cross the boundary lines of ranges I and II, I and III, II and IV, III and IV and cross the point  $b$  (depending on the ratio  $U^D/U^\delta$ ). Thus, though only one solution is possible at high temperatures, additional solutions can result from a decrease of temperature. The phase with the smallest  $\mu_T$  corresponds to the stable solution. It is easy to see that the stable solution always changes in a stepwise fashion, provided that the expression

$$f^{\max} > C > f^{\min}, \tag{28}$$

where  $f^{\max}$  and  $f^{\min}$  are maximum and minimum values of the function  $f(y)$  ( $0 < y < 1$ ), holds for a certain temperature. Let us consider the case where  $U^D = 0$ . Figure 5a shows that ( $A < 4$ )  $f(y)$  has no extrema and, therefore, there is one stable solution. With a decrease of temperature, the straight line  $C$  descends (we neglect the dependence of  $\Delta\mu$  upon  $T$  near the phase transition),  $f(y)$  acquires the minimum  $f^{\min}$  and the maximum  $f^{\max}$  when  $A > 4$ . If, under these conditions, the maximum is situated below the straight line  $C$ , which is always possible, and if  $C > 0.5 - \ln 2$  (when  $A = 4$  and  $f^{\min} = f^{\max} = 0.5 - \ln 2$  in the point of a bend), then with the decrease of temperature, when  $T < T_1$ , the straight line  $C$  will cross  $f(y)$  in three points ( $T_1$  stands for the temperature at which the straight line will be contiguous to

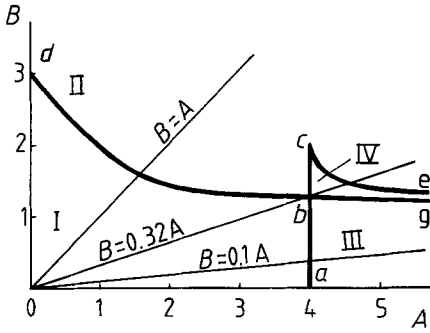


Fig. 6. The ranges of  $A$  and  $B$  values, where one (I), two (II, III) and three (IV) solutions are possible.

$f^{\max}$ ). With a further decrease of temperature, the straight line  $C$  goes down lower, and the minimum value  $f^{\min}$  goes upward, and  $C < f^{\min}$  at  $T < T_2$ ; i.e., the straight line  $C$  once again will cross  $f(y)$ . At  $T_1 < T < T_2$  one of the extreme solutions holds for the stable phase, and the other for the metastable phase. Since at  $T > T_1$ , the left-hand solution  $y < 2^{-1}$  is stable, and at  $T < T_2$  the right-hand solution is  $y > 2^{-1}$ , the right-hand solution must apparently become stable within the range  $T_1 < T < T_2$  i.e., the chemical potential  $\mu_T$  corresponding to this solution will become smaller than  $\mu_T$  of the left-hand solution; at worst, the left-hand solution will just disappear at  $T = T_2$ . We can reason analogously when we deal with the case where  $U^D \neq 0$ . Figure 7 shows the area, limited by the curve  $agb$ , in which expression (27) is correct. In this range  $f^{\max}$  and  $f^{\min}$  (depending on  $A$ ), are presented for different  $B$ . The function can have an additional maximum and minimum in the given range, limited by the broken line  $cdgb$ . However, when  $C < -0.617$ , whatever  $A$  and  $B$  may be, there can be no break in the filling of the cavities. An example can be provided by Figure 8, where the  $y(T)$  dependence is presented, the parameters  $A, B, C$  at certain temperatures being in the range  $bcgd$ . As we seen, the degree of filling undergoes two steps (jumps) at the points  $T_1$  and  $T_2$ .

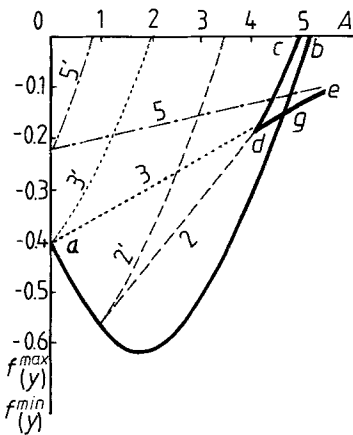


Fig. 7.  $f^{\max}$  and  $f^{\min}$  dependence upon  $A$ , when  $B$  has the values given on the curves. Lines 2', 3', 5' correspond to  $f^{\max}$ ; lines 2, 3, 5 correspond to  $f^{\min}$ . The  $f^{\max}$  dependence when  $B = 0$  is described by the line  $cd$ , and  $f^{\min}$  dependence is described by the line  $dge$ .

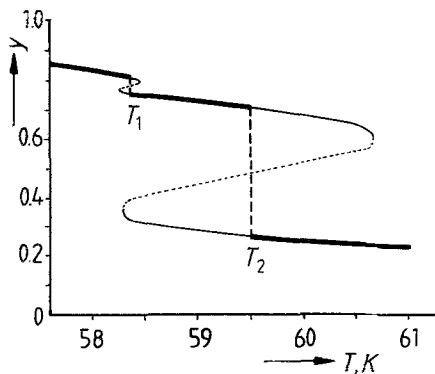


Fig. 8. The dependence of the degree of filling of the cavities upon temperature in range IV (Figure 6), when  $U^\delta = -2135 \text{ J mol}^{-1}$ ,  $U^D = -628 \text{ J mol}^{-1}$ ,  $\Delta\mu/v = -77.9 \text{ J mol}^{-1}$ ; — is used for a stable phase; - - - for a metastable phase and . . . for a labile state. The phase transition at temperature  $T_1$  and  $T_2$ .

There are one stable and two metastable degrees of filling near the temperature range  $T_1$  and there are one stable and one metastable degree near  $T_2$ . At the temperature  $T = T_2$  the phase transition representing guest component condensation in the framework takes place, and at  $T = T_1$  the degree of filling changes in a stepwise fashion, which is due to a stepwise appearance of the order parameters.

3.5. CLATHRATES WITH ONE TYPE OF CAVITY AND TWO TYPES OF GUEST MOLECULES ( $M = 2$ ,  $K = 1$ )

In this case, the clathrate thermodynamics are described by Equations (19)–(22), where we can omit index  $t$  and sum over the index and take  $M = 2$ . Let us study the gas phase with a constant composition consisting of two types of guests (the host vapour pressure being neglected) and the solid clathrate phase, including both types of guests. Let us assume that the guest molecules have no constant dipole moment, i.e.,  $U_i^D \equiv 0$  and that the gas phase is governed by the ideal gas laws. The guest-molecule chemical potential in the gas phase  $\tilde{\mu}_i^{(g)}$  ( $i = 1, 2$ ), as a function of partial pressures  $p_i^{(g)}$ , can be expressed as follows:

$$\tilde{\mu}_i^{(g)} = -kT \ln(p_i^{(g)}/kT\phi_{iR}(T)). \tag{29}$$

The general pressure  $p$  for ideal mixtures is connected with  $p_i^{(g)}$  by the equation

$$p_i^{(g)} = x_i p$$

where  $x_i$  stands for the molar portion of the  $i$ -type guest in the gas phase ( $x_1 + x_2 = 1$ ). The relevant equilibrium is described by the equations  $\mu_i^{(g)} = \tilde{\mu}_i^{(g)}$ , where  $\mu_i^{(g)}$  is determined according to Equation (22), which after transformation will look as follows:

$$x_1 p = \frac{kT}{4\pi a^3 g_1} \frac{y_1}{(1 - y_1 - y_2)} \exp\{[W_1(0) + y_1 U_{11}^\delta + y_2 U_{12}^\delta]/kT\} \equiv f_1(y_1, y_2), \tag{30}$$

$$x_2 p = \frac{kT}{4\pi a^3 g_2} \frac{y_2}{(1 - y_1 - y_2)} \exp\{[W_2(0) + y_2 U_{22}^\delta + y_1 U_{21}^\delta]/kT\} \equiv y_2 f_2(y_1, y_2). \tag{31}$$

While obtaining (30), (31) we assumed that  $\phi_{t\Gamma}(T) = \phi_t(T)$  which, as we shall see further on, does not affect the final conclusions. In (30) all the variables and parameters have the same meaning as before, but the index  $t$  ( $= 1$ ) is omitted for the sake of simplicity. At a given temperature and composition of the gas phase, the two nonlinear equations allow us to determine  $y_1(p)$  and  $y_2(p)$ . To solve the system of Equations (30) and (31), it is necessary to use numerical methods. Here we shall consider the case where  $x_2 \ll 1$ , and find the solution using the perturbation theory. We shall assume  $x_2 = 0$  in the zero approximation. From Equation (31) it follows, that  $y_2 = 0$ , and Equation (30) acquires the form of Equation (26), in which it is necessary to assume  $S = 0$ , and to use 2 instead of 4 in the denominator, and carry out the integration over the whole cavity. This is explained by the fact that, in the absence of a dipole, there is no preferred orientation of the guest-molecule in the host cavity. Equation (26), for the case, where  $U^D = 0$ , as derived in [13], is analogous to Langmuir's equation (see, e.g., [21]), describing the gas adsorption on a surface, taking account of the interaction between the adsorbed molecules. From this point of view, clathration and adsorption are quite similar, when the guest-guest interaction is absent, as has already been pointed out in [5]. The analysis of solution (30), when  $y_2 = 0$ , is analogous to the analysis of Langmuir's equation with corrections for interaction. The analysis of a similar equation for the case of adsorption is performed in [21]. A stepwise change of the degree of filling is probable, when  $p$  changes, as well as in the case discussed in Section 3.4 (when temperature changes).

In the following approximation, Equations (30) and (31) can be represented by expanding the functions  $f_1, f_2$  in powers of  $y_2$ , retaining the term  $\sim y_2$ . If we further designate the solution obtained in a zero approximation,  $\tilde{y}_1(p)$ , Equations (30) and (31) will have the following form:

$$p(1 - x_2) = f_1(y_1, 0) + y_2 f_1(\tilde{y}_1(p), 0)[(1 - \tilde{y}_1(p))^{-1} + U_{12}^{\delta}/kT], \quad (30')$$

$$y_2 = x_2 f_2^{-1}(\tilde{y}_1(p), 0)p. \quad (31')$$

After the substitution of (31') into (30') we obtain the equation with respect to  $y_1$ . Obviously, the nature of the solution  $y_1(p)$  remains the same, since corrections in (30') are small, i.e., under a certain pressure  $p_0$  both  $y_1(p)$  and  $y_2(p)$ , as follows from (31'), change in a stepwise fashion. When  $p = p_0$ , the monovariant equilibrium concerned becomes a nonvariant equilibrium in which, in addition to the gas phase, there exist two clathrate phases whose degrees of filling  $y_1, y_2$  are different within the same framework.

#### 4. Discussion of the Results

As has already been pointed out in [14], hydroquinone clathrates are convenient objects for model evaluation and quantitative calculations, due to their nature and to the amount of knowledge available about them. In spite of the values of their guest-guest interaction energy  $\mathcal{E} = U/2$  being significantly smaller than those of other clathrates (e.g., in the xenon hydroquinone clathrate  $\mathcal{E} = 1200 \text{ J mol}^{-1}$ , and in the xenon gas hydrate with structure I  $\mathcal{E} = -2650 \text{ J mol}^{-1}$ ), hydroquinone clathrates are an excellent illustration of these interaction effects on stoichiometry, because the degree of filling in monovariant equilibrium (24) is far from being 1, which is not true of hydrates.

##### 4.1. THE ESTIMATION OF THE GUEST-GUEST INTERACTION AND THE DEGREE OF FILLING

To calculate the guest-guest interaction energy we shall use the Lennard-Jones potential [22]:

$$\mathcal{E} = 2\varepsilon[(\sigma/R)^{12} g_{12} - (\sigma/R)^6 g_6], \quad g_{12} = \sum_j' p_{ij}^{-12}, \quad g_6 = \sum_j' p_{ij}^{-6}, \quad (32)$$

where  $p_{ij}R$  stands for the distance between the atom  $i$  concerned and any other atom  $j$ , expressed as the distance between the nearest neighbours  $R$ ;  $\varepsilon$  and  $\sigma$  stand for the parameters of the Lennard–Jones potential. Parameters  $g_{12}$  and  $g_6$ , are defined by the host structure for  $\alpha$  and  $\beta$ -hydroquinone:  $g_{12}^\alpha = 2.0005$ ,  $g_6^\alpha = 2.0379$ ,  $g_{12}^\beta = 2.0041$ ,  $g_6^\beta = 2.2350$  (the following parameters of elementary cells are used: for  $\alpha$ -hydroquinone  $a = 38.3$  and  $c = 5.6$  [28, 29], for  $\beta$ -hydroquinone  $a = 16.5$  and  $c = 5.5$  Å [1, 2]). The values of the guest-guest interaction energy of the parameters concerned for the simplest guest molecules are also listed in Table II.

Table II. Guest-guest interaction energy  $\mathcal{E} = U/2$  in  $\alpha$ - and  $\beta$ -hydroquinone clathrate frameworks, calculated according to Lennard–Jones rules [22].

Guest	$\sigma$ (Å)	$\varepsilon/R$ (K)	$-\mathcal{E}_\alpha$ (kJ mol <sup>-1</sup> )	$-\mathcal{E}_\beta$ (kJ mol <sup>-1</sup> )
Ar	3.40	119.8	0.20	0.24
Kr	3.60	171	0.38	0.46
Xe	4.10	221	0.98	1.19
CH <sub>4</sub>	3.82	148	0.45	0.55
SO <sub>2</sub>	4.29	252	1.38	1.68

In spite of the guest-guest interaction being small (of the order of several per cent of the guest-host interaction) its influence on stoichiometry is rather significant. Thus, for xenon at 55 and 80°C the degrees of filling under experimental conditions (when equilibrium (24) takes place) are 0.39 and 0.37 [23], when the Xe–Xe interaction and the solubility of xenon in  $\alpha$ -hydroquinone [14] (0.386 and 0.359) is taken into account. However, the van der Waals model gives values of 0.314 and 0.296 [5]. If the guest solubility in  $\alpha$ -hydroquinone is taken into account and the Xe–Xe interaction is not, the degrees of filling will be 0.350 and 0.330. This means that consideration of the guest-guest interaction improves the agreement between calculation and experiment. In [14] we cite a similar comparison for some other guests.

To our mind, consideration of the guest solubility in  $\alpha$ -hydroquinone (when the equilibrium between clathrate and gas and  $\alpha$ -hydroquinone is monovariant) as well as the guest-guest interaction allowed us to correctly determine the value of  $\Delta\mu = -326 \pm 10$  J mol<sup>-1</sup> [14], which, as it should be in the case of the nondistorted  $\beta$ -framework, becomes independent (within the limits of error) of the guest nature.

#### 4.2. ON THE PROBABILITY OF A STEPWISE CHANGE IN THE DEGREE OF FILLING OF THE CAVITIES

When studying a fragment of the hydroquinone-methanol-*n*-propanol diagram at 25°C (see Figure 9a), the clathrate composition at the eutectic point was found [5] to correspond to a 47% filling of the  $\beta$ -framework cavity. Using the data obtained by Powell [24], who determined the composition of a clathrate in the hydroquinone–methanol binary system, van der Waals and Platteeuw [5] have compiled a picture of the phase equilibrium whose scheme is presented in Figure 9a. A more detailed investigation of Q–CH<sub>3</sub>OH–third component (LiCl, LiBr, HCl, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr, (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr) ternary phase diagrams has shown that the hydroquinone with methanol clathrate has an almost constant composition  $(0.99 \pm 0.01)\text{CH}_3\text{OH} \cdot 3\text{Q}$ , which does not depend on the guest concentration in the equilibrium liquid phase [8, 9]. The compound corresponding to a cavity degree of filling of 0.47, obtained by van der Waals and Platteeuw, was observed over the whole range of its existence,

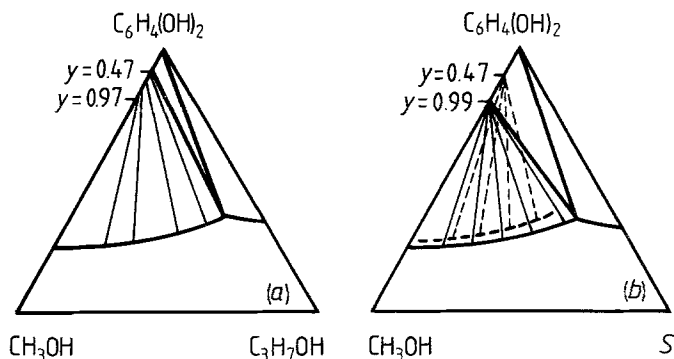


Fig. 9. Schematic picture of possible phase equilibria in the hydroquinone-methanol-*n*-propanol system: (a) the variant, suggested by van der Waals [5], (b) variant corresponding to data [8,9], including experiment [5].

but only as a metastable phase. If the degree of filling exceeding 0.34 could be explained by host framework distortion (i.e., if assumption (1) was not observed), as was the case with the acetonitrile clathrate [5], the existence of two phases with one and the same host component structure [5] would cause insuperable difficulties with the ideal solid solution clathrate theory. The distortion of the framework in the case of the hydroquinone methanol clathrate is not large (for the methanol clathrate  $a = 16.56$ ,  $c = 5.55$  Å, for the empty framework  $a = 16.61$ ,  $c = 5.48$  Å [26], while for the acetonitrile clathrate  $a = 16.00$ ,  $c = 6.248$  [26]). Thus, we observe a picture that is qualitatively described by the situation, represented in Figure 8, near either temperature  $T_1$  or  $T_2$ . The application of our model to the hydroquinone clathrates in the cluster approximation yielded a good quantitative description of this experiment [18]. Experimental results cited in Section 2.2 are explained qualitatively by Equations (30) and (31), if we study the composition rather than  $p$ . In reality the picture is more complex since, during the transition from a phase with one degree of filling to that with another, the  $\beta$ -framework is also distorted, which is shown by the scheme in Figure 10. It should be noted that the framework distortion causes a kind of additional attraction for the guests of one type, whilst filling the empty cavities by the molecules of another type results in a defective structure. For clathrates of  $\text{CH}_3\text{OH}$  and  $\text{HCl}$ , the difference between the elementary cell parameters is small, and it seems that only a significant difference in the guest-guest interaction can explain

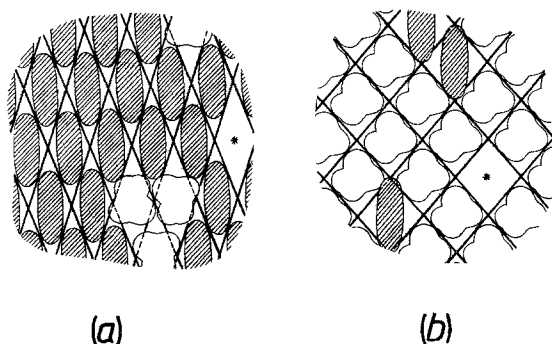


Fig. 10. Schematic picture of the guest molecule arrangement in mixed crystals of the acetonitrile clathrate (a) and formic acid clathrate (b) basis. The cavities which are not occupied by the guests are designated by asterisks.



the fact that when a methanol-hydroquinone clathrate is crystallized from an HCl solution in methanol (up to 29% wt.) the HCl content in the solid phase is too small to be detected [8,9].

The analysis described above shows that, just as in the case of guests of one type, where the phase transition of the guest (of the liquid-gas type) in a framework matrix is possible, in the case with guests of two types the phase transition of the guest subsystem of the liquid-liquid type within the same framework is also possible, at the cost of a preferable interaction between guest molecules of the same kind. At lower temperatures, phase transitions of the type of the polymorphous guest-component transformation within the framework can be expected. To describe such transitions it is necessary to use the methods of quasi-chemical or cluster approximation.

The formation of clathrates with a different stoichiometry is possible at the cost of both the stepwise change of the filling degree within the same framework (which has already been discussed in the present paper) and the replacement of frameworks (which is characteristic of water systems [27]). The equations cited here make possible a description of this case, too: this latter, however, goes beyond the scope of this communication.

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