

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

### On the stoichiometry of clathrates

Yuri A. Dyadin<sup>a</sup>

<sup>a</sup> Institute of Inorganic Chemistry, Russian Academy of Sciences, Novosibirsk, Russia

To cite this Article Dyadin, Yuri A.(1995) 'On the stoichiometry of clathrates', *Supramolecular Chemistry*, 6: 1, 59 – 70

To link to this Article: DOI: 10.1080/10610279508032520

URL: <http://dx.doi.org/10.1080/10610279508032520>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# On the stoichiometry of clathrates

YURI A. DYADIN\*

*Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, 630090 Novosibirsk, Russia*

(Received August 5, 1994)

## INTRODUCTION

There are two aspects to this problem: stoichiometry determined by the framework structure and changes in composition of clathrate phase due to the possibility of the partial filling of the cavities in it. In the simplest case structural stoichiometry is defined as the ratio of the number of the host molecules to the number of cavities in a unit cell but more complicated cases are not difficult to understand either.

As for clathrate phases of variable composition which is due to different filling degrees of the cavities (we named this kind of clathrate phases “iskhoric solutions” from the Greek  $\epsilon\iota\sigma\chi\omega\rho\acute{\omega}$ , which means “to penetrate”) there are two versions we are going to discuss. Iskhoric solutions of the first type (IS-I) form on the basis of a stable (under conditions concerned) crystalline host modification. The filling degree of the cavities ( $y$ ) is within  $0 \leq y < 1$ . IS-II form on the basis of a metastable crystalline host modification. In this case  $y_0 < y < 1$  and  $0 < y_0$ .

However, there are many clathrates (some hydrates, clathrates of urea and thiourea and so on) whose composition remains constant when conditions change in a wide range. The existence of these compounds is possible only if the host framework is absolutely unstable in the absence of the guest.

The transformation from one type of the stoichiometric interrelations to another is illustrated by means of the summarized P,T,X-phase diagram of the guest—host system.

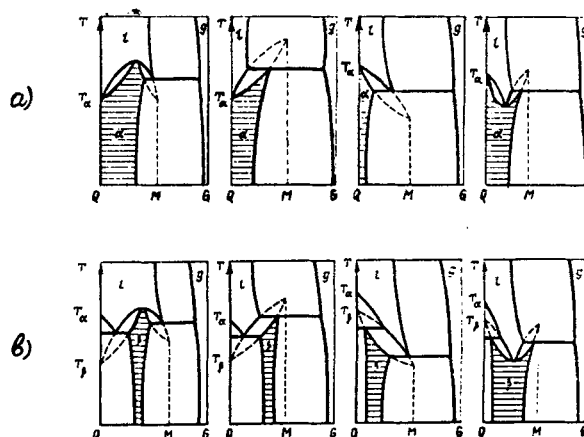
Two more types of clathrate solid solutions are possible in three (and more) component systems: *alloxenic solutions* (resulting from the substitution of one guest for another) and *allokirc solutions* (the substitutions of one host for another).

## ISKHORIC SOLUTIONS OF THE FIRST TYPE

In this case the initial stable crystal modification of the host has cavities of molecular size and can, therefore, accommodate guest molecules. It is not typical for molecular crystals because quite large vacant cavities result in a high energy loss but this occurs when molecules are connected with one another by directed bonds (for example, H-bonds) or are of complex, uneven shape, or both. The composition of the clathrate phase is changing from a pure host to a host with a certain amount of the guest continuously (Fig. 1,a), i.e. *it is not a new chemical individual*. Let us consider some real systems of this type.

### The hydroquinone—noble gas systems

In the  $\alpha$ -hydroquinone structure the cavities (free diameter is 4.35Å) are similar to the ones in  $\beta$ -quinol ( $d=4.48$ ) [1]. When  $\alpha$ -hydroquinone ( $\alpha$ -Q) dissolves relatively small guest molecules, which do not distort its structure (for example, Ar, Xe or  $H_2S$ ), we can see the increase of its melting point with the increase of the guest content,



**Figure 1** Some kinds of the phase diagrams with iskhoric solutions of the first (a) and second type (b); M is “imaginary” compound composition. *l* is liquid, *g* is gas,  $\alpha$  is solid solution on the basis of the initial stable host modification,  $\beta$  is solid solution on the basis of the metastable host modification.

\*To whom correspondence should be addressed.

i.e. these guests stabilize the  $\alpha$ -modification additionally.  $\alpha$ -Hydroquinone melts at  $173.3^\circ$ , while its phase with Xe dissolved in it melts at  $174^\circ\text{C}$  (Fig. 2). The composition corresponding to the full occupation of the cavities in  $\alpha$ -Q is not reached (the vertical dotted line at the composition Xe:18Q) as at higher guest concentrations  $\beta$ -quinol containing six times more cavities is more stable (classic clathrates).

Other heavy noble gases (beginning from Ar) behave similarly as well as many gaseous guests ( $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  [2],  $\text{SO}_2$  [3]). As for the light noble gases they are not able to stabilize the  $\beta$ -quinol phase but they are dissolved in  $\alpha$ -Q [2], forming the solid solutions concerned only.

### The water—helium (hydrogen, neon) systems

Common ice (ice Ih) is rather a porous structure with an extremely low packing coefficient ( $k=0.43$  [4]). However, in spite of this, the cavities in this structure are very small and they can accommodate He, Ne and  $\text{H}_2$  molecules only (Fig. 3). It has been found that the ice Ih phase melting point is considerably higher in the presence of helium than that of ice without gas (at 2.1 kbar it is higher  $10.3^\circ\text{C}$  [5], Fig. 4, *a*). This clearly indicates that the solubility of helium in ice is rather high and exceeds its solubility in liquid water (Fig. 4, *b*). If the pressure is lower than 2.1 kbar (the triple point "ice Ih-ice III-liquid water"), as it can be seen in Figs. 4–5 we deal with IS-I.

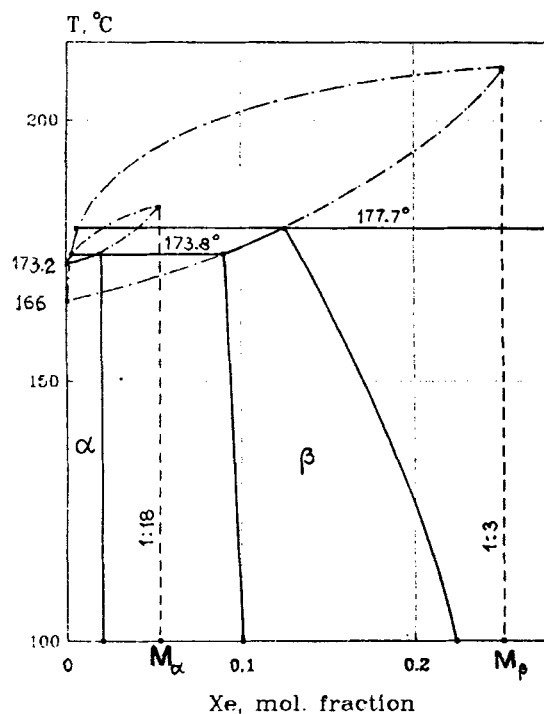
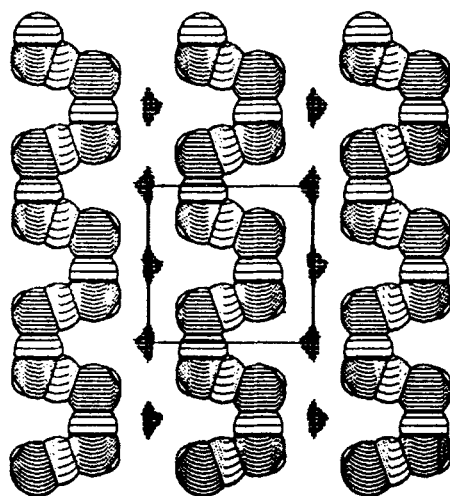
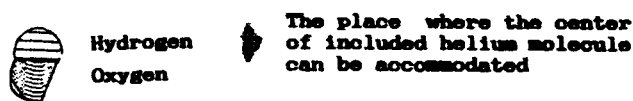
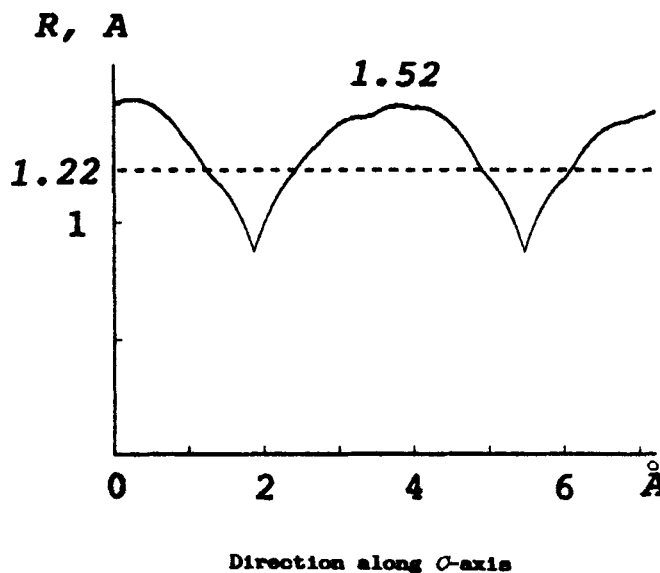


Figure 2 Isobaric section (10 bar) in the Xe—hydroquinone (Q) system. The structural composition 1:18 for  $\alpha$ -Q (imaginary compound  $M_\alpha$ ) and 1:3 for  $\beta$ -Q (imaginary compound  $M_\beta$ ) is not reached (dotted lines).

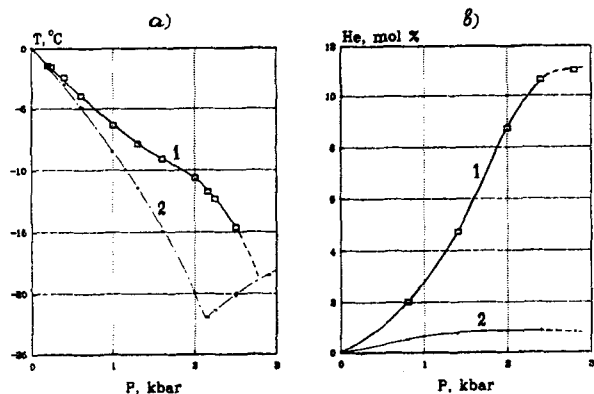


*a)*



*b)*

Figure 3 The dimensions and the shape of the channels in the (1,1,0)-section (*a*) of the ice Ih structure. The maximum radius of a sphere inscribed in the channel along the C-axis (hydrogen disorder neglected) (*b*).



**Figure 4** The pressure dependence of *a*) the decomposition temperature of the solid solution of helium (1), in ice Ih, melting points of ices (2) and *b*) the compositions of helium solutions in ice (1) and water (2) at the monovariant  $l, \alpha, g$ -equilibrium (they were calculated on the basis of Fig. 4(a) by V. I. Belevantsev and R. K. Udachin).

We notice once again that in this type of systems *no new chemical individual is formed*. In some cases the guest inclusion leads to the destabilization of the host framework. This is possible if the dimensions of the guest molecules are big enough and their inclusion leads to some distortion of the host framework but I would not like to discuss this problem in detail here.

## ISKHORIC SOLUTIONS OF THE SECOND TYPE

This is a classical case: the host component has a metastable modification with the cavities of molecular size, which becomes stable above a certain value of the filling degree of the cavities ( $y_0 < y$  and  $0 < y_0$ ). Some types of phase equilibria in the binary guest-host systems are presented in Fig. 1, b. We can see a new phase, *a new chemical individual of berthollide type*\*

### Classic hydroquinone clathrates

Let us again look at Figure 2, at the part of the diagram, where the existence area of the  $\beta$ -phase is shown. Neither the  $\beta$ -modification of hydroquinone with completely vacant cavities nor the compounds  $Xe \cdot 3Q$  (with completely occupied cavities) on whose basis this phase is formed are stable under conditions concerned, and according to Kurnakov they are the *imaginary modification and imaginary compound*, respectively. The vast majority of  $\beta$ -hydroquinone clathrates are the phases of berthollide type.

\*A *berthollide* is a solid phase of variable composition, solid solution of two (or more) compounds that are not stable, i.e. they do not have their own stable crystallization field, but only a part of the solid solution crystallization field between them is stable. Kurnakov [6] called such compounds "imaginary compounds".

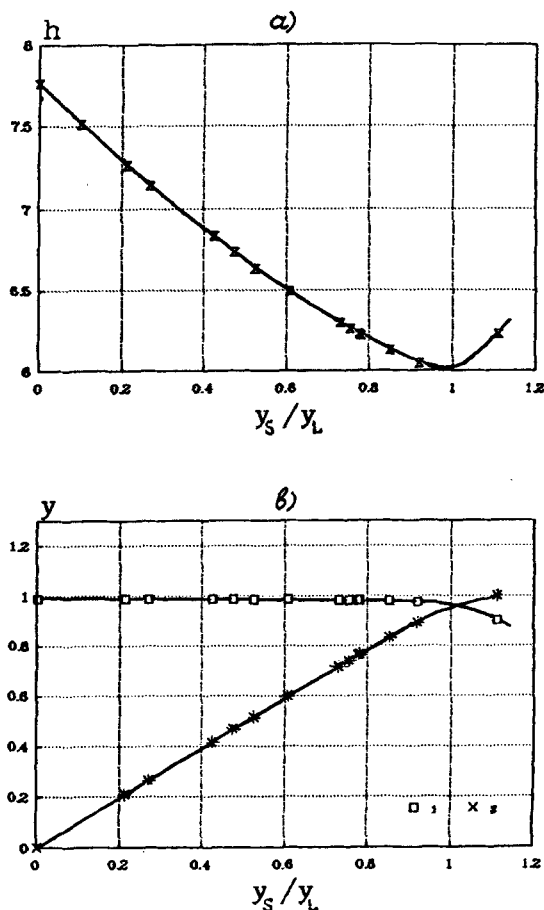
## Clathrate hydrates

A more complicated case takes place in water systems. There are two kinds of cavities in the water clathrate frameworks which are occupied by the guest molecules in different ways: the big cavities must be occupied almost completely whereas the small (dodecahedral) ones can be completely vacant. Figure 5 drawn on the basis of the data of Collins, Ratcliffe and Ripmeester [7] illustrates that.

### Structural Stoichiometry

We have already said that in the simplest case the structural hydrate number is defined as the ratio of the number of host molecules to the number of the cavities in a unit cell. If in the process of the hydrophylic-hydrophobic inclusion of the guest particles some water molecules are displaced this should be necessarily taken into account. For example, the formula

$$h = \frac{V - CZ - nZ}{Z}, \quad (1)$$



**Figure 5** The guest molecule cage occupancy ratio dependence of the hydrate numbers  $h$  of the CS-I hydrates (*a*) and the filling degree (*b*) of the T- (1) and D-cavities (2).

(where  $C$  is the anion charge,  $n$  is the number of water molecules displaced by one anion,  $Z$  is the number of formula salt units in the unit cell) is true for the hydrates of peralkylonium salts. In Table I some structural data on the water frameworks needed for that are given.

#### Filling of the Small and Large Cavities

We could see that the filling degree of large cavities is equal or almost equal to one. Therefore, the variable hydrate composition can be due to the variable filling degree of the small cavities only, which can be seen in

**Table 1** Structural information on idealized water clathrate frameworks

type, space group	cell parameters (A), $\rho$ (g cm <sup>-3</sup> )	unit cell formula	structural hydrate number	examples of guest molecules
<b>Ice frameworks</b>				
hexagonal Ih, $P6_3/mmc$	$a$ 4.48 $c$ 7.31 $\rho$ 0.917	$2C*4H_2O^*$	2	H <sub>2</sub> , He, Ne
cubic Ic	$a$ 6.35 $\rho$ 0.92	$8C*8H_2O$	1	H <sub>2</sub> , He, Ne
$F\bar{4}3m$ trigonal ice II, $R\bar{3}$	$a$ 7.78 $\alpha$ 113.1° $\rho$ 1.15	$2C*12H_2O$	6	H <sub>2</sub> , He, Ne
<b>Frameworks containing D-cavity</b>				
cubic I, CS-I, $Pm\bar{3}n$	$a$ 12.0 $\rho$ 0.796	$6T*2D*46H_2O^{\&}$	$7\frac{2}{3}^a$ $5\frac{3}{4}^b$	cyclo-C <sub>3</sub> H <sub>6</sub> , PF <sub>6</sub> , Xe, CH <sub>4</sub> , H <sub>2</sub> S, BF <sub>3</sub>
cubic II, CS-II, $Fd\bar{3}m$	$a$ 17.1 $\rho$ 0.812	$8H*16D*136H_2O$	$17^a$ $5\frac{2}{3}^b$	SF <sub>6</sub> , THF, CCl <sub>4</sub> , Ar, Kr,
hexagonal I, HS-I, $P6/mmm$	$a$ 12.4 $c$ 12.5 $\rho$ 0.719	$2P*2T*3D*4OH_2O$	$10^a$ $38^c$	Br <sub>2</sub> (?), i-Am <sub>4</sub> NF
hexagonal II, HS-II, $P6_3/mmc$	$a$ 12.1 $c$ 19.7 $\rho$ 0.812	$4H*8D*68H_2O$	$17^a$ $15^d$	(CH <sub>3</sub> ) <sub>2</sub> CHNH <sub>2</sub> , (CH <sub>3</sub> ) <sub>4</sub> NF + (C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NF
hexagonal III, HS-III, $P6/mmm$	$a$ 12.3 $c$ 10.2 $\rho$ 0.768	$E*2D'*3D*34H_2O$	$34^c$	cyclo-CH <sub>3</sub> C <sub>6</sub> H <sub>11</sub> + H <sub>2</sub> S
tetragonal I, TS-I, $P4_2/mnm$	$a$ 23.5 $c$ 12.3 $\rho$ 0.757	$4P*16T*10D*172H_2O$	$8.6^a$ $32.4^c$	Br <sub>2</sub> , Bu <sub>4</sub> NBr, Bu <sub>4</sub> NF
Orthorombic, RS, $Pbam$	$a$ 23.5 $b$ 19.9 $c$ 12.1 $\rho$ 0.782	$4P*4T*4H*14D*148H_2O$	$12^{1a}$ $34.5^c$	Br <sub>2</sub> (?), Bu <sub>3</sub> PO
<b>Frameworks without D-cavity</b>				
tetragonal II, TS-II, $I4/mcm$	$a$ 15.4 $c$ 12.0 $\rho$ 0.709	$8P*4d*68H_2O$	$8.5^a$ $7.5^c$ $32^c$	(CH <sub>3</sub> ) <sub>4</sub> NOH, i-Am <sub>4</sub> PBr
tetragonal III, TS-III	$a$ 16.9 $c$ 17.1 $\rho$ 0.710	$16P'*4Q*116H_2O^5$	$7.25$ $27$	- i-Am <sub>4</sub> NF
cubic $I\bar{4}3d$	$a$ 18.8 $\rho$ 0.701	$16A*8Q*156H_2O^5$	$9.75$	(CH <sub>3</sub> ) <sub>3</sub> CHNH <sub>2</sub>
cubic $Im\bar{3}m$	$a$ 7.68 $\rho$ 0.793	$2B*12H_2O^5$	$6$ $5^c$	HPF <sub>6</sub> , (CH <sub>3</sub> ) <sub>4</sub> NOH

<sup>a</sup>) C is a wide part of channel (cavity) in the ice structures where the guest molecules (H<sub>2</sub>, He, Ne) are able to arrange.

<sup>&</sup>) d, D, T, P, H, E is decahedron (4<sup>2</sup>5<sup>8</sup>), dodeca- (5<sup>12</sup>), tetradeca- (5<sup>12</sup>6<sup>2</sup>), pentadeca- (5<sup>12</sup>6<sup>3</sup>), hexadeca- (5<sup>12</sup>6<sup>4</sup>) and eicohedron (5<sup>12</sup>6<sup>8</sup>) cavity, respectively.

<sup>5</sup>) Q, B, P', A is 8-hedron (4<sup>4</sup>5<sup>4</sup>), 14-hedron, 15-hedron (4<sup>2</sup>5<sup>9</sup>6<sup>3</sup>7<sup>1</sup>) and 17-hedron, respectively. Q-cages are very small to arrange any guest molecules,

<sup>a</sup>) large cavities are occupied only,

<sup>b</sup>) all cavity kinds are occupied,

<sup>c</sup>) see formula (1),

<sup>d</sup>) (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> arranges in H-cavity, (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N<sup>+</sup> occupies D<sub>4</sub>-cavity, F<sup>-</sup> includes by hydrophilic way and this double hydrate formula is (CH<sub>3</sub>)<sub>4</sub>NF\*O.5(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NF\*15H<sub>2</sub>O,

<sup>e</sup>) double hydrate can exist only, D' is 12-hedron (4<sup>3</sup>5<sup>6</sup>6<sup>3</sup>) cage.

Figure 6 where the solid solution field of the ethylene oxide CS-I hydrate is shown [8]. This field is within the limits of the hydrate numbers 5.75–7.67. The same picture for other hydrates of the CS-I is shown in Figure 7 [9]. One can see the hydrate numbers are in the range from 5.8 to 7.8, i.e. (within the experimental error) in the interval allowed by different filling degree of the dodecahedral cavities. At present the most reliable value of the maximum hydrate number for the CS-I hydrates is 7.76 and  $y=0.987$  [10]. But I would like to note that the increasing accuracy of the experiments resulted in the decrease of the upper limit from 8.47 [11] to 7.76 [10] which is quite close to the ideal value 7.67.

As for hydrates of CS-II it was shown that this framework was stable if the large cavities were fully occupied [12]. Therefore, with the large guest molecules the hydrates of this structure are the constant composition compounds.

### CLATHRATE CONSTANT COMPOSITION COMPOUNDS

Now it is universally believed that all clathrates are solid solutions of the guest component in a host framework which is metastable in the absence of the guest component. In our terms this means that only isohoric solutions of the second type are assigned to clathrates. Clathrates with constant composition are looked upon rather as nonsense. That is why this section requires more profound and detailed reasoning.

### Hydrates

As we have already seen if the guest molecules are able to be arranged in the large cavities of the water frameworks, the structure is stable only when all large cavities are occupied, i.e. the hydrate composition is equal to the structural one.

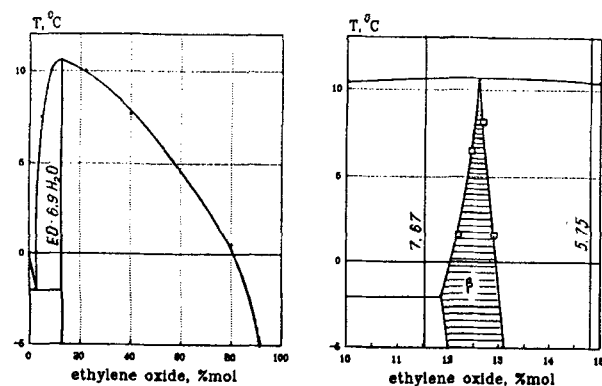


Figure 6 The fusibility diagram of the ethylene oxide—water system, □—is the experimental data of Glew and Rath [8].

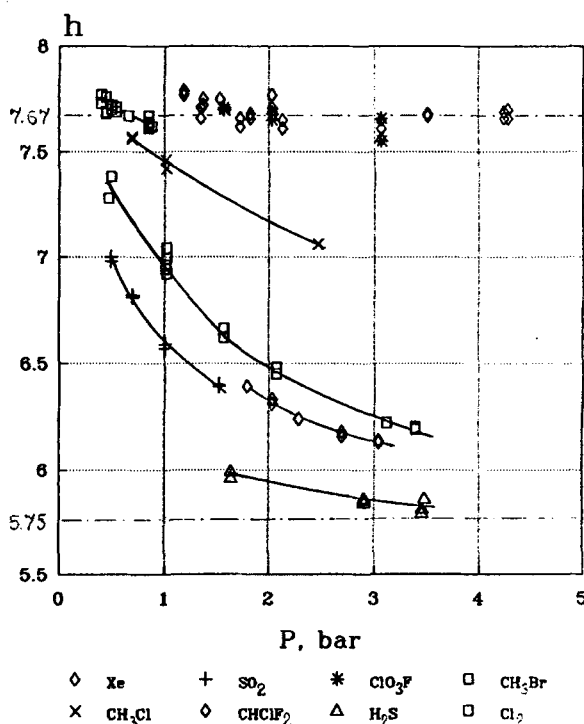


Figure 7 The pressure dependence of the compositions of the CS-I hydrates in the gas—water—hydrate equilibria at 0 °C [9].

### Hydrates of Peralkylonium Salts

The water—tetrabutylammonium bromide system (TBAB) was studied in detail. In addition to the fusibility diagram of the binary system considered 15 isotherms in 9 three-component systems water—TBAB—indifferent component were studied by the Schreinemakers technique and 280 Schreinemakers' rays were analyzed. It turned out that four polyhydrates were formed in this system\*: the hydrate numbers are 24, 26, 32.4 and 36, i.e. their compositions are very close and change from 96.0 to 97.3 mol % of water (Table 2). In Figure 8 the phase diagram of water—TBAB system and one of the isotherms of the tricomponent systems are shown. I would like to concentrate your attention on: *first*, all the 4 polyhydrates forming in the system have (within the experimental error) constant composition everywhere over the stability range in the temperature interval studied (-2 - +10°C), *second*, comparison of the obtained composition with the structural one indicates that the structure is stable if all the large cavities are completely occupied.

A similar picture is observed for other systems with peralkylonium salts (alkyl = butyl or isoamyl). Figure 9 shows the fusibility diagram of the water—i-AmBu<sub>3</sub>NBr

\*In addition to the enumerated polyhydrates, di- and trihydrates crystallize in the system [15], but we will not consider them here in detail.

**Table 2** Compositions of tetrabutylammonium bromide polyhydrates defined by Schreinemakers' method in the  $Bu_4NBr-H_2O-A$  systems (A is a third indifferent Component)

Hydrate	A	$T, ^\circ C$	$n$	$h_a$	$h_w$	A: $Bu_4NBr$
Bu <sub>4</sub> NBr*36H <sub>2</sub> O	CH <sub>3</sub> OH	0	4	36,07(37)	35,75(23)	0,006(74)
	C <sub>2</sub> H <sub>5</sub> OH	0	7	35,86(26)	35,8(19)	0,02(18)
	C <sub>3</sub> H <sub>7</sub> OH	0	5	35,97(61)	35,89(92)	0,013(22)
	C <sub>4</sub> H <sub>9</sub> OH	0	9	36,24(15)	36,60(16)	0,007(11)
	CH <sub>3</sub> COOH	-4	6	36,00(12)	35,64(20)	-0,012(10)
	CH <sub>3</sub> COOH	0	20	35,88(10)	35,96(7)	0,008 (7)
	CH <sub>3</sub> COOH	-2	13	36,09(18)	36,36(12)	-0,000(10)
	C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	0	14	36,05 (8)	35,92(16)	-0,007(17)
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0	5	36,56(39)	38,14(70)	0,015(10)
	HBr	0	9	36,77(80)	35,68(37)	-0,062(35)
	NH <sub>4</sub> Br	0	13	35,95(31)	35,60(31)	0,003(22)
Bu <sub>4</sub> NBr*32H <sub>2</sub> O	NH <sub>4</sub> Br	8	4	36,66(35)	37,4(13)	-0,007 (9)
	CH <sub>3</sub> COOH	8	5	31,85(22)	31,47(11)	-0,008 (3)
	C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	0	24	31,92 (4)	31,88(4)	-0,007 (8)
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0	12	31,91 (6)	31,89(8)	-0,001(10)
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	10	6	32,16(80)	31,08(31)	0,030(18)
Bu <sub>4</sub> NBr*26H <sub>2</sub> O	NH <sub>4</sub> Br	8	4	31,24(42)	31,4(16)	-0,004(17)
	CH <sub>3</sub> COOH	10	12	25,89 (8)	25,93(8)	-0,001 (1)
	CH <sub>3</sub> COOH	8	15	25,99(13)	25,99(6)	0,015 (4)
	CH <sub>3</sub> COOH	4	9	25,98(10)	26,12(14)	0,021(17)
	CH <sub>3</sub> COOH	-2	6	26,15(22)	26,47(9)	-0,047 (9)
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	10	9	26,15 (9)	26,26(6)	-0,009 (5)
Bu <sub>4</sub> NBr*24H <sub>2</sub> O	NH <sub>4</sub> Br	8	8	26,77(43)	25,94(5)	0,021 (9)
	CH <sub>3</sub> OH	0	8	23,81(39)	23,91(21)	0,19(23)
	C <sub>2</sub> H <sub>5</sub> OH	0	4	24,12(25)	24,10(22)	-0,102(37)
	C <sub>3</sub> H <sub>7</sub> OH	0	9	24,22(35)	22,83(23)	0,120(54)
	C <sub>4</sub> H <sub>9</sub> OH	0	5	24,00(14)	23,25(21)	0,055(24)
	CH <sub>3</sub> COOH	10	10	23,99(11)	24,07(10)	0,001 (1)
	CH <sub>3</sub> COOH	8	2	23,35(53)	24,71	
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	10	6	23,86(11)	23,66(10)	
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	0	2	24,03(29)	20,97	
	HBr	0	4	24,00(42)	23,84(28)	0,035(25)
	NH <sub>4</sub> Br	0	8	23,55(27)	23,41(40)	-0,034(33)
	NH <sub>4</sub> Br	8	2	23,39(76)	24,12(19)	

$n$  - the number of the Schreinemakers' rays,

$h_a$  - the mean arithmetical hydrate number defined by intersecting the Schreinemakers' rays with the axis of the binary  $Bu_4NBr - H_2O$  system,

$h_w$  - the mean weighed hydrate number defined by intersecting the Schreinemakers' rays with each other.

system and one of the isotherms (14°) of the ternary system with triethylamine as a third component.

#### Bromine Hydrates

Bromine as well as TBAB forms four polyhydrates. Three of them had been observed by other authors before we did this (see the bibliography in reference [14]): Lowig, Alekseev, Roozeboom and Harris (*decahydrate*), Giran, D'Ans and Hofer, Mulders, Allen and Jeffrey (*octahydrate*), Zernike, Cady (*heptahydrate*). It is very curious each of them believed that only the hydrate discovered by him or her existed in the system. We succeeded in obtaining these three hydrates and one more with twelve water molecules. All the known hydrate compositions are shown in Figure 10. All of them are the constant composition compounds within the mentioned accuracy (Table 3).

#### Hydrates on the Basis of Ice Ic and Ice II Frameworks

Thanks to the kindness of Professor J. Ripmeester I learned about the very interesting investigation of the

American scientists W. Vos, L. Finger, R. Hemley and Ho-kwahg Mao [16] on the formation of the hydrogen hydrates under high pressures. It was found that the hydrate  $H_2*6H_2O$  (hydrogen molecules are arranged in the ice II cavities) is stable up to about 26 kbar and 115°C, after that the hydrate  $H_2*H_2O$ , constructed on the ice Ic framework, becomes stable. Undoubtedly, under these extreme conditions it is quite impossible to assume that ice II and, the more so as ice Ic, can exist with vacant cavities (theoretical conclusions show that ice Ic is absolutely unstable even at a temperature of 0 K at a pressure of 19.5 kbar [17]). These are compounds of constant composition although it will be difficult to demonstrate.

#### Urea and thiourea clathrates

The analogous picture is observed in the urea (thiourea)—guest systems. The classic urea clathrates with normal paraffins are the constant composition compounds in the whole stability area at the indicated

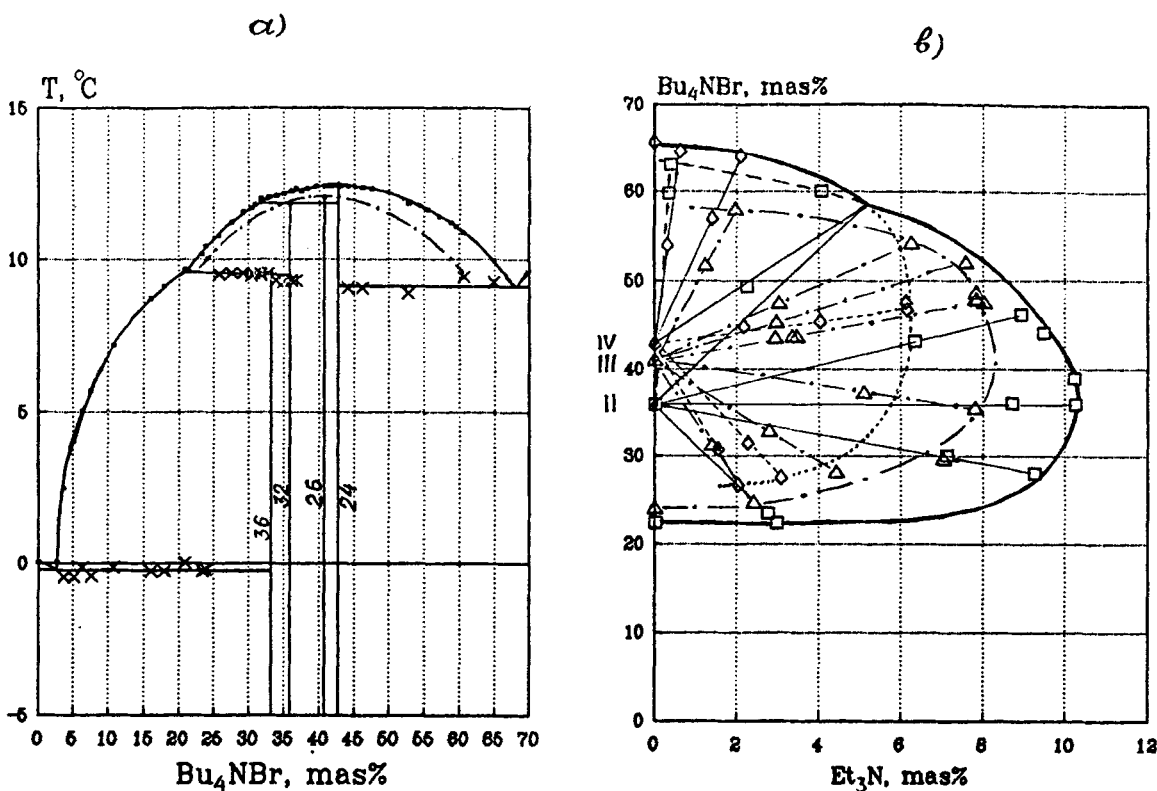


Figure 8 The fusibility diagram of the  $\text{Bu}_4\text{NBr}-\text{H}_2\text{O}$  system (a) and isotherm ( $10^\circ\text{C}$ ) in the  $\text{Bu}_4\text{NBr}-\text{H}_2\text{O}-\text{Et}_3\text{N}$  system in the clathrate formation field (b).  $\square$ ,  $\triangle$ ,  $\diamond$  stands for the data on the crystallization fields of the  $\text{Bu}_4\text{NBr}\cdot 32\text{H}_2\text{O}$  (II),  $\text{Bu}_4\text{NBr}\cdot 26\text{H}_2\text{O}$  (III) and  $\text{Bu}_4\text{NBr}\cdot 24\text{H}_2\text{O}$  (IV) hydrates, respectively. Metastable parts of the solubility branches are observed vividly and one can see the hydrate-III has no stable solubility branch.

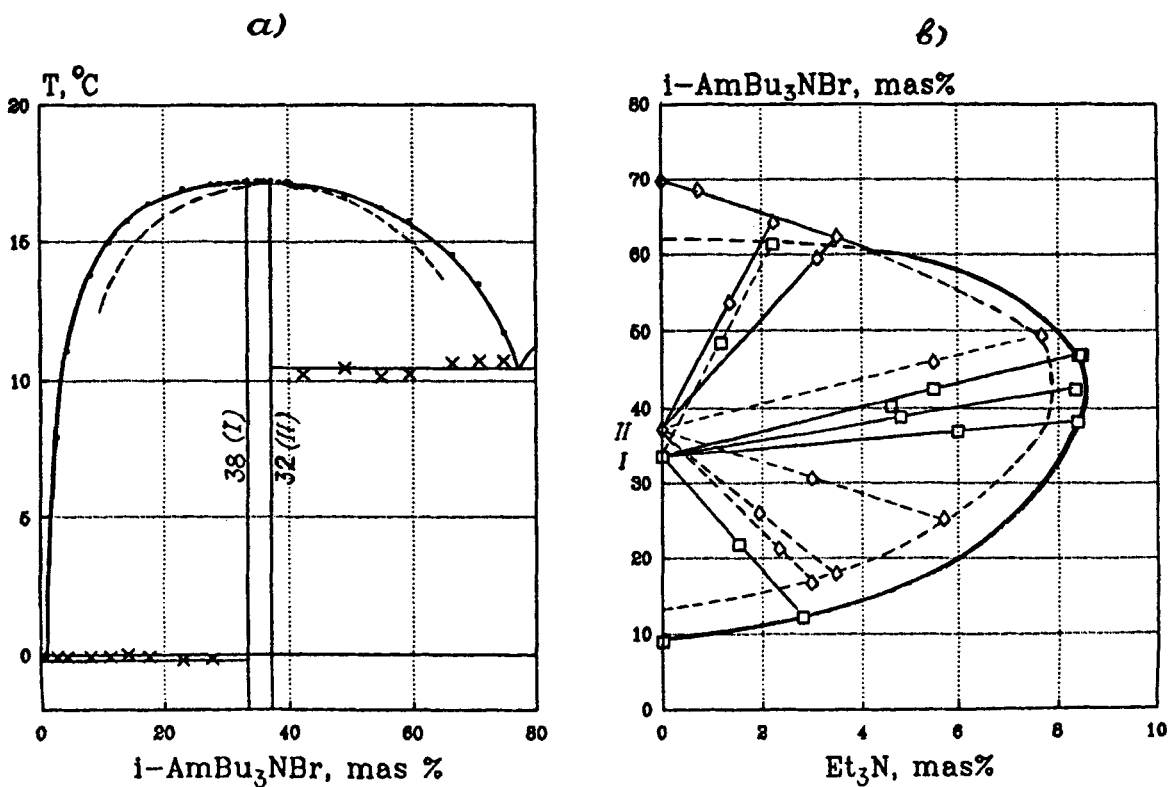


Figure 9 The fusibility diagram of the  $i\text{-AmBu}_3\text{NBr}-\text{H}_2\text{O}$  system (a) and isotherm ( $14^\circ\text{C}$ ) in the  $i\text{-AmBu}_3\text{NBr}-\text{H}_2\text{O}-\text{Et}_3\text{N}$  system in the clathrate formation field (b).  $\square$ ,  $\diamond$ , stand for the data on the crystallization fields of the  $i\text{-AmBu}_3\text{NBr}\cdot 38\text{H}_2\text{O}$  (I) and  $i\text{-AmBu}_3\text{NBr}\cdot 32\text{H}_2\text{O}$  (II) hydrates, respectively.



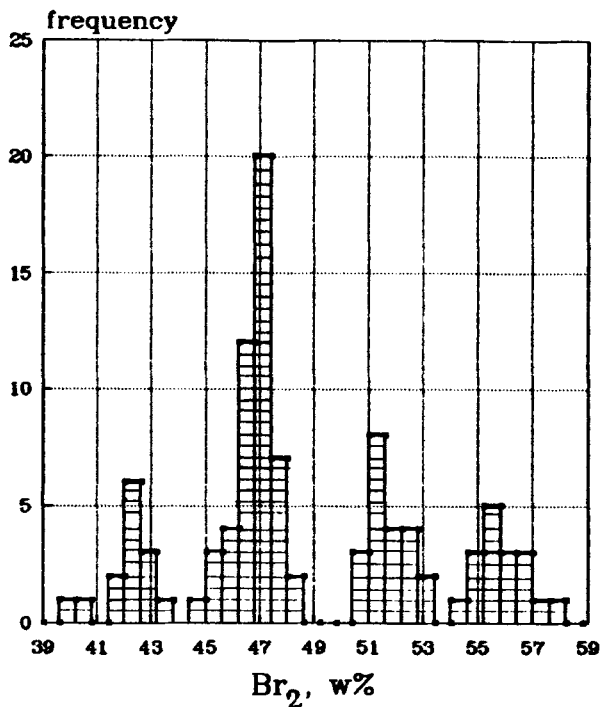


Figure 10 The histogram of the compositions of bromine hydrates.

temperature [18]. The composition corresponds to the closest packing of the guest molecules in the channels of the urea clathrate framework. The hollow clathrate framework density is very low for a solid: the density ratio of the urea clathrate network to the common initial urea is only 0.69. Of course, such structures can not be stable without the guest "support". This conclusion is still more true of thiourea clathrates in which the above mentioned ratio is only 0.60. In Figure 11 the ternary guest—urea (thiourea)—indifferent component systems are given [17, 18]. In either case the forming compound composition is constant in the whole stability area and corresponds to the closest packing of the guest molecules in the channels. It is clear that such situation can only be observed if the host network is not stable at all without the guest support.

#### Schaeffer's clathrates

Now we will consider quite an interesting case where the host molecules themselves are unstable out of the clathrate or, in other words, these host molecules can exist

Table 3 The arithmetical ( $h_a$ ) and mean-weighted ( $h_w$ ) compositions of bromine hydrates [14]

Hydrate	$h_a$	$h_w$	the number of data, $n$
$\text{Br}_2 \cdot 12\text{H}_2\text{O}$	12.02(6)	12.03(5)	12
$\text{Br}_2 \cdot 10\text{H}_2\text{O}$	10.10(5)	10.00(1)	50
$\text{Br}_2 \cdot 8.6\text{H}_2\text{O}$	8.28(6)	8.32(4)	21
$\text{Br}_2 \cdot 7\text{H}_2\text{O}$	7.02(7)	6.98(6)	17

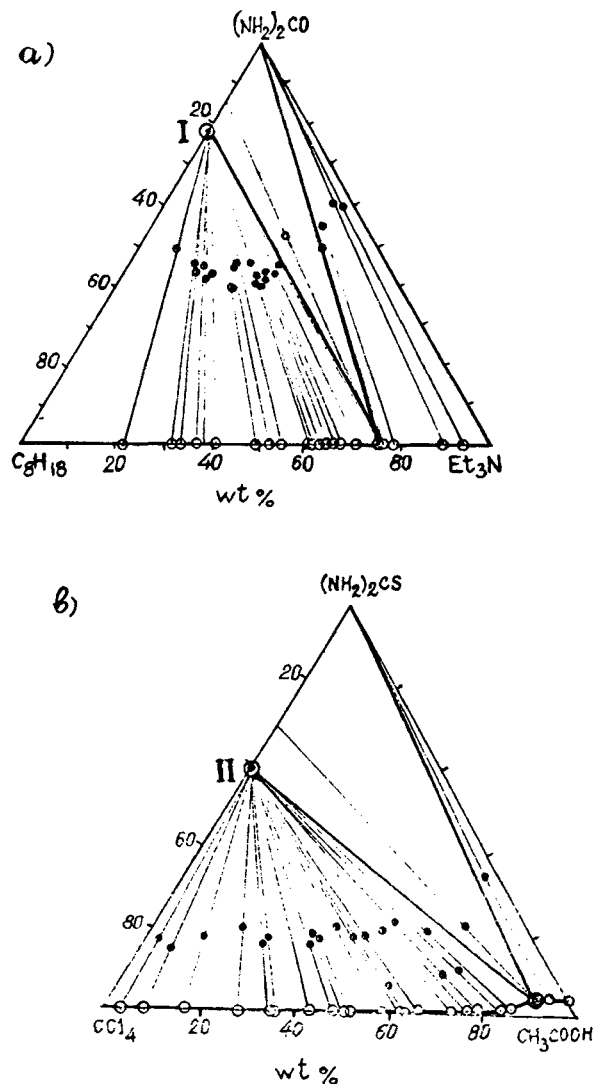


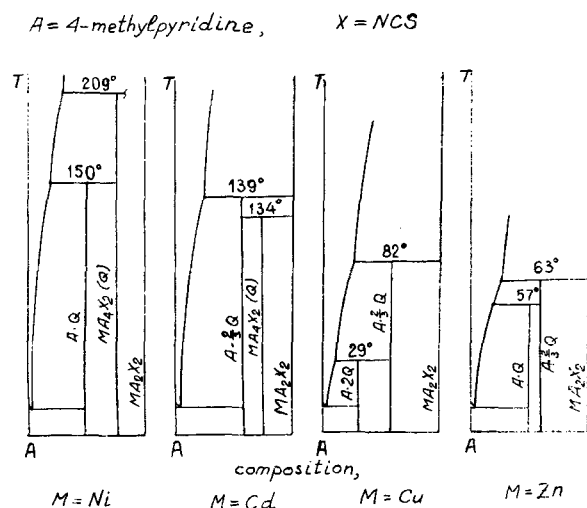
Figure 11 Isothermic sections ( $20^\circ\text{C}$ ) in the ternary *a*) urea—n-octane—triethylamine system, I is  $\text{C}_8\text{H}_{18} \cdot (6.71 \pm 0.01)(\text{NH}_2)_2\text{CO}$  (*a*) and in *b*) thiourea—carbon tetrachloride—acetic acid system, II is  $\text{CCl}_4 \cdot (2.86 \pm 0.02)(\text{NH}_2)_2\text{CS}$ .

only in a clathrate structure [20]. We illustrate this case with the Schaeffer's clathrates. The complexes, which are the hosts, with the chemical formula  $[\text{MA}_4\text{X}_2]$  are known to be able to form clathrates  $[\text{MA}_4\text{X}_2] \cdot m\text{G}$  (more often than not, M is the transitional metal (II), A is 4-methylpyridine, X is isothiocyanate, G is the guest,  $m$  changes from  $\frac{2}{3}$  to 2). The nickel complex clathrates have been studied in sufficient detail. Its host molecules of the mentioned composition are quite stable independent of the guest presence: it is stable up to about  $209^\circ\text{C}$  whereas its clathrate  $[\text{NiA}_4\text{X}_2] \cdot \text{A}$  (here G is A, i.e. 4-methylpyridine) decomposes at about  $150.5^\circ\text{C}$ . But this picture is not always observed. If M is Cd the host complex decomposes into the clathrate  $[\text{CdA}_4\text{X}_2] \cdot \frac{2}{3}\text{A}$  and the bipicoline complex  $[\text{CdA}_2\text{X}_2]$  at  $134^\circ$ , i.e. about

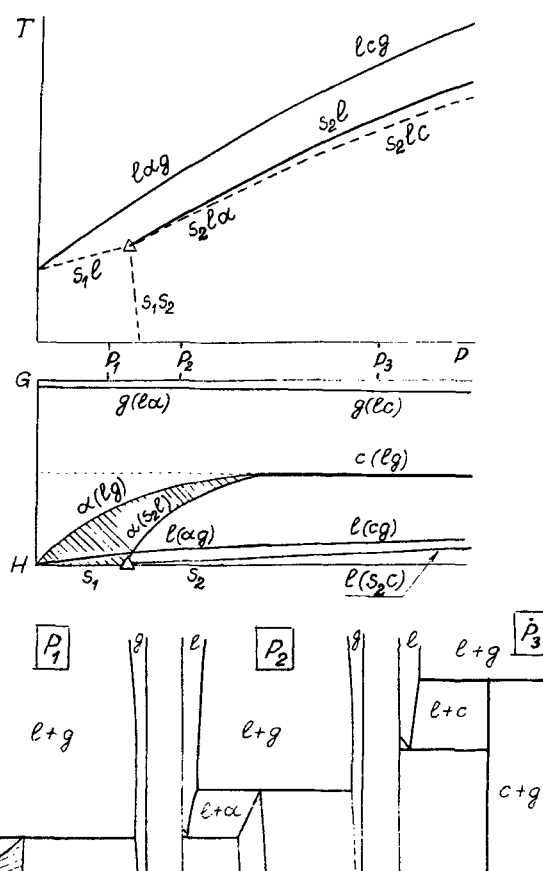
5 degrees below the point at which the clathrate itself does (Fig. 12). In other words in the interval 134–139, 2° the host molecule  $[CdA_4X_2]$  is not able to create its own phase and can exist as a noncovalent support of the guest molecules only. If M is Cu or Zn, the host molecules do not exist at all in the whole investigated field. Thus, in this case the instability of the host framework is due to the instability of the host molecules themselves.

### THE SUMMARIZED P,T,X-DIAGRAM

In Figure 13 the summarized P,T,X-phase diagram where the transformation from iskhoric solutions of the first type to constant composition compound via solid solution of the second type is shown. Indeed, if the initial host modification has cavities of molecular size, it will sooner or later become metastable under pressure and on further pressure increase it must become absolutely unstable (as is the case with, for example, ice Ic, as we mentioned above). The binary system water—hydrogen is very vivid. Being based on reference [16] and our data (Fig. 14) I have tried to reproduce the P,T-phase diagram of this system schematically (Fig. 15). The uncertainty caused by the ambiguity of the experimental data for the pressure range 2.3–3 kbar results in two versions of phase equilibria presented in Fig. 15 (b and c). For our purposes these differences are not critical. Of course, this actual system is more intricate than the summarized one shown above. However the transition on the basis of ice II structure from the iskhoric solutions of the first type to the constant composition compound ( $H_2 \cdot 6H_2O$ ) via the iskhoric solutions of the second type is seen distinctly enough (Figure 16).



**Figure 12** Schematic phase diagram in the binary  $MA_4X_2$ —A systems, where M is Ni, Cd, Cu and Zn, A is 4-methylpyridine, X is  $NCS^-$ .



**Figure 13** Summarized P,T,X-phase diagram in a host—guest system. a) P,T-projection, b) P,X-projection, c-e) characteristic isobaric sections.  $\alpha$ , l, g is solid solution, liquid and gas, respectively,  $s_1$ , c is solid host modifications and clathrate constant composition compound, respectively

### ALLOXENIC AND ALLOKIRIC SOLUTIONS

The fact that there is an extensive group of constant composition clathrate compounds with absolutely unstable frameworks has made it reasonable to distinguish two more types of clathrate solid solutions in three- (and more) component systems.

#### Alloxic solutions

Alloxic (from the Greek words  $\alpha\lambda\lambda\omicron\zeta$  another, different and  $\xi\epsilon\nu\omicron\zeta$  guest) solutions are solid clathrate solutions in which one guest is substituted for another. This is the most widely distributed kind of clathrate solutions. Since the guest subsystem is more mobile than the host one, and its properties under usual conditions resemble those of liquids or even gases, the formation of solutions in it occurs almost as readily as it does in liquids or gases. In Figure 17, a alloxic solutions in the thiourea (host)— $CCl_4$  (guest-1)—cyclo- $C_6H_{12}$  (guest-2) are shown. Both of these guests are similar in their clathrate formation ability, therefore they form almost an ideal

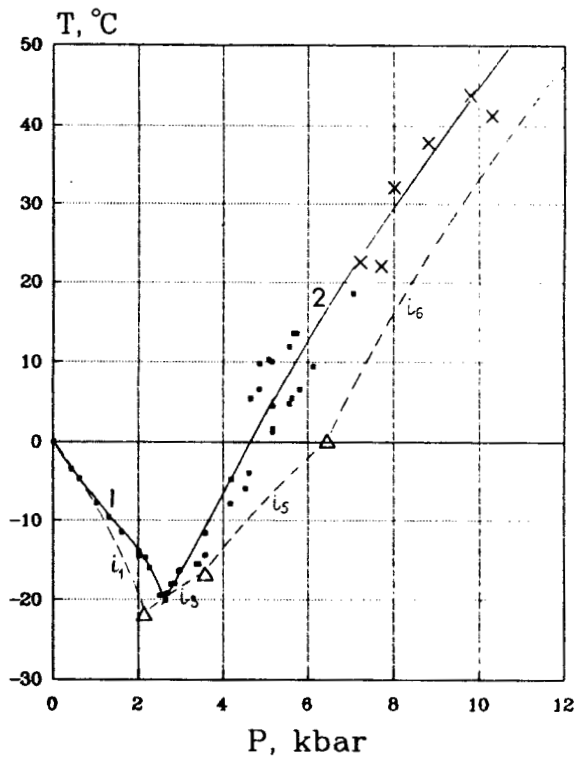


Figure 14 The decomposition curves of the hydrogen solid solutions in ice Ih (1) and in ice II (2); × are data of references [16].

solution. If the ability of the guests to form clathrates is different, the alloxic solutions have large deviation from ideality (Figure 17, b).

**Alloxic solutions**

Alloxic (αυριος means “host”) solutions are solid clathrate solutions in which one host is substituted for another. Such solutions are more difficult to form because the restrictions on the formation of solid substitution solutions by molecular crystals are extended over to a “rigid” host subsystem, too. They are more rare than the alloxic solutions. Especially this has to do with water systems since no molecules are close to the water molecule in size and ability to form the H-bonds and, therefore, neither ice, nor clathrate hydrates form this kind of solid solutions with a homogeneity region anywhere to be appreciable. An interesting exception is ammonium fluoride which can form solid solutions in a wide range, substituting two water molecules for its ion pair [19]: in the cubic hydrate  $Bu_4NF \cdot 28.6H_2O$  framework, under conditions depicted in Figure 18, the content of the water molecules is only about 30%.

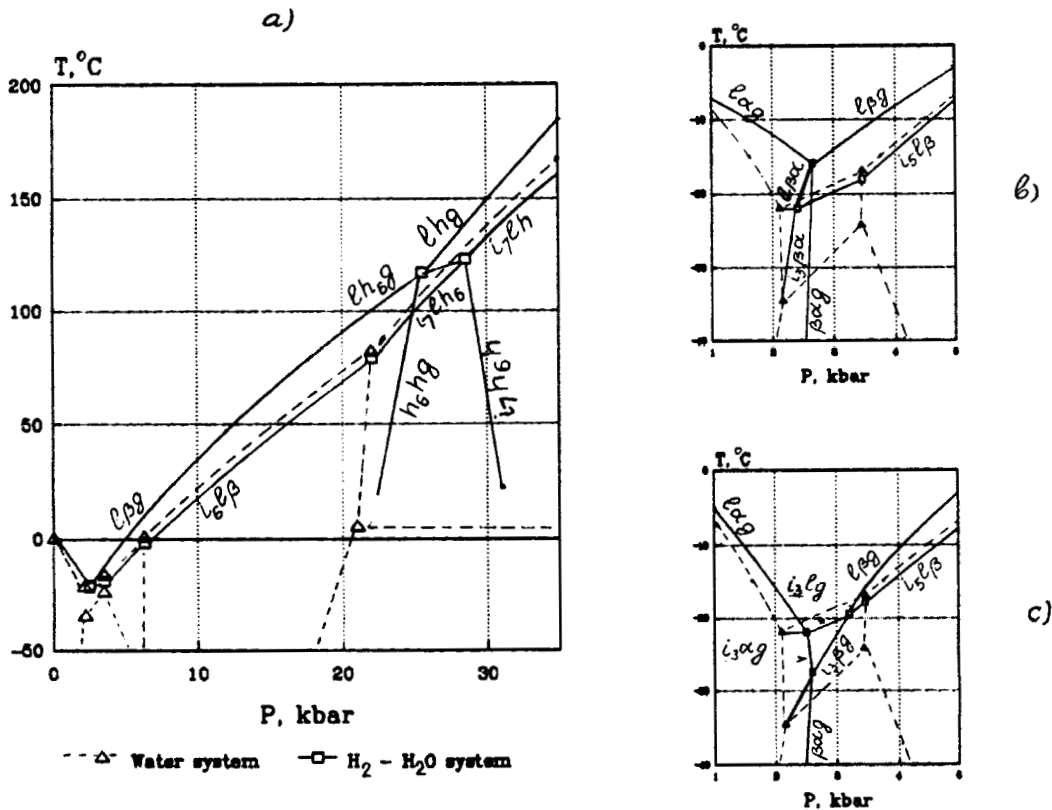


Figure 15 P,T-Phase diagram of the  $H_2-H_2O$  system (a) (see Fig. 14 and [16]).  $h_6$  and  $h$  are the  $H_2 \cdot 6H_2O$  and  $H_2 \cdot H_2O$  hydrates, respectively,  $l$  is the water rich liquid,  $g$  is the hydrogen rich fluid,  $i_3, i_5$  and  $i_6$  is the corresponding ice modifications,  $\alpha$  and  $\beta$  is solid solutions on the basis of ice Ih and ice II, respectively. b) and c) are possible versions of the phase equilibria in the range from 2 to 3.5 kbar.



## REFERENCES

- 1 V.R. Belosludov, Yu. A. Dyadin, G.N. Chekhova and S.I. Fadeev, *J. Inclusion Phenom.*, **1**, 251 **1984**.
- 2 H.M. Powell, *Non-stoichiometric compounds*. Ed. L. Mandelcorn, Academic Press, N-Y, London **1964**; Russian translation, Khimia, Moskva, 398 **1971**.
- 3 G.N. Chekhova, T.M. Polyanskaja, Yu. A. Dyadin and V.I. Alekseev, *Zh. Strukt. Khim.*, **16**, 1054 **1975**; *Ch. A.*, **84**, 172412m **1976**.
- 4 Yu. A. Dyadin, I.V. Bondaryuk and F.V. Zhurko, *Inclusion Compounds*, Eds. J. Atwood, E. Davies and D. MacNicol, Oxford University Press, **5**, 213, **1991**.
- 5 Yu. A. Dyadin, E. Ya. Aladko, K.A. Udachin and M. Tkacz, *Polish J. Chem.*, **68**, 343 **1994**.
- 6 N.S. Kurnakov, *Vvedenie v Fiziko-Khimicheskij Analiz*, Izd. Akademii Nauk SSSR, Moskva, **7** **1940**.
- 7 M.J. Collins, C.I. Ratcliffe and J.A. Ripmeester, *J. Phys. Chem.*, **94**, 157 **1990**.
- 8 D.N. Glew and N.S. Rath, *J. Chem. Phys.*, **44**, 1710 **1966**.
- 9 G.H. Cady, *J. Phys. Chem.*, **85**, 3225 **1981**, **87**, 4437 **1983**.
- 10 D.W. Davidson, Y.P. Handa and J.A. Ripmeester, *J. Phys. Chem.*, **90**, 6549 **1986**.
- 11 Van der Waals and J.H. Platteeuw, *Adv. Chem. Phys.*, **2**, 1 **1959**.
- 12 D.W. Davidson, "Water. *Comprehensive Treatise*". Ed. F. Franks, Plenum Press, N-Y, **2**, Ch.3, 115 **1973**.
- 13 Yu. A. Dyadin and K.A. Udachin, *Zh. Strukt. Khim.*, **28**, 75 **1987**, *Ch. A.* 107:167544v **1987**.
- 14 Yu. A. Dyadin and L.S. Aladko, *Zh. Strukt. Khim.*, **18**, 51 **1977**, *Ch. A.* 87:12297m **1977**.
- 15 Yu. A. Dyadin, I.I. Yakovlev, I.V. Bondaryuk, L.S. Aladko and L.S. Zelenina, *Doklady AN SSSR*, **203**, 1068 **1972**.
- 16 W. Vos, L. Finger, R. Hemley, Ho-kwang Mao, *Phys. Rev. Lett.*, **71**, 3157 **1993**.
- 17 Yu. A. Dyadin, G.N. Chekhova and T. Ya. Arapova, *Izv. Sib. Otd. AN SSSR, ser.khim.*, vyp.4, 68 **1979**; *Ch. A.*91:163771v **1979**.
- 18 G.N. Chekhova, Yu. A. Dyadin and T.V. Rodionova, *Izv. Sib. Otd. AN SSSR, ser.khim.*, vyp.5, 78 **1979**; *Ch.A.*92:100212p **1980**.
- 19 Yu. A. Dyadin and N.V. Kislykh, *Mendeleev Commun.*, **4**, 134 **1991**.