

## Clathrate Formation in Binary Aqueous Systems with $\text{CH}_2\text{Cl}_2$ , $\text{CHCl}_3$ and $\text{CCl}_4$ at High Pressures

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**Abstract.** *P*, *T*, *X* phase diagrams of the  $\text{CH}_2\text{Cl}_2$ – $\text{H}_2\text{O}$ , the  $\text{CHCl}_3$ – $\text{H}_2\text{O}$  and the  $\text{CCl}_4$ – $\text{H}_2\text{O}$  systems have been studied by DTA in the pressure range  $10^{-3}$  to 5.0 kbar. Under pressure the cubic structure II (CS-II) hydrates forming in all the systems are replaced by hydrates with the composition  $\text{M} \cdot 7.3 \text{H}_2\text{O}$  whose stoichiometry and positive  $dT/dP$  values of melting lead us to believe that they are CS-I hydrates.

In the  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  systems the nonvariant point coordinates of the hydrate transformation  $Q_2^h$  ( $l_1h_{17}h_7l_2$ , where  $l_1$  and  $l_2$  are liquid phases abundant in water and hydrate former, respectively,  $h_{17}$  and  $h_7$  are hydrates with hydrate numbers 17 and 7, respectively) are  $P = 0.6$  kbar,  $T = -1.5^\circ\text{C}$  and  $P = 2.65$  kbar,  $T = -10.5^\circ\text{C}$ , respectively. In the  $\text{CCl}_4$  system the 4-phase  $Q_3^h$  point ( $l_1h_{17}h_7s$ , where 's' is crystalline  $\text{CCl}_4$ ) has coordinates  $P = 0.75$  kbar and  $T = 0.4^\circ\text{C}$ .

The main obstacle of the present study, the very slow achievement of equilibrium, has been eliminated by adding small amounts (0.25% by mass) of surfactants followed by ultrasonic mixing. We have shown that this accelerates the achievement of equilibrium without changing its position.

**Key words.** High pressure, clathrate formation, clathrate hydrate, phase diagrams.

### 1. Introduction

The application of pressure destroys cubic structure II (CS-II) clathrates which are then replaced by hydrates of the denser cubic structure I (CS-I). This regularity has been established for liquid hydrate formers dissolved in water in any proportion (cyclic ethers, acetone) [1, 2].

It was of interest to investigate systems with guest components unable to form H-bonds so as not to complicate the interpretation of hydrate formation. Mutual solubility in such systems is usually low and it was difficult to make the clathration reaction go to completion. This is more evident in such systems as  $\text{H}_2\text{O}$ – $\text{CCl}_4$ , where the mutual solubility of the liquids is negligible and a great difference in densities results in rapid phase separation. On cooling, clathrate formation practically stops long before equilibrium is attained. These difficulties have been overcome by adding small amounts (0.25% by mass) of surfactants which resulted in stable emulsions. This allows easier hydrate formation and the reactions go almost to completion [3]. The study of clathrate formation in the  $\text{CH}_2\text{Cl}_2$ – $\text{H}_2\text{O}$  system,<sup>1</sup> with and without surfactant, has revealed that the addition of small proportions of a surfactant does not appreciably affect the equilibrium state, but considerably increases the reaction rate and decreases the time required to reach equilibrium.

<sup>1</sup> Since in this system the mutual solubility of liquids is still appreciable it was possible to achieve the equilibrium state without a surfactant, but it was more time consuming.

At low pressures ( $P \geq 1$  atm) the hydrate formers chosen by us form CS-II hydrates quite readily.  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  can be accommodated not only in the CS-II 16-hedral H-cavity, but also in the CS-I 14-hedral T-cavity. For  $\text{CCl}_4$ , whose molecular size is large even for the H-cavity, the arrangement of the guest molecule is not so evident. Therefore,  $\text{CCl}_4$  is of interest as a hydrate former.

## 2. Materials and Methods

We used substances labelled 'pure' and additionally purified them by washing with water followed by distillation. At  $20^\circ\text{C}$  the products obtained had the following densities:  $\rho_{\text{CCl}_4} = 1.5933(5) \text{ g cm}^{-3}$ ,  $\rho_{\text{CHCl}_3} = 1.4891(3) \text{ g cm}^{-3}$ ,  $\rho_{\text{CH}_2\text{Cl}_2} = 1.3350(2) \text{ g cm}^{-3}$ . Water was distilled twice. The oxyethylated nonylphenol surfactant, with an average number of oxyethylene groups of 10 (ON-10), was not additionally purified.

The mixture of the required concentration was prepared on an ultrasonic disperser USD H-2M at 22–40 kHz for 1 to 4 minutes. The composition of the resulting emulsion was determined on the basis of the densities at  $20^\circ\text{C}$  which was necessitated by the guest components being rather volatile, especially during ultrasonic mixing. The emulsions obtained were poured into Teflon ampoules with a capacity of 0.12 mL.

The DTA technique used under pressure is described in [3, 4]. In the phase diagrams only heating curves are depicted because these systems are prone to supercooling. Heating and thermostating rates were regulated with the aid of a precision PL-element RIF-101. For the general case the heating rate was  $1.0^\circ\text{C}/\text{min}$ .

To determine the composition of a high pressure hydrate a Tammann triangle was constructed at pressures where only this hydrate is stable. Because of the low rate of clathrate formation in the systems concerned three endothermic effects

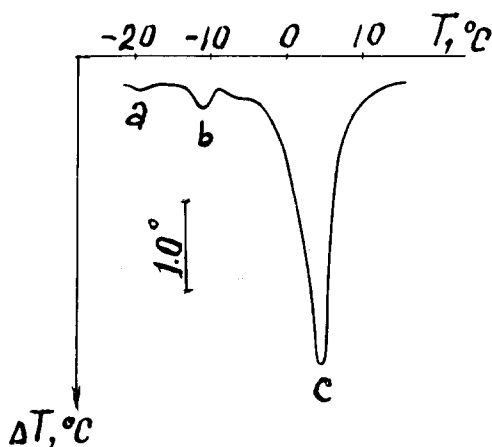


Fig. 1. The heating curve showing the relation between the values of the endothermic effects of: (a) the polymorphic transition  $\text{I} \rightleftharpoons \text{II}$ ; (b) the water eutectic melting; (c) the decomposition of the clathrate at high pressure under conditions close to equilibrium, which are used to construct Tammann triangles at  $P = 1.25$  kbar and with the composition of the sample 1 : 7.8  $\text{H}_2\text{O}$  for the  $\text{CCl}_4$ - $\text{H}_2\text{O}$  system.

(melting of the eutectic abundant in the guest,<sup>2</sup> water and hydrate decomposition) have always been observed on the heating curves of the initially frozen binary mixtures of any composition.

An equilibrium or near equilibrium state was achieved in the following way: mixtures of certain compositions were frozen, heated to 1 to 2°C below the decomposition point of the hydrates and kept at this temperature for 20 to 30 minutes. Then the system was cooled and heated again to 1 to 2°C below the decomposition point of the hydrates. The procedure was repeated until the thermal effects of one of the eutectics (or both, if the mixture composition was close to that of the hydrate) disappeared or became fairly small. In this case the endothermic effect corresponding to the hydrate decomposition effect increased. In several cases it took 3 to 4 cycles to achieve a state close to equilibrium. However, with mixtures of composition close to that of the hydrate it took many more cycles (12 to 15). As an example the  $\text{CCl}_4\text{-H}_2\text{O}$  system is presented in Figure 1 for the heating thermogram (after 14 cycles) showing the relation among the values of endothermic effects of the polymorphic  $\text{I} \rightleftharpoons \text{II}$  transition, of the water eutectic melting and of the decomposition of the high pressure clathrate under conditions close to equilibrium at  $P = 1.25$  kbar and the composition of the sample was 1:7.8  $\text{H}_2\text{O}$ . These endothermic effects are used to construct Tammann triangles.

### 3. Results and Discussion

#### 3.1. UNARY SYSTEMS

The  $P, T$  phase diagrams of the unary systems of chloromethane derivatives were first studied by Bridgman [5, 6], with the results being confirmed by later investigators [7–13].

Our data on the melting of the hydrate formers  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  under pressure agree closely with reported data [5–7] and we do not cite them here. The data on the unary  $\text{CCl}_4$  system in the range studied are also in good agreement with previous work [10–13], both on the melting (the upper curve) and on the polymorphic  $\text{I} \rightleftharpoons \text{II}$  transition<sup>3</sup> (the lower curve). We will discuss only the problems which, in our opinion, are of interest. On the  $P, T$  phase diagram of this system between the points  $\pi_1$  and  $\pi_2$  (Figure 2) we have discovered small but well reproducible effects (Figure 3) whose values are essentially smaller than those of the transition  $\text{I} \rightleftharpoons \text{II}$  effects.<sup>4</sup> The nature of these effects has not been investigated, but we think they belong to the polymorphic  $\text{CCl}_4$  transition, which we designate  $\text{I} \rightleftharpoons \text{V}$ .<sup>5</sup>

<sup>2</sup> In the  $\text{H}_2\text{O-CCl}_4$  system at atmospheric pressure it was also convenient to study the excess  $\text{CCl}_4$  in the clathrate formation process by following the  $\text{CCl}_4$  polymorphic transition thermal effect since its value was several times greater than that of the thermal melting effect. At pressures above 0.6 kbar (Figure 6) this is the only way to study the excess  $\text{CCl}_4$ , since its melting temperature becomes higher than the hydrate decomposition temperature and the eutectic abundant in the guest disappears.

<sup>3</sup> Phase I corresponds to phase Ib in the common notation [10–13].

<sup>4</sup> On the  $\text{CCl}_4$  heating curve from  $-40^\circ\text{C}$  to  $-70^\circ\text{C}$  (depending on pressure) prior to the endothermic effect at temperatures 6° to 10° lower an exothermic effect was observed which disappeared when the thermogram was recorded repeatedly.

<sup>5</sup> Five (V) has been chosen because at high pressure in the range of approximately (6–15 kbar) phases III and IV have already been observed [9–11].

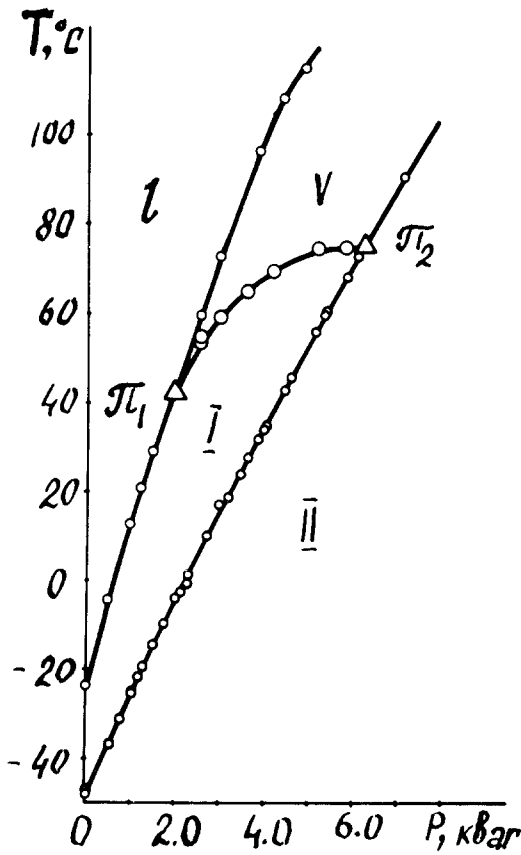


Fig. 2. The  $P, T$  phase diagram of the  $\text{CCl}_4$  unary system.  $\pi_1$  and  $\pi_2$  are the 3-phase nonvariant points.

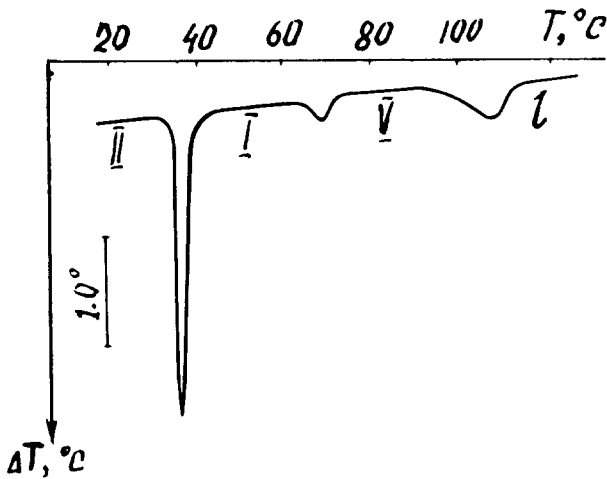


Fig. 3. The heating curve showing the relation among the values of the endothermic effects for the polymorphic  $\text{I} \rightleftharpoons \text{II}$ ,  $\text{I} \rightleftharpoons \text{V}$  transitions and melting  $\text{V} \rightleftharpoons \text{I}$  in the  $\text{CCl}_4$  unary system at  $P = 3.7$  kbar (see the caption to Fig. 1).

To simplify the figure and the description of the  $P, T$  phase diagram of the  $\text{CCl}_4$  system we do not describe the equilibria with the metastable Ia modification and phase transitions in the pressure range from 5 kbar and above. Sometimes we observed equilibria with the Ia phase in our studies at  $P < 1$  kbar, but we eliminated them by repeated recording of the heating thermogram. Neither we nor other

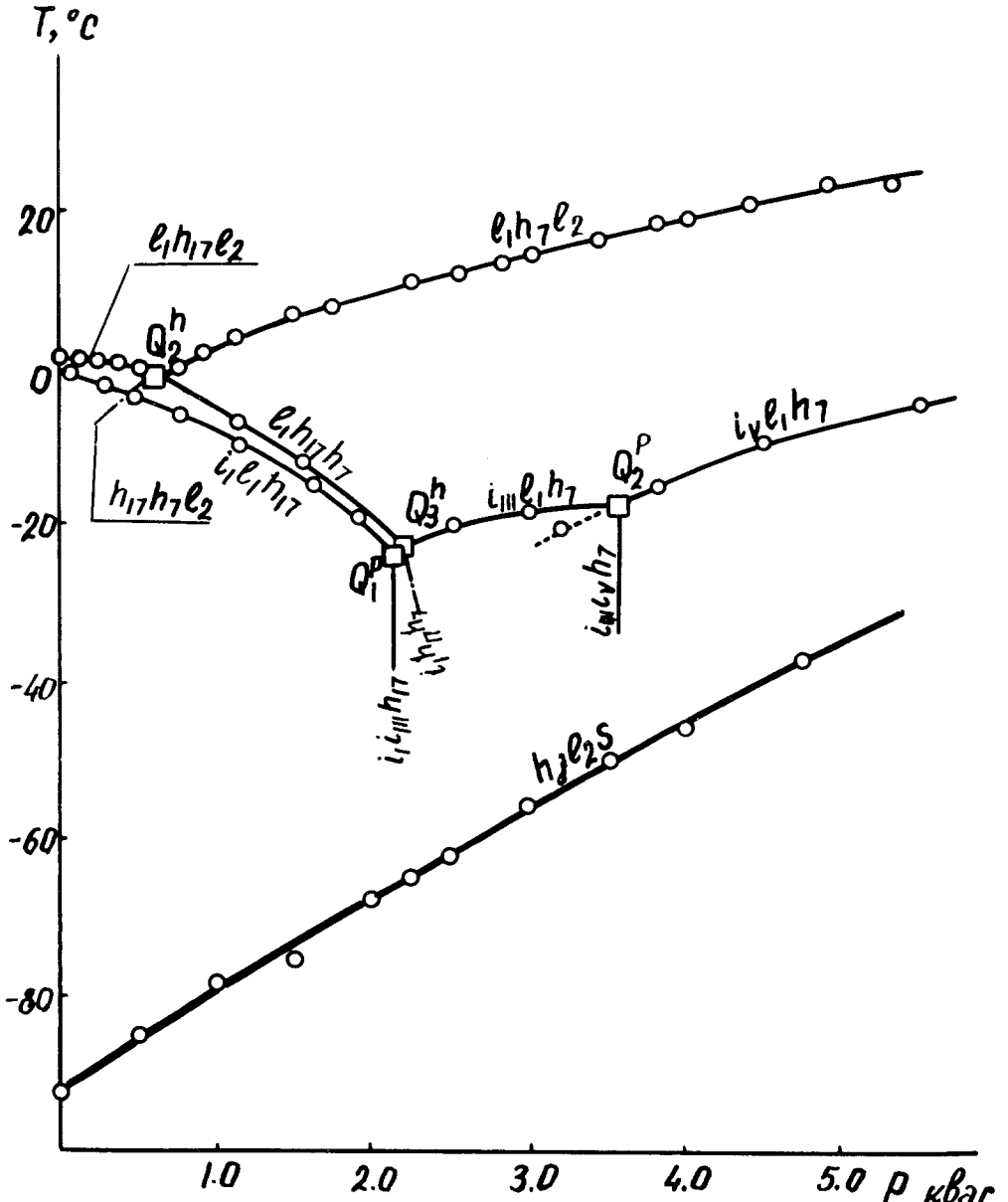


Fig. 4. The projection of the  $P, T$  phase diagram of the  $\text{CH}_2\text{Cl}_2$ - $\text{H}_2\text{O}$  binary system; the  $P, T$  melting lines in the unary system practically coincide with the eutectic lines and are not shown in the figure.

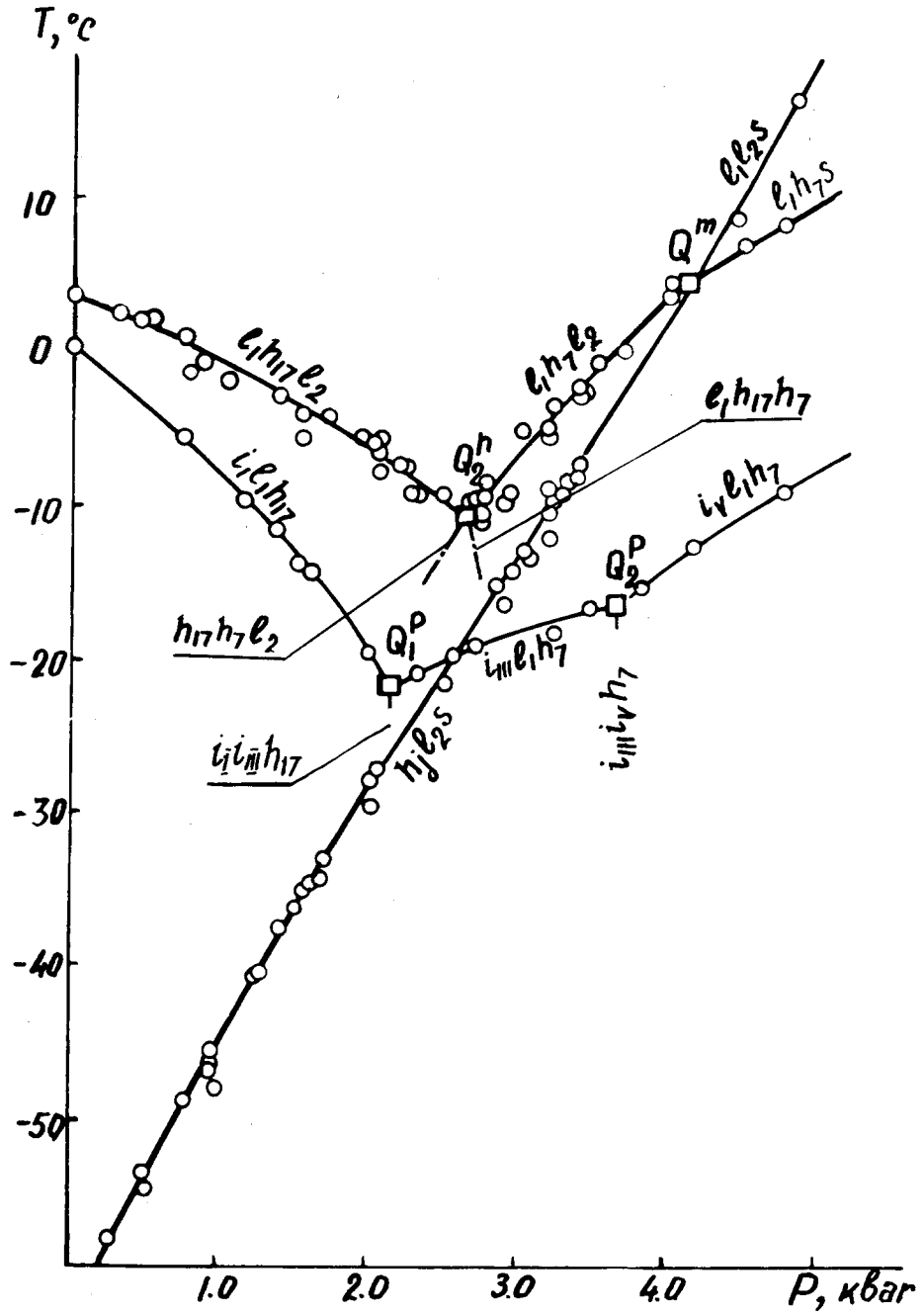


Fig. 5. The projection of the  $P, T$  phase diagram of the  $\text{CHCl}_3\text{-H}_2\text{O}$  binary system (see also Table I).

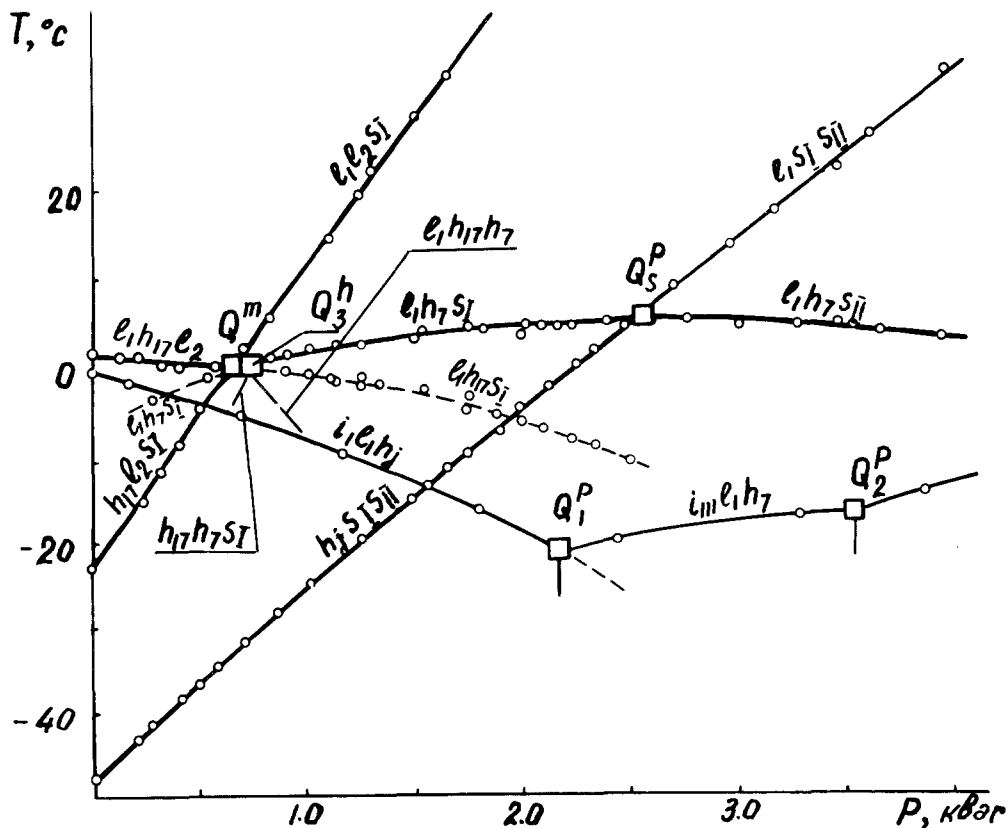


Fig. 6. The projection of the  $P, T$  phase diagram of the  $\text{CCl}_4\text{-H}_2\text{O}$  binary system.  $h_i$  stands for  $h_{17}$  or  $h_7$ . The cause of this uncertainty is that we have not managed to register the location of the quadruple points ( $h_{17}h_7s_{\text{I}}$  and  $i_1l_1h_{17}h_7$ ). The dashed lines show the 3-phase equilibria curves with the participation of the metastable phases; the dashed-dotted lines depict the curves of the supposed equilibria; the solid lines represent the curves of the stable equilibria. The experimental points of the water eutectic melting lines are not marked in the figure, since they practically repeat the melting lines of the ices (within the experimental accuracy) which is due to the binary system components being almost insoluble in each other.

authors [10–13] who have studied this system can confirm the data of Trappeniers [8].

A typical  $\text{CCl}_4$  heating thermogram without the exothermic effect mentioned in note 5 at a pressure of  $\approx 3.7$  kbar is shown in Figure 3. In this case the recorder made two curves: the signals from a simple thermocouple (the sample temperature) and a differential thermocouple (the difference in temperature,  $\Delta T$ , between the sample and the standard) vs time. Since the device provided the direct proportional dependence between temperature and time with good accuracy we do not show here the record of the signals from a simple thermocouple, and the temperature scale is transferred to the  $X$ -axis (time).

## 3.2. BINARY SYSTEMS

3.2.1. Systems at  $P \geq 1 \text{ atm}$ 

Figures 4 to 6 show the  $P, T$  projections of the phase diagrams of the binary water–chloromethane system based on our experimental data. For discussion it is convenient to pick out two groups of lines. One of them is determined by the unary systems because the mutual solubility of the components is negligible. Under pressure the melting curve of the eutectic rich in water essentially repeats that of ices under pressure, and melting curves of the eutectic rich in the hydrate former coincide with those of pure hydrate formers under pressure. This is also true of the monotectic lines and those of polymorphic transitions in ices and  $\text{CCl}_4$ .

However, of most interest to us are monovariant lines describing the transformation of the hydrates forming in those systems. As mentioned previously in all the systems under consideration at atmospheric pressure CS-II hydrates of composition  $\text{M} \cdot 17.0 \text{ H}_2\text{O}$  ( $h_{17}$ ) are formed which, at positive temperatures, decompose into practically pure liquid abundant in water  $l_1$  and liquid which is practically pure hydrate former  $l_2$ . Thus, under pressure, the syntectic equilibrium  $h_{17} \rightleftharpoons l_1 + l_2$  is monovariant (henceforth such equilibria will be referred to as  $l_1 h_{17} l_2$ , the phases

Table I. Coordinates of quadruple points ( $Q$ ) in binary systems.

$Q$ Coexistent Phases in the Nonvariant Points	The Aqueous Systems with					
	$\text{CH}_2\text{Cl}_2$		$\text{CHCl}_3$		$\text{CCl}_4$	
	$P$ , kbar	$T$ , °C	$P$ , kbar	$T$ , °C	$P$ , kbar	$T$ , °C
$Q_2^h l_1 h_{17} h_7 l_2$	0.6	−1.5	2.65	−10.5	—	—
$Q_3^h i_{111} l_1 h_{17} h_7$	2.18	−22.5	—	—	—	—
$l_1 h_{17} h_7 s^c$	—	—	—	—	0.75	0.4
$Q^m l_1 h_7 l_2 s$	—	—	4.10	4.5	—	—
$l_1 h_{17} h_7 s$	—	—	—	—	0.6	0.4
$Q_s^p l_1 h_7 s_1 s_{II}$	—	—	—	—	2.55	5.3
$Q_1^p i_1 i_{111} l_1 h_{17}$	2.08	−24.0	2.08	−24.0	2.08	−24.0
$Q_2^p i_{111} i_v l_1 h_7$	3.55	−18.0	3.55	−18.0	3.55	−18.0
$Q_1 i_1 l_1 h_{17} g$	$1.62 \times 10^{-4a}$	0.1 <sup>a</sup>	—	—	—	—
$Q_2 l_1 h_{17} l_2 g$	$2.18 \times 10^{-4a}$	1.85 <sup>a</sup>	—	—	—	—
$Q_3 h_{17} l_2 g s$	$5.0 \times 10^{-5b}$	−96.7 <sup>b</sup>	—	—	—	—
$Q_1^h h_{17} h_7 l_2 s$	$-10^{-3} < P < 0.6^b$	$-96.7 < T < -85.0$	—	—	—	—

$h_{17}$  and  $h_7$  – hydrates  $\text{M} \cdot 17 \text{ H}_2\text{O}$  and  $\text{M} \cdot 7 \text{ H}_2\text{O}$ , respectively.

$i_{i-v}$  and  $s$  – ice and solid hydrate former; lower index indicates polymorphic modification of the phase.

$l_1$  and  $l_2$  – liquid phases rich in water and in hydrate former, respectively.

$g$  – gaseous phase.

$Q_1^h, Q_2^h, Q_3^h$  – quadruple points, in which at least two hydrates coexist.

$Q^m$  – quadruple points, in which the liquid ( $l_2$ ) and solid hydrate former coexist.

$Q_s^p, Q_1^p, Q_2^p$  – quadruple points, in which the unary systems exist in two polymorphic modifications.

$Q_1, Q_2, Q_3$  – quadruple points of hydrate formation at various phase surfaces.

<sup>a</sup> Data [10, 11];

<sup>b</sup> evaluated data,  $-96.7^\circ\text{C}$  = the melting point of the  $\text{CH}_2\text{Cl}_2$  [24];

<sup>c</sup> See Figures 4, 5 and 6.



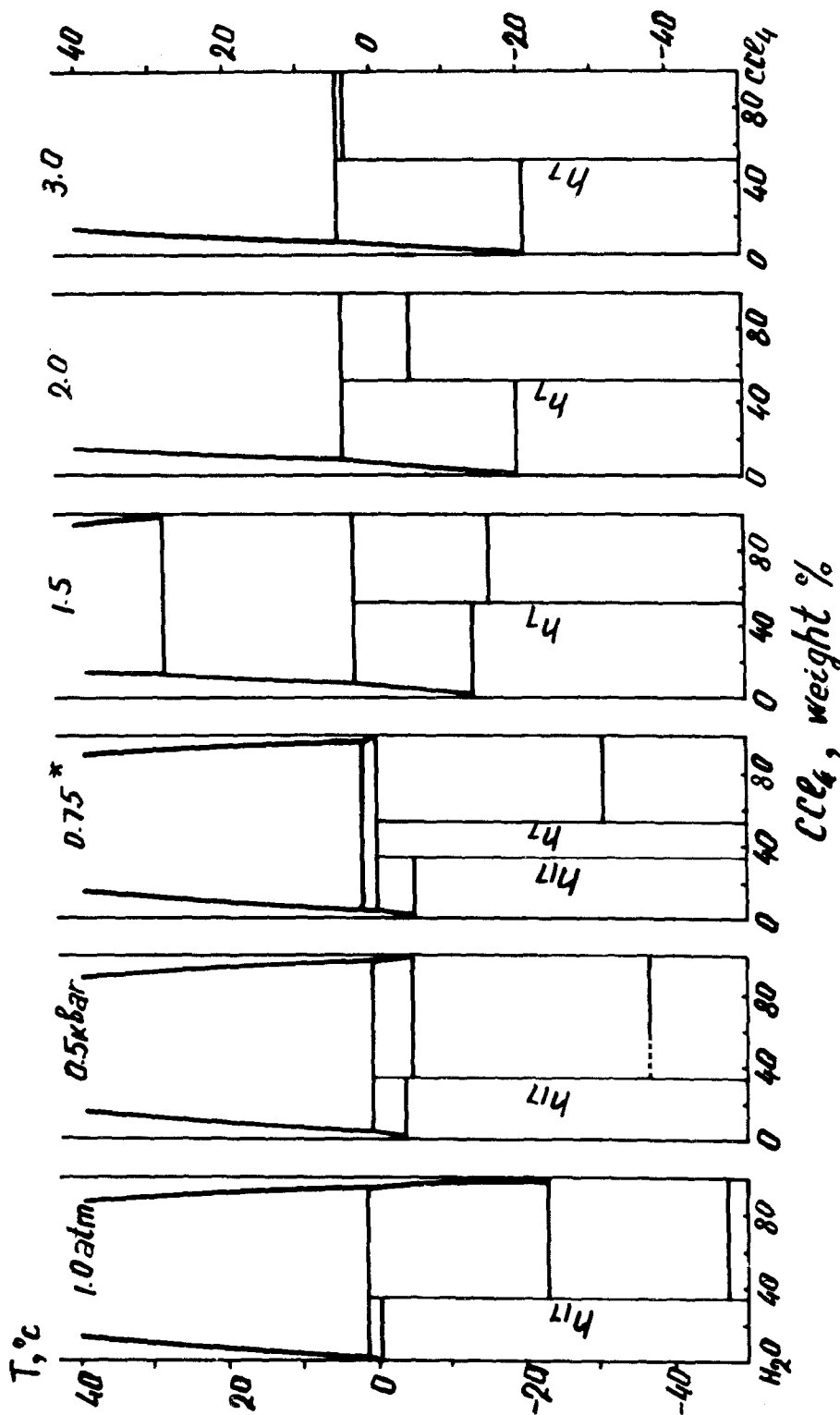


Fig. 7. The characteristic isobaric sections of the  $P, T, X$  phase diagram of the  $\text{CCl}_4\text{-H}_2\text{O}$  binary system. The section marked with an asterisk passes through the quadruple point  $Q_3$ . The dashed line on the 0.5 kbar isobar is due to the uncertainty in the location of the quadruple point -  $h_{17}, h_7, s_{II}$  ( $s_I \equiv I, s_{II} \equiv II$ ). For clarity the liquidus lines are shifted relative to the axes towards the side of the greater solubility. This is also true of Figure 9.

being written in the order of increasing content of the hydrate former). As one would expect for CS-II hydrates [1, 2] under pressure in this kind of system monovariant lines  $l_1h_1l_2$  are directed to the low temperature range and in the  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  systems end in the monovariant point  $Q_2^h$ , where 4 phases ( $l_1h_1l_2h_2$ ) are in an equilibrium state. In  $\text{CCl}_4$  it ends in the point  $Q_3^h$  ( $l_1h_1l_2h_2s$ , for the notations see Table I), since transformation of the hydrates occurs at pressures higher than the  $\text{CCl}_4$  crystallization pressure, i.e., point  $Q^m$  ( $l_1h_1l_2s$ ) is located in a lower pressure region than point  $Q_3^h$ .

With pressure increase syntectic decomposition of  $\text{CH}_2\text{Cl}_2 \cdot 7.1 \text{H}_2\text{O}$  and  $\text{CHCl}_3 \cdot 7.3 \text{H}_2\text{O}$  hydrates (the composition will be discussed later) is observed at higher temperatures. This is also true of the peritectic melting ( $l_1h_1l_2s$ ) in the systems

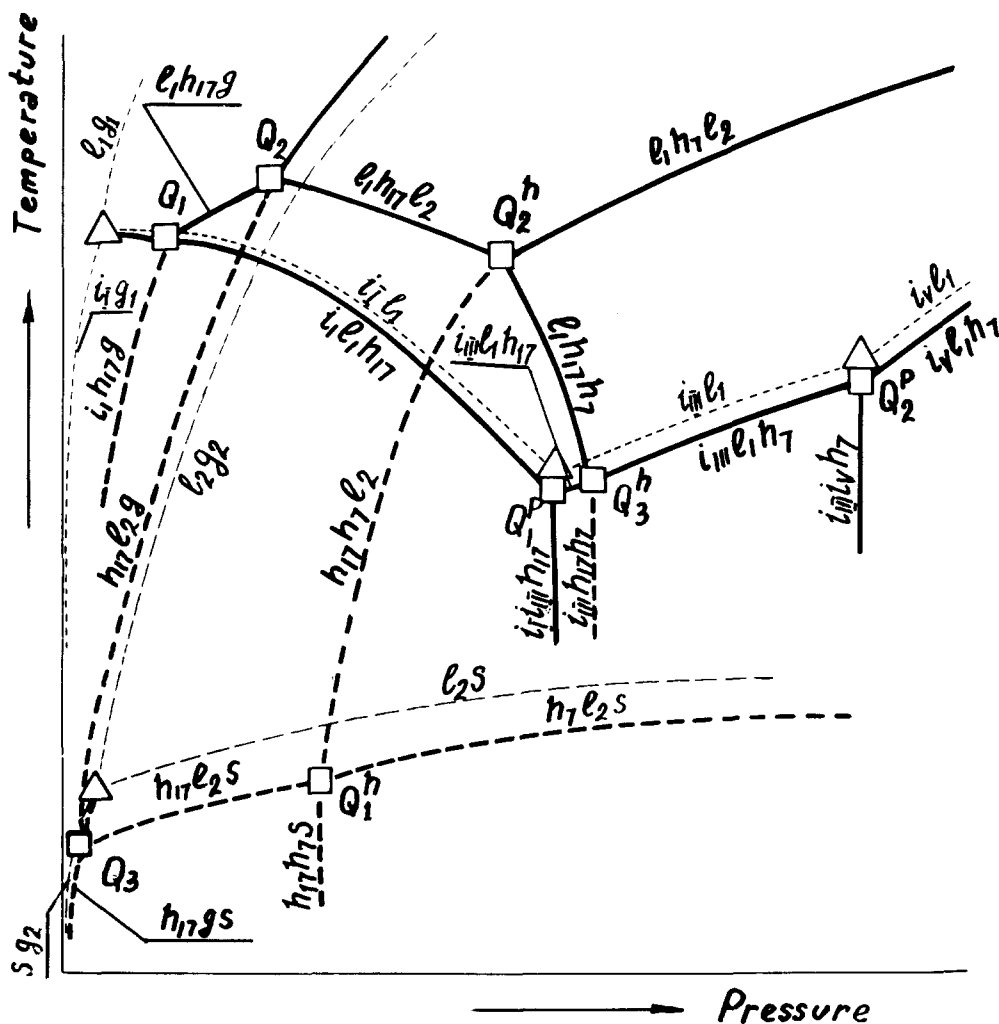


Fig. 8. The general scheme of the  $P, T$  projection of the phase diagram of the  $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$  system. The solid lines show the stable equilibria; the dotted-dashed lines represent the assumed equilibria; the dashed lines depict the curves of the unary systems.

with  $\text{CCl}_4$  and  $\text{CHCl}_3$  after point  $Q^m$ . In the  $\text{CCl}_4$  system at a pressure above 2.55 kbar (point  $Q_s^p$ ) the peritectic lines ascend more slowly and with further pressure increase the value of  $dT/dP$  becomes negative. The phase diagram evolution under pressure is clearly shown in Figure 7, illustrating characteristic isobaric sections in the  $\text{CCl}_4$ - $\text{H}_2\text{O}$  system.

### 3.2.2. The Complete $\text{CH}_2\text{Cl}_2$ System Phase Diagram

Literature data [14, 15] on phase equilibria of this system, provided there is a gaseous phase, allow us to picture its complete phase diagram. Schematically the phase equilibria of this system are shown in Figure 8. For convenience we use conventional notations for  $Q_1, Q_2$  and further they will be used as a basis for other notations. The index 'h' refers to the points of the transformation of the hydrates; the index 'P' stands for the quadruple points corresponding to polymorphic transformations. The coordinates of points  $Q_3$  and  $Q_1^h$  are not known to us.  $Q_3$  has been evaluated by extrapolation of the melting and boiling lines of  $\text{CH}_2\text{Cl}_2$  as functions of pressure up to their crossing. As to point  $Q_1^h$  one can say that it is probably located in the pressure range  $10^{-3} < P < 0.6$  kbar and its temperature is located near the  $\text{CH}_2\text{Cl}_2$  melting line in this pressure range.

### 3.2.3. The Compositions of the Hydrates

We did not determine the compositions of the CS-II hydrates, because they have already been determined accurately by other authors [14–18]. Of much greater interest to us were the compositions of the high pressure hydrates determined by constructing the Tammann triangles on the invariants (at constant pressure) of water eutectic, rich in hydrate former and syntectic decomposition line. For instance, for the  $\text{CH}_2\text{Cl}_2$  hydrate the determination was carried out at  $P = 3.1$  kbar (Figure 9a). Since the equilibrium is reached slowly, the determination was conducted as described in Section 1. The hydrate  $\text{CCl}_4$  composition was determined at  $P = 1.25$  kbar, but since at this pressure the hydrate melts incongruently, in the mixture with surplus  $\text{CCl}_4$  its amount was followed by observing the size of the endothermic effect of the polymorphic transformation (Figure 9b). Hydrate numbers determined as described above are; for the  $\text{CH}_2\text{Cl}_2$  hydrate  $7.1 \pm 0.8$ ; for the  $\text{CCl}_4$  hydrate  $7.4 \pm 0.8$ ; for the  $\text{CHCl}_3$  hydrate  $7.3 \pm 0.8$  (the hydrate numbers are given with mean-square uncertainty).

For the  $\text{CHCl}_3$  system the Tammann triangles were not constructed. Our judgment of its composition is based on the fact that on the heating curves of the sample with the ratio of components  $\text{CHCl}_3 : \text{H}_2\text{O} = 1 : 7.3$  at  $P = 3.0$  kbar thermal effects of the eutectics rich in water on the one hand and the eutectics rich in the hydrate former on the other hand were extremely small.

### 3.2.4. The Nature of High Pressure Hydrates

While studying the  $\text{H}_2\text{O}$ -THF [19] system an assumption has been made that the hydrate forming at high pressure ( $\text{THF} : 7.1 \text{H}_2\text{O}$ ) is CS-I. It is evidenced by the hydrate composition, a positive value of  $dT/dP$  and modelling using Stuart-Brigled

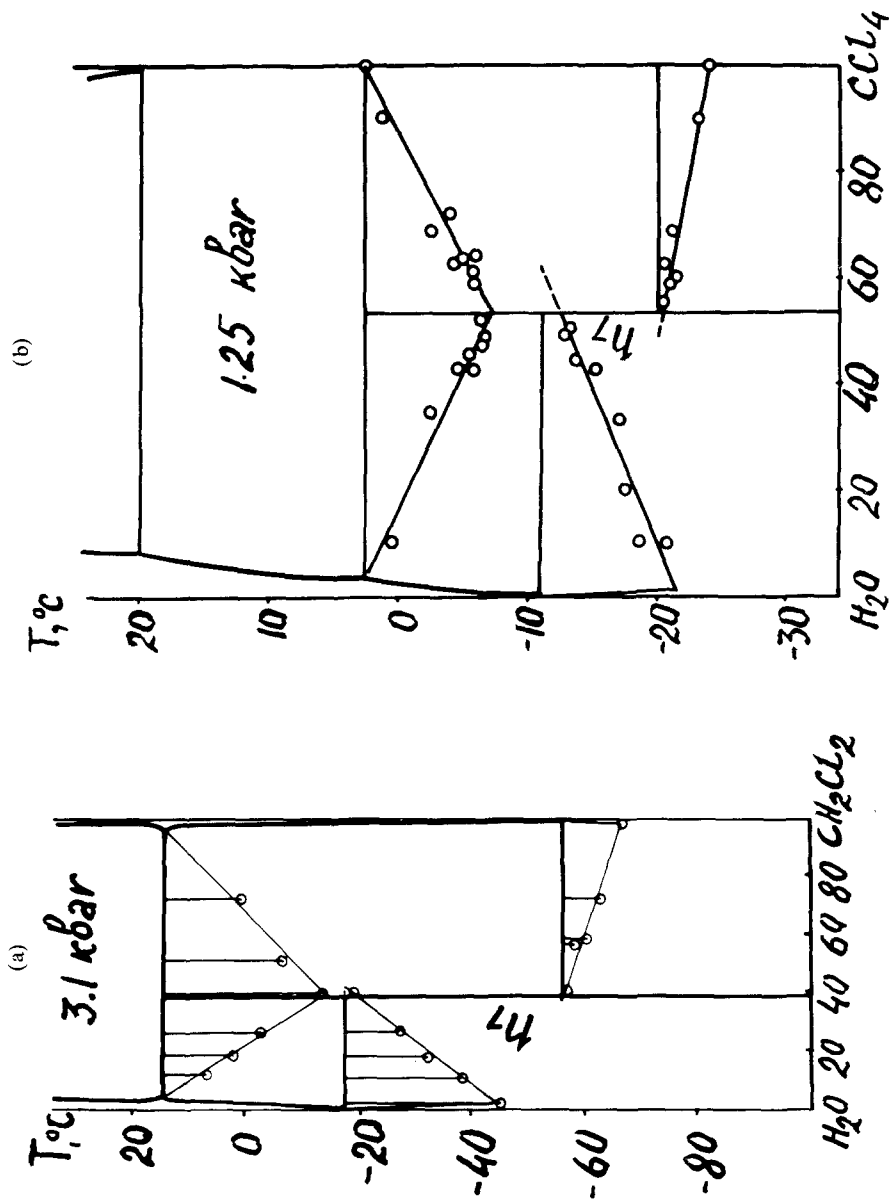


Fig. 9. The isobaric sections of the  $P, T, X$  phase diagrams and Tammann Triangles in the systems: (a)  $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$  at  $P = 3.1$  kbar; (b)  $\text{CCl}_4\text{-H}_2\text{O}$  at  $P = 1.25$  kbar. The values of the endothermic stops in the relative units are marked on the corresponding invariants (Tammann triangles). The low heating effects beyond the composition line (see the dashed lines in (b)) are probably explained by the fact that the clathrate formation reaction does not go to completion.

models. One more argument in favour of this opinion was Andersson's and Ross' experiments [20]. By measuring thermophysical properties of the hydrate in the  $\text{H}_2\text{O}$ -THF system at high pressure they have shown that the  $\text{THF}:7.1 \text{H}_2\text{O}$  hydrate, like the  $\text{THF}:17 \text{H}_2\text{O}$  hydrate, has a clathrate nature. The clathrate nature of the high pressure is also proved by the experiments aimed at the investigation of hydrate formation in the  $\text{H}_2\text{O}$ -TMO (trimethyleneoxide) system at high pressures. In this system, even at atmospheric pressure, hydrates of both CS-II and CS-I form. The structure of the hydrates has been determined by the X-ray technique [21, 22]. The appearance of this system under pressure is similar to those of the water-cyclic ethers and the water-acetone systems [1, 2, 23]. From the above, and on the basis of the composition of the high pressure hydrates forming in the systems studied in this work, one draws the conclusion that they are also of CS-I.

As mentioned previously  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  molecules can fill the CS-I T-cavities quite easily. As to the  $\text{CCl}_4$  molecule it can occupy this cavity with difficulty, using empty space in the 'walls' which is likely to be promoted by pressure.

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