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Gas Hydrates

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This review states contemporary views about gas hydrates, and also about non-stoichiometric clathrates with the general formula $M.nH_2O$. The known types of the hydrates and their crystal structure are described. The thermodynamics of hydrate formation is considered. Methods of determining the composition of the hydrates are described. Factual information concerning the hydrates of individual gases and organic liquids and mixed hydrates (binary and multicomponent) is given. The problem of the stabilisation of hydrates by an auxiliary gas is considered. Information is given about the density of hydrate crystals and the physical kinetics of the hydrate formation. Equations are given which are obtained by the methods of statistical mechanics and are based on the use of Lennard-Jones and Kihara potentials, and allow the main thermodynamic properties of the hydrates to be calculated. The problems of the industrial utilisation of the hydrates are examined (desalination of sea water, separation of liquid and gaseous mixtures, etc.). The theoretical principles of the inhibition of hydrate formation processes are stated. Bibliography of 180 references.

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I. INTRODUCTION

Gas hydrates are solid crystalline substances with the appearance of snow or loose ice and the general formula $M.nH_2O$, where M is the hydrate-forming molecule. There is considerable theoretical interest in the investigation of gas hydrates, as they allow general laws to be formulated which describe the unique physical properties of an extensive group of clathrate compounds† in which the crystal

† Contemporary views about gas hydrates as non-stoichiometric clathrates are presented in Chapter II of this review.

lattice is constructed from water molecules but nevertheless differs appreciably from the lattice of ordinary ice (stability at temperatures > 0°C, presence of cavities of strictly determined diameter, etc.).

Practical interest in gas hydrates is connected with the following features. A series of processes which are carried out in the oil, gas, and petrochemical industries is accompanied by the formation of hydrocarbon hydrates which clog pipelines and equipment. To prevent hydrate formation it is necessary to know the conditions of formation of the hydrates for various compositions of the gas phase, temperatures, pressures, and other parameters, which determine this process. Three prospective directions for the industrial use of gas hydrates must also be noted: (1) the desalination of sea water (semi-industrial plants are already known to be in operation); (2) the separation of binary and multicomponent gas and liquid mixtures; (3) the storage of gases.

Davy[1] first obtained a gas hydrate of chlorine in 1811 on cooling a saturated aqueous solution of chlorine at 9°C. In the first half of the XIXth century hydrates of Br_2, SO_2, and H_2S were obtained in this way.

Thanks to the work of Cailletet, Vroblevskii, Villard, de Forcrand, and other investigators[1] in the 1850s to 1890s, the hydrates formed by CO_2, CS_2, C_2H_2, PH_3, AsH_3, CH_4, C_2H_6, C_2H_4, C_3H_8, N_2O, Ar, Kr, and Xe became known.

A large group of so-called "double hydrates"‡ was then studied, formed by H_2S or H_2Se with hydrocarbons and their halogen derivatives (predominantly of the aliphatic series): CH_3Cl, C_2H_5Br, C_2H_5I, etc. and also hydrates formed by the mixtures: $CO_2 + PH_3$, $CS_2 + PH_3$, $C_2H_2 + CCl_4$, and hydrates obtained from halogen-substituted aliphatic hydrocarbons and such compounds as C_2H_4, CO_2, SO_2, and others.

In the first third of the XXth century the investigation of gas hydrates was mainly connected with the defining of the conditions for the formation of previously known hydrates and of obtaining some new hydrates (CF_4, CHF_3, SO_2Cl_2, I_2, etc.)[1-3]. There was an appreciable increase in interest in studying gas hydrates after the publication of Hammerschmidt's first work[4], who showed in a study of the hydrates of individual C_1–C_4 aliphatic hydrocarbons, that the serious difficulties arising in the transport of natural gas were connected with the formation in the pipelines of the so-called "mixed hydrates". During these years there appeared a great number of papers devoted to defining the equilibrium conditions for the formation of hydrates by individual hydrocarbons, their mixtures, the composition of the hydrates, and methods of preventing hydrate formation. All these problems have been covered completely enough in Frost and Deaton's monograph[5]. As a result of the fundamental investigations made by Stackelberg[6-18], Claussen[19,20], and also Pauling and Marsch[21], in the 1950s the structure of the hydrate crystals was determined, the ideas about "mixed hydrates" were significantly extended, the stabilising influence of foreign gases was studied, and the thermodynamics of hydrate formation and other problems were considered.

At the end of the 1950s and start of the sixties theoretical studies devoted to the statistical mechanics of gas hydrates appeared[22-29]. Between 1960 and 1966 the existence of hydrates of oxygen and nitrogen at high pressures was shown experimentally[30,31] and the theoretical investigations were pursued further[32-37].

‡ As will be shown below, "double hydrates" are particular examples of "mixed hydrates".

II. CONTEMPORARY VIEWS ABOUT GAS HYDRATES

Current literature[38] devoted to the structure of gas hydrates recognises the viewpoint first expressed by Nikitin[39-43]. According to this viewpoint, gas hydrates (formed by individual gases or their mixtures) are non-stoichiometric inclusion compounds, "gas clathrates"[28,44,45], in which the "included" molecules of gas are held by van der Waals forces in a metastable crystal lattice, the "host", which is constructed from water molecules.

The investigations of Claussen[19,20], Pauling and Marsch[21], Stackelberg and Müller[8,9], and Mandelcorn[46] have shown conclusively that gas hydrates crystallise in one of two cubic structures, (I) or (II), the interaction between the water molecules from which the lattice is constructed being effected by means of hydrogen bonds.

The hydrates of structure (I) are described by space group $Oh^3 = Pm3n$ and are characterised by the crystal lattice parameter 12 Å. The unit cell is constructed from 46 water molecules and in it there are eight cavities available for gas molecules, including 2 "small" cavities and six "large". The "small" cavities of structure (I) are regular pentagonal dodecahedra with mean free diameter ~ 5.1 Å; each of the six "large" cavities is tetrahedral with a mean free diameter of ~ 5.8 Å, formed by two opposing hexagons and 12 pentagons situated between them.

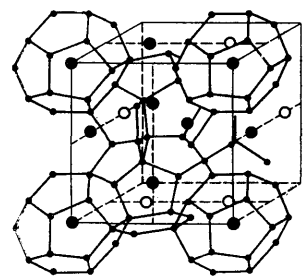


Figure 1. Crystal lattice of a gas hydrate of structure (I).

The hydrates of structure (II) are described by space group $Oh^7 = Fd3n$ with crystal lattice parameter 17.4 Å. The unit cell is constructed from 136 water molecules, contains 24 cavities, including 16 "small" and 8 "large". The "small" cavities, as for structure (I), are pentagonal dodecahedra, but somewhat deformed, as a result of which the mean free diameter is ~ 5 Å. The "large" cavities of structure (II) are hexadecahedra, each of which is constructed from four hexagons and 12 pentagons. The mean free diameter of this cavity is ~ 6.7 Å.

When the effective diameter of the hydrate-forming molecule ($d_{\text{eff}}^{M_1}$) < 5.1 Å, then a hydrate of structure (I) is formed in the presence of water; in principle, all the eight cavities can be filled (hydrates of Ar, CH_4, H_2S, etc.) and consequently the ideal formula of this hydrate will be $8M_1.46H_2O$ or $M_1.5.75H_2O$, where M_1 can be a molecule of Ar, CH_4, H_2S, etc. When 5.8 Å > $d_{\text{eff}}^{M_2}$ > 5.1 Å, then the hydrate-forming molecules can fill only the six large cavities: in this instance the ideal formula of the hydrate will be $6M_2.46H_2O$ or $M_2.7\frac{2}{3}H_2O$ ($M_2 = C_2H_6$, Cl_2, SO_2, etc.). When two types of molecule are present simultaneously in the gas mixture (a mixture of $M_1 + M_2$) a so-called "mixed hydrate" with the ideal formula $2M_1.6M_2.46H_2O$ is formed, which can

be considered as a solid solution[28,40-42] with a composition which changes during fusion of the hydrate. An example of a "mixed hydrate" of structure (I) is $2H_2S.6C_2H_6.46H_2O$.

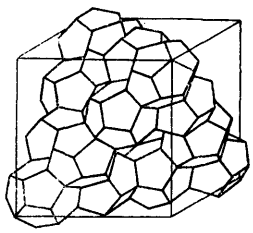


Figure 2. Crystal lattice of a gas hydrate of structure (II).

Analogous considerations apply for a hydrate of structure (II). When 5 Å $< d_{eff}^{M_3} <$ 6.7 Å (C_3H_8, iso-C_4H_{10}, $CHCl_3$, etc.), then the ideal formula of the hydrate will be $8M_3.136H_2O$ or $M_3.17H_2O$. For the mixture $M_3 + M_4$ (under the conditions: $d_{eff}^{M_4} < 5$ Å), the "mixed hydrate" which is formed is characterised by the ideal formula $16M_4.8M_3.136H_2O$ or $2M_4.M_3.17H_2O$; for example, $2H_2S.C_3H_8.17H_2O$ or $2CH_4.C_3H_8.17H_2O$.

Figs. 1 and 2 show schematically hydrates of structures (I) and (II).

III. CONDITIONS FOR THE FORMATION OF HYDRATES

A clear presentation of the conditions of formation of hydrates according to the equation $M + nH_2O \rightleftharpoons M.nH_2O$ can be obtained by considering the diagram of heterogeneous equilibrium in P–t coordinates proposed by Roozeboom[47] and given in one of Stackelberg's papers[10]. On this diagram (Fig. 3): (a) curve *I* characterises the saturation vapour pressure of the hydrate-forming substance P_M which in its turn is saturated with water vapour; (b) curve *II*, the vapour pressure of the hydrate-forming substance M over the hydrate in the presence of liquid water; (c) curve *II′* is the vapour pressure of M over the hydrate in the presence of ice; (d) curve *III* is the variation of the melting point of the hydrate with the pressure; (e) curve *IV* is the depression of the freezing point of water during the dissolution of M in it under pressure.

As Fig. 3 shows, the region of existence of hydrates is situated to the left of curves *II* and *III*. The intersection of these curves gives the so-called "critical point for the decomposition of the hydrate" P_c, which is simultaneously the upper quadruple point of the system; at this point hydrate + M_{gas} + M_{liq} + water coexist. It should be noted that point P_c is absent from the hydrates formed by such gases as Ar, CH_4, C_2H_4, Kr, Xe, N_2, and O_2, since owing to the low values of the critical temperature, curve *I* for these gases falls below curve *II* up to the intersection point. The intersection of curves *II′* and *II* gives the so-called "lower quadruple point" at which hydrate + ice + water + M_{gas} coexist. When the pressure in the system is below P_c, then on heating the hydrate decomposes into water and gas (on crossing curve *II*).

When the pressure in the system exceeds P_c, then on raising the temperature (passage through curve *III*) the hydrate decomposes into two liquid phases, H_2O and M_{liquid}.

Curve *III* itself characterises the P–t_f dependence for condensed systems. For the hydrates this curve is almost vertical. The slope of the curve to left or right ($dt/dp < 0$ or $dt/dp > 0$) will depend on how much the volume of the solid hydrate is greater or less than that of the liquid phase which is formed in the fusion of the hydrate§. From the equation given above for the formation of a hydrate comes the idea of dissociation pressure (P_{diss}). Evidently each hydrate is characterised at a given temperature by a definite value of P_{diss}. In principle

$$P_{diss} = P'_M + P'_{H_2O},$$

where P'_M is the vapour pressure of the hydrate-forming substance M over the hydrate and P'_{H_2O} the vapour pressure of the water above the crystal lattice of the same hydrate, constructed from H_2O molecules. In practice, $P_{diss} \simeq P'_M$ (since $P'_M \gg P'_{H_2O}$).

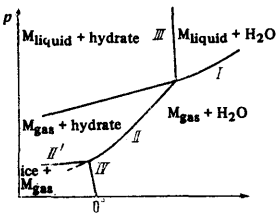


Figure 3. P–t phase diagram.

From what has been said above, at constant temperature there are two boundary conditions[48], which determine the possibility of existence of a hydrate: (1) $P'_M < P_M$, and (2) $P'_{H_2O} < P_{H_2O}$, that is, the equilibrium pressure of the vapour of M above the solid hydrate (P'_M) should be less than the pressure P_M in the system, and simultaneously the equilibrium pressure of water vapour above the hydrate crystal (P'_{H_2O}) should be less than the partial pressure of water vapour (P_{H_2O}) in the same system. Investigations made by many authors have shown[4,5] that this second condition is observed in practice only for the presence of drops of liquid water in the system (that is, at 100% humidity at the given temperature).

The relation between the equilibrium pressure of the hydrate-forming substance over the hydrate (in the literature it is usually denoted simply by the symbol P) and the temperature is described by the well-known equation[49-51]:

$$\lg P = A - B/T,$$

where T is in °K. Tamman and Kriege[52] showed that for most gas hydrates the connection between the equilibrium pressure and temperature can be represented by an equation of the type:

$$t = a(\lg P + B).$$

Diagrams[53] constructed on a semilogarithmic scale for methane, ethane, propane, and isobutane well reflect the linear character of the relation between $\lg P$ and t and allow the equilibrium conditions for hydrate formation for each of these hydrocarbons to be found readily by interpolation.

§ For hydrates of structure (I) $dt/dp > 0$; for structure (II) $dt/dp < 0$.[10]

IV. METHODS OF PREPARATION AND OF DETERMINING THE COMPOSITION OF HYDRATES

Experimental methods for the preparation of hydrates are considered in the papers of Frost and Deaton[51], Hammerschmidt[4], and the reviews of Czaplinski[2,3]. Hydrates can be formed both in a closed system (most convenient for laboratory investigations) and in a flow system (gas pipes, petrochemical industrial plant).

The formation of hydrates can in principle be compared with crystallisation from a supersaturated solution or the freezing of a supercooled melt[2]. Therefore the general rules formulated by Eucken[54] for crystallisation can be transferred to the process of hydrate formation. This process is greatly facilitated[4] by increasing the rate of gas flow, saturation with water vapour, pressure pulsations, the introduction of small crystals of the hydrate or other nuclei for the crystallisation (for example, crystallites of AgI[55]).

From the very definition of gas hydrates as non-stoichiometric clathrates it follows that in the formula $M.nH_2O$ the value of n is variable¶, depending on the degree of filling of the cavities†. The minimal value of n is reached when all the cavities of the clathrate crystal are filled with molecules of the hydrate-forming substance.

In this sense it is possible to speak about the "ideal" formula of the hydrate. For hydrates of structure (I) the ideal formula $8M.46H_2O$ or $M.5.75H_2O$ (when only the six large cavities are filled, $6M.46H_2O$ or $M.7\frac{2}{3}H_2O$). For the hydrates of structure (II) the eight large cavities ($d_{eff} < 6.7$ Å) are usually filled and the ideal formula of such a hydrate is $8M.136H_2O$ or $M.17H_2O$.

1. DIRECT EXPERIMENTAL DETERMINATION OF COMPOSITION

The direct determination of the composition of a hydrate is carried out as follows[2,51]: a definite quantity of liquid water and of compressed gas is put in a thick-walled glass tube at ~ 0°C and, with periodic shaking, the system is kept for several days. After complete bonding of the water in the hydrate the tube is cooled below the temperature at which $P_{diss} = 1$ atm, and the excess of gas, bonded with the water, is removed. Then the hydrate is decomposed by heating and the volume of gas liberated is measured, after which the composition of the hydrate is calculated from the ratio between the initial amount of water and the volume of gas liberated.

It should be noted that for any one hydrate many authors have obtained quite different results[51,55]. The explanation is firstly that the conditions of carrying out the experiment are not comparable and secondly the serious experimental difficulties that arise in carrying out the method. Of the many studies devoted to the direct experimental determination of the composition of hydrates, the most precise are those of Marshall and coworkers[57] and Ceccoti[55]. The former determined the composition of methane hydrate in the pressure range 150–680 atm, and in the calculations they took account of the compressibility of methane and its solubility in water. The same authors observed an interesting fact: the occlusion of water by the hydrate lattice which is formed prevents the interaction between gas and water proceeding to completion.

Ceccoti studied the formation of hydrates by propane directly in the gas phase in the presence of microcrystallites of AgI, which, as he showed, serve as effective catalysts for hydrate formation. In this instance the result of the experiment was not distorted by the occlusion of the liquid phase (aqueous or hydrocarbon) of the crystal lattice of the hydrate. At a temperature somewhat above the lower quadruple point the propane hydrate was found to have the composition $C_3H_8 . 19.7H_2O$ (which corresponds to 86% filling of the large cavities). Ceccoti first suggested that propane hydrate, by analogy with bromine hydrate[58], has a tetragonal structure. A method first proposed by Bigorné[59] belongs among the direct experimental methods of determining the composition of hydrates. He found that when the hydrate is formed from an aqueous solution of a salt (for example, $NiSO_4$), which does not itself react with a hydrate-forming substance (ClO_2), then after the formation of the hydrate the quantity of "free" water in the system decreases, since part of it is converted into the hydrate lattice, but the concentration of the salt in the solution rises correspondingly. Knowing the decrease in the hydrate-forming substance in the system, it is easy to calculate the composition of the hydrate. The precision work of Khayano and Takasi[60] was based on the principle stated above; they determined the composition of isobutane hydrate ($M.17.1H_2O$) with the aid of a series of NaCl solutions of different concentration.

2. SEMIEMPIRICAL METHOD OF CALCULATING THE COMPOSITION OF HYDRATES

This method, first proposed by de Forcrand[61] and perfecte by Scheffer and Meyer[62], allows the value of n at the lower quadruple point to be determined, that is, the point of intersection of the two curves "ice–hydrate–gas" and "water–hydrate–gas". As stated above, each of these curves is described by an equation of the type $\lg P = A - B/T$, in which the constants A and B are found by experiment. The number of water molecules connected with one molecule of the hydrate-forming substance is calculated by the simple formula:

$$n = \frac{\Delta H_1 - \Delta H_2}{Q},$$

where ΔH_1 and ΔH_2 are the molar heats of formation of the hydrate from liquid water and from ice, and Q is the molar heat of fusion of ice (at 0°C, $Q = 1430$ cal mole^{-1}). The values of ΔH_1 and ΔH_2 for the specific hydrate were calculated in the usual way, by combining the equation given above with the Clausing–Clapeyron equation:

$$T\frac{\Delta P}{\Delta T} = \frac{\Delta H}{\Delta V}.$$

In this way the compositions of the hydrates of methane, ethane, propane, and natural gas were determined for the lower quadruple point[49–51].

In the same way van Cleef and Diepen[31] calculated the composition of the hydrates of oxygen and nitrogen which they obtained for the first time at high pressures. The calculations were sufficiently rigorous: the density of the hydrated crystals, the solubility of the gas in water, and its coefficient of compressibility were calculated. For nitrogen hydrate at the lower quadruple point ($t = -1.3$ °C, $P = 141.5$ atm) the composition $N_2(6.01 \pm 0.23)H_2O$ was

¶ According to van der Waals (grandson) and Platteeuw[28,55], with rise in temperature along curves *II* and *III* on the *P–t* diagram the degree of filling of the cavities of the hydrate lattice increases, that is, the value of n decreases.

† When a hydrate is formed directly from an aqueous solution, for example, ethylene oxide hydrate[56].

found and for oxygen hydrate ($t = -1.0°C$, $P = 104.2$ atm), the value $n = 6.06 \pm 0.21$.

It is interesting to note that even at $P > 100$ atm not all the cavities of the hydrate lattice are completely filled.

Among the indirect methods of determining n must be included the method proposed by Miller and Strong[48].

On applying the law of mass action to the formation of propane hydrate

$$C_3H_8 + nH_2O \rightleftarrows C_3H_8 \cdot nH_2O\,(\text{hydr.})$$

in terms of activities

$$[a_{C_3H_8}][a_{H_2O}]^n = K[a_{C_3H_8} \cdot n_{H_2O}]$$

and then converting to fugacities the authors obtained the expression:

$$f_2(a)^n = f_1(a_1)^n = K,$$

where f_2 is the fugacity of propane in equilibrium with the hydrate and pure liquid water, f_1 the fugacity of propane in equilibrium with the hydrate in aqueous solution, a the activity of pure liquid water ($a = 1$), and a_1 the activity of water in the solution. From the equation given above,

$$n = \frac{\lg (f_2/f_1)}{\lg (a_1/a)} = \frac{\lg f_1 - \lg f_2}{-\lg a_1}.$$

By using aqueous 2 M solutions of methanol, ethanol, acetone, and KOH for hydrate formation, Strong and Miller obtained at 1.9°C for all four solutions the value $n \simeq 6$. It should be noted that this result does not agree with the values of n for propane hydrate found by other investigators[51] ($n = 17.95$).

V. THERMODYNAMICS OF HYDRATE FORMATION

Problems connected with the calculation of the energy of formation of hydrates, the entropy and enthalpy of this process, and the work of expansion of the crystal lattice of the hydrate were considered in detail by Stackelberg[13]. On the basis of the general premises that simple gas hydrates are formed from molecules of water and the hydrate-forming substance with the aid of van der Waals forces and that in energetic respects the crystal lattice of the gas hydrate differs very little from the lattice of ordinary ice[12]. Stackelberg suggested that the entropy of the reaction:

$$M_{gas} + nH_2O_{solid} = M.nH_2O_{hydr.}$$

equals the entropy of freezing of 1 mole of gas (ΔS):

$$\Delta S = \Delta S_1 + \Delta S_2.$$

In this instance ΔS_1 (the entropy of condensation of 1 mole of gas) according to Trouton's rule is 21 cal deg^{-1} and ΔS_2 (entropy of freezing of 1 mole of liquefied gas) was 1 cal deg^{-1}, and consequently $\Delta S = -22$ cal deg^{-1}. By analogy with physical adsorption, according to Eucken[54] the energy of formation of the hydrate is

$$W_{ads} = W_{hydr} \simeq -\sqrt{21 T_b} \times 8000,$$

where T_b is the boiling point of the hydrate-forming substance at atmospheric pressure in °K, 8000 cal mole^{-1} is the heat of vaporisation of water not entering into the pseudocrystalline group; hence $W_{hydr} \simeq -400\sqrt{T_b}$.

The change in free energy (ΔG) in hydrate formation is here described by the equation (for 273°K):

$$\Delta G = W_{hydr} - T\Delta S = -400\sqrt{T_b} + 6000. \quad (1)$$

At the same time

$$\Delta G = RT \ln P_{diss}, \quad (2)$$

where P_{diss} is the dissociation pressure of the hydrate in atmospheres.

On combining Eqns. (1) and (2) it is easy to obtain the relation

$$\lg P_{diss.} = 4.8 - 0.32\sqrt{T_b}. \quad (3)$$

Eqn. (3), which connects P_{diss} with the boiling point of the hydrate-forming substance, is true only at 0°C.

For $t > 0°C$ ($M_{gas} + nH_2O_{liquid} \rightarrow M.nH_2O_{hydr}$), Stackelberg obtained the general equation:

$$4.57 \lg P_{diss.} = -400\sqrt{T_b} - n1437 + 22T + 1437T/273. \quad (4)$$

With the aid of Eqn. (3) he calculated P_{diss} at 0°C for hydrates which had been studied well and obtained values which were compared with experimental data (Table 1).

Table 1.

M	B.p., T_b, °K	P_{diss}, atm	
		expt	calc.
CH_4	112.0	26	26
C_2H_4	171.0	5.5	4.2
C_2H_6	180.0	5.2	3.2
C_2H_2	189.0	5.7	2.5
C_3H_8	228.0	1.0 (1.7)	0.9

As noted above, one of the main conditions for the existence of a hydrate is the relation[48]: $P'_M = P_{diss} < P_M$, where P_M is the saturated vapour pressure of the hydrate-forming substance.

By using the combined Clausing–Clapeyron and Trouton equation $\lg P_M = 4.60 - 0.0169\, t_b$ and Eqn. (3) the boundary condition for the formation of the hydrate can be obtained ($P_M = P_{diss}$): $t_b = 60°C$. Hence gases and volatile organic liquids with $t_b > 60°C$ cannot form hydrates. The extensive experimental results agree with this statement (an exception is chloroform, for which $t_b = 61°C$).

ENTHALPY OF FORMATION OF HYDRATES

Stackelberg showed[7,13] that for the process $M_{gas} + nH_2O_{liquid} \rightleftharpoons M.nH_2O_{hydr}$ the enthalpy calculated on the basis of calorimetric and tensimetric measurements for $n \simeq 6$, varies within limits from −14 to −17 kcal mole^{-1}; at $n \simeq 9$, from −19 to −20 kcal mole^{-1} and at $n \simeq 17$, from −29 to −32 kcal mole^{-1}. For the process $M_{solid} + nH_2O_{solid} \rightleftharpoons M.nH_2O_{hydr}$ both the enthalpy (±2 kcal mole^{-1}) and entropy (±5 cal deg^{-1}) are almost equal to zero. Simultaneously with this Stackelberg found that for the formation of "double hydrates":

$$M_{gas} + 2H_2S_{gas} + 17H_2O_{liquid} \rightleftarrows M \cdot 2H_2S \cdot 17H_2O_{hydr},$$

the enthalpy and entropy are rather significant ($\Delta H =$ 70 kcal mole^{-1} and $\Delta S = -200 - 250$ cal deg^{-1}).

The work of expansion of the crystal lattice of the hydrate on increasing the diameter of the molecule introduced into its internal cavities was calculated by Stackelberg and Jahns[14].

As a result of careful X-ray diffraction measurements of the crystal lattice parameters of the hydrates of structures (I) and (II) they found that the parameters a increase with the diameter of the molecule of the hydrate-forming substance. Thus a change in d_{eff} from 5.2 to 5.7 Å increases the lattice parameter of structure (I) by 1%. The same effect is observed in structure (II) for "double hydrates", where the increase in a becomes noticeable at $d_{eff} > 6.3$ Å. Evidently the value of the work of expansion of the crystal lattice of the hydrate produced by large molecules allows the stability of the hydrate to be evaluated.

Starting from the general definition, the work of expansion is $-W_{exp} = \int_{v_0}^{v} p\,dv$, where p is the dissociation pressure of the hydrate, and introducing the value of the coefficient of compressibility of the hydrate, which characterises the force opposing the expansion of the lattice,

$$\chi = -\frac{1}{v_0} \cdot \frac{dv}{dp},$$

the authors[14] obtained the following expression for the work of expansion:

$$-W_{exp.} = \frac{[9Na_0^4(\Delta a)^2]}{8 \cdot 2 \cdot \chi \cdot a_0^3 \cdot 41} = \frac{8{,}3 \cdot 10^{21} \cdot a_0^3}{\chi}\left(\frac{\Delta a}{a_0}\right)^2 \text{ cal}, \quad (5)$$

where a_0 is the parameter of the normal lattice (before expansion), $a = a_0 + \Delta a$ is the parameter of the expanded lattice.

On converting to numerical values: $\chi = 4 \times 10^{-5}$, $a_0 = 12 \times 10^{-8}$ cm, structure (I), and $a_0 = 17.3 \times 10^{-8}$ cm, structure (II), the final form can be obtained.

$$-W_I = 36\left(100\frac{\Delta a}{a_0}\right)^2 \text{ cal, structure (I)} \quad (6)$$

$$-W_{II} = 107\left(100\frac{\Delta a}{a_0}\right)^2 \text{ cal, structure (II).} \quad (7)$$

The work performed in the expansion of the crystal lattice increases the chemical potential of the molecule of the complex-forming substance by $\Delta\mu$:

$$-W_{exp} = \Delta\mu = RT\ln(P/P_0). \quad (8)$$

From this equation, on increasing the chemical potential, P_{diss} for the hydrate increases and consequently the "upper quadruple point" of the hydrate is shifted to lower temperatures. This depression of the critical temperature for the decomposition of the hydrate (ΔT_C) is described by the equation:

$$\Delta T = (-W_{exp} \cdot T)/(\lambda_{hydr} - \lambda_M) = -W_{exp} \cdot T/\lambda \quad (9)$$

where λ_{hydr} is the heat of the reaction $M.nH_2O \rightarrow M_{gas} + nH_2O_{liquid}$; λ_M the heat of vaporisation of the hydrate-forming substance, and λ the heat of the reaction $M.nH_2O \rightarrow M_{liquid} + nH_2O$.

For structure (I) (at $n \simeq 6$), $\lambda_I \simeq 10\,000$ cal, λ_{II} (at $n \simeq 17$) = 25 000 cal, and consequently after substituting in Eqn. (9) the corresponding values of W_{exp}^{I} and W_{exp}^{II} the approximate formula

$$\Delta T = 1.1\left(100\frac{\Delta a}{a_0}\right)^2 \quad (10)$$

can be obtained; it is true for structures (I) and (II).

From Eqn. (10) it follows that an increase of 3% in the lattice dimensions depresses the temperature of the upper quadruple point by 10 deg. This conclusion agrees with the experimental results[14].

VI. STABILISATION OF HYDRATES WITH THE AID OF AN "AUXILIARY GAS"

The stabilising action on hydrate formation of a so-called "auxiliary gas", that is, a gas the molecules of which are not held in the internal cavities of the hydrate crystal, was first observed by Villard in 1897.[63] In studying the hydrate of N_2O, Villard found that in pure compressed N_2O at 14°C the decomposition pressure of the hydrate formed is 250 atm.

When the experiment is carried out at the same temperature but in the presence of air the decomposition pressure of the hydrate is reduced to 100 atm. In 1923 Villard[1] observed a still more interesting effect: iodine, which itself is incapable of hydrate formation (b.p. 183°C), forms in the presence of oxygen or nitrogen (which form hydrates only at very high pressures[31]) a brick-red, crystalline hydrate, stable at 3°C (P_{N_2} = 200 atm) and even at 8°C (P_{O_2} = 330 atm). Further investigations of the "stabilisation effect" carried out by Stackelberg and Meinhold[11] allowed a general experimental rule to be established: certain gases (N_2, O_2, CO_2, etc.) which fill only an insignificant part of the cavities of the hydrate lattice appreciably raise the critical temperature for the decomposition of a hydrate by their presence (usually at $P > 1$ atm). The degree of elevation of the decomposition temperature of the hydrate depends on the nature of the gas. Thus in studying the influence of CO_2 and N_2 on the decomposition temperature of hydrates (CCl_4, $CHCl_3$, CH_2Cl_2)‡ Stackelberg and Meinhold established that the effect which could be produced by the presence of CO_2 is twice as much as that obtainable in the presence of N_2 (~ 10 deg and 5 deg). It is also interesting to note that the stabilising influence of n-butane§, which was recently unambiguously shown not to form hydrates itself[60], but nevertheless on being present as one of the components of a gaseous mixture considerably alters the value of the equilibrium pressure over the "mixed hydrate". Extensive investigations of the stabilising action of "auxiliary gases" were made by Barrer and Ružicka[64]. In studying the hydrates of chloroform the authors established that such gases as H_2, Ne, N_2, Ar, O_2, CH_4, Kr, Xe, C_2H_4, C_2H_6, and CO_2 not only appreciably change the equilibrium conditions of hydrate formation but also partially fill the small cavities of structure (II), that is, here it is possible to speak not about an individual hydrate of chloroform but about its "mixed hydrates".

VII. HYDRATES OF INDIVIDUAL GASES AND VOLATILE ORGANIC LIQUIDS

Schroeder's monograph[1] contains the most complete information about the hydrates of the individual gases and the volatile organic liquids relating to the experimental results published up to 1923. Frost and Deaton's monograph[5] contains data embracing the period up to 1945 and relating mainly to hydrates of hydrocarbon gases. The studies made in the last two decades are surveyed in the review part of Stackelberg's papers[10,11], the fundamental handbook edited by Katz[65], and also in a series of articles published between 1960 and 1966.

‡ Carbon tetrachloride forms hydrates only in the presence of a stabilising gas.

§ In this connection indications of the possibility of the formation of hydrates of n-butane[3,53] must be considered extremely doubtful.

Methane

Villard first obtained a hydrate of methane[66] at $t > 0°C$ and $P > 1$ atm; the maximal temperature at which he succeeded in obtaining the hydrate was 21.5°C. Methane hydrate was then investigated by Deaton and Frost[67] and Roberts[68] who studied the $P-t$ dependence for temperatures from 0.5° to 12.8°C. The part of the $P-t$ diagram in the region of existence of ice (from −10° to −5°C) was also investigated[68]. The construction of apparatus needed for working at high pressures allowed Kobayashi and Katz[69,70] to obtain the $P-t$ dependence at pressures from 333 atm (22.5°C) to 762 (28.8°C).

Campbell and McLeod[71] studied methane hydrate in the same pressure interval and obtained results agreeing with those of Kobayashi and Katz. In 1964, Marshall and coworkers published a study[72] in which with the aid of a specially constructed chamber, using an original method of "pressure jump" they studied hydrates of CH_4 in the pressure range from 157 atm (17°C) to 3915 atm (47°C). Table 2 gives their equilibrium $P-t$ data.

Table 2.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
17.05	157	28.44	645.3
17.33	157.2	33.55	1093.1
22.05	295.8	37.16	1506.2
21.94	295.1	39.55	1847.2
22.61	332.8	40.5	2033.0
24.9	437.0	41.05	2208.3
25.0	431.8	43.66	2679.2
27.0	561.3	45.16	3152.8
28.4	645.3	46.44	3627.1
		46.88	3915.4

In their monograph[28] van der Waals and Platteeuw give the following physicochemical characteristics for the hydrate of CH_4, structure (I): $P_{diss} = 26$ atm at 0°C; the heat of formation from water and the gas is 14.5 kcal mole^{-1} at 0°C; the decomposition temperature at $P = 1$ atm is $t = -29.0°C$.

Ethane

The hydrate of C_2H_6 was first obtained by Villard[73]. Deaton and Frost[74] obtained the $P-t$ dependence for ethane hydrate at pressures of 5.4–54 atm and temperatures 0–14.4°C. Roberts[68] studied ethane hydrate at pressures up to 64 atm (this also embraces the region of existence of the liquid hydrocarbon phase). Deaton and Frost[51] obtained equilibrium $P-t$ data in the region of negative temperatures; they investigated temperatures from −9.6° to −1.1°C and pressures from 3.09 to 4.51 atm. Their results are presented in Table 3.

On the basis of the equilibrium data given above and obtained earlier[74,75] for $t > 0°C$ and pressures up to $P =$ 68 atm, Deaton and Frost calculated the heats of decomposition of ethane hydrate at $t > 0°C$ (17 796 cal mole^{-1}) and $t < 0°C$ (6069 cal mole^{-1}) and used Forcrand's method to determine the composition of the hydrate at the lower quadruple point: $C_2H_6 \cdot 8.25H_2O$. The most recent results on the equilibrium $P-t$ data are given in Reamer and coworkers' work, carried out at a high experimental level. These results, which agree well with those obtained by other authors, are given in Table 4.

The following constants for ethane hydrate, structure (I), are given by van der Waals and Platteeuw[28]: $P_{diss} = 5.2$ atm at 0°C; maximal temperature of existence of the hydrate 14.5°C; heat of hydrate formation at 0°C, $\Delta H = 16.3$ kcal mole^{-1}.

Table 3.

t_{equil}, °C	P_{equil}, atm
−9.6	3.09
−6 6	3.52
−3.5	3.99
−1.1	4.51

Table 4.

t_{equil}, °C	P_{equil}, atm
6.73	9.6
9.66	16.42
11.52	21
14.2	32.5

Table 5.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
1.5	9.26	9.6	23.75
5.22	11.41	9.76	24.7
5.16	12.18	10.2	29.1
5.55	13.81	10.5*	26.2*
6.41	17 5	11.5	30.9
6.5	20.5	12.05	32.2
7.26*	19.1*	19.93	34.9
8.55	21.9		

* Values of P_{equil} too low.

Stackelberg gave[10] $\Delta H = 15.0$ kcal mole^{-1}, decomposition temperature of hydrate $t = 15.8°C$ at $P = 1$ atm.

Ethylene

Ethylene hydrate was first obtained by Villard[66], who determined P_{diss} for the hydrate at 0° and 17°C (5.5 atm and 44.8 atm). More extensive investigations in this field were made by Deaton and Frost[67], Kobayashi and Katz[69], and by Diepen and Scheffer[77], who investigated ethylene hydrate at pressures up to 50.5 atm. Reamer and coworkers[76] made a careful determination of the equilibrium $P-t$ values; their results are given in Table 5.

Snell and coworkers[78] studied the conditions of formation of ethylene hydrate and of the hydrate of a $CH_4 + C_2H_4$ mixture at pressures up to 612 atm. Fig. 4 shows the $P-t$ dependence they obtained.

Stackelberg[10] gives the following values of the constants for ethylene hydrate, structure (I); $P_{diss} = 5.5$ atm at 0°C (5.44 according to Diepen), $\Delta H = 15.2$ kcal mole^{-1}; decomposition temperature −13.4°C at $P = 1$ atm; composition found by Claussen[20] by an X-ray diffraction method $C_2H_4 \cdot 7.4H_2O$.

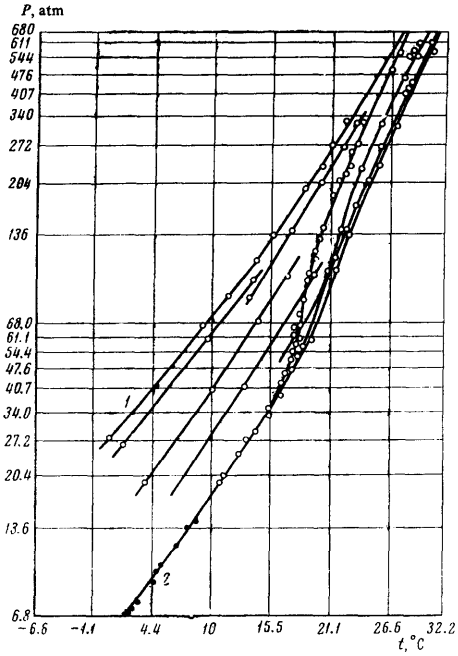


Figure 4. Conditions of formation of the mixed hydrate of CH_4 (*1*) and C_2H_4 (*2*).

Acetylene

Acetylene hydrate was first obtained from the compressed gas in 1877 by Cailletet[1]. Villard[73] measured the pressure of C_2H_2 vapour over its hydrate at 0°C (P = 5.5 atm) and 17°C (P = 44.8 atm). In a summary table Stackelberg[10] gives: (a) decomposition temperature of hydrate 15.4°C at P = 1 atm; (b) temperature of upper quadruple point, 16°C; (c) heat of formation of hydrate 15 000 cal mole^{-1}.

Propane

Propane hydrate was first obtained by Villard[73]. Deaton and Frost determined the equilibrium P–t values for this hydrate[74,75] (Table 6). On the basis of the P–t values given above the heats of formation of propane hydrate at $t > 0$°C and $t < 0$°C and its composition at the lower quadruple point ($C_3H_8 \cdot 17.95H_2O$) were calculated[79].

The conditions of formation of propane hydrate at high pressures (in the region of existence of the liquid hydrocarbon phase) were also studied by Wilcox and coworkers[79], Reamer and coworkers[76] (at temperatures from 1.1° to 5.7°C and pressures from 2.4 to 20 atm), and Teodorovich[80].

The following values of the constants for propane hydrate structure (II), are given by van der Waals and Platteeuw[28]: P_{diss} = 1.74 atm at 0°C (Stackelberg[10] gave P_{diss} = 1 atm), maximal temperature of existence of hydrate t = 5.69°C, heat of formation 32 000 cal mole^{-1} at 0°C, crystal lattice constant 17.4 Å.

Propene

The first information about propene hydrate is contained in a paper by Reamer and coworkers[76]. They succeeded in obtaining P–t values for the pressure range 5–20 atm and temperatures from 0.5° to 1.7°C (the pressure interval also embraces the region of existence of the liquid hydrocarbon phase). A precision investigation of propene hydrate, during which even the pressure of water vapour in the system was calculated, was made by Clarke and coworkers[81]. Table 7 gives their equilibrium results. They obtained the following expression for the volatility (f) of propene over its hydrate:

$$\lg f = 24.8309 \pm 0.0001 - (6610 \pm 20)\ 1/T$$

Table 6.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
−11.95	0.984	+0.222	1.787
− 9.0	1.137	+0.444	1.895
− 6.27	1.318	+0.611	1.901
− 5.56	1.328	+0.723	2.018
− 3.33	1.462	+2.388	2.875
− 0.278	1.698	+3.78	3.958

Table 7.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
−0.161	4.569	0.493	5.330
−0.134	—	0.558	5.404
−0.113	4.622	0.594	5.452
−0.064	4.674	0.798	5.709
+0.006	4.746	0.897	5.851
0.217	4.988	0.943	5.913
0.325	5.114	0.958	—
0.442	5.253		

and calculated the heat of decomposition of the hydrate at t = 0°C (ΔH = 30230 ± 90 cal mole^{-1}). P–t values in the range of negative temperatures (from −3.7° to −14.7°C) were found by Byk and coworkers[82], who obtained an equation for the above temperature range, $\lg f = 4.4853 - 1072/T$ and calculated the heat of decomposition of the hydrate for $t < 0$°C (ΔH = 4920 cal mole^{-1}).

According to Clarke and coworkers[81] the temperature of the lower quadruple point of propene hydrate is −0.134°C, that of the upper is 0.958°C, and the composition of the hydrate is $C_3H_8 \cdot 17H_2O$.

Isobutane

Deaton and Frost obtained the first reliable experimental equilibrium P–t data for isobutane hydrate[83]. Kayano and Utida[60] made a careful investigation of isobutane hydrate, including the determination of its composition (iso-$C_4H_{10} \cdot 17H_2O$ and quadruple points (0°C and 847 mmHg for the lower point; 1.8°C and 1268 mmHg for the upper); they obtained the following equations:

$$\lg P_{mm} = 29.33 - 7210/T \ (\text{at } t > 0°),$$
$$\lg P_{mm} = 9.106 - 1688/T \ (\text{at } t < 0°).$$

Their calculated heats of decomposition of the hydrate are respectively ΔH = 32 960 cal mole^{-1} (t > °C) and ΔH = 7716 cal mole^{-1} (t < 0°C).

Hydrogen Sulphide

Hydrogen sulphide hydrate was first obtained in 1840 by Beller[1]. Systematic investigations of this hydrate were carried out by de Forcrand and Villard[84], who measured P_{diss} of the hydrate at 0.5°C (1.1 atm) and 28.5°C (16 atm). Sheffer[85] determined the quadruple points of the hydrate (−0.389°C and 0.917 atm for the lower point; 29.6°C and 22 atm for the upper), and Kolvezce and Scheffer[86] its composition: $H_2S.6H_2O$.

Careful measurements of the equilibrium P–t values (the water–hydrate–H_2S_{gas} system in the region close to the freezing point of water) were made by Wright and Maas[87].

The most extensive investigation of the H_2S–H_2O system (in the region of existence of the hydrates) was made by Selleck and coworkers[88], who obtained equilibrium P–t values for the temperature range from −0.389° to 29.45°C and pressures from 0.917 to 22.10 atm. These results are given in Table 8.

Table 8.

Hydrate–water–gas		Hydrate–ice–gas	
t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
− 0.389*	0.917	0	0.435
+ 4.4	1.55	−15	0.496
+10	2.75	−12.2	0.556
+15.5	5.925	− 9.45	0.631
+21.1	8.79	− 6.6	0.714
+26.6	15.7	− 3.89	0.803
+29.6*	22.0	− 1.11	0.891
− 0.389	0.917*	− 0.233*	0.917
+ 1.8	3.4	−22.7	0.340
+18.6	6.8	—	—
+22.6	10.2		
+25.3	13.6		
+27.4	17		
+28.8	20.4		
+29.45	22.10*		

* Quadruple point.

For the system hydrate + H_2O_{liquid} + H_2S_{gas} these same authors obtained the equation:

$$\lg P_{atm} = 15.11835 - \frac{6867.98}{T}.$$

Sulphur Dioxide

Sulphur dioxide hydrate, with m.p. 4–5°C was obtained in 1829.[1] Having obtained a hydrate from liquid SO_2, Villard[73] proposed the formula $SO_2.6H_2O$. Roozeboom[47] determined, in a sealed glass ampoule, the critical decomposition temperature of SO_2 hydrate (12.1°C) and the decomposition temperature at P_{SO_2} = 1 atm (7.1°C).

Tamman and Kriege[52] proposed for sulphur dioxide hydrate the equations $t = 16.75\,(\lg P + 0.4179)$ at $t > -2.6$°C, and $t = 41.60\,(\lg P + 0.4904)$ at $t < -2.6$°C, where t is the temperature of hydrate formation, and P the dissociation pressure, atm. The same authors found that $t = -2.6$°C is the eutectic point, at which the hydrate has the composition $SO_2.6H_2O$. Stackelberg[10] gives the following values for the constants of sulphur dioxide hydrate, structure (I): P_{diss} = 0.39 atm at 0°C; heat of hydrate formation from gaseous SO_2 and H_2O = 16.6 kcal mole^{-1}, crystal lattice constant 11.94 Å.

Carbon Dioxide

Carbon dioxide hydrate was obtained in 1882 by Wroblewsky[89] at ~ 0°C and a CO_2 pressure of ~ 30 atm. Villard[76] proposed the formula $CO_2.6H_2O$ for the hydrate Tamman and Kriege[52] measured P_{diss} of the hydrate in the temperature range from −20° to −43°C (106.4 mmHg and 9.2 mmHg) and obtained the equation $t = 22.0\,(\lg P - 1.0904)$, where t is in °C and P in cmHg.

Wiebe[90], having studied the $CO_2 + H_2O$ system at pressures up to 700 atm, obtained for carbon dioxide hydrate the formula $CO_2.7H_2O$. Deaton and Frost[74] obtained equilibrium P–t data for a wide temperature range (including $t > 0$°C).

Table 9.

t_{equil}, °C	P_{equil}, atm
4.6	20.1
6.0	25.5
7.7	31.8
9.2	36.4
9.2	42.4

Unruch and Katz[91] studied the conditions of hydrate formation in the $CO_2 + H_2O$ system up to the upper quadruple point (9.8°C, 42.4 atm). Their results are given in Table 9.

Dinitrogen Oxide (N_2O)

Villard obtained dinitrogen oxide hydrate in 1888.[79] He measured P_{diss} of this hydrate at −9.1°C (P_{diss} = 3.6 atm) and 10.7°C (P_{diss} = 34.7 atm), and also proposed for it the formula $N_2O.6H_2O$. Tamman and Kriege[52] obtained for dinitrogen oxide hydrate the equation:

$$t = 1.9\,(\lg P - 0.9795),$$

where t is in °C, and P_{diss} in atm.

Stackelberg[10] gives the following constants for dinitrogen oxide hydrate, structure (I): P_{diss} = 10 atm at 0°C, decomposition temperature −19.3°C at P_{N_2O} = 1 atm. The critical decomposition temperature is 12.0°C, the heat of formation of the hydrate (from water and gas) 14.7 kcal mole^{-1}. The crystal lattice constant is 12.03 Å.

Hydrogen Selenide (H_2Se)

Hydrogen selenide hydrate was obtained by de Forcrand in 1902.[1] Experimental P–t values have not been published. Stackelberg[10] gives the following constants for this hydrate: P_{diss} = 0.45 atm at 0°C, decomposition temperature of the hydrate 8.0°C at P = 1 atm; t_c = 30°C; lattice parameter 12.06 Å.

Sulphur Hexafluoride (SF_6)

Sulphur hexafluoride hydrate was studied by Sortland and Robinson[36]. The authors obtained P–t data for the temperature range from −9 to 15° they calculated the composition of the hydrate at the lower (~ 0°C) quadruple point: $SF_6.17.02H_2O$, determined the upper quadruple point (14.0°C, 19.9 atm), and also calculated the heat of formation of the hydrate at $t < 0$°C (5140 cal mole^{-1}) and at $t > 0$°C (29570 cal mole^{-1}).

PH_3, AsH_3, and SbH_3

1. Phosphine hydrate was obtained by Skinner[1] by condensing phosphine vapour in the presence of water. The same author measured P_{diss} at 1°C (P = 2 atm) and 25.0°C (P = 16 atm).

According to Stackelberg[10] P_{diss} = 1.6 atm at 0°C, decomposition temperature of the hydrate = −6.4°C at P_{PH_3} = 1 atm, critical decomposition temperature = 28.0°C.

2. According to Schroeder[1] arsine hydrate has the composition $AsH_3 . 6.14H_2O$ and is characterised by the following values: t = 0°C at P = 613 mmHg; t = 1.6°C at P = 760 mmHg; t = 21°C at P = 8.85 atm.

According to Stackelberg[10], the constants of arsine hydrate are: decomposition temperature = −1.8°C at P = 1 atm. Critical decomposition temperature 28.3°C.

3. For stibine hydrate, Schroeder[1] gives the value P_{diss} = 760 mmHg at t = 10.9°C.

Chlorine

Chlorine hydrate, as already stated above[1], was obtained in 1810 by Davy. The decomposition temperature of this hydrate (determined in a sealed glass ampoule) is 28.7°C, according to Schroeder[92].

van der Waals and Platteeuw[28] give data for chlorine hydrate: P_{diss} = 252 mmHg at 0°C; heat of formation 16.0 kcal mole^{-1}; crystal lattice parameter 12.03 Å. Tamman and Kriege[52] proposed for this hydrate the formula $Cl_2.8H_2O$ and for $t < 0$°C (the ice–hydrate–vapour system) obtained the equation $t = 49.0\ (\lg P + 0.4757)$, where t is in °C and P in mmHg. Careful X-ray diffraction investigation of chlorine hydrate was made by Pauling and Marsh[21,93], and also Allen[94]. The latter found that at the lower quadruple point the Cl_2 molecule (for the formation of a hydrate from liquid chlorine) occupies only 16% of the small cavities of the crystal lattice, the parameter of which is 11.82 Å. The composition of this hydrate is $Cl_2 . 7.27 + 0.17H_2O$. Investigations, made by Glew and Rath[56], showed that when the hydrate is in equilibrium with gaseous chlorine, then 81% of the small cavities of structure (I) are occupied and the hydrate has the composition $Cl_2 . 6.04 \pm 0.13H_2O$.

Bromine (Br_2)

As already mentioned above, bromine hydrate was first obtained by Levig[1]. Roozeboom[47] determined the critical decomposition temperature of the hydrate (in a sealed ampoule), ~ 6.2°C, and proposed for the hydrate the formula $Br_2.10H_2O$. Tamman and Kriege[52] obtained for Br_2. $.10H_2O$ the formula $t = 43.0\ (\lg P + 0.2465)$ ($t < 0$°C), where t is in °C and P in mmHg. Mulders[28] determined P_{diss} = 43.90 mmHg at 0°C, maximal temperature of existence of the hydrate 5.81°C, heat of hydrate formation 20.83 cal mole^{-1} at 0°C and he proposed the composition $Br_2 . 8.47H_2O$ for the lower quadruple point. From Stackelberg's review[10], bromine hydrate is characterised by structure (I) with lattice parameter 12.0 Å. In addition Jeffrey and McMullan[58] proposed in 1963 that bromine hydrate crystals are tetragonal.

Iodine (I_2)

Iodine hydrate can be obtained, as was shown experimentally in 1923 by Villard[1], only in the presence of "stabilising" gases (N_2, O_2, CO_2). The highest positive temperature (8.0°C) at which the crystalline iodine hydrate is still stable could be attained in the presence of oxygen under a pressure of 300 atm.

Inert gases (Ar, Kr, Xe)

Villard obtained hydrates of Ar, Kr, and Xe in 1896[95] and then de Forcrand[96] in 1925. Nikitin[43] in 1956 also mentioned the ability of radon (Rn) to form a hydrate.

Waller[97] carried out an X-ray diffraction investigation of the hydrates of Ar, Kr, and Xe and found that all three hydrates have structure (I), with ideal formula $M . 5.75H_2O$.

Godhot[98] obtained hydrates of Kr and Xe with heavy water, $Kr.6D_2O$ and $Xe.6D_2O$.

Argon. According to Diepen, cited by van der Waals and Platteeuw[28], P_{diss} = 95.5 atm at 0°C (according to Stackelberg[10] P_{diss} = 105 atm, and the decomposition temperature of the hydrate is −42.8°C at P = 1 atm). Tamman and Kriege[52] obtained an equation for argon hydrate ($Ar.5–6H_2O$): $t = 19.6(\lg P - 2)$, where t is in °C and P in atm. The equilibrium P–t values were obtained by Marshall and coworkers[72] for the wide temperature range 1.65° to 31.0°C and pressures from 105 to 3780 atm (Table 10).

Table 10.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
1.16	105.0	25.6	1807.4
3.7	130.2	26.7	2040.6
2.9	121.2	26.8	2049.8
6.3	167.6	27.7	2204.1
11.8	316.5	28.9	2662.2
11.1	314.8	29.7	3031.4
15.3	494.0	30.4	3336.7
17.8	659.9	31.0	3717.2
19.3	807.5	31.1	3777.4
23.5	1400.1	30.9	3729.1

Krypton. According to de Forcrand[96], P_{diss} = 14.5 atm at 0°C and at t = 12.5°C P_{diss} = 47.5 atm. Tamman and Kriege[52] obtained for krypton hydrate the equation: $t = 21.2\ (\lg P - 1.1698)$ where t is in °C and P in atm. Stackelberg[10] gives the following values of the constants for ($Kr.5–6H_2O$): decomposition temperature −27.8°C at P = 1 atm, heat of hydrate formation 13.9 kcal mole^{-1}.

Xenon. According to Waller's results[97] xenon hydrate is the most stable in the series Ar < Kr < Xe. de Forcrand[96] measured its P_{diss} at the temperatures 1.4°C (P = 1.45 atm) and 23.5°C (P = 17 atm). For Xe($n \simeq 6H_2O$) Stackelberg[10] gives the following values of the constants: P_{diss} 1.5 atm at 0°C (van der Waals and Platteeuw[28] give P_{diss} = 1.15 atm). The decomposition temperature of the hydrate is −3.4°C at P = 1 atm. The heat of hydrate formation is 16.7 kcal mole^{-1}; the crystal lattice parameter is 11.97 Å.

Nitrogen

As already stated above, nitrogen hydrate was first obtained by van Cleef and Diepen[30] in a specially constructed apparatus which allows hydrates to be studied at very high pressures, ~ 1000 atm. On the basis of the experimental P–t data they found for the temperature range from 0° to 18°C, they obtained the equation given below for the hydrate–water–gas system and calculated the heat of formation of the hydrate:

$$\lg P_{atm} = 14.1293 \pm 0.0006 - \frac{3257 \pm 23}{T};$$

$$\Delta H_1 = 12380 \pm 310 \text{ cal mole}^{-1}.$$

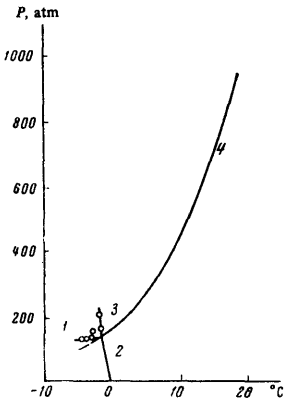


Figure 5. Conditions of hydrate formation by nitrogen: *1*) hydrate–ice–gas; *2*) ice–water–gas; *3*) hydrate–ice–water; *4*) hydrate–water–gas.

Subsequently the same authors[31] determined the equilibrium P–t values at t < 0°C for the temperature range −1.17° to −4.45°C and obtained the equation $\lg P_{atm}$ = 5.5598 ± 0.0002 − (927 ± 17)/T, calculated the heat of hydrate formation ΔH_2 = 3810 ± 110 cal mole^{-1} and also determined the lower quadruple point of the hydrate in the ice–hydrate–gas system, t = −1.3°C, P = 141.5 atm. Fig. 5 shows a correlation of the P–t results of van Cleef and Diepen for N_2.6.01 ± 0.23H_2O¶.

Nitrogen hydrates were also studied by Marshall and coworkers[57] over a wide range of temperatures and pressures. Table 11 shows their experimental P–t values.

¶ Composition of the hydrate calculated by the same authors.

Oxygen

Oxygen hydrates were first obtained by van Cleef and Diepen[31] and published P–t equilibrium data for oxygen hydrate over a wide range of temperatures from −1.8° to +18.0°C and pressures from 100 to 938 atm. The same authors proposed the equations:

$$\lg P_{atm} = 14.3082 \pm 0.0005 - \frac{3340 \pm 21}{T}$$

(for the hydrate–water–gas system), and

$$\lg P_{atm} = 5.1168 + 0.0006 - \frac{838 \pm 38}{T}$$

Table 11.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
4.4	245.2	24.6	1665
8.0	362.8	25.7	1825
13.6	628.0	26.0	2030
18.4	1005	27.4	2170
19.8	1135	29.4	2640
21.1	1270	31.6	3130
23.4	1520	32.9	3250

Table 12.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
−1.8	100.5	1.5	139	10.1	373
−1.4	104.0	1.7	142	10.1	376
−1.2	106.2	2.0	147.5	10.3	381
−1.0	108.5	2.7	158	10.6	404
−1.0	108.7	3.6	175	11.0	438
−0.8	110.6	4.7	194	12.1	471
−0.6	113.5	5.0	208	13.1	520
−0.3	116.5	5.3	214	13.2	543
0.0	119.5	5.4	214	14.1	597
0.0	120.2	6.0	232	14.2	599
0.0	120.5	7.0	260	16.0	662
0.5	126.3	8.1	296	16.1	744
0.5	127.5	8.6	308	17.1	836
1.0	136.5	8.8	320	17.6	880
				18.0	938

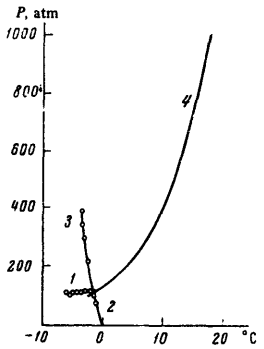


Figure 6. Conditions of hydrate formation by oxygen: *1*) hydrate–ice–gas; *2*) ice–water–gas; *3*) hydrate–ice–water; *4*) hydrate–water–gas.

(for the hydrate–ice–gas system), and calculated the heats of formation of the hydrate (O_2. 6.06 ± 0.21H_2O): ΔH_1 = 11 840 ± 260 cal mole^{-1} and ΔH_2 = 3190 ± 160 cal mole^{-1} corresponding to the parts of the P–t curves above and

below the quadruple point ($t = -1.0°C$, $P = 109.2$ atm). The experimental results of van Cleef and Diepen are given in Table 12 and Fig. 6.

HYDRATES OF VOLATILE ORGANIC LIQUIDS

The review part of Stackelberg's paper[10] and the monograph of van der Waals and Platteeuw[28] give the characteristics of a series of hydrates formed by volatile organic liquids. All these results are given in Table 13, which also contains information about certain hydrates taken from later original papers.

Table 13.

Hydrate-forming substance	Dissociation pressure at 0°C, mmHg	Decomposition temp. of hydrate, °C, at $P = 1$ atm	Max. temp. of existence of hydrate, °C	Heat of hydrate formation at 0°C from gas and water, kcal mole^{-1}	Crystal lattice parameter, Å	Reference
CH_3Cl	311	7.5	21	18.1	12.00	
C_2H_5F	251	3.7	22.8	18.0	—	
CH_3Br	187	11.1	14.5	19.5	12.09	
CH_3SH	239	10 (8)	12	16.6	12.12	
ClO_2	160	15.0	18.2	6.5	—	
SO_2Cl_2	—	—	—	—	—	1
BrCl	125	14	—	—	—	
$CHCl_2F$	115	—	8.61	32.7	—	104*
C_2H_5Cl	201	0.78	4.8	31.9	17.30	
CH_2Cl_2	116	1.7	1.7	29	17.33	
$C_2H_4Cl_2$	555	1.5	0.09	29.4	--	
C_2H_5Br	152	1.4	0.22	—	—	
CH_3I	74	—	14.3	31.4	17.14	
$CHCl_3$	50	—	1.6	31	17.33	
$(CH_3)_2O$	—	—	—	—	17.44	
$(CH_3)_3CH$	—	—	—	—	17.53	

* $CHCl_2F.17 \pm 0.5\ H_2O$.

There are also reports[1] of the existence of hydrates of such compounds as CF_4, CHF_3, $C_2H_2F_2$, and C_2F_4. Ethylene oxide (C_2H_4O) hydrate was investigated by Glew and Rath[56] and also by Jeffrey and McMullan[58]; Glew and Rath found that the hydrate of C_2H_4O belongs to structure (I). Depending on the C_2H_4O concentration in the aqueous solution, which is found in equilibrium with the hydrate, there is a different degree of filling the cavities of the hydrate lattice. At the temperature of congruent fusion of the hydrate (11.1°C) the filling is 100% of all six of the large cavities of the crystal and 34% of the small cavities. This corresponds to the composition $C_2H_4O \cdot 6.89 \pm 0.06H_2O$.

Glew[99] studied the hydrate of bromochlorodifluoromethane ($CBrClF_2$) and found that this hydrate belongs to structure (II). Tetrahydrofuran hydrate $[CH_2]_4O.17H_2O$, was obtained by Stackelberg[18], who found its melting point to be 5.1°C.

Pinder's investigation of this hydrate[100] showed that the melting point of $[CH_2]_4O.17H_2O$ depends on the THF concentration in the equilibrium solution.

Ponyet and Mealier[101] obtained the hydrate of propylamine and Jordan and Mac[102] studied the structure of diethylamine hydrate.

McMullan and coworkers[103] investigated the hydrate of t-butylamine.

VIII. MIXED HYDRATES

As already stated above, when the hydrate-forming substance is not an individual gas, but a mixture of gases or volatile organic liquids, then the hydrate which is formed is a solution, the composition of which varies during its fusion. Such a hydrate is usually called "mixed".

The simplest examples of a "mixed hydrate" are the so-called "double hydrates" formed by a mixture of two types of molecule: $M_1 + M_2$ or $M_3 + M_4$†.

1. DOUBLE HYDRATES, FORMED BY H_2S AND H_2Se

de Forcrand[1] first observed the ability of hydrogen sulphide to form "double hydrates" when mixed with other gases. Somewhat later[1], double hydrates of hydrogen selenide were obtained. de Forcrand established the experimental fact that H_2S forms hydrates with halogen derivatives of aliphatic hydrocarbons. These hydrates are readily obtained on passing moist H_2S through the corresponding liquid at $t \simeq 0°C$.

Below, in Table 14, are listed the organic compounds which, according to de Forcrand, readily form double hydrates

Table 14.

1. CH_3Cl	8. $C(NO_2)Cl_3$	15. C_2H_5I	22. C_3H_5Br
2. CH_2Cl_2	9. C_2H_5Cl	16. C_3H_3I	23. iso-C_4H_9Cl
3. $CHCl_3$	10. $C_2H_4Cl_2$	17. C_3HCl_3	24. iso-C_4H_9Br
4. CCl_4	11. $C_2H_3Cl_3$	18. C_3H_7Cl	
5. CH_3Br	12. $C_2H_2Cl_2$	19. C_3H_7Br	
6. CH_2Br_2	13. C_2H_5Br	20. iso-C_3H_7Br	
	14. $C_2H_4Br_2$	21. C_3H_5Cl	

de Forcrand studied the $H_2S + CHCl_3$ system most carefully, having shown that the hydrates formed by this system belong to structure (II).

Lui[1] studied a group of double hydrates formed by H_2Se and halogen derivatives of hydrocarbons and found that hydrates of the type $M.2H_2Se.17H_2O$ are formed from the following compounds: CCl_4, $CHCl_3$, CH_3Br, CH_3I, C_2H_5Cl, C_2H_5Br, C_2H_5I, $C_2H_2Cl_2$, iso-C_3H_7Br, iso-C_4H_9Cl. As already stated, CCl_4 itself does not form hydrates.

At the end of the 1890s it was shown[1] that acetylene forms double hydrates with CCl_4, $CHCl_3$, $C_2H_4Cl_2$, CH_3I, $CHBr_3$, C_2H_5Br, CH_2Cl_2, and CH_2I_2.

Halogen substituted hydrocarbons also give double hydrates with C_2H_4, CO_2, and SO_2. Hydrates of such mixtures as $PH_3 + CS_2$, $PH_3 + CO_2$, and $(C_2H_5)_2O + CO_2$ are known[1]. The mixed hydrate[105] $Cl_2.Br_2.7\frac{2}{3}H_2O$, decomposition temperature 14°C, is interesting.

The double hydrates formed by H_2S with the hydrocarbons CH_4 and C_3H_8 were studied comparatively recently (1940s to 1950s). The hydrate of the mixture $CH_3 + H_2S$ was obtained by Noaker and Katz[106] and simultaneously with their obtaining equilibrium P–t values (15–19°C, 47–60 atm), the authors determined the composition of the coexisting equilibrium phases for the hydrate $2H_2S.6CH_4.46H_2O$.

The results of a study of the hydrate $2H_2S.C_3H_8.17H_2O$, which was made by van der Waals and Platteeuw in 1959[29] are of independent interest for the following reason. Up to 1959 the literature devoted to "double hydrates" had been dominated by Stackelberg's viewpoint[12], according to which

† See Chapter I of the present review.

the "double hydrates" formed by hydrogen sulphide (or H_2Se) differ from other binary mixed hydrates by their being compounds of constant composition with a definite, stable dissociation pressure at a given temperature whereas all other double hydrates are characterised by variable composition and corresponding different values of P_{dis}. Van der Waals and Platteeuw showed that the hydrate $2H_2S.C_3H_8.17H_2O$ does not differ in principle from other binary hydrates in which H_2S or H_2Se is absent and is an ordinary non-stoichiometric binary clathrate.

3. DOUBLE HYDRATES FORMED BY HYDROCARBONS

Hydrates Formed by Mixtures of Alkanes

Campbell and McLeod studied[71] hydrate formation in the binary systems: (a) $CH_4 + C_2H_6$; (b) $CH_4 + C_3H_8$; (c) CH_4 + iso-C_4H_{10}, and Deaton and Frost[5] that in the system (d) $CH_4 + C_3H_8$ and (e) $CH_4 + C_2H_6$.

System (a) was investigated at temperatures from 11.6° to 31.0°C and pressures from 68 to 680 atm (at ethane concentrations from 5.4 to 19.1%).

Table 15.

P_{equil}, atm	t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm	t_{equil}, °C
gas No.2		gas No.3		gas No.4	
675	28.8	676	30.9	70.4	17.4
612.5	28.02	611	29.9	61.6	19.4
475	25.8	480	281	680	30.7
339	23.4	351	25.8	340	26
239	20.4	137	20.1	476	28.3
137	16.5	103	18.5	612.5	30.5
103	14.6	69	15.6	137	21.4
71.4	11.7			103	20.1
				71.4	17.5
gas No.5		gas No.8		gas No.9	
73	19.9	470	26.8	66.3	21.1
73	19.6	340	24.6	66.3	20.6
341	27.4	332	24.4	137	24.4
476	29.4	207	22.0	138	23.8
615	31.7	485	26.7	229	25
232	25.4	67	15.4	342	27.3
137	23	615	28.9	476	29.3
				624	31.8
				484	29.9
				235	25.1
				138	24.5
				104	22.1

For system (b), containing 3.5 and 5.5% C_3H_8, the equilibrium $P-t$ values were found in the temperature range 17.2–31.0°C and pressures from 68 to 680 atm.

System (c), containing 1.4 and 4.6% iso-C_4H_{10} was investigated at 15.5–32.2°C and pressures 68–680 atm. The same authors found that the equilibrium $P-t$ values for the CH_4 + n-C_4H_{10} system (with 0.5, 2.0, and 5.3% n-C_4H_{10}) agree, within the limits of error of the experiment with the $P-t$ values of pure CH_4.

Experimental $P-t$ data for mixtures (d) and (e) are given in Deaton and Frost's monograph[5]. They studied the $CH_4 + C_3H_8$ system at temperatures from 0° to + 6°C and pressures from 1 to 50 atm and the $CH_4 + C_2H_6$ system at temperatures from 2° to 10°C and pressures from 2 to 60 atm.

The experimental $P-t$ data of McLeod and Campbell for mixtures (a) (gases Nos. 2 and 3), (b) (gas No. 5), and (c) (gases Nos. 8 and 9) are given in Table 15.

Carson and Katz[107] obtained equilibrium $P-t$ data for the four-phase, three-component system $CH_4 + C_3H_{8\,liquid} + C_3H_{8\,gas} + H_2O_{liquid}$ in the temperature range 12.3–22.5°C and pressures from 12 to 71.5 atm. Their results are given in Table 16.

Table 16.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
22.5	71.5	12.8	15.6
20.9	52.6	16.6	27.7
18.6	35.4	18	34.5
16.6	27.4	21	56.5
14.7	21.0	20.4	50.9
18.5	36.3	21.8	53.6
10.6	12.0	13.6	17.4
17.8	32.5	12.2	17.8
10.8	12.7		

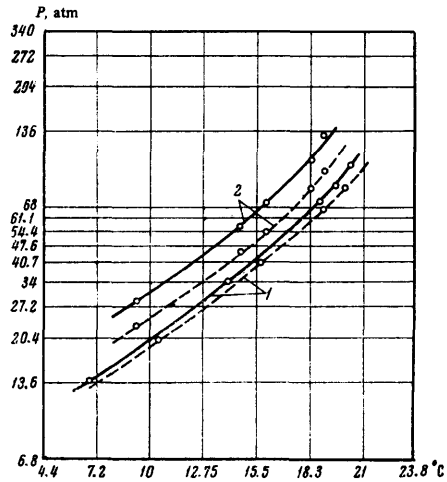


Figure 7. Conditions of formation of hydrates in mixtures containing CH_4, C_2H_4, and C_3H_6:
1) CH_4 0.326, C_2H_4 0.606, C_3H_6 0.068; *2*) CH_4 0.604, C_2H_4 0.347, C_3H_6 0.049. Continuous curves: experimental; broken lines: predicted.

Hydrates Formed by Alkane–Alkene Mixtures

Hydrate formation in the binary systems (a) $CH_4 + C_2H_4$, (b) $CH_4 + C_3H_6$, and (c) $C_3H_8 + C_3H_6$ were studied by Snell and coworkers[78] (a), Otto and Robinson[108] (b), and also Reamer and coworkers[76], Teodorovich[80], and Byk and coworkers[82] (c).

For system (a) with from 1.9 to 92.4% C_2H_4 equilibrium $P-t$ data were obtained in the temperature range from 1.1° to 21.0°C and pressures up to 600 atm. Some $P-t$ values were also obtained[82] for the ternary system with CH_4 32.6, C_2H_4 60.6, C_3H_6 6.8% (Fig. 7).

System (b) with from 0.5 to 23.0% C_3H_6, was studied at pressures up to 130 atm in the temperature range from 0° to 21.1°C (Fig. 8).

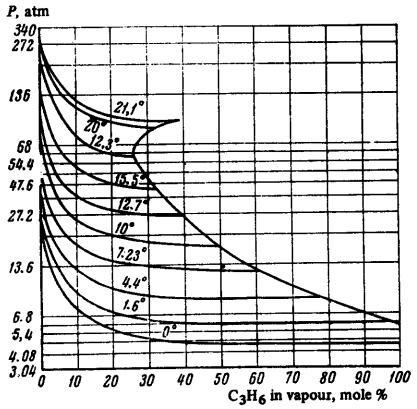


Figure 8. Effect of composition on the conditions of formation of a mixed hydrate containing CH_4 and C_3H_6.

The conditions of hydrate formation in system (c) were studied[76] for two propane–propene mixtures of different composition (C = 0.3148 and C = 0.5246, where

$$C = \frac{X_{C_3H_6}}{X_{C_3H_6} + X_{C_3H_8}},$$

at pressures from 2.9 to 26 atm (including the range of existence of a liquid hydrocarbon phase) and temperatures from 0.55° to 3.8°C (Table 17). Teodorovich[80] concluded, on the basis of the P–t values they obtained, that propene does not enter into the composition of the hydrate (contrary to the results of other authors). Byk and coworkers[82] obtained equilibrium P–t data for two gaseous mixtures which are characterised by the ratio $X_{C_3H_6}/X_{C_3H_8}$ = 2.87 and 0.67. The experimental results relating to this system are given in Table 18.

Table 17.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
C = 0.5246			
0.55	2.96	3.50	7.94
1.27	3.49	3.50	8.11
1.16	3.65	3.56	9.36
1.22	3.66	3.56	12.46
1.44	3.92	3.78	18.00
2.00	4.27	3.78	18.82
1.83	4.44	3.78	19.61
1.83	4.52	3.84	27,00
3.00	4.92		
2.78	4.95	C = 0.3148	
2.44	4.95	0.67	3.88
2.94	4.98	1.33	4.39
3.50	6.68	1.89	4.90
		2.00	5.0[illegible]
		2.06	5.26

Double Hydrates Formed by Methane with Carbon Dioxide, Nitrogen, and Argon

Unruch and Katz[91] studied the conditions of hydrate formation in the CH_4 + CO_2 system. They obtained P–t equilibrium data for pressures from 27 to 68 atm and temperatures from 1.1° to 11.0°C.

The CH_4 + N_2 system was studied by Ichaveri and Robinson[109], who experimentally determined P–t values for mixtures with various N_2 concentrations from 18 to 90% at temperatures from 0° to 22°C and pressures up to 350 atm.

Table 18.

C = 2.87		C = 0.67	
t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
0	3.4	0.2	2.4
0.1	3.5	1.1	2.75
0.5	3.75	1.5	3
1	4.2	1.9	3.05
1.85	4.93	2.15	3.24
2.2	5.05	2.2	3.57
2.5	5.35	3.3	4.21
		3.4	4.25
		4.2	5.18
		4.3	5.21
		4.35	5.24

Equilibrium P–t values for the systems: (1) CH_4 + Ar and (2) Ar + N_2 were obtained experimentally by Saito and Kobayashi[34] in a specially constructed apparatus by the "pressure jump" method. System (1) was investigated at temperatures from 2.7° to 25.7°C and pressures from 56 to 1120 atm; system (2) at temperatures from 2.2° to 17°C and pressures from 142 to 605 atm.

Mixed Hydrates Formed by Inert Gases

Hydrates formed by molecules of inert gas (Ar, Kr, Xe) with molecules of organic liquids (acetone, methylene, dichloride, chloroform, carbon tetrachloride) were first obtained by Waller[97]. With ideal filling of all the cavities of structure (II) these hydrates can be characterised by the general formula A.2B.17H_2O, where A is the organic component and B the inert gas.

Table 19.

Gas	Temperature, °C, at which P_{diss} of the mixed hydrate equals 1 atm			
	organic liquid			
	acetone	methylene dichloride	chloroform	carbon tetrachloride
Ar	−8.0	−7.0	− 4.8	− 1.6
Kr	−5.0	+6.2	+ 9.0	+11.3
Xe	+3.0	+8.6	+10.9	+13.7

As was shown by Waller, argon forms hydrates of the above type at pressures of 200–400 atm, krypton at $P \simeq$ 30 atm, and xenon at $P \simeq$ 1 atm. Table 19 shows the relative stability of the A.2B.17H_2O hydrates.

From Table 19, xenon gives the most stable hydrates with organic solvents. These hydrates could be obtained by simply bubbling the moist gas through the organic liquid at P = 1 atm and $t \sim$ 0°C. Waller also states that O_2 forms mixed hydrates with acetone and N_2 with acetone and carbon tetrachloride.

Mixed Hydrates Formed by Organic Liquids

Binary hydrates A.B.17H_2O, where A and B are organic liquids (for example, A = C_2H_5Cl, B = CH_3CHCl_2, or A = C_2H_5Cl, B = $CHCl_3$ were studied by Stackelberg and Meinhold[11].

A large group of mixed (binary) hydrates formed by chloroform (or methyl iodide) with such gases as H_2, Ne, N_2, Ar, O_2, CH_4, Kr, Xe, C_2H_4, C_2H_6, and CO_2 was studied by Barrer and Ružicka[64] and is of considerable interest. Barrer and Ružicka showed that even such gases as hydrogen and neon, which themselves are incapable of hydrate formation, are retained by the small cavities of structure (II) in quantities appreciably greater (34 times for H_2 and 220 times for Ne) than in the ordinary physical dissolution of H_2 and Ne in liquid water at 0°C.

Hydrates of Multicomponent Gas Mixtures

Natural Gas

The first systematic study of the conditions of formation of hydrates was made by Hammerschmidt[4], who showed that the so-called "freezing" of gas pipes, in which natural gas is present at high ($P \gg 1$ atm) pressures and temperature $\simeq 0°C$, is connected with the formation of solid crystalline hydrate "plugs". The natural gas investigated by Hammerschmidt had the composition (vol.%): CH_4 82.5, C_2H_6 5.99, C_3H_8 3.26, n-C_4H_{10} 0.49, iso-C_4H_{10} 0.30, CO_2 0.20, C_5 0.07, N_2 (residue) 7.19.

On the basis of their treatment of the experimental P–t values they obtained the relation: $y = 8.9(x)^{0.285}$, where y is in °F and x in lbf dm^{-2}.

In the same work, as stated above, the general premises of the hydrate formation process (thermodynamic, hydrodynamic, etc.) were examined. After the appearance of Hammerschmidt's work, which in application to natural gas can be considered classical, a large number of papers were published by foreign and Russian investigators devoted to various aspects of hydrate formation in natural gas. Carson and Katz[73] [? wrong ref. (Ed. of Translation)] studied the relation between the conditions of formation of hydrates of natural gas and its density (actual composition). They showed that an increase in the concentration of the C_2 and C_3 hydrocarbons in the natural gas appreciably raises (at constant pressure) the temperature of hydrate formation or lowers the pressure of hydrate formation (at t = const). The same problem was dealt with in a paper by Katz[110] who had studied various specimens of natural gas, the density of which varied between broad limits (from 0.55 to 1.0). Fig. 9 shows the influence of the density of natural gas on the equilibrium P–t values.

The presence in the natural gas of the impurities N_2, CO_2, and H_2S appreciably raises the temperature of hydrate formation (Fig. 10 shows the effect of N_2).

The presence of H_2S is especially effective on the equilibrium P–t values, as was shown by Molinero[111].

Campbell and McLeod[71] studied the conditions of formation of hydrates of natural gas at high pressures (up to 700 atm). Among the Russian investigations devoted to the hydrates of natural gas, the series of papers by Trebin and Makogon stand in the forefront[112–117].

Of this series of papers the investigation dealing with the problem of the formation and decomposition of hydrates of natural gas at negative temperatures[115] is of considerable interest. Trebin and Makogon showed that at the time of decomposition of the hydrate at $t < 0°C$ (by reducing the pressure) there is a rearrangement of the crystal lattice of the hydrate into the ice lattice according to the scheme: hydrate → water → ice.

On passage of the hydrate from the region of positive into that of negative temperatures, the rearrangement of the hydrate lattice does not take place. In the above papers detailed consideration is given to the methods of calculation and application of appropriate nomograms which allow the conditions and place of formation of hydrates in pipelines to be determined.

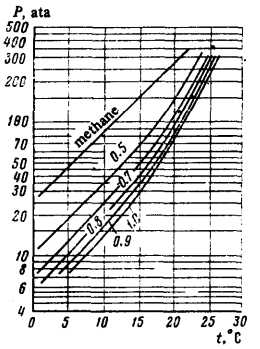


Figure 9. Conditions of hydrate formation for natural gases of various densities relative to air.

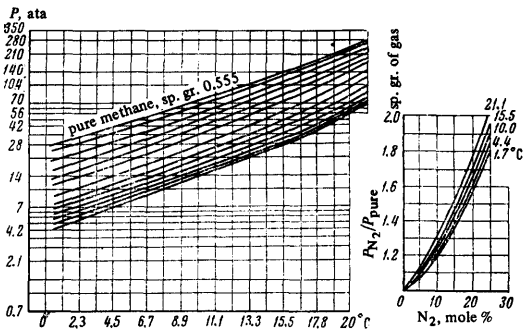


Figure 10. Conditions of hydrate formation in the presence of nitrogen in natural gas. Density of gas (from top to bottom): *1*) pure methane 0.555; *2*) 0.56; *3*) 0.57; *4*) 0.58; *5*) 0.59; *6*) 0.60; *7*) 0.62; *8*) 0.64; *9*) 0.66; *10*) 0.68; *11*) 0.70; *12*) 0.80; *13*) 0.90.

The influence of stabilising gases was considered simultaneously[115].

Ponomarev's studies[118,119] examined the problem of the formation of hydrates of natural gas of different composition, and also commercial gases containing a relatively large proportion of propane. For natural gas, Ponomarev obtained numerical values of the constants K and B in equations of the type $t = K \lg P - B$ where t and P are respectively the temperature and pressure of hydrate formation.

Khoroshilov[120–122] gives methods of calculating the equilibrium parameters of hydrate formation for natural gas.

Liquefied Hydrocarbon Gases

Hydrate formation in mixtures of liquid hydrocarbon gases (C_3H_8 + n-C_4H_{10}) has been considered by Musaev[123-125].

The same author investigated the hydrate formed by the liquid products of the thermal treatment of petroleum, having the following fractional composition (wt.%) C_2 4.3, C_3 16.9, iso-C_4 8.2, n-C_4 18, iso-C_5 18.4, n-C_5 17.0, C_6 17.3. Musaev's conclusions concerning the influence of n-C_4H_{10} on hydrate formation in C_3H_8 + n-C_4H_{10} mixture and also the influence of the rate of cooling on the temperature of formation of the hydrate of liquid propane are interesting. According to Musaev, n-C_4H_{10} does not participate in the hydrate formation.

Hydrocarbon Mixtures Formed in the Pyrolysis of Petroleum Products

The conditions of formation of hydrates of pyrogas were studied by Byk[126]. The material selected for investigation was an industrial gas from the pyrolysis of benzines of the following composition (vol.%): H_2 14.8, CH_4 45.1, C_2H_4 21.9, C_2H_6 10.0, C_3H_6 5.3, C_3H_8 0.9, ΣC_4, C_5 5.0. For two pressure ranges (20–35 and 35–50 atm) empirical equations connecting the temperature of hydrate formation (°C) and the corresponding equilibrium pressure (atm) were obtained: (1) $t = 0.27P + 2.4$, and (2) $t = 0.105 P + 8.5$.

IX. CALCULATION OF THE CONDITIONS OF HYDRATE FORMATION AND OF THE COMPOSITIONS OF THE SOLID (HYDRATE) AND GAS PHASES

As already stated above, mixed hydrates formed by binary and multicomponent mixtures are now considered to be solid solutions, the composition of which varies during the decomposition of the hydrate. On the basis of the analogy between the solid and liquid solutions (from the standpoint of the gas or vapour phase found in equilibrium with them) Wilcox and coworkers[79] proposed a method of calculating the conditions for the formation of hydrates from gas mixtures. The method is based on the use of numerical values of the "equilibrium constant" $K_{v/is} = y_i/x_i$ where y_i is the mole fraction of component i in the gas (vapour) phase, and x_i the mole fraction of the same component in the solid hydrate phase. The value of $K_{v/is}$, just as for liquid solutions, depends on the temperature, pressure, and composition of the mixture. The conditions of formation of a mixed hydrate from an i-component gas mixture is determined by the equality:

$$\sum_{i=1}^{i=n} \frac{y_i}{K_{v/s}} = \sum_{i=1}^{i=n} x_i = 1.$$

Hence when the nature of the dependence $K = f(t, P)$ is known for all the components of a gas mixture (the authors considered natural gas), then by carrying out the simplest linear interpolation the temperature at which the condition $\sum_{i=1}^{i=n} x_i = 1$ is observed for a given pressure can be determined (or, on the other hand, for a specified temperature the corresponding equilibrium pressure can be calculated).

This method was developed further in a series of later papers by Carson and Katz[107,127,128], who constructed $K_{v/s} = f(P)$ and $K_{v/s} = f(t)$ diagrams for the individual components of natural gas: methane, ethane, propane, and isobutane. In constructing such diagrams naturally it is necessary to locate experimental data on the compositions of coexisting solid (hydrate) and gas phases.

These results were taken from Hammerschmidt's work[4] (gas phase: natural gas at a pressure of 41 atm, Table 20) and from the publications of Deaton and Frost[83], who studied the compositions of the coexisting phases in the systems: (1) $CH_4 + C_2H_6$, (2) $CH_4 + C_3H_8$, and (3) CH_4 + iso-C_4H_{10}. For natural gas containing hydrogen sulphide and carbon dioxide as impurities in order to carry out calculations by the method of Wilcox and coworkers it is necessary to allow for the values of $K_{v/s}$ for H_2S and CO_2.

Table 20.

Component	Composition of gas phase, vol. %	Composition of hydrate, vol. %
CH_4	82.5	56.95
C_2H_6	5.99	5.66
C_3H_8	3.26	24.97
iso-C_4H_{10}	0.30	4.69
n-C_4H_{10}	0.49	0.83
C_5H_{12}	0.07	0.00
CO_2	0.20	0.44
N_2	7.19	0.46

The nature of the dependence $K_{v/s} = f(P, t)$ for these two gases was investigated by Noaker and Katz[106] (H_2S + CH_4 system) and by Unruch and Katz[91] (CO_2 + CH_4 system). A handbook[65] edited by Katz gives $K = f(P, t)$ diagrams for CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, CO_2, and H_2S.

It should be noted that on all these diagrams the maximal pressure is ~ 280 atm. Consequently the conditions of hydrate formation for mixtures of the natural gas type can be calculated by the method of Wilcox and coworkers only at $P_{dis} \leq 280$ atm.

In this connection the work of McLeod and Campbell[71] is interesting; they proposed a method for calculating the temperature of hydrate formation of natural gas in the pressure range 400–680 atm.

The authors, using a modernised form of the Clausius–Clapeyron equation $d \ln P/dT = m$, obtained in the general form the equation $C = mT^2$, where $C = \Delta H/zR$.

Having found that in C_1–C_4 alkane mixtures (not containing n-C_4H_{10}) in the pressure range 400–680 atm, m = const = 0.066, McLeod and Campbell obtained the formula $C = 0.066T^2$, in which the temperature is expressed in degrees Rankine.

To calculate the hydrate formation temperature the value of C for the specified pressure must be found by using the additivity rule ($\sum_{i=1}^{i=n} C_i = C$). Naturally, in making such calculations it is necessary to know the value of C for each hydrocarbon at various pressures. These values were obtained by McLeod and Campbell experimentally for methane ethane, propane, and isobutane and given in the form of Tables[7].

It should be noted that the number of papers in which the information given about the composition of the coexisting solid (hydrate) and gas phases was found directly by experiment is comparatively small.

Apart from those mentioned above, they include:

1. An investigation by Otto and Robinson[108], who determined the compositions of the equilibrium phases in the

$CH_4 + C_3H_8$ system in the temperature range from 0° to 21°C and pressures from 7 to 204 atm.

2. An investigation of the compositions of the coexisting phases in the system $CH_4 + C_2H_4$ made at temperatures from 0° to 29°C and pressures from 6.8 to 612 atm by Snell and coworkers[78].

3. Equilibrium compositions in the $C_3H_6 + C_3H_8$ system‡, determined at 0.3°C by Fomina and Byk[129] and presented as a P–X diagram in Fig. 11.

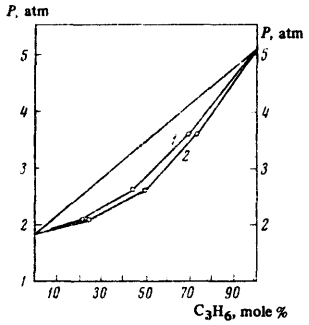


Figure 11. P–X isothermal equilibrium diagram for the C_3H_6–C_3H_8–H_2O system.
1) Hydrate; *2*) gas.

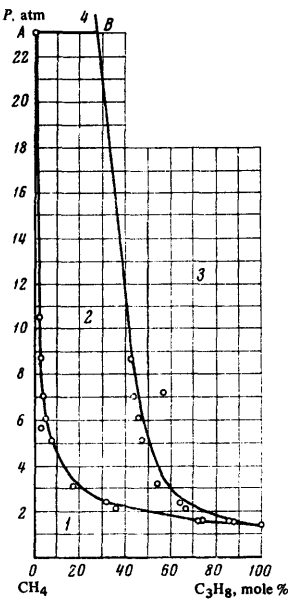


Figure 12. P–X isothermal equilibrium diagram for the C_3H_8–CH_4–H_2O diagram.
1) Gas-ice; *2*) hydrate-gas-ice; *3*) hydrate-ice; *4*) hydrate$_I$–hydrate$_{II}$-ice.

‡ The first attempts to determine the compositons of the equilibrium phases in the $C_3H_6 + C_3H_8$ system was made by Reamer[76] but the relative volatilities (α) found were almost equal to 1.

4. The same authors[130] determined, at 0.65° and 1.2°C, the compositions of the coexisting phases in two systems containing 2-methylpropene:

(a) $C_3H_8 + i\text{-}C_4H_{10} + i\text{-}C_4H_8$;

(b) $C_3H_8 + i\text{-}C_4H_{10} + i\text{-}C_4H_8 + C_3H_6$.

During the investigations a mixed hydrate was obtained which contained up to 82.5 vol.% 2-methylpropene and by extrapolation for the temperature range 0.66–1.2°C the equation $\lg P = 27.9298 - 7629/T$ was found, where P is the dissociation pressure of the hypothetical hydrate of pure 2-methylpropene.

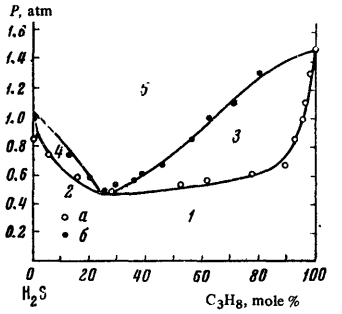


Figure 13. P–X isothermal equilibrium diagram for the H_2S–C_3H_8–H_2O system:
a) composition of gas phase; *b*) composition of hydrate.
1) Gas-ice; *2*) hydrate$_I$–gas-ice; *3*) hydrate$_{II}$–gas-ice; *4*) hydrate$_I$–gas-ice; *5*) hydrate$_{II}$-ice.

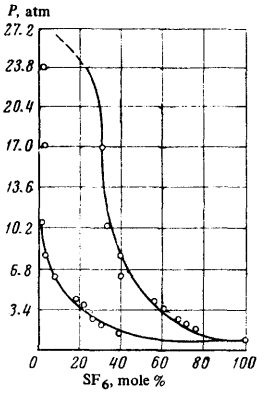


Figure 14. P–X isothermal equilibrium diagram for the CH_4–CF_6–H_2O system.
Continuous curves: experimental; points: calculated.

5. The isothermal "hydrate–gas phase" equilibrium ($t = -3$°C) in the $CH_4 + C_3H_8$ and $C_3H_8 + H_2S$ systems, including the determination was investigated by van der Waals and Platteeuw[28,29]; this involved the determination of the compositions of the coexisting phases. Figs. 12 and 13 give their P–X equilibrium diagrams they obtained. In the $C_3H_8 + H_2S$ system they observed an interesting phenomenon, analogous to anisotropy in liquid solutions: at $t = -3$°C and $P_{diss} = 0.48$ atm the compositions of the hydrate and gas phases agree (~ 75 mole % H_2S).

Hence the constancy of the value of P_{diss} for this hydrate observed by Stackelberg and Frühbuss[12] is connected with the existence of an azeotrope.

6. Ichaveri and Robinson[109] studied the compositions of the coexisting gas and hydrate phases in the $CH_4 + N_2$ system at −0.1° and 6.6°C.

In this system methane is the less volatile component ($K_{v/s} < 1$).

The compositions of the equilibrium gas and hydrate phases in the $CH_4 + SF_6$ system were studied at $t = -3$°C over the whole concentration range and pressures from 0.72 to 23.2 atm by Sortland and Robinson[36]. Fig. 14 shows their experimental results as a $P-X$ diagram.

X. USE OF THE PRINCIPLES OF STATISTICAL MECHANICS IN STUDYING GAS HYDRATES

The possibility of using the principles of statistical mechanics in studying solid non-stoichiometric clathrates, and consequently, hydrates, was shown in the studies[22-28] of Barrer, and of van der Waals (grandson) and Platteeuw. This subject is covered most fully in the monograph of the last two authors[28].

By applying the methods of statistical mechanics to a three-dimensional Langmuir model for the ideally localised adsorption of spherical molecules in the cavities of a clathrate (hydrate) lattice and by considering the hydrate phase as a solid solution obeying Raoult's law, van der Waals and Platteeuw obtained equations which allow several fundamental (principally thermodynamic) properties of gas hydrates to be calculated (dissociation pressure of the hydrates at various temperatures, their heats of formation, the compositions of the coexisting equilibrium phases, etc.). The main equations of van der Waals and Platteeuw are:

$$\text{(I)}\ \Delta\mu = kT\Sigma\nu_i \ln(1 + \Sigma C_{K_i} f_K),$$

$$\text{(II)}\ y_{K_i} = C_{K_i} f_K/(1 + \Sigma C_{K_i} f_K),$$

where $\Delta\mu = \mu^\beta - \mu^\alpha$ is the difference in chemical potentials of the empty crystal lattice of the hydrate (μ^β) and stable ice (μ^α), f_K is the fugacity of the adsorbed substance (K); v_i, the crystallographic constant of the cavities of the hydrate lattice with radius a_i, characterises the number of molecules of K per molecule of water. For structure (I), $\nu_1 = \frac{1}{23}$ and $\nu_2 = \frac{3}{23}$. For structure (II), $\nu_1 = \frac{2}{17}$ and $\nu_2 = \frac{1}{17}$. y_{Ki} is the probability of finding a molecule of gas K in a cavity of a hydrate lattice of type i, and C_{Ki} is the Langmuir constant for molecules of K in cavities i.

$$\text{(III)}\ C_{K_i} = \frac{4\pi}{kT}\int \exp[-\omega(r)/kT]\, r^2\, dr.$$

Here $\omega(r)$ is the spherical symmetrical potential of molecule K at distance r from its centre to the wall of the cavity. In the general form for a characteristic of the interaction between the cavity walls and the molecule K the authors employed the Lennard-Jones–Devonshire (12–6) potential:

$$\{\omega(r) = 4\varepsilon\{(\sigma/R)^{12} - (\sigma/R)^6\}.$$

On the basis of Eqns. (I), (II), and (III) given above, van der Waals and Platteeuw[28] calculated the dissociation pressure of a series of hydrates at 0°C (Table 21).

As Table 21 shows, good agreement between experimental and calculated values of P_{diss} is observed for hydrates of Kr and Xe (monatomic molecules) and to a lesser extent for almost spherical molecules (C_2H_4, C_2H_6).

The fundamental equations (I), (II), and (III) given above allow the composition of a solid hydrate phase in equilibrium with a gas phase to be calculated. Such calculations were made by van der Waals and Platteeuw[28,29] for the systems $CH_4 + C_3H_8 + H_2O$ and $C_3H_8 + H_2S + H_2O$ with the aid of the equations:

$$\text{(a)}\ y_{A_1} = C_{A_1} P_A/(1 + C_{A_1} P_A);\quad y_{A_2} = C_{A_2} P_A/(1 + C_{A_2} P_A),$$

$$\text{(b)}\ \nu_1 \ln(1 - y_{A_1}) + \nu_2 \ln(1 - y_{A_2}) = \frac{-\Delta\mu}{kT},$$

$$\text{(c)}\ Y_A = \nu_1 y_{A_1} + \nu_2 y_{A_2},$$

Table 21.

Hydrate-forming substance	P_{diss} at 0°C, atm	
	expt.	calc.
Ar	95.5*	95.5*
Kr	14.5	15.4
Xe	1.15	1.0
CH_4	26	19
CF_4	1	1.6
C_3H_8	5.2	1.1
C_2H_4	5.44	0.5

* The experimental value of P_{diss} for argon hydrate was used in the calculation. The constant thus found was used to calculate P_{diss} for the remaining hydrates.

where y_{A_1} is the fraction of small cavities of the hydrate lattice filled with molecules of A, y_{A_2} the fraction of large vacancies of the hydrate lattice filled with molecules of A, P_A the partial pressure of component A in the equilibrium gas phase, C_{A_1} the Langmuir constant of component A for when it fills the small vacancies, C_{A_2} that for when it fills the large vacancies, and Y_A the concentration of component A in the equilibrium hydrate.

As the authors showed, for a mixed hydrate of structure (I) $\Delta\mu = 0.167$ kcal mole^{-1} (Br_2 hydrate model). For a hydrate of structure (II), $\Delta\mu = 0.196$ kcal mole^{-1} SF_6 hydrate model). The results of the calculations for $t = -3$°C showed good agreement with experimental results, as is clear from the $P-X$ diagrams for the two systems (Figs. 12 and 13).

A theory of solid hydrate solutions using the principles of statistical mechanics has obtained its furthest development in the studies of Saito and coworkers[32,34], who somewhat modified the equations of van der Waals and Platteeuw[28] and proposed a method of calculating several properties of gas hydrates at temperatures above the lower quadruple point (in practice at $t > 0$°C). The objects of their investigations were the hydrates of methane, argon, and nitrogen, and also mixed hydrates in the $CH_4 + Ar + H_2O$ and $Ar + N_2 + H_2O$ systems. P_{diss} for the individual hydrates of CH_4, Ar, and N_2 were calculated as functions of temperature and pressure up to 3000 atm and agree well with the experimental results, the heats of formation of the hydrates, and also the number of water molecules (n).

In finding the nature of the $n = f(P)$ dependence, Saito and coworkers[32] showed that for the hydrates of Ar and N_2 complete filling of the small and large cavities of the hydrate lattice ($n = 5.75$) is attained only at very high equilibrium pressures, of the order of 3400 atm. For $CH_4 \cdot nH_2O$ complete filling is attained at $P = 1300$ atm. Their calculated values of the heats of formation of these (Ar, N_2, and CH_4) hydrates agreed well with the values obtained from $P-t$ results with the aid of the Clausius–Clapeyron equation. Saito and Kobayashi[34] calculated for $CH_4 + Ar$ and $Ar + N_2$ mixtures the conditions of hydrate formation over a wide range of temperature and pressures, which also

agreed well with those they obtained experimentally. The same authors calculated the composition of a mixed argon–methane hydrate which coexists in equilibrium with the gas phase at the temperatures 4.4°, 10.0°, 15.5°, and 21°C.

All the above-mentioned calculations of the properties of hydrates were based on the use of the Lennard-Jones–Devonshire potential, which is known not to take into consideration the form and size of the gas molecules. The first successful attempt to calculate P_{diss} of hydrates by use of the values of the Kihara potential, the value of which, in principle, depends on the form and size of the interacting molecules, was made by McLeod and McKoy and Sinanoglu[33]. The authors calculated P_{diss} for a series of hydrates by using the Lennard-Jones (28–7) potential, the Lennard-Jones (12–6) potential, and the Kihara potential. They showed that the least satisfactory agreement with the experimental results is given by using the Lennard-Jones (28–7) potential. As might be expected, the (12–6) potential gives satisfactory results for molecules of monatomic gases and CH_4 but is not very satisfactory for the molecules C_2H_6, CO_2, N_2, O_2, C_2H_4. Furthermore, the use of the Kihara potential allows sufficiently good agreement with experimental values of P_{diss} to be obtained for the above rod-shaped molecules. The Kihara potential found further use in Nagata and Kobayashi's work[35,37]. In the first of these papers, on the $CH_4 + N_2$ binary system, the hydrate formation pressure was calculated for a mixture with 55% CH_4 and also the compositions of the coexisting hydrate and gas phases in equilibrium at −0.1° and 6.6°C. Satisfactory agreement was shown with experimental P–X data published earlier[109]. In the second paper the authors calculated P_{diss} for the mixed hydrates formed in the $CH_4 + C_2H_6$ and $CH_4 + C_3H_8$ systems, using only the constants given in the literature which characterise the individual hydrates of CH_4, C_2H_6, and C_3H_8. Their results also agree well with the experimental data.

Use of statistical mechanical methods allowed Barrer and Stuart[23] and then Barrer and Ružicka[64], to make quantitative evaluations of the stabilising influence of an auxiliary gas on the hydrate formation temperature. Their approximate calculations for the mixed hydrate formed by chloroform and nitrogen showed that when the N_2 is in the small cavities of structure (II) and partly in the large cavities, then $\Delta\mu = \mu^{\beta} - \mu^{\alpha} = -115.2$ kcal mole^{-1}. In the absence of nitrogen the value is −112 kcal mole^{-1} and consequently the difference is 3.2 kcal mole^{-1} and is due to the effect of the rise in the $CHCl_3$ hydrate formation temperature in the presence of nitrogen.

XI. PHYSICAL KINETICS OF THE FORMATION OF HYDRATES

The problem of the dependence of the rate of formation of gas hydrates on various factors in one form or another is treated in many papers devoted to the determination of their formation conditions. They include the investigations of Hammerschmidt[4], Ceccoti[55], Tesner and co-workers[131], Musaev[125], etc. Indications of the promoting action of certain additions (which by themselves do not enter into the composition of the hydrate) are contained in the work of van der Waals and Platteeuw[28] and also van Cleef and Diepen[31]. We know of only five studies specially devoted to the physical kinetics of hydrate formation, and with the exception of one[132] which examined the kinetics of hydrate formation, they all deal solely with the hydrates of organic liquids, and the conclusions drawn in these papers cannot, according to the authors's own statements, be extended to purely gas hydrates. Pinder[100] studied the dependence of the rate of formation of tetrahydrofuran hydrate $[CH_2]_4O.17H_2O$ on the processes of mutual diffusion of the two complexes with a hydrogen bond which exist in the initial solution. Keneth and Pinder[133] investigated the rheological properties of the hydrate system of tetrahydrofuran + hydrogen sulphide. The hydrate they investigated exhibits high stability (at $P = 1$ atm, $THF.2H_2S.17H_2O$ is destroyed at $t > 21$°C). They also studied the viscosity of hydrate *slush* at a function of time, rate of growth of individual crystals, etc.

Saito and Sadanaga[134] studied the process of formation of the hydrate of dichloromonofluoromethane ($CHCl_2F.17H_2O$) and obtained a series of empirical equations connecting the rate of formation of crystalline hydrate nuclei with the degree of supercooling of the solution and the number of revolutions of the stirrer.

The most fundamental investigation on the physical kinetics of the hydrate formation process is, perhaps, the work by Barrer and Ružicka[135]. They measured the rate of formation of binary hydrates produced by chloriform or THF with Ar, Kr, Xe, and CH_4, at various temperatures (−78° and ~ 0°C).

Their method of investigation (measurements of the quantity of gas absorbed after definite intervals of time) allowed them to obtain at constant P, t a series of single-valued curves (almost straight lines) which characterise the rate of formation of the hydrates mentioned above. With the binary hydrate of THF + argon as example, these authors also examined in detail the factors which determine the growth of the crystallisation nuclei in the formation of the hydrate.

XII. DENSITY OF HYDRATE CRYSTALS

The density of the crystals of the hydrates was first measured by Stackelberg[7,11] for the following organic compounds (Table 22).

Table 22.

Hydrate	Density, g cm^{-3}
SO_2	1.23
$CHCl_3$	1.11
C_2H_5Cl	<1.0
$CCl_4 + H_2S$	1.272±0.01
$CHCl_3 + H_2S$	1.216±0.01
Cl_2*	1.29±0.1

* Calculated from the slope of the curve (dT/dP).

Precision measurements of the density of hydrate crystals were made by Saito and Sadanaga[136]. In a specially equipped room with a temperature of 0°C they used a float method to measure the density of hydrates of propane and also of several chlorofluoro-derivatives of methane (CHF_2Cl, $CHFCl_2$, CF_2Cl_2, and $CFCl_3$).

From propane hydrate, $d = 0.88$ g cm^{-3}; for the hydrates of the above chlorofluoromethanes, the density lay within the limits 1.04–1.24 g cm^{-3}.

Saito and Sadanaga also proposed formulae for calculating the density of hydrates of structures (I) and (II):

$$d_I = \frac{(46\,H_2O + 6\,M\cdot\alpha_1)\,1/N}{a^3}; \quad d_{II} = \frac{(136\,H_2O + M\cdot\alpha_2)\,1/N}{a^3}$$

where M is the molecular weight of the hydrate-forming substance, α_1 and α_2 are the degree of filling of the cavities in the crystal lattice of the hydrate ($1 \geqslant \alpha > 0$), N is Avogadro's number, and a the crystal lattice parameter of the hydrate, Å. They found good agreement between experimental and calculated values of the density of the hydrates mentioned.

Van Cleef and Diepen[31] give the values of the densities they found for the hydrates of oxygen ($d = 1.03 \pm 0.02$ g cm^{-3}) and nitrogen ($d = 1.02 \pm 0.02$ g cm^{-3}).

XIII. INDUSTRIAL USE OF GAS HYDRATES

1. DESALINATION OF SEA WATER

A process first proposed by Donath[137] for the desalination of sea water is based on the use of hydrocarbon hydrates (of ethane, propane, and isobutane), and also of hydrates formed by halogen derivatives of methane, mainly the Freons and certain other gases (Cl_2).

The paper by Kuoch and coworkers[138] gives the principles of the method in greatest detail, and also the technological scheme of the process, based on the formation and subsequent decomposition of propane hydrate.

According to the scheme given, the hydrate ($C_3H_8.17H_2O$) is made in a special reactor at 1.1°C and a pressure of 3.9 atm. In a second reactor, into which the hydrate mud is brought by means of a conveyor belt, the hydrate is decomposed at 7.2°C and 4.7 atm, with the liberation of pure distilled water (the salt dissolved in sea water is known not to permeate the hydrate lattice). In this way, 40% of the sea water put into the first reactor was desalinated.

The process for the desalination of sea water with the aid of hydrates is covered by a series of foreign patents[139,140] and also by papers of Caryofcky[141], Barduhn[142], and Medvedev[143].

2. USE OF HYDRATES FOR THE STORAGE OF GASES

The storage of natural gas as hydrates is considered in several patents and publications[48,49,144]. Mock[145] has proposed an interesting method for the storage of inert gases (Ar, Kr, Xe).

3. SEPARATION OF GASEOUS AND LIQUID MIXTURES WITH THE AID OF HYDRATES

The separation of these mixtures with the aid of hydrates has been considered in detail in a paper by Barrer and Ružicka[64] which gives the principles of the method and considers some specific separable gaseous and liquid mixtures ($O_2 + N_2$, Kr + Ar, Xe + Kr, $CH_3I + CHCl_3$, $C_6H_5CH_3 + CHCl_3$, $C_6H_6 + CHCl_3$, $CH_2Cl_2 + CHCl_3$). These problems are also covered in the patent literature. Thus, Crowther[146] proposed a method of separating the gaseous mixture $CH_4 + C_2H_6$. Glew's patent[147] deals with the separation by hydrate formation of the liquid hydrocarbon mixture $C_3H_6 + C_3H_8$. Kinney and Kahre[148] proposed a method of separating helium from natural gas. The patent proposes that in the last stage of the process an N_2 + He mixture is separated by adding propane, which forms a mixed hydrate with the nitrogen. Byk and Fomina's patent[149] covers the separation of the gaseous mixtures n-C_4H_{10} + iso-C_4H_{10}, and $C_3H_6 + C_3H_8$.

XIV. PREVENTION OF HYDRATE FORMATION

Methods for preventing hydrate formation derive directly from the equilibrium conditions for their existence given above (P_{gas}, P_{H_2O}, and t°C): (1) raising the temperature in the system where a hydrate has already formed or can be formed; (2) reducing the pressure of the hydrate-forming gas; (3) reducing the concentration of water in the gas by drying it or by using special inhibitors which lower the partial pressure of water vapour in the system.

Detailed consideration of all the methods for preventing hydrate formation has been given in the extensive Russian and foreign literature on the subject, dealing mainly with the problems of the drying of gases[150-155] and the use of various inhibitors[117,156-174].

Measures against hydrate formation are considered in the Russian monographs by Sarkis'yants and Makagon[175,176], and also in Frost and Deaton's monograph[5].

The theoretical principles of the inhibition of hydrate formation, which are of independent interest, and also the specific possibility of using individual inhibitors (methanol, ethanol, isopropyl alcohol, glycine solutions, propanol, aqueous solutions of $CaCl_2$, NaCl, LiCl, $AlCl_3$, NH_3, etc.) have been considered[177-180].

The most complete theory of the inhibiting action of a "third" component has been given by Pieroen[180], who by using the concepts of the chemical potentials of the components, participating in the hydrate formation, and of the "activities" of the aqueous solutions obtained the equation

$$\Delta T = -\frac{nRT_0^2}{\Delta H} X_{t.c.},$$

in which ΔH is the heat of formation of one mole of hydrate containing n moles water at T_0; $\Delta T = T_0 - T$; T_0 is the equilibrium temperature (°K) of formation of the hydrate in the absence of inhibitor; T that in the presence of the inhibitor; and $X_{t.c.}$ the mole fraction of the inhibiting third component in the water. For the natural gas–water system, the above equation acquires the form:

$$\Delta T = \frac{nRT_0^2}{\Delta H} \frac{18\omega}{(100-\omega)M} (1 - X_{t.c.}),$$

since $X_{t.c.} \ll 1$, then

$$\Delta T \sim \frac{nRT_0^2}{\Delta H} \frac{18\omega}{(100-\omega)M},$$

where w is the inhibitor concentration (wt.%) in the water, M the molecular weight of the inhibitor at $T = 280$°K, and $\Delta H \simeq -41$ kcal mole^{-1}, so that

$$\Delta T \sim 1240 \frac{\omega}{M(100-\omega)}.$$

Earlier[178], Hammerschmidt obtained an analogous formula with the numerical coefficient equal to 1297 for inhibiting aqueous solutions of electrolytes.

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Synthesis of Technical Tanning Agents

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The review gives data mainly on Soviet investigations on the preparation and application of synthetic tanning agents, comprising auxiliary syntans and substitutes for vegetable tannins. A detailed account is given of the processes used in the synthesis of Soviet heavy-duty syntans and some information on the production of substitute syntans abroad. The bibliography contains 83 references.

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I. INTRODUCTION

Since the earliest times tanning agents, found in the bark, wood, leaves, and roots of various plants, have been used for the production of leather. The structure of these substances, which are known generally as "tannins", was elucidated as a result of the large amount of work done during the second half of the nineteenth century and the beginning of the twentieth century. All natural tanning agents are derivatives of polyhydric phenols, and are divided into two groups: the chief structural unit of hydrolysable tannins is digallic acid, which forms esters with hexoses; non-hydrolysable tannins are based on catechol units linked together either directly or through carbon atoms [1].

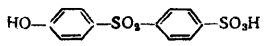
At the same time as the investigation of the structure of vegetable tannins, and directly connected with it, work was also done on the synthesis of tanning agents with the above main structural units as starting materials. Such syntheses were undertaken by Schiff, Baeyer, Fischer, Melau, and others, who by various methods obtained condensation products of arenepolyols and hydroxybenzoic acids.

The work of Schiff is of especial interest for the history of synthetic tanning agents. Having obtained digallic acid from gallic acid by the action of phosphoryl chloride, he applied this method to pyrogalloisulphonic acid and hydroxybenzenesulphonic acid [2], and assigned to the products the formulae

$$C_6H_2(OH)_3-SO_2-O-C_6H_2(OH)_2-SO_3H,$$
$$C_6H_4(OH)-SO_2-O-C_6H_4-SO_3H.$$

While differing from digallic acid in composition, these compounds showed some analogy with it in molecular structure: they contained phenolic rings linked by ester groups (-CO.O- or $-SO_2.O-$) and one of the rings contained an acidic group (-COOH or $-SO_3H$). Both compounds possessed tanning properties, and underwent all the reactions characteristic of vegetable tannins.

Schiff also obtained a tanning agent [3], probably hydroxyphenylsulphonylbenzenesulphonic acid



by dehydrating hydroxybenzenesulphonic acid at a high temperature.

These compounds obtained by Schiff must be regarded as direct precursors of modern synthetic tanning agents.

The history of modern industrial synthetic tanning agents, usually termed syntans (synthetic tannins), began in 1911, when Stiasny made a patent application covering the production of tanning materials by the condensation of hydroxybenzenesulphonic acids with formaldehyde [4,5]. Synthetic tanning agents have come a long way. More than a thousand patents have been issued on processes for their production, while the total number of brands manufactured in various countries reaches two hundred.

Synthetic tanning agents can be divided into two main groups—"light" and "heavy"—from the point of view of leather technology. Those of the first group possess weak