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Gas hydrates, a new class of impurities in high purity gases and gas – vapour mixtures

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Abstract. The conditions of formation and structural features of gas hydrates are considered. The existing physicochemical models of formation of gas hydrates are analysed and an algorithm for calculating the parameters which influence the efficiency of gas purification is proposed. Theoretical values of dissociation pressure and water vapour pressure over the surface of mixed hydrates in mixtures of volatile inorganic hydrides are given as well as the distribution coefficients of the components between phases in the process of their formation. It is shown that the appearance of impurities in the form of gas hydrates in hydrides can markedly affect the efficiency of their refinement. The bibliography includes 43 references.

I. Introduction

The chemical nature of impurities determines their behaviour in the processes of separation and refinement of substances. In studies of suspended particles of submicro-size it was established that the transition of the same compound from the molecular to the heterogeneous form substantially alters its behaviour as an impurity in these processes. Therefore, suspended particles of submicro-size are regarded as a new class of impurities in substances of high purity. The interaction of impurity components (especially, water) with the main substance yielding donor – acceptor complexes or new chemical compounds substantially broadens the array of impurities in the substance under purification. At the same time, the appearance of a 'new' impurity component may be due to the formation of molecular complexes, that are bound only by van der Waals forces. Certain complexes of this kind known as gas hydrates and suspended submicro-size particles may also be attributed to a new class of impurities in ultrapure substances. It is interesting to study their structure, the formation conditions, and behaviour in the process of gas refinement. The aim of this paper is to analyse the existing physicochemical models of gas hydrate formation and to devise algorithms for calculating their parameters which affect the efficiency of gas refinement: the pressure of saturated water vapour over the surface of hydrates and dissociation pressure as well as distribution coefficients of gas mixture components between the gas and solid phases.

Gas hydrates were first detected and given this name as early as 1810 when Davy synthesised a chlorine gas hydrate. Nikitin suggested [1] that gas hydrates are solid solutions. Several reviews and monographs have been published [2 – 7] which present in detail both historical aspects and physicochemical data on gas hydrates.

At present, over 120 gas hydrates are known. Many of them have found practical uses: for example, gas hydrates of Freon 12 are applied to desalinating sea water and in the concentration of heavy water.[8]

Gas hydrates formed in gas mains can block the transportation of natural gas resulting in pipeline failures.[5] In addition, gas hydrates can be formed in the process of purification of volatile substances under high pressure and change the solubility of the water impurity in such substances.[9]

Clathrate compounds are formed by the inclusion of one species of molecules called 'guests' into the cavities of a crystalline network built of molecules of another species called 'hosts'. The term 'inclusion compounds' was introduced by Schlenk, and the term 'clathrate compounds' was proposed by Powell.[10] Originally, only compounds with cellular cavities were regarded as clathrates. Nowadays, both terms are synonyms defining the compounds in question irrespective of the type of cavities. Their major difference from common chemical compounds consists in their reacting components ('host' and 'guest') being generally coordinationally saturated compounds and their interaction is, as a rule, based on van der Waals forces. Therefore, the clathration is accompanied by a slight gain of energy and plays a crucial role only when no chemical reactions take place. The crystalline lattice of the 'host' per se is thermodynamically unstable if it is not filled with a minimum number of gas molecules, and thus cannot exist in the 'pure' form. This peculiarity distinguishes it from the crystalline lattice of ice.

II. Structure of gas hydrates

All the known gas hydrates have basically one of the following structures: I, II and H. The structures I and II are characterised respectively by a cubic symmetry (space group $Pm3n$, $Fd3m$) and the structure H, by hexagonal (space group $P6/mmm$) symmetry. Structure H was discovered in 1987.[2] Some compounds possess a different structure; for example, Br_2 and Me_2O have tetragonal (space group $P4_2/mnm$) symmetry, while Me_3CNH_2 has cubic (space group $I43d$) symmetry.

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There are five fundamental types of cavities in the crystalline network of which structures I, II, and H are constructed. The basic characteristics of these cavities are presented in Table 1.

Table 1. Structural properties of clathrate hydrates.[2]

Parameter	Structure I	Structure II	Structure H
Space group	*Pm3n*	*Fd3m*	*P6/mmm*
Unit cell parameters /Å			
a	12.03	17.31	12.26
c	—	—	10.17
Number of water molecules per unit cell	46	136	34
Number of cavities in the unit cell with D_{mean} /Å			
7.8	2	16	3
8.7	6	0	0
9.4	0	8	0
7.8	0	0	2
10.7	0	0	1
Composition of the structure			
all cells are occupied	$M \cdot \frac{23}{4} H_2O$	$M \cdot \frac{17}{3} H_2O$	see [a]
large cells are occupied	$M \cdot \frac{23}{3} H_2O$	$M \cdot 17H_2O$	$M \cdot 34H_2O$

[a] Structure H is stabilised only due to filling of the smallest cavities with xenon and hydrogen sulfide.

Gas molecules intercalating into structures I, II, and H differ substantially in size and shape. There is a relationship between the maximum van der Waals diameter of gas molecules and the lattice structure. Gas molecules will not occupy the cavities if their van der Waals diameter is larger than the free diameter of these cavities. The latter is roughly equal to the difference between the geometric size of the cavity indicated in Table 1 and the van der Waals diameter of the oxygen molecule (2.8 Å). For example, when the van der Waals diameter of a gas (d_g) is in the range from 4.2 to 5.5 Å, the gas hydrate with structure I is formed; when $3.8 < d_g < 4.0$ Å or $5.6 < d_g < 7.0$ Å, structure II is formed, and when $d_g = 8.2-8.3$ Å, structure H is formed.[2]

Certain gas hydrates include more than one substance as their 'guests'. If different compounds occupy cavities randomly, a mixed gas hydrate is formed. When large cavities are filled with gas molecules of large size and small cavities are occupied by those of small size, double hydrates are formed. All hydrates with structures H and II for relatively large gas molecules (> 6.8 Å) are of the double type. In such hydrates, the 'auxiliary' gases, xenon and hydrogen sulfide, occupy small cavities and stabilise the crystal.

III. Physicochemical models of gas hydrate formation

1. An ideal solution model

First, a model of ideal solutions has been used by van der Waals for a description of the non-stoichiometric nature of clathrate crystals.[11] Initially, it was used for clathrates of hydroquinone with cavities of only one type. However, the equations derived for this molecule had to be modified considerably because of the specificity of gas hydrates (the presence of cavities of different size and shape in structures I and II, crystalline lattices of water molecules, *etc.*). The modifications were first done by Barrer and Stuart [12] and then by van der Waals and Platteeuw.[13]

By assuming that only one molecule occupies each cavity, van der Waals obtained the following expression for the distribution function for an ensemble of molecules of water W and gas M forming a clathrate crystal:

$$Z = \exp\left(-\frac{F_0}{kT}\right) \sum_{N_{M_i}} \prod_{i=1}^{2} \left[N_{M_i} B_{M_i} A_M \frac{N_i!}{(N_i - N_{M_i})! N_{M_i}!} \right], \quad (1)$$

where F_0 is the free energy of water molecules in an empty clathrate lattice; N_{M_1} and N_{M_2} are the numbers of gas molecules in the respective cavities; B_{M_i} is the molecular distribution function of molecules M in cavities *i*; A_M is the absolute activity; and N_1 and N_2 are the numbers of large and small cavities, respectively. For Eqn (1), it is assumed that, first, F_0 is independent of the extent of cavity filling and the nature of gas M and, second, the value of B_{M_i} is the same for each cavity of the *i*th type and is independent of whether or not the cavity is occupied. The first condition is not strictly true for large gas molecules nor is the second condition, for strongly polarised gas molecules.

In the case of an equilibrium distribution of gas molecules M over cavities, all the known thermodynamic functions are included in Z in accordance with the following equation:

$$kT\mathrm{d}(\ln Z) = \frac{U}{T}\mathrm{d}T + P\mathrm{d}V + N_M kT\mathrm{d}(\ln A_M) - \mu_W \mathrm{d}N_W, \quad (2)$$

where U is the internal energy, $N_M = N_{M_1} + N_{M_2}$ is the equilibrium number of intercalated gas molecules with activity A_M, μ_W is the chemical potential and N_W is the number of water molecules in the clathrate lattice.

Using the method of molecular dynamics, Rodger has attempted to establish how far the assumptions underlying the cellular theory of gas hydrates are valid.[14] It was shown that one of the approximations, according to which the free energy of the 'water crystal' is independent of the presence of 'guest' molecules in the cell structure, does not hold for gas hydrates. Analysis of the results obtained suggested that the conditions of gas hydrate formation may equally depend on kinetic and thermodynamic factors.

Disregarding the kinetic factors, Eqns (1) and (2) may be transformed to yield an expression for the determination of the chemical potential of water molecules in the equilibrium distribution of 'guest' molecules over the cavities of a gas hydrate:[12, 13]

$$\mu_W = \mu_W^0 + kT \sum_i n_i \ln(1 - Q_i), \quad (3)$$

where μ_W^0 is the chemical potential of an empty hydrate lattice, n_i is the ratio of the number of *i*-type cavities in the elementary cell to the number of its constituent water molecules, Q_i is the fraction of gas-filled cavities calculated using the known Langmuir formula:

$$Q_i = \frac{C_{M_i} f_M}{1 + C_{M_i} f_M}, \quad (4)$$

where, C_{M_i} are the Langmuir coefficients depending on temperature and pressure (the latter dependence is very weak), f_M is the gas fugacity.

It was shown [15] that one should take into account the fugacity of gas molecules in calculations. Sufficient accuracy in the calculation of this parameter is achieved using the Redlich–Quong equation.

Equation (3) makes it possible to determine the minimum value of the fraction of filled cavities, and in combination with Eqn (4), it allows the estimation of the minimum pressure of gas M (dissociation pressure P_{dis}) necessary for the hydrate stabilisation at a given temperature.

The results of studies [16–18] demonstrate that there is also a maximum pressure under which gas hydrates may exist in a steady state (15 000 – 20 000 atm). With hydrates of tetrahydrofuran and SF_6 as examples it was shown [18] that at 77 K and 10 000 – 20 000 atm they are transformed to a denser modification with a 19% decrease in volume.

Barrer and Stuart [12] have derived an expression for the determination of the saturated vapour pressure over the surface of gas hydrate for the case of thermodynamic equilibrium of a gas hydrate with water vapour:

$$P_W = P_W^0 - \sum_i n_i \ln(1 + C_{M_i} f_i), \quad (5)$$

where P_W^0 is the saturated vapour pressure (dependent on temperature and the structural type) over an empty clathrate lattice. Using the experimental data for the most thoroughly studied hydrates of methane (structure I) and propane (structure II), the authors of Ref. 19 showed that the dependence $P_W^{0(I,II)}$ is satisfactorily (with an error of $\sim 3.5\%$) described by two three-membered equations for the temperature range 260–290 K

$$\ln P_W^{0(I)} P = -128.0009 + 22.0937 \ln T - \frac{193.6439}{T}, \quad (6)$$

$$\ln P_W^{0(II)} P = -111.0433 + 20.2241 \ln T - \frac{690.3979}{T}. \quad (7)$$

Thus, if the Langmuir coefficients are known, Eqns (5)–(7) permit us to calculate the pressure (or fugacity) of gas hydrate dissociation or the saturated water vapour pressure above its surface.

In recent years, more accurate models for the thermodynamic description of gas hydrates have been developed.[7, 10] It has been shown that the most important factors to be taken into account in the construction of such models are the interactions of intercalated molecules (interaction of a 'guest–guest' type). The refinement of a thermodynamic description of gas hydrates is made in a way analogous to that used in the theory of solutions when a model of a regular solution is considered instead of a model of an ideal solution. The model thus obtained is called the 'regular clathrate model'. It should be emphasised that at higher degrees of filling of cavities in the hydrate network and similarity of parameters characterising the 'guest–guest' interactions for different gases (*e.g.*, in narrow groups of gas mixtures such as natural gas, hydrides, *etc.*), their contributions to the formulae describing the interaction of intercalated molecules are virtually constant and independent of the gas phase composition. In this case, the 'guest–guest' interaction may formally be included in μ_0 (Ref. 7). It is for this reason that the possibilities of practical application of the ideal gas hydrate model are noticeably extended. Therefore, this paper discusses in sufficient detail the model of an ideal gas hydrate rather than a model of a regular clathrate, which is more complex and cumbersome for practical calculations.

2. Calculation of Langmuir coefficients

In order to determine the Langmuir coefficients, van der Waals and Platteeuw [20] used a spherical cell model. By substituting the mean cavity radius R_i formed by Z_i water molecules for the mean cell radius formed by the neighbouring molecules in liquid, these authors obtained the equation

$$C_{M_i} = \frac{4\pi}{kT} \int_0^{R_i} \exp\left(-\frac{W(r)}{kT}\right) r^2 dr, \quad (8)$$

where $W(r)$ is the radial potential function derived using the interaction potential of the gas molecules with the surrounding water molecules and r is the radial distance of the intercalated gas molecule from the cavity centre.

The energy of gas–water interaction is usually determined by the Lennard-Jones potential. The interaction between gas molecules in the hydrate cavities may be disregarded, as it is insignificant compared to the gas–water interaction and the accuracy of its determination is low (20%–40%).[21]

Calculations of the dissociation pressure by Eqns (3) and (8) using Kihara's potential (*e.g.*, in studies [22, 23] for methane, nitrogen, ethane, and propane) agree well with the experimental values of dissociation pressure of the corresponding gas hydrates. As regards the parameters of Kihara's potential, preference was given to those values which gave the best fit of the μ_W values calculated by Eqns (3) and (4) and found in experiments. The model for calculating the Langmuir coefficients was further improved in studies [24–27] to allow a more adequate description of experimental data.

To calculate the Langmuir coefficients of a spherical gas molecule in a real non-spherical hydrate cavity, the following equation was proposed:[24]

$$C_{M_i} = \frac{1}{kT} \int_0^{2\pi} \int_0^{\pi} \int_0^{R_i} \exp\left(-\frac{W}{kT}\right) r^2 \sin\theta \, dr \, d\theta \, d\varphi, \quad (9)$$

where $W = W(r, \theta, \varphi)$ is the interaction potential in the cavity. To estimate it, the spherical Kihara potential was used, because this potential is believed to permit a better prediction of hydrate equilibria than other potentials do.[24, 25] Kihara's potential has the following form:

$$F(x) = \infty \quad \text{at } x < 2a,$$

$$F(x) = 4\varepsilon\left[\left(\frac{\sigma}{x - 2a}\right)^{12} - \left(\frac{\sigma}{x - 2a}\right)^{6}\right] \quad \text{at } x > 2a, \quad (10)$$

where $F(x)$ is the potential energy of a binary interaction for a distance x between the water and gas molecules, ε is the potential well depth, σ is the distance between molecular centres for which $F(x) = 0$ and a is the nuclear radius of interaction between water and gas molecules. When the distribution of cavity-forming water molecules is known, the summation of binary interactions of a gas molecule with each water molecule allows the estimation of the interaction potential in the cavity $W(r, \theta, \varphi)$ for selected coordinates of the gas molecule.

The spherically symmetrical, smoothed potential derived from the cell model, $< W(r) >$, is expressed through Kihara's parameters in the following manner:

$$< W(r) > = 2Z\varepsilon\left[\frac{\sigma^{12}}{R^{11} r}\left(B^{10} + \frac{a}{R} B^{11}\right) - \frac{\sigma^6}{R^5 r}\left(B^4 + \frac{a}{R} B^5\right)\right], \quad (11)$$

where Z is the coordination number and R is the radius of the cavity.

$$B^n = \frac{1}{n}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-n} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-n}\right],$$

n is 4, 5, 10 and 11.

By comparing the results of calculations using Eqns (9), (10), and (11), the radius and coordination number were determined for each cavity,[24] which allow the use of $< W(r) >$ for the approximation of the interaction potential in a cavity for all distances at which the potential is negative or 'slightly positive'. In this case, the coordination number of an equivalent spherical cavity is not necessarily equal to the real coordination number of the cavity (Table 2).

The effects of the second and third layers of water molecules in the hydrate lattice on the accuracy of calculation of Langmuir constants were studied.[25] It is assumed that the binary interaction between a gas and a water molecule is described by the quasi-spherical Kihara potential (10). The characteristics of smoothed potential in the form of Eqn (11) were obtained, as before,[23] by comparing the results of calculations by Eqn (11) with the results of the summation of the binary interactions. The data reported in Ref. 28 on the distribution of water molecules in a hydrate cell were used for the estimation of the effects of the second and third levels of water molecules. When the effective radius and coordination number of the second and third levels of water molecules were introduced, it was assumed that the gas and water molecules interact only due to the attractive forces. To determine the effective radius of the second level (R_{2i}), the following expression was used:

Table 2. Effective radii of shells of water molecules for various types of cavities in gas hydrates.

Cavity	First shell [22]		First shell [23]		Second shell		Third shell	
	R_i, Å	Z	R_i, Å	Z	R_i, Å	Z	R_i, Å	Z
Structure I								
Small cavity	3.95	20	3.875	20	6.593	20	8.056	50
Large cavity	4.3	24	4.152	21	7.078	24	8.285	50
Structure II								
Small cavity	3.91	20	3.870	20	6.667	20	8.079	50
Large cavity	4.73	28	4.703	28	7.464	28	8.782	50

$$\frac{Z}{(R_{2i})^6} = \sum_j \frac{Z_j}{(r_j)^6}, \tag{12}$$

where Z_j is the number of the second level molecules at the distance r_j from the cavity centre. The effective radius of water molecules at the third level R_{3i} was determined similarly. However, whereas the second layer of water molecules may be correctly described using the crystallographic data, it is not always possible to distinguish the third and subsequent layers. Therefore, the contribution from the third level is determined by those from the subsequent layers of water molecules. The results of calculation of the effective radius for the second and third layers are presented in Table 2. The calculation of the smoothed interaction potential between gas and water molecules by Eqn (11) for the three water layers has shown [25] that although the contributions from the molecules of more distant layers are small compared to that of the first-layer molecules and make up only a few percent, nonetheless their consideration leads to a nearly tenfold increase in the Langmuir constant. Consequently, accurate calculation of the Langmuir constants requires consideration of no less than three layers of water molecules.[25]

To make it possible to use the parameters of Kihara's potential obtained by independent calculations based on the data on viscosity and the second virial coefficient in Eqn (11), it was proposed [26, 27] to introduce a correction factor into Eqn (8) to account for the irregularity of the shape of gas molecules and the cavity. To this end, it was proposed to calculate the Langmuir constant by the following equation:

$$C_0 = CQ, \tag{13}$$

$$Q = \exp\left\{-A_0\left[U\left(\frac{\sigma}{R-a}\right)\frac{\varepsilon}{rT}\right]^n\right\}, \tag{14}$$

where C is calculated by Eqn (8), A_0 and n are empirical constants depending on the cavity type, and U is the empirical parameter taking into account the shape of the gas molecules. For small and spherical molecules, $U = 0$. The largest deviation of the coefficient Q from 1 is observed for the gas molecules localised in large cavities of structure I, which are the most asymmetrical. The results of calculations of the dissociation pressure for a number of substances based on the above model agree well with the reported experimental data.[26, 27] The Q value may also be larger than 1. Relatively high Q values are observed for small Langmuir constants (for large gas molecules). This may be explained by strong fluctuations of the cell potential $W(r, \theta, \varphi)$.[26]

The method of molecular dynamics was used [29] to study the potential field in a small cavity of type I gas hydrate. The thermal motion of 'host' molecules of the lattice was found to change the natural potential in the cavity and to result in its substantial anisotropy and temperature dependence. An equation for the potential in the form of a polynomial of the sixth power was proposed and its parameters were determined for methane. It was shown that Kihara's potential may also be applied using the dependence of parameters a and R on angles θ and φ. The form of these dependences can be determined from the results of simulation by the method of molecular dynamics.

Thus, a system of Eqns (8), (11), (13), and (14) makes it possible to calculate the Langmuir constants necessary for determination of the conditions for the existence of gas hydrates by the Eqns (3)–(5).

3. Calculation of gas hydrate parameters for argon, krypton and xenon

Using the model of ideal solutions for the calculation of the conditions for the existence of gas hydrates and the spherical cell model for the determination of the Langmuir constants, an algorithm for the computation of parameters of gas hydrates in the separation and refinement of gases was derived and the corresponding programs for an IBM PC were developed.[30]

To check the applicability of Eqns (8) and (11)–(14) for the determination of the Langmuir constants, these were calculated [30] for the gas hydrates of argon, krypton, and xenon because of the availability of experimental data on these compounds.[31]

The calculation of the Langmuir constants within the framework of the above model requires that the parameters of Kihara's potential for the substances under study be known. The literature data on these parameters are contradictory; in some cases, the discrepancy reaches 50%–100%. The authors of Ref. 32 have used the parameters of Kihara's potential reported in Ref. 27, whereas in another study,[31] double hydrates were used for the experimental determination of the Langmuir constants. In the latter work, the absorption of the above-mentioned gases in structure II of $CHCl_3$ hydrate under different gas pressures was investigated. All large cavities were occupied by $CHCl_3$, while the inert gas filled the small cavities. The linear dependence obtained between the pressure and the volume of the gas absorbed confirmed once again the applicability of the Langmuir isotherm. Figure 1 shows the plots of the dependence of the logarithm of the Langmuir constant for argon, krypton, and xenon on $1/T$. All the

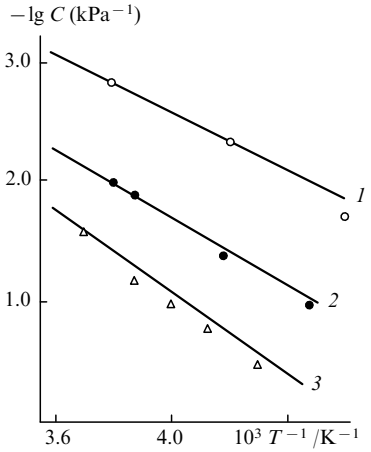


Figure 1. The temperature dependence of the Langmuir constants for argon (*1*), krypton (*2*), and xenon (*3*). The solid line corresponds to the theoretical calculations, the points represent the experimental data.

dependences proved to be linear thus allowing the determination of the enthalpy of dissociation for each gas in 12 water cavities, and the results obtained coincided with the theoretical data.[31] Figure 1 also shows the results of calculations based on the above model. However, the parameters of Kihara's potential differ from those reported [27] (Table 3) by the magnitude of the error of their determination (5%–7%). The use of accurate ε and σ values results in underestimation of the Langmuir constants for krypton and xenon by more than an order of magnitude.

To check the applicability of Eqns (5)–(7) for the calculation

Table 3. Parameters of Kihara's potential used to calculate the Langmuir constants.

Parameter	Ar	Kr	Xe
σ /Å	3.29 3.29	3.53 3.3	3.65 3.43
ε/k /K	156.08 156.08	216.4 230.0	314.51 340.0
a /Å	0.217 0.217	0.232 0.217	0.252 0.252

Note. Numbers above the line are potential parameters given in Ref. 26, those below the stroke are parameters used by us. For all gases in all cases we assumed $U = 0$.

of the vapour pressure of water above the surface of hydrates, calculations were performed [30] for the hydrates of the same inert gases under their dissociation pressure. As follows from the above-mentioned theory of gas hydrate formation, under the pressure of hydrate dissociation, the pressure of water vapour above its surface is equal to that above the ice surface at the same temperature. For example, at 273 K the pressure of water vapour calculated by the algorithm mentioned is 0.54, 0.53, and 0.57 kPa for argon, krypton, and xenon, respectively. The literature data value for the same parameter for ice is 0.6 kPa,[32] *i.e.* fairly good agreement is observed between the theoretical and experimental results.

Thus, the theoretical model of gas hydrate formation allows an accurate calculation of the dissociation pressure of a hydrate-forming gas and the minimum content of water at which the formation of hydrates is still possible. In the refinement of some substances, *e.g.*, Freons and volatile inorganic compounds capable of forming gas hydrates in the vapour phase, their effect on the efficiency of this process may be substantial.[33–36]

IV. Vapour pressure of water over the surface of gas hydrates in mixtures of volatile inorganic hydrides

In volatile inorganic hydrides, the content of water and some other impurities should not exceed a certain level. Demands for higher purity of substances and a larger set of impurities to be controlled make it necessary to consider the possible presence of different forms of water.

Under elevated pressures, the impurity of water can form finely dispersed, solid gas hydrates with some volatile inorganic hydrides.[15] The presence of gas hydrates in the vapour phase may lead to incorrect determination of the water concentration in a given gas.[34]

Using the algorithm for the calculation of the parameters of gas hydrates,[30] the pressure of water vapour above the surface of methane and hydrogen sulfide hydrates for different temperatures and gas pressures was calculated [34] (Table 4). For these compounds, the temperature dependences of dissociation pressure of gas hydrates and the parameters of Kihara's potential have been studied in sufficient detail.[27]

Analogous calculations for other hydrides are problematic due to the absence of the respective parameters of Kihara's potential. Therefore, the Lennard-Jones potential was used [34] to calculate the Langmuir constants by Eqn (4).

To check the applicability of the Lennard-Jones potential for this purpose, the Langmuir constants were calculated for the gas hydrates of argon, krypton, and xenon, because the experimental values of the constants are known.[2] The parameters of the Lennard-Jones potential necessary for such calculations are presented in Table 5. The use of literature values of ε and σ leads to the underestimation of the Langmuir constants for all gases by more than one order of magnitude. Therefore, to calculate the Langmuir constants, preference was given to the values of ε and σ, which are within the range of their error estimates. For water, the following parameters were used: ε_W/k = 102.1 K, σ_W = 3.564 Å.[27] When calculating ε and σ for the cases of cross-interaction of water molecules with molecules of hydrides, the Lorentz–Berthelot rule was used:[34]

$$\varepsilon_0 = (\varepsilon_W \varepsilon)^{1/2}; \sigma_0 = \tfrac{1}{2}(\sigma_W + \sigma),$$

where ε_0 and σ_0 are parameters describing the gas–water interaction.

Analogous formulae were also used for the calculation of the vapour pressure of water above the surface of hydrates of some volatile inorganic hydrides. The results of calculations for gas hydrates of arsine, hydrogen selenide, and phosphine, as well as methane, characterised by structure I are given in Table 4 as examples.[34] Comparison of the results of calculations for hydrogen sulfide and methane shows that the deviation of values derived using the interaction potentials of Kihara and Lennard-Jones does not exceed 10%. The percentage of water in gas given in the table, which is equal to the ratio of water vapour and gas pressures, determines the minimum content of water in the molecular form at which the formation of gas hydrates is possible under given conditions. If the concentration of molecular water exceeds the indicated value, it is decreased owing to the formation of hydrates and tends to reach the level given in the table. Consequently, the given value of water concentration determines the maximum concentration of water in the molecular form for specified conditions.

The results of calculations presented in the tables indicate that if one disregards the formation of hydrates and takes into account only the condensation of water to form ice, then the value of the vapour pressure of water and hence the concentration of molecular water may be overestimated by a factor of 1.5 or more. With a decrease in temperature, the ratio of the vapour pressure of water above the ice surface to that of gas hydrate increases (Table 6) with a concomitant increase in the scatter of values of this parameter for different hydrides (except for arsine and hydrogen sulfide), which becomes significant at temperatures below 273 K. It seems so far impossible to calculate this parameter for a wider temperature range since the required initial data are unavailable. Nonetheless, this parameter may be estimated using the equations given in Ref. 34 by approximating the data shown in Table 6 by the least-squares method.

For arsine and hydrogen sulfide at $T < 273$ K

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{189.1}{T} - 0.328, \quad (15)$$

for phosphine at $T < 273$ K

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{613.4}{T} - 1.879, \quad (16)$$

for hydrogen selenide at $T < 273$ K

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{49.5}{T} + 0.587, \quad (17)$$

Table 4. Results of the calculations of water vapour pressure over the surface of various hydrates.

T/K	Methane hydrate [a]						Hydrogen sulfide hydrate [b]						Arsine hydrate			Phosphine hydrate			Hydrogen selenide hydrate		
P_{dis}	P'_{dis} P_W	P'_W	c'_{H_2O} (%) c_{H_2O} (%)		P_{dis}	P_W	c_{H_2O} (%)		P'_{dis}	P'_W	c'_{H_2O} (%)		P_{dis}	P_W	c_{H_2O} (%)	P_{dis}	P_W	c_{H_2O} (%)	P_{dis}	P_W	c_{H_2O} (%)
252	–	–	–	1130	0.09	0.80	42	0.10	0.24	42	0.09	0.21	32	0.09	0.29	31	0.09	0.30	28	0.09	0.32
	–	–	–	10000	0.07	0.07	300	0.08	0.03	300	0.06	0.02	200	0.07	0.04	500	0.06	0.01	100	0.08	0.08
	–	–	–	20000	0.06	0.03	515	0.07	0.01	517	0.05	0.01	485	0.06	0.01	1022.7	0.05	0.005	231	0.07	0.03
259	1550	0.19	1.23	1550	0.17	1.10	55	0.19	0.35	55	0.17	0.30	45	0.18	0.40	55	0.17	0.31	33	0.18	0.54
	10000	0.15	0.15	10000	0.13	0.13	300	0.15	0.05	300	0.13	0.04	300	0.13	0.05	600	0.12	0.02	150	0.14	0.10
	20000	0.13	0.07	20000	0.12	0.06	650	0.13	0.02	653	0.11	0.02	602	0.12	0.02	1242	0.11	0.01	301	0.13	0.04
	2030	0.35	1.74	2030	0.32	1.55	71	0.36	0.51	72	0.32	0.44	60	0.34	0.55	91	0.31	0.35	38	0.34	0.88
266	10000	0.28	0.28	10000	0.25	0.25	400	0.28	0.07	400	0.24	0.06	350	0.26	0.07	700	0.23	0.03	200	0.27	0.13
	20000	0.25	0.13	20000	0.23	0.12	815	0.25	0.03	818	0.22	0.03	740	0.23	0.03	1493	0.20	0.01	387	0.24	0.06
	2620	0.64	2.44	2620	0.58	2.19	92	0.67	0.72	92	0.58	0.63	83	0.61	0.74	160	0.55	0.35	45	0.64	1.41
273	10000	0.53	0.53	10000	0.48	0.48	500	0.52	0.10	500	0.45	0.09	400	0.49	0.12	800	0.43	0.05	250	0.50	0.20
	20000	0.48	0.24	20000	0.44	0.22	1010	0.46	0.05	1012	0.40	0.04	900	0.43	0.05	1778	0.38	0.02	490	0.45	0.09
	5940	1.07	1.80	5940	0.93	1.34	204	1.12	0.55	204	0.98	0.48	190	1.02	0.54	319	0.94	0.30	90	1.09	1.21
280	10000	0.99	0.99	10000	0.88	0.88	600	0.95	0.16	600	0.83	0.14	500	0.89	0.18	900	0.80	0.09	300	0.92	0.31
	20000	0.89	0.45	20000	0.81	0.40	1240	0.84	0.07	1240	0.74	0.06	1081.1	0.790	0.073	2100	0.71	0.03	614	0.82	0.13
	12800	1.75	1.37	12800	1.56	1.22	436	1.84	0.42	437	1.61	0.37	415	1.69	0.41	612	1.57	0.26	175	1.84	1.05
287	20000	1.64	0.82	20000	1.47	0.74	1000	1.62	0.16	1000	1.42	0.14	600	1.60	0.27	1000	1.46	0.15	350	1.66	0.48
	40000	1.46	0.37	30000	1.39	0.46	1500	1.51	0.10	1505	1.34	0.09	1290	1.43	0.11	2457	1.28	0.05	761	1.48	0.20
	26100	2.84	1.09	26100	2.54	0.98	865	3.00	0.35	865	2.65	0.31	880	2.75	0.31	1140	2.61	0.23	327	3.06	0.94
294	35000	2.71	0.78	30000	2.49	0.83	1200	2.85	0.24	1200	2.53	0.21	1000	2.70	0.27	1400	2.53	0.18	450	2.92	0.65
	50000	2.56	0.51	35000	2.42	0.69	1800	2.66	0.15	1809	2.38	0.13	1524	2.55	0.17	2856	2.29	0.08	933	2.63	0.28

Note. The following designations are used: P'_{dis}, P'_W, and C'_{H_2O} are values obtained using Kihara's potential, P_{dis}, P_W, and C_{H_2O} are those obtained with the Lennard-Jones potential (the gas pressures P'_{dis}, P_{dis} and water pressure P_W are given in kPa).
The following parameters of Kihara's potential were used: [a] ε/k = 197.39 K, σ = 3.501 Å, a = 0.13 Å, U = 0; [b] ε/k = 414.88 K, σ = 2.747 Å, a = 0.36 Å, U = 0.

Table 5. Parameters of the Lennard-Jones potential used to calculate the Langmuir constant.

Substance	ε/k /K			σ /Å		
	I	II	III	I	II	III
H_2S	301	309	290	3.623	3.722	3.8
H_2Se	320	334	310	3.86	3.876	3.86
PH_3	270	260	275	3.897	3.992	3.77
AsH_3	277	293	280	4.06	4.069	3.8
CH_4	148.6	153.4	148.6	3.758	3.413	3.6
Ar	93.3	117.2	100	3.542	3.405	3.3
Kr	178.9	—	185	3.655		3.55
Xe	231	—	250	4.047		3.75

Note. The following designations are used: I — the data from Refs 37 and 38; II — calculation by the procedure proposed in Ref. 39, III — our results.

Table 6. Ratios of the vapour pressure of water over hydrates at the dissociation pressure to that at the saturated vapour pressure for some hydrides.

T /K	AsH_3	PH_3	H_2Se	H_2S
252	1.53	1.74	1.39	1.52
259	1.50	1.63	1.40	1.49
266	1.46	1.54	1.41	1.47
273	1.43	1.44	1.41	1.45
280	1.29	1.33	1.32	1.32
287	1.18	1.22	1.24	1.21
294	1.08	1.11	1.16	1.11

for all hydrides at $T > 273$ K

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{940.6}{T} - 3.089, \tag{18}$$

where P_1 and P_2 are the pressures of water vapour above the gas hydrate surface at the pressure of saturated hydride vapour and at the pressure of dissociation, respectively. Thus, for phosphine at 200 K, this parameter and hence the ratio of the real concentration to its theoretical value is 3.28.

In addition, the presence of water in the form of a finely dispersed phase requires the use of an appropriate purification technique. Specifically, this concerns the formation of double or mixed hydrates, when other hydrides or gases may be intercalated as impurities into the crystalline lattice of gas hydrates.

Thus, the above data indicate that the appearance of impurities in hydrides in the form of gas hydrates can substantially affect the process of their refinement.

V. The formation of mixed hydrates in inorganic hydrides and atmospheric air

A large contribution to the development of theory and experimental techniques for studying mixed gas hydrates was made by Nikitin [1] who proposed and developed a method of isomorphous co-precipitation in mixed hydrates of rare components from the gas phase irrespective of their concentration. It was shown that there is no need to apply high pressures to form gas hydrates of a large number of gases, since the gas in question under a partial pressure lower than the pressure of its hydrate dissociation, can form a gas hydrate in the form of an isomorphous mixture with hydrates of other gases. Based on the results obtained and general theoretical concepts, Nikitin formulated the 'analogy rule', according to which two substances having the same van der Waals forces and commensurable molecules should form with a third substance analogous molecular compounds possessing similar stability and the ability to form mixed crystals with each other. Thus, taking into account the 'analogy rule' and the law of isomorphous co-precipitation, it may be inferred that a mixed hydrate can contain different quantities of the all gas phase components that can form isomorphous structures.

Let us consider the methods employed for the quantitative assessment of the conditions for formation of mixed gas hydrates.

1. The effect of gas mixture composition on conditions of gas hydrate formation and vapour pressure of water above its surface

One of the critical parameters characterising the process of gas hydrate formation at a given temperature is its dissociation pressure P_{dis}. The dissociation pressure determines the minimum pressure of a gas mixture at which the hydrate is thermodynamically stable. To carry out processes of refinement of substances that form gas hydrates, one should know the dependence of the dissociation pressure of gas hydrates and the vapour pressure of water over their surface on the composition of gas mixture. This dependence may be determined using the model proposed by Barrer and Stuart.[12]

The application of the model of ideal solutions for the case of thermodynamic equilibrium yielded an equation for the calculation of the pressure of saturated water vapour over the surface of a gas hydrate formed by a mixture of gases M_1, M_2, ..., M_i.[12]

$$\ln\left(\frac{P_W}{P_W^0}\right) = \frac{1}{m(n+1)}\left[n\ln\left(1-\sum_i Q_{1i}\right) + \ln\left(1-\sum_i Q_{2i}\right)\right], \tag{19}$$

where P_W is the pressure of saturated vapour over the hydrate surface; P_W^0 is the pressure of saturated vapour above an empty clathrate lattice (which depends on the structural type and temperature; these may be found in Ref. 32); m is the number of water molecules per cavity; n is the ratio of large-to-small cavities in the elementary crystalline hydrate cell ($n = 3$, $m = 5.75$ for structure I hydrates and $n = 2$ and $m = 5.67$ for structure II hydrates [32]); Q_{1i} and Q_{2i} are the fractions of small and large cavities filled with gas M_i.

The filling of cavities in gas hydrates is well described by the Langmuir adsorption isotherm:[15]

$$Q_{ji} = \frac{C_{ij}f_i}{1+\sum_i C_{ij}f_i}, \tag{20}$$

where $f_i = \varphi_i P_i$ is the fugacity of gas M_i, φ_i is the fugacity coefficient, P_i is its pressure and C_{ij} are the Langmuir coefficients calculated using the spherical cell model.[32]

The model used for calculating the fraction of filled cavities in mixed gas hydrates describes well the experimentally found (most probably, derived in an indirect way)[5] compositions of equilibrium phases formed by hydrates of natural gas (Table 7).

Table 7. Composition of the equilibrium phases formed by natural gas ($T = 269.5$ K; $P = 4150$, $P_W^s = 0.455$, $P_W^h = 0.367$ kPa).

Natural gas		Q_i	c_i	
components	percentage	calculation	calculation	experiment
CH_4	82.50	51.42	56.93	56.95
C_2H_6	5.99	13.44	14.88	5.66
C_3H_8	3.26	20.67	22.88	24.97
iso-C_4H_{10}	0.30	2.75	3.05	4.69
N_2	7.19	1.07	1.18	0.46
CO_2	0.20	0.23	0.25	0.44
Other	0.56	0.75[a]	0.83[a]	0.83
$\sum$	100	90.33	100	94.0

[a] Found experimentally.

Since an empty hydrate lattice cannot be formed directly from water or ice, the following relation [2] is valid: $P_W^0 > P_W^{l,s}$, where $P_W^{l,s}$ is the pressure of saturated water vapour above the surface of liquid (l) or ice (s). It follows from Eqn (19) that the intercalation of the gas forming the hydrate into the hydrate lattice cavities reduces the pressure of water vapour above the hydrate surface. As soon as it becomes equal to or lower than $P_W^{l,s}$, crystalline lattice formation becomes possible. Thus, the dissociation pressure is determined from the condition

$$P_W = P_W^{l,s}. \tag{21}$$

By substituting (19) and (20) into (21), one obtains an expression for the calculation of the dissociation pressure:[35]

$$\ln\left(\frac{P_W^{l,s}}{P_W^0}\right) = \frac{1}{m(n+1)}\left[n\ln\left(1+\sum_i C_{1i}f_i\right) + \ln\left(1+\sum_i C_{2i}f_i\right)\right]. \tag{22}$$

Equation (22) was solved for the dissociation pressure by numerical methods on a PC. The computations were performed for gas mixtures of different composition containing hydrides of arsenic, phosphorus, sulfur, and selenium, as well as krypton at different temperatures of hydrate formation. In the calculations by Eqn (22), it was assumed that $P_W^{l,s} = 2.52$ kPa at $T = 294$ K and $P_W^{l,s} = 0.092$ kPa at $T = 252$ K.[32] The results of calculations are presented in Fig. 2.

As is seen from the Figures showing a ternary gas mixture (two hydrides and water), in all cases when values of P_{dis} of individual components are different, the dissociation pressure depends substantially on the fraction of the main substance and the temperature of hydrate formation. With the decrease in the amount of the main component, P_{dis} varies monotonically from the value of dissociation pressure of a pure major component to that of a pure component, which serves as an impurity (Fig. 2 *a,* curves *1–4*; Fig. 2 *b*, curve *1*).

For four-component systems, the content of the second component was arbitrarily taken to be equal to 10% of that of the main substance, and this ratio was maintained constant. The portion of the major component varied in the same way as in the case of ternary systems, though at the expense of the fourth component. The character of changes in the dissociation pressure was analogous to that in the first case, though at definite ratios of concentrations of the second and the fourth components (this ratio varies for different systems and depends on the temperature and P_{dis} of each component) extrema may appear in the curve of dependence of P_{dis} on composition (Fig. 2 *a*, curve *2*).

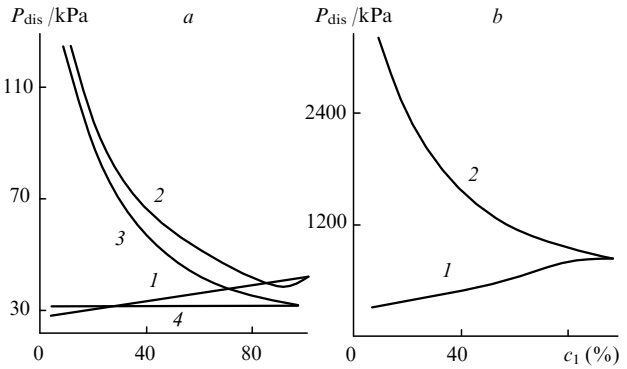


Figure 2. Dissociation pressure of gas hydrates *vs.* concentration of the main component of a gas mixture for different systems at 252 K (*a*) and 294 K (*b*).
(*a*): (*1*) $H_2S + H_2Se + H_2O$; (*2*) $H_2S + H_2Se + H_2O + Kr$; (*3*) $AsH_3 + PH_3 + H_2O + Kr$; (*4*) $AsH_3 + PH_3 + H_2O$;
(*b*): (*1*) $H_2S + H_2Se + H_2O$; (*2*) $H_2S + H_2Se + H_2O + Kr$.

Thus, the presence in a gas mixture of components with lower and higher values of dissociation pressure than that of the main substance under purification may substantially alter the conditions of formation of hydrates and in some cases prevent their formation in the process of purification.

The maximum concentration of water in a gas mixture containing gas hydrates is determined by the pressure of saturated water vapour above the hydrate surface.[34] Let us consider the influence of gas mixture composition on the pressure of water vapour above the surface of a gas hydrate.

Under real conditions, the composition of a gas mixture changes due to changes in the partial pressures of its components.[33, 35, 36]

Let us consider first a ternary gas system comprising two hydrides and water. The variation of partial pressures occurs in the following manner:[35, 36] first, the pressure of a major component, equal to the pressure of its saturated vapour at a given temperature, is assumed to be constant, while the partial pressure of an impurity component increases from zero to a maximum value equal to the pressure of its saturated vapour at this temperature. After the maximum partial pressure of impurity is reached, further decrease in the proportion of the major substance is possible only owing to the reduction of its partial pressure. In this situation, the pressure of the impurity component is maintained constant. As a result, the total pressure of the gas mixture first increases and then decreases. The vapour pressures of water above the hydrate surface calculated for this case by Eqn (19) are presented in Fig. 3.[36]

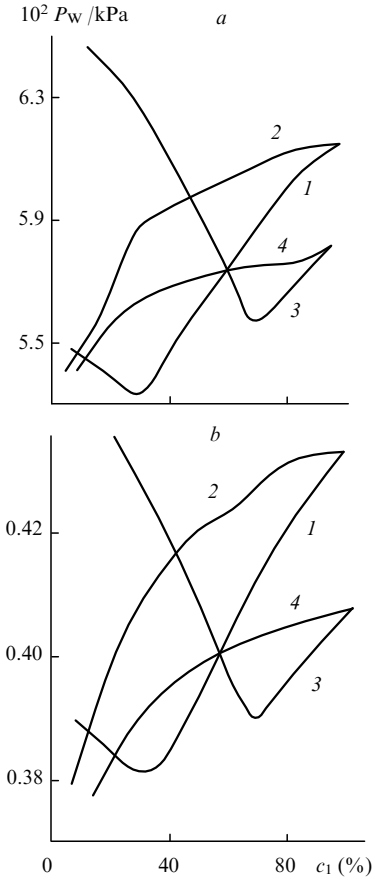


Figure 3. Pressure of water vapour above the surface of gas hydrates *vs.* concentration of the main component of a gas mixture at 252 K (*a*) and 273 K (*b*).
(*a*): (*1*) $AsH_3 + PH_3 + H_2O$; (*2*) $AsH_3 + PH_3 + H_2O + Kr$; (*3*) $H_2S + H_2Se + H_2O$; (*4*) $H_2S + H_2Se + H_2O + Kr$;
(*b*): (*1*) $AsH_3 + PH_3 + H_2O$; (*2*) $AsH_3 + PH_3 + H_2O + Kr$; (*3*) $H_2S + H_2Se + H_2O$; (*4*) $H_2S + H_2Se + H_2O + Kr$.

As seen from the Figures, there is a minimum in P_W corresponding to the maximum value of the total pressure of the gas mixture. This is due to the maximum filling of hydrate cavities by gas molecules resulting in higher stability of the clathrate lattice and a lower pressure of water vapour above its surface.

In the calculations of four-component systems, the content of the second component was also arbitrarily assumed to be equal to 10% of the content of the main substance (see above), and this ratio was maintained constant.[35] As the temperature of the gas mixture was higher than the critical temperature of the fourth component (krypton), the total pressure increased monotonically with the decrease in the level of the major component, and the vapour pressure of water over the surface of mixed hydrate was substantially decreased (Figs 3 *a* and 3 *b*, curves *2* and *4*).

Thus, the increase in the pressure of a gas mixture due to the addition to it of a component which does not condense at a given temperature, allows a significant decrease in the content of molecular water in the gas mixture.

2. Distribution coefficients of constituent molecules of a gas mixture in the cavities of mixed hydrates

In the process of separation and refinement of multicomponent systems M_1, M_2, ..., M_i, mixed hydrates may be formed at appropriate temperatures and pressures. This is accompanied by redistribution of gas mixture components between the gas hydrate and the gas mixture. The gas hydrate (or the gas mixture) is enriched or depleted in one or several components because of differences in the composition of equilibrium phases: gas phase and solid phase (on an anhydrous base).[30] In order to estimate the purification efficiency, it is necessary to know the composition of gas hydrates, which is determined by distribution of molecules of the major substance and impurities in the cavities.

The distribution of the hydrate-forming molecules in the cavities of a gas hydrate is characterised by the distribution coefficient [33, 36]

$$K_i = \frac{Q_i P_s}{P_i \sum_i Q_i}, \tag{23}$$

where Q_i is the fraction of hydrate cavities filled with molecules M_i, P_s is the total pressure of the gas mixture, and P_i is the partial pressure of M_i molecules in the gas phase.

The fraction of filled cavities is determined from the Langmuir isotherm [Eqn (20)]. If n_j is the fraction of type j cavities in the gas hydrate, then

$$Q_i = \sum_j n_j Q_{ij}. \tag{24}$$

To characterise the redistribution of gas mixture components upon formation of gas hydrates, it is convenient to use the relative distribution coefficient [33, 36]

$$K_{i1} = \frac{K_i}{K_1}, \tag{25}$$

where the mixture component with $i = 1$ is arbitrarily assumed to be the major substance (the one to be purified).

By substituting Eqn (23) into Eqn (25) the following relation is obtained:

$$K_{i1} = \frac{Q_i P_1}{Q_1 P_i}. \tag{26}$$

The relative distribution coefficient makes it possible to assess whether the gas hydrate will be enriched (when $K_{i1} > 1$) or depleted (when $K_{i1} < 1$) in impurities from the substance subject to purification. It follows from Eqns (24) and (26) that the relative distribution coefficient may substantially depend on the conditions of hydrate formation and the impurity concentration in the gas mixture.

The dependences of relative distribution coefficient on the conditions of gas hydrate formation were studied [36] in mixtures containing inorganic hydrides of arsenic, sulfur, selenium, phosphorus and antimony, as well as methane and nitrogen.

Under real conditions, the composition of a gas mixture changes as a result of changes in the partial pressures of the components of a mixture.

Let us consider first a ternary gas mixture containing two hydrides and water. In the temperature range studied (250 – 290 K), the pressure of water vapour is negligible in comparison with the total pressure of the gases [34] and hence may be disregarded. Thus, the total gas pressure is determined by the partial pressures of the hydrides. If the partial pressure of the major component (equal to the pressure of its saturated vapour at a given temperature) is assumed to be constant, then the decrease of its fraction in the mixture may occur at the expense of an increase in the partial pressure of the impurity component, up to its maximum level (equal to the pressure of its saturated vapour at a given temperature). This results in an increase in the total pressure of the gas mixture. The increase in the partial pressure of impurity above its maximum level leads to condensation of the impurity component. Thus, further decrease in the fraction of the major substance is possible only at the expense of a decrease in its partial pressure, the pressure of the impurity component being maintained constant. This results in the reduction of the total pressure of the gas mixture. The relative distribution coefficients calculated for this case by Eqn (26) are presented in Fig. 4 *a*,*b*. The

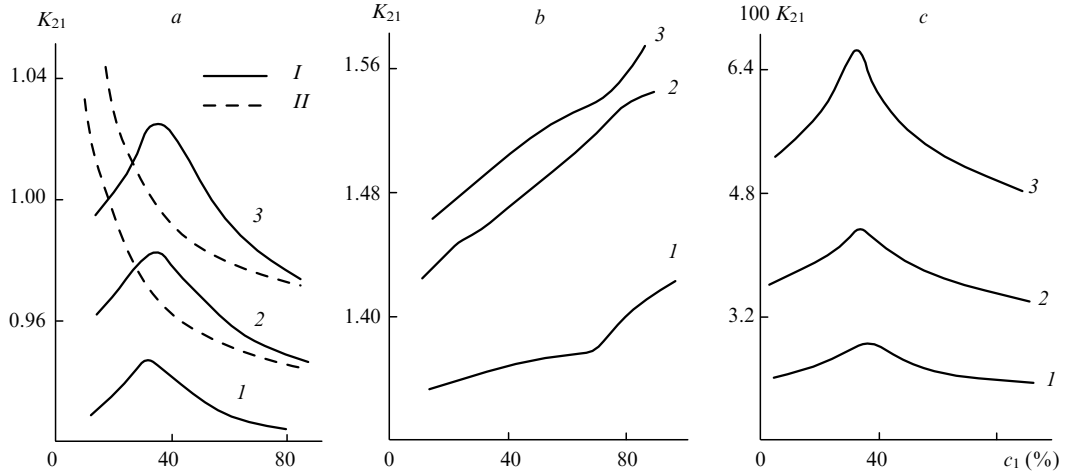


Figure 4. Relative distribution coefficient *vs.* concentration of principal (*I*) and the second (*II*) components of gas mixture for the systems: $AsH_3 + PH_3 + H_2O$ (*a*), $H_2S + H_2Se + H_2O$ (*b*), $AsH_3 + CH_4 + H_2O + PH_3$ (*c*) at 252 K (*1*), 273 K (*2*) and 294 K (*3*).

Langmuir constants, which are required for the determination of the fraction of the cavities filled from Eqn (20), were calculated using the spherical cell model.[32]

As is seen from these figures, in all cases the relative distribution coefficient depends substantially on the fraction of the main substance. This is due to the fact that changes in the partial pressures (fugacity) of the components of the gas mixture result in redistribution of molecules of different gases between the gas hydrate cavities according to Eqn (20). The presence of extrema in curves *1–3* shown in Fig. 4 *a* and inflection points in all curves of Fig. 4 *b* may be explained by non-monotonic changes in the fugacity of the components of the mixture upon the non-monotonic changes in the total pressure of the gas mixture.[37] Incidentally, depending on the fraction of the components of the mixture, the relative distribution coefficient of the second component may be either >1, *i.e.* the hydrates accumulate predominantly the impurity from the substance subject to purification, or <1, *i.e.* the hydrates accumulate mostly the major substance.

In calculations of four-component systems, the content of the second component was arbitrarily assumed to be equal to 10% of that of the main substance, and this proportion was maintained constant. The fraction of the main component varied in the same manner as in the case of ternary systems, though at the expense of changes in the concentration of the fourth component. If the temperature of the gas mixture is below the critical temperature of the third component, then the total pressure is first increased and then decreased as the fraction of the main component is increased. This leads to the formation of extrema in curves *1–3* (Fig. 4 *c*). If the temperature of the gas mixture is above the critical temperature of the fourth component, the total pressure of the mixture grows monotonically with the decrease in the fraction of the main component. In this case, the relative distribution coefficient of the second component changes monotonically (Fig. 4 *a*, curves *II*). Figure 4 *a* shows that in this case, too, K_{21} may be either >1 or <1, depending on the fractions of the gas mixture components.

If the total pressure of the gas mixture remains invariant despite changes in its composition, the partial pressure of each component is subject to variation. Then, the dependence of the relative distribution coefficient of the second component on the fraction of the main component in the gas phase is virtually linear for different mixture compositions and conditions of hydrate formation (Fig. 5).

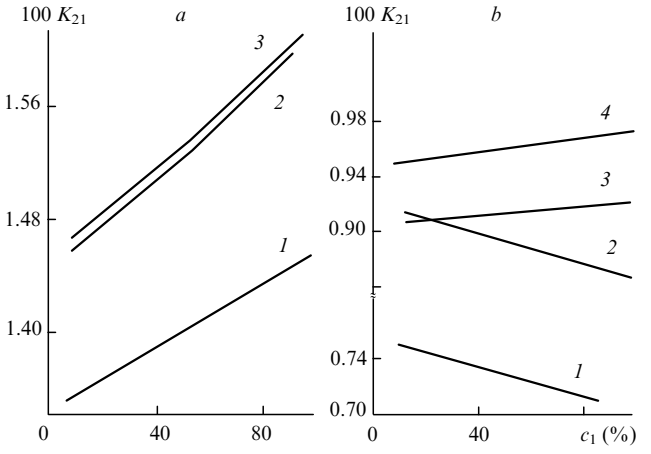


Figure 5. Relative distribution coefficient *vs.* concentration of the main component of a gas mixture for the systems: $H_2S + H_2Se + H_2O$ (*a*), $AsH_3 + SbH_3 + H_2O + PH_3$ (*b,1,2*), and $AsH_3 + SbH_3 + H_2O$ (*b,3,4*).

(*a*)	*1*	*2*	*3*
T/K	294	252	294
P_s/kPa	930	230	150

(*b*)	*1*	*2*	*3*	*4*
T/K	294	252	294	252
P_s/kPa	1520	500	1520	500

The above data indicate that under the same conditions of hydrate formation the relative distribution coefficient depends substantially on the ratio of components in gas mixtures, and in some cases it may differ greatly from unity (see, *e.g.*, Fig. 4 *b*). Hence, substantial enrichment or depletion of the main component in the impurities present may already occur at the stage of hydrate formation. Separation of gas hydrates from the gas mixture allows additional purification of the main substance or air – gas mixtures.

3. Concentration of technogenic impurities in atmospheric gas hydrates

The atmosphere continuously receives strong fluxes of gases containing deleterious compounds, such as sulfur and carbon dioxides, carbon and nitrogen monoxides, chlorinated organic compounds, *etc*. Such noxious compounds are released by natural and industrial sources. Nowadays, the natural and anthropogenic fluxes are commensurable, though in some instances the latter may dominate.[40] Such compounds are either uniformly dispersed in space or concentrated on some carriers (aerosols, various colloidal particles, *etc*.). Concentration of hazardous impurities on specific carriers may lead, on the one hand, to environmental cleaning by the 'storage' of such impurities in relatively small quantities of microparticles. On the other hand, these 'stores' are a serious threat to biosystems, since such a redistribution of minor components in atmospheric air may radically affect various physicochemical processes in the biosphere.[41] The role of carriers in which the components of gas mixtures can be concentrated may be played by water molecules, water-based clusters, or gas hydrates.[35,41]

When technogenic impurities are released into the atmosphere in quantities sufficient for the formation of gas hydrates, it is necessary to know their composition and the conditions of their stability at a given temperature.

The use of Eqn (22) makes it possible to determine whether or not gas hydrates are formed under given conditions.

Knowing the fraction of cavities filled with molecules of a gas mixture, one can determine their concentration in the gas hydrate. Since, on average, there are 5.75 water molecules per cavity in structure I hydrate and 5.67 water molecules per cavity in structure II hydrate,[5] then we obtain for structure I

$$c_i = \frac{Q_i}{5.75}, \tag{27}$$

and for structure II

$$c_i = \frac{Q_i}{5.67}. \tag{28}$$

Let us consider an air mixture (with nitrogen and oxygen as the main components) containing sulfur and carbon dioxides, nitrogen monoxide, Freon 12 and chloroform as impurities.[42,43] The results of calculations performed using the above equations allowing the determination of relative distribution coefficients and the concentrations of impurities in gas hydrates are presented in Table 8.

For the temperature range under study, $P_W^s = 0.2566$ kPa at 263 K and $P_W^s = 0.6067$ at 273 K. The gas mixtures indicated above do not form any gas hydrates at 273 K, because condition (21) is not fulfilled, whereas in all other cases the formation of gas hydrates is possible. When the temperature increases, the probability of hydrate formation decreases. It is of note that the hydrates formed will contain predominantly the impurity components. Gas hydrates concentrate preferentially the compounds with minimum dissociation pressures at given temperature. For example, at 273 K the dissociation pressures of nitrogen, sulfur dioxide, and chloroform are 11 000, 18.7, and 3.5 kPa, respectively. In addition, the extent of concentration of individual impurity in a hydrate or the relative distribution coefficient (relative to the coefficient of nitrogen distribution) depends substantially on the composition of a gas mixture, temperature,

Table 8. Relative distribution coefficients and concentration of an impurity in the gas hydrates.

Gas	P_i /kPa	P_i/P_s (%)	$T = 263$ K			$T = 273$ K		
			Q_i (%)	c_i (%)	K_{i1}	Q_i (%)	c_i (%)	K_{i1}
Structure I; $P_s = 159$ kPa								
			$P_W = 0.2446$ kPa			$P_W = 0.6184$ kPa		
N_2	78	49.1	0.31	0.05	1	0.34	0.06	1
O_2	21	13.2	0.11	0.02	1.32	0.12	0.02	1.30
CO_2	15	9.44	1.0	0.17	16.7	1.08	0.19	16.5
N_2O	20	12.6	12.8	2.23	160	13.1	2.28	151
SO_2	25	15.7	77.9	13.6	778	73.9	12.9	679
Structure I; $P_s = 219$ kPa								
			$P_W = 0.2223$ kPa			$P_W = 0.5675$ kPa		
N_2	78	35.6	0.18	0.03	1	0.21	0.04	1
O_2	21	9.59	0.06	0.01	1.30	0.07	0.01	1.28
CO_2	30	13.7	1.08	0.19	15.2	1.18	0.21	14.3
N_2O	40	18.3	12.9	2.26	137	13.3	2.31	121
SO_2	50	22.8	81.0	14.1	686	77.9	13.6	567
Structure II; $P_s = 112.1$ kPa								
			$P_W = 0.2435$ kPa			$P_W = 0.6103$ kPa		
N_2	78	69.6	1.42	0.25	1	1.26	0.22	1
O_2	21	18.7	0.44	0.08	1.17	0.39	0.07	1.14
CO_2	0.1	0.09	0.01	0.002	6.90	0.01	0.002	6.80
$CHCl_3$	2.0	1.78	22.6	3.98	623	20.0	3.52	642
CF_2Cl_2	10	8.92	33.1	5.83	182	27.0	4.75	168
SO_2	1.0	0.89	3.67	0.65	203	3.00	0.53	186
Structure II; $P_s = 122.1$ kPa								
			$P_W = 0.2223$ kPa			$P_W = 0.5675$ kPa		
N_2	78	63.9	1.13	0.20	1	1.07	0.19	1
O_2	21	17.2	0.35	0.06	1.16	0.32	0.06	1.13
CO_2	0.1	0.08	0.009	0.002	6.35	0.008	0.001	5.97
$CHCl_3$	5.0	4.10	25.4	4.47	350	23.0	4.05	346
CF_2Cl_2	15	12.3	34.5	6.07	159	28.0	4.93	136
SO_2	3.0	2.45	7.65	1.35	177	6.00	1.06	151

and pressure. This is due to the redistribution of gas mixture molecules among hydrate cavities according to the Langmuir coefficients determined by the character of the van der Waals interaction.

Thus, gas hydrates may be formed under the conditions of the environmental presence of technogenic impurities over a wide range of ambient temperatures (the temperate climate zone). Such gas hydrates become sites of predominant concentration of typical technogenic impurities.

VI. Conclusion

The appearance of impurities in the form of gas hydrates in gases undergoing cleaning may significantly influence the process of their refinement: at the stage of hydrate formation the content of water in the gas phase decreases accompanied by changes in its composition due to redistribution of components between the solid and gas phase.

The presence in a gas mixture of components with higher or lower values of dissociation pressure than that of the principal substance subject to purification may change substantially the conditions of gas hydrate formation and in some instances even prevent their formation in the process of purification.

The relative distribution coefficient for the same conditions of hydrate formation depends appreciably on the ratio of the components in the gas mixture and in some cases it differs markedly from unity. Therefore, even at the stage of hydrate formation, the substance can be considerably enriched or depleted in impurities. Thus, the separation of gas hydrates from the gas mixture may provide additional purification of the major substance or air–gas mixtures.

The existing models which simulate gas hydrate formation allow an accurate determination of the dissociation pressure of a hydrate-forming gas, the minimum water content at which the formation of hydrates is still possible, as well as the distribution coefficients of molecules of a gas mixture over the cavities of gas hydrates.

The computational results provide evidence that gas hydrates can be formed under environmental conditions (in the range of temperatures characteristic of the temperate climate zone). Under these conditions, they predominantly accumulate deleterious impurities released into the atmosphere from technogenic exhausts. Concentration of such impurities becomes hazardous for biological systems.

Thus, the gas hydrates formed in the vapour phase in the process of refinement of gases (Freons, volatile inorganic hydrides, *etc*.) as well as the suspended particles of submicro-size form a new class of impurities in ultrapure substances, and it is necessary to account for their influence on the processes of refinement of gases.

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