Russian Chemical Reviews

August 1986

Translated from *Uspekhi Khimii*, **55**, 1233-1257 (1986)

U.D.C. 541 : 54.058 + 541.572

The Role of Molecular Complexes in the Preparation of Highly Pure Materials

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Various aspects of the influence of molecular complexes on the efficiency of two-phase methods for purifying substances have been examined (for the case of the volatile inorganic hydrides of the elements of groups IIIa-VIIa). Data published in the last 10 years on the experimental and theoretical study of intermolecular interactions in these systems have been discussed. Chemical methods for purifying hydrides, including the formation of stable molecular complexes, have been examined briefly. The bibliography contains 172 references.

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I. INTRODUCTION

Highly pure substances contain individual impurities at the level of 10^{-4}–10^{-8}% and below, and a total concentration of impurities of 10^{-3}–10^{-4}%.[1]

Methods for preparing highly pure materials are based on differences between the properties of the impurity and the substance being purified, which in turn are generally revealed as differences in the interactions between the particles (atoms, molecules, ions) of the impurities and the main material.[2] The forces of interparticle interaction can be classified as long-range (van der Waals) and short-range (chemical or specific).[3] Methods of purification, in turn, can be classified as physicochemical or chemical, according to the type of interactions responsible for the separation effect. Both types of purification method are being intensively developed, and have been the subject of a number of books and reviews (see Refs.2 and 4 and references therein, and also Refs.5–7).

An important case of interactions occupying an intermediate position between van der Waals and chemical interactions is the formation of molecular complexes.[8] This term covers electron donor–acceptor (EDA) complexes or charge-transfer complexes (CTC), and also complexes with hydrogen bonding (H-complexes).

The formation of molecular complexes, taking place against a background of non-specific van der Waals interactions, influences the efficiency of purification processes; previously, however, there was practically no discussion of this question in the literature. The aim of the present review is to examine various aspects of extensive purification processes, associated with the formation of molecular complexes. The examination will be restricted to only a few classes of substance and purification methods. The discussion will deal chiefly with the two-phase methods of fractional distillation and, to a lesser extent, crystallisation, the theory of which in systems with non-specific interactions is most fully developed at the present time.[5,7] Molecular complexes of different stability play an important role in methods of purification by extraction. Since however these methods are relatively unsuitable for preparing highly pure materials, and since there are no rigorous theories to describe two-phase equilibria in extraction systems,[9,10] this group of methods is not examined in the present review.

The materials chosen to examine the influence of the formation of molecular complexes on the efficiency of extensive purification are the volatile inorganic hydrides of the elements of groups IIIa–VIIa. This choice was made for the following reasons. Volatile inorganic hydrides are fairly widely used to obtain highly pure elements and structures based on them.[11,12] In spite of the considerable progress made in their purification,[1,12] however, the removal of some impurities (for example water) still represents a difficult problem. There are indications that in a number of such cases, hydride–impurity molecular complexes may be formed, leading to a decrease in the efficiency of purification. Finally, the weak specific and more particularly non-specific intermolecular interactions (IMI) in systems based on the hydrides examined, although insufficiently studied, have nevertheless been more fully studied at the present time than other classes of substance obtainable in a highly pure state. The review covers data on non-specific and weak specific interactions in volatile inorganic hydrides, obtained by various experimental methods and also by quantum-chemical calculations and semi-empirical estimates.

In spite of these restrictions, the procedure used to analyse the role of molecular complexes is general in character, and can be used to examine other purification methods and other systems.

II. BASIC IDEAS FROM THE THEORY OF MOLECULAR COMPLEXES

A large number of papers have been devoted to various aspects of the theory and practical utilisation of molecular complexes of both types (EDA and H-complexes). It is sufficient to mention the most important monographs and reviews published chiefly in the last 10 years in the Soviet Union and other countries.[13–20]

The theory of molecular complexes (usually referred to in the literature as the theory of donor–acceptor interaction) was developed by Mulliken in the early fifties and applied to systems consisting of molecules, one of which has a low ionisation potential (the electron donor D) while the other has a high electron affinity (the electron acceptor A). The nature of the interacting orbitals of the donor and acceptor molecules formed the basis for the generally accepted classification of molecular complexes.[20]

Donor–acceptor interactions in the sense of Mulliken's classical theory are closely related to the problem of the hydrogen bond. In H-complexes, the hydrogen atom acts as a bridge joining atoms X and Y, which generally have a high electronegativity: X–H...Y. In the case of organic molecules, the fragment Y may be a π-electron system.

Intermolecular interactions in molecular complexes of both types can be classified as weak (ΔE = 0.1–1 kcal mole^{-1}, $R_{DA(HY)}$ = 0.30–0.35 nm) medium (ΔE = 5–15 kcal mole^{-1}, $R_{DA(HY)}$ = 0.27–0.30 nm), and strong (ΔE = 20–60 kcal mole^{-1}, $R_{DA(HY)}$ = 0.22–0.25 nm).[3,21] Thus the energies of formation of molecular complexes at one extreme are close to those of van der Waals systems ($\Delta E = 10^{-2}$–10^{-1} kcal mole^{-1},

Table 1. The impurity composition of volatile inorganic hydrides (mass %).[12]

Hydride	Impurity									
	B_2H_6	SiH_4	GeH_4	NH_3	PH_3	AsH_3	SbH_3	H_2S	H_2Se	HCl
C_2H_4	—	$7\cdot10^{-4}$	$1.1\cdot10^{-1}$	—	—	$3\cdot10^{-2}$	$2.6\cdot10^{-2}$	—	$1.4\cdot10^{-3}$	—
C_4H_{10}	—	$7.5\cdot10^{-4}$	0.74	—	—	—	—	—	—	—
$C_2H_5+C_2H_5OH$	—	$3.5\cdot10^{-2}$	—	—	—	—	—	—		—
$(CH_3)_2CO$	—	$1.1\cdot10^{-1}$	—	—	—	—	—	—	—	—
$(C_2H_5)_2O$	—	$1\cdot10^{-4}$	—	—	—	—	—	—	—	—
$(CH_3)_2O$	—	$6.8\cdot10^{-5}$	—	—	—	—	—	—	—	—
$CH_3OC_2H_5$	—	$3.5\cdot10^{-5}$	—	—	—	—	—	—	—	—
C_2H_5Cl	—	$5\cdot10^{-4}$	—	—	—	—	—	—	—	—
CH_3Cl	$1.9\cdot10^{-4}$	—	—	—	—	—	—	—	—	—
CH_3CHO	—	$1.4\cdot10^{-4}$	—	—	—	—	—	—	—	—
CH_4	$1\cdot10^{-3}$	—	1.2	—	—	$1.6\cdot10^{-1}$	—	—	—	$2.6\cdot10^{-3}$
C_2H_6	$2.5\cdot10^{-4}$	—	0.51	—	$2.7\cdot10^{-2}$	$4.6\cdot10^{-2}$	—	—	$1.2\cdot10^{-2}$	—
C_3H_8	$2.5\cdot10^{-4}$	—	0.33	$1\cdot10^{-3}$	—	$4\cdot10^{-4}$	—	—	$1.2\cdot10^{-2}$	$7\cdot10^{-4}$
C_4H_8	—	—	$4.2\cdot10^{-2}$	$5.2\cdot10^{-4}$	—	$5.2\cdot10^{-2}$	$3.6\cdot10^{-3}$	—	$1.4\cdot10^{-2}$	$9.6\cdot10^{-4}$
C_6H_6	—	—	—	$7\cdot10^{-2}$	—	—	—	$1.7\cdot10^{-2}$	—	—
$CHCl_3$	—	—	—	—	—	-	$8.6\cdot10^{-3}$	—	—	—
C_2H_2	—	—	—	—	—	—	$1.2\cdot10^{-3}$	—	—	$1.2\cdot10^{-1}$
CS_2	—	—	—	—	—	—	—	$1.2\cdot10^{-1}$	$2.8\cdot10^{-2}$	—
CO_2	—	—	—	—	—	—	—	—	—	$1.1\cdot10^{-2}$
AsH_3+GeH_4	—	$4.5\cdot10^{-3}$	—	—	—	—	—	—	—	—
B_5H_9	—	$4.3\cdot10^{-3}$	—	—	—	—	—	—	—	—
PH_3+H_2S	—	$6.8\cdot10^{-2}$	—	—	—	—	—	—	—	—
HCl	$3.8\cdot10^{-1}$	$7.3\cdot10^{-3}$	—	—	$2.5\cdot10^{-2}$	$3.6\cdot10^{-2}$	$9\cdot10^{-2}$	$2\cdot10^{-2}$	$5\cdot10^{-1}$	—
NH_3	—	$1.5\cdot10^{-3}$	—	—	—	—	—	—	—	—
SiH_4	—	—	$1\cdot10^{-4}$	—	—	—	—	—	—	—
PH_3	—	—	$1\cdot10^{-5}$	—	—	—	$3.4\cdot10^{-1}$	—	—	—
H_2O*	—	—	1—2	$5\cdot10^{-1}$	$7\cdot10^{-1}$	$8\cdot10^{-1}$		0.5	1.1	$1.8\cdot10^{-4}$
$SiH(OC_2H_5)_3$	—	—	—	$2.5\cdot10^{-2}$	—	—	—	—	—	—

*The concentration of water in unpurified HF reaches 8.4 mass %.

R = 0.30–0.40 nm), and at the other extreme are close to those of chemically combined molecules (ΔE = 80–100 kcal mole^{-1}, R = 0.10 nm).

Table 1 gives a number of typical impurities in unpurified volatile inorganic hydrides of elements of groups IIIa–VIIa.[12] In spite of the fact that the impurity composition of the hydrides depends to a large extent on the method of synthesis, it is possible to distinguish two groups of impurity in these compounds: inorganic impurities, including the hydrides of analogue elements, higher hydrides, and various gases (CO, N_2), and organic impurities, including saturated, unsaturated, and aromatic hydrocarbons, and also hydrocarbons containing heteroatoms with a lone pair of electrons. All this is responsible for the complex character of the IMI in the hydrides being considered. For highly pure hydrides containing most impurities at the level of 10^{-5}–10^{-7} mass %, it is mainly the weak specific interactions of the hydride–hydride and hydride–impurity type that are important. In starting materials containing from 0.5–1.0 mass % to 10^{-5} mass % impurities (Table 1), impurity–impurity molecular complexes are probably also formed.

As noted above (section I), the weak specific interactions leading to the formation of molecular complexes are present against a background of non-specific van der Waals interactions. It is therefore appropriate to discuss in more detail the contributions made to the energy of the interaction of a pair of molecules of a volatile inorganic hydride by specific and non-specific interactions.

The van der Waals interactions in volatile inorganic hydrides are usually characterised quantitatively using the familiar Lennard-Jones potential. Since the model is approximate, the numerical values of the parameters of the potential ε and σ depend on the set of properties from which they are determined.[3] Since the purification processes examined below are based on phase equilibria, it is appropriate to use the values of ε and σ calculated from the vapour pressure and the density of the liquid on the liquid–vapour equilibrium line.[5] The relationships required for this were obtained in Ref.22; Table 2 gives the values of ε and σ obtained in the work cited for volatile inorganic hydrides. The values of ε for different substances lie mainly in the range 400–800 kcal mole^{-1}, and the values of σ in the range 0.30–0.45 nm. The values given are the effective values, including the contribution from weak specific interactions when these are present. Specific interactions have comparatively little influence on the magnitude of σ, but have a considerable influence on the value of the parameter ε, characterising the depth of the potential well.

Table 2. The parameters of the Lennard-Jones potential for the volatile inorganic hydrides of the elements of groups IIIa–VIIa.[22]

Substance	ε, cal mole^{-1}/σ, nm	Substance	ε, cal mole^{-1}/σ, nm
CH_4	296/0.374	NH_3	723/0.330
SiH_4	443/0.398	PH_3	517/0.399
GeH_4	503/0.426	AsH_3	584/0.407
SnH_4	604/0.444	SbH_3	719/0.427
H_2O	882/0.305	HF	918/0.312
H_2S	614/0.372	HCl	471/0.352
H_2Se	666/0.388	HBr	588/0.375
H_2Te	767/0.426	HI	674/0.401

General information on the structure and the nature of the chemical bonding in the molecules of the hydrides of the elements of groups IIIa–VIIa [11] can be used in a preliminary discussion of their tendency to form molecular complexes.

The chief characteristic of the hydrides is the presence of a hydrogen atom forming a covalent bond with the central atom of the element. In the examination of these compounds, therefore, it is necessary first of all to take account of the tendency for an intermolecular hydrogen bond to be formed. In addition, the hydrides of boron and aluminium may act as strong ν-type electron acceptors in EDA complexes, using the unoccupied p orbitals of the B and Al atoms.

The polarity of the bonds in the hydrides increases on going from left to right along the periods. The ability of these compounds to form intermolecular H-bonds should increase in the same order. On the other hand, the polarity of the bond decreases on going down the groups, and this should lead to a decrease in the proton-donor power of the hydrides of periods 3–7. The elements of groups Va and VIa have lone pairs of electrons, so that the corresponding hydrides, having low ionisation potentials,[23] can not only form intermolecular H-bonds but also act as n-type electron donors towards inorganic and organic electron acceptors.

This is illustrated by the values of ε given in Table 2. The systematic decrease down the groups in the values of ε for the hydrides of the elements of groups Va–VIIa, due to the decrease in the contribution of van der Waals interactions, breaks down for ammonia, water, and hydrogen fluoride, because of the large contribution made to the value of ε by the energy of the hydrogen bond, which is much greater than the corresponding values for phosphine, hydrogen sulphide, and hydrogen chloride. No significant change in the contribution of H-bonds is observed on going from left to right along periods 3–5.

Experimental and theoretical data on the ability of the volatile inorganic hydrides of the elements of groups IIIa to VIIa to form molecular complexes are examined in more detail below. Particular attention will be paid to the systems in Table 1, or related systems.

III. TWO-PHASE METHODS OF EXTENSIVE PURIFICATION AND THE FORMATION OF MOLECULAR COMPLEXES

Among the physicochemical methods of extensive purification used at present, two-phase distillation and crystallisation methods have found extensive application. The difference between the compositions of the equilibrium phases is characterised by the distribution coefficient of the impurity:

$$K^{vl} = x_2^v/x_2^l;\ K^{sl} = x_2^s/x_2^l \qquad (1)$$

where x_2 is the concentration of the impurity in the vapour (v), liquid (l), or solid (s) phases (in mole fractions). The phase equilibrium condition gives the relationship between the distribution coefficients and the chemical potentials of the impurities in the equilibrium phases. Thus the study of the influence of specific interactions on the efficiency of two-phase purification methods is directly related to the study of their influence on the thermodynamic properties of dilute solutions. The methods used for this purpose have been reviewed,[24] and their details will not be discussed further. Interesting data have been published[25] on the purification of the chlorides of various elements tending to form complexes.

Before analysing the influence of specific interactions, the nature of two-phase equilibria in dilute solutions with non-specific interactions can be discussed briefly. A statistical-thermodynamic description of phase equilibria in dilute solutions with non-specific interaction between the molecules, and methods for calculating the distribution coefficient based on it, have been described.[5–7,24] From these methods, that based on the theory of conformal solutions can be selected,

since it is simple and at the same time sufficiently exact.[26,27] By applying this method to a solution for which the interaction between the molecules is described by the Lennard-Jones potential, an expression for the liquid–vapour distribution coefficient has been found in the approximation of an ideal vapour phase.[27,28] Here, only the quantities on which the distribution coefficient depends will be given:

$$K^{vl} = f\left(\frac{kT}{\varepsilon_{11}}, \frac{\varepsilon_{21}}{\varepsilon_{11}}, \frac{\sigma_{21}}{\sigma_{11}}\right) \quad (2)$$

where T is the temperature.

The parameters of the interaction potential of the particles of the impurity and the base are given by the equations:

$$\sigma_{21} = (\sigma_{11}+\sigma_{22})/2;\ \varepsilon_{21} = \xi(\varepsilon_{11}\varepsilon_{22})^{1/2} \quad (3)$$

where ε_{ii} and σ_{ii} are the parameters characterising the interaction of the particles of the base ($i = 1$) and the impurity ($i = 2$) components. The parameter ξ in the Lorentz–Berthelot combination rules (3) for solutions with non-specific interactions is usually taken as 1.

Table 3 compares experimental data with the results of calculations of the distribution coefficients from Eqn.(2) for a number of systems in which specific interactions are weak or non-existent. The calculation of the distribution coefficient using the Lennard-Jones potential for $\xi = 1$ in most cases gives correctly the nature of the deviations from Raoult's law, so that this potential can be regarded as a satisfactory effective potential for this case. The deviations from 1 in the values of ξ found from the values of K^{vl}_{expt} are relatively small, confirming that there are no appreciable donor–acceptor interactions between the components of the solutions studied. The values of $\xi \leqslant 0.97$ are apparently due to the inaccuracy of the values of the experimental distribution coefficient used.

Table 3. Results of the calculation of the distribution coefficient in systems based on volatile inorganic hydrides at their normal boiling points.[6]

System	$K^{vl}_{id} = p_{02}/p_{01}$	K^{vl}	K^{vl}_{expt}	ξ
SiH_4—GeH_4	0.23	0.26	0.26	1.00
SiH_4—PH_3	0.22	0.26	0.23	**1.01**
SiH_4—AsH_3	0.05	0.075	0.078	**1.00**
SiH_4—H_2S	0.02	0.076	0.093	0.99
SiH_4—B_2H_6	0.28	0.26	0.73	0.95
SiH_4—HCl	0.17	0.35	0.35	1.00
SiH_4—C_2H_4	0.60	0.63	0.76	0.99
SiH_4—C_2H_6	0.23	0.46	0.26	1.03
SiH_4—C_3H_8	0.009	0.013	0.03	0.97
GeH_4—SiH_4	2.92	3.11	2.52	1.01
GeH_4—AsH_3	0.27	0.33	0.38	0.99
GeH_4—H_2S	0.18	0.32	0.31	1.00
GeH_4—C_2H_4	2.26	2.09	2.23	1.00
GeH_4—C_2H_6	1.01	1.62	1.21	1.02
GeH_4—C_3H_8	0.071	0.082	0.081	1.00
PH_3—AsH_3	0.29	0.30	0.68	0.96
AsH_3—PH_3	2.57	2.83	3.03	1.00

Notes. p_{01} and p_{02} are the saturated vapour pressures of the pure base and the impurity; the values of the parameter ξ in Eqn.(3) were found from Eqn.(2) using the experimental values of the distribution coefficient K^{vl}_{expt}.

Donor–acceptor interactions make the phase equilibria more complex. In solutions whose components form molecular complexes, azeotropes are fairly frequently produced. In this case, the estimation of the distribution coefficient from Raoult's law may lead to a qualitatively incorrect result, namely to an incorrect indication of the phase in which the impurity is concentrated.

The influence of specific interactions on the distribution coefficients can be analysed in two ways. In the first, the interaction potential, which in some form takes account of the specific components, is directly related to the distribution coefficient. In the second, explicit account is taken of the presence of various complexes and associates formed as a result of specific interactions, and the expression for the distribution coefficient includes the equilibrium constant of the complex formation process.

In the first approach, the main consequences of the existence of specific interactions follow directly from Eqns. (2) and (3) when the depth of the potential well ε_{ij} is separated into non-specific ε^0_{ij} and specific $\delta\varepsilon_{ij}$ components:

$$\varepsilon_{ij} = \varepsilon^0_{ij} + \delta\varepsilon_{ij};\quad \varepsilon^0_{ij} = (\varepsilon^0_{ii}\varepsilon^0_{jj})^{1/2} \quad (4)$$

(for the separation of these components, see also section VI). It follows from Eqns.(4) and (5) that

$$\xi = \frac{\varepsilon^0_{21} + \delta\varepsilon_{21}}{[\varepsilon^0_{11}\varepsilon^0_{22} + (\varepsilon^0_{11}\delta\varepsilon_{22} + \varepsilon^0_{22}\delta\varepsilon_{11} + \delta\varepsilon_{11}\delta\varepsilon_{22})]^{1/2}}. \quad (5)$$

For $\delta\varepsilon_{ij} = 0$, $\xi = 1$. A relatively small contribution of specific interactions to ε_{21} gives values of $\xi < 1$, and increase in the contribution $\delta\varepsilon_{21}$ (or decrease in $\delta\varepsilon_{ii}$) gives $\xi > 1$. It follows from Eqn.(3) that decrease in ξ leads to an increase in the value of K^{vl}, and a positive azeotrope may be produced, whereas increase in ξ decreases K^{vl} and leads to the production of a negative azeotrope.

Special mention may be made of cases when specific interactions lead to qualitative (from the viewpoint of the sign of $\ln K^{vl}$) deviations from Raoult's law. If the boiling point of the impurity component is higher than that of the main component, these qualitative deviations ($K^{vl}_{id} < 1$, $K^{vl}_{expt} > 1$) are produced when $\xi < 1$ (for example if $\delta\varepsilon_{11} = \delta\varepsilon_{21} = 0$ and $\delta\varepsilon_{22} \neq 0$). If the boiling point of the impurity component is lower than that of the main component, qualitative deviations ($K^{vl}_{id} > 1$, $K^{vl}_{expt} < 1$) are observed when $\xi > 1$ (for example if $\delta\varepsilon_{11} = \delta\varepsilon_{22} = 0$ and $\delta\varepsilon_{21} \neq 0$).

The quantitative estimation of the distribution coefficients of impurities in solutions in which the interactions have a specific component $\delta\varepsilon_{11}$ can be carried out using the methods[5–7] for solutions with non-specific interactions only when the specific component makes a small contribution: $\delta\varepsilon_{11} \leqslant 0.1\varepsilon_{11}$. In other cases, quantitative estimates require more rigorous models of the impurity–base and base–base interaction potentials (see section VI).

The properties of dilute solutions with specific interactions can be examined further by taking explicit account, via the equilibrium constants, of the processes of molecular complex formation. When the energy of formation of impurity–impurity and impurity–base complexes is sufficiently high, when their lifetime becomes greater than the characteristic time of the thermal motions in the liquid, $\tau \cong 10^{-12}$ s, it is reasonable to regard the complexes as different molecular forms of the impurity.

The formation of a molecular complex can be represented by the equation

$$iA + jB \rightleftharpoons A_iB_j \quad (6)$$

where A is the main component, and B the impurity. The equilibrium constants of the complex formation reactions in the vapour K_V and liquid K_l phases

$$K_{v,l} = \frac{[A_iB_j]_{v,l}}{[A]^i_{v,l}[B]^j_{v,l}} \quad (7)$$

and the distribution coefficients of the impurity in the monomeric and associated forms

$$K_m^{vl} = [B]_v/[B]_l;\ K_{ass}^{vl} = [A_iB_j]_v/[A_iB_j]_l \qquad (8)$$

can be introduced. The generalised distribution coefficient of the impurity[29,30] [compare Eqn.(2)]:

$$K^{vl} = \frac{[B]_v + j[A_iB_j]_v}{[B]_l + j[A_iB_j]_l} \qquad (9)$$

characterises the equilibrium distribution of the impurity B, irrespective of its specific molecular form.

Eqn.(9) can be examined for two particular cases: the formation of impurity–base and impurity–impurity dimers. In the first case, Eqn.(9) gives two equivalent relationships:

$$K^{vl} = \frac{1 + K_v}{1 + K_l} K_m^{vl};\ K^{vl} = \frac{(1 + K_v)K_l}{(1 + K_l)K_v} K_{ass}^{vl} \qquad (10)$$

It follows from Eqns.(10) that K^{vl} takes values intermediate between K_m^{vl} and K_{ass}^{vl}. When K_v and $K_l \ll 1$, $K^{vl} \cong K_m^{vl}$, and when K_v and $K_l \gg 1$, $K^{vl} = K_{ass}^{vl}$. Similarly, the cases where $K_V \gg K_l$ and $K_V \ll K_l$ reduce only to a renormalisation of the quantity K^{vl}.

Eqn.(9) has more interesting consequences when impurity–impurity dimers are formed:

$$K^{vl} = K_m^{vl} \frac{1 + 2K_vK_m^{vl}[B]_l}{1 + 2K_l[B]_l} \qquad (11)$$

In this case, K^{vl} depends on the concentration. In the absence of specific interactions, the distribution coefficient becomes independent of concentration at $[B]_l \leqslant 10^{-2}$.[24] It follows from Eqn.(11) that at high values of the equilibrium constants of the complex formation process, a concentration dependence may also be observed at lower concentrations. It also follows from Eqn.(11) that $K^{vl} = K_m^{vl}$ as $[B]_l \to 0$ as the equilibrium for the dimerisation is displaced towards the formation of the monomers with decrease in the concentration of the impurity. Since usually $K_v \leqslant 1$ and $K_m^{vl} \cong 1$, Eqn.(11) shows that for a concentration dependence in the range $[B]_l \cong 10^{-3}$, it is necessary that $K_l \cong 5 \times 10^2$.

Quantitative estimates of the proportions of impurities in different molecular forms require methods for calculating the equilibrium constants in the liquid phase. These calculations can be based on published rigorous statistical-thermodynamic expressions[31] for the quantities K_l (see also the published review[32]).

The possibility of considerable deviations from the laws of ideal solutions and the production of different molecular forms of the impurities have a significant influence on the behaviour of impurities during purification, so that their study is important for the practical preparation of highly pure materials. It also follows that the chief question which must be investigated is whether molecular complexes are formed in the given system, and if so, whether they are stable or unstable.

Since at present there is no single theory which might be used to predict reliably the formation of donor–acceptor complexes (including H-complexes) the question raised can be answered by undertaking: 1) an experimental study of complex formation under the actual conditions of the given method of purification, or, if this is difficult, under model conditions with subsequent extrapolation of the results obtained to the real conditions; and 2) a theoretical (quantum-chemical) calculation, in a given approximation, of the energy of formation of the complex (the energies of the interaction of the complex-forming molecules) and other thermodynamic parameters.

IV. EXPERIMENTAL METHODS FOR STUDYING MOLECULAR COMPLEXES

Practically all present-day physicochemical methods are used in the study of molecular complexes. Exhaustive reviews of these topics have been published.[13–16,18,20] The information on weak EDA and H-complexes is of greatest interest. At the present time, therefore, most experimental studies of molecular complexes are aimed at increasing the sensitivity of existing methods both by introducing new techniques and by improving existing methods. Molecular complexes are studied in all states of aggregation. Since their formation is exothermic, and since the reactions take place with a decrease in the number of moles, the most significant results should be obtained by using low temperatures and/or high pressure.

All methods of studying molecular complexes can be provisionally divided into two large groups: spectroscopic (in practically all ranges of the electromagnetic spectrum) and non-spectroscopic (calorimetry, chromatography, measurement of dipole moments, second virial coefficients, etc.).

The first group of methods can be examined in slightly more detail. The traditional method of studying EDA complexes of different stability is electronic spectroscopy in the ultraviolet or visible ranges, used to record the charge-transfer (CT) band. The spectroscopic characteristics of the CT bands are used to determine the thermodynamic characteristics of EDA complexes, usually in the liquid or gas phases (extensive reviews of these data have been published,[14,15,23,68] chiefly for organic compounds). This method has been used to study various complexes of hydrogen sulphide.[34] It can obviously also be used for other systems based on hydrides having a lone pair of electrons (n-donors).

The use of vibrational spectroscopy to study EDA complexes is most effective when strong donor–acceptor bonds are formed, since it is only then that the corresponding intermolecular vibrations are completely characteristic. Far infrared spectroscopy is particularly promising in this connection.[35] On the other hand, infrared spectroscopy is still the chief source of information on the hydrogen bond in H-complexes of different stability, as indicated by recent reviews.[18,20,36] Measurement of the spectroscopic characteristics of the ν_{XH} stretching band (its displacement to shorter wavenumbers and the increase in its strength when a complex is formed) gives valuable information on the nature of the hydrogen bond and the thermodynamic characteristics of H-complexes in the liquid or gas phase.

Comparatively few experimental papers have been published on the study of H-complexes formed by the volatile inorganic hydrides of the elements of groups IIIa–VIIa in solution or in the gas phase (see Table 5). Exceptions are water (although in this case most attention has been paid to associates $(H_2O)_n$[37–39]) and, to some extent ammonia and hydrogen halides.[40,41] The spectroscopic study of intermolecular interactions in these systems encounters considerable difficulty. Thus most complexes based on the hydrides being considered are very weak (see section V). At the same time, in systems such as H_2O–HCl, NH_3–HCl, and NH_3–H_2O at high concentrations of the components in solution in a polar substance or even in the gas phase, protonated species (ion pairs) may be formed.[42] The nature of the IMI in these systems should be different, however, in dilute solutions based on one of these components.

Extensive possibilities for studying H-complexes of both types (with and without proton transfer) are provided by infrared spectroscopy in low-temperature matrices of nitrogen and noble gases. This method is now being used in many laboratories (see the published reviews[43,44]). Unfortunately, the H-complexes of volatile inorganic hydrides have been insufficiently studied by this method. Data on the ν_{HHal} stretching wavenumbers and the relative wavenumber displacements $\Delta\nu/\nu$ in the spectra of H-complexes of hydrogen halides with the molecules of a number of substances which are potential impurities in these compounds have been reviewed[45] (see Table 1). Attempts have been made to establish correlations between the properties of H-complexes and the molecular characteristics reflecting the nature of the electronic structure of the partner molecules.[41,45,46] Most frequently, use is made of the proton-acceptor (electron-donor) power of the base PA, determined by various methods. Although the absolute magnitude of the relative wavenumber displacement of the ν_{HHal} band of the complex generally increases with increase in the PA, there is no simple relationship between these quantities. The H-bonds formed by hydrogen halides with molecules containing atoms with lone pairs of electrons (water, dimethyl ether, etc.) are fairly strong.

The study of IMI in systems based on water by infrared spectroscopy in low-temperature matrices is important, since, as can be seen from the data in Table 1, water is a universal impurity, most difficult to remove, in all volatile inorganic hydrides, and also in many other volatile compounds (for example the chlorides of the elements of groups IIIa–Va [47]). The study of these complexes by ordinary infrared spectroscopic methods is fairly complicated. On the other hand, comparatively few papers on matrix-isolation studies have been published. Most have been devoted to the dimers $(H_2O)_2$ and the polymers $(H_2O)_n$ (see the published review[48] and other papers[49,53]).

Table 4 gives the wavenumbers of the stretches (ν_1 and ν_3) and deformations (ν_2) of the O–H bond in a molecule of free water and water combined with proton acceptors (argon matrix). Like the H–Hal stretching wavenumbers, ν_1 and ν_3 decreases relative to monomeric water on complex formation, and the magnitude of the wavenumber shift $\Delta\nu$ characterises in a definite sense the stability of the H-complexes formed. According to this characteristic, the strength of the H-bonds in matrix-isolated water systems changes in the order:

$$NH_3 < (CH_3)_2O > H_2O > HCl \approx H_2S \approx Cl_2 > CO_2$$

Table 4. Wavenumbers of the principal vibrations of the H_2O molecule (cm^{-1}) in the free state and combined in a complex[50–52,54–56] (the type of matrix is given in brackets).

Type of vibration	H_2O (monomer)				Complex H_2O–X				
	(Ar)	(N_2)	X=$(CH_3)_2O$ (Ar)	X=HCl (Ar)	X=H_2S (N_2)	X=H_2O (Ar)	X=CO_2 (N_2)	X=Cl_2 (N_2)	X=NH_3 (N_2)
ν_1	3638	3634	3506	3631	3628	3575	3632	3631	3414–3374
$\Delta\nu_1$	—	—	132	7	6	63	2	7	240 (cp.)
ν_2	1589	1597	1615	1590	1597	1611	1598	1597	—
ν_3	3734	3728	3706	—	3719	3710	3725	3726	3697
$\Delta\nu_3$	—	—	28	—	9	24	2	8	31

Among the systems of interest for the present review, mention may be made of published data on the complexes formed by hydrogen sulphide and ammonia, obtained by matrix-isolation methods.[53,54,56–60]

The chief disadvantage of the matrix-isolation method is that in the rigid matrix the systems being studied are in a non-equilibrium state, so that the experimental determination of the thermodynamic functions of the complex is impossible. An alternative method of study is provided by infrared cryospectroscopy, where liquid noble gases, which are highly transparent, are used as solvents.[61–64] In the study of the state of impurities in inorganic hydrides and similar compounds which have a simple molecular structure and which are liquefied at low temperatures, it is probably possible to use the compounds themselves as solvents, at temperatures close to the boiling point (if they are transparent in the given spectral range).

Important information on the structural, electric, and in some cases energy characteristics of the weak molecular complexes of simple molecules in the gas phase at low pressure can be obtained by various forms of rotational spectroscopy developed in the last ten years: microwave spectroscopy with Stark modulation; electron-resonance spectroscopy in molecular beams; and pulse microwave Fourier spectroscopy in a supersonic gas beam with adiabatic expansion from a vessel at high pressure.[65–67] These methods have been used to study a number of systems containing the hydrides of the elements of groups Va–VIIa and the molecules of potential impurities (see for example Refs.65 and 68).

In non-spectroscopic methods for studying molecular complexes, in contrast to spectroscopic methods, the thermodynamic parameters of the complexes are determined by measuring properties of the solution which depend only on the number of particles in it, and not on the physical parameters of the particles of different type. An important representative of this group of methods is gas–liquid chromatography.[69,70] The advantages of this method are the direct determination of the equilibrium constants from the retention volumes without the more complicated measurement of the concentrations of the substances in two phases, and also the possibility of working with low concentrations at which the laws of dilute solutions are applicable. This last feature is particularly important in the study of the state of impurities in highly pure volatile substances, and gas chromatography has for long been used successfully for the quantitative analysis of these materials.[71]

The above brief review of various physical methods for studying molecular complexes shows that it is still necessary and important to identify and determine the thermodynamic properties of both EDA and H-complexes and complexes formed in a large excess of one of the components (in dilute solution) or at equivalent ratios of the components at low temperatures (NH_3–HCl, NH_3–H_2O, etc.).

At the same time, primary information on the energy and structure of these complexes can also be obtained from quantum-chemical calculations. The number of published papers in this field, including those devoted to the complexes formed by the volatile hydrides of the elements of groups IIIa–VIIa, is increasing continuously. Some of these will be examined in the next section.

V. QUANTUM-CHEMICAL METHODS FOR STUDYING MOLECULAR COMPLEXES

The use of modern methods of quantum chemistry to solve the problems being discussed in the present review, related to the theory and practice of the preparation of highly pure materials, is necessary for the following reasons. Firstly, after establishing the impurity composition of the substance being purified, it is necessary to estimate quantitatively the

possibility of specific interaction beween the impurity molecules and the molecules of the main material, and of impurity–impurity interactions when the concentration of individual impurities is appreciable. Calculation methods now available often make it possible to obtain information on at least the relative stability of possible associates more easily than by experiment. It must be remembered, however, that the result obtained will relate to an isolated molecule of the complex, without allowance for the solvation energy.

Secondly, one of the principal problems in the theory of the preparation of highly pure materials is the development of reliable methods of calculating the distribution coefficient of an impurity for two-phase purification methods. In most cases, increase in the accuracy of calculations of the distribution coefficient requires primarily refinement of the interaction potentials. Quantum chemistry can now be used to calculate these potentials. Quantum-chemical interaction potentials can be used for the *a priori* estimation of other quantities characterising the preparation of a highly pure substance: solubility, diffusion coefficient, rate of the introduction of impurities from the material of the apparatus into the substance being purified.

The most reliable data on the energy and geometry of molecular complexes (EDA and H-bonded) are obtained from non-empirical (*ab initio*) calculations by the method of molecular orbitals (MO) in the self-consistent field (SCF) approximation. The present state of different versions of these calculations has been reviewed.[15,20,72–74] The present section deals briefly with the principal concepts of the method and discusses published data on the stability of some of the two-component systems with weak specific interactions discussed in Table 1. Since they are particularly important for the problems being discussed in the present review, topics related to the construction of quantum-chemical IMI potentials are discussed separately in the next section.

In the MO SCF approximation, a molecular complex is regarded as a supermolecule whose energy of formation (the IMI energy) is equal to the difference between the total energy of the complex E_{DA} and the energies of the components E_D and E_A:

$$\Delta E = E_{DA} - E_D - E_A$$

The accuracy of non-empirical calculations of ΔE depends chiefly on the number of basis atomic orbitals (AO) used to construct the MO. The generally accepted notation used below for different basis sets is explained, for example, in Ref.74. In the SCF approximation, no account is taken of the correlation of the motion of the electrons at each moment of time, as a result of which the electrons in individual orbitals are situated as far as possible from one another. The correlation energy ΔE^{corr} corresponding to this process constitutes only a small fraction of the total energy ΔE, but allowance for it is important in rigorous calculations of the stability of complexes. For example, for the dimer $(H_2O)_2$, $\Delta E = -4.5$ kcal mole^{-1}, and the contribution of the correlation energy is -1.1 kcal mole^{-1}.[75] In practice, allowance for ΔE^{corr} reduces to the calculation of the dispersion energy using either perturbation theory[76] or multipole expansion, in which the coefficients are determined from experimental data on the polarisability of the molecules.[77] An alternative method of taking account of the correlation energy is the configuration interaction (CI) method.[75,78] Even when a minimum basis set is used without allowance for correlation energy, non-empirical calculations are usually carried out for molecules containing a comparatively small number of atoms (10–15) belonging to the second and third periods.

For more complex molecules and complex compounds, extensive use is made of semi-empirical methods, usually based on the neglect of differential orbital overlap and using SCF equations (CNDO, INDO, etc. methods).[79] These methods are much less laborious and therefore more accessible. For molecular complexes, however, these methods give absolute values of the energy of IMI which are systematically several times too high. Data on the use of these methods to calculate the energy and geometry of EDA and H-complexes have been reviewed.[74,80] Recently, interesting parametrisation schemes for familiar versions of the CNDO and INDO methods have been proposed, making it possible to obtain various geometric and energy characteristics of complexes containing hydrogen bonds of the type O–H...O, O–H...N, and N–H...O.[81,82] Semi-empirical methods are useful for estimating the relative characteristics of IMI in a series of structurally related molecular complexes. Thus it is possible to obtain information fairly rapidly on the relative stability of practically all the hydride–impurity and impurity–impurity dimers given in Table 1.

The results of non-empirical calculations of the complex-forming power of the molecules of the hydrides of the elements of the second and third periods, given in Table 1, both with respect to one another (dimers) and with respect to various inorganic and organic molecules (heterodimers) can be discussed in more detail. Detailed calculations have been carried out for complexes involving BH_3, AlH_3, NH_3, PH_3, H_2O, H_2S, HF, and HCl. There are no published data on the quantum-chemical description of the IMI in silane, although a number of papers (for example Refs.83 and 84) give detailed calculations of the structure and properties of the SiH_4 molecule by non-empirical methods.

Table 5. Energies of the hydrogen bonds (kcal mole^{-1}) for the hydrides of the elements of the second and third periods, from the results of non-empirical quantum-chemical calculations*.[85–87]

Electron donor	Proton donor					
	NH_3	PH_3	H_2O	H_2S	HF	HCl
NH_3	4.3 (4.5±0.4) [88]	1.2	8.9	4.4	16.3	10.8 (15.2±±0.3) [89]
PH_3	2.2	0.8	4.0	2.1	6.9	4.3
H_2O	4.1	1.1	8.1 (5,1) [91]; (6±3) [90]	3.8	13.4	8.2
H_2S	2.1	0.6	3.9	1.8 (1.7±0.3) [92]	5.8	3.5
HF	3.6	1.0	5.4	2.5	5.8 (5—7) [93]	4.6
HCl	1.6	0.4	2.5	1.1	3.4	2.0
H_2CO	1.4	0.2	3.4	0.6	6.2	5.3

*The experimental values of the energies of the complexes (from infrared spectroscopy) are given in brackets.

Note. Numbers in square brackets denote references (Ed. of Translation).

As already noted, the chief aim of this section of the present review is a comparative analysis of the stability of weak complexes of various hydrides, that is a comparison of the energies of IMI found under identical conditions. The data obtained for ~40 dimers and heterodimers in a 4-31G restricted basis set[85–87] are of particular interest in this connection (Table 5). The results of these calculations agree satisfactorily with experimental data (gas-phase infrared spectra). According to published estimates,[86] the data given in Table 5 are all slightly high (5–50%), relative to

the experimental data and the best non-empirical results, and the more stable the complex, the greater the error. Nevertheless, these data lead to the following conclusions.

1. All the hydrides considered tend to undergo self-association by H-bonds of low or medium energy.

2. The tendency to form dimers decreases in the order $H_2O > HF > NH_3 > HCl > H_2S > PH_3$. The energy of the hydrogen bond varies from -16.3 kcal mole^{-1} for HF–NH_3 to -0.4 kcal mole^{-1} for PH_3–HCl. The strongest bonds are formed with hydrogen fluoride or hydrogen chloride as proton donor.

3. The proton-acceptor power decreases sharply on going from the hydrides of the second period to those of the third period.

4. In the heterodimers of the hydrides of the elements of the second period, ammonia shows electron-donor properties with respect to water and hydrogen fluoride; water acts as electron donor only towards HF. In the heterodimers of the hydrides of the third period, the hydride of an element of a group with a smaller number acts as an electron donor with respect to that of an element of a subsequent group. For the heterodimers of the hydrides of the elements of the second and third periods, the following apply: HCl is a proton donor towards NH_3, H_2O, and HF; H_2S is a proton donor towards NH_3, but an electron donor in the complex with HF. In its reaction with H_2O, hydrogen sulphide shows both electron-donor and proton-donor properties, to equal extents. Finally, PH_3 forms weak complexes with ammonia, water, and hydrogen fluoride, in which it is an electron donor.

5. The most stable complexes with other hydrides are formed by HF, H_2O, and HCl.

6. Judging from the calculated values of the H-bond energy, in practically all these hydrides at least part of the impurity water must be present in the combined state, and the probability of water–hydride molecular complex formation decreases in the order: $HF > NH_3 > HCl > H_2S \cong PH_3$.

In connection with the relative role of specific interactions, it is of interest to compare the energies of the dimers (Table 5) with the effective energies ε of the paired interactions (Table 2). The difference between these quantities for a given substance are related to two factors: firstly, the quantity ε includes a contribution from hydrogen bonds, averaged over all nearest neighbours, and not only over those forming bonds; and secondly, the absolute magnitude of the average energy of a hydrogen bond in the condensed phase is lower than that of the energy of the bond in the gas phase. Thus the values of ε in Table 2 are lower than the values of the energy given in Table 5 for systems with a high hydrogen bond energy, and are close to those for systems with a low bond energy. This comparison for systems for which data are given in both Tables shows that the role of the hydrogen bond is a minimum for phosphine and a maximum for water.

Calculations of the energies of the molecular complexes formed by various hydrides with carbon dioxide, carbon monoxide, nitrogen, fluorine, and sulphur dioxide have been published.[94–100]

To estimate the efficiency of the extensive purification of such strongly polar hydrides as water and ammonia, it is important to have information on the IMI in the complexes with the ions of the elements of groups Ia and IIa, and also with the molecules of the halides of these elements. Data on these complexes have been published;[101–105] their stabilisation energy is several tens kcal mole^{-1}.

In Refs.106–109 it was shown for the first time by a non-empirical method in an expanded basis set that many of the hydrides examined in the present review form EDA complexes with the neutral atoms of the metals of the groups Ia–IIIa, and that the latter act as electron acceptors. The formation of associates of this kind must apparently be taken into account in the examination of: a) the contaminating effect of the apparatus (hydride–surface interaction); b) the state of suspended particles in hydrides; and c) the preparation of highly pure elements by the thermal or photochemical decomposition of the volatile hydrides.

The above results of non-empirical quantum-chemical calculations for dimers and heterodimers based on various volatile hydrides make it possible to estimate their stability in the sense of the IMI energy in the ideal-gas state. For the theory of the preparation of highly pure materials, however, it is no less important to have information on the ability of these complexes to dissociate at the temperature of the separation process, characterised by the Gibbs free energy. The processes of complex formation described by Eqn.(6) are generally accompanied by a decrease in entropy. Thus for weak IMI at comparatively high temperatures, the entropy factor may play an important role in the formation of molecular complexes, and conclusions about their stability based only on the values of ΔE (the enthalpy of formation) may generally speaking be incorrect. The thermodynamic stabilities of weak molecular complexes, based on theoretically determined ΔE values, have been analysed in a series of papers,[110–113] where the values of ΔG_T^0 were calculated for the formation of the H-complexes H_2O–HF, H_2O–H_2O, HF–HF, HF–HCl, HCl–HCl, CO_2–HF, $Si(OH)_4$–H_2O, and $(H_3Si)_2O$–H_2O at temperatures of 100, 298.2, and 500 K.

Thus present-day methods of quantum chemistry make it possible to obtain comparatively reliable data on the stability of weak molecular complexes of different types, including those formed by the volatile hydrides of the elements of the second and third periods in the gas phase or in a non-polar solvent. In the study of the same processes of complex formation in polar media, and processes involving molecules formed by the elements of lower periods, experiment provides the only source of reliable information at present.

VI. THE INTERACTION POTENTIALS OF SYSTEMS WITH MOLECULAR COMPLEXES AND THE RESULTS OF THEIR STUDY BY NUMERICAL EXPERIMENT METHODS

The problem of selecting optimum potential functions, whose components would have a rigorous physical significance, to describe interactions with a specific contribution has not yet been solved. Various versions of paired potentials are used: atom–atom potentials and their extentions, namely site–site potentials, and combinations of spherically symmetrical and non-central compounds. The most systematic models, however, are apparently those in which the contributions of specific and van der Waals interactions are separated:[114]

$$U_N = \sum_{i<j} \{\Phi_{ij} + B(ij)\,u(ij)\} \qquad (12)$$

Here, Φ_{ij} is the potential energy of the paired-additive interaction of the molecule, characterising the non-specific interactions (for example the Lennard-Jones potential); $u(ij)$ the energy of the donor–acceptor interactions; and $B(ij)$ the characteristic function of bond formation between the given molecules i, j, equal to unit if a saturated (specific) interaction is localised between the molecules, and otherwise equal to zero.

Various interaction potential parametrisation methods are used. The first, traditional method uses an empirical paired potential, whose parameters are determined from the

condition for the minimum mean-square deviation of the calculated from the experimental values of some characteristic. For a system with hydrogen bonds, this empirical potential is a combination of Lennard-Jones and Coulomb terms and a Morse function, which is assumed (see for example Ref.115) to describe effectively the contribution made by charge transfer to the total energy of the H-bond. A large number of other empirical potentials, of simpler form, for calculating the IMI energy in liquids with weak hydrogen bonds are known.[116] In this traditional approach for dilute solutions, the separation of the contribution of donor–acceptor interactions has been used[117,118] to calculate the distribution coefficient in solutions of various volatile hydrides (see section III). In this method, the components describing the non-specific and weak specific interactions are separated in the parameter ε of the Lennard-Jones potential (1). For hydrogen sulphide it was found[117] that the contribution of hydrogen bonds to the depth of the potential well (see Table 2) is 60–70 cal mole^{-1}. The estimated non-specific component for water, 360–480 cal mole^{-1},[118] also agrees with published data.[119]

Care must be taken, however, when using these parametrisation methods. For example, a calculation of the structure of liquid ammonia using a model potential whose parameters were obtained from data on the second virial coefficient[120] showed the complete absence of any association in the liquid, contrary to experimental data.

A second method of IMI potential parametrisation is based on the results of non-empirical quantum-chemical calculations. In recent years it has become possible to determine comparatively rapidly the energy of dimers at different points of configuration space, that is to obtain fairly complete information on the potential energy surface of the interacting molecules. The parameters of the analytical expressions for the paired potential functions (usually in the form of the sum of the electrostatic and atom–atom contributions) are selected to reproduce most effectively the calculated potential surface.

The IMI potential constructed using the approximate first method or the more accurate second method is then used for a statistical-thermodynamic calculation of the structure and characteristics of pure liquids and solutions with donor–acceptor interactions.

Promising possibilities for practical application to the calculation of the structure and properties of systems with both van der Waals and donor–acceptor interactions are provided by the methods of computational physics: the method of molecular dynamics (MD) [121] and the Monte Carlo (MC) method[122] (see also the published monographs[123,124] and reviews[125,126]). These methods are well known, and will not be described here. It may be noted, however, that algorithms for calculating[127,128] thermodynamic quantities, including the entropy component, for systems with specific interactions have apparently not yet been developed. For these systems, quantities such as the pressure (density), energy, heat capacity, and structural characteristics are calculated.

The principal results of the study of the structural and thermodynamic properties of various liquid hydrides of the elements of the second and third periods with weak specific interactions by numerical experiment methods using rigorous quantum-chemical IMI potentials can be examined.

Water. The familiar exceptional chemical and biological importance of water is responsible for the vast amount of published information on various properties of this most widely encountered associated liquid (see for example the published reviews[38,130–132]). The preparation of highly pure water[133] and, on the other hand, as noted repeatedly above, the removal of traces of water from various inorganic and organic materials, are extremely urgent problems. It is in the case of aqueous systems, whose properties are determined to a large extent by comparatively strong intermolecular H-bonds, that the methods usually employed to calculate the distribution coefficient[5–7] and the solubility[134] do not give the desired results.

In pioneering work by Clementi and co-workers,[135] 216 different geometries of the $(H_2O)_2$ dimer, corresponding to four types of configuration, were calculated in an almost Hartree-Fock basis set. The results were approximated by a fairly cumbersome expression consisting of the sum of 16 paired contributions, nine of which describe the electrostatic interaction between the hydrogen atoms and the lone pairs of electrons of the oxygen atoms, while the others describe the attraction and repulsion between the oxygen and hydrogen

Table 6. Thermodynamic functions of liquid hydrides from the results of computer experiments using non-empirical potentials.

Hydride	Calculation method, ensemble	Basis set	N	T, K	E	C	ΔE_{vol}	Experiment			
								E_v	C_v	C_p	E_{vol}
H_2O	MC, (NVT) (Ref.75)	SCF CI	343	298	−6.8±0.2	13.5±2	—	−8.1	17.9	18.1	—
	MC, (NPT) (Ref.129)	SCF CI	100	298	−7.1±0.3	20.6±7					
	MC, (NVT) (Ref.143)	STO-3G	125	298	−6.6	12.7					
HF	MC, (NVT) (Refs.144, 145)	STO-3G	108	273	−4.33	17.1	5.46	—	≤17	—	6.7
		6-31G	108	273	−5.62	11.8	6.85				
	MD, (NPT) (Refs.146–147)	SCF	216	278	−3.97	14.3	5.2				
HCl	MD, (NVT) (Ref.150)	4-31G	216	296	−2.28	—		−2.48			
	MD, (NVT) (Ref.154)	SCF CI	216	304	−2.33	8.4			7.3		
NH_3	MC, (NVT) (Ref.156)	STO-3G	128	239.7	−3.05	13.3	4.88	−3.75	12.7	—	5.58
	MD, (NVT) (Ref.157)	SCF	108	269.6	−5.2	—					

Notation: E is the internal energy, kcal mole^{-1} (E_v in an NVT ensemble, and E_p in an NPT ensemble); C the heat capacity, kcal mole^{-1} K^{-1} (C_v in an NVT ensemble, and C_p in an NPT ensemble); N is the number of particles.

atoms, due to non-electrostatic forces. The potential found in this way was used to calculate the structure of liquid water in an isochoric–isothermal ensemble (NVT ensemble).

The thermodynamic functions of liquid water (Table 6) show good agreement with experiment. A calculation[129] of the thermodynamics of liquid water in an isobaric–isothermal ensemble (NPT ensemble, see Table 6) using the Clementi potential gave good agreement with published data.[135]

The Clementi potential,[75,135,136,141] obtained on the basis of rigorous non-empirical calculations with allowance for CI, is still the best for the theoretical determination of the structure and properties of liquid water, although a number of other potentials, which give sufficient accuracy when used in calculations, were later proposed.[137–140]

On the other hand, a number of authors have studied the possibility of using minimum and restricted basis sets to construct the IMI potentials of associated liquids. The most fruitful results using this approach have been obtained by Jorgensen.[141–145] The potential surface of the water dimer was calculated[142] in an STO-3G minimum basis set (291 configurations) and approximated by a 12-6-3 potential:

$$U = \sum_{i<j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{\mu,\nu} \left(\frac{b_{mn}}{r_{\mu\nu}^3} + \frac{c_{mn}}{r_{\mu\nu}^6} + \frac{d_{mn}}{r_{\mu\nu}^{12}} \right) \qquad (13)$$

The first term takes account of the long-range electrostatic interaction between four point charges, and the summation is carried out over all pairs of charges belonging to N monomeric molecules. The second sum is taken for all pairs of atoms μ, ν of type m (O atom) and n (H atom). Liquid water has been modelled by the MC method using potential (13).[143] The data in Table 6 show that the thermodynamic functions of water obtained by Jorgensen by much less laborious calculations also show good agreement with experiment and with Clementi's data.

Hydrogen fluoride. A potential of type (13) has also been used to model liquid HF by the MC method.[144,145] The potential surface of the dimer $(HF)_2$ was found in a 6-31G basis set for 250 configurations[144] and in an STO-3G minimum basis set for 285 configurations. An analysis of the calculated atom–atom distribution functions showed that liquid hydrogen fluoride consists of long highly bent chains of molecules (in the solid and gas phases, on the other hand, the chains are linear).

The structure and properties of liquid HF have been studied by the MD method.[146,147] The potential was constructed using the results of calculations of the potential surface of the dimer $(HF)_2$ in an almost Hartree–Fock basis set.[148] The radial distribution functions g_{FF}, g_{HH}, and g_{FH} and various equilibrium and non-equilibrium properties of liquid HF were calculated (see Table 6).

The main conclusion about the structure of liquid hydrogen fluoride, reached in the works cited, agree with Jorgensen's conclusions,[145] but the first peak of the function g_{FF} in Ref.147 was found to be split into two, and the second and third peaks of all the radial functions were broadened considerably, which does not agree with the fairly high structural order of liquid HF beyond the first coordination sphere. These anomalies are possibly related to the neglect of many-particle interaction, whose contribution reaches 10% of the total energy. The potential of the HF–HF intermolecular interaction has also been obtained.[149]

Hydrogen chloride. It follows from what was said above that the ability of HCl molecule to form intermolecular H-bonds is weaker than that of water and hydrogen fluoride. Computer modelling of liquid hydrogen fluoride has been carried out using quantum-chemical potentials.[150–154] In Refs.150 and 151, liquid HCl was studied by the MD method using several potentials which approximated the potential surface of the $(HCl)_2$ dimer, calculated in a 4-31G basis set. The best agreement with experiment (Table 6) was obtained using the potential from Refs.146 and 147. According to these data, hydrogen chloride is a weakly associated liquid, in which chains are formed to a smaller extent than in HF.

In Ref.154, liquid HCl was modelled by the MD method using a paired potential obtained by calculating the IMI in the dimer in an expanded basis set. The second virial coefficient of gaseous HCl and the atom–atom radial functions of liquid hydrogen chloride and some of its thermodynamic functions were calculated (Table 6). The experimental and calculated heat capacities of liquid HCl showed good agreement. In a preliminary report[155] a potential was proposed for the description of hydrogen chloride, including Lennard-Jones, dipole, and quadrupole components, and also polarisation terms. This gave a good description of the structure of the dimers in the gas phase and the structure of the liquid and the solid.

Ammonia. The dimerisation energies of various hydrides, given in Table 1, indicate that the tendency of ammonia to form H-bonded dimers is intermediate between those of water and hydrogen chloride. The potential surface of the $(NH_3)_2$ dimer has been calculated[156] in an STO-3G basis set (250 configurations). The results were described by a 12-6-3-1 potential (13), which was subsequently used to model the liquid by the MC method. The structural and thermodynamic data obtained in this way, however, showed insufficiently good agreement with experimental data (see Table 6). The agreement was much better when the modified potential (13) was used.

Various properties of liquid NH_3 have been determined by the MD method.[157] The potential surface of the dimer was calculated in an almost Hartree–Fock basis set with allowance for correlation energy (61 configurations). Although the thermodynamic functions found for liquid NH_3 showed satisfactory agreement with published data (Table 6), none of the three potentials used[157] made it possible to obtain simultaneously with sufficient accuracy both the thermodynamic functions in Table 6 and the second virial coefficient. The data on the structure of liquid ammonia obtained in Refs.156–158 agree well with one another and indicate only weak (compared with HF and H_2O) association in the liquid phase.

The use of quantum-chemical potentials in model pure associated inorganic liquids is at present practically limited to the above systems.

Dilute solutions. For a wide range of applied problems, including the calculation of the distribution coefficient, it is necessary to have structural and thermodynamic information on solutions of associated liquids, including their dilute solutions. For this it is necessary to carry out a non-empirical calculation of the potential surface of the base–impurity heterodimer. The number of published papers dealing with this topic is fairly small.

Some of these papers deal with aqueous solutions of simple organic molecules, because of the considerable interest in the hydrophobic effect.[159] The water–methane system[129] provides an example. The potential surface of this heterodimer was calculated in a 4-31G basis set for 28 configurations. The IMI paired potential took account of the interaction between the nuclei and the interaction between the lone pair of electrons of the oxygen atom and the hydrogen atoms in the methane molecule. The Clementi potential was used for the potential of the water–water dimer. The MC

method for an NPT ensemble (number of particles 64, $T = 298$ K, 4-31G basis set) was used to determine the partial molar internal energy, equal to -11 ± 15 kcal mole^{-1}. The large uncertainty in its calculation is due to the fact that it represents the difference between the two large values of the energy of the solution and the individual components.

The H_2O-CH_4 system was also studied[160,161] in an NVT ensemble, where the potential surface was calculated in a 6-31G basis set for 225 configurations. Data have also been published on the quantum-chemical potentials of the water–ethane,[162] water–benzene,[163] and various other systems.

The results examined in this section demonstrate the fruitfulness of the approach to the study of the structure and properties of liquids, which are characterised by more or less strong specific interactions between the molecules, based on computer modelling with the use of non-empirical quantum-mechanical potentials. Two fundamental difficulties are encountered in this approach. The first is that all the calculations assume the paired additivity of the IMI. This is obviously not completely correct, particularly for systems with fairly strong donor–acceptor bonds. This is indicated in Refs.141 and 164–166, where it is pointed out, in particular, that the magnitude of the correction for the three-particle interaction of water molecules may be comparable with that of the correlation energy. On the other hand, other authors[167,168] assume that the non-additivity observed in the H-bonded systems $H_2S-(H_2O)_2$, $(CH_4)_3$, $(NH_3)_3$ does not play a significant role in the calculation of the structure of associated liquids. To some extent, a way out of this position involves the use of data on the properties of condensed systems in the parametrisation of the potential. This makes it possible to take effective account of the role of non-additive interactions.[169]

The other difficulty in obtaining analytical expressions for the potentials from non-empirical calculations is that the results of the latter depend on the basis set chosen. As already noted, the results with the most reliable accuracy are obtained in calculations in almost Hartree–Fock basis sets taking full account of electron correlation. These methods are laborious and expensive, however, so that they can as yet be used only to solve problems of fundamental importance. If however account is taken of the fact that the rate of increase in the efficiency of computers shows no sign of decreasing,[170,171] then in spite of the above difficulties, it can be expected that further progress in the calculation of various parameters characterising the efficiency of the preparation of highly pure associated liquids will in one way or another be related to the approaches examined in this section, based on the methods of quantum chemistry and numerical experiments.

VII. CHEMICAL METHODS OF PURIFICATION AND THE FORMATION OF MOLECULAR COMPLEXES

The data examined in sections II–VI relate to the formation of weak molecular complexes by the volatile inorganic hydrides of the elements of groups IVa–VIIa. It has been shown that even in this case, appreciable deviations may be expected from the regular relationships familiar from the theory of extensive purification, based on allowance for only non-specific IMI.

At the same time, complex-forming substances giving stable molecular complexes with energies of several tens of kcal mole^{-1}, either with impurities or with the main material, have for long been used to separate and purify various compounds. These methods, based on the marked difference in the complex-forming power of the components, represent a form of chemical method for purifying substances.[2,4]

In chemical methods of purification based on the formation of molecular complexes, the separation factor is proportional to the ratio of the equilibrium constants of the processes of complex formation involving the main material and involving the impurity, and is higher, the greater the difference in the complex-forming power of the impurity and the main material with respect to the complex-forming reagent.[2]

Examples of the use of the ability of various hydrides of the elements of groups IIIa, Va, and VIa to form stable EDA complexes with various Lewis acids and bases in the preparation of highly pure materials can be found, for example, in Refs.9–11.

New interest in chemical methods of purification are also being stimulated by work on the preparation of materials for fibre light carriers, where it is necessary to remove one particular impurity which leads to the absorption of electromagnetic radiation in the range of the spectrum where the fundamental mechanisms of absorption make the minimum contribution. To use these methods successfully in practice, it is necessary to carry out a detailed preliminary study (theoretical and experimental) of the processes of molecular complex formation in each specific case. Studies of this kind are also necessary for the development of new methods of reaction gas chromatography, used successfully to analyse highly pure substances.[172]

VIII. SUMMARY

The material discussed in the present review makes it possible to point out various important problems in the preparation of highly pure substances, whose solution is related to some extent to the problem of molecular complexes. Firstly, the determination of the state of impurities in substances being subjected to extensive purification. Secondly, the theoretical and experimental determination of the parameters characterising the efficiency of extensive purification. Thirdly, the development of methods of extensive purification and analysis using effective complex-forming reagents.

Complete information on the state and behaviour of impurities in a substance being purified would make possible a directed and justified selection of the method of purification. This requires an experimental and theoretical study of the possible formation of molecular complexes both under model conditions (at comparable concentrations of the components or with a slight excess of one of them) and under real conditions (dilute solutions).

High demands are made of experimental methods for studying molecular complexes, particularly at micro-concentrations of one of the components. It is desirable to use methods which simultaneously give information on the quantitative concentration of impurities and on their molecular state (for example infrared spectroscopy). In some cases, useful information on the state of impurities can be obtained by both semi-empirical and non-empirical quantum-chemical calculations. It is difficult to overestimate their role in the study of the structure and properties of molecular liquids with weak specific interactions. The numerical data obtained by these methods are necessary for predicting at a quantitative level the efficiency of two-phase methods of purification in systems of this kind. The fairly fully developed and universal character of many present-day methods in quantum chemistry makes the approaches described in sections V and VI accessible for the solution of practical problems, including those in the field of extensive purification.

The investigation of the chemical form of impurities in a solution of a substance being purified is also important in connection with the use of complex-forming substances as additives to systems in which the distribution coefficient of

an impurity is close to 1. Selective complex formation should probably also be more widely used in the gas-chromatographic analysis of highly pure substances.

The role of molecular complexes in the preparation of highly pure substances has been examined in the present review for the case of the volatile inorganic hydrides of the elements of groups IIIa–VIIa of the second and third periods, which are important compounds in the preparation of highly pure elements and structures based on them. It can be seen from published data, however, that the intermolecular interactions of different strength in hydrides (particularly in the liquid phase), with a few exceptions (boron hydrides, water, ammonia, hydrogen halides) have as yet been insufficiently studied. There are even fewer published data on the hydrides of the elements of the same groups from the fourth, fifth, and sixth periods. With increase in the requirements to be satisfied by the purity of volatile inorganic hydrides, allowance for the influence of the formation of molecular complexes on the efficiency of extensive purification will become even more necessary. This applies particularly to the extensive purification of inorganic chlorides and organometallic compounds, that is substances whose molecules have a much greater tendency to form molecular complexes than most of the hydrides examined in the present review. Thus both theoretical and experimental work on the detailed study of IMI in systems of this kind is extremely urgent. The data obtained will also undoubtedly increase knowledge of the nature of intermolecular interactions as a whole.

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