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Development of the Physical Chemistry of the Solvated Electron

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The principal results of experimental and theoretical studies of excess electrons in condensed media are examined and the physical nature of localised (solvated) electrons as well as the characteristics of the chemical and electrochemical reactions in which they participate are discussed.
The bibliography includes 131 references.

CONTENTS

I. INTRODUCTION

In 1808 Davy observed the phenomenon involving the acquisition of a bronze colour by potassium in liquid ammonia,[1] which was evidently the first description of the effects associated with the formation of the solvated electron. Approximately 50 years later, a similar observation was made by Weyl,[2] who is traditionally regarded as the first investigator of the unusual physicochemical properties of metal–ammonia solutions. After Weyl's investigations, the interest in metal–ammonia solutions continued without interruption, passing through periods of growth and decline. It was shown that the unusual metal-like properties of metal–ammonia solutions are caused[3,4] by the "abstraction" of an electron from the metal. During the last decades it has been established that the states of thermalised excess electrons, whose nature is analogous, arise in many disordered condensed media, without intrinsic conductivity, under the influence of radiation or the injection (emission) of electrons.

The phenomena occurring following the introduction of excess electrons into the media indicated have become the subject of continued attention from investigators working in a number of branches of the physics of condensed media, chemical physics, radiation chemistry, and even biology. Since 1964, international conferences, called the Weyl Colloquia, have been held regularly on this topic. The proceedings of these conferences, containing important information about the state of research into the properties of excess electrons in condensed media, have been published.[5-10] The results of such studies are also presented in books and reviews whose authors have concentrated their attention on the physicochemical,[11-16] physical,[17-21] chemico-physical, and radiation-chemical[22-28] aspects of the problem.

Initially, mainly localised electronic states in polar liquids attracted the attention of investigators. Such electrons were called solvated and were designated by the symbol e_s. The interest in solvated electrons increased especially after the discovery at the beginning of the 1960's of the short-lived solvated (hydrated) electron e_{aq} in water and aqueous electrolyte solutions.[29] The very important role of e_{aq} in radiation-chemical transformations and in the alteration of the physical properties of irradiated aqueous systems was then established.[23-26] There exist a number of hypotheses concerning the possible involvement of e_{aq} in various biochemical reactions[30-34] and in the synthesis of organic substances accompanying the binding of nitrogen and involved in the origin of life on Earth.[26]

States analogous to e_s in polar liquids and differing sharply from the excited states of electrons in crystals have been discovered and investigated also in non-polar liquids—liquid inert gases and hydrocarbons.[19,22,35-39] The electrons captured in vitreous matrices at low temperatures have properties similar to those of e_s.[40] The extensive experimental data obtained proved in many instances to be unexpected and did not fit the existing theoretical schemes. Together with e_s, the so called "dry" excess electrons, resembling the delocalised conductivity electrons in metals, were discovered and investigated.† Bielectrons $(e_s)_2$—systems with a double charge exhibiting a specific reactivity—

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†Historically the term solvated electrons was given to localised equilibrium states of excess electrons in polar media. The term "dry" electrons is usually understood as the delocalised states of excess electrons, which have not as yet attained equilibrium with the "slow subsystem"—the polar medium. We may note that delocalised equilibrium states of excess electrons are also possible (if one leaves aside the consideration of chemical reactions involving excess electrons), which are called quasi-free electrons. Furthermore, the term "captured electron" (in the English language literature "trapped" electrons) is frequently encountered in the literature—this represents a non-equilibrium (quasi-equilibrium) localised state of the electron in frozen polar media (glasses). If one also takes into account the fact that excess electrons can exist in different excited states, the terminological difficulties of the authors become understandable. In subsequent exposition, the term "solvated electron" (e_s) should be understood in its initial (historically) sense, unless it is specially stipulated which particular quantum-mechanical state of the excess electron is being considered. We may point out that the questions of terminology have been considered in fair detail by Pikaev;[23,28] we shall be forced to return to them again in the Section devoted to the consideration of the energetic characteristics of excess electrons.

have also been discovered.[41] The synthesis of the latter aroused special interest among investigators in connection with the hypothetical possibility of constructing superconductors of a new type on the basis of their Bose condensate properties.[42,43]

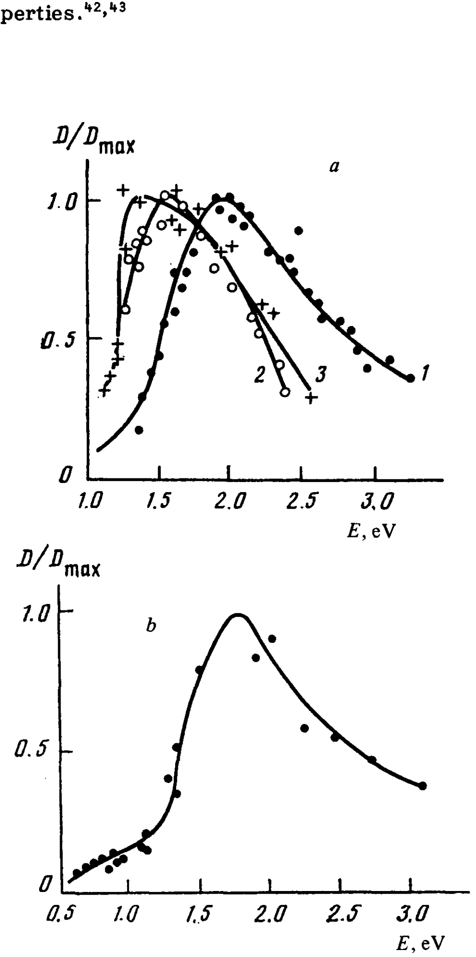

Figure 1. The absorption spectra of e_s in methanol at different temperatures (°C): *a*: *1*) 20; *2*) 148; *3*) 208; *b*: 244.[44]

The optical absorption curves for solvated electrons in different substances, their mixtures, and solutions, which have many properties in common, have been investigated in detail. In most cases these curves consist of a single broad structureless peak located in the visible or in the near ultraviolet depending on the microscopic structure of the solvent. The characteristic universal features of the shape of the absorption curves, to which we shall frequently refer below, are presented in Fig.1. Evidently the absorption peak is asymmetric: with increase of the energy, the comparatively sharp increase of the absorption is replaced by a slower descent. Such asymmetry is unusual in atomic and molecular spectroscopy (if one disregards the absorption spectra of a number of negative ions), but has analogies in nuclear physics.[21] In particular, the shape of the peak resembles very closely, after the appropriate alteration of the energy scale, the frequency dependence of the photosplitting of the deuteron. It was found that the shape of this absorption peak is extremely stable; for example, in the case of water it is almost invariant at temperatures from −4 °C up to a supercritical temperature. An important characteristic feature of the behaviour of the absorption peak from the standpoint of theory is its tendency to undergo a bathochromic shift with increase of temperature. It is seen in Fig.1 that the spectra of e_s in alcohol have the same features.

After a brief description of the various methods for the detection and investigation of e_s, we shall consider in the present review its physical nature, its chemical reactions, and its electrochemical behaviour. Special attention is devoted to the unusual nature of the chemical reactions of the solvated electron, the most active reductant, which is caused to a large extent by the possible occurrence of tunnel processes involving e_s. The characteristics of the thermodynamics of the solvated electron, including the thermodynamic relations between e_s and the quasi-stable "dry" electrons, will also be discussed.

II. EXPERIMENTAL RESEARCH METHODS

It is difficult to name an experimental physicochemical method which has not been used in the study of excess electrons in condensed media. This can be naturally accounted for by the fact that solvated electrons constitute unique experimental objects—the simplest anions which interact strongly with the medium and are characterised by both specific EPR and optical absorption spectra, readily generated by various procedures (pulsed and steady), having a wide variety of chemical properties, and, as already mentioned above, participating in many physicochemical processes. Therefore, regardless of whether the investigator is interested in quantum chemistry, magneto-resonance analytical methods, conductivity, the optics of condensed media, the chemistry of solutions, radiation chemistry, electrochemistry, cooperative phenomena, or other questions, the analysis of the nature and behaviour of excess electrons in various media enables him to test the selected method, to obtain interesting information, and to assess critically the existing theoretical schemes.

The possibility of using well tested physical methods, with a high time resolution, is an appreciable advantage in the study of solvated electrons (including the kinetics of their reactions). Here we have in mind in the first place the optical spectroscopic and EPR methods and also the method of induced pulsed electrical conductivity developed recently (and various modifications and combinations of the methods indicated). Most information about e_s has been obtained by studying the optical absorption spectra by an extremely wide variety of methods. High speed spectrometry with time resolution down to several picoseconds[45–53] with e_s generated by pulse radiolysis[48,50–52] and flash photolysis[45–47,49] has been used in the study of kinetics of the solvation and chemical reactions of e_s. Stationary and nanosecond spectra of e_s generated in different ways have been investigated as a function of temperature,[44,54] pressure,[55] the state of aggregation of the matrix (glass, liquid, and crystal), etc. Attempts (albeit with negative results) to observe the luminescence of solvated electrons have been described.[45,56]

Apart from the optical spectra, the IR and UV spectra of solvent–excess electron systems have been investigated.[57–59] Combined electro-optical,[60] magneto-optical,[61] and ellipsometric[62,63] methods are extremely promising. Excess electrons have also been investigated in experiments on photoemission and thermoemission from a metal into a solution and from a solution into a vacuum.[64–66] Many experiments concerning the influence of photoannealing on e_s spectra have been performed.[45–53] At the present time, one may claim that the optical properties of e_s have been more fully investigated than those of other colour centres in condensed media, including the usual halide ions. At the same time, to this day there is no generally accepted theoretical scheme which would explain the characteristic optical properties of e_s.

Various pulsed and stationary NMR and EPR methods have been used to investigate the immediate environment of solvated electrons.[7-12,19] Particularly valuable results have been obtained for frozen systems by the spin-echo modulation method.[67-69] The spin-echo modulation method, developed specially[67] for the investigation of solvated ions, has already yielded extensive information about the solvation shells of various metal ions in frozen electrolytes. However, in the case of e_s the results obtained must be treated with greater caution, according to Golden and Tuttle,[70] because in their interpretation one usually employs effective constants for spin interactions, which, as a consequence of the comparatively broad distribution of the e_s electron density, always have values as if the electron were localised in a cavity even when in fact there is no increase in the distances between the molecules of the medium at the site of the localisation of the excess electron.

There exist examples of the employment of fairly rare methods, such as the annihilation of positrons,[10,14] mass-spectrometric analysis of charged clusters of the type $(H_2O)_n^-$ in vapours,[71] and measurement of ultrasonic absorption.[10,14] Some of the results obtained by these procedures do not fit in any way the familiar theoretical schemes, which, incidentally, may be attributed to the inadequate accuracy and reliability of the selected experimental method.

Clearly, even a brief description of the experimental methods employed and the results obtained would occupy too much space. For this reason, we confined ourselves above to mentioning only the principal and most thoroughly developed fields of experimental research. We shall only state that, by analysing the nature of e_s, it is possible to assess fairly reliably various experimental and theoretical approaches in various fields of chemical physics.

III. THEORETICAL DESCRIPTION

The problem of the selection of an adequate model for the description of the solvated electron—an excess localised electron in a disordered, usually polar, condensed medium—is complex and interesting. Any progress towards its solution appears important not only for specialists, directly concerned with the solvated electron, but also for the general theory of condensed media.

During the period from 1940 to 1946, Ogg[72] developed the first quantitative theory of the electron solvated in ammonia. It was postulated that a spherical cavity with a radius R is formed around the electron in ammonia and that the ammonia molecules at the boundary of the cavity create for the electron an effective spherical potential well with infinitely high walls. The energy of the electron is made up of the positive kinetic energy T_e, determined with the aid of the uncertainty principle from the formula $T_e = (2\pi\hbar)^2/2mR^2$, and the energy of the interaction with the polarisation field:

$$V=-\frac{e^2}{R}\left(1-\frac{1}{\varepsilon_0}\right) \tag{1}$$

where ε_0 is the dielectric constant of the medium and m and e are the mass and charge of the electron.

The equilibrium value of the radius R_{eq} corresponds to the condition for a minimum in the total energy of the system. Ogg compared the "pushing apart" of the molecules by the electron in the cavity with the observed increase in the specific volume of ammonia following the dissolution of alkali metals in it. On excitation with light, the electron leaves the cavity. The threshold frequency Ω of the light absorbed by the solvated electron is determined from the relation

$$\hbar\Omega = T_e + V \tag{2}$$

The frequencies Ω and the high value R_{eq} = 20 Å obtained by Ogg clearly conflict with experiment. The main cause of this discrepancy is, as has now become clear, the unduly high kinetic energy of the solvated electron in the model of the potential well with infinite walls, which provides a poor description of the states of e_s, which are in reality comparatively weakly bound. However, the idea itself of the formation of a "cavity" greatly stimulated further theoretical investigation of e_s. In essence, an analogous computational scheme (with, however, the minimisation not of the energy but of the free energy of the electron—medium system) has been used as the basis of the modern description of the localised states of excess electrons in inert gases.[17,35-39]

Davydov[73] was the first to use for the description of solvated electrons in ammonia the Landau–Pekar theory of large radius polarons, developed previously[74] for the description of electronic states in ionic crystals. Subsequently this approach was used by Deigen.[75] Within the framework of the Davydov–Deigen theory, which its authors put forward in opposition to Ogg's cavity theory, it has been possible to obtain the quantitative values of a whole series of characteristics of the electron in ammonia in agreement with experiment, and in the first place the position of the maximum of the optical absorption band, which was related to the Franck–Condon 1s – 2p transition. This theory has played an important role in the prediction of the existence of and the determination of the frequency range in the optical absorption of the short-lived hydrated electron e_{aq}. On its basis, many attempts have been made to refine the calculations of the energy parameters and other characteristics of the ground and excited states of solvated electrons (see, for example, Mazurenko and Mukhomorov[76]).

The computational scheme, in which longitudinal optical phonons appear as collective excitations, has been most frequently used in the solvated electron theory. The appearance of such collective excitation is associated with the movement of a system of dipoles, whose orientation changes after the introduction of a charge into the system. The direct use of the theory of the interaction of electrons with phonons is possible only in the case of weak interactions with the aid of the procedures of the perturbation theory. Another limiting case, that of the strong interaction, is of greatest interest for the theory of solvated electrons. A special approach, whose main element is the use of an analogue of the Hartree self-consistent field method frequently used in quantum chemistry, has been developed for this purpose.

One of the most logical and clearest schemes for the representation of the above approach is as follows.[77] The complete vector of the state of the system $|\Psi\rangle$ is expressed approximately in the form of the direct product of the vector of the state $|\phi\rangle$, which depends solely on the electronic parameters, and the vector of the state $|\chi\rangle$, which depends only on the characteristics of the phonon field:

$$|\Psi\rangle = |\varphi\rangle|\chi\rangle \tag{3}$$

The exact Hamiltonian of the system H, i.e.

$$H = H_0^{el} + H_0^{ph} + \sum_{\mathbf{q}}\left(Q_{\mathbf{q}}a_{\mathbf{q}}e^{i\mathbf{qr}} + Q_{\mathbf{q}}^{*}a_{\mathbf{q}}^{+}e^{-i\mathbf{qr}}\right)$$

is then replaced by the approximate Hamiltonian $\tilde{H}$, which depends explicitly on the time t:

$$\tilde{H}=H_0^{el}+H_0^{ph}+\sum_{\mathbf{q}}[Q_{\mathbf{q}}a_{\mathbf{q}}\rho_{\mathbf{q}}(t)+Q_{\mathbf{q}}^{*}a_{\mathbf{q}}^{+}\rho_{\mathbf{q}}^{*}(t)]+$$
$$+\sum_{\mathbf{q}}[Q_{\mathbf{q}}A_{\mathbf{q}}(t)\,\mathrm{e}^{i\mathbf{qr}}+Q_{\mathbf{q}}^{*}A_{\mathbf{q}}^{*}(t)\,\mathrm{e}^{-i\mathbf{qr}}]+F(t) \tag{4}$$

where the summation is carried out with respect to the wave vectors of the phonons $\mathbf{q}$, H_0^{el} and H_0^{ph} are the Hamiltonians of the non-interacting electron and phonons respectively, $Q_{\mathbf{q}}$ is the shape factor of the electron–phonon interaction,# $a_{\mathbf{q}}$ ($a_{\mathbf{q}}^{+}$) the operator of the annihilation (generation) of the phonon, $\rho_{\mathbf{q}}(t)$, $A_{\mathbf{q}}(t)$, and $F(t)$ are certain (non-operator) time functions, and the asterisk * implies the complex conjugate. It follows from the condition for the minimum deviation of $\tilde{H}$ from H, which is formulated as the requirement for a minimum in the functional $\langle\Psi|(\tilde{H}-H)^2|\Psi\rangle$ for all the vectors of the state $|\Psi\rangle$ of type (3) that the following equations must hold:

$$\rho_{\mathbf{q}}(t)=\int\varphi^{*}(\mathbf{r},t)\cdot\varphi(\mathbf{r},t)\cdot\mathrm{e}^{i\mathbf{qr}}\mathrm{d}^3r$$
$$\varphi(\mathbf{r},t)=\langle\mathbf{r}|\varphi(t)\rangle$$
$$A_{\mathbf{q}}(t)=\langle\chi|a_{\mathbf{q}}|\chi\rangle$$
$$F(t)=-\sum_{\mathbf{q}}[Q_{\mathbf{q}}A_{\mathbf{q}}(t)\cdot\rho_{\mathbf{q}}(t)+Q_{\mathbf{q}}^{*}A_{\mathbf{q}}^{*}(t)\cdot\rho_{\mathbf{q}}^{*}(t)] \tag{5}$$

When the ground state is considered, the c-number term $F(t)$, which is independent of the coordinates and momenta of the electron and phonons can be rejected in the Hamiltonian (4), because its retention leads only to a change in the phase of the wave function which is insignificant when stationary states are considered. From Eqns.(4) and (5), it is possible to obtain dynamic equations which can be conveniently formulated for the wave function $\phi(\mathbf{r}, t)$ of the electrons in the Schrödinger representation and for the phonon operators $a_{\mathbf{q}}$ in the Heisenberg representation:

$$i\hbar\frac{\partial\varphi}{\partial t}=\left\{H_0^{el}+\sum_{\mathbf{q}}[Q_{\mathbf{q}}A_{\mathbf{q}}(t)\cdot\mathrm{e}^{i\mathbf{qr}}+Q_{\mathbf{q}}^{*}A_{\mathbf{q}}^{*}(t)\,\mathrm{e}^{-i\mathbf{qr}}]\right\}\varphi$$
$$i\hbar\frac{\partial a_{\mathbf{q}}\ (s)}{\partial t}=[\tilde{H},a_{\mathbf{q}}]=\hbar\omega_{\mathbf{q}}a_{\mathbf{q}}+Q_{\mathbf{q}}^{*}\rho_{\mathbf{q}}^{*}(t) \tag{6}$$

where $\omega_{\mathbf{q}} = \omega$ for the optical phonons and $\omega_q = C_s q/\hbar$ for the acoustic phonons.

In Eqns.(6), the electronic (phonon) field depends on the phonon (electronic) field solely via the average values of the corresponding operators, analogously to what happens in the Hartree method. The second Eqn.(6) represents the equation for an oscillator in the presence of an external force. The basis set of the so called coherent states, which remain coherent in the course of the evolution of the system in time, i.e. each coherent state passes to another specific coherent state corresponding to it, is convenient in this case. By selecting, in terms of the Heisenberg representation considered, a coherent state with an eigenvalue $\alpha_{\mathbf{q}}$ of the operator $a_{\mathbf{q}}$ at time $t = -\infty$, we have

$$a_{\mathbf{q}}(t)|\alpha_{\mathbf{q}}\rangle=\alpha_{\mathbf{q}}(t)|\alpha_{\mathbf{q}}\rangle,\ |\alpha_{\mathbf{q}}\rangle=\sum_{n_{\mathbf{q}}=0}^{\infty}\frac{\alpha_{\mathbf{q}}^{n_{\mathbf{q}}}}{n_{\mathbf{q}}!}|n_{\mathbf{q}}(t)\rangle\cdot\mathrm{e}^{-|\alpha_{\mathbf{q}}|^2/2} \tag{7}$$

where $|n_{\mathbf{q}}(t)\rangle$ is a state with a specified number of phonons and a wave vector $\mathbf{q}$. Bearing in mind that phonons with different $\mathbf{q}$ are independent in terms of the given approximation, it is sufficient to consider, instead of the second operator equation (6), the usual differential equation for the average values of $a_{\mathbf{q}}$ in terms of coherent states which enter into the first Eqn.(6):

$$A_{\mathbf{q}}(t)\equiv\langle\alpha_{\mathbf{q}}|a_{\mathbf{q}}|\alpha_{\mathbf{q}}\rangle \tag{8}$$

Thus, the second Eqn.(6) is replaced by the equation for the classical field $A_{\mathbf{q}}(t)$. Its solution is

$$A_{\mathbf{q}}(t)=A_{\mathbf{q}}^{0}\cdot\mathrm{e}^{-i\omega t}-i\hbar^{-1}Q_{\mathbf{q}}^{*}\int_{-\infty}^{t}\mathrm{e}^{i\omega(t'-t)}\rho_{\mathbf{q}}^{*}(t')\,\mathrm{d}t' \tag{9}$$

In the majority of the calculations carried out hitherto, the following two additional assumptions have been used (explicitly or implicitly). Firstly, the first term on the right-hand side of Eqn.(9) is rejected, which can be interpreted as abandonment of allowance for the influence on e_s of the real free phonons arising in the medium even at equilibrium due to thermal excitation. Secondly, the adiabatic approximation, consisting in the replacement of $\rho_{\mathbf{q}}^{*}(t')$ in the integrand in Eqn.(9) by $\rho_{\mathbf{q}}^{*}$—the average for the electronic ground state considered along a finite trajectory—is applied. The validity of the latter approximation is justified by the different time scales of the movements of the inertial phonon and rapid electronic subsystems.

After the replacement of the summation by integration, the problem of finding the stationary electronic function is reduced, in accordance with the usual rule, to its solution for the eigenvalues for a non-linear integro-differential operator:

$$E^{e}\varphi(\mathbf{r})=[H_0^{el}-V_{sc}(\mathbf{r},\varphi(\mathbf{r}))]\,\varphi(\mathbf{r}) \tag{10}$$

where

$$V_{sc}(\mathbf{r},\varphi(\mathbf{r}))=\int\mathrm{d}^3r'\,[|\varphi(\mathbf{r}')|^2 z(\mathbf{r},\mathbf{r}')]$$
$$z(\mathbf{r},\mathbf{r}')=\frac{1}{8\pi^3}\int\mathrm{d}^3q\left\{\frac{|Q_{\mathbf{q}}|^2}{\hbar\omega_{\mathbf{q}}}\cos[\mathbf{q}(\mathbf{r}-\mathbf{r}')]\right\}$$

After solving the problem formulated above for the eigenvalues, the overall energy of the system can be represented in the form

$$E=E^{e}+E^{m} \tag{11}$$

where E^m is the energy of reorganisation:

$$E^{m}=\left\langle\alpha\left|\sum_{\mathbf{q}}\hbar\omega a_{\mathbf{q}}^{+}a_{\mathbf{q}}\right|\alpha\right\rangle=\sum_{\mathbf{q}}\frac{|Q_{\mathbf{q}}|^2\cdot|\rho_{\mathbf{q}}|^2}{\hbar\omega}=$$
$$=\frac{1}{2}\iint\mathrm{d}^3r\,\mathrm{d}^3r'\,[|\varphi(\mathbf{r})\cdot\varphi(\mathbf{r}')|^2 z(\mathbf{r},\mathbf{r}')]=\frac{1}{2}\mathrm{d}^3r\varphi^{*}(\mathbf{r})V_{sc}\varphi(\mathbf{r}) \tag{12}$$

In calculating E^m, Eqn.(9) was used for $A_{\mathbf{q}}$ without taking into account the free phonons.

The direct solution of Eqn.(10) with substitution in it of a particular specific expression for $z(\mathbf{r}, \mathbf{r}')$ represents an extremely complex problem, which is usually solved by variational methods.

#In the "classical" theory of the polaron, the shape factor $Q_{\mathbf{q}}$ assumes the form $Q_{\mathbf{q}} = -i(\pi\alpha_F/V)^{1/2}(\hbar^5\omega^3/m)^{1/4}q^{-1}$, where $\alpha_F = (\varepsilon_\infty^{-1}-\varepsilon_0^{-1})(e^2/\hbar\omega)(m\omega/\hbar)^{1/2}$ is a dimensionless coupling constant (Fröhlich constant), ω and $\mathbf{q}$ are the frequency and the wave vector of the optical phonon, ε_∞ and ε_0 are the high-frequency and static dielectric constants of the medium, and V is the volume of the system. If interactions with acoustic phonons are considered, then $\omega = \omega(q) = C_s q/\hbar$ and $Q_{\mathbf{q}} = -i\sigma(\hbar q/2MC_sV)^{1/2}$, where C_s is the velocity of sound, M the mass of the unit cell, and σ the constant of the deformation potential.

The question of the limits of applicability of the numerous approximations introduced in the description of the strong coupling of electrons with phonons set out above is fairly complex. In the first place it is known that the Hartree type self-consistent field approximation cannot be characterised as an expansion in terms of a small dimensionless parameter and is justified in definite specific cases only as a result of certain numerical cancellations. One can only claim that such approximation is known to be applicable to a large number of phonons or, what amounts to the same thing, at high temperatures *T* in the system considered, because the correct classical limit for phonon equations is then obtained in terms of the basis set of coherent states. The additional adiabatic approximation used is known to be unjustified in the description of excited electronic states in the vicinity of the boundary of the continuous spectrum. The question of the methods of calculation of excited states with the aid of the variational procedure considered remains in general open. Its logical realisation requires expressions for the wave functions of higher states, which are so far unknown. Indirect estimates of the difference between the energies of the excited and ground states, which are in principle feasible, are extremely inaccurate. Referring to adiabatic conditions, the excited states in optical transitions are frequently calculated using the Hamiltonian of the ground state. This approach is quite justifiably disputed by Devreese et al.[78]

To the considerations presented in the studies quoted above, one must add that, when optical transitions are considered, one cannot simply reject, which is frequently done, the time(t)-dependent *c*-number terms $F(t)$ in Eqn.(4), such terms being different in different states. The fact that the theory must take into account quantitatively the effects arising owing to the disorder in the medium is significant. Logical allowance for these effects and also for microscopic interactions, symbolically introduced into Eqn.(4), within the framework of polaron models remains so far a matter for the future.

In connection with the uncertainty of the initial postulates of the theory, comparison of the conclusions which follow from it with experimental data is especially important. As already stated, many attempts have been made at a direct application of the large-radius polaron theory, in which the interaction with longitudinal optical phonons is specified by the Fröhlich Hamiltonian and there are no microscopic interactions, to the description of solvated electrons (see Refs.73–76 and the references in the last paper). However, this theory proved to be unable to explain many properties of solvated electrons. It has not been possible to interpret with its aid the shape of the optical absorption curve, the temperature dependence of the position of the maximum on this curve, and the influence of the phase state and pressure of the medium.§

The fundamental questions concerning the mechanism of the solvation of the electron have been investigated experimentally in a series of studies.[80–82] The authors investigated the optical spectra of e_s in mixtures of associated polar liquids having different or similar dielectric constants and also the changes in the spectra of e_s following the dilution of polar liquids by a non-polar solvent which is neutral as regards association. The most important result is the conclusion that the properties of e_s are correlated with the microstructure of the mixtures and that there is no dependence of the spectroscopic characteristics of e_s on the macroscopic parameters of the system (dielectric constant, density, etc.). On the basis of their experimental data, the authors[80–82] claim that the intrinsic structural elements of the medium—hydrogen bonded complexes of different molecules or self-associated species which function as electron traps—are of decisive importance for the mechanism of the solvation of the electron. The main cause of the broadening of the spectrum is the distribution of e_s among different associated species.[82]

Subsequently the approach proposed[80–82] was extended to dilute solutions of ammonia in various alkanes. The optical absorption corresponding to the photoexcitation of electrons localised in the associated polar molecules was then observed and investigated. The very fact of the solvation of the electron at very low concentrations of the polar component in the mixture (approximately 0.1 mole %) is of interest. The spectrum of e_s then remains almost the same as in pure NH_3 even when the medium is non-polar. The solvated electrons in such systems can probably be regarded as analogous to excess electrons in the vapours of polar liquids[83] and the spectrum of e_s then makes it possible to infer the energy characteristics of the electron in an "isolated" cluster of polar molecules.

The need to take into account in the solvated electron theory the influence of specific chemical interactions of e_s with the medium, which follows from the analysis of the experimental data, led to the development of semicontinuous models. Apart from the long-range interactions of e_s with long wavelength phonons, in such models account is taken, mainly phenomenologically, of the interactions with the molecules in the immediate environment—the solvation shell. Analysis of such models and of the difficulties associated with their use in the interpretation of experimental data, in the first place of the absorption spectra of e_s, has been carried out.[22]

The difficulties arising when the interactions of the electron with the solvent as a continuous system are considered stimulated the development of alternative theoretical models based on microscopic interactions of e_s with clusters—a small number of molecules surrounding the electron. These clusters are investigated by quantum-chemical methods. Such calculations for e_s are sometimes referred to as *ab initio* calculations for the electron. Using the terminology of solid state physics, the cluster models are seen to be closest to small radius polaron models. By virtue of the characteristics of a disordered medium, a tunnel electron jump is in this case difficult, because the equivalent position may prove to be fairly remote. If the characteristic time of any kind of processes involving e_s, for example optical transitions, is shorter than the characteristic time of the jumps, then the latter can be altogether neglected in the study of the given processes, i.e. the electron may be regarded as fixed at a specific molecular cluster.

In one of the first studies on these lines,[84] the states of the excess electrons in systems comprising water and ammoni dimers for a specific fixed geometry of the molecules in the dimers were calculated within the framework of a simplified version of the molecular orbital theory. For excitation energies identified with the difference between the energies of the lowest and highest orbitals, $\hbar\Omega = 2.5$ eV in the case o H_2O and 1.63 eV in the case of NH_3 were obtained.

The first quantum-chemical calculations for e_s revealed also the main difficulties encountered. It was found that (1) the state of e_s in the dimeric model is relatively unstable as regards the escape of the electron to a quasi-free state

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§ The question of the influence of temperature and pressure on optical spectra has not been finally solved even for the classical case of large radius polarons.[79]

and (2) the electron (especially in an excited state) is not localised within the limits of the cluster. In order to eliminate these difficulties, clusters consisting of a large number of molecules were considered in subsequent studies and also attempts were made to take into account the influence of the dielectric continuum outside the solvation sphere (cluster). Such *ab initio* calculations for clusters consisting of four water or ammonia molecules have been carried out.[85,86] They yielded not only extensive numerical information, in general in agreement with experimental data (we have in mind the optical transition energies $\hbar\Omega$ and the geometrical dimensions of the clusters), but also involved a discussion of the question of the stability of the states of e_s. It was found that the overall energy E_s represents the difference between two quantities: the energy gain in the localisation (capture) of the electron in the cluster with the optimum configuration and the energy expenditure necessary for the formation of such a cluster (or defect). The overall solvation energy E_s is positive although not large.[86]

However, in our view the energy gains obtained in the solvation of the electron are comparable to the accuracy of the calculation and the question of the stability of the clusters (i.e. of their existence in the vapour phase) should still be regarded as open. The above studies[85,86] have confirmed but not eliminated the difficulties arising in quantum-chemical models in view of the large effective radius of e_s in the excited state. In view of this result, the calculations of the characteristic excited states of e_s must be treated with a great deal of scepticism, because the interactions of the electron with the molecules of the second solvation shell should be significant for such states.

An evident deficiency of the above studies is their complete neglect of the interactions of the electron with the medium surrounding the cluster. Such interactions should lead to at least two effects; firstly, owing to the influence of the medium, the discrete lines in the absorption spectra of the cluster e_s should spread (or the corresponding vibronic bands should be modified); secondly, the presence of the medium can lead to an increased stability of the localised e_s (for example, via the polaron mechanism).

A configurational model of e_{aq} has been proposed.[87] The states of the H_2O^- ion, in the field of six dipoles interacting with one another which consist of the molecules in the first solvation shell, have been calculated by the LCAO method. The local energy minima of the cluster, corresponding to the electronic ground state of e_s, have been calculated as a function of the orientation of the dipoles. The "Franck–Condon" excited states of e_s were then found for each such local minimum in the energy of the cluster. The optical absorption spectral lines for such a cluster *in vacuo* should correspond to the differences between these energies. The attempt at a quantitative calculation of not only the main characteristics of the optical absorption band of e_s but also of the dependence of the spectrum on temperature and pressure must be regarded as a fundamentally new step in the study of Byakov et al.[87]

For the description of the absorption spectrum of the solvated electron, the above workers[87] resorted, apparently for the first time in quantum-chemical calculations of this kind, to the general theory of the absorption of light by impurity species in the medium. This general theory, developed by Ovchinnikov and Ovchinnikova,[88] relates the broadening of the discrete lines to the interaction of the electron with the optical phonons of the medium. Analysis of the spectrum of e_{aq} within the framework of the configurational model showed that, depending on the disposition (orientation) of the dipoles in the first solvation shell, there are several groups of stable "ground" states of e_{aq} (i.e. local energy minima of the electronic ground state). Its own "Franck–Condon" excited state corresponds to each of these ground states. It has been observed that the energies of the Franck–Condon transitions decrease on average with increase in the energy of the "ground" state. This finding explains the effect of the bathochromic temperature-induced shift of the absorption maximum: with increase in temperature, increasingly high "ground" states, which correspond to absorption in a longer-wavelength region, are populated. The interaction of the cluster with the medium leads to the spreading of the discrete spectral lines and to the appearance of a structureless spectral band, which is displaced to the left along the frequency axis if the temperature is increased. Since the band width is mainly related to the disposition of the initially discrete lines, its temperature dependence may not follow the proportionality to $\varepsilon_\infty^{-1} - \varepsilon_0^{-1}$ predicted by the polaron theory[76] and this also applies to the asymmetry of the band.

The experimental EPR data for e_s, indicating (in terms of the usual interpretation) the symmetry of the electron density distribution among the 4–6 protons of the immediate environment, may constitute an evident objection against the above model.[87] However, the authors[87] took into account this possible objection and carried out an analysis of the EPR spectra of e_s in terms of their model. An unexpected conclusion arising from this analysis is that of the possible equivalence of protons from the standpoint of EPR spectroscopy accompanied by a clear geometrical asymmetry of the disposition of the molecules in the configurational model (we recall that initial localisation of the electron in the cluster on one central H_2O molecule is postulated). The observed uncertainty in the reproduction of the geometrical structure of e_s on the basis of EPR data must be borne in mind also in the interpretation of complex spin echo experiments (see also Golden and Tuttle[70]). Unfortunately the authors[87] did not continue an analogous analysis of e_s for other media and it therefore remains unclear whether the mechanisms of the bathochromic shift, broadening, and asymmetry of the optical absorption band of e_{aq} which they quote[87] are universal for all (or the majority) of solvents or whether they apply only to H_2O.

The attempt to take into account the dielectric continuum has also been undertaken in a study[89] whose author reformulated the usual self-consistent field problem in terms of the Hartree potential and included the corresponding polaron contribution to the minimised energy functional in the quantum-chemical calculation for a negatively charged cluster consisting of four molecules of the medium. The calculation confirmed yet again the conclusion that the state of e_s in the gas phase is unstable, that the electron cloud incorporating the molecules of the medium adjoining the cluster has a large radius, and that the electron is almost fully delocalised in the excited state. Unfortunately, in the above study[89] the question of the shape of the absorption band and of its temperature dependence was not considered. The broadening of the band was explained qualitatively by the presence of geometrically different clusters, i.e., as is usual for cluster models, a heterogeneous mechanism for the broadening of the band was postulated.

It is noteworthy that a non-empirical calculation for a negatively charged cluster incorporating 4–6 molecules is at the limit of feasibility as regards modern computers and many natural questions, for example, concerning the infrared spectra of such clusters or the constants for the interaction of an additional electron with the intramolecular vibrations therefore still remain unanswered. It must be emphasised yet again that the quantum-mechanical methods used in the study of e_s provide only more or less approximate results and it would be naive to expect to obtain with their aid answers to all the questions. Experiments still remain the principal source of information.¶

The complex problems arising in the comparison of different theoretical computational schemes for e_s, the presence of a large number of parameters, and the uncertainty of the initial data led to studies in which the structure of e_s was investigated with the aid of methods of analysis of optical spectra unrelated or weakly related to model representations.[22,90–95] Such analysis indicates primarily the short-range character of the interactions leading to the localisation of e_s and makes it possible to treat optical absorption as electron transition from a bound state to a continuum.

We believe that the most convincing confirmation of the transition from the bound state to a continuum is provided by the results of the analysis of absorption spectra with the aid of optical sum rules, the virial theorem, and threshold formulae.[22,90–95] In an early study[96] it was already noted that the region of the characteristic absorption peak of the solvated electron corresponds virtually to the maximum value of the oscillator strength. Hence it was possible to conclude that at least the given peak corresponds to the transition of e_s to a continuum. Detailed analysis of the experimental results based on a wide variety of sum rules and model-free threshold formulae[22] demonstrates quite convincingly that the optical section of the absorption spectrum of the solvated electron does indeed correspond to the "bound state–continuum" transition. The long-energy sections of the spectrum can then correspond in certain specific cases to contributions by "bound state–resonance level" transitions. The contributions of such transitions are apparently extremely significant in the case of the electron in ammonia. The conclusions reached in a review[22] and in subsequent communications[92–95] concerning the analysis of the moments (optical) of the spectral absorption curves of the solvated electron are mainly in agreement. A significant feature of the above studies[92–95] was the discussion in the latter of the influence of the temperature of the system on the sum rules.

One of the most important conclusions from the model-free analysis of the optical absorption spectra of solvation electrons with the aid of sum rules and threshold formulae is that the interactions retaining the electron in the localised state are short-range in character.[22] A direct consequence of this conclusion has been an attempt to describe the optical spectra of the solvated electron within the framework of the stationary short-range potential model. The first study based on this approach was apparently that of Kajiwara et al.[97], in which the radial dependence of the potential was represented by a rectangular well characterised by two parameters. This approach has definite features in common with the cavity model adopted as early as the 1940's in Ogg's studies.

The studies summarised by Frankevich and Yakovlev[22] dealt with the so called zero radius potential with a single parameter expressed directly in terms of a quantity having a direct physical significance, namely in terms of the energy of the bound state of the electron. The zero radius potential, actively employed in nuclear physics, has the significance of the limit of the potential of the rectangular well (in terms of the zeroth spherical harmonic) when the width of the well tends to zero and its depth tends to infinity so that the single stationary level (or the antibonding state) does not change. Systems in a short-range potential field, the energy of the systems being close to the continuous spectrum threshold, are satisfactorily described in a similar way.

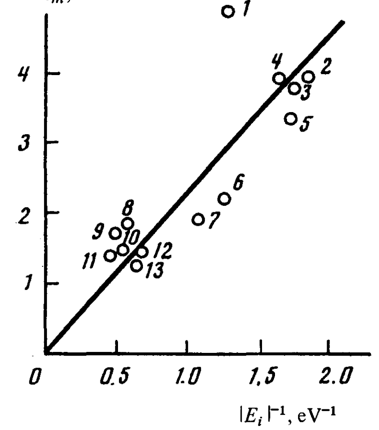

Figure 2. The extinction coefficient at the absorption maximum expressed as a function of $|E_i|^{-1}$. Straight line—theoretical relation corresponding to the zero radius potential model; circles—experimental data: *1*) ammonia; *2*) diethyl ether; *3*) methyltetrahydrofuran; *4*) tetrahydrofuran; *5*) dimethoxyethane; *6*) 1,3-propylenediamine; *7*) ethylenediamine; *8*) water; *9*) methanol; *10*) ethanol; *11*) ethylene glycol; *12*) isopropyl alcohol; *13*) 1-propanol.[44]

It is possible to extend the zero radius potential to the case of certain bound states, including states with the highest angular momenta, which is usual for specific systems with solvated electrons. The number of "adjustable" parameters can be increased by passing to potentials with a finite radius. In the case of the zero radius potential, the dependence of the cross-section σ of the photoinduced "bound state–continuum" transition on the frequency of the incident light Ω and on the energy of the initial state E_i is expressed by the simple formula

$$\sigma(\Omega, E_i) = \frac{32\pi^2 e^2}{3c\hbar} k_i \left(\frac{k_f}{k_f^2 + k_i^2}\right)^3 ,$$
$$\hbar^2 k_i^2 = 2m|E_i|;\ \hbar^2 k_f^2 = 2m(E_i + \hbar\Omega) . \qquad (13)$$

Eqn.(13) reproduces very satisfactorily in many instances the principal characteristics of the main absorption peak of the solvated electron. For example, according to Eqn.(13), there should be a linear relation, with a rigorously defined coefficient, between the extinction coefficient ε_m at the absorption maximum [which is proportion to $\sigma(\Omega_m)$] and the reciprocal of the frequency Ω_m^{-1}, corresponding to the absorption maximum. The corresponding theoretical curve together with the experimental points for a series of substances[90] is shown in Fig.2. The only deviation of the experimental points from the theoretical curve, exceeding the experimental

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¶In this connection one cannot fail to mention again the study[62] in which an ellipsometric investigation of e_s in hexamethylphosphoramide revealed a change in the vibration frequency of the non-polar C–H bond but no influence of the excess electrons on the polar C–N and P=O bonds was observed. This information necessitates in many respects a re-examination of the initial postulates for the construction of cluster models.

error, is observed in the case of the electron in ammonia. This finding is attributed[90] to the comparatively large interaction region (the presence of a "cavity") in the case of ammonia. Agreement with experiment can be attained if it is assumed that the size of this "cavity" in ammonia is in the range 1–2 Å. The relation between Ω_m and the threshold energy, which follows from Eqn.(13), also holds very satisfactorily:[22]

$$\hbar\Omega_m \cong 2|E_i| \; . \tag{14}$$

It is useful to quote the results of the analysis of the expression for the polarisability of the solvated electron α. In the general case of the motion of the localised electron with an energy E_i in an external potential field, the polarisability is given by

$$\alpha = K\frac{e^2\hbar^3}{mE_i^2} \; , \tag{15}$$

where K is a numerical multiplier. For the zero radius potential, the multiplier K assumes the minimum value $K = 1/16$ for the ground 1s state, while for a long-range potential of the Coulombic type, this quantity is 70 times greater and amounts to 9/2. For the remaining monotonic potentials, K lies in the range between 1/16 and 9/2. The polarisabilities obtained using the sum rule[22] for electrons in different media and the theoretical relation (15) for $K = 1/16$ are compared in Fig.3. The satisfactory agreement of the results constitutes important additional evidence in support of the short-range character of the interactions promoting the localisation of the electron in the solvated state.

However well the behaviour of the solvated electron is described with the aid of the zero radius potential model, such description is known beforehand to be incomplete, since it does not take into account the influence of many-particle effects. However, precisely these effects determine interesting phenomena such as the dependence of the shape and position of the absorption peak in the optical frequency range on the structure of the medium and temperature and also the manifestation of absorption in the infrared region associated with the modification of the collective modes as a result of the introduction of an excess electron into the medium. They also influence the kinetics of processes with participation of the solvated electron.

The question of allowance for many-particle effects in the solvated electron theory has been frequently posed in the literature. The problem has been most often considered in terms of a linear treatment based on the formulation of the Hamiltonian H taking into account the interaction and dynamics of the motion of all the particles in the system considered or, at least, sufficiently large clusters. One of the examples of this approach has been given by Golden and Tuttle.[98] In an approach of this kind, the introduction of insufficiently well-founded approximations and hypotheses of a model character is inevitable even when large computers are used for the calculations. Without denying the importance of such studies, we nevertheless doubt if real advances can be achieved on these lines, especially if an explanation can be found for the observed simple and universal characteristics of the behaviour of the spectra of solvated electrons.

We believe that another approach, corresponding to a scheme actively and successfully used in modern physics of condensed media is more promising. According to this scheme, the short-range interactions to which correspond the greatest changes in the energy of the system when a solvated electron is introduced into it are assumed to be specified and parametrised with the aid of a finite number of parameters, which can be calculated, in principle, by quantum-chemical methods. In the case of the solvated electron, the parameters of the zero radius or separable potential can be used as parameters of this kind. On the other hand, the long-range interactions are regarded as interactions with long-wavelength low-energy collective excitations of disordered media. Precisely such interactions determine, for example, the temperature effects for a constant density and also the principal kinetic features of the phenomena considered. The approach described has much in common with the semicontinuous model mentioned above, the only difference being that the interactions are separated in accordance with their energy and not spatial scale. An attempt to apply the above approach to the elucidation of the temperature dependence of the optical spectra was made in our earlier study.[99]

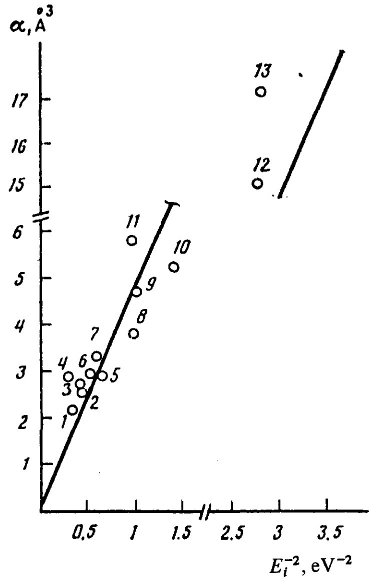

Figure 3. Dependence of the polarisability α on E_i^{-2}. The theoretical straight line corresponds to the zero radius potential model; circles—expermental data: *1*) methanol; *2*) 1-propanol; *3*) ethanol; *4*) 10 M KOH; *5*) diethylene glycol; *6*) 1-butanol; *7*) isobutyl alcohol; *8*) isopropyl alcohol; *9*) water (25 °C); *10*) 2-aminoethanol; *11*) water (−4 °C); *12*) *NN*-dimethylaminopropylamine; *13*) diethylenetriamine.[44]

IV. CHEMICAL REACTIONS

The chemical reactions of e_s in water, alcohols, ketones, and other polar liquids have been studied in especially great detail in the radiation chemistry of solvating compounds. The corresponding reactions have been described in a number of monographs[16,19–21,71] and we shall not deal with them in detail. In recent years much attention has been devoted to the detailed mechanism and other features of the reactions of e_s in mixtures of various solvents and to the reactions of stable e_s with a number of compounds dissolved in liquids such as ammonia, amines, and hexamethylphosphoramide.

We shall consider initially the bimolecular and unimolecular reactions of solvated electrons with water as the most important examples:

$$2\,e_{aq} + 2\,H_2O \rightleftarrows H_2 + 2\,OH^- \,, \tag{16a}$$

$$e_{aq} + H_2O \rightleftarrows H + OH^- \,. \tag{16b}$$

The analogous reactions in pure ammonia, i.e.

$$2e_s + 2NH_3 \rightleftarrows H_3 + 2NH_3^- \tag{17a}$$

$$e_s + NH_3 \rightleftarrows H + NH_2^- \,, \tag{17b}$$

hardly occur and e_s is extremely stable. The kinetic and thermodynamic characteristics of reactions (16) and (17) are presented below (at room temperature):

Reaction	k, litre mol^{-1} s^{-1}	ΔH^0, kJ mol^{-1}	ΔS^0, J mol^{-1} K^{-1}
(16a)	$5\cdot10^9$	−397	−12
(16b)	10^3	10	−48
(17a)	$\leqslant 1$	−168	−466
(17b)	$\leqslant 1$	125	−272

The kinetic data for the reactions were taken from Antropov[16] and the thermodynamic data from Schindewolf.[100]

Thus the absence of appreciable reactions of e_s in ammonia is caused by kinetic and not thermodynamic factors. The high absolute entropy of the solvated electron in ammonia $|S^0| = 169$ J mol^{-1} K^{-1} [101] (the entropy of the hydrated electron is $|S^0| = 13$ J mol^{-1} K^{-1}) leads to a high activation energy for the reactions of e_s in ammonia according to the activated complex (transition state) theory.[100–103]

The above arguments should also indicate a low probability of the reaction of the electron solvated in ammonia with admixtures of water ($\Delta H^0 = 52$ kJ mol^{-1}, $\Delta S^0 = -316$ J mol^{-1} K^{-1}):[103]

$$2e_s + 2H_2O \rightleftarrows H_2 + 2OH^- \,. \tag{18}$$

The possibility of an endothermic unimolecular reaction is apparently ruled out in this instance. However, direct experiments have shown[104–106] that the electron in ammonia reacts with added water at an appreciable rate, which has not so far been unambiguously explained. It has been suggested[103] that the acceleration of this reaction is caused by the formation of an unknown intermediate X in accordance with the scheme

$$2e_s = (NH_3) + 2H_2O \rightarrow [2X] \rightarrow H_2 + 2OH^- \,. \tag{19}$$

Evidence for the formation of intermediates in the reaction of e_s with water had been obtained earlier in experiments involving flash photolysis with additional lower-frequency illumination displaced in time relative to the initial pulse.[107,108] It was suggested that such intermediates may be the bielectron $(e_s)_2$, formed via the recombination of two solvated electrons, and, in a sodium–ammonia solution, the neutral complex (Na^+e_s), which is much larger than the Na atom. The question of the possible formation of $(e_s)_2$ and of complexes of the type $[Na(e_s)_2]$ has attracted much attention.[25] The detailed microscopic mechanism of even the most thoroughly investigated reactions of e_s with water cannot so far be regarded as unambiguously elucidated.

Much attention has been devoted recently to the reactions of e_s with aromatic and unsaturated hydrocarbons in various solvents and to reactions modelling processes involving charge transfer (electron capture by an acceptor). Studies of reactions with aromatic compounds[109–113] made it possible to identify the ranges of parameters within which the rates are controlled either by diffusional or kinetic limitations. In the case of diffusion-dependent control, the fact that the localised solvated electron e_s is in equilibrium with a delocalised "quasi-free" electron e_d assumes special importance. Although the fraction of delocalised electrons is small, their mobility is high and may determine the characteristic features of the migration. On the other hand, in most reactions (except perhaps the reactions of H atoms) the rate of interaction with e_s is much greater than the rate of interaction with e_d in conformity with the Franck–Condon principle. Thus, as noted for the first time by Frankevich and Yakovlev,[22] when the reactions of the solvated electron are considered account must be taken of both possible (localised and delocalised) states of the latter.

After the publication of the study of Frankevich and Yakovlev,[22] other communications appeared in which a system of two differential equations, corresponding to different states of the electron linked to one another by an equilibrium constant, is used instead of a single (diffusion) equation for the formal diffusional description of e_s capture and neutralisation processes.[18,114] The exact solution of such equations is difficult. The usual simplification is the hypothesis that the mobility (diffusion coefficient) of the electron in the localised state is much lower than the mobility (diffusion coefficient) of the quasi-free electron. On this hypothesis, it is possible to retain the form of the experimental relaxation curves and the values of the "adjustable" parameters become more reasonable.

This type of approach has been used in a study[114] whose authors began with generalised Noyes formula[115] for the effective reaction rate constant:

$$k_{\text{eff}} = [pk_s + (1-p)\,k_d] \Big/ \left[1 + \frac{pk_s + (1-p)\,k_d}{R_r D_{\text{eff}}}\right] \,, \tag{20}$$

where p is the probability of the localisation of the electron, k_s and k_d are the rate constants for the reactions with acceptors in the localised and delocalised states respectively, D_{eff} is the effective diffusion coefficient of the electron, and R_r is the reaction radius. In this way it has been possible, in particular, to explain the observed non-monotonic nature of the dependence of k_{eff} on the mobility of the solvated electron μ in the reactions of the latter in various hydrocarbons. Qualitatively, this phenomenon can be explained as follows. For low values of μ, the reaction proceeds under diffusion controlled conditions and the reaction rate constant is proportional to the mobility. The increase of the mobility promotes an increasing delocalisation of the electrons, which reduces the effective rate constant (subject to the condition that the reaction with the acceptor in the localised state is much faster than in the delocalised state). With the aid of the model considered, the authors[114] were able to explain also the dependence of the activation energy of the reaction on the effective mobility of the electron in hydrocarbons.

In the study of the kinetics proper of the reactions of solvated electrons with aromatic compounds, the validity of correlations involving a linear dependence of the rate on the free energy change in accordance with the Hammett equation was considered.[111] After the studies of Marcus[116] and Levich,[117] most attention was devoted (see Kestner[118] and the literature quoted therein) to the general theory of processes of the type

$$T^- + A \rightarrow T + A^- \tag{21}$$

where T denotes a trap for the solvated electron ($e_s \equiv T^-$), which disappears over a finite period after it loses its charge.

One of the reasons for the interest in reaction (21) is that it is the simplest example of charge transfer. Furthermore, reactions (21) are included among the elementary steps of many electrochemical and biological processes. Processes involving e_s can be followed directly with the aid of effective optical methods with a short resolution time. Additional difficulties in the theoretical study of reactions (21) are associated with the need to allow for non-adiabatic effects. The most important qualitative result of the theoretical and experimental studies of the above reactions is the conclusion that electron transfer over a large distance is impossible and that this process is influenced by the orientation of the molecules of the medium, especially in biological systems and glasses.[119]

In conclusion of the present Section, we may point to the possibility, established recently (see the review of Glausinger et al.[42] and the literature quoted therein), of the formation (in the form of films or powders) of new compounds—electrides, obtained for the first time on evaporating solutions of solvated electrons. Electrides is the name given to salts in which the localised electrons behave as anions and the positive ions are alkali metal complexes. The salts $Cs^+.(18C6)e^-$, where the symbol 18C6 denotes a complex-forming crown compound (a macrocyclic polyether), is an example of an electride.[120] As a result of the strong electron–electron interaction and the delocalisation of electrons, electrides exhibit extremely unusual properties, approaching the properties of metals, including high electrical conductivity and absorption spectra of the plasma type.[42] The hypothesis that electrides are Wigner crystals is of interest.

V. ELECTROCHEMICAL PROPERTIES

Chemically stable systems with solvated electrons include in the first place solutions of metals in ammonia (the counterions in such systems are usually alkali metal ions) and also in aprotic solvents such as hexamethylphosphoramide (HMP), dimethyl sulphoxide, diglyme, etc.

The method of electrochemical generation of solvated electrons in such systems, which makes it possible to investigate e_s under stationary conditions in controlled chemical reactions in the bulk of the solution and on the electrode, is very interesting. Although the electrochemical generation of solvated electrons in ammonia was reported as early as 1948,[121] the qualitative investigation of this process did not begin until the 1970's (see the relevant reviews[24,26]) after the investigation of the characteristics of photoemission into electrolyte solutions.[64,65] Clearly the photoemission and the electrochemical e_s generation processes are in many respects analogous and differ essentially only in the detailed mechanisms of the excitation of the electron from the Fermi level of the metal: in the first case the excitation is optical and in the second thermal.

For high negative potentials of the cathode, the cathodic generation of electrons should be observed theoretically in all electrolytes. However, in fact the actual occurrence of cathodic generation requires that (1) the solution should be stable in relation to the cathodic reduction of positive ions at fairly high negative potentials of the cathode and (2) that the reaction of the electrons in the bulk phase with positive ions should be at least hindered. Otherwise, instead of the cathodic generation of e_s, the reduction of counterions either on the electrode (deposition of the metal) or immediately in the region near the electrode is observed. We may note that a number of workers[24,122] hold the view that many of the known electrochemical reduction reactions proceed precisely via a mechanism involving the generation of e_s with subsequent interaction (in the part of the solution near the electrode) of the solvated electrons and positive ions.

This type of mechanism has been discussed in the literature even for the usual discharge of H^+ ions in the electrolysis of water. However, detailed study has shown that in water the "classical" discharge of H^+ ions nevertheless takes place on the electrode.[24] Among all the solutions, the conditions specified are satisfied best by the aprotic systems enumerated above (HMP, diglyme, etc.). It is therefore not in any way surprising that the greatest number of data on the cathodic generation of e_s have in fact been obtained using HMP, which is a liquid under normal conditions.

In the cathodic generation of e_s, two reaction pathways are possible in principle. In the realisation of the first of these, the electrons of the metal, thermally excited above the level corresponding to the electrochemical potential of the delocalised electron on the "bottom of the conductivity band of the solution",† overcome the surface barrier, move along the conductivity band, and are thermalised and solvated at a certain distance from the electrode. The possibility of the generation of solvated electrons under these conditions is determined by the activated excitation of the electron to the V_0 level. The second reaction pathway involves the tunnel transition of the electrons of the metal to the E_s level of the solvated electrons in solution. The electron must then "tunnel" over a certain distance into the solution. The activation energy for such a process, equal to $E_s - E_F$ (E_F is the Fermi level in the metal), is naturally smaller than the activation energy for the first pathway, but we have here instead kinetic limitations associated with the low probability of tunnelling over comparatively large distances. Clearly, for different potentials and states of the surface of the cathode, one or other mechanism of the cathodic generation of e_s takes place preferentially.

There is experimental evidence for the operation of both mechanisms of the generation of e_s.[24,123,124] In the above studies it was also concluded that there is a possibility of a change in the generation mechanism when the state of the electrode surface changes (the surface is passivated). Indeed, at a fixed potential of the electrode, the formation on the latter of a passivating film increases the tunnelling distance. For a sufficient thickness of the film, the process involving the excitation of the electron to the conductivity band of the solution, whereupon the electron passes over the surface barrier, is more probable.

The study of the anodic oxidation reactions of solvated electrons showed that they are controlled by diffusion and that the oxidation potential depends on the state of the electrode surface. Apart from the discharge of the solvated electrodes on the anode, the polarisation curves for HMP revealed yet another limiting current plateau, corresponding to the discharge of non-paramagnetic complexes containing two electrons and an alkali metal ion. In relation to discharge on the anode, the monoelectrons are significantly more active than the non-paramagnetic complexes;[124] their oxidation potentials differ by approximately 0.5 eV. The study of the anodic reactions of solvated electrons made it possible

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†The very concept of the "conductivity band" in a disordered system with a strong electron–phonon (electron–exciton) interaction requires discussion. Being in a delocalised state, the electron "does not have time" to interact with the slow orientational polarisation of the medium. Here it is more appropriate to speak of the influence of the electronic and nuclear polarisation of the medium, i.e. of the interaction of the electron with high-frequency phonons and excitons, which can be regarded as weak. In this case one can actually use the ideas about the conductivity band developed for ordered media. The validity of the hypothesis of the "bottom of the conductivity band of the solution" has been demonstrated by experiments on photoemission into solutions and from solutions (see Brodskii and co-workers[64,65]).

to estimate accurately their concentrations in solution from the limiting discharge current and to establish, on the basis of the concentration of the electrons, the concentration dependence of the equilibrium "electronic" potential and to calculate the standard potential of the reversible electron electrode in HMP.[124] An analogous study has been carried out also for ammonia.[103]

Investigation of the bulk-phase reactions of cathodically generated electrons is extremely promising. Since solvated electrons are "rapidly moving" species, i.e. have high diffusion coefficients, in many cases it is more convenient to carry out the reaction in the bulk phase by supplying electrons to the latter than to ensure the transport of the reducible species to the electrode. Furthermore, the change in many solvents of the density of the medium near the sites where the electron is localised promotes the mixing of the solution by convection, which also accelerates the reaction in the bulk phase. Solvated electrons, whose standard potential is close to the standard potentials of alkali metal ions, are one of the most powerful reductants and, since they can be generated at large concentrations, it is possible to achieve many reactions with organic compounds which are difficult to reduce. At the present time there already exist many examples of such processes.[24,26,122–124]

VI. PRINCIPAL ENERGETIC CHARACTERISTICS

The following scheme of the states of solvated electrons can be put forward. The delocalised "dry" electron moves along the "conductivity band", whose bottom is at the level V_0 reckoned from the energy level of the electron *in vacuo*. After solvation, accompanied by a possible rearrangement of the medium and the localisation of the electron, the energy of the self-consistent "electron–medium" system is $E_s^e + E^m$, where E_s^e is the energy of the electron and E^m the energy of the reorganised medium. Apart from the ground and delocalised (quasi-free) states of the electron, excited localised states may arise, which can be regarded as resonances in the continuous spectrum of the electron–phonon system. In an optical transition, which proceeds in accordance with the Franck–Condon principle without change in the "slow" coordinates of the medium, the electron passes from the ground state to one of the excited states or to a "band" state. The medium then remains in the initial state and the excited levels are therefore non-equilibrium in nature and their energies, generally speaking, differ from the energies of the corresponding equilibrium levels. We shall denote the "Franck–Condon" excited levels by an asterisk: for example, $(2p)^*$ is the $2p$ state of the electron not adjusted for consistency with the state of the medium and $(2p)$ is the state adjusted for such consistency.

In order to find the difference between the chemical potentials of the delocalised (quasi-free) and localised solvated electrons ($\mu_d - \mu_s$), it is necessary to take into account the entropy factor. When the Boltzmann formula is used, we obtain

$$\mu_d - \mu_s = -E^e - E^m + V_0 + kT\ln\left[\frac{(mkT/2\pi h^2)^{3/2}a^3c_s}{c_dg}\right]\ . \qquad (22)$$

The formula for the chemical potential of an ideal gas was used here for the delocalised electron and the degeneracy factor g, effectively allowing for the change in the number of states of the phonon subsystem on localisation of the electrons, was introduced; the factor a is approximately equal to the average radius of e_s, i.e. corresponds in order of magnitude to the intermolecular distance, and $c_{s(d)}$ is the concentration of localised (delocalised) electrons. We emphasise that the concept of the "solvated electron" refers to the entire many-particle excess electron + medium system. At equilibrium ($\mu_d = \mu_s$), we have

$$c_s/c_d = c(g)\cdot\exp\left(\frac{V_0 - E_s^e - E^m}{kT}\right) \qquad (23)$$

and the numerical coefficient $c(g)$ attains 10^3 at room temperature even if $g = 1$. We may note that the possible existence of systems in which the localisation of electrons is favoured by thermodynamic factors when the energy of the localised state exceeds that of the delocalised electron at the bottom of the "conductivity band" follows from the previous treatment. In the description of the interaction with electromagnetic radiation, such a system can be regarded as one with inverse population and laser action is possible in it as a result of the energy of the phonon subsystem.

Table 1. Thermodynamic and energy parameters of solvated electrons determined in different experiments.

Type of experiment	Quantity determined
Measurement of the optical absorption spectrum	Oscillator strength of optical transitions (Refs,22, 90–94]; the position of the absorption maximum (corresponds to the energy differences $E_{(2p)*}^e - E_s^e$ if a discrete level exists and to $\sim 2(V_0 - E_s^e)$ if the spectrum corresponds to the photoionisation of e_s and there are no autoionisation states)
Measurement of the photoconductivity excitation spectrum	Photoconductivity threshold, energies of autoionisation states: $V_0 - E_s^e$, $E_{(2p)*}^e - E_s^e$, etc.
Photoemission into a liquid	Position of the bottom of the conductivity band V_0 (if the emission is into the "band"), the energy E_s^e (if there is a tunnel transition to a bound level)
Cathodic generation	Thermodynamic parameters of the ground state of e_s
Photoemission from the solution to a vacuum (vapour)	The photoemission threshold E_s^e
Thermal emission from the solution to a vacuum (vapour)	Free energy of activation for thermal emission $E_s^e + E^m - T\Delta S$
Dissolution of the metal	Free energy of solvation $E_s^e + E^m - T\Delta S$

Table 1 shows a systematic arrangement of the energy and thermodynamic characteristics of solvated electrons obtained in different experiments. It also includes the differences ΔS between the specific entropies of the delocalised and localised states which can be written in the following form by analogy with Eqn.(22):

$$\Delta S = kT\left[c_s\ln\left(\frac{a^3c_s}{g}\right) + c_d\ln\left(\left(\frac{mkT}{2\pi\hbar^2}\right)^{-3/2}\right)\right] \qquad (24)$$

We may note that we never use the thermodynamic characteristics of the electrons *in vacuo*, because they cannot form a homogeneous equilibrium system *in vacuo*.

A number of comments may be made concerning the amount of information yielded by the different experiments indicated in Table 1. The greatest number of data naturally refer to the spectroscopic characteristics of the solvated electron.

However, when the nature of the transition has been established, these data by themselves say nothing about the energy parameters of the different states of e_s. Only careful analysis of the spectroscopic data using the sum rules, additional thermodynamic information, and other data would make it possible to estimate the energy parameters of e_s from the optical spectra. For example, in the measurement of the spectra of e_s in ammonia–alcohol and hydrazine–alcohol mixtures the superficially strange conclusion is reached that the electrons "solvated in ammonia and hydrazine", absorbing at lower frequencies than the "alcoholic" electrons, are favoured by energy factors.[80–82] However, if it is assumed that the spectrum of e_s in ammonia is determined by transitions between bound states and the spectrum of the electron in alcohol is determined by transitions of the "bound state–conductivity band" type then the observed facts can find a natural explanation.

The study of photoemission from a metal to a vacuum, an electrolyte, or a dense electrolyte vapour can yield much information about the position of the solvated electron at the bottom of the conductivity band as a function of the density of the electrolyte.[64,83] Joint measurements of the absorption and photoconductivity spectra and the spectra of the photoemission from the metals to the solution and from the solution to a vacuum would then make it possible to obtain all the energy characteristics of the ground and excited states of e_s. Unfortunately at the present time there are no photoconductivity data at all and the remaining data have been obtained in different systems and are non-systematic.

There exist certain data on thermal emission from solutions,[126] but these have been subjected to a justified criticism[64] in view of the lack in the relevant communication of information about the temperature dependence of the density of the vapour phase (and hence about the energy characteristics of the electron in it).

Table 2. Certain energy characteristics of e_s.

Characteristic	Medium		
	ammonia	HMP	water
Maximum of absorption spectrum, eV	0.88 [14]	0.45 [129]	1.72 [16]
Position of bottom of conductivity band, eV	—	−0.9 [128]	−1.3 [128]
Solvation energy, eV	1.7 [127]	1.0 [126]	1.5 [128]
Solvation entropy, J mol^{-1} K^{-1}	154 [103]. 47 [130]	—	49 [130]. 12 [101]
Threshold of photoemission from the solution to a vacuum, eV	1.53 [131]	0.9 [131]	—

Note. The numerals in square brackets represent references (Ed.of Translation).

Presumably experiments on the electrochemical generation of e_s [24,108,111,124] can yield the most accurate thermodynamic data. The same may be said of data on the thermodynamics of electrochemical reactions obtained from measurements of the e.m.f.'s of cells containing solvated electrons. Unfortunely, the majority of experiments on the cathodic generation of e_s have been carried out in HMP and the e.m.f. data have been obtained solely for electrons in ammonia. Altogether, there exist at the present time an enormous number of different experimental data referring to different systems but a sufficiently complete set of information has been accumulated for only one system—that in ammonia.

Table 2 summarises the known energy and thermodynamic characteristics of solvated electrons in a number of solvents. The very large positive entropies of solvation of the electron in ammonia and HMP, greatly exceeding the entropies of solvation of ions in these solvents, are noteworthy.# Furthermore, the similarity of the heats of solvation of the electron in HMP and ammonia to the thresholds of the photoemission of electrons from these solvents, i.e. the closeness of the value of E^m to zero, is striking, although the photoemission data for these solvents should be regarded as estimates only. Hitherto no experiments have been carried out on the photoconductivity of electrons solvated in liquid solvents, although there is a genuine need for them. Furthermore, from our standpoint, the lack of photoconductivity data to a large extent vitiates the existing extensive information about the spectra of e_s.

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As shown in the introduction, different physicochemical effects associated with the solvated electron have come to the centre of attention during different periods. In particular, during the 1960's, the role of solvated electrons in the radiation chemistry of aqueous systems aroused special interest. At the present time, the study of the details of the dynamics of various reactions involving e_s, especially reactions with charge transfer in polar solutions and vitreous matrices, electrochemical reactions, and complex biochemical processes, including the role of e_s in photosynthesis, is of greatest current interest. Comparison of the data obtained with theoretical conclusions provides unique possibilities for testing various concepts in chemical kinetics.

It follows from the foregoing that numerous problems concerning the characteristics of e_s have not yet been solved. It is especially important to determine theoretically and experimentally the dependence of the transport properties of the solvated electron on temperature over the widest possible range of the latter and to study the photoconductivity. The possibilities of investigating the chemical and electrochemical reactions of solvated electrons and of the unusual compounds such as the electrides formed with their participation have not been fully utilised. There is no doubt that the interest in the role of the solvated electron in photosynthetic processes and in the transfer of excitations in biological systems will grow. Finally, in the immediate future the quantum chemistry of e_s should develop further. It is significant that the theoretical study of an exotic anion such as e_s makes it possible to compare effectively and to assess the approaches developed both in quantum chemistry and in the electronic theory of disordered media.

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