

EXCESS ELECTRONS IN NONAQUEOUS SOLVENTS

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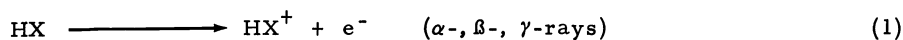
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Abstract - By forced or spontaneous ionization excess electrons are formed in any solid, liquid or gaseous solvent. Depending on the conditions the electrons are localized, or even solvated, like normal ions; or they are delocalized as in the metallic state or as in vacuum. Transitions between these states can be observed by varying the electron concentration or the solvent density resp. Optic, electric, magnetic, thermodynamic and kinetic properties of excess electrons in ammonia and their transitions between different states are described, with a short outlook on other solvents.

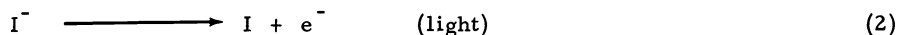
INTRODUCTION

The expression "excess electrons" is coined for electrons dissolved in a solid, liquid or gaseous phase, but not bound to any distinct atom or molecule of the solvent. At high concentration the excess electrons form by mutual interaction the Fermi-gas which is responsible for the metallic properties of all metals. At low concentration the interaction with the solvent leads to widely different (nonmetallic) states with the fully localized or even solvated electron as the one extreme and the delocalized or quasifree electron as the other.

Excess electrons are formed by forced ionization of the solvent or a solute by nuclear radiation



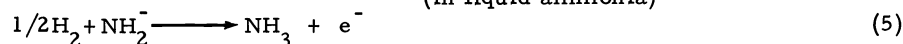
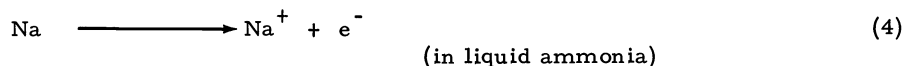
or photochemical processes



or they can be injected from a metallic electrode into the solvent by cathodic polarization (electrolysis) or by the photoelectric effect



or they are formed by spontaneous ionization of dissolved species



The excess electrons (besides those of pure metallic systems) are unstable, their lifetime is restricted by reactions with the solvent or other solutes. Depending on the system and its state the electron lifetime varies within wide limits; it can be well below nano-seconds, e.g. in acidic media, or immeasurably long, e.g. in liquid ammonia. The mobility of the electrons in an electric field can approach in some liquids values as high as $10^4 \text{ cm}^2/\text{V} \cdot \text{sec}$, defining the delocalized state as in vacuum; in other liquids where the electrons are

localized or even solvated mobilities down to $10^{-3} \text{ cm}^2/\text{V}\cdot\text{sec}$ are found, as for normal ions in polar liquids. Finally in solid solvents the electrons can be almost completely immobilized.

A wealth of information on the behaviour of excess electrons in many solvents has been collected (Ref. 1-16); but the following review will predominantly be devoted to electrons in ammonia formed by reaction (1) to (5), but most conveniently by dissolving alkali metals according to reaction (4). The very long electron lifetime in ammonia allows the extensive study of their physical and chemical properties.

MODEL OF EXCESS ELECTRONS

Simplified, in any medium the excess electron can occupy two extreme states, the quasi-free, unbound or delocalized state of high mobility or the bound or localized state of low mobility. The distribution between the two states depends on their energy which can be estimated by the formalisms of wave mechanics (Ref. 17).

The ground state energy (relative to vacuum) is given by two terms, one describing the potential and kinetic energy of the electron, the other describing the change in energy of the solvent due to rearrangement of its molecules in the electric field of the electron. For a quasifree electron the last term is zero because it is delocalized over a large volume and therefore its charge density is too small to cause any reorientation of the solvent molecules. The electron energy then is given only by the long range attractive potential of the polarized medium (polarization: charge shift within the solvent molecules) and the short range repulsive (scattering) potential of the molecules. With proper boundary conditions the Schrödinger equation yields a periodic wave function, extending over the whole system, which confirms the delocalized state of the electron. And it yields the energy of the electron which is identical to the energy V_0 of the lower edge of the conduction band. In liquids of high volume polarizability, like liquid xenon, the attractive forces predominate. The electron energy will be negative ($V_0 < 0$), and energy is gained when transferring the electron from vacuum into the liquid. In liquids like helium with low polarizability $V_0 > 0$ is found.

In the localized state the electron is fixed in a small volume with high charge density which by repulsion leads to the formation of a solvent cavity (bubble); the strong polarization of the medium around the cavity results in a potential dropping steeply inside the cavity where the electron occupies an $1s$ -state. Outside the cavity the wave function goes asymptotically to zero. Inside it has a maximum value which confirms that the electron is confined to the volume of the size of the cavity.

In thermal equilibrium the electron will occupy the lowest energy state; it is delocalized and therefore has a high mobility when $V_0 < E_{1s}$. This case is realized in liquid argon, krypton, xenon, methane, neopentane and others. On the other hand, when $E_{1s} < V_0$ (localization criterium) the electron is localized and has a low mobility, as in helium, neon, n-hexane, n-pentane, benzene etc.

In liquid polar solvents (water, ammonia, alcohols, ethers etc.) the electron always will be in a localized state because the orientational polarization of the solvent molecules around the cavity adds strongly to the attractive potential thus causing rather low lying $1s$ -levels. In these media we even talk of solvated electrons, indicating some similarities with solvated ions. In Fig. 1 the energetics of the two electron states are visualized for several solvents.

The energy of the V_0 - and of the $1s$ -level depend on the density of the solvent; therefore in its overcritical state a continuous transition of localized \rightleftharpoons delocalized electrons can be observed by changing the density as found in helium or ammonia.

The localized electrons also will have (as a "particle in a box") higher energy levels ($2p$, $3p$... etc.) to which they can be excited by photon absorption. Therefore they have an intense light absorption, by which they are easily detected.

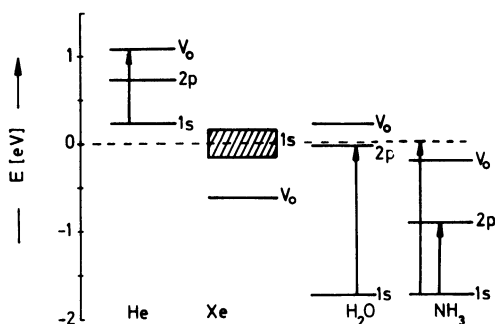


Fig. 1. Energy levels of excess electrons in liquid helium, xenon and ammonia relative to the energy of the electron in vacuum. V_0 is the energy of the delocalized state (lower edge of the conduction band); 1s and 2p indicate energy of the ground state and first excited state of the localized electron. Arrows describe observed optical transitions (Ref. 17).

SOLVATED ELECTRONS IN AMMONIA

a) Volume

The density of metal ammonia solutions is smaller than that of the pure components and decreases with increasing metal concentration (Ref. 18). Normally electrolytes cause the contrary effect owing to electrostriction. Therefore the volume expansion must be due to the presence of solvated electrons which break the structure in ammonia. In terms of the cavity model, an idea of which was born on the basis of the density measurements, the electron volume of about 75 ml/mol corresponds to a cavity radius of $3.1 \cdot 10^{-8}$ cm.

b) Light absorption

The most obvious property of electrons in ammonia is the intense blue colour of their solutions caused by light absorption in the red, but extending to the near infrared and to the near ultraviolet spectral range. The wide structureless absorption band (Fig. 2; maximum absorption at $\lambda(\text{max}) \approx 1500$ nm; decadic molar extinction coefficient $\epsilon(\text{max}) \approx 50000 \text{ l mol}^{-1} \cdot \text{cm}^{-1}$; half width almost 1 eV; Ref. 19) is mainly due to the 1s \rightarrow 2p transition.

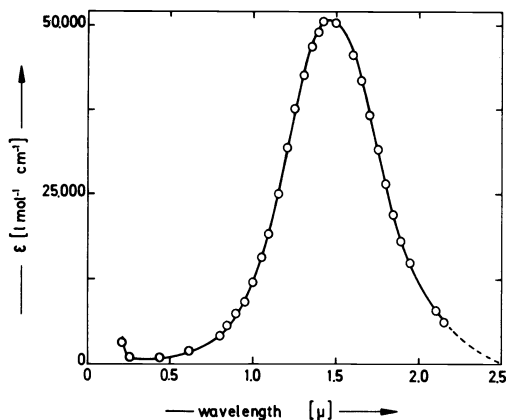


Fig. 2. Absorption spectrum of solvated electrons in ammonia (-50°C ; ϵ is the decadic absorption coefficient; Ref. 19).

According to the theory of a particle in a box the energy of the transition ΔE or the wavelength of light absorption

$$\Delta E = E_{2p} - E_{1s} \sim 1/\lambda \sim 1/R^2 \quad (6)$$

depend on the radius R of the cavity.

The wide absorption spectrum is due to thermal fluctuations of the cavity radius around a most probable (average) value, which defines $\lambda(\max)$. The more sophisticated theory taking into account orientation and polarization of the ammonia molecules around the cavity describes the main features of the spectrum well, assuming a most probable cavity radius around $3 \cdot 10^{-8}$ cm. Only the high energy tail of the spectrum is not understood on this basis. It might be due to transitions to higher bound states ($3p$, $4p \dots$) or even to the conduction band (V_0 -level). According to eq. (6) the compression of the cavity or its thermal expansion by outside pressure or temperature increase cause a blue- and a red-shift of the spectrum (Ref. 20).

c) Nonmetal-metal transition

In Fig. 3 the equivalent conductivity $\Lambda = 1000 \sigma/c$ (σ , specific conductivity, c , molar concentration) of sodium-ammonia solutions is plotted versus the sodium mole fraction x (Ref. 21; thumb rule: $c \approx 40x$).

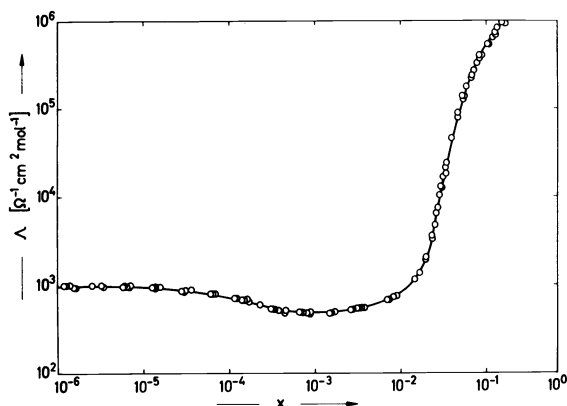


Fig. 3. Equivalent conductivity of sodium in ammonia (-35°C ; x mole fraction of sodium; Ref. 21).

As in normal electrolyte solutions the equivalent conductivity approaches with dilution a constant value, given by the sum of the equivalent conductivities $\lambda^0(i)$ of cations and anions, which here is close to $1000 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Subtracting the value for the sodium ion ($\lambda^0(\text{Na}^+) \approx 130 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) yields $\lambda^0(e^-) \approx 870 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ or the mobility $\mu(e^-) = \lambda^0(e^-)/F \approx 0.87 \cdot 10^{-2} \text{cm}^2 \text{V}^{-1} \cdot \text{sec}^{-1}$ (F , Faraday number). This value is considerably above that expected on the basis of Walden's rule ($\lambda(i) \sim 1/(\eta R(i))$; η , viscosity of the solvent, $R(i)$ radius of the solvated particle) for a particle as "large" as the electron. It excludes a normal migration of the electron cavity in the viscous medium. However the electron can tunnel or jump from its cavity into a neighbouring solvent site where by thermal fluctuation of the solvent molecules a shallow potential trap is formed. Here it finally forms the stable cavity again.

The steep increase in equivalent conductivity by almost three powers of ten at concentrations above $x = 0.02$ ($\approx 1\text{M}$) defines the transition to the metallic state which can be formulated as a concentration dependent equilibrium



It is shifted to the right by increasing temperature and to the left by increasing pressure (Ref. 21, 22).

The highly concentrated solutions have all the characteristics of a liquid metal such as high thermal conductivity, metallic reflectivity, Knight shift etc. The mechanism of the transition is not understood at present, but, qualitatively it can be described by theories as contradicting as the theory of the Mott-transition (Ref. 23) and that of the percolation concept (Ref. 24).

d) Paramagnetic-diamagnetic transition

In the highly diluted metal ammonia solutions the dissolved metal or rather the solvated electrons have a paramagnetic mole susceptibility as calculated according to the Curie law for electrons with spin $1/2$. The ESR spectrum displays only one sharp line. This proves that the solvated electron is an individual particle without magnetic interaction with cations or solvent molecules (which would result in further line splitting).

With increasing concentration the susceptibility decreases (Fig. 4; Ref. 18, 25) and becomes negative (diamagnetic) around $x = 0.02$.

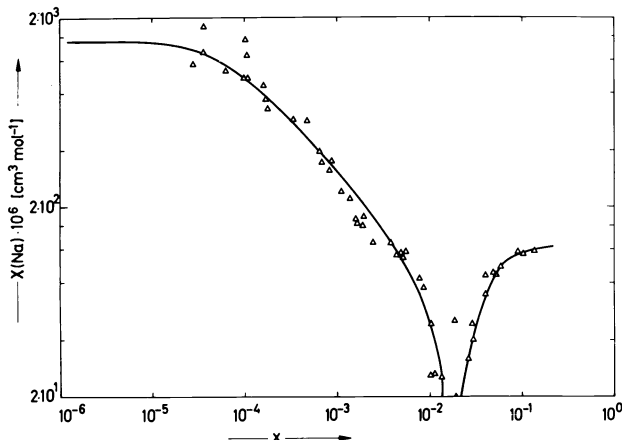


Fig. 4. Molar magnetic susceptibility of sodium in ammonia (-35°C ; x mole fraction of sodium; Ref. 18, 25).

The diamagnetic state is formed by spin compensation of two electrons, which again can be described by a concentration dependent equilibrium



With increasing temperature it is shifted to the left. The optical spectra as well as the mobilities of electrons in the paramagnetic and diamagnetic state differ only very little (Ref. 21, 26).

Parallel to the transition to the metallic state as reflected by the mobility increase above $x = 0.02$, the paramagnetic susceptibility increases with concentration and finally the temperature independent paramagnetism of the Fermi gas (Pauli-Landau paramagnetism) is obtained.

e) Localized-delocalized transition

Radiation chemical experiments (reaction (1); Ref. 27) revealed that in supercritical ammonia at high densities solvated electrons are formed as detected by their intense light absorption. The radiation chemical yield (number of electrons formed per unit mass of ammonia per unit radiation dose) does not depend on the density down to 0.1 g/cm^3 ; but below this "critical" density it very sharply drops to zero. It is concluded that only above this critical density the interaction of the primarily free electron with the solvent is strong enough to form the localized or solvated state (the solvation process in normal liquids requires less than 50 p sec; Ref. 28, 29). Below the critical density the electrons are in a delocalized state.

This is proven by measurement of the mobility of electrons injected by the photoelectric effect according to reaction (3) into ammonia vapour of varying density (Fig. 5; Ref. 30). At high densities the electrons have the low mobility of the localized state (extrapolation to the liquid density gives about the same value as obtained from conductivity experiments). But with decreasing density the mobility steeply rises by five powers of ten to values of the delocalized state. The localized-delocalized transition can be described by the equilibrium



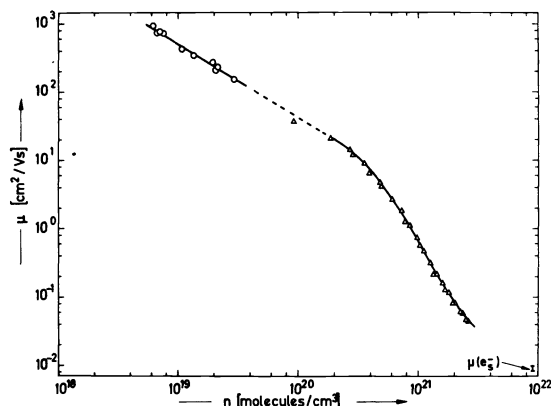
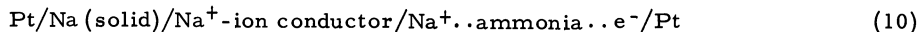


Fig. 5. Mobility of excess electrons in ammonia vapour (n , number density of ammonia molecules; \bullet -60 to -35°C ; Δ 130°C ; $\mu(e_{\text{sol}}^-)$ indicates the mobility of solvated electrons in liquid ammonia at -35°C (Ref. 30).

which is shifted to the right by increasing solvent density and to the left by increasing temperature.

f) Thermodynamics of sodium-ammonia solutions

Numerous investigations on the thermodynamic properties of metal ammonia solutions have been carried out with partly contradicting results in restricted temperature and concentration ranges. Recently we succeeded (Ref. 31) by electrochemical means to measure the chemical potential $\mu(\text{Na}^+)$ of dissolved sodium (relative to that of solid sodium) in the concentration range from $x = 10^{-6}$ to saturation $x = 0.16$, in the temperature range from -75 to 25°C and at pressures up to 500 bar. The cell used was



The left hand side of the cell with the solid Na^+ -ion conductor ($\text{Na}^+\text{-}\beta\text{-alumina}$) responds reversibly to Na^+ -ions, the right side responds to electrons. The EMF of this cell

$$E = E^{\circ} - \frac{RT}{F} \ln (a(\text{Na}^+) \cdot a(e^-)) \quad (11)$$

(E° , standard potential with a hypothetical 1M ideal solution of Na^+ -ions and electrons) is equivalent to the osmotic work obtained by the dissolution of 1 mol solid sodium in solutions with the activities $a(\text{Na}^+)$ and $a(e^-)$. The temperature and pressure dependences give the partial molar entropy $S^{\circ}(\text{Na})$, molar heat capacity $C_p^{\circ}(\text{Na})$ and volume $V^{\circ}(\text{Na})$ of the dissolved sodium, again relative to those of solid sodium.

Very clearly in the enthalpy diagram (Fig. 6) two plateaus are recognized describing the enthalpy of the dissolved sodium with electrons in the paramagnetic and in the diamagnetic state resp. The enthalpy drop between the plateaus indicates that spin compensation is an exothermic process ($\Delta H^{\circ} \approx -30 \pm 1 \text{ kJ mol}^{-1}$; in accordance with the temperature dependence of magnetic data; Ref. 25). The other drop above $x = 0.02$ is due to the transition to the metallic state, which also is exothermic.

The concentration dependence of the chemical potential $\mu(\text{Na})$ also reflects the two transitions. Below $x = 0.02$ it is definitely shown that the diamagnetic species contains, besides the two spin paired electrons, one cation to diminish the Coulombic repulsion of the two electrons. The spin-pairing consequently must be described by



with the equilibrium constant $K = 6 \cdot 10^4 \text{ M}^{-2}$ at -35°C . The solutions behave ideal only below $x = 10^{-5}$ where eq. (8) or (12) is shifted primarily to the left and the Coulombic interaction is negligible. Extrapolation of the EMF concentration curve to the ideal standard state 1M

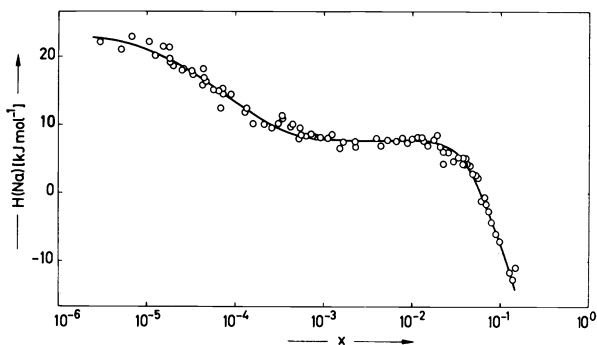


Fig. 6. Partial molar enthalpy of sodium in ammonia relative to that of solid sodium (-35°C ; x mole fraction of sodium; Ref. 31).

and taking into account the newly determined standard potential of the sodium electrode ($E^{\circ}(\text{Na}^+) = -1.828 \pm 0.018 \text{ V}$ at -35°C ; Ref. 32) relative to the normal hydrogen electrode (NHE) yields the standard electrode potential of the solvated electrons $E^{\circ}(e^-) = -1.908 \pm 0.019 \text{ V}$, practically independent of temperature between -65 and 25°C . This value falls well within the literature data scattering between -1.86 to -2.04 V (Ref. 33).

The partial molar volume $V^{\circ}(\text{Na})$ as obtained from dE/dp also reflects the two transitions by a characteristic concentration dependence. In very dilute solutions where density measurements fail to give results $V^{\circ}(\text{Na})$ is larger than reported (Ref. 12) (the absolute value is around $74 \pm 3 \text{ cm}^3/\text{mol}$ which is mainly due to the large electron cavity with $R \approx 3 \text{ \AA}$).

Surprisingly, the partial molar heat capacity $C_p^{\circ}(\text{Na})$ is very negative, $-350 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ at infinite dilution; this as well as the rather positive entropy $S^{\circ}(\text{Na})$ of $60 \pm 2 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ or the large volume $V^{\circ}(\text{Na})$ is due to the structure breaking (cavity forming) action of the electrons. Normal electrolytes never have C_p° , S° or V° values of this magnitude. Due to electrostriction or structure enhancing these quantities very often have even opposite sign.

g) Thermodynamics of the electron reaction with ammonia: dissociation constant of ammonia

The electrons in ammonia as in other solvents are unstable; they react with the solvent



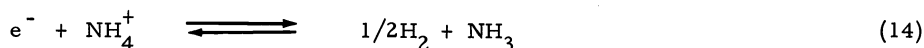
until an equilibrium is achieved which is far on the right side. This decomposition reaction is the reverse of the formation reaction (5) in which low electron concentrations are formed.

The electrochemical cell (10) with dissolved sodium amide (10^{-3} to 10^{-2} M) and saturated with hydrogen has been applied to obtain the thermodynamic data of reaction (13) (Ref. 32). The EMF was evaluated to obtain the activities of solvated electrons and Na^+ -ions (compare eq. (11)) which with known concentrations of Na^+ and NH_2^- -ions and their activity coefficients finally yield the equilibrium constant K ; from its temperature dependence the enthalpy ΔH° is obtained:

$$K = 1.5 \cdot 10^6 \text{ M bar}^{1/2}; \Delta G^{\circ} = -28 \pm 3, \Delta H^{\circ} = -88 \pm 4 \text{ kJ/mol (all at } -35^{\circ}\text{C)}$$

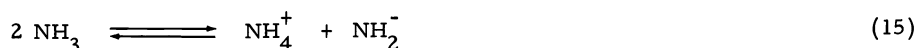
The dissociation constant for the weak electrolyte $\text{NaNH}_2 (\text{NaNH}_2 \rightleftharpoons \text{Na}^+ + \text{NH}_2^-)$ was determined by conductivity: $K = 1.9 \cdot 10^{-5} \text{ M}$, $\Delta H^{\circ} = -8 \pm 1.5 \text{ kJ/mol}$ (both at -35°C); ΔH° is negative as that of many weak acids in water above room temperatures).

The standard potential of the electron electrode vers. NHE, $E^{\circ}(e^-) = -1.908 \text{ V}$ and its temperature dependence gives the free enthalpy change and enthalpy change of reaction



$$K = 2.4 \cdot 10^{40} \sqrt{\text{bar}} / M; \quad \Delta G^\circ = -184 \pm 2, \quad \Delta H^\circ = -182 \pm 4 \text{ kJ/mol } (-35^\circ).$$

Subtracting eq. (14) from eq. (13) yields



i. e. the autoprotolysis reaction of ammonia. The thermodynamic data are $K = 6 \cdot 10^{-35}$; $\Delta G^\circ = 156 \pm 3$, $\Delta H^\circ = 94 \pm 6 \text{ kJ/mol } (-35^\circ\text{C})$.

The good agreement of the ΔH° for reaction (14) and (15) determined by EMF measurements with those obtained by calorimetry (Ref. 34, 35) confirms that also the dissociation constant of ammonia given here is rather precise. It is in the range between 10^{-25} and 10^{-37} given by other authors for temperatures between 25 and -50°C (Ref. 36).

h) Thermodynamic of other equilibrium reactions

Also the thermodynamic data of other chemical equilibria in which solvated electrons are involved can be obtained by means of the electrochemical cell (10). As an example, the data for the formation of aromatic radical anions are summarised



(φ , dissolved aromatic hydrocarbon), which were obtained by potentiometric titration with a sodium ammonia solution (Ref. 37). The titration curves for nine different aromatic substances are displayed in Fig. 7.

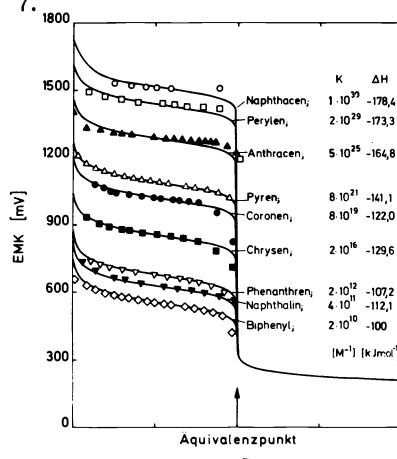


Fig. 7. Potentiometric titration curves of aromatic hydrocarbons in liquid ammonia with sodium ammonia solution (-40°C ; Ref. 37).

In pure ammonia the potential is given by the activity of the added sodium according to eq. (11). In the presence of a reactive partner the electron activity depends on the equilibrium constant of reaction (16)

$$K = \frac{[\varphi^-]}{[e^-] \cdot [\varphi]} \quad (17)$$

and the concentrations of φ and φ^- . Eqs. (11) and (17) combine to give

$$E = E^\circ - \frac{RT}{F} \ln \frac{[\text{Na}^+][\varphi^-]}{[\varphi]} + \frac{RT}{K} \ln K \quad (18)$$

i. e. the EMF is the more positive the larger the equilibrium constant K (activity coefficients neglected). The data are included in Fig. 7.

K , ΔG° and ΔH° of reaction (16) as calculated from the EMF of eq. (18) and its temperature dependence are given (besides solvation effects) by the electron affinities of the aromatic molecules which again are related to the energies of their lowest unoccupied molecular orbital (LUMO). Thus there is a linear relationship between the MO-coefficient x_α (Ref. 38) and the thermodynamic data as demonstrated in Fig. 8.

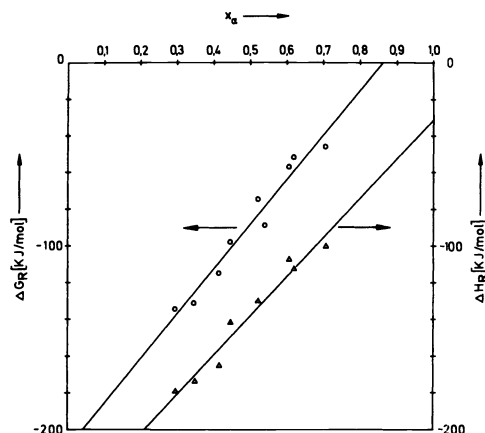
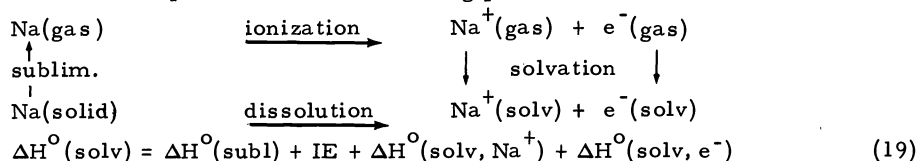


Fig. 8. Relationship between the thermodynamic data of the electron attachment reaction of aromatic hydrocarbons in ammonia and their energy parameter of the MO theory (Ref. 37).

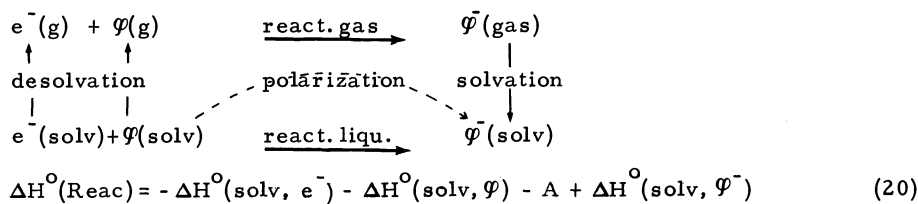
i) Energetics of solvated electrons

The EMF of cell (10) yields the enthalpy change of dissolving solid sodium to form Na^+ -ions and solvated (paramagnetic) electrons, $\Delta H^\circ(\text{sol}) = 22 \pm 0.4$ kJ/mol. By a Haber-Born cycle the reaction can be separated into the following process



The sublimation enthalpy $\Delta H^\circ(\text{subl})$ of sodium is 105 ± 5 kJ/mol, its ionisation energy IE is 496 kJ/mol; therefore the sum of the solvation enthalpies $\Delta H^\circ(\text{sol})$ of Na^+ -ions and electrons is -580 ± 6 kJ/mol. The solvation enthalpy of the electron can only be determined if that of the Na^+ -ion is known; but the latter cannot be measured. Estimations vary, depending on the method, between -545 and -432 kJ/mol (Ref. 39, 40), leading to a solvation enthalpy of the electrons in ammonia between $\Delta H^\circ(\text{sol}, \text{e}^-) = -44$ and -156 kJ/mol. The latter value is considered to be better because it fits the adopted theory; but it is not necessarily the best. From electrochemical experiments a value of -130 ± 3 kJ/mol is deduced (Ref. 41).

With the data of section h) we can obtain another estimation of $\Delta H^\circ(\text{sol}, \text{e}^-)$. Reaction (16) whose enthalpy change $\Delta H^\circ(\text{Reac})$ we know for nine aromatic molecules can be separated into the following process:



The electron affinity A is known (Ref. 42). The difference $\Delta H^\circ(\text{pol}) = -\Delta H^\circ(\text{sol}, \varphi) + \Delta H^\circ(\text{sol}, \varphi^-)$ can be calculated according to Born as the change in polarization energy of the solvent when transferring unit charge from vacuum to a spheric particle with radius r in a dielectric medium with dielectric constant ϵ (Ref. 43).

$$\Delta H^\circ(\text{pol}) = \frac{Ne^2}{2r} \left\{ \frac{1}{\epsilon} - 1 + \frac{T}{\epsilon} \frac{d\epsilon}{dT} \right\} \quad (21)$$

(N, Loschmidt number, e, electronic charge)

The Born approximation can be applied for large ions where due to the small charge density no special solvation effects are expected.

For the aromatic substances of Fig. 7, $\Delta H^{\circ}(\text{Reac})$ varies between -100 and -178 kJ/mol, the electron affinity between 8 and 106 kJ/mol and $\Delta H^{\circ}(\text{pol})$ between -164 and -188 kJ/mol. With these quantities we get according to eq. (20) the solvation enthalpy of the electrons in ammonia $\Delta H^{\circ}(\text{solv}, e^{-}) = -84 \pm 9$ kJ/mol as an average. This value could be as good as the other reported values for which a number of assumptions have been made. The wide spread of data for the same property reflects the general difficulty encountered when trying to resolve thermodynamic data of electrolytes into the contribution of the individual ions. But whatever value is correct it follows that the solvation enthalpy of the electron in ammonia is small compared to that of normal univalent ions (< -200 kJ/mol). This is due to the structure breaking effect of the electrons which requires energy. The large positive solvation entropy of the electrons $\Delta S^{\circ}(\text{solv}, e^{-}) = 170 \pm 20$ J/mol·K (Ref. 31, 37, 44) also is due to the dissolution of the structure.

h) Kinetics of electron reactions

The very negative standard potential of the solvated electrons or the equilibrium constant of reaction (13) $K = 1.5 \cdot 10^6 \text{ Mbar}^{-1/2}$ show that the solvated electrons are instable with respect to hydrogen formation. Nevertheless the hydrogen formation proceeds extremely slowly (the lifetime of sodium ammonia solutions exceeds many months). Without giving any proof we might say that the formation of hydrogen is prevented by a high overvoltage (in water the corresponding reaction (13) has a half-time $< 10^{-3}$ sec). Another explanation can be given on the basis of the transition state theory of chemical kinetics whereby the rate constant is expressed in terms of a universal frequency factor and the activation parameters ΔS^{\ddagger} and ΔH^{\ddagger}

$$k = \frac{RT}{Nh} \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \quad (22)$$

(h Planck constant).

The activation parameters are given by the difference of the thermodynamic quantities S or H of the activated complex A^{\ddagger} and the reaction partners e^{-} and A ; the activation entropy is given by

$$\Delta S^{\ddagger} = S^{\ddagger}(A^{\ddagger}) - S(e^{-}) - S(A) \quad (23)$$

For all known electron reactions, irrespective of rate, the activation enthalpy ΔH^{\ddagger} is close to 16 kJ/mol; therefore it must be the entropy term in (22) which is responsible for the slow reaction. It is indeed rather negative because of the very positive entropy of the solvated electron in ammonia.

Other factors may contribute as reasons for a slow electron reaction in ammonia as compared to water. An example is benzene that does not react at all with electrons in ammonia but relatively fast in water to form cyclohexadiene. Preceding the hydrogenation is the formation of the radical anion $C_6H_6^{\cdot -}$ which is protonated by the solvent and then reacts further



The equilibrium (24) with benzene is far to the left in both solvents (Ref. 37, 45); but it is disturbed in water by the protonation step (25) which does not proceed in ammonia because of its small dissociation constant. Our investigations in water-ammonia mixtures (Fig. 9) prove this concept displaying the influence of the entropy term and the protonation rate on the overall rate constant (Ref. 45).

The reduction or hydrogenation reactions in ammonia with dissolved alkali metals are known as Birch reactions (Ref. 46). As useful as they are in organic chemistry, little is known about their kinetics.

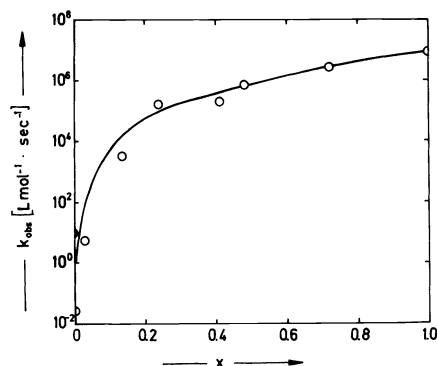


Fig. 9. Second order rate constant for the reaction of benzene with solvated electrons in ammonia-water mixtures (25°C; x mole fraction of water; Ref. 45).

The electron reactions of higher aromatic hydrocarbons and many other substances in ammonia are diffusion controlled, their rate constant follows the Smoluchowski equation of diffusion controlled reactions:

$$k_{\text{diff}} = 4\pi\sigma DN/1000 \left[\text{M}^{-1} \text{sec}^{-1} \right] \quad (26)$$

where the collision parameter σ is the distance from which the electron can jump or tunnel to the reaction partner, and D the sum of the diffusion coefficients of both. The upper limit of the diffusion controlled rate constant in ammonia is about $10^{11} \text{M}^{-1} \text{sec}^{-1}$, about four fold larger than in water because of the lower viscosity.

ELECTRONS IN OTHER SOLVENTS

a) Absorption spectra

As stated before, the excess electrons exhibit an absorption spectrum whenever they are in a localized state. The spectra in a series of polar solvents which have solvated electron states are displayed in Fig. 10 (Ref. 47).

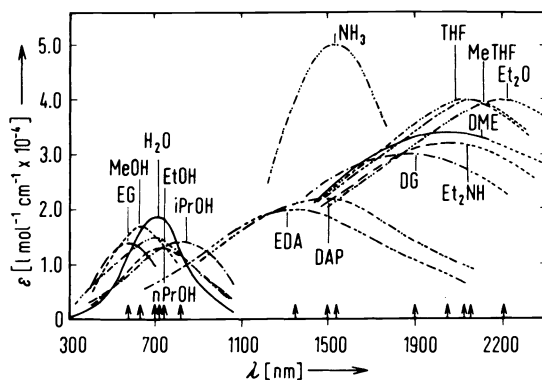


Fig. 10. Absorption spectra of solvated electrons in polar solvents at room temperature (H_2O , water; MeOH, methyl alcohol; EtOH, ethyl alcohol; iPrOH, isopropyl alcohol; nPrOH, n-propyl alcohol; EG, ethylene glycol; NH_3 , ammonia (-33°C); EDA, ethylenediamine; DAP, 1,3-diaminopropane; Et_2NH , diethylamine; DG, diglyme; DME, dimethoxyethane; Et_2O , diethyl ether; THF, tetrahydrofuran; MeTHF, methyl tetrahydrofuran Ref. 47).

All spectra are rather broad and lack any structure. A relationship clearly exists between $\lambda(\text{max})$ and the nature of the solvating group: in solvents containing OH-groups (water, alcohols) the absorption maximum is located around 700 nm, in solvents having NH_2 -groups (ammonia, amines) between 1200 and 1600 nm, and finally in ethers between 1900 and 2200 nm.

All attempts to find a simple relationship between $\lambda(\text{max})$ and typical macroscopic properties of the solvent (dielectric constant, refractive index or polarizability, surface tension etc.) have failed. However since the size of the cavity in which the electrons are trapped plays a decisive role in determining its energy (comp. eq. (6)) the dependence of $\lambda(\text{max})$ on the solvent might indicate a variation of cavity size. An evaluation on the basis of the simplified theory (Ref. 47) leads to cavity radii of around 0.9 to 1.5 Å in water and alcohols, 2.5 to 3 Å in ammonia and amines and 3.1 to 4 Å in ethers. An independent experimental prove of this, as we have for ammonia, is still missing.

In water and ammonia vapour at high densities the same spectra are observed as for the liquid (Ref. 27). Only little information is available about the absorption spectra of localized electrons in nonpolar solvents. In hexane, cyclohexane, methylcyclohexane and isopentane the absorption maximum is located at slightly higher wave lengths than in ethers (Ref. 48). According to theory the electrons even in helium should absorb light (Ref. 49).

b) Electron mobilities

In polar solvents (alcohols, ethers, amines, water, ammonia) the mobility of solvated electrons is between 10^{-3} and $10^{-2} \text{ cm}^2/\text{V}\cdot\text{sec}$ (Ref. 50); it is two to five fold larger than that of normal ions. To a first approximation it increases with decreasing viscosity η of the solvent. However Walden's rule ($\mu \sim 1/\eta$) can not be expected to apply strictly because of different solvation structure due to different structure of the solvents or the solvent molecules. But in water and ammonia the mobility of electrons and that of normal large ions have the same temperature coefficient as the fluidity ($\sim 1/\eta$) of the solvent. This proves that the viscosity has a decisive influence on the mobility of the solvated electrons, although they may still move by jumping or tunneling.

In nonpolar solvents the electron mobility varies between 10^{-3} and $3 \cdot 10^3 \text{ cm}^2/\text{V}\cdot\text{sec}$ (Ref. 50) A general trend is obvious: the mobility is the higher the lower the energy V_0 of the conduction band (Fig. 11).

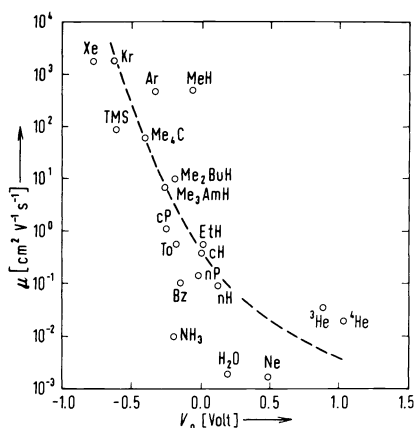


Fig. 11. Electron mobility μ in liquids of varying V_0 values, just below the normal boiling points or at room temperature (liquified rare gases He, Ne, Ar, Kr, Xe; MeH, methane; TMS, tetramethylsilane; Me_4C , neopentane; Me_2BuH , 2,3-dimethyl butane; Me_3AmH , 2,2,4-trimethylpentane; cP, cyclopentane; cH, cyclohexane; EtH, ethane; nP, n-pentane; nH, n-hexane; T₀, toluene; Bz, benzene; NH_3 , ammonia; H_2O , water; Ref. 50).

Three groups can be distinguished.

- 1.) In liquid helium and neon, the electrons are localized because of the high energy of the conduction band ($V_0 > E_{1s}$); consequently the electron mobilities are small ($\leq 10^{-2} \text{ cm}^2/\text{V}\cdot\text{sec}$) Walden's rule is roughly followed.
- 2.) In liquid argon, krypton, xenon, methane, tetramethylsilane, electrons have high mobility

($>4 \cdot 10^2 \text{ cm}^2/\text{V}\cdot\text{sec}$), comparable to those of semiconductors. They indicate the quasifree or delocalized electron state in solvents of low lying conduction band ($V_0 < E_{1s}$).

3.) In solvents with electron mobilities between the extremes of group 1 and 2 the lower edge of the conduction band is slightly above the $1s$ -level. Therefore as in semiconductors thermal activation of the localized electrons into the conduction band is possible. The observed mean mobility is approximated by the product of mobility and the relative concentration of electrons in the delocalized state. With temperature increase a gradual transition from the localized to the delocalized state according to eq. (9) is possible.

c) Kinetics

In aqueous systems the kinetics of electron reactions with almost a thousand substrates have been investigated (Ref. 51). In nonaqueous systems only sparse kinetic information is available. The rate constant of reaction



cover a range between $k < 1$ up to $10^{15} \text{ M}^{-1} \text{ sec}^{-1}$. However the rate constant describes only the overall rate with which the electrons disappear from the solution without revealing any details of a reaction mechanism.

The experimental data so far show the electron reaction rates to be strongly dependent on the solvent

- 1) via its viscosity or other properties which influence the mobility or the rate of diffusion of the electrons
- 2) via its influence on the properties or the reactivity of the electrons and their reaction partners
- 3) via its dielectric constant which is decisive for the Coulombic interaction in reactions with ions
- 4) via its participation in consecutive reactions.

Point 1 is demonstrated by Fig. 12 in which the rate constant of selected reactions in a series of solvents are plotted vs. the electron diffusion coefficient as calculated from the mobilities of Fig. 11.

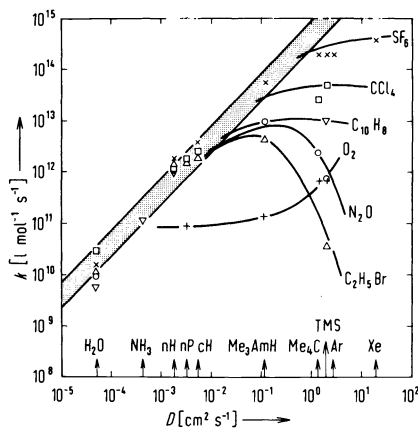


Fig. 12. Relation between rate constant k of some reactions of excess electrons and their diffusion coefficient in several solvents. The reaction partners are given on the right-hand side, the solvents on the abscissa. The hatched area is calculated for diffusion-controlled reactions according to eq. (26) with the collision distance $\sigma = 3 \cdot 10^{-8}$ to $1 \cdot 10^{-7}$ cm. (H_2O , water; NH_3 , ammonia; nH, n-hexane; nP, n-pentane; cH, cyclohexane; Me_3AmH , trimethylpentane; Me_4C , neopentane; TMS, tetramethylsilane; Ar, argon, Xe, xenon; C_{10}H_8 , naphthalene; Ref. 50).

The relation between the rate constant and the diffusion coefficient according to eq. (26) for diffusion controlled reactions with $\sigma = 3 \cdot 10^{-8}$ to 10^{-7} cm is shown hatched. All reactions with rate constants in the hatched area are diffusion controlled. Here the individual

properties of the solvent, of the reaction partner and of the electron are without influence on the reaction rate. The sole decisive factor of the rate is the electron diffusion coefficient.

For non diffusion controlled reactions point 2 has to be considered, which in the transition state theory is covered by the activation entropy in eq. (22). The activation enthalpy ΔH^\ddagger (being almost constant for all reactions in all solvents) has only minor impact on the rate. It is assumed that the electron reactions proceeds via tunneling (Ref. 52). Since tunneling is possible only between states of identical energies the electron transfer to the reaction partner will occur only when it has a free orbital in the energy range of the excess electron, which in turn depends on the solvent. Thus a relation between rate constant and solvent is given. The rate constant depends on tunneling probability which is given besides other factors by the density of energy states. Since probabilities can be expressed by an entropy term the tunneling concept leads back to the transition state theory.

Point 3 is a rather trivial effect to be considered for all reactions between charged particles. In accordance with theory, the rates of solvated electron reactions with negative ions are decreased, with positive ions increased with decreasing dielectric constant of the solvent (Ref. 53).

Participation of the solvent in consecutive reactions (point 4) is of importance whenever the electron attachment is governed by an equilibrium reaction like eq. (24) which is unfavourably to the left and has to be disturbed by succeeding reactions. The electron reaction with benzene in water ammonia mixtures given above stands as one example among many.

CONCLUDING REMARKS

In the preceding pages we have tried to explain some of the properties of excess electrons. By far we do not understand them all, and many problems have still to be solved. Not only from the academic point of view is it worthwhile to be engaged in these studies. Many chemical, biological or even technical aspects might be involved which could redeem our efforts. At least the concepts of three different technical processes (Ref. 54) are the results of research on excess electrons.

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