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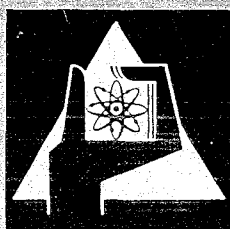
Institut für Kernverfahrenstechnik

Beiträge zur Diskussionstagung über

Solvatisierte Elektronen in festen und flüssigen Lösungen

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Isothermal Compressibilities of Sodium- and Potassium-Ammonia Solutions

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The isothermal compressibility of alkali metal-ammonia solutions, measured at several pressure intervals up to 1000 at, is compared with the adiabatic compressibility and is used to calculate the apparent molar volume of the dissolved metal at various pressures.

Die in mehreren Druckbereichen bis 1000 at gemessene isotherme Kompressibilität von Alkalimetall-Ammoniaklösungen wird mit der adiabatischen Kompressibilität verglichen und zur Berechnung des scheinbaren Molvolumens des gelösten Metalls bei verschiedenen Drücken herangezogen.

Whereas adiabatic compressibilities of metal-ammonia solutions, as derived from sound velocity measurements, have been known for some time, no data on the isothermal compressibility of these solutions were available. By applying high pressure techniques we have measured integral isothermal compressibilities of Na-NH₃ and K-NH₃ solutions in the pressure intervals of 60–160 at, 100–500 at, and 500–1000 at, at temperatures between –30 and –60°C.

To cover several pressure ranges two different autoclave systems were used, employing the compression of edge welded steel bellows (applicable up to 200 at) and a piston displacement method (up to 2000 at), respectively.

The isothermal compressibility of the Na-NH₃ and K-NH₃ solutions increases with increasing metal concentration, opposite in tendency to the behavior of normal electrolyte

solutions, e.g. KI-NH₃. It increases with increasing temperature.

For comparison with existing data on the adiabatic compressibility of metal-ammonia solutions the low pressure isothermal compressibility (60–160 at) of both Na-NH₃ and K-NH₃ solutions at –35°C, found to be alike within the limits of error, was used. Although similar in trend with concentration, the isothermal compressibility, as expected, is higher than the adiabatic compressibility. The ratio of the two, i.e. the ratio of the specific heats, as function of concentration shows a maximum at about 2.4 MPM \cong 1 mole/l (Fig. 1).

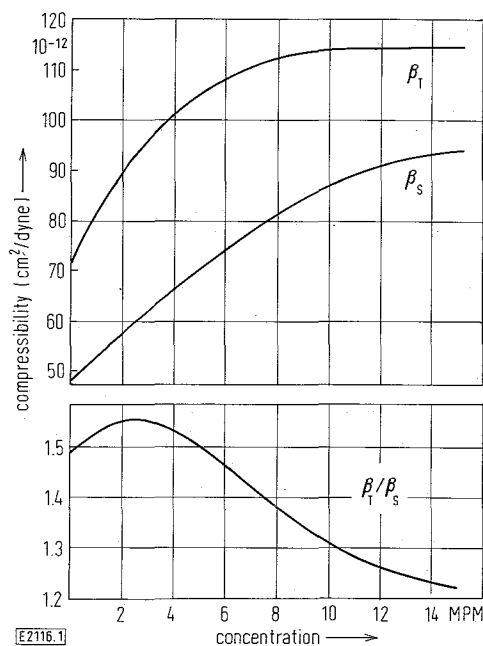


Fig. 1

Concentration dependence of the isothermal and adiabatic compressibility of potassium-ammonia solutions and of the ratio of specific heats c_p/c_v

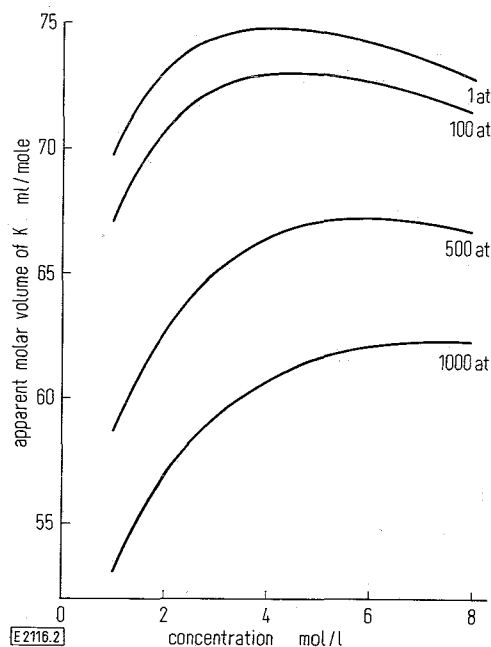


Fig. 2

Concentration dependence of the apparent molar volume of potassium in ammonia at different pressures

From the densities of K-NH₃ solutions at 1, 100, 500, and 1000 at the apparent molar volume of dissolved potassium as function of concentration at these pressures was calculated (Fig. 2). The data were used to estimate the isothermal compressibility of potassium in the dissolved state, anticipated to relate to the compressibility of the solvated electrons in their various solution states in liquid ammonia.

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Pressure and Temperature Dependence of Optical Properties of Potassium-Ammonia and of Potassium Iodide-Ammonia Solutions

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The absorption spectra of dilute potassium-ammonia solutions, in which solvated electrons are present, and of potassium iodide-ammonia solutions (ctts-spectrum) are in a restricted temperature range shifted with increasing temperature to longer wave-lengths and with increasing pressure to shorter wave-lengths. These shifts are interpreted in terms of thermal expansion and of compression resp. of the solvation shells around the electrons and the iodide ions resp. (cavities) the size of which determines the wave-length of light absorption. At higher temperature however the effects reverse their signs, indicating that the relationship between cavity size and position of the absorption maximum is not unambiguous.

The reflectivity of concentrated potassium ammonia solutions increases with temperature but decreases with pressure. The reflectivity behaviour of the solutions therefore parallels their behaviour of electrical conductivity.

Die Absorptionsspektren verdünnter Kalium-Ammoniaklösungen, in denen solvatisierte Elektronen vorliegen, und die von Kaliumjodid-Ammoniak-Lösungen (ctts-Spektren) werden in beschränktem Temperaturbereich mit steigender Temperatur in den längerwelligen, mit steigendem Druck in den kürzerwelligen Spektralbereich verschoben. Diese Verschiebungen werden auf die thermische Ausdehnung bzw. die Kompression der Solvathüllen zurückgeführt, in denen die Elektronen bzw. die Anionen eingefangen sind und deren Größe die Wellenlänge der Lichtabsorption bestimmt. Bei höheren Temperaturen haben die Effekte jedoch entgegengesetztes Vorzeichen. Das zeigt, daß der Zusammenhang zwischen Größe der Solvathülle und Lage des Absorptionsmaximums nicht eindeutig ist.

Die Reflektivität der konzentrierten Kalium-Ammoniaklösungen steigt mit der Temperatur und nimmt mit dem Druck ab. Das Reflexionsverhalten der Lösungen steht damit in Parallele zu ihrem elektrischen Leitfähigkeitsverhalten.

In the past it has been shown, that the electrical conductivity [1], the paramagnetic susceptibility [2] and the miscibility gap [3] of the metal-ammonia solutions as well as their equilibria with added substrates [4, 5] depend strongly on pressure. In the following we will report about the pressure and temperature dependence of the optical properties, i.e. of the absorption spectrum of dilute and of the reflexion spectrum of concentrated metal-ammonia solutions. In addition we give some data on the pressure and temperature dependence of the absorption spectrum of iodide ions in ammonia and in ammonia-water mixtures.

I. Absorption Spectrum of Dilute Potassium-Ammonia Solution

The light absorption of dilute metal-ammonia solutions is corresponding to theory [6] caused by a $1s-2p$ transition of the electrons caught in a solvent cavity (solvated electron). The transition energy depends on the cavity size and on the potential which acts on the electron. With the simplifying assumption of a square well potential the transition energy $\Delta E = E_{2p} - E_{1s}$ is inversely proportional to the square of the cavity radius R :

$$\Delta E \sim 1/\lambda_{\max} \sim 1/R^2$$

(λ_{\max} wave-length at maximum absorption).

This relationship is closely followed in case of F centres (electrons on anionic vacancies in ionic crystals) the geometry of which is given by the lattice constant [7].

The more sophisticated treatment of the solvated electron by Jortner [6] on the basis of the SCF-theory with a Coulomb like potential gives a more complicated relationship between cavity radius and transition energy, but still with the same tendency, that — all other parameters kept constant — λ_{\max} increases with the cavity radius.

Therefore an increase of temperature which leads to an expansion of the cavity should lead to a redshift of the spectrum, whereas compression of the cavity by application of pressure should yield a blue shift.

At low temperatures the redshift of the spectrum with increasing temperature has been observed already [8]. With a high pressure optical cell [9] we could extend the studies up to 150°C and to pressures up to 2000 at.

The results of these studies ($1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ m K-NH₃ solution, window distance of the cell 0.024 to 0.11 cm) are plotted in Fig. 1. In the temperature range from -80° up to 40°C at normal pressure the position of the absorption maximum is shifted by about 3000 Å to longer wave-length. The data taken from literature [8] (full circles) are in poor agreement with each other and with ours, however they give the same tendency. Further temperature increase above 50°C has little effect on the absorption maximum; above 120°C however there seems to be a reversal of the effect, i.e. a slight blueshift with further temperature increase. — At higher pressures the temperature shift of the spectrum is less pronounced.

In the temperature range around 1°C an increase in pressure up to 1500 at leads to a blueshift of the ammoniated electron spectrum by about 1600 Å. At lower temperatures the pressure dependency of the spectrum is less. At higher temperatures (60°C) again the effect is very small.

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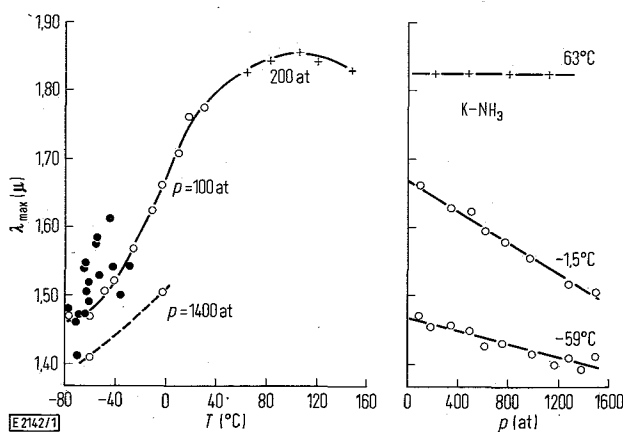


Fig. 1

Wave-length of maximum absorption of ammoniated electrons versus temperature and pressure (● data from literature [8], normal pressure; + obtained from $\text{H}_2 - \text{KNH}_2 - \text{NH}_3$ solution with low equilibrium concentration [4] of electrons, 200 at)

The leveling off of the curves and the slight reversal of the effect at higher temperatures show that the simplified cavity model with square well potential has only limited application and that more parameters but cavity radius have to be discussed in explaining the position of the absorption maximum of solvated electrons. — In contrast to the ammonia system the spectrum of the solvated electrons in water is continuously shifted to longer wave-lengths [10] (from 0.7μ at 0°C to 1.29μ at 372°C).

II. Reflexion Spectrum of Concentrated Potassium-Ammonia Solution

The bronze luster of the concentrated metal-ammonia solutions is caused by the high reflectivity in the red and the low reflectivity in the blue part of the spectrum. The reflectivity increases with the metal concentration [11], i.e. with the electron density or the electric conductivity of the solution, as is described by the theory of reflectivity of metals.

The conductivity of the metal-ammonia solutions show an anomalous temperature- and pressure dependence: in contrast to solid and liquid metals it increases with temperature and decreases with pressure [1]. The reflexion measurements reported about in the following show that the reflectivity of the metal-ammonia solutions also has anomalous temperature- and pressure dependence.

The results are exhibited in Fig. 2 where the reflectivity of the solutions relative to the reflectivity of mercury at normal conditions is plotted versus wave-length for four different concentrations: at all concentrations the reflectivity increases with increasing temperature and decreases with increasing pressure. The temperature and pressure coefficient of the reflectivity $R(\lambda = 2 \mu)$

$$k_T = \frac{\Delta R}{R \cdot \Delta T}, \quad k_p = \frac{\Delta R}{R \cdot \Delta p}$$

(referred to the reflectivity at -48°C and 1 at resp.) are plotted in Fig. 3. The positive temperature coefficient and the negative pressure coefficient of reflectivity go through a maximum

value at a concentration around 1 m, i.e. in the concentration range of the transition from nonmetal to metal. The curves of Fig. 3 parallel the corresponding curves of the temperature and pressure coefficients of electrical conductivity [1], which also exhibit maxima at concentrations around 1 m and can be interpreted in the same way: shift of the equilibrium

nonmetal \rightleftharpoons metal

to the right by increasing temperature and to the left by increasing pressure. Formal application of thermodynamics to these shifts leads to the conclusion that the transition to the metallic state is an endothermic ($\Delta H > 0$) process connected with a volume expansion of the system ($\Delta V > 0$). The same conclusions follow from our studies of the magnetic properties [2] and from the miscibility gap of the metal-ammonia solution [3].

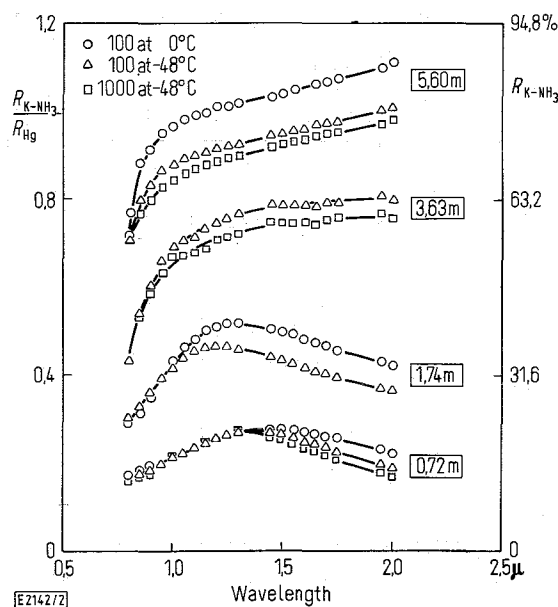


Fig. 2

Reflexion spectrum of potassium-ammonia solutions of different concentrations (\square 1000 at, -48°C ; \triangle 100 at, -48°C ; \circ 100 at, 0°C)

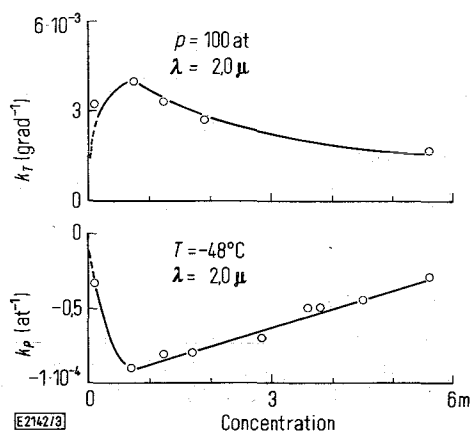


Fig. 3

Temperature and pressure coefficient of the reflectivity of potassium-ammonia solutions versus concentration (wave-length 2μ)

III. Absorption Spectrum of Potassium Iodide Solutions

The spectra of dissolved halogenide ions depend like those of solvated electrons on the solvent [12]. The theory [13] of these anion spectra is based on the assumption that light absorption is caused by a transition of one outer sphere electron from the anion to the solvent shell (charge transfer to solvent: cttS-spectra).

The transition energy according to theory depends on the size of the solvent shell in a similar way as that of the 1s-1p transition of the solvated electrons. Consequently we expect for the cttS-spectra similar changes with temperature and pressure as observed for the solvated electrons.

This is born out by the experimental results, shown in Fig. 4. At moderate temperatures we observe a redshift with increasing temperature and a blueshift with increasing pressure. However at higher temperatures again we obtain a reversal of the effects, i.e. blueshift with temperature and a redshift with pressure.

The pressure and temperature dependence of the absorption spectrum of iodide ions in several water-ammonia mixtures are shown in Fig. 5. As for solvated electrons [15] the wave-length of maximum absorption increases with the ammonia

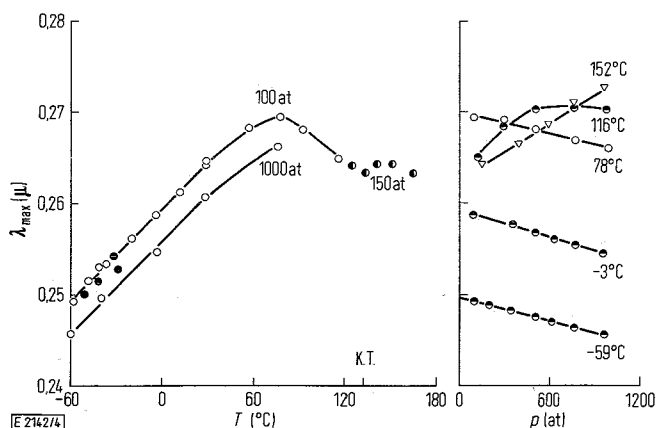


Fig. 4

Wave-length of maximum absorption of iodide ions in ammonia versus temperature and pressure (● data from literature [14])

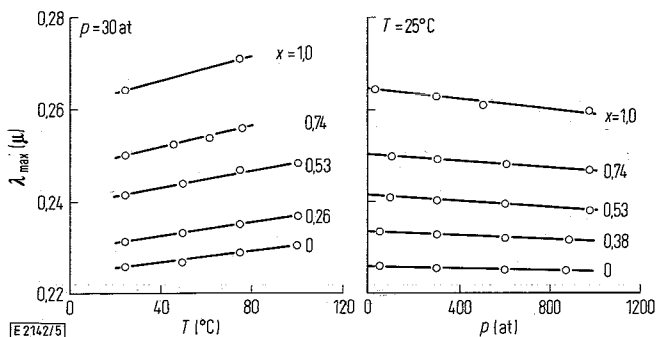


Fig. 5

Wave-length of maximum absorption of iodide ions in ammonia-water mixtures versus temperature (30 at) and pressure (25°C; x mole fraction of ammonia)

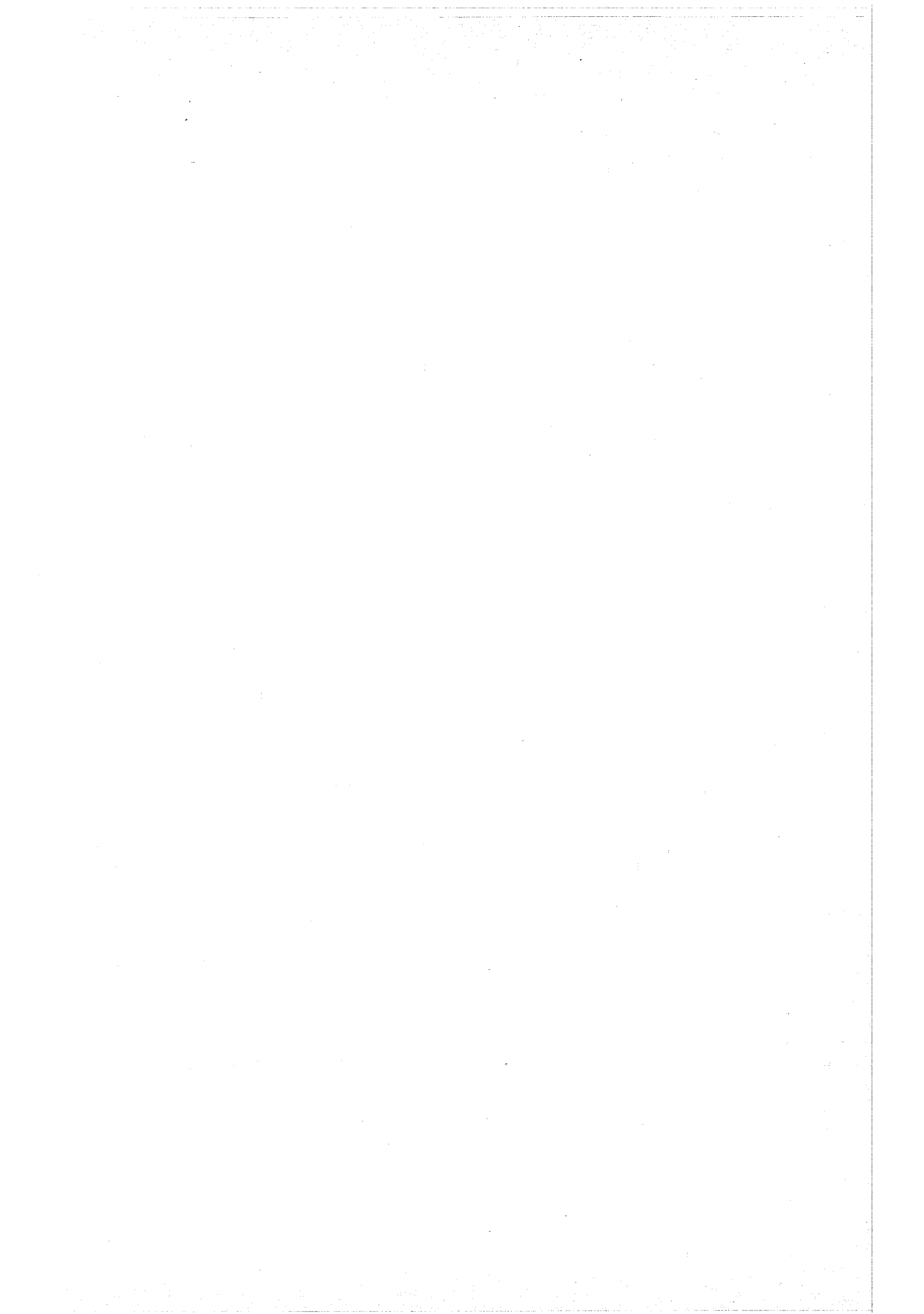
content of the mixture and in the restricted temperature range show the usual redshift with temperature and blueshift with pressure.

Our data indeed show that the spectra of solvated electrons and ions with cttS-spectra depend in a similar way on solvent parameters like solvent composition, temperature and pressure. Therefore the concept is supported that the theory of both spectra should be based on the same principles. The results however also indicate that the relationship "the bigger the cavity the longer the wave-length of maximum absorption" definitely does not hold under all conditions and therefore has only limited value.

This is also born out by experiments in ethers like tetrahydrofuran. The absorption maximum of solvated electrons in all ethers [16] investigated so far lies around to 2 μ, i.e. in the further infrared as compared to ammonia. However the molare volume of the solvated electrons or the cavity size must be very small in ethers, because here equilibria like $e^- + C_6H_6 \rightleftharpoons C_6H_6^-$ are not affected by pressure [5] whereas in ammonia we find a pressure shift of the equilibrium corresponding to a reaction volume of 60 ml/mol, reflecting the large molare volume or the large cavity size of the ammoniated electrons [5].

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Experiments Concerning Electrochemical Production of Solvated Electrons

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Solvated electrons are known to be produced by electrolysis of liquid ammonia solutions of alkali salts. It is doubtful however if solvated electrons also are formed as precursor of hydrogen during electrolysis of aqueous solutions.

Experiments were undertaken to detect by optical means solvated electrons injected into liquid water or ammonia by cathodic polarisation of a light reflecting silver electrode. The experimental set up allowed us to detect changes of $1 \cdot 10^{-6}$ in intensity of the reflected light which would be connected with the concentration of $3 \cdot 10^{-14}$ mol hydrated electrons per cm^2 electrode surfaces.

In aqueous solutions the intensity of the reflected light changes with cathodic polarisation of the electrode. The dependence of this effect on the wave length of the reflected light however rules out the hypothesis that it is due to solvated electrons formed as intermediate during electrolysis. On the other hand in liquid ammonia the effects are larger by several orders of magnitude and show the wave length dependence as expected for ammoniated electrons.

Bei der Elektrolyse von flüssigem Ammoniak mit gelösten Alkalisalzen werden kathodisch solvatisierte Elektronen gebildet. Zweifel bestehen dagegen, ob auch bei der Elektrolyse wäßriger Lösungen als Vorstufe der Wasserstoffbildung an der Kathode solvatisierte Elektronen entstehen.

Experimente werden beschrieben, um mit optischen Methoden bei kathodischer Polarisation an einer lichtreflektierenden Silberelektrode in wäßrigem System eventuell entstehende solvatisierte Elektronen nachzuweisen. Die experimentelle Anordnung gestattet noch Änderungen der Intensität des reflektierten Lichtes von $1 \cdot 10^{-6}$ nachzuweisen, die sich bei einer Konzentration von $3 \cdot 10^{-14}$ mol hydratisierter Elektronen je cm^2 Elektrodenoberfläche ergeben würden.

Im wäßrigen System ändert sich die Intensität des reflektierten Lichtes während der kathodischen Polarisation der Elektrode. Die Wellenlängenabhängigkeit des Effektes schließt jedoch aus, daß er durch hydratisierte Elektronen bedingt ist. In flüssigem Ammoniak ist der Effekt unter sonst gleichen Bedingungen einige Größenordnungen größer und zeigt die für Elektronen in Ammoniak erwartete Wellenlängenabhängigkeit.

Due to the high overvoltage of hydrogen at most electrode materials in liquid ammonia the electrolysis of alkali salts leads to ammoniated electrons at the cathode [1]. In analogy to this several authors [2-7] have put forward the hypothesis that in aqueous systems also solvated electrons are formed as precursors of hydrogen during electrolysis. Due to the high reactivity of solvated electrons toward water their concentration however will be very low and therefore their detection requires equipment of high sensitivity.

Walker [2] has tried to detect the hydrated electrons formed at a highly reflecting silver electrode by following the changes in the intensity of the reflected light during ac-electrolysis. To increase sensitivity he constructed a tube like silver electrode at the inner of which he got multiple reflection of a light beam tangentially introduced.

Indeed Walker could show that when applying alternating current the intensity of the multiply reflected light was decreased during cathodic polarization of the silver electrode. This decrease of light intensity was ascribed to solvated electrons.

However to get this multiple reflection a beam of parallel light was required. As light source a gas laser was applied the wave length of which agreed fairly well with the absorption maximum of solvated electrons in water (0.72μ).

Since the frequency of the laser cannot be changed the experiment could be carried out only at this one frequency. Therefore the interpretation of the effect observed by Walker is not conclusive. To prove solvated electrons as intermediates

during electrolysis it has to be shown that the effect depends on the wave length of the reflected light just as the extinction coefficient of hydrated electrons does.

The experimental set up we describe in the following enables us to detect changes of the intensity of the reflected light of a silver electrode during polarization down to $1 \cdot 10^{-6}$ in the range from 0.5 to 1.6μ . The arrangement was checked with liquid ammonia as solvent where we positively could detect the solvated electrons at the cathode. In aqueous systems however the observed changes of intensity of reflected light definitely cannot be due to hydrated electrons, they must be ascribed to other effects.

Experimental Arrangement

Fig. 1 describes the experimental set up. It consists of the electrolysis cell, with the electrodes, the power supply, and the optical detection system with its electronics.

a) As electrolytic cell we used a glass beaker (\varnothing 70 mm) which fitted exactly into a steel container with two sapphire windows (Fig. 1). The lid of the container was provided with two insulated electrical leads for the electrodes. The lead for the silver electrode was put exactly in the middle of the lid, the one for the platinum counter electrode was further outside. Two steel capillaries through the lid, one of which was extended far enough that it almost touched the bottom of the glass beaker, allowed to evacuate the system and to flush the solution with any desired gas.

The electrodes could be connected with an ac sine wave generator (up to 5000 cycles/sec, 500 mA), a square wave pulse generator (1 μ sec to 1 sec, up to 300 mA) for single pulses and for periodic repetition of pulses symmetric to zero voltage.

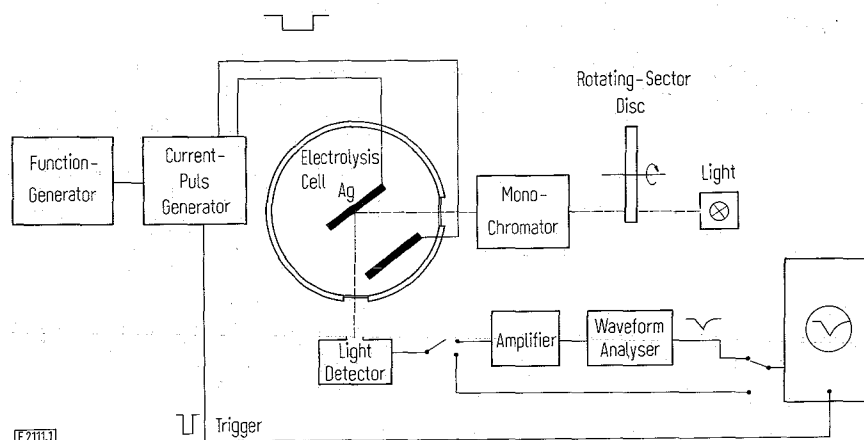


Fig. 1

Experimental arrangement for the detection of solvated electrons during electrolysis

b) The optical detection system consisted of a tungsten lamp, a monochromator and a fast responding solid state light detector for 1.8 down to 0.4 μ . — The silver electrode in the cell was placed so that the incoming light was reflected into the light detector. The signal of the light detector which is proportional to the reflected light intensity is amplified and fed directly into the oscilloscope, when the signals (as in ammonia) were large enough to be observed directly. In this case the single pulse technique with a storage oscilloscope was applied. — When the signal was too small and not to distinguish from the noise (as in water) ac-current or periodic pulses were used. The light detector output was further amplified (factor 10000) and fed into signal integrator (PAR Wave Form deductor) which eliminates the noise and further amplifies the signal. The integrator was triggered by the generator. The outcoming signal of the integrator was displayed on the oscilloscope. The optical arrangement was calibrated with a rotating sector disc.

With the first arrangement changes of light intensity down to $5 \cdot 10^{-3}$ could be followed. The more sensitive second arrangement allowed us to detect changes of light intensity down to $1 \cdot 10^{-6}$.

Triply distilled water was filled into the beaker, made 10^{-2} m in sodium hydroxide. The steel container with the beaker was evacuated to remove oxygen and finally saturated with hydrogen. — Anhydrous ammonia was distilled into the beaker after cooling down the closed autoclave to -80°C . The ammonia was made 10^{-2} m in potassium iodide and also saturated with hydrogen.

Results

(a) Ammonia. The oscillographic trace of the change of intensity of the reflected light obtained with cathodic polarization of the silver cathode is shown in Fig. 2 together with the trace of the applied square wave current pulse through the cell. After an induction period the light intensity decreases during the 55 msec pulse almost linearly with time; after pulse end it returns within 100 msec to the original value. Anodic polarization of the silver electrode does not give any comparable effects.

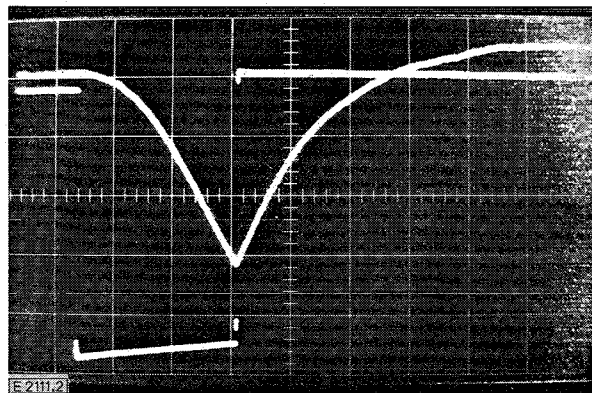


Fig. 2

Oscilloscopic traces of the polarizing current (square wave curve: current density 6.5 mA/cm^2 per division) and of the intensity of light ($\lambda = 0.7 \mu$; $\Delta I/I_0 = 0.013$ per division) reflected during cathodic polarization of the silver electrode in ammonia (ac-coupling of the oscilloscope; 20 msec per division)

In Fig. 3 we have plotted the obtained changes in optical density versus the wave length up to 1.6 μ . The curve increases with wave length, and has the typical form of the absorption spectrum of ammoniated electrons, the absorption maximum of which under our experimental conditions is around 1.7 μ .

We have no doubts that the optical effects at the cathode are due to the electrochemical production of ammoniated

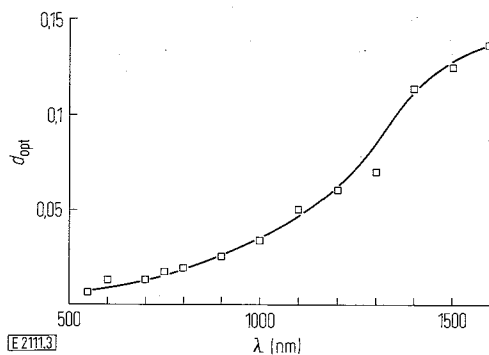


Fig. 3

Wave length dependence of the optical density during cathodic polarization of the silver electrode in ammonia

electrons. The relatively short lifetime we observe is due to reactions with impurities. The induction period probably is caused by reducible species adsorbed on the silver surface, which quickly react with the electron. For by repetition of the pulses in short sequence the induction period vanishes and the optical changes during pulses become higher.

From the maximum optical density 0.14 and the maximum extinction coefficient of the ammoniated electrons $\approx 5 \cdot 10^7 \text{ cm}^3/(\text{mol} \cdot \text{cm})$ follows a concentration of electrons of around $2.8 \cdot 10^{-9} \text{ mol/cm}^2$ electrode surface. This is lower by factor of around 6 compared to the expected production of $1.7 \cdot 10^{-8} \text{ mol/cm}^2$ (30 mA, 55 msec). The losses should be due to reactions with impurities.

(b) Water. With the same single pulse technique applied to aqueous systems effects were too small and due to noise could not even be observed by higher amplification. The use of the signal averager to increase the signal to noise ratio requires periodic repetition of pulses. However the repeated applications of negative current pulses to the cathode finally leads to evolution of hydrogen by which the light beam is scattered. Therefore ac-technique had to be used whereby absorbed or already dissolved hydrogen is reoxidized before formation of bubbles.

The oscilloscopic traces in Fig. 4 show, that indeed as already reported by Walker the light intensity changes with

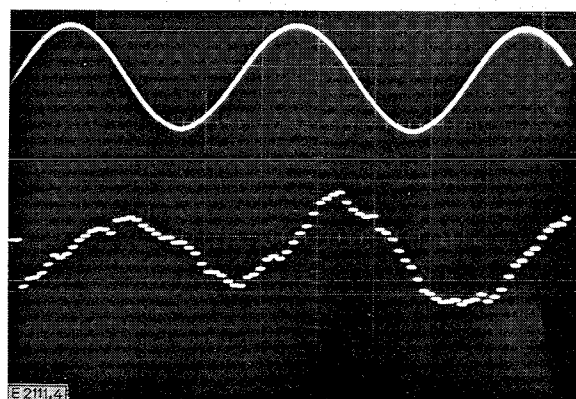


Fig. 4

Oscilloscopic traces of the polarizing current (upper curve: current density 30 mA/cm^2 per division) and of the intensity of light reflected ($\lambda = 0.55 \mu$; lower curve: $\Delta I/I_0 = 2 \cdot 10^{-4}$ per division) during cathodic polarization of the silver electrode in water (20 msec per division)

ac-polarization of the electrode. However the light changes are not in phase with the applied polarisation. The intensity of the effect observed with only single reflection is appreciable lower than observed by Walker with the multiple reflection cell.

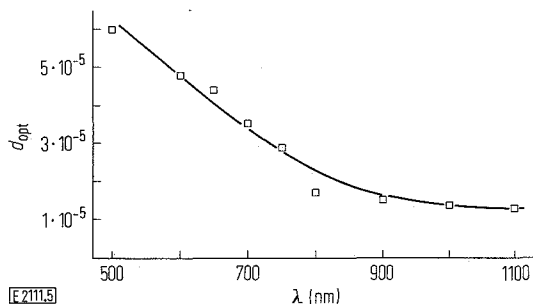


Fig. 5

Wave length dependence of the changes of optical density during ac-electrolysis with the silver electrode in water

The dependence of this effect on the wave length is plotted in Fig. 5. The changes of optical density during polarization increase with decreasing wave length. The figure shows no increased absorption around 0.7μ where the hydrated electron spectrum has its maximum.

Only 10% of the optical density of $3.6 \cdot 10^{-5}$ at 0.7μ could be due to hydrated electrons; with the molar extinction coefficient [8] of around $1.5 \cdot 10^7 \text{ cm}^3/(\text{mol} \cdot \text{cm})$ it follows that the concentration of hydrated electrons during polarisation (30 mA/cm^2) of the electrode is smaller than $1 \cdot 10^{-13} \text{ mol/cm}^2$ electrode surface (the light beam passes the electron containing surfaces layer twice under an angle of 45°).

In the following we will try to estimate the expected concentration of hydrated electrons at the electrode surface under the following assumptions: 1. they are formed with 100% yield (production rate per cm^2 : $r = j/F$; j current density, F Faraday number); 2. they are moving into the solution by diffusion only (diffusion coefficient [8] $D = 4.8 \cdot 10^{-5} \text{ cm}^2/\text{sec}$; the drag of the electrons into the solution by the applied field is neglected); 3. they react with water only by the bimolecular reaction $2e^- \xrightarrow{\text{H}_2\text{O}} \text{H}_2 + 2\text{OH}^-$ (reaction rate $v = -\frac{dc}{dt} = kc^2$; bimolecular rate constant [8] $k = 5 \cdot 10^{12} \text{ cm}^3/(\text{mol} \cdot \text{sec})$, c hydrated electron concentration).

For steady state condition*), under which the change in concentration of electrons in a volume element due to the

reaction with water equals the change in concentration due to diffusion into and out of the volume element, we obtain

$$\frac{d^2c}{dx^2} = \frac{k}{D} c^2. \quad (1)$$

With the boundary condition $c = 0$ for $x \rightarrow \infty$ Equation (1) integrates to

$$c = \left(\frac{1}{\sqrt{c_0}} + \sqrt{\frac{k}{6D}} x \right)^{-2} \quad (2)$$

(x distance from the electrode)

with $c_0 = c(x=0)$. c_0 follows from the condition that electrons are injected through the electrode surface at rate j/F and can be removed only by diffusion

$$j/F = -D \cdot \frac{dc(x=0)}{dx} = \sqrt{\frac{2k \cdot D}{3}} c_0^{3/2}. \quad (3)$$

The electron concentration per cm^2 electrode surface is

$$\int_0^\infty c(x) dx = \sqrt{\frac{6D}{k}} \cdot c_0. \quad (4)$$

With the known data for k and D and $j = 0.03 \text{ A/cm}^2$ the volume concentration c_0 of hydrated electrons at $x=0$ is calculated according to Equation (3) to be $8.2 \cdot 10^{-8} \text{ mol/cm}^3$. From Equation (4) follows the concentration of hydrated electrons referred to 1 cm^2 electrode surface $2.2 \cdot 10^{-12} \text{ mol/cm}^2$. Compared with the observed upper limit $1 \cdot 10^{-13}$ it follows that the yield of electrolytic production of solvated electrons is smaller than 5%. (This estimate is based on the assumption that extinction coefficient, rate and diffusion constant in close vicinity of the electrode surface have the same values as in bulk solution.)

On the basis of our results we have to assume that Walker in his experiments did not observe hydrated electrons, but registered the same effects as we did which might e.g. be due to coverage of the electrode with hydrogen atoms.

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*) Steady state condition can be applied because the life time of the hydrated electrons is small compared to period of ac-current applied.



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Density Dependence of the Absorption Spectrum of Solvated Electrons in Supercritical Ammonia

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Preliminary experiments are reported on the density dependence of the absorption spectrum of the solvated electron in supercritical ammonia. Solvated electrons were produced by pulse radiolysis in a heated high pressure optical cell. The intensity of the absorption spectrum diminishes with decreasing the ammonia density, and could be detected at 150°C down to densities of 0.1 g/ml. The shape of the spectrum and its position are only slightly changed indicating that normal solvation even at the low densities is possible. The spectroscopic data can be adequately interpreted by a theoretical molecular model for electron localization in a polar dense fluid.

Die Abhängigkeit des Absorptionsspektrums solvatisierter Elektronen in Ammoniak wurde in Abhängigkeit von der Dichte des Lösungsmittels im überkritischen Bereich untersucht. Die solvatisierten Elektronen wurden in einer thermostatisierbaren, optischen Hochdruckzelle durch Pulsradiolyse erzeugt. Die Intensität ihres Absorptionsspektrums nimmt mit abnehmender Dichte des Lösungsmittels ab. Solvatisierte Elektronen konnten bei 150°C noch bis herab zu einer Dichte von 0,1 g/ml festgestellt werden. Die Form des Spektrums und seine Lage sind nur wenig verändert, so daß selbst bei diesen geringen Dichten noch normale Solvation möglich erscheint. Die spektroskopischen Resultate können interpretiert werden mit Hilfe eines molekularen Modells für Elektronlokalisierung in einer polaren Flüssigkeit.

Solvated electrons have been so far produced by pulse radiolysis in a series of solvent systems at room temperature and at normal densities. It is of theoretical interest to obtain information concerning the critical minimum solvent density at which electron localization will occur in a polar dense fluid.

In normal fluid systems the density can be decreased at will only in the supercritical state. In liquid water Hart [1] has extended the studies up to the critical temperature of 372°C at which the density is 0.323 g/cm³. He found a red shift of the spectrum from 0.72 μm at room temperature to 1.29 μm at the critical point. However, he could not decrease the density any further to find the limits of formation of the solvated electrons.

Some time ago Schindewolf, Vogelsgesang, and Böddiker [2] investigated the spectrum of ammoniated electrons formed in the equilibrium reaction $1/2 \text{H}_2 + \text{NH}_2^- \rightleftharpoons \text{e}^- + \text{NH}_3$ above the critical temperature up to 150°C. It was demonstrated that the solvated electron spectrum did not undergo any substantial changes. In the experiments ammonia density could not be decreased below 0.36 g/cm³ by decreasing the pressure, because at lower densities in the supercritical ammonia the potassium amide was precipitated.

This work reports some preliminary experiments in which solvated electrons were produced in supercritical ammonia by pulse radiolysis and in which we could repeatedly change the density between 0.6 and 0.05 g/cm³ by varying the pressure between 1.000 and 100 at. These experimental data can be interpreted in terms of a molecular model for electron localization in a dense polar gas.

Experimental Procedure

The experiments were carried out in the high pressure apparatus already described [3] which was modified for working at higher temperatures [4]. The set up consisted of the pulsed linear accelerator, the optical part and the high pressure cell.

a) The linear accelerator delivers 5 μsec pulses of 0.4 A 10 MeV electrons to which the solution under investigation is exposed.

b) The solution is kept in the optical cell the axis of which is perpendicular to the beam of the electron accelerator. The cell is made of stainless steel with two sapphire windows and withstands pressures up to 1500 at. The static pressure is produced by the hand driven pressure generator. The thermostating was achieved by blowing electrically heated air through the mantle of the autoclave.

c) The optical system for the detection of the solvated electrons consists of a modified spectral photometer with a fast responding light detector which is connected to the oscilloscope.

The solutions were prepared in a storage autoclave which was connected with the high pressure cell and the pressure generator. The solutions were made 10⁻³ molar in potassium amide and saturated with 150 at hydrogen in order to remove other primary and secondary radiolysis products which might react with the solvated electrons. The additives were chosen in analogy to the radiolytic experience in aqueous systems that hydroxyde and hydrogen are very effective in scavenging unwanted reaction products.

Experimental Results

Fig. 1 shows the absorption spectra for different mass densities at temperatures around 150°C and for liquid ammonia at 25°C obtained under otherwise identical conditions. In liquid ammonia we find the broad absorption spectrum as it is known for ammoniated electrons — due to the logarithmic scale the spectrum in this plot looks broader than usual.

From the maximum of this curve together with the maximum extinction coefficient (48000 l/mol · sec) and the light path (2.4 cm) we calculated a concentration of solvated electrons immediately at the end of a 5 μsec pulse of $4 \cdot 10^{-6}$ mol/l. In the supercritical state we get similar spectra, the intensity of which however decreases with decreasing density. The spectra seem to be sharper than it is at room temperature. However, the strong absorption of ammonia above 1.5 μm interferes with the weak solvated electron absorption under our conditions so that data become increasingly poorer. The position of the maximum of the absorption curves is only little affected by changing the density.

Assuming a constant extinction coefficient at the band maximum the decrease of the intensity of the spectra is due to decreasing yield of solvated electrons per cm³ of solvent. Since the energy absorption of the ionizing radiation, the highly accelerated electrons here, is proportional to the density of the solution, the light absorption spectra or the yield should be referred to the density of the solution.

In Fig. 2 the maximum light absorption divided by the mass density is plotted as function of the density. In the upper right corner we have the value for liquid ammonia at room temperature. At 150°C and at slightly smaller density (0.5 g/cm³) the value has decreased by the factor of about 7, but stays more or less constant down to a mass density of 0.2 g/cm³. We cannot comment on the slight increase of the curve around 0.2 g/cm³ which has been shown in all experiments we carried

out. Below 0.2 g/cm³ the yield per g solution decreases sharply and at densities below 0.09 g/cm³ we were unable to detect any absorption.

Although the observed spectra in supercritical, low density ammonia are sharper than expected we believe to have observed ammoniated electrons. Fig. 2 indicates that these electrons are formed with approximately constant yield in the density range between 0.5 and 0.2 g/cm³. Below this density the yield decreases sharply.

From these experiments, it follows that solvation of electrons in ammonia is still possible down to densities of about 0.1 g/cm³. Below this we cannot give any information because the sensitivity of our experimental arrangement was too low.

Experiments are now planned utilizing deuterioammonia, the light absorption of which does not interfere with that of the solvated electron.

Electron Localization in Ammonia Gas

The experimental spectroscopic data reported herein conclusively demonstrate that in dense ammonia fluid over the density range 0.7–0.1 gm/cm³: a) The excess electron is localized, b) the vertical optical excitation energy of the localized electron is practically density independent. These experimental observations can be adequately interpreted in terms of a molecular model for electron localization in a dense polar fluid. The model proposed involves an extension of the potential field previously introduced by Copeland, Kestner, and Jortner [5, 6] for electron localization in polar solvents. We assume [7] that the localization centre consists of a cluster of properly aligned molecules and the polarized medium beyond this cluster. An electrostatic microscopic potential will be used to account for the electron-molecular cluster attractive interactions. Long range attractive interactions exerted by the polar gas beyond the first molecular layer were treated by the Landau polaron potential. Finally, short range repulsive interactions were handled by the energy V_0 of the quasi-free electron state [5, 6] in the polar medium.

The electron-medium potential was recast in the form

$$\begin{aligned}
 V(r) &= -\frac{N\mu e \langle \cos \theta \rangle}{r_d^2} - \frac{\beta e^2}{r_c}; & r < r_d - \tilde{a}_s \\
 V(r) &= -\frac{N\mu e \langle \cos \theta \rangle}{r_d^2} - \frac{\beta e^2}{r_c} + V_0; & r_d - \tilde{a}_s < r < r_d \\
 V(r) &= -\frac{\beta e^2}{r_c} + V_0; & r_d < r < r_c \\
 V(r) &= -\frac{\beta e^2}{r} + V_0; & r_c < r
 \end{aligned}
 \tag{1}$$

where μ is the static molecular dipole moment, r_d represents the distance of the centre of the solvent molecule (which is characterized by a radius $r_s = 1.5 \text{ \AA}$ and an effective hard core repulsive radius $\tilde{a}_s = 1.0 \text{ \AA}$) from the centre of the cavity. The continuum onset is located at $r_c = r_s + r_d \cdot \langle \cos \theta \rangle$ corresponds to the thermally averaged cosine of the angle between μ and r_d , being $\langle \cos \theta \rangle = \coth \xi - \xi^{-1}$, where $\xi = \mu e C_g / r_d^2 k T$ and C_g is the fraction of the ground state electronic charge enclosed in the spatial region $r < r_d$. The polaron coupling parameter $\beta = D_{op}^{-1} - D_s^{-1}$ is expressed in terms of the optical dielectric

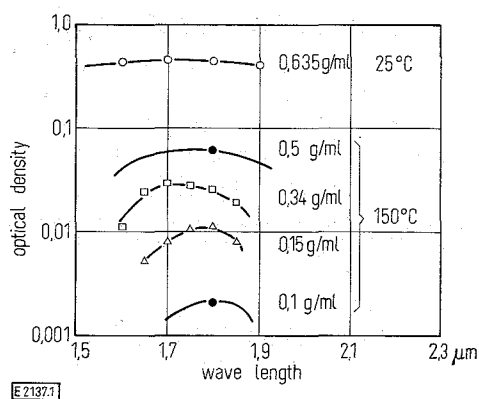


Fig. 1

Density dependence of the absorption spectra of solvated electrons in supercritical ammonia gas

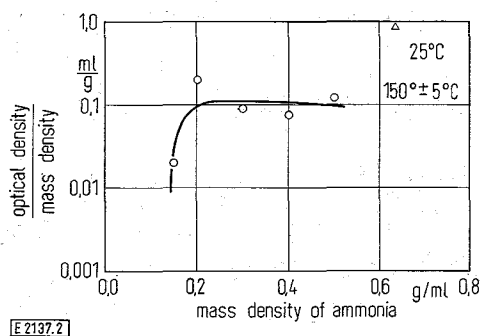


Fig. 2

Density dependence of the yield of solvated electrons in supercritical ammonia

constant, D_{op} , (computed at various ammonia densities by the Clausius Mossotti relation) and by the static dielectric constant D_s (the density dependence of which was calculated from the Onsager relation). Finally, the quasi-free electron energy [5, 6] is $V_0 = T + U_p$ consisting of the short range repulsive term T (determined by \tilde{a}_s and by the gas density ρ) and of the long range polarization contribution (determined by the molecular polarizability and by ρ). It should be stressed that within the framework of this model the density dependence of the energy levels of localized electrons in ammonia (or other polar) gas is embedded in the "coarsely grained" parameters V_0 and β . The electronic energies $E_E^i(r_d)$ for the ground s type ($i = g$) and for the lowest excited p type state ($i = e$) were computed variationally setting $E_E^i = \langle \varphi_i | -\frac{\hbar^2}{2m} \nabla^2 + V(r) | \varphi_i \rangle$. The variational wave function for the ground state, φ_g , was chosen to correspond to the solution for a finite rectangular potential well

$$V'(r) = V(r); \quad r < r_d \quad (2)$$

$$V'(r) = 0; \quad r > r_d$$

where $V(r)$ is given by Equation (1). In the limit $\rho \rightarrow 0$ (whereupon $\beta \rightarrow 0$ and $V_0 \rightarrow 0$) this solution is exact. For the lowest optically allowed excited state we have used a variational p type function, φ_e , which for low densities corresponds to the solution of the potential (2), while for high densities a hydrogenic 2p wave function was utilized. The calculations were performed [7] in a self-consistent manner. The total ground state energy $E_t^g(r_d) = E_E^g(r_d) + E_M(r_d)$ consists of the electronic energy and of the medium rearrangement energy E_M . To evaluate the latter the following contributions were included: (1) dipole-dipole repulsions $E_{dd} = D\mu^2 \langle \cos \theta \rangle^2 / r_d^3$. (2) Medium polarization energy $\pi = \beta e^2 C_g^2 / r_c$. (3) Short range molecule-molecule repulsions in the first layer [8], $E_{HH} = F(N)A(\sigma/R_m)^3$ where $A = 0.173$ eV, $\sigma = 2.8$ Å, while R_m corresponds to the distance of neighboring molecules. The equilibrium ground state energy is obtained from $(\partial E_t^g / \partial r_d)_{r_d=R_0} = 0$. The vertical optical excitation energy is $h\nu(r_d) = E_E^e(r_d) - E_E^g(r_d)$.

In Fig. 3 we display the density dependence of β and V_0 in ammonia gas. The remarkable feature of these results is that β is almost constant down to $\rho = 0.16$ g/cm³, while V_0 is small and negative changing gradually over this density region. In Fig. 4 we present the density dependence of the total ground

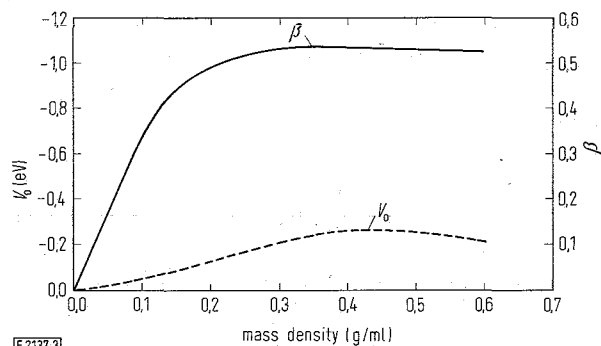


Fig. 3
Density dependence of β and V_0 in ammonia gas

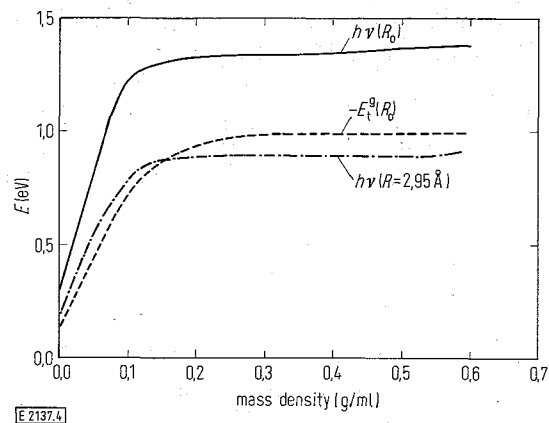


Fig. 4

Density dependence of the total ground state equilibrium energy and of the vertical excitation energy of a localized electron in ammonia gas. The calculation for $\rho = 0.596$ g/ml performed at 300°K, all other data for $T = 405$ °K. In view of the small absolute value of V_0 , we took $V_0 = 0$. Data for $N = 4$

state energy and the vertical excitation energy at equilibrium ($R_0 = 2.25$ Å) for localized electrons in ammonia gas calculated for $N = 4$ at $T = 405$ °K. We have also included $h\nu$ values at $r_d = 2.95$ Å, which provide a good fit to the experimental data (and which may be applicable in view of the uncertainty in calculating E_{HH}). From these results we conclude that:

a) An adequate theoretical scheme is provided for the persistence of the spectrum of the localized electron and for the insensitivity of the vertical excitation energy to density changes down to 0.1 g/cm³ in gaseous ammonia. As β is practically constant while V_0 is small over this density region the energy levels and thus the vertical excitation energy are practically constant over a wide density region. The sharpening of the spectrum at lower densities (Fig. 1) may be due to a dominating role of a single cluster configuration at lower densities while at high ammonia densities equilibrium between several structures will prevail.

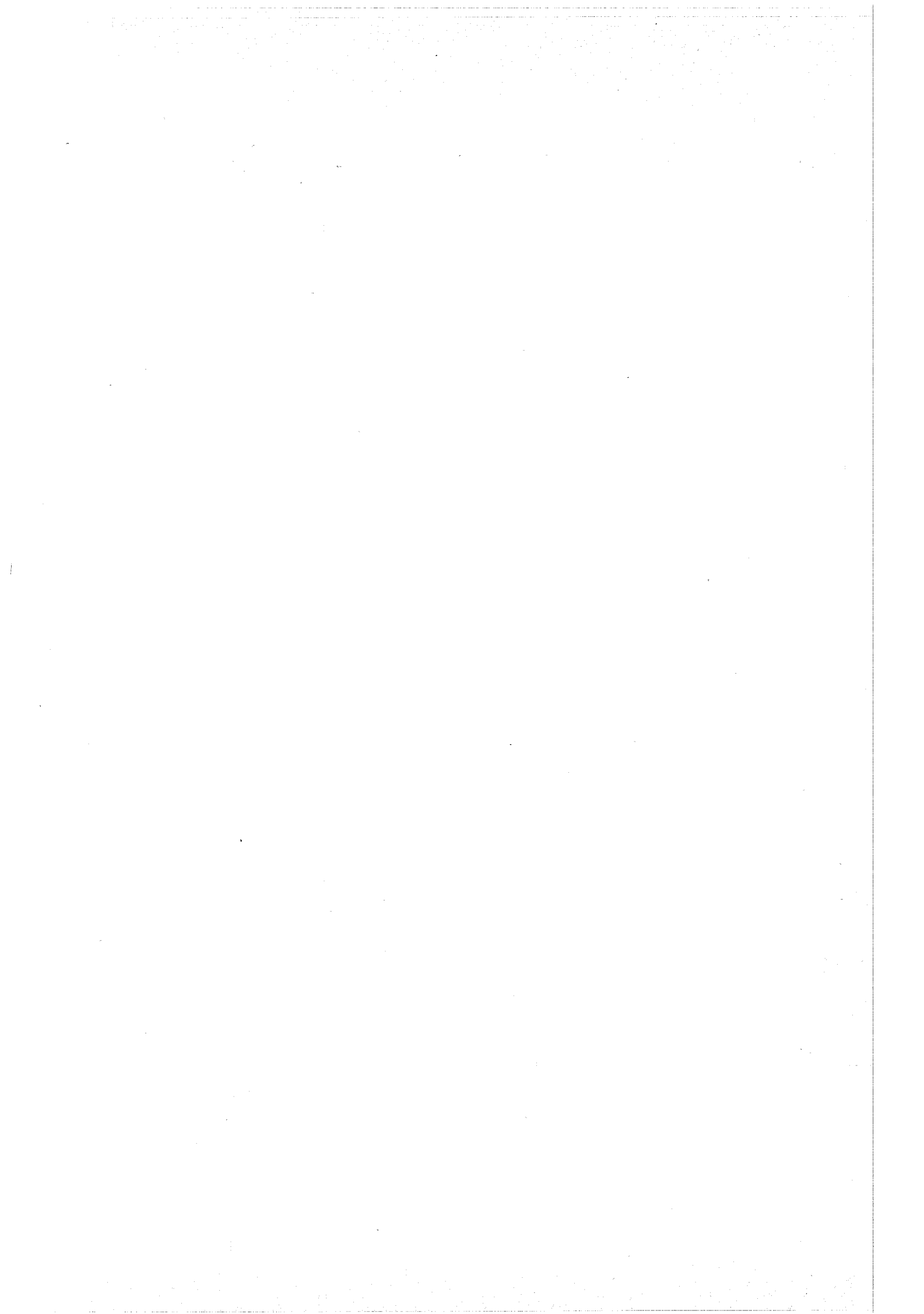
b) The situation will be drastically different in water vapor where theoretical calculations [7] indicate that V_0 (for $\tilde{a}_s = 1$ Å) changes from $V_0 \approx 1.6$ eV at $\rho = 1$ g/cm³ ($T = 300$ °K) to $V_0 = 0.25$ at $\rho = 0.5$ g/cm³ ($T = 661$ °K). Over this density region the calculated optical excitation energy decreases by about 30% in agreement with Hart's [1] experimental data.

c) Over the whole ammonia gas density region we have (see Figs. 3 and 4) $V_0 > E_t^g(R_0)$ whereupon the localized excess electron state will be energetically stable at all densities. The same situation prevails in water vapor [7]. Thus in a polar dense fluid electron localization will be energetically favored even at low density, and the possibility of observing the localized excess electron state at low density will be determined by kinetic rather than by energetic factors. This behavior is drastically different from the features of electron localization in a non polar electron repulsing gas [6] (such as Helium [9] or Hydrogen), where the quasi-free electron state is energetically favored at low density.

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Solvent Dependence of Optical and Kinetic Properties of Solvated Electrons in Water-Ammonia Mixtures

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The absorption spectrum and the lifetime of solvated electrons was determined in water-ammonia mixtures with special consideration of the temperature- and pressure dependence. The solvated electrons were produced by pulseradiolysis.

With increasing ammonia content the light absorption maximum of the solvated electrons is shifted to longer wave lengths. — The lifetime of the solvated electrons, restricted by the reaction with water, increases almost exponentially with the ammonia content whereas the activation energy and the activation volume decrease down to negative values.

The optical data indicate that there is a smooth transition from hydrated to ammoniated electrons and that the molare volume of the electrons increases continuously with the ammonia content. The kinetic data can be explained on this basis and under the assumption that the entropy of the solvated electrons is the bigger the higher their volume.

Das Absorptionsmaximum und die Lebensdauer radiolytisch erzeugter solvatisierter Elektronen in Wasser-Ammoniak-Mischungen wurde unter besonderer Berücksichtigung der Druck- und Temperaturabhängigkeit bestimmt.

Das Absorptionsmaximum wird mit steigendem Ammoniakgehalt zu längeren Wellenlängen verschoben. — Die Lebensdauer der solvatisierten Elektronen, die durch die Reaktion mit Wasser begrenzt ist, steigt nahezu exponentiell mit dem Ammoniakgehalt an. Die Aktivierungsenergie und das Aktivierungsvolumen nehmen dagegen bis zu negativen Werten ab.

Die optischen Daten deuten auf einen kontinuierlichen Übergang von hydratisierten zu ammoniierten Elektronen hin, wobei der Raumbedarf der Elektronen mit dem Ammoniakgehalt steigt. Die kinetischen Daten können nach der Transition State Theorie erklärt werden unter dieser Annahme und der Voraussetzung, daß die Entropie der Elektronen mit ihrer Größe steigt.

Solvated electrons in ammonia occupy a volume of 60 to 80 cm³/mole which is explained by the cavity model [1]; on the other hand the solvated electrons in water require negligible volumes as is inferred from optical data [2].

The difference in volume is revealed by differences in the pressure dependence of equilibria and rates of electron reactions in ammonia and in water. These dependencies are described by

$$\frac{d \ln K}{dp} = - \frac{\Delta V}{RT}; \quad \frac{d \ln k}{dp} = - \frac{\Delta V^\ddagger}{RT} \quad (1)$$

K and k are the equilibrium constant and rate constant resp., ΔV and ΔV^\ddagger describe the reaction volume and the activation volume, i.e. the differences in volume of the reaction products or the activated complex resp. and the reactants.

Pressure has only little effect on the rate constants for both directions and consequently on the equilibrium constant of the reaction [3, 4]

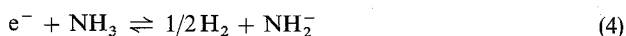


and on the rate constant of the reaction [4]



i.e. the reaction volume and the activation volume resp. of these reactions of solvated electrons in water are close to zero.

On the other hand the equilibrium constants of the reactions [5, 6]



and



in liquid ammonia are increased up to a factor of ten by a pressure increase of 1000 at, corresponding to a reaction volume of up to -60 cm³/mol.

So the results of these pressure experiments give an independent support to the ideas about the electron volumes as inferred from other experimental evidence.

The electrons in water are very reactive and even in the absence of other reactants their life time is restricted to 1 msec or below due to reactions (2) and (3) yielding hydrogen atoms or molecules [1b]. On the other hand the electrons in pure ammonia have a life time of weeks, months or even longer although their reaction with ammonia formally described by Equation (4) is thermodynamically favoured.

Is the difference in kinetic behaviour a question of the reactivity of water and the inertness of ammonia or do the kinetic properties of the solvated electrons depend on the solvent as for instance their size does? The investigation of the properties of solvated electrons in water-ammonia mixtures should give an answer to this question.

In the following we will report about the absorption spectrum and the lifetime of solvated electrons at various temperatures and pressures in water-ammonia mixtures. Some of our preliminary results were mentioned in a former review paper [7]. Later Dye et al. [8] gave a full account of their experiments on the absorption spectrum of solvated electrons in the same solvent mixtures with only very preliminary remarks about the kinetics. Elaborate work on the kinetics of the reaction of electrons with traces of water in ammonia was done by Dewald et al. [9].

Experimental Part

The solvated electrons were produced by pulse radiolysis with an electron accelerator. The experimental set up for the high pressure experiments has been described in detail before [10].

In analogy to radiolysis in aqueous systems all solutions were made 0.01 M in potassium hydroxide and saturated with hydrogen, to eliminate other primary and secondary radiolysis products which might react with the solvated electrons. These additives here too are very effective, only in their presence the kinetic observations reported below have been possible.

Because the strong light absorption of water and ammonia in the near infrared would interfere with the absorption spectrum of solvated electrons, mixtures of heavy water and deuterio ammonia were used whose absorption bands are in the farther infrared. The deuterio ammonia in amounts of 350 g was prepared by hydrolysis of about 1 kg sodium cyanide with about 800 g heavy water in a heatable 2 liter pressure autoclave [11].

Experimental Results and Discussion

a) Spectra

In Fig. 1 the optical density (product of extinction coefficient, concentration and light path) of water and several water ammonia mixtures after a single pulse of the electron accelerator under identical conditions is plotted versus the

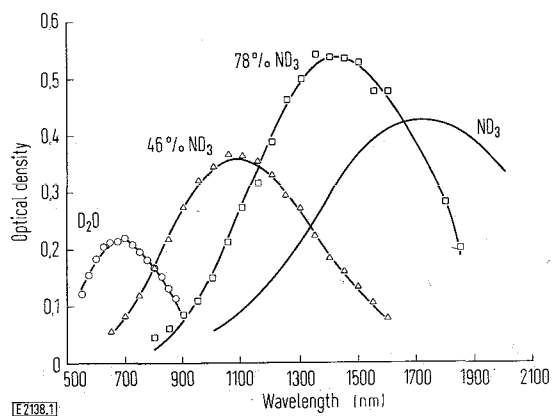


Fig. 1

Absorption spectra of solvated electrons in water-ammonia mixtures at 20°C (the electron concentration in water after one linac-pulse is around $3 \cdot 10^{-6}$ mol/l); the right curve is for ammonia under the assumption of equal yield as in water

wave length. In all cases we obtain the broad absorption spectrum which is typical for solvated electrons. The optical density at maximum light absorption increases with the ammonia content, the maximum is shifted to longer wave length. Extrapolation of the maximal optical density to pure ammonia yields a value 3.2 times bigger than the value obtained in pure water. Taking into consideration the different densities of the pure solvents and the different maximum extinction coefficients of the electrons in both solvents, we obtain for ammonia a 1.6 times bigger electron yield than in water. From the curves in Fig. 1 we conclude that the maximum extinction coefficient and the yield of the radiation chemical formation of solvated electrons increases with the ammonia content.

In Fig. 2 the wave length of maximum light absorption of the solvated electrons is plotted versus the ammonia content. The position of maximum absorption does not change linearly with the ammonia content, as we reported earlier [7]; the dependence is rather S-shaped as Dye et al. pointed out later [8]. The data of Fig. 2 are in good agreement with theirs.

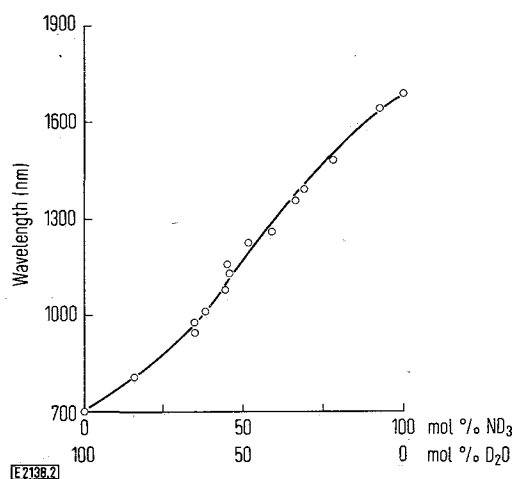


Fig. 2

Position of the light absorption maximum of solvated electrons in water-ammonia mixtures at 20°C

According to the theory [2] which relates the position of the absorption maximum of the solvated electrons to the size of their cavity, it follows qualitatively from the spectra in Fig. 1 and 2 that the electron cavity increases with the ammonia content of the mixture. Since the spectra have only one maximum and not even exhibit a shoulder we can assume to have a smooth transition from hydrated to ammoniated electrons, the solvent shell of which is composed of water and ammonia molecules in about the same ratio as in the solvent mixture.

All spectra are with increasing pressure up to 1000 at shifted to shorter wave lengths, with increasing temperature in the range from -10 to $+30$ °C to longer wave lengths as shown before for pure water [4] and pure ammonia [12]. We can interpret the shifts by compression and thermal expansion of the electron cavities [2].

b) Kinetics

The lifetime of the solvated electrons increases with increasing ammonia content as shown in Fig. 3: In the mixture with 20% water it is more than 10^7 times longer than in pure

water under otherwise identical conditions. In all mixtures but in pure water (2. order kinetics) we observe 1. order kinetics with respect to electrons.

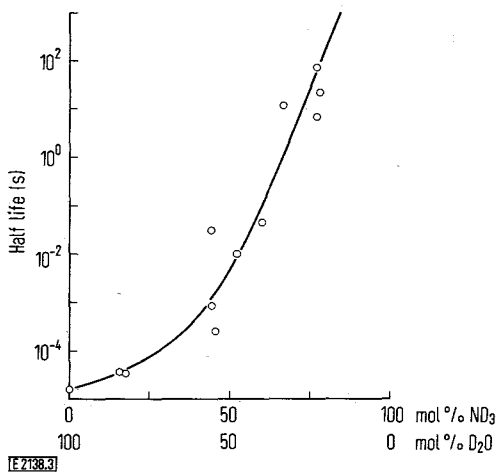


Fig. 3

Halftime of the reaction of solvated electrons with water in water-ammonia mixtures at 25°C

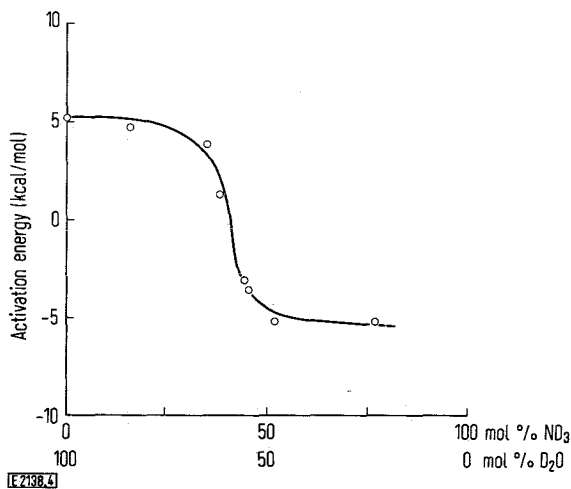


Fig. 4

Arrhenius activation energy of the reaction of solvated electrons with water in water-ammonia mixtures (rate data taken between -10° and $+30^\circ\text{C}$)

The Arrhenius energy of activation calculated from the temperature dependence between -10 and $+30^\circ\text{C}$ of the lifetime is shown in Fig. 4. In water rich mixtures the activation energy is in agreement with data for pure water from other authors [1b] around 5 kcal/mol. With increasing ammonia content it decreases and in ammonia rich mixtures finally becomes negative.

The volume of activation, as calculated from the pressure dependence of the lifetime of the electrons is plotted in Fig. 5. In water it is — in agreement with earlier data [4] — close to zero (no pressure effect on kinetics) and becomes increasingly negative with increasing ammonia content down to $-35\text{ cm}^3/\text{mol}$ (4 fold increase of rate at 1000 at) in the 20% water mixture. The point for pure ammonia is ΔV from the equilibrium reaction (4).

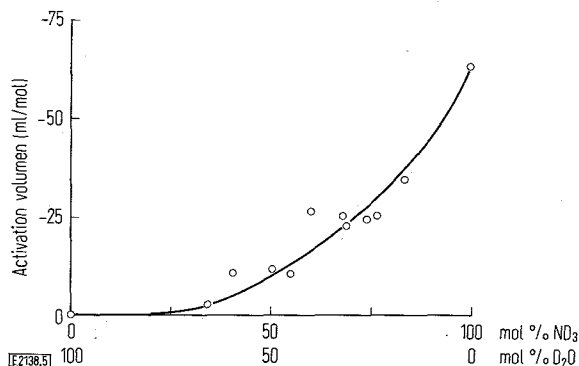


Fig. 5

Activation volume of solvated electrons in water-ammonia mixtures at 25°C (rate data taken between 100 and 1000 at)

The quantitative interpretation of the results is obscured because the mechanism of the reaction of the electrons is not known. What ever the mechanism may be it is most remarkable that the reaction of the electrons with water molecules which is so fast in water is slowed down by many orders of magnitude in ammonia. The effect of five fold dilution of the reactive water with inert ammonia should bring only a comparatively small increase of electron life time.

Jolly [13] and Dewald [9] interpret their results of the kinetic measurements of the reaction of dilute metal-ammonia solutions with traces of water (10^{-4} m) by a two step mechanism: in the first step ammonium ions are formed ($\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$) which in the second step react with the solvated electrons ($\text{NH}_4^+ + e^- \rightarrow \text{NH}_4 \rightarrow 1/2\text{H}_2 + \text{NH}_3$). They exclude the direct reaction (2) on energetic grounds: it is due to insufficient solvation of the OH^- -ions too endothermic to be possible. In our mixtures with at least 20% water however the OH^- -ions should find enough water molecules for solvation. Therefore we think it is possible that we observe the direct reaction of the water molecule with the electron, where the activated complex is formed by the transfer of the electron from the cavity to the water molecule.

The rate constant k_r according to the transition state theory is given by

$$k_r = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} = \frac{kT}{h} e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT} \quad (6)$$

with ΔG^\ddagger , ΔS^\ddagger , and ΔH^\ddagger the free enthalpy, the entropy and the enthalpy of activation, i.e. the differences of these functions between the activated complex and the reactants.

Since the activation energy which is about equal to the activation enthalpy does not increase with the ammonia content (Fig. 4) the increase in lifetime of the solvated electrons by seven orders of magnitude (Fig. 3) must be due to a decrease of the activation entropy to large negative values.

If we put $\Delta S^\ddagger = S^\ddagger - S_{\text{H}_2\text{O}} - S_{e^-}$ and assume in first approximation that the entropy of the activated complex S^\ddagger and of the reactant water $S_{\text{H}_2\text{O}}$ cancel or that at least their difference is about constant, then we can ascribe the decrease in ΔS^\ddagger to an increase of the entropy of the solvated electron S_{e^-} with increasing ammonia content [14]. This can be related

to the increasing size of the solvated electron or its bigger structure breaking effect.

The strongly negative entropy of activation in ammonia rich mixtures not only would explain the slow reaction of the electrons with water but also the negative activation energy: according to the transition state theory the activation energy can be written:

$$E_a = RT + \Delta G^\ddagger + T\Delta S^\ddagger. \quad (7)$$

ΔG^\ddagger must be positive because the equilibrium constant for the formation of the activated complex must be small. Therefore the activation energy can be negative only if the activation entropy is strongly negative.

Laidler et al. [15] have established a linear relationship between activation entropy and activation volume for a series of ion reactions in the one solvent water. A similar relationship is observed here for the one reaction of solvated electrons with water in a series of solvent mixtures: both the activation volume and the activation entropy decrease with the ammonia content of the mixtures. — The negative activation volume directly reflects the size of the solvated electrons, which — as deduced from the spectra — increases with the ammonia content.

We conclude that the rate of the electron reaction with water in ammonia which is highly susceptible to pressure is mainly controlled by the entropy term of the rate constant just as the pressure sensitive equilibria of its reactions (4) and (5) also are highly influenced by the entropy term of the equilibrium constant.

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