in an effort to determine the role played by impurity molecules.

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† National Research Council Post-doctorate Fellow 1957–59. Present address: William Ramsay and Ralph Forster Laboratories, University College, London, England.

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Spectrum and Radius of OH^- in Solution

Joshua Jortner, Baruch Raz, and Gabriel Stein

Department of Physical Chemistry, Hebrew University, Jerusalem, Israel

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Electron affinities[1] and ionic radii[2] of anions in solution can be calculated from their absorption spectra. We now investigated the hydroxyl ion, the size of which in aqueous solution is not accurately known. The ionic radius of OH^- in crystals cannot be directly obtained from the investigation of the structure of solid hydroxides[3]; effective radii of 1.32–1.84 A were obtained, depending on the cation.

The absorption spectrum[4] of OH_{aq}^- was accurately determined at several temperatures, using a Hilger Uvispek spectrophotometer fitted with a special fused silica prism, and checked for absence of stray light effects to 188 mμ; $\lambda_{\max}$ was determined to an accuracy of 0.15 mμ by the method of means.[2b,5] Solutions were prepared in the absence CO_2 from A.R. KOH, triply distilled water saturated with N_2, diluted and transferred to closed fused silica cells. Figure 1 shows the effect of temperature; $d(h\nu_{\max})/dT = 14.5\ \text{cm}^{-1}\ \text{deg}^{-1}$.

From the relations[2]

$$h\nu_{\max} = E_X - L_X + 0.77e^2/r_0 - 1.58\ \text{ev} \tag{1}$$

and

$$K = -d(h\nu_{\max})/dT = (0.77e^2/r_0^2)(dr_0/dT), \tag{2}$$

using $E_{OH} = 2.17$ ev[6] and $L_{OH} = 0.27$ ev,[7] the mean ionic cavity radius $r_0(OH_{aq}^-)$ at 30°C = 1.78 A; $dr_0/dT = 0.52 \times 10^{-3}$ A deg^{-1}. In these calculations the known equilibrium value of the electron affinity was used instead of the required vertical value; r_0 is the equivalent radius of the (presumably nonspherical) cavity occupied by the ion.

For I_{aq}^{-2}, $dr_0/dT = 0.93 \times 10^{-3}$ A deg^{-1}. These results are consistent with Latimer's assumption[8] of a linear correlation between ionic radii in solution and their temperature coefficients. The radius r_0 represents [2a] the cavity at the disposal of the ion at a certain temperature. The intensity distribution along the absorption band may be assumed to be due to different apparent ionic radii. For I_{aq}^- it was shown [2b] that K the temperature coefficient, decreases when passing from the band onset to shorter wavelengths. From the linear dependence between K and $h\nu$ at constant T, $h\nu(K=0)$ gave a value of effective radius about equal to the crystallographic radius of I^-. Similarly for OH^-, in Fig. 2 $h\nu$ vs K is plotted at the band onset ($\epsilon = 5$), band half-width, and band maximum. Lines for different temperatures yielded on extrapolation $h\nu(K=0) = 5.77 \times 10^4$ cm^{-1}. From Eq. (1), $r = 1.63$ A, corresponding to the virtual limit for the shrinking of the ionic cavity.

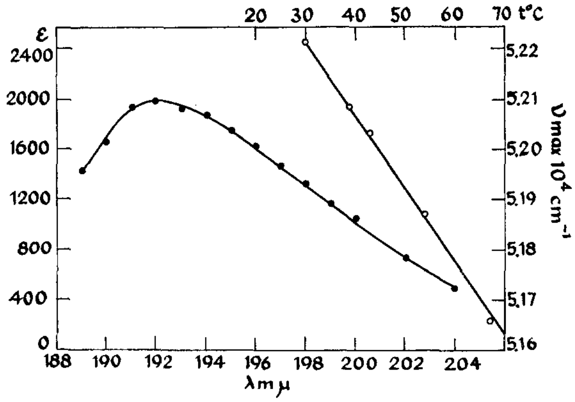

Fig. 1. Full circles: the spectrum of OH^-_{aq} at 43°C; open circles: $\nu_{\max}$ as a function of temperature.

The oscillator strength of OH_{aq}^-, $f = 4.31 \times 10^9\ \epsilon_{\max}\Delta\nu$; $\epsilon_{\max}$ being $\sim 2 \times 10^3$ we obtain $f = 0.04$.[9] This value fits the correlation[10] between ionic radius and oscillator strength for anions in solution, based on the investigation of the halide series.

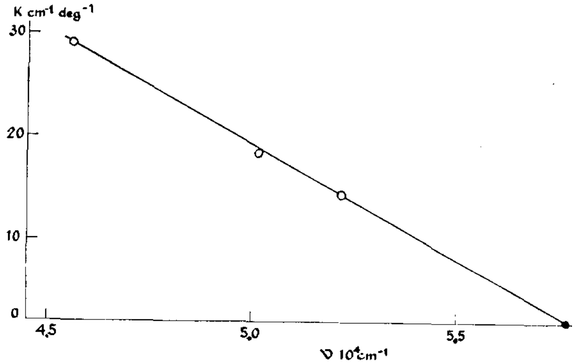

Fig. 2. The temperature coefficient K as a function of ν along the absorption band. Open circles: experimental values at 30°C. Full circle: extrapolated value of ν for $K = 0$.

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Transitions between Different Forms of Ice

R. H. Beaumont,* H. Chihara,* and J. A. Morrison

Division of Pure Chemistry, National Research Council, Ottawa, Canada

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UNDER special conditions (deposition from the vapor onto a surface at low temperatures) ice can be prepared in forms other than the ordinary hexagonal crystal. One of these, a cubic crystalline form, has been studied by both electron[1,2] and x-ray[3] diffraction techniques. A second form, which gives only diffuse diffraction halos, has been variously described as vitreous, amorphous, or microcrystalline. Its transparent glassy appearance[4] suggests, however, that it is best viewed as vitreous. The transitions from one form to another have been examined by different methods including simple calorimetry,[4–6] but estimates of the transition temperatures vary (see Fig. 8 of the work cited in footnote 1). Also, it has been suggested[3] that the formation of the cubic phase is sensitive to the nature of the substrate upon which the ice is deposited.

Preparatory to an extensive calorimetric study of the ice system, we have investigated the transitions between the different forms of ice using x-ray diffraction and simple thermal analysis with the object of establishing their reproducibility. Although different apparatus was used for each set of experiments, the conditions of deposition of the ice were kept as similar as possible. The results show that vitreous ice transforms cleanly to cubic ice over the temperature range 140°–156°K with an energy release of approximately 12 cal/g. The cubic ice in turn transforms into hexagonal ice over a wider temperature range beginning at about 200°K. No release or absorption of energy was detected in the latter transition, but the method used would not have "seen" energies less than about 1.5 cal/g.

The thermal analyses were carried out using an experimental arrangement similar to that of de Nordwall and Staveley.[6] Water vapor was brought into the calorimeter vessel (immersed in liquid nitrogen), which was a thin-walled copper cylinder, through a heated German silver tube. During the analysis the vessel was heated by maintaining a constant temperature head between it and a surrounding thermal shield. When ice, which had been deposited, at a slow enough rate, was heated up, an exothermic change took place between 140° and 156°K. The shapes of the heating curves were much like those found by de Nordwall and Staveley (Fig. 2 of work cited in footnote 6). The energies were, however, somewhat higher. For rates of deposition less than 0.01 g/cm^2 hr, the resulting energies were reproducible and the average of six separate measurements was 12 cal/g with an average deviation of 2 cal/g. At deposition rates higher than this, the energy was smaller and in some cases not detectable. From this we conclude that at high deposition rates the temperature of the deposit exceeded the transition temperature.

For the x-ray measurements a simple low-temperature vacuum camera was used, which could be attached to the goniometer head of a Norelco diffractometer equipped with a copper target. The camera was made from a brass cylinder and had two beryllium windows on its cylindrical side. The specimen holder was a lead-covered copper plate supported on a German silver tube. The plate was cooled by means of a copper rod which ran through the tube and into liquid nitrogen in a Dewar flask. Water vapor was brought in through a second tube with a funnel at its end directed at the specimen holder. After deposition of the water the camera was sealed off. With this arrangement the specimen holder was the coldest point in the camera. The temperature was measured with a copper-constantan thermocouple soldered to the holder.

The two crystalline modifications were distinguished by means of the diffraction lines (220) and (311) for cubic ice and (11.0), (10.3), and (11.2) for hexagonal ice. As long as the temperature of the holder was kept below 135°K during the deposition (deposition rate less than 0.04 g/cm^2 hr), no distinct diffraction lines were apparent.[7] When the deposit was warmed slowly ($\sim$0.5°/min), the characteristic lines of cubic ice appeared rather suddenly at about 150°K, and their intensities increased with time, reaching a maximum within a few minutes. With continued heating the deposit remained cubic until a temperature of about 200°K was reached. At this point the (10.3) line of the hexagonal phase could just be distinguished. Its intensity increased slowly in the temperature region 200° to 240°K. On several occasions deposits were cooled down again but there were no indications that the transformations reversed.

We conclude from the foregoing results that the transitions in ice show sufficient reproduciblity and consistency to merit a more detailed study. It is also apparent that the temperature of deposition is the important parameter, which suggests that uncontrolled variation of temperature may have been the cause of the different estimates of transition temperatures recorded previously. The agreement between the