practically unchanged (0.506 and 0.412 M) the concentration of molecular iodine was varied by a factor of 14, which led to a reduction in the limiting current from 226 mA cm^{-2} for a solution of 0.506 M KI + 0.0123 M I_2 to 73 mA cm^{-2} for a solution of 0.412 M KI + 0.174 M I_2, which represents a decrease by a factor exceeding 3. The rate of the anodic process depends on the concentration of both I^- and I_2, and the complex ion I_3^- has a remarkably great effect. The electrode reaction itself limits the velocity of the process.

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ENERGY OF HYDRATION OF IONS AND THE "EXPULSION EFFECT"

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The sums A_{ch} of the chemical energies of hydration of cations and anions and the differences in energies of hydration of ions of the same sign can be determined from experimental data; in order to derive from these quantities the energies of individual ions, an assumption must be made about the energy of hydration of one of the ions, or something else must be assumed, for example that these quantities are equal for a certain cation and a certain anion. Izmailov[1] avoids this difficulty by a method which consists essentially in finding such sums or differences for the combination of a certain ion, *e.g.* H^+ or Ag^+, with an ion of sufficiently large radius and of the opposite or the same sign respectively, on the assumption that, with increase in r, the chemical free energy of hydration tends to zero as $1/r$. Limiting values of these sums or differences as $1/r \to 0$ are found by extrapolation from data for halide and alkali-metal ions having different values of r. In a discussion of this question I pointed out that the part of the energy of hydration depending on van der Waals forces does not decrease with increase in r, but increases as r^2 for sufficiently large r. This view, to which reference was made in the above paper, has not yet been published. The purpose of the present communication is to make this idea more precise.

As an example, let us consider the value of the term due to van der Waals forces in the free energy of hydration for tetra-alkylammonium ions. For this purpose, such an ion can be regarded to a first approximation (ignoring the charge) as a hydrocarbon droplet of radius r†. We shall now utilise a method which has already been applied repeatedly in analogous calculations[3,4]. In order to introduce this droplet into an aqueous medium, we create a void of radius r in the latter, the work involving in doing this being $4\pi r^2\sigma_1$, where σ_1 is the surface tension of water. Filling this void with the hydrocarbon produces a gain in energy of $4\pi r^2 a$, where a is the free energy of adhesion of the hydrocarbon to water per cm^2, equal to $\sigma_1 + \sigma_2 - \sigma_{12}$, σ_2 being the surface tension of the hydrocarbon and σ_{12} the water–hydrocarbon interfacial tension. The net work done in transferring the hydrocarbon droplet from the gas phase to the aqueous medium is therefore $4\pi r^2(\sigma_{12} - \sigma_2)$, a result which can be obtained directly by comparing the initial and final states of the system. On substituting 50.8 and 21.8 ergs cm^{-2} (the experimental values for octane C_8H_{18} at 20°) for σ_{12} and σ_2 respectively[5], and 5.29×10^{-8}, *i.e.* the radius of the $N(C_5H_{11})_4^+$ cation[6], for r, we obtain 14.7 kcal × × g-ion^{-1} for the quantity in which we are interested. The employment of a macroscopic model to determine the energy of hydration of this ion is apparently justified, since, for example, a calculation based on Stokes's formula gives a correct value for its mobility[6]; however, the value obtained is too high, since our calculation has made no allowance for the effect of radius of curvature on the value of σ. Another source of error is the fact that the values of σ_{12} and σ_2 used relate to a hydrocarbon with an unbranched chain; it would be more correct to use values for hydrocarbons of the type CR_4, but apparently such data have not been published. An analogous calculation can be carried out for the change in total energy, using data from ref. 5; the resulting value of 4.9 kcal is considerably lower than, but has the same sign as, the change in free energy.

The existence of this "expulsion effect" is revealed in the considerable capacity of tetrapentylammonium ions to be adsorbed[7], and should lead to high values for their partition coefficients between non-aqueous solvents and water. The quantitative dependence of partition coefficients on ionic size could be determined from the variation of the potential difference at the boundary between aqueous and non-aqueous solutions with the nature of the electrolyte, but apparently such measurements have not yet been made for ions of this type (*cf.* ref. 8).

The influence of the expulsion effect on the free energy of hydration of organic ions can also be assessed from published data on uncharged long-chain molecules. It follows from the increase in fugacity with increase in chain length of unbranched aliphatic compounds, *e.g.* alcohols, dissolved in water that the free energy of hydration at 20°

† A recent paper[2] has made use of the hypothesis that the term in the expression for the free energy of a large ion which depends on non-Coulombic interaction with the solvent is identical with that for an uncharged molecule of the same radius.

changes by 0.16–0.175 kcal when one CH_2 group is added to the chain[9,10]. Hence the reduction in free energy of hydration due to the expulsion effect should be about 3.2 kcal greater for the cetyltrimethylammonium ion, $C_{16}H_{33}.N(CH_3)_3^+$, than for the NH_4^+ ion. Application of this method of calculation to the $N(C_5H_{11})_4^+$ ion, using the fugacities given in ref.9 for methyl and t-butyl alcohols, indicates that 0.2 instead of 0.17 kcal should be added for each CH_2 group, which gives an increase in the expulsion effect on passing from NH_4^+ to $N(C_5H_{11})_4^+$ of about 4 kcal.

Thus appreciably lower values are obtained for the non-Coulombic component of the free energy of hydration by the second method of calculation compound with the first (the expulsion effect for the NH_4^+ ion is probably small). The difference between the two calculated values is still greater if we consider the corresponding component for the total energy of hydration. The first method of calculation gives a value which, as indicated above, is of the same sign as, although less than, that for the free energy; with increase in chain length in homologous series, however, the free and the total energy of hydration of gaseous organic compounds change in the opposite sense[9]. In spite of the diminution in solubility with increase in chain length, the energy evolved in the dissolution of gaseous organic compounds increases under these conditions. Since the first method of calculation involved several dubious assumptions, the results obtained by the second method must be regarded as the more reliable, whence it follows in particular that the expulsion effect of large organic ions is entropic in origin.

In any case, rough estimates of the van der Waals component of the free energy of hydration show that it reaches very considerable values for the organic ions with which we deal in practice in electrochemical research. This is seen particularly well from the fact that the gain in free energy, calculated from the formula $\frac{1}{2}Ne^2(1-1/D)/r$, for the transfer of an ion from a vacuum to water, is only ~30 kcal for an ion with $r = 5.29 \times 10^{-8}$. For an ion with r about 10 Å, the expulsion effect should thus reduce the free energy of hydration to zero.

It is difficult to carry out similar calculations for inorganic ions with $r = 1.5-2.0 \times 10^{-8}$. Although the expulsion effect is not usually allowed for in calculating the energy of hydration, its hypothetical existence has been used to explain the increase, in the sequence $Cl^- < Br^- < I^-$, of the capacity of inorganic anions for adsorption at the free surface of aqueous solutions and at the water–mercury interface[3,11].

The partition coefficient of anions between alcohols and water is considerably greater than that of cations‡. It might be concluded, by analogy with the behaviour of the above organic ions, that the halide anions were exhibiting an expulsion effect, which reduced the numerical value of their free energy of hydration and which increased with increase in radius. Great caution is necessary, however, in reaching such a conclusion, since there is apparently a considerable difference between aliphatic compounds and the very simple inorganic ions with respect to the effect of molecular size of the non-Coulombic part of the free energy of hydration. In the dissolution of gaseous organic compounds in water the difference in entropy between the initial and final states (negative entropy of hydration) increases with increase in chain length, which also leads to an increase in their fugacity in aqueous solution[9]. In the case of the halide and alkali-metal ions, however, the negative entropy of hydration falls with increase in radius, reaching a value which cannot be explained by a decrease in the orienting action of the electric field of the ion on the water dipoles[6,13]. If, nevertheless, the existence of an expulsion effect of the anions which increases with radius is accepted, a correction would have to be introduced into Izmailov's calculation, since values of free energies of hydration which did not include the expulsion effect would have to be used in the extrapolation. It is readily seen from a consideration of the method of extrapolation employed in ref.1 that such a correction would lead to an increase in the calculated values of the free energies of hydration of cations and to a decrease in those for anions.

Although this correction would probably be small, such a result would be of definite interest, since chemical energies of hydration and the actual values A_r which can be determined experimentally are linked by the relation

$$A_{ch} = A_r + nF\chi_{H_2O}, \qquad (1)$$

which enables us to determine χ_{H_2O}, the potential difference at the water–gas interface, n being the number of positive charges on the ion, and free energies of hydration being regarded as positive. Calculation based on Eqn.(1) using the more reliable of the published values of A_{ch} yields negative values between -0.3 and -0.48 V for χ_{H_2O}, whereas a number of other considerations suggest a small positive value[14,15] (~0.1 V) as the more probable. This difference is diminished when the values of A_{ch} quoted in ref.1 are used in combination with Randles' most trustworthy experimental values[16] of A_r§. The mean for Na^+, K^+, Rb^+, Cs^+, Cl^-, Br^-, and I^- (Li^+ is rather out of line) gives $-2.6 \pm \pm 0.8$ kcal for the difference $A_{ch}-A_r$, whence $\chi_{H_2O} = -0.11$¶. An increase in the calculated A_{ch} for cations would reduce still further the discrepancy between this value and that indicated above. Still more exact calculations of A_{ch} are thus extremely desirable.

In conclusion, I wish to express my gratitude to B.V. Deryagin, Corresponding Member of the Academy of Sciences of the USSR, and to Professor A.B.Taubman for valuable discussion of some of the questions dealt with in the present paper.

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§ Randles' data are undoubtedly more accurate than the earlier results[17]. It is still not altogether clear, however, whether an adsorbed film of moisture was not present on the mercury surface in Randles' experiments; the value used for the electronic work function of mercury in the calculation, by means of which A_r is found from experimental values of the Volta potentials, relates to a clean surface.

¶ Izmailov has kindly informed me that a similar calculation which he carried out by a somewhat different method yielded $\chi_{H_2O} = -0.17$.

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THE SURFACE CONDUCTIVITY OF THE GERMANIUM–ELECTROLYTE JUNCTION

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The study of surface conductivity provides valuable information on the surface properties of semiconductors and of their junctions with other media. The present work concerns an estimate of the surface conductivity of the *n*-germanium–electrolyte junction, the calculations being based essentially on the assumptions about the properties of the junction made in ref. 1.

A logarithmic relation between current and voltage is observed in the anodic dissolution of germanium at low currents; this can be obtained in several ways. It is reasonable to suppose that the charge distribution is closely related to the kinetics of dissolution, and therefore the investigation of surface conductivity will undoubtedly help to elucidate the electrochemical aspects of dissolution.

The conductivity of the region adjacent to the junction differs from that of the homogeneous semiconductor, for the following reasons. The contact potential difference results in a difference in the number of carriers at the surface and in the bulk of the semiconductor. Similarly, the concentration of ions at the junction differs from the bulk value away from the junction. The mobility of the current carriers at the surface also differs from that in the bulk of the material. This is because the width of the surface layer is comparable with the mean free path of the carriers, and therefore collision of the carriers with the surface leads to a substantial decrease in their mobility. Finally, the electrolyte ions adjacent to the semiconductor may be arranged in an ordered fashion, and therefore the occurrence of electronic conduction in this region of the electrolyte is not impossible. This last case, however, will not be examined here.

Let us now calculate the surface conductivity σ_p of the semiconductor, which is defined as follows,

$$\sigma_p = \Gamma_p \mu_{eff}, \tag{1}$$

where Γ_p is the total charge due to holes per unit surface and μ_{eff} the surface mobility of the holes. In conformity with the assumptions made in ref. 1, we regard the surface as being enriched with holes, and neglect the surface conductivity due to electrons. Therefore the total surface charge can with good approximation be put equal to the charge due to holes Γ_p. The total charge can be readily found from the equation

$$\frac{d^2\varphi}{dx^2} = -4\pi\rho(x), \tag{2}$$

where $\rho(x)$ is the density inside the semiconductor at a distance x from the junction, and $\varphi(x)$ is the potential at the point x.

In this case Γ_p is given by

$$\Gamma_p = \int_0^\infty \rho(x)\,dx. \tag{3}$$

On integrating both sides of Eqn. (2) with respect to x, we obtain

$$\int_0^\infty \frac{d^2\varphi}{dx^2}\,dx = -4\pi \int_{x=0}^\infty \rho(x)\,dx.$$

Since the electric field in the interior of the semiconductor is zero, we find that

$$\frac{E_j}{4\pi} = \Gamma_p, \tag{4}$$

where E_j is the electric field at the semiconductor junction.

In determining μ_{eff}, we shall follow ref. 2, but will not repeat the calculations made there, noting only the important physical assumptions involved. The reflection of holes from the surface is assumed to take place by diffusion. This means that particles which have collided with the surface are scattered at all angles. Mathematically this implies that application of an electric field parallel to the boundary surface does not affect the Boltzmann velocity distribution at the surface itself. For simplicity, we shall further suppose that a constant electric field E_j exists in the semiconductor at equilibrium. We shall see later that this hypothesis yields too low a value for the conductivity.

In the present case, in conformity with ref. 2, we have

$$\mu_{eff} = [1 - \exp(1 - \operatorname{erf}\alpha)]\,\mu_b, \tag{5}$$

$$\operatorname{erf}\alpha = \frac{2}{\sqrt{\pi}} \int_0^\alpha \exp(-x^2)\,dx. \tag{6}$$

The value of α is given by

$$\alpha = \frac{\sqrt{2mkT}}{eE_j\tau}, \tag{7}$$

where τ is the relaxation time in germanium, and μ_b is the bulk mobility in the interior of the semiconductor.

According to ref. 1, the junction field E_j is high (it was required in ref. 1 that $y_j > 1/t_0$, where y_j is a quantity proportional to the electric field, and t_0 is proportional to the length of the Helmholtz layer). It is easily shown that for