

Fig. 3

during 20–300 h, the slow adsorption stage obeys a parabolic law, which points to the diffusive character of the phenomena occurring at the surface.

The existence of such surface films of oxygen, able to volatilise in vacuo, is indicated also by the investigations of other authors. The work of Dell[3] has shown that oxygen is readily adsorbed at 25° by the surface of germanium powder purified from surface oxide by heating in vacuo at 650°. The initial rapid-adsorption stage is replaced by a slow process, and even after 5 h oxygen is still absorbed. In the range 0.1–0.6 mm Hg the amount of oxygen absorbed is practically independent of pressure. For the first 2 h Dell found a logarithmic relationship between adsorption and time, which does not contradict our own results.

Zettlemoyer et al. [4] also noted that, on nickel, cobalt, and copper, apart from the usual chemisorption and physical adsorption, firmly bound oxygen layers, able to volatilise on warming up, are formed at -195°. It may be that this form of adsorption, which these authors term "stable physical adsorption", is similar in nature to the adsorption which we have observed.

Additional information on the nature of this reversible adsorption could be obtained from optical and electron-diffraction studies. We have recently shown[5] that, with oxygen at atmospheric pressure, the thickness of the oxygen layers which can volatilise in vacuo may reach 25 Å and even higher. It has been suggested that the oxygen molecules in such layers are arranged with their major axes normal to the metal surface. [6]

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THEORY OF THE HYDRATION OF IONS IN AQUEOUS SOLUTION

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In connection with the study of the hydration of ions in aqueous solution great interest attaches to the work of Connick and Poulson, [1] in which they used a nuclear magnetic resonance method to determine the rates of exchange of water molecules immediately surrounding various cations. This is the first estimate of the mean periods of time during which water molecules stay within the primary hydration shell of the ions (τ_i values). It was found in particular that at room temperature $\tau_i \leq 9.10^{-7}$ sec for Fe^{3+}, and $\tau_i \leq 1.10^{-7}$ sec for Mn^{2+}.

We have previously proposed[2,3] the quantities τ_i/τ and ΔE_i as quantitative measures of the short-range hydration of ions in aqueous solution. The quantity τ represents the average time spent by a water molecule in water in one position of equilibrium, and ΔE_i is the difference between the activation energy for the replacement of water molecules from the primary hydration shell of the ions by other water molecules in the solution ($E + \Delta E_i$) and the activation energy for the exchange of neighbouring molecules in water (E). The ratio τ_i/τ and the quantity ΔE_i are connected by the relationship

$$\frac{\tau_i}{\tau} \cong e^{\Delta E_i / RT} \qquad (1)$$

We may write this approximate relationship in the more accurate form

$$\frac{\tau_i}{\tau} = \frac{\tau_{0i}}{\tau_0} e^{\Delta E_i / RT},$$

where τ_0 and τ_{0i} are the factors multiplying the exponential terms in the expressions for τ and τ_i respectively. The multiplier τ_0 is approximately equal to half the period of vibration of the water molecules close to equilibrium positions in water, and the multiplier τ_{0i} to half the period of vibration of the molecules in the primary hydration shell of the ions. For ions close to the boundary between positive and negative hydration it can be assumed that $\tau_{0i} = \tau_0$. For ions characterised by positive hydration $\tau_{0i} < \tau_0$, and therefore for such ions relationship (1) gives an upper limit to the value of τ_i (just as in the results of Connick and Poulson).

The value of τ was determined from data on the Raman spectra of water and on self-diffusion in water. It was found that at 25° $\tau = 1.7 \times 10^{-9}$ sec. [4] A method was worked out for estimating values of ΔE_i for individual ions from data on self-diffusion in water and on the temperature coefficients of ionic mobilities in solution. [3,4] From the values of ΔE_i thus obtained it appeared that in a solution exchange of water molecules next to the ions for other water molecules occurs extremely rapidly. Among the ions examined the cation Mg^{2+} has the largest value of τ_i, but even here the upper limit to τ_i was only 1.5×10^{-7} sec ($\tau_i/\tau \leq 86.3$, $\Delta E_i \leq 2.61$ kcal/mole). It would appear that such high rates of exchange of water molecules surrounding the ions contradict the extremely high values of the energies of hydration of the ions. It has been shown that in fact this is not so. [3,4] However, no data

have yet been published with which the results obtained could be compared (even if only as to order of magnitude). Such data are first given in the work of Connick and Poulson, [1] from whose results $\tau_i \leq 10^{-7}$ sec for Mn^{2+}, i.e. $\tau_i/\tau \leq 59$ and $\Delta E_i \leq 2.4$ kcal/mole.

The values of τ_i/τ depend on the radius of the ion, increasing as the latter decreases. Since the radius of Mg^{2+} is 0.74 Å and that of Mn^{2+} 0.91 Å, [5] the value obtained by Connick and Poulson for the upper limit to τ_i for Mn^{2+} can be regarded as experimental confirmation of the quantitative characteristics of short-range hydration of the ions given earlier.

Estimates of ΔE_i from existing experimental data are of an extremely rough character. It is scarcely possible to obtain values of ΔE_i directly even from data on the self-diffusion of water in aqueous solutions of electrolytes (here a number of complicating factors exist, which have been considered by Wang [6]). For this reason special interest attaches to the equation recently obtained [7] relating ΔE_i with the coordination numbers of the ions in aqueous solution (mean numbers of constantly interchanging water molecules immediately surrounding the ions):

$$\frac{n_i}{4\pi R_i^2} = \frac{n}{4\pi R_0^2} \frac{j_0}{j_{0i}} e^{\Delta E_i / RT}, \qquad (2)$$

where n_i and R_i are the coordination number and radius respectively of the primary hydration shell of the ion in solution, n and R_0 are the corresponding values for water molecules in water, and j_0 and j_{0i} are the factors by which the exponential terms are multiplied in the expressions for the average numbers (during 1 sec) of activated exchanges of water molecules in water (j_0) and water molecules from the primary hydration shell of the ions (j_{0i}). The values of j_0 and j_{0i} are related to the vibration frequencies of the molecules in the transient equilibrium positions (they are approximately equal to twice the frequencies). Since n, R_0, and j_0 are known, [4] Eqn. (2) enables ΔE_i to be calculated from n_i and R_i, determined, for example, by X-ray diffraction, if the vibration frequencies of the water molecules in the primary hydration shell of the ion are known. In a number of cases (for ions close to the boundary between positive and negative hydration) it can be assumed that $j_0/j_{0i} \cong 1$. In addition, Eqn. (2) can be used also to estimate values of j_{0i}.

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ISOTOPE EXCHANGE BETWEEN CARBON DIOXIDE AND THE CARBONATE ION IN THE SEPARATION OF THE ISOTOPES OF CARBON AND OXYGEN

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It is known [1,2] that the separation of carbon isotopes by the bicarbonate method at atmospheric pressure is not very effective because of the low solubility of CO_2 in aqueous salt solutions. Thus Tunitskii and his coworkers, [2] using optimum packing in a two-metre column, achieved a separation with an effectiveness of about three theoretical plates, i.e. the height equivalent to one theoretical plate was 62 cm. The separation of carbon isotopes by this method, i.e. by using the exchange reaction

$$C^{13}O_2 + HC^{12}O_3^- (soln.) \rightleftharpoons C^{12}O_2 + HC^{13}O_3^- (soln.)$$

is improved by raising the pressure in the system because of the resulting increase in the solubility of CO_2. [1-3] However, the time required to reach a steady state is then considerably increased, [2] and difficulties arise with the apparatus owing to the use of high pressure.

The solubility of CO_2 can be raised by adding to the aqueous bicarbonate solution certain water-miscible organic solvents, such as alcohols, acetone, etc. The solubility [4] of CO_2 at 20° in one volume of solvent is $l = 0.900$ in water, $l = 3.57$ in pure methyl alcohol, and $l = 6.98$ volumes in acetone.

This principle, namely the employment of mixed solvents, can be applied also to other isotope-exchange reactions, the effectiveness of separation of the isotopes being governed by the solubility of the reactants (especially of gases).

We carried out experiments with addition of 5 vol. % of methyl alcohol and 5 vol. % of acetone to a 20% solution of potassium bicarbonate. For comparison an experiment was also carried out without added solvents. The packing used consisted of a synthetic aluminosilicate catalyst in the form of cylindrical pellets containing 16.0% Al_2O_3 and measuring 3.5 × (5–6) mm. Before use the packing was washed with warm hydrochloric acid solution and with distilled water. During the experiments the column, 2 metres high 16 mm in diameter, was cooled to 20° with thermostated water. The solution of potassium bicarbonate entered the column at the rate of 4.0 ± 0.1 ml/min. The results (Fig. 1) show that addition of 5 vol. % of methyl alcohol has practically no effect on the separation of carbon isotopes. However, addition of 5 vol. % of acetone leads to an increase in the overall separation factor from 1.044 (without addition) to 1.100 in the course of 24 h operation of the column, the height equivalent to a theoretical plate decreasing from 53 to 25 cm.

It may be assumed that this effect is due both to the increase in the solubility of CO_2 in the water–acetone system and to the possible occurrence of another competing exchange reaction* of the type:

* Urey et al. [5] have shown that a solution of CO_2 in pure acetone is ineffective for the separation of carbon isotopes.