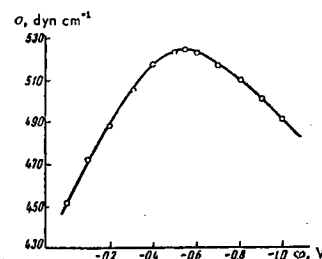


Fig. 2. Critical curves for water:

1) isochore; 2) constant-entropy curve; 3) constant-enthalpy curve; 4) $U = \text{constant}$ curve; $v_c = 3.26 \text{ cm}^3 \times \text{g}^{-1}$; $S_c = -1.058 \text{ kcal kg}^{-1} \text{ deg}^{-1}$; $U_c = 484.3 \text{ kcal kg}^{-1}$; $t_c = 501.5 \text{ kcal kg}^{-1}$.



It is well known that the zero-charge potentials of metals φ^0 can be related to the work function ψ by the approximate relation $\varphi^0 = \psi - 4.78$.³ Tsarev⁴ gives ψ_{In} a value of 4.0 V, emphasising its unreliability. If this is substituted in the above equation, -0.78 V is obtained for the zero-charge potential of indium, relative to the normal hydrogen electrode, i.e. near to our value. It may therefore be assumed that the value of ψ_{In} quoted by Tsarev is not far wrong.

It may be observed further that the surface tension σ_{In} at the zero-charge potential of indium is 523 dyn cm⁻¹. Timofeevicheva and Pugachevich⁵ find that σ_{In} in a vacuum at the same temperature is 531 dyn cm⁻¹.

The relations are illustrated graphically in Fig. 2, using the experimental data for water as an example.

It must also be mentioned that the equations obtained, including of course Eqn. (1), hold for any point within the two-phase range of parameters describing the state of a substance.

THE ZERO CHARGE POTENTIAL OF INDIUM

V. A. Kuznetsov and L. S. Zagainova

This paper describes a determination of the zero-charge potential of indium by measurement of the potential at the maximum of the electrocapillarity curve. The metal was of grade B-4. Analysis showed that the total content of impurities was less than $2 \times 10^{-4}\%$. The electrolyte used was a fused LiCl-KCl eutectic mixture, prepared from the carefully purified salts. Potentials of the capillary electrode were measured at 450° relative to a fused-lead electrode in the LiCl-KCl mixture. The experimental method has been described previously¹.

The electrocapillarity curve of indium in the Figure shows that the zero-charge potential of indium is -0.52 V with respect to the lead electrode. This is 0.05 V more negative than the zero-charge potential of lead but 0.11 and 0.13 V more positive than that of cadmium and thallium (-0.47†, -0.63 - -0.65 V respectively²). Since the difference in zero-charge potentials of metals changes little on passing from melts to solid metals in aqueous solutions, it may be expected that the potential of indium in an aqueous solution would be -0.75 to -0.80 V with respect to the normal hydrogen electrode.

† -0.67? (Ed. of Translation).

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THE MECHANISM OF THE CATHODIC REDUCTION OF ZINC OXIDE LAYERS ON A ZINC ELECTRODE

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The cathodic reduction of zinc oxide layers on a zinc electrode in alkaline solutions may take place in two ways: (1) via the solution, with the participation of zincate ions formed by dissolution of zinc oxide in alkali, and (2) in the solid phase, due to the slight electronic conductivity of zinc oxide or to diffusion or surface displacement of zinc ions through the zinc oxide. That the reaction can take place by the first mechanism is obvious, in view of the ready solubility of zincate ions in alkali and the ease of their cathodic reduction.

To show that it is possible in principle for the reaction to take place by both of the above mechanisms, we studied the reduction of zinc oxide under conditions where reaction by the first method is hindered, namely in absolute ethyl alcohol, in which zinc oxide is almost insoluble. The experiments were carried out at electrodes obtained by anodic oxidation of smooth zinc and on "coated" electrodes prepared by depositing a layer of zinc oxide, up to 0.5 mm thick, on a zinc plate with polyvinyl alcohol as binding agent. The polarisation curves were recorded in an atmosphere of hydrogen. A special apparatus was used to record the polarisation curves in a period of several seconds. At high current densities the individual points of the polarisation curve were sometimes recorded at different, always fresh electrodes. This made it possible to avoid the influence of preliminary polarisation on the structure of the electrode and on the changes in concentration close to the electrode. The potential was measured relative to an auxiliary mercuric oxide reference electrode in 10 N KOH.

"Chemically-pure" grade reagents were purified before use. "TsO" grade zinc (not less than 99.96%) was used. Ethyl alcohol was dehydrated with calcium oxide and metallic calcium and its purity was checked by the specific gravity. The solutions were saturated with anhydrous LiNO_3 or K_2SO_4 to increase the electrical conductivity.

The polarisation curves recorded in absolute ethyl alcohol saturated with LiNO_3 at a "coated" zinc oxide electrode are shown in Fig. 1 (curves 1). Fig. 2 gives the same curves recorded at electrodes prepared by oxidising smooth zinc with an anodic current of $1 \times 10^{-6} \text{ A cm}^{-2}$ for 10 min (curve 2) and with an anodic current of $8 \times 10^{-6} \text{ A cm}^{-2}$ for 1 h (curve 1). The same figures also give the polarisation curves recorded at smooth air-oxidised zinc (curve 2 in Fig. 1 and curve 3 in Fig. 2) and the polarisation curves obtained for measurements in the reverse sense (broken curves).

It was observed that after the sharp displacement of the potential to more negative values, there was considerable evolution of hydrogen, which with the "coated" electrode took place at current densities greater by one and a half powers of ten than with the air-oxidised smooth zinc electrode. At

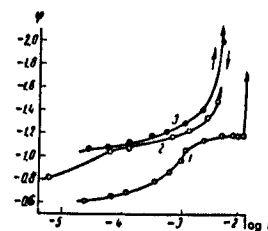


Fig. 2. Polarisation curves in absolute ethyl alcohol saturated with LiNO_3 :
1) smooth zinc oxidised by an anodic current of $8 \times 10^{-6} \text{ A cm}^{-2}$ for 1 h; 2) smooth zinc oxidised by an anodic current of $1 \times 10^{-6} \text{ A cm}^{-2}$ for 10 min; 3) smooth zinc oxidised in air.

electrodes obtained by the anodic oxidation of smooth zinc, the limiting current depended on the quantity of oxide formed (curves 1-3 in Fig. 2). A trace of water in the alcohol does not alter the situation qualitatively, as can be seen from Fig. 3, which gives polarisation curves at "coated" (curve 1) and smooth (curve 2) zinc electrodes in 98% ethyl alcohol saturated with LiNO_3 .

The reverse course of the polarisation curves recorded at "coated" electrodes after the onset of hydrogen evolution is similar to that of the curves at smooth electrodes.

The solubility of zinc oxide in absolute ethyl alcohol, found by analysis, was 10^{-6} mole litre $^{-1}$. This value is evidently high, since it was not possible to remove completely the suspension of zinc oxide in the solution in which the solubility was determined.

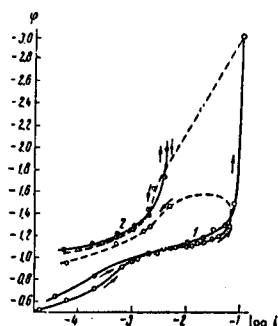


Fig. 1. Polarisation curves in absolute ethyl alcohol saturated with LiNO_3 :
1) "coated" zinc oxide electrode;
2) smooth zinc.

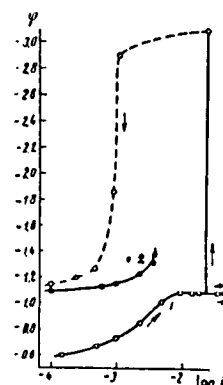


Fig. 3. Polarisation curves in 98% ethyl alcohol saturated with LiNO_3 :
1) "coated" zinc oxide electrode;
2) smooth zinc.

The data show that in absolute ethyl alcohol, in which zinc oxide is almost insoluble, reduction of zinc oxide by a cathodic current takes place, the limiting current of this process being fairly high, ~ 0.1 A per cm^2 of the apparent surface of the "coated" electrode.

It is difficult to attribute the reduction of zinc oxide on "coated" and smooth electrodes in absolute ethyl alcohol to participation of zincate ions in the solution, even if, like Kabanov and Popova in their work on the reduction of PbSO_4 ,¹ we allow for the fact that the source of dissolved substance lies in the diffusion layer. Taking the dimensions of the zinc oxide particles as $1 \times 10^{-4} - 1 \times 10^{-5}$ cm $\dagger$, and assuming that the effective thickness of the diffusion layer $\delta = 10^{-5}$ cm, we in fact obtain for the order of magnitude of the limiting current

$$i_{\text{lim}} = \frac{nFDc}{\delta} \ll 1 \times 10^{-4} \text{ A cm}^{-2},$$

instead of the experimentally-observed value 10^{-1} A cm^{-2} .

The data thus indicate that in solutions where the dissolution of the oxide is difficult, the reduction of zinc oxide on zinc takes place directly in the solid phase, as in the case of manganese dioxide² and nickel oxide electrodes³.

We wish to thank Professor B. N. Kabanov for valuable discussion of this problem.

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DETERMINATION OF THE SINGLE-STAGE SEPARATION FACTORS FOR SULPHUR ISOTOPES. SULPHUR DIOXIDE COMPLEXES

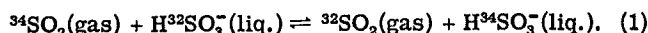
G. M. Panchenkov and L. I. Pechalin

A suitable method of separating sulphur isotopes in appreciable quantity has not yet been found. The individual sulphur isotopes are of importance in a number of biochemical and physiological investigations where the use of radioactive ^{35}S is not possible.

There have been many publications dealing with the separation of stable sulphur isotopes by various methods.

$\dagger$ The particle size of the zinc oxide powder used to prepare the electrodes was determined by means of an electron microscope by I. I. Astakhov, whom we thank.

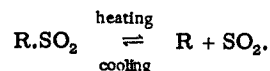
Most of these are based on the exchange reaction between sulphur dioxide gas and a bisulphite solution:



The separation factor for the ^{32}S and ^{34}S isotopes in this reaction is 1.019.^{1,2} However, this method suffers from the great disadvantage that reversal of the phases requires large quantities of expensive reagents.

It is therefore of interest to search for a suitable chemical exchange system for separating the sulphur isotopes, similar to those used in the separation of the boron isotopes on an industrial scale³. In such systems, reversal of the phases is brought about by simple thermal decomposition, thus avoiding the consumption of chemical reagents.

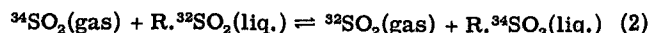
Our work has been directed at finding suitable molecular compounds of sulphur dioxide and determining the single-stage separation factors for the sulphur isotopes. Of the numerous compounds forming complexes with SO_2 , xylidine and dimethylaniline were chosen. They absorb vigorously large quantities of SO_2 , forming molecular compounds $\text{R} \cdot \text{SO}_2$ which, on heating, readily and completely dissociate to the original compounds:



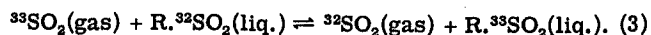
Xylidine was diluted with water in the ratio 1:2 to avoid the crystallisation that occurs in pure xylidine with an SO_2 concentration of 108 g litre $^{-1}$.⁴ Dimethylaniline does not require dilution with water. Technical grade SO_2 from a cylinder and "pure" grade *m*-xylidine and dimethylaniline were used.

The saturated complexes $\text{R} \cdot \text{SO}_2$ are coloured dark red. At 20° their compositions are: 1 mole dimethylaniline + 1.6 mole SO_2 , and 1 mole xylidine + 1.2 mole SO_2 .

Since determination of the single-stage separation factor α by direct measurement of the isotopic compositions of the phases with a mass spectrometer is not possible on account of the small value of α and the insufficient precision of the apparatus, a multi-stage enrichment of the sulphur isotopes was carried out in order to magnify the single-stage separation effect. α was determined experimentally for the reactions



and



The SO_2 was slowly evolved (separate bubbles) from one portion of complex and passed, with stirring, into another portion, which, after saturation, was used in another cycle of the process. With xylidine the process consisted of five stages and with dimethylaniline — of three. SO_2 evolved from the complexes obtained in the final stages was subjected to mass-spectroscopic analysis.

Isotopic analysis was performed with an MI-1305 mass spectrometer, with automatic recording of the 48, 49, and 50 mass spectra, corresponding to the SO^+ ion, on an EPP-09 recording potentiometer. Correction for the oxygen isotopes was not made.

The results of the experiments (see Table) show that the exchange reaction results in a separation of the sulphur