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1ST AND 2ND ORDERS

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ca

2

Platinum electrode. II. Adsorption properties of the platinum electrode. A. Shlygin, A. Frumkin and V. Medvedovskii. *Acta Physicochim. U. R. S. S.* 4, 911-28 (1936) (in German); cf. C. A. 30, 4008[8]. In salt solns. the alkali adsorption is little affected by anodic polarization. The induction period is much longer in alk. than in acid solns. In acid, NaBr-NaOH and Na_2SO_4-H_2SO_4 solns. alkali is replaced by acid with further polarization. The converse change takes place in alkali and alkali-salt solns. The shape of the adsorption curve is explained by assuming that the acids and H atoms affect the metal-soln. p. d. in the pos. direction. The satn. of the electrode surface with H leads to increase of metal-soln. p. d. and reduction in capacity of the double layer. Amts. of adsorption are in general parallel to the amts. of electricity. Changes due to slow oxidation were also observed. III. **Adsorbed atoms and ions on the surface of the platinum electrode.** A. Frumkin and A. Shlygin. *Ibid.* 5, 819-40 (in English). *Bull. acad. sci. U. R. S. S., Classe sci. math. nat., Ser. chim.* 1936, 773-91. Curves show p. d. and adsorption as affected by charging current, soln. compn. and electrode area. By use of these the relation between adsorbed H and the thermodynamic p. d. can be calcd. A differential equation is derived enabling the calcn. of adsorption curves from the charging curves made at 2 different p_H values. George M. Evans

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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1ST AND 2ND ORDERS

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3rd AND 4TH ORDERS

7

The Platinum Electrode. III. Adsorbed Atoms and Ions on the Surface of a Platinum Electrode. A. Frumkin and A. Slygin (*Izvestia Akademii Nauk S.S.S.R.* (*Bull. Acad. Sci. U.R.S.S.*), 1936, (Chim.), (5), 773-792. [In Russian.] See abstract from periodical printed in English, *Met. Abs.*, this vol., p. 402.—S. G.

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BC

A-1

Theory of the hydrogen overvoltage. A. FRUMKIN (J. Phys. Chem. Russ., 1937, 10, 568—574).—The formation of H_2 occurs in two steps, viz., (1) metal + H_3O^+ → metal–H + H_2O, and (2) metal–H + H_3O^+ → metal + H_2O + H_2. On metals which readily adsorb H_2 the second reaction is slow and determines the overvoltage; on metals like Hg the decomp. of metal–H compound is rapid, and the overvoltage is due to the slowness of the first reaction.

J. J. B.

METALLURGICAL LITERATURE CLASSIFICATION

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1ST AND 2ND ORDERS

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Cu

2

Phenomena of wetting and the adhesion of bubbles. I. A. Frumkin. *J. Phys. Chem.* (U. S. S. R.) 12, 337-45 (1938)(in Russian); *Acta Physicochim. U. R. S. S.* 9, 313-37(1938)(in German).—Theoretical. In the general case, the curve expressing the relation between surface tension, σ, and area per mole, has a max. and a min. For a finite angle of contact between $0 < s < s_f$ ($s = s_f$ corresponding to the layer in equil. with the vol. phase) the layer is metastable or labile. The position of points is detd. by the condition of equality of the areas *abcd* and *def* on the σ-s diagrams. For cases where the contact angle is not finite, for $s_f < s < s'_f$, the layer is stable, while for $s'_f < s < s_f$ it is metastable or labile. The results are applied to the theory of the adhesion of bubbles. **II. The mechanism of the adhesion of bubbles to a mercury surface.** A. Frumkin and A. Gorodetskaya. *Acta Physicochim. U. R. S. S.* 9, 327-40(1938)(in English).—Data are given for the adhesion of H_2 bubbles to a Hg cathode for various concns. of the Na_2SO_4 soln. from 10^{-4} to 1.0 *N* and for various degrees of polarization. The time of adhesion varies from a fraction of a second to 15 min. (if adhesion occurs at all), and is least for low pos. polarizations (0.2-0.8 *V*) and higher concns. of soln. Below 10^{-4} *N*, small lenses appear on the Hg surface. The equation $P = (D/2\pi)\, e^{2h/\kappa}\cdot(\varphi^2 h/\kappa^2)$ is derived for the pressure acting upon 2 charged surfaces at a distance h, a soln.-metal potential difference φ, and a double layer thickness κ.

F. H. Rathmann

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BC

A-1

Maxima on current-voltage curves. B. BRUNS, A. FRUMKIN, S. JOVA, L. VANJUKOVA, and S. ZOLOTARWSKAJA (Acta Physicochim. U.R.S.S., 1938, 9, 359—372; cf. A., 1934, 1079).—Current-voltage curves at a Hg cathode in solutions of $Hg_2(NO_3)_2$ under various conditions have been measured. A theory is outlined which attributes the max. on the current-voltage curve to the "auto-stirring" caused by the movements of the Hg surface, which are related to local differences of interfacial tension or to variations of this tension with time. A method of measuring the potential of a Hg cathode at different points in the surface is described. O. J. W.

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BC

R-1

Properties of unimolecular layers on salt solutions. I. A. I. PANKRATOV. II. A. N. FRUMKIN and A. I. PANKRATOV (J. Phys. Chem. Russ., 1938, 12, 541—548, 549—555).—I. At a const. area the surface pressure and the surface potential of cetyl alcohol and Et palmitate (I) films increase when the underlying solution contains much (1—8 N.) salt. The effect of the salts rises in the series sulphates < chlorides < bromides < iodides.

II. The chemical potential of (I) on various underlying solutions is calc. The calculation makes it probable that the salt effect is due to interaction between the salt ions and the dipoles. J. J. B.

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3RD AND 4TH ORDERS

2

Investigation of thin layers of organic substances at the mercury-solution boundary by the method of capacity measurements. I. High-molecular alcohols and acids. A. Gorodetskaya and A. Frumkin. *Compt. rend. acad. sci. U. R. S. S.* 18, 630-42(1938)(in English); cf. Tomilek and Přibl, *C. A.* 30, 3219[4]; Borisova and Proskurnin, *C. A.* 30, 7483[2].—A new method for the study of thin layers of org. liquids spread over the surface of a polarized Hg electrode. From the authors' measurements, the effective thickness of a layer (d) from its capacity, for cetyl alc. and oleic acid is calcd. Thus, under max. compression of the Hg surface, these values are $d = 1.9 \times 10^{-7}$ and $d = 1.5 \times 10^{-7}$, resp. The value for cetyl alc. is fairly close to the length of the mol. detd. by other methods, although the value for oleic acid is lower. It should, however, be borne in mind that with even a partial penetration of the soln. of the electrolyte between the mols. of a monolayer, the effective thickness of the monolayer as calcd. from capacity measurements will be much lower than its true value. With polylayers, calcns. of the thickness from capacity afford quite reasonable results as long as the thickness does not exceed the value of 2-3 monolayers. For thicker layers, too low values result.

W. A. Cook

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1ST AND 2ND DEGREE

PROCESSES AND PROPERTIES INDEX

BC

A-1

Influence of stirring on current voltage curves obtained with a mercury cathode. S. Joza and A. Frumkin (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 293—296).—Both for an amalgamated Pt cathode and a dropping Hg cathode in $Hg(NO_3)_2 + HNO_3$ solutions, the max. in the current–voltage curve disappears when a vigorous stream of electrolyte is directed against the electrode. O. D. S.

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3RD AND 4TH ORDERS

A-1

Electrokinetic behaviour of platinum at different potentials. N. BALABCHOVA and A. FRUMKIN (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 449—452).—The potential and the deflexion of a fine Pt wire immersed in an electrolyte between two charged plates have been determined under various conditions. Results are related to the formation of polarisation films and are in agreement with measurements of cataphoresis of Pt sols and of adsorption at Pt electrodes. J. A. K.

COMMON ELEMENTS

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1st AND 2nd ORDERS

PROCESSES AND PROPERTIES

4

Basic problems in electrochemistry. A. N. Frumkin and V. A. Pleskov. *Sbornik "Matem. i Estestvozn. v S. S. S. R."* 1938, 401-15; *Khim. Referat Zhur.* 2, No. 1, 13/14(1939). A review of the most important electrochem. investigations in U. S. S. R. for the last 20 years. Considerable progress was made in the electrochemistry of nonaq. solns. (relation between elec. cond. and the formation of complexes; properties of liquid NH_3 solns.); theory of aq. electrolytes, nature of electrodeposition; mechanism of reactions in the elec. discharge through gases; potential drops at different phase boundaries; problems of surface phenomena, theory of electrode processes; measurements of dipole moments and problems of applied chemistry (development of different types of storage batteries, methods of electrolysis of fused salts, electro syntheses, etc.).

W. R. Henn

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PROCESSES AND PROPERTIES INDEX

CP

2

Properties of unimolecular layers on solutions of salts. I. A. Pankratov. *Acta Physicochim. U. R. S. S.* 10, 45-54 (1939) (in English).—Exptl. data on the surface tensions and elec. properties (contact potential as measured by a Guyot-Frumkin radioactive air electrode at 20°) of Et palmitate and cetyl alc. films on pure water and on solns. of K_2SO_4, KCl, KBr, KI, NaCl and $CaCl_2$ in pure water are given. The surface tensions and contact potentials increase in both cases in the order given above, i. e., the order of decreasing ion hydration or increasing anion adsorption leading to an increasing neg. charge of the substrate-air interface. The increasing vertical component of the dipole moment of the polar carbonyl group is attributed to a rotation of the acid H or ester alkyl to a higher position resulting from electrostatic interaction with the surface-adsorbed anions. II. A. Frumkin and A. Pankratov. *Ibid.* 55-64.—A theoretical discussion of data in I from a thermodynamic viewpoint. Owing to electrostatic interaction between the double-layer ions and the mol. dipoles, the work of adsorption for both the salt and the org. film-producing substance increases, increasing the effective dipole moment and increasing the repulsive forces in the surface layer. Hence, independently of the mechanism of adsorption, the work of adsorption, the intermol. repulsive forces in the film and the surface tension increase as the concn. of adsorbed salt increases. F. H. Rathmann

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3RD AND 4TH ORDERS

CA

No. 3

2

Electrocapillary curves of concentrated solutions of acids. Z. A. Iofa and A. Frumkin. *Acta Physicochim. U. R. S. S.* 10, 473-80(1939)(in English).—Data on HCl in concns. from 0.1 to 10 *N* are given and discussed by means of Lippmann's equation. Cl adsorption is pos. on the anodic branch of the electrocapillary curve; it becomes strongly neg. on the cathodic branch. Adsorption of the H ion is pos. in dil. solns. and neg. in concd. solns.

F. H. Rathmann

COMMON ELEMENTS

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1ST AND 2ND ORDERS

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Q + FRUMKIN A

Hydrogen overvoltage on nickel. [illegible], S. Levina and A. Frumkin. *Acta Physicochim. U. R. S. S.* 11, 21-44([illegible]).—The H overvoltage on Ni in HCl solns. from 0.0008 to 0.15 *N* and for c. d. from 10^{-4} to 10^{-4} amp./sq. cm. obeys Tafel's equation $\eta = a + b \log i$ with $b = 0.100$. In NaOH, concns. from 0.001 to 8.8 *N*, $b = 0.108$–0.115 at 20°. In acid solns. the overvoltage increases on addn. of neutral salts (NaCl, $LaCl_3$); in alkalies, it decreases. A satn. current similar to that predicted by Horiuti and Okamoto (*C. A.* 32, 4861[9]) was observed only at much higher c. ds., and can be more satisfactorily explained as due to concn. polarization of H and to the oxidation of Ni and not by the velocity of H adsorption. The exptl. results can be explained by assuming that the slow process is ionic and influenced by the elec. field of the double layer. F. H. Rathmann

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PROCESSES AND PROPERTIES INDEX

BC

A 1

Maxima on current-voltage curves. B. BRUNS, A. FRUMKIN, S. JOPA, L. VASJUKOVA, and S. ZOLOTAREVSKAJA (J. Phys. Chem. Russ., 1939, 13, 786—793; cf. A., 1935, 1079; 1939, I, 140).—The max. are traced to mixing of the Hg by surface movements caused by differences of surface tension between various parts of the surface and by variations of surface tension with time.

R. C.

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PROCESSES AND PROPERTIES INDEX

Electrocapillary curves of concentrated solutions of acids. I. Derivation of an adsorption equation. A. Frumkin and Z. A. Iofa. *J. Phys. Chem.* (U. S. S. R.) 13, 931-3(1939).—The equation $\partial\varphi_1/(1/F)\partial\mu_{HA} = -\Gamma_A'/(\Gamma_A' - \Gamma_H)$ is derived, where φ = potential difference, μ = chem. potential, Γ = adsorption of Hg salt or of acid. **II. Adsorption of ions in solutions of HCl, HBr and H_2SO_4.** Z. A. Iofa, B. Ustinskii and F. Ilman. *Ibid.* 934-41.—From 0.1 to 20.0 *N* the course of the electrocapillary curves and of the adsorption of anions and cations as a function of concn. is given by the equations given in part I. The exptl. data are given in 10 tables and 3 figures.

F. H. Rathmann

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FRUMKIN4A8 600

1. LUKOVTSEV, P. : LEVINA, S.: FRUMKIN, A.

2. USSR (600)

"The Supertension (Perenapryazheniye) of Hydrogen over Nickel," Zhur. Fiz. Khim., 13, No. 7, 1939. Moscow Physico-Chemical Institute imeni L. Ya. Karpov, Lab of Superficial Phenomen/ Received 29 December 1938.

9. [redacted] Report U-1615, 3 Jan. 1952.

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PROCESSES AND PROPERTIES INDEX

Capacity of double layer of mercury electrode in dilute solutions of hydrochloric acid and of potassium chloride. M. A. Vorsina and A. N. Frumkin (Compt. rend. Acad. Sci. U.R.S.S., 1939, 25, VIII—681).—The method described (see preceding abstract) has been used to plot the capacity curves of a Hg electrode in dil. KCl (1, 10^{-1}, 10^{-2}, 10^{-3}N.) and HCl (10^{-3}, 10^{-4}N.). The curve of 0·1N-KCl consists of two almost horizontal branches which correspond with a double layer formed of anions and cations respectively, and a connecting branch with intermediate capacity vals. At high positive or negative surface charges the capacity val. increases owing to the deformation of ions. This curve does not indicate a diffuse structure. The data are compared with the requirements of Stern's theory.

W. R. A.

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1ST AND 2ND ORDERS — 3RD AND 4TH ORDERS

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(a) 7.

Diffuse and nondiffuse double layers. A. N. Frumkin. *Bull. acad. sci. U. R. S. S., Classe sci. chim.* 1940, No. 1, 3-12; cf. *C. A.* 34, 3000[9].—A general review of the methods for investigating the structure of double layers is presented. By assuming that the Helmholtz double layer has a const. capacity, the ζ potential can be detd. from the first equation of the Stern theory: $\epsilon = K(\varphi + \psi')$, i. e., by measuring the capacity in dil. solns. and detg. the av. value of the potential (ψ') at the distance of one ionic radius from the surface of metal. This potential (ψ') had somewhat lower value than the ζ potential obtained from the electrokinetic data; this fact was explained by insufficient accuracy of the assumptions taken for the basis of the theory of electrokinetic phenomena. Twenty-five references.

A. A. Podgorny

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M 9

ON THE OVERVOLTAGE THEORY OF H. EYRING. A. FRUMKIN (ACTA PHYSICOCHEM., U.R.S.S., 1940, 12, (4), 481-484) (In English) The overvoltage theory of Eyring, Glasstone, and Laidler (Met. Abs. 1939,6, 418), which proceeds from modifications of the theory of retarded discharge, is criticized and the following objections are raised; (1) the assumption that the overvoltage is independent of the hydrogen-ion concentration is contrary to experimental evidence (2) the assumption that the surface of a metal in aqueous solutions is covered with a mono-molecular layer of water molecules which are firmly bound to the metal in the form of H-atoms and OH- groups is again contrary to experimental data on the adsorption of water on metals, and (3) the explanation of the fractional value of the coefficient α — 0.5 which appears in the formula for the current strength is inaccurate. E.N.

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M

9

***Kinetics of Processes on the Platinum Electrode. III.—The Influence of the Diffusion of Molecular Hydrogen on the Capacity of the Platinum Electrode.** A. Frumkin, P. Dolin, and B. Krukke (*Acta Physicochim., U.R.S.S.*, 1940, **13**, (6), 793-802). [In English]. Cf. preceding abstract. It is shown that Krüger's equation for the polarisation capacity cannot be applied directly to the platinum electrode, because the assumption about the instantaneous establishment of equilibrium between the hydrogen ions in the solution and the hydrogen adsorbed on the surface is too rough an approximation. A relation between the capacity of the ohmic component of the platinum electrode and the frequency of the current is derived which allows for the finite rate of the reaction of evolution of molecular hydrogen, this relation being confirmed by experimental data.—E. N.

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KUCHINSKIY, Ye.; BURSHTEYN, R.; FRUMKIN, A.

Moscow

Laboratory of Surface Phenomena, Physico-Chemical Institute imeni L. Ya. Karpov, (-1940-).

"The Adsorbtion of Electrolytes on Coal."

Zhur. Fiz. Khim., Vol. 14, No. 4, 1940.

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FRUMKIN, A. N.

"Comparison of the Rate of Discharge of H Ions with the Rate of the Total Process of Depositing Hydrogen on Pt," Part II," with P. DOLIN and V. ERSHLER, in Zhur. Fiz. Khim., Vol. 14, No. 7, 1940.

"The Effect of the Diffusion of Molecular Hydrogen on the Polarization Capacity of the Pt. Electrode,"(Part 3), with P. Dolin, B. Ershler and A. Frumkin, Zhur. Fiz. Khim., Vol. 14, No. 7, 1940.

"Adsorption of Electrolytes on Charcoal," Acta Phys., 12, No. 6, 1940.

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1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

A

A-1

Nos. 9-10

Electrochemical methods of studying the surface of catalysts. A. N. Frumkin (*J. Phys. Chem. Russ.*, 1940, 14, 1200—1207).—Electrochemical charging of metal electrodes with H_2 or O_2 gives information about the surface of metals; a review of the results thus obtained is given. J. J. B.

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MA

7

*Hydrogen Over-Voltage and Dissolution of Metals. I.—Dissolution of Lead in Acids. Y. Kolotirkin and A. Frumkin (*Zhur. Fizich. Khimii (J. Phys. Chem.)*, 1941, 15, 346-356; *Brit. Chem. Abs.*, 1942, [A I], 131).—[In Russian.] The rate v of hydrogen evolution by spongy lead in 2N-HCl or 8N-H_2SO_4 is determined by the equilibrium potential of lead and the overvoltage η corresponding with this potential. If the spongy lead is made a cathode and the straight line log. v–η is determined, it joins the point representing the v in the absence of external current. At small c.d. ($<3 \times 10^{-6}$ amp./cm.^{2}), v is < equivalent to the external current as the latter is used up for reduction of oxygen at the cathode. The equilibrium potential of lead in 8N-H_2SO_4 is that of the electrode Pb | $PbSO_4$ | 8N-H_2SO_4.

Also in Acta. Phys. 14, No. 4, 1941

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7

MA

"**Ohmic Resistance of Local Elements During the Solution of Metals in Acids.** V. G. Levich and A. N. Frumkin (*Zhur. Fizich. Khimii* (*J. Phys. Chem.*), 1941, **15**, 748-759; *C. Abs.*, 1942, **36**, 5411).—(In Russian.) Theoretical—mathematical. For a local element due to a disc-shaped inclusion of radius r, assuming a non-polarizing anode, the specific resistance per unit of central cathode surface is given by $2r/\pi\chi$, where χ = specific conductivity of the electrolyte. In the case of zinc dissolving in H_2SO_4, the ohmic fall of potential should not exceed 13 mv. The change in concentration of the electrolyte at the cathode surface is an equally important factor.

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1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

CA

2

The applicability of Nernst's formula to amphoteric adsorbents. A. N. Frumkin. *Doklady Akad. Nauk S. S. S. R.* 30, 414-17(1941).—The difference of potentials between the surface of an amphoteric nonconducting adsorbent and the soln. is expressible by the same relation as that for the H electrode, provided that the no. of the adsorbing groups on the surface is sufficiently great, i. e., $4\pi\lambda_0 q/D \gg 2kT/\epsilon$ and $q^{-1/2} \ll \lambda$, where λ is the thickness of the double layer and q is the no. of the groups.

G. M. Kosolapoff

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Applicability of Nernst formula to amphoteric adsorbents. A. N. Frumkin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 417—419).—The p.d. between the surface of an amphoteric non-conducting adsorbent and the solution can be expressed by the same relation as for a H electrode provided that the no. of adsorbing groups on the surface is great enough. W. R. A.

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No. 5

Hydrogen peroxide formation on the adsorption of acids by activated charcoal. K. Burschtein and A. Frumkin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 32/327–329).—10 c.c. of aq. H_2SO_4 were added to 0·5 g. of charcoal, and O_2 was passed through the mixture. After filtration through a glass filter the adsorbed anion was determined by titration with standard alkali and H_2O_2 by $KMnO_4$. As $[H_2SO_4]$ is increased the yield of H_2O_2 rises. H_2O_2 is, however, formed only when gaseous O_2 is present; in the cathodic reduction of O_2 with C electrodes the rate of formation of H_2O_2 depends on the c.d.

W. R. A.

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The solution of Ni in acids. Ya. Kolotyrkin and A. A. Frumkin. *Compt. rend. acad. sci. U. R. S. S.* 33, 445-9 (1941); *N. C. A.* 37, 3672[3].—The rate of soln. of Ni in acids at different potentials was calcd. by use of the equation $i = P_2 - P_1$, where pos. values of i correspond to a cathodic current, P_2 is the rate of discharge of H ions and P_1 is the rate of ionization of Ni ions. The exptl. procedure consisted in obtaining an accurate H-overvoltage curve and in measuring simultaneously the vol. of H evolved during fixed time intervals, both in the presence and absence of an external polarization. The overvoltage curve obtained on starting from high c. ds. after a prolonged preliminary cathodic polarization of the electrode at high c. d. is situated higher and has a steeper slope than the same curve measured in the reverse direction, i. e., from low c. ds. to high ones. If after the latter treatment the electrode is not subjected again to a prolonged cathodic polarization, the last curve can be fairly well reproduced in both directions. The state of high overvoltage is unstable. H-overvoltage curves in a half-logarithmic scale obtained by measuring c.-d. and those obtained from the rate of H evolution in a $N\,H_2SO_4$ soln. are given. In contrast to the c.-d. curve, the curve obtained from H-vol measurements strictly follows Tafel's equation down to the potential of spontaneous soln. The law of H evolution expressed by Tafel's equation is observed for Ni as well as for Pb in the case when there is no external polarization. The rate of H evolution was also measured at potentials more pos. than the stationary potential, under anodic polarization of the electrode, the c. d. corresponding to a given anodic polarization being measured along with the rate of H evolution. The curve obtained by plotting the rate of soln. of Ni in acids at different potentials in a half-logarithmic scale gives a nearly straight line. The decrease in the rate of metal soln. during cathodic polarization is a direct consequence of the cathodic shift of the metal potential. A. Sindinkov at Moscow State University has confirmed the values of the rate of soln. of Ni in acids by direct analytical measurements. R. R. Heiks

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No. 7

Influence of Acid Concentration and of the Addition of Platinum on the Dissolution of Nickel. Ya. Kolotkin and A. Frumkin (*Compt. rend. (Doklady) Acad. Sci. U.R.S.S.*, 1941, 32, 450-453; *Brit. Abs.*, 1945, [A II], 31). The rate of anodic dissolution of nickel in HCl and H_2SO_4 is independent of acid concentration for concentrations not greater than N HCl and 10N H_2SO_4. Platinum deposited on the nickel electrode has no influence on the rate of dissolution at a given potential, but has a strong influence on the rate of spontaneous dissolution. This is possibly due to platinum forming centres of lowered hydrogen overvoltage. As a result evolution of hydrogen is increased without affecting the dissolution of nickel. The rate of spontaneous dissolution increases because of the shift of the stationary potential in the anodic direction following the increased rate of hydrogen ion discharge.

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*Academy of Sciences, U.S.S.R. *Transactions of the Second Conference on the Corrosion of Metals.* [Held January 15-19, 1941.] Volume II. [In Russian.] Edited by **A. N. Frumkin, E. I. Gurovich,** and **B. N. Kabanov.** 25 x 17 cm. Pp. 208, illustrated. 1943. Leningrad and Moscow: Izdatel'stvo Akademii Nauk S.S.S.R. (18.50 Rbls.)

[Among papers of non-ferrous interest are: "On the Solution of Aluminium in Acids and Alkalies" (M. Straumanis); "The Mechanism of Depolarization of Local Cathodes in Corrosion with Oxygen Depolarization" (N. D. Tomashov); "Irreversible Electrode Potentials of Metals" (G. B. Clark and G. V. Akimov); "On the Passivity of Platinum" (B. V. Krshler); "The Anodic Passivation of Lead in Sulphuric Acid" (B. N. Kabanov); "The Structure and Mechanism of Formation of Surface Films on Metals" (P. D. Dankov); "The Laws of Formation and Growth of Crystals in Electrolysis" (K. M. Gorbunova); "The Effect of Some Metallic Salts (Mercury, Tin, Lead) on Cathodic Processes in Zinc Electrolytes" (N. T. Kudryatsev); "Quality Control of Electrodeposits" (D. S. Abramson); "Electrodeposition at the Stalin Automobile Works" (A. I. Levin); "On the Work of the State Institute of Applied Chemistry on Corrosion" (Ts. A. Adzhemyan); "On the Question of the Effect of Mineral Acids on Metals and Alloys" (I. Ya. Klinov); "Electrodeposits of Manganese from Aqueous Sulphate Solutions" (P. I. Terikhov, A. K. Reikhshtadt, and A. N. Ivanovna).]

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CA

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Free energy of a diffusion double layer. A. Frumkin. *J. Phys. Chem.* (U. S. S. R.) 17, 310-12(1943). — Theoretical. The free elec. energy, E, of a diffusion double-layer is given by the equation $E = {}^1/_2\, W_c$ (and not by $E = W_c$) where W_c is the elec. work necessary to charge the condenser.

F. H. Rathmann

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VORSINA, N.; FRUMKIN, A.

Lab. of Surface Phenomena, Physico-Chemical Inst. imeni L. Ya. Karpov, Moscow (-1943-)

"The Capacity of the Mercury Electrode in the Presence of Polyvalent Cations." Zhur. Fiz. Khim., Vol. 17, No. 5-6, 1943

[redacted]

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Discharge of hydrogen ions. I. Mercury. A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 23—57).—The vol. of H_2 liberated on a Hg cathode was determined in 3N-HCl, 2·2N-HBr, and 3N-KI + 0·1N-HBr. The results confirm the dependence of overvoltage (η) on c.d. Tafel's equation, $\eta = a + b \log i$ (i = current, a and b = const.) holds for Hg up to a high c.d. Using a dropping Hg electrode, measurements of η at const. i should give a mean val. 0·005 v. - the val. at const. potential. Comparison of electrocapillary curves of acidified and alkaline solutions shows the absence of at. H on the surface of the Hg. The mean val. of η on Hg for 0·1N-HCl, 0·2N-HBr, and 0·1N-H_2SO_4 at 20° is 1·428 + 0·115 log i. When salts of multivalent cations (La^{+++} and Th^{++++}) are added to dil. solutions of acids, the val. of the ϕ_1 potential changes from to . The increase of η produced by the addition of these ions is - the increase in the ϕ_1 potential. When salts with a common anion are added to HCl or HBr, a decrease of η is observed for low c.d., but an increase for high c.d., except when Na_2SO_4 is added to H_2SO_4, when there is an increase of η for all c.d. A. J. M.

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Theory of the discharge of hydrogen ions. II. Mercury. Concentrated solution of acids. S. Joffa and A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 183—193; cf. A., 1939, I, 614).--The decrease in overvoltage (η) in conc. acid solutions is determined by the change in the boundary layer structure and the increase in [H^+]. The change in activity coeff. is relatively ineffective. Changes in η in HCl-KCl and HCl-LiCl solutions at equal concns. are approx. equal. A linear relation is found between the adsorption potential of H^+ (ϕ_H) and log (mean a val. for positive and negative ions) in the acid. The change in η is < the val. calc. from the change in ϕ_H. [J.]

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The capacity of a Hg cathode in the presence of multivalent cations. M. Versina and A. Frumkin. *Acta Physicochim. U. R. S. S.* 18, 242-63(1943)(in English); *J. Phys. Chem.* (U. S. S. R.) 17, 295-310(1943)(in Russian).—The capacities of the surface of a Hg electrode in dil. soln. of $BaCl_2$, $LaCl_3$ and $ThCl_4$ have been measured. Throughout the cases examd. capacity maxima were observed at potentials corresponding to not very high neg. values of the surface charge. The magnitude of the surface charge, that of the potential at the distance of one ionic radius from the interface and the equiv. capacity of the electrode were calcd. from expt. data. These calcns. show that the presence of multivalent cations brings about a reversal of the neg. charge of the electrode surface. Possible interpretations of this effect are discussed from the viewpoint of the double-layer theory.

R. H. Rathmann

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Ohmic resistance of local voltaic cells in the process of the solution of metals in acids. B. Levich and A. Frumkin. *Acta Physicochimica U. R. S. S.* 18, 325–40(1943) (in English).—The conditions detg. the behavior of the cathode of a local cell are considered, the cathode being treated as an inclusion having the shape of a disk of radius r_0 embedded in the surrounding mass of the metal. The calcn. is carried out by assuming the anode to be non-polarizable and the cathode strongly polarized. Under these conditions the sp. resistance per unit area of the cathode surface at its center, where it is at a max., is $2r_0/\pi\kappa$, where κ is the cond. of the electrolyte. A calcn. carried out by this formula shows that the ohmic potential drop in the soln. of Zn with inclusions of Ni, in H_2SO_4, does not exceed 13 mv. if r_0 is about 10^{-4}. In the cases where the ohmic potential drop in the soln. cannot be neglected, the change of the electrolyte concn. at the cathode surface should simultaneously be taken into account. F. H. Rathmann

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Effect of the anion on the capacity of a mercury electrode in dilute solutions. M. Vereina and A. Frumkin. *Acta Physicochim. U. R. S. S.* 10, 641-50(1942)(in English).—The magnitude of the min. value of the differential capacity and of the corresponding value of the potential in dil. solns. depend on the adsorbability of the anion. The increase of the latter is followed by an increase of the min. capacity, and the position of the min. is shifted toward more neg. potentials. In presence of strongly adsorbed anions (I^-) at not too low concns., the min. on the capacity curve disappears altogether. The values of min. capacity observed in electrolyte solns., which do not lower the interfacial tension at the Hg-soln. boundary and in which the specific adsorption of anions is, consequently, least marked ($NaOH$, Na_2SO_4), still considerably exceed the values calcd. from the double-layer theory. A qual. interpretation of the effect of specific adsorption of anions on the magnitude and position of the capacity min. may be given on the basis of the Stern double-layer theory.

F. H. Rathmann

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Free energy of a diffusion double layer.—A. Frumkin
Acta Physicochim. U. R. S. S. 18, 473-6(1943).—See
C. A. 38, 5129.
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Overvoltage on a mercury cathode in concentrated solutions. II. Peculiarity and [illegible] and acidified salt solutions. Z. A. Jofa and A. N. [illegible] Phys. Chem. Russ., 1944, 18, 265—268; cf. A., 1939, I, [illegible].—Theoretical and practical work on anomalies in the [illegible] to concn. and c.d. in conc. solutions. A special [illegible] method is used to determine c.d. from the vol. of H_2 liberated at the cathode. From measurements of η in relation to calc. c.d. it is shown that the decrease of η and the departure from linearity on η–log c.d. curves in a solution containing surface-active ions are caused by anion adsorption and not by any depolarization process. In the case of η on Pb, on the other hand, the deviation found in H_2SO_4 solutions has to be explained by depolarization (cf. A., 1940, I, 131). Experiments with solutions of KCl + HCl and LiCl + HCl indicate that at equal acid concn. the η vals. are similar in spite of differences in the activity coeff. of the acid ions. In solutions of HCl, HBr, $HClO_4$, and H_2SO_4 the adsorption potential, calc. from electro-capillary curves (Jofa et al., J. Phys. Chem. Russ., 1939, 18, 934), is a linear function of the log of the activity of the acid, except at low concns. where the curve tends asymptotically to zero. The existence of a log relation between the max. of the electro-capillary curve and the activity of the electrolyte was first demonstrated by Esin and Markov on solutions of KI (A., 1939, I, 520).

G. S. S.

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*On the Theory of Hydrogen Overvoltage on Palladium. A. Frumkin and N. Aladzhalova (*Zhur. Fiz. Khim.*, 1944, 18, (11/12), 493 517). [In Russian.] The hydrogen overvoltage was measured in a hydrogen atmosphere on smooth and diffusion palladium electrodes, the surfaces of which were activated first by anodic and subsequently by cathodic polarization treatments. The following features were investigated: (*a*) the change of overvoltage with time on the smooth electrode and on each side of the diffusion electrode; (*b*) the effect of the electrode hydrogen concentration and the strength of acid and basic solutions on the magnitude of the overvoltage; and (*c*) the effect of palladium hydrogen phase change on the overvoltage. The results obtained can be explained by considering that the total hydrogen overvoltage on palladium is the sum of two separate overvoltage effects: (1) the overvoltage which is independent of the nature of the electrolyte, and which has the same value on both sides of the diffusion electrode, and is considered as the equilibrium overvoltage of the dissolved hydrogen in the palladium electrodes, and (2) the overvoltage which is especially high in the case of basic electrolytes and is independent of the formation of the molecular hydrogen is considered as dependent on the electrochemical reaction. These conclusions are supported by the theoretical considerations of the kinetics of slow decomposition. 12 references are given. V. K.

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Theory of hydrogen ion discharge. III. Palladium. A. Frumkin and N. Aladjakova (*Acta Physicochim.*, 1944, **19**, 1—35).—The properties of Pd electrodes depend largely on the nature of their surface. Experimental results indicate that the overvoltage of Pd during evolution of H consists of two parts. One of them is almost independent of the nature of the solution, and is slowly attained after switching on the current. It also disappears slowly when the current is switched off, and can be transmitted to the diffusion side of the electrode. This indicates that it is an equilibrium potential between H_2 dissolved in the metal and that in the electrolyte. The other part of the overvoltage, which may reach high vals. in alkaline solutions, is not connected with evolution of H, but depends on the electrochemical reaction itself quite apart from the electrodes. This overvoltage is not affected by transition of Pd from the α to the β phase. It is independent of the area of Pd covered by the H_2. The mechanism of the process accounting for these facts is based on the theory of slow discharge. Equations are deduced showing the overvoltage to be composed of two parts, one depending on the intensity of current, the other on the equilibrium potential of adsorbed H_2, in accordance with the experimental facts. The theories of Farkas (A., 1937, I, 78, 253) and of Hickling *et al.* (A., 1943, I, 18) are discussed in the light of the experimental results. The poisoning of Pd electrodes is briefly considered. A. J. M.

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CA

Physical chemistry in the Academy of Sciences of the U.S.S.R. A. N. Frumkin and A. F. Kapustinskii. *Vestnik Akad. Nauk S.S.S.R.* 1948, 91-102 (in Russian). Historical review.

N. Thon

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FRUMKIN, A.N.

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New electrocapillary phenomena. A. N. Frumkin (Colloid-Electrochem. Inst., Acad. Sci. U.S.S.R.). Doklady Acad. Sci. U.R.S.S., Classe sci. chim. 1945, 223-32(in Russian).—Two groups of phenomena arising under the action of an external elec. field on the interface of a particle and its surrounding liquid medium are treated from a common point of view, namely electrokinetic and electrocapillary motions. In the first class, in catapheresis, spherical particles move in an external elec. field E with velocities U, of the order of microns per sec. per volt/cm., detd. by the double layer of elec. charges arising at the interface, of surface d. ϵ and thickness d ($\sim 10^{-7}$ cm.), according to $U = \epsilon Ed/\eta$, where η is the viscosity of the liquid medium; such velocities are by several powers of 10 less than those that would have been acquired under identical conditions but in the absence of a double layer by a spherical particle of radius a, namely $U = (2/3)\epsilon Ea/\eta$; the actual small electrophoretic velocities are due to the fact that the applied force is compensated everywhere by viscous tension in the double layer. In electrocapillary phenomena, any elec. surface charge ϵ lowers the surface tension γ. On a positively charged Hg drop placed in an external field, ϵ decreases and γ increases at the point where the current enters the drop, and the reverse occurs where the current passes from the Hg into the soln.; this gives rise to flow along the surface in the direction of increasing γ, and to reactive repulsion from the bulk of the liquid, resulting in an overall motion of the drop in the direction of the field. With the simplifying assumption of a plane (nondiffuse) Helmholtz double layer, under conditions of ideal polarizability (absence of Hg ions and O), the present analysis of the forces acting on a Hg drop in an electrolyte soln. shows that application of an external field produces a dissymmetry of field strength within the double layer, its d. being greater at the farther end of the sphere than on the nearer side, counting in the direction of the external field; all elec. force components perpendicular to the surface of the drop give a resultant in the direction of the external field; the sum of all normal and tangential components over the total surface area of the sphere is zero. If the external field E is made to coincide with the y-axis, surface elements of the Hg sphere farthest from that axis are subject to forces opposed to E, on portions of the surface nearest to the y-axis, forces in the direction of E are predominant. Although in the case of a solid sphere this would result only in internal stresses, the surface of a liquid metal sphere of radius a can be shown to acquire a velocity $U = \epsilon Ea/(2\eta + 3\eta')$ where η' is the viscosity of the liquid metal (Hg); this velocity is of the same order of magnitude as it would be if the surface charge were free, that is in the absence of a double layer. It is thus theoretically demonstrated that the same set of conditions, namely action of an external elec. field on a double layer, which in dielec. particles produces the usual electrokinetic motions, with its small velocities, gives rise to electrocapillary motions in liquid metal droplets, with velocities comparable to those of freely charged spheres. Exptl. support can be inferred even from older data of Christiansen. By I. Bogotskaya's recent expts. at the author's Inst., the mobility of Hg droplets of $a = 2.5 \times 10^{-6}$ cm. in water-glycerol mixts. of $\eta = 2.5$ is 6×10^{-1}

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cm./sec. whereas the ordinary electrokinetic mobility at the same η would not exceed 3×10^{-4} cm./sec. per 1 v./cm. This observation cannot however be extended to very dil. solns. and correspondingly much stronger elec. field intensities; in fact, it is found that upon dilu., electrocapillary mobility falls and tends toward the low values of common electrokinetic velocities. This behavior can be linked with observations with Hg dropping from a capillary orifice under the sole action of gravity: T. A. Kryukova's and B. N. Kabanov's findings (*C.A.* **36**, 6420[1]) according to which tangential motions at the surface of a Hg drop, present at higher concns., disappear on dilu., are ascribable to asymmetrical distribution of elec. charges as between the upper and the lower parts of a falling droplet, resulting in the appearance of an elec. field, with a damping action on the tangential motions at the surface; in concd. electrolyte solns., high elec. cond. counteracts and wipes out this potential difference between the two sides of a drop but this will not be the case in poorly conducting dil. solns.; actually, in dil. solns., drops will grow by pure perpendicular expansion and consequently the Ilkovich-Rideal equation is applicable. Depending on whether the magnitude defined by $\epsilon^2/\kappa(2\eta + 3\eta')$ where κ = cond. of the soln., is $\ll 1$ or $\gg 1$, the damping effect will be either absent or decisive. Supporting evidence is found in recent expts. of T. A. Kryukova according to which movements of the electrolyte in the neighborhood of a Hg surface are observable at all potentials in a 1 *N* KCl soln. but in a 10^{-4} *N* soln. only within ± 0.2 v. from the electrocapillary nullpoint. A further conclusion is that at const. η, the dropping rate of Hg must increase with increasing κ of the soln. A similar asymmetrical distribution of elec. charges must be expected in the case of motion under the action of an external elec. field; here the potential difference arising between the farthest and the nearest side of a drop will oppose the external field and counteract it and thus result in "self-damping" of the motion; the effect can also be described in terms of convective elec. cond. of the mobile metal surface. With this correction, the accurate expression for the velocity becomes $U = \epsilon E\kappa/(2\eta + 3\eta' + (\epsilon^2/\kappa))$ of which the previously quoted expression is a limiting case valid for $\epsilon^2/\kappa(2\eta + 3\eta') \ll 1$. Inasmuch as in highly dild. solns. the latter magnitude is $\gg 1$, the velocity becomes $U = E\kappa/\epsilon$ which accounts for the rapid fall of the mobility with increasing dilu. Under the accurate formula, U as a function of dilu. (or cond.) had to be expected to have a max. at the elec. surface charge density $\sigma = (2\eta + 3\eta')^{1/2}\kappa^{1/2}$ and this was actually found. In the case of *solid* metals, electrocapillarity manifests itself in the relation of *hardness*, defined in the broad sense of resistance to elastic and plastic deformations and brittleness, and the potential difference across the double layer at the interface metal/electrolyte soln., in conformity with P. A. Rebinder's prediction of diminishing hardness with decreasing value of the surface tension in microinterstices in solids. P. A. Rebinder's and E. K. Venstrem's (*Acta Phys. Chim. U.S.S.R.* **19**, 1, 1945, and unpublished data) measurements of hardness by the damping of the amplitude of oscillations of a pendulum supported by the substance under investigation, which could be polarized to known potentials across a drop of an electrolyte soln., led to plots of hardness against potential analogous to the common electrocapillary curves of Hg and its amalgams; this is illustrated particularly by the practical coincidence of hardness curves for solid Tl and surface tension curves for a 41.5% Tl amalgam; the same deformation of the curves in the presence of adsorbable matter (C_4H_9OH) repeats itself in both instances. Relative to the potential of the max. of the electrocapillary curve of Hg, taken as 0.0 v., the electrocapillary max. of molten Tl, Zn, Pb (at 420°–450°) and Te (at 550°) in fused KCl + NaCl, lies at, resp., −0.67, −0.45, −0.37, and +0.70 volts (Karpachev and Stromberg, cf. *C.A.* **37**, 3322[2]); on the same scale, the max. of the hardness curve of the same metals in the solids state in 1 *N* Na_2SO_4 soln. lies at, resp., −0.49, −0.42, −0.37, and +0.79 volts. For graphite in NaCl the max. of hardness lies at +0.13 although judging by detns. of wettability the electrocapillary max. appears to be situated at about +0.28 v. Detns. of hardness curves as a function of polarization potential lead directly to the detn. of the abs. electrochem. zero potential.

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The movement of solid and liquid metal particles in electrolyte solutions. I. The movement in electric field. A. N. Frumkin and V. Levich. *J. Phys. Chem.* (U.S.S.R.) 19, 673-800; *Acta Physicochim. U.R.S.S.* 20, 709-818(1945).—The forces acting on an insulating, a partially polarizable, and a perfectly polarizable drop in a soln. in an electrostatic field are calcd. The mobility of partially polarizable drops is only a small fraction of that, u_0 of perfectly polarizable drops. The u depends on the stirring of the soln. caused by the flow of the drop surface between the regions of a high and a low interfacial tension. When this stirring is intense, u is inversely proportional to the charge d. σ on the drop; when it is small, u is proportional to σ and almost as great as the mobility of a particle carrying the free charge equal to the charge of the double layer surrounding the drop. J. J. Bikerman

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—Life and scientific work of Academician Vladimir Aleksandrovich Kistyakovskii. A. N. Frumkin. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1946, 121-5(in Russian).—Summary of scientific work, with portrait.
G. M. Kosolapoff

COMMON ELEMENTS

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3RD AND 4TH ORDERS

In memory of A. W. Bakh. A. N. Frumkin. Bull. acad. sci. U.R.S.S., Classe sci. chim. 1946, 467-70(in Russian).—Obituary. G. M. Kosolapoff

COMMON ELEMENTS

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1 AND 2ND ORDERS

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CA

1

New electrocapillary phenomena. A. N. Frumkin (Inst. of Colloid- and Electro-chemistry, Acad. of Sciences of the U.S.S.R., Moscow). *J. Colloid Sci.* 1, 277-91(1946); cf. *C.A.* 40, 2056[6].—The effect of the double layer on (1) the dynamic behavior of metals in the liquid state and (2) the mech. hardness of metals in the solid state is considered. The action of an elec. field on the charges of the double layer, which in the case of a dielec. particle in electrolyte solns. gives rise to the usual electrokinetic movement, induces electrocapillary movement in the case of a liquid metal drop in an electrolyte soln. The velocity of electrocapillary movement is a function of the field intensity, surface charge, particle radius, η of the liquid metal, and of the electrolyte soln. The nature of the damping effect exercised by the charges of the double layer on the movement of the liquid metal surface is considered. The motion of the surface is related to the polarographic max. observed in the current-voltage curves of *dropping-Hg electrodes*. The values of the potential observed at the max. of the electrocapillary curve for molten Te, Pb, Zn, and Tl (as measured by Karpachev and Stromberg, *C.A.* 37, 3322[1]) correspond closely to the potentials observed by Rebinder and Venstrem (*C.A.* 39, 2440[3]) at the max. hardness of the solid metal.

H. K. Livingston

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Cy

3

Surface phenomena in electrochemistry. A. N. Frumkin. *Uspekhi Khim.* 15, 385-402(1946). [illegible] 5322[illegible]. Review with 14 references. G. M. K.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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CA

PROCESSES AND PROPERTIES INDEX

No. 2

2

The motion of solid and liquid metallic masses in solutions of electrolytes. II. Motion in the field of gravity. A. N. Frumkin and V. Levich (Inst. Phys. Chem. Moscow).—*Acta Physicochim. U.R.S.S.* 21, 193-212(1946)(in English); cf. *C.A.* 40, 3235[6].—Equations are given that show the dependence of the sedimentation potential and the current caused by the fall of Hg drops in an electrolyte soln. on the radius of the drops, charge d., elec. cond., and viscosity of the soln. The behavior of the drop varies, depending on the value of the dimensionless quantity $\epsilon^2/\kappa(2\mu + 3\mu')$. At small values of this no. the Hg drops behave like liquid drops, whereas at large values the elec. fields set up retard the motion of the surface and the drops act as if they were solid. Values calcd. on the basis of these derivations were in fair agreement with Bakh's (*C.A.* 29, 3812[8]) measurements of currents caused by falling Hg drops. The flow of Hg from a capillary into a soln. also depends on the value of the same no. At small values the flow is accompanied by eddy motions of the Hg inside the drop, the Hg on the surface flowing from the lower to the upper part of the drop. At large values the drop grows only by radial motion of the liquid, as is usually assumed in the theory of *polarography*. These conclusions were checked by exptl. data on the motion of the liquid when Hg flows into KCl solns. of various concns

Otto H. Müller

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FRUMKIN, A. N.

"Physico-Chemical Phenomena in the Movement on the Boundary between Two Liquids," by A. N. Frumkin, included in a collection of papers given at Jubilee Symposium of the AS USSR, dedicated to the 30th Anniversary of the Great October Socialist Revolution. Published by AS in 1947.

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

"Excited Form of Cathode Hydrogen," Zhur. Fiz. Khim., 21, 1947.

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1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

2

Adhesion of mercury to glass in electrolyte solutions. A. V. Gorodetskaya, A. N. Frumkin, and A. S. Titievskaya (Acad. Sci. U.S.S.R., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 675-88(1947)(in Russian).—A horizontal glass plate is slowly lowered onto a Hg meniscus in an aq. electrolyte soln., and the time t is detd. that is required by Hg to displace the aq. film and to make contact with the glass. After the contact is established, the plate is lifted, and the max. value of the contact angle θ between glass, Hg, and soln. is detd. In solns. of Na_2SO_4, NaOH, and H_2SO_4 t is smaller and θ is greater the more dil. the soln.; there is no "adhesion" in N solns. θ is max. at a pos. charge of Hg, characteristic for a given electrolyte and a given concn., Cl^-, Br^-, I^-, and $N(C_4H_9)_4^+$ reduce the "adhesion," and Th^{++++} eliminates it at 10^{-4} N and greater concns. The effects are explained by the properties of the thin film remaining between Hg and glass when a visible contact is established. J. J. Bikerman

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FRUMKIN, A. N.

USSR/Physics Jul 47
Wetting Agents
Wetting Phenomena

"The Relation of the Wettability of Mercury to the Nature of the Solvent," I. P. Tverdovskiy, A. N. Frumkin, 5½ pp

"Zhurnal Fizicheskoy Khimii" Vol XXI, No 7

With the method of measuring the extreme angle, the relation of wettability of mercury to the composition of water-alcohol solutions was studied. With the increase of the content of ethyl alcohol in the solution, the extreme angle decreases, approaching zero (or very nearly zero) in pure alcohol. Simultaneously the dependence of its magnitude on polarization also decreases which indicates the thickening of the layer under a bubble. With alcohol content exceeding 90%, almost complete independence of the extreme angle from polarization arises, which indicates the approach of the concentration of electrolytes in the solution under a bubble to the concentration in the volume phase.

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FRUMKIN, A.

2

Movement of solid and liquid metal particles in an electric field. II. Currents of falling drops. A. Frumkin and V. Levich (Inst. Phys. Chem., Acad. Sci. U.S.S.R., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 953-66 (1947)(in Russian); cf. *C.A.* 40, 3326[6]; 42, 2160a.—Equations are derived for the *sedimentation potential* of Hg drops in electrolyte solns. Depending on the charge d. on the drop, the viscosities of Hg and ambient soln., and the elec. cond. of this soln., the drops behave either as a liquid (i.e., there is convection streaming in the surface) or as a solid (no convection in the surface). This deduction is in agreement with the data by Bakh (*C.A.* 29, 2812[9]). Similar rules are valid also for drop formation of Hg at the orifice of a capillary. They agree with Kryukova's observations (*C.A.* 41, 6160e). I. J. B.

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4

The potentials of falling drops. I. Bagotskaya and A. Frumkin (Inst. Phys. Chem., Acad. sci. U.S.S.R., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 1061-43(1947) (in Russian).—Hg drops, 1.2 mm. in diam., were forced from a capillary and fell in a KBr soln. in glycerol 98.99, H_2O 1.2%. When still attached to the Hg in the capillary, they were polarized by means of an auxiliary electrode. The polarization altered their surface charge σ which was calcd. from $i = \sigma A$, i being the current carried by the drops and A the area of the Hg/soln. interface formed in 1 sec. The *sedimentation potential* E between the top and the bottom of the glycerol column was measured as a function of σ. In N KBr E was almost independent of σ at large pos. σ, became zero at very small neg. σ, and changed its sign at greater neg. σ values. In 0.03 N and 0.015 N KBr E showed a max. at small pos. σ and a min. (i.e., a max. of the neg. E) at small neg. σ values. These results were observed after air was displaced from the soln. by H_2; in the presence of O_2 E was almost independent of σ because the charge on the falling droplet was detd. by the compn. of the soln. rather than by the original polarization. The E values increased when the concn. of KBr decreased and reached about 0.1 v., i.e., were much greater than the sedimentation potentials of solid insulating particles. A simplified theory of the effect is given (Levich, *C.A.* 42, 2156a). It shows, e.g., that the potential difference between the back and the front of a falling Hg drop was as high as 0.4 v. The theory predicts, in agreement with the expt., that the max. of E occurs at $\sigma = (3\mu)^{1/2}$, μ being the viscosity and κ the elec. cond. of the soln.

J. J. Bikerman

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1ST AND 2ND ORDER

PROCESSES AND PROPERTIES INDEX

2

Cd

Effect of surface-active substances on movements at the boundaries of liquid phases. A. Frumkin and V. Levich (Inst. Phys. Chem., Acad. Sci. U.S.S.R., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 1183-1204(1947); cf. preceding abstr.—Math. When a drop covered with an adsorbed film moves in a liquid, the adsorbed substance is forced to the rear of the drop. This causes variation of surface tension along the meridian of the drop. The unequal distribution of the adsorbed substance is counteracted by its diffusion through the bulk phases and its surface diffusion along the interface. J. J. Bikerman

Reaction characteristics of solid materials and their significance to industry. J. Arvid Hedvall. *Suomen Kemistilehti* 20A, 119-35(1947)(in German).—A review. S. A. Karjala

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

Movement of solid and liquid metal particles in aqueous electrolytes. IV. Maxima on the current-voltage curves of a dropping electrode. A. Frumkin and V. Levich (Inst. Phys. Chem., Acad. Sci. U.S.S.R., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 1435-40(1947)(in Russian); cf. C.A. 41, 6118a.—The theory (cf. C.A. 42, 2156i) developed for the movement of an isolated drop in an elec. field is extended to include drops connected to an electrode. The rate of motion of the drop depends on the potential gradient, which is detd. by the asymmetry of the polarization of the drop, and on the movements along the drop surface which are a function of the charge on the drop. This charge can assume max. values and thus cause max. on the current-voltage curves. The potential gradient within the soln. near the drop depends on the length of the path of the current and on the supply of the reducible substance to different parts of the dropping cathode. When the soln. is stirred by the surface movements of the drop, the difference between this supply at pos. and neg. voltages causes the difference between the pos. and neg. *polarographic* max. J. J. Bikerman

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2

The velocity of fall of mercury drops in a viscous medium. I. A. Bagotskaya and A. N. Frumkin. *Compt. rend. acad. sci. U.R.S.S.* 55, 131-6(1947)(in English); cf. *C.A.* 40, 3339[9], 6044[4].—The velocity of fall of Hg drops, 0.4-0.5 mm. in radius, in glycerol contg. 1-3% H_2O and Na_2SO_4 or KBr as electrolyte was detd., with suitable corrections by Faxen's formula for the effect of the vessel walls and the hydrodynamic interaction of the falling drops in the column. In the presence of dissolved O_2 and with a small elec. cond. the drops fell at a rate in agreement with Stokes' formula. The charge on the drops after a certain time of contact with a soln. contg. dissolved O_2 is independent of its initial value. After removal of dissolved O_2 by bubbling H_2 through the soln. for 20 hrs., the values of the ratio, u_1, the velocity of fall of the liquid drop, u, to that of the velocity of fall of a solid sphere, u_s, varies between 1.03 and 1.47, depending on the charge, and approaches 1.5 times the value of u_1 at small charges. The addn. of surface-active agents, such as amyl and octyl alcs., did not cause any appreciable change in the form of the curves. Values calcd. by the theoretical equation derived, agreed with the observed values. A. F.

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FRUMKIN, A. N.

"Physico-Chemical Phenomena in the Movement on the Boundary Between Two Liquids," by A. N. Frumkin, presents the basic results of research conducted in the Institute of Physical Chemistry of the Academy of Sciences of the USSR devoted to the explanation of the role of physico-chemical phenomena in the movement on the boundary between two liquids or between a liquid and a gas. The theoretical part of the work was done by V. G. Levich and the author. The experimental part was done by T. A. Kryukova and I. A. Bagetska.

SO: Sum. #8, 26 Apr 48.

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1ST AND 2ND ORDERS

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A

P

3C-4. Determination of the Zero Point of Solid Metals on the Basis of Results of Measurement of the Capacity of the Double Layer, Lead. (In Russian.) A. Frumkin. Zhurnal Fizicheskoi Khimii (Journal of Physical Chemistry), v. 22, Aug. 1948, p. 925-929.

Attempts to apply the method of measuring the capacity in dilute solutions for the determination of the zero point of charge for solid metals. This point for lead was found to be —0.97 volts. 12 ref.

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4

The potential of falling [mercury] drops. A. Frumkin and I. A. Bagotskaya (Univ. Moscow). *J. Phys. & Colloid Chem.* 52, 1-11(1948); cf. *C.A.* 41, 7202*f*.—In an O-free soln. of KBr and glycerol with a viscosity of 8-14 poises, Hg drops fall from a dropping-Hg electrode with a drop time of about 0.4 sec. at the rate of 1.0-1.2 cm./sec. The drops are polarized by an e.m.f. which is applied between the dropping-Hg electrode and a large Hg electrode in the same soln. The potential arising from the fall of the drops is measured against 3 Ag-AgBr electrodes spaced along the path of the drops. It is shown that the tangential motion of the surface of falling drops displaces the charges of the double layer from the lower to the upper end of the drop, giving rise to a p.d. between the two ends. For drops of radius 0.0 mm., viscosity of the soln. 13, and elec. cond. 4×10^{-4}, the p.d. between the lower and the upper ends of the drop reaches 0.4 v. Measurements of the p.d. between various points of a liquid column in which the drops are falling are in fair agreement with values expected theoretically. In accordance with the theory of Frumkin and Levich (*C.A.* 40, 6944[9]) with increase in the charge density the abs. value of the potential of falling drops first increases, reaches a max., and then drops off. It also follows from these measurements that the relaxation time of the elec. double layer at the Hg soln. interface in glycerol is less than 2×10^{-5} sec. Otto H. Muller

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FRUMKIN, A. N.

22988 Tormozheniye tangentsial'nykh dvizheniy poverkhnosti rtutnoy kapli rastvorami l-butilovogo spirta. Zhurnal fiz. Khimii, 1949, Vyp. 7, C. 819-27. Bibliogr: C. 827.

SO: LETOPIS' NO. 31, 1949

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PROCESSES AND PROPERTIES INDEX

4

Retardation of tangential movements of the surface of mercury drops by butyl alcohol solutions. T. A. Kryukova and A. N. Frumkin. *Zhur. Fiz. Khim.* 23, 819-27 (1949).—Hg is dropped from a glass capillary, radius 0.006 cm., into 3 *N* KCl + 0.003 *N* $HgCl_2$ at the rates (v) of 1 drop in 0.6 or 2.2 sec. It was cathodically polarized. At, e.g., −0.6 v. against *N* HgCl/Hg electrode the limiting current strength i_l was 4.7 or 14.1 microamp. at the above rates of drop. When the tangential movement of the drop surface was stopped by addn. of gelatin, the current (i_0) became 2.2 and 4.0. When BuOH (I) was added instead of gelatin, the current was reduced; minima of this current (i_m) were observed in 0.03 *M* I and at about −0.7 v. At e.m.f. less than −0.4 v. and above −1.4 v. the effect of I was very small. From the values of i_l, i_0, and i_m the rate of tangential movement of the drop can be calcd., cf. Frumkin and Levich, *C.A.* 42, 3244*b*. The retardation of this movement by I is semi-quantitatively accounted for by assuming that the diffusion of I toward the growing drop is the rate-detg. factor. The diffusion mechanism is confirmed by the effect of v on the degree of retardation; if the adsorption process were the slowest part of the reaction, the retardation would have been independent of v; this gives the lower limit for the rate of the adsorption process. For the above calcn., the *adsorption* of I by Hg at different e.m.f. was needed. It was detd. from new measurements of the *electrocapillary* curve of Hg in 3 *N* KCl without and in the presence of I (0.006–0.3 *M*).

I. I. Bikerman

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1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

B

14

Distribution of the Corrosion Process Along a Tube. (In Russian.) A. N. Frumkin. *Zhurnal Fizicheskoi Khimii* (Journal of Physical Chemistry), v. 23, Dec. 1949, p. 1477-1482.

Theoretically analyzes distribution of corrosion in an endless tube filled with electrolyte having a fixed potential applied at the exit. Such a situation is exemplified by having a tube of one metal inserted into the wall of a large reservoir of another metal filled with the same electrolyte. Corrosion is thus studied as an anodic process on the wall of the tube. Formulas for determination of distribution of potential inside the tube are proposed and interpreted for different values of the variables.

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FRUMKIN, A. N.

Effect of Electrolytes on Hydrogen Over-voltage and the Theory of Damped Discharge.

Zhur. Fiz. Kim., XXIV,2, 244-253
State U. in M.V. Article Submitted Nov. 24, 1949.

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CA

2

Dependence of the adsorption of electrolytes on potential and concentration. A. N. Frumkin. *Doklady Akad. Nauk S.S.S.R.* 69, 821-4(1949).—Thermodynamic considerations give, for the dependence of the charge σ, ϵ on the equil. potential φ and the concn. c of the cations, in the case of a negatively charged surface, the functional relation $\epsilon = f[\varphi - (RT/nF)\ln c]$, which, when the H^+ ion is potential-deg., can be written $\epsilon = \Phi([H^+]/c^{1/n})$, and, in terms of Gibbs' surface σ, Γ of the cations, $\Gamma = -(1/nF)\Phi([H^+]/c^{1/n}) = \rho_s[pH - (1/n)pM]$, where M = metal cation. The specific form of the functions Φ or f_1 is not given by thermodynamics, and must be assumed. Gapon (*C.A.* 36, 4003[9]) assumes a linear function f_1, which gives $\Gamma = \alpha + \beta pH - \gamma pM$, with $\gamma = \beta/n$. For const. c, this goes over into the equation of Lange and Berger (*C.A.* 24, 2657, 4201) $\Gamma = \alpha + \beta pH$ which renders the constancy of the capacity C of the double layer, $\epsilon = C\varphi$. If so, the equation of Gapon would appear to be in conflict with a const. capacity of the double layer. This difficulty is resolved in the light of the theory of the double layer of Stern (C. 1, 19, 720); const. capacity refers not to the total potential difference φ, but only to the potential drop $\varphi - \varphi_1$, where φ_1 is the potential at a distance of an ion radius from the surface, i.e., $\epsilon = k(\varphi - \varphi_1)$. This leads to $\Gamma = (k/nF)[(RT/F)pH - (RT/nF)pM]$, identical with the equation of Gapon. From Stern's theory in a simplified form, namely with the helmholtzian part of the double layer disregarded and only the diffuse part taken into consideration, and with the assumption that c is very much larger than $[H^+]$ in the surface layer, Γ, derives, in combination with Gapon's equation, $\epsilon = k[\varphi - (RT/nF)\ln c] + (2RTk/nF)\ln[\varphi - (RT/nF)\ln c] +$ const., which permits an estn. of the error of the G. equation. With $n = 2$, variation of the factor in brackets from 0.2 to 1.0 v. causes the 1st term to vary by 0.8 k, the 2nd only by 0.04 k. The conclusion that potential-deg. adsorption of cations leads to the equation of Gapon, is not reversible; a linear relation between the amt. adsorbed and the log of the concn. need not indicate potential-deg. adsorption, but may be due to penetration of the adsorbed substance into the solid lattice, as in the β-phase of the Pd-H_2 system, and, possibly, also in the sorption of cations by zeolites.

N. Thon

(BA - A1 Mr '53:196)

1951

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MA

Electrometallurgy-9

The Influence of Electrolytes on Hydrogen Overvoltage and the Theory of Slow Discharge. A. N. Frumkin (*Zhur. Fiz. Khim.*, 1950, **24**, (2), 244-253).—[In Russian]. F. shows that, after a secondary correction by de Béthune (*J. Amer. Chem. Soc.*, 1949, **71**, 1556; *M.A.*, **17**, 369) the overvoltage theory of Eyring and his collaborators (*J. Chem. Physics*, 1939, **7**, 1053) gives the same basic kinetic relations as the slow-discharge theory previously developed by F. and his collaborators (*Z. physikal. Chem.*, 1933, [A], **164**, 121). The only remaining difference between the two theories is that the American workers, having split the jump in potential at the cathode into two parts and calculated the surface concentration of H ions, do not deduce from this any phys. based picture of the structure of the double layer, do not give any experimental data on the magnitude of the surface charge, and do not admit that the charge is const. on the inner part of the ionic sheath in the double layer. F. shows that the equations obtained in this way must be regarded as approximations to the equations which arise from the theory of the double layer, and that the approximation used is valid only in certain conditions. He shows that, in the presence of n-valent cations, the potential at a distance of one ionic radius from the electrode surface varies with the cation concentration $[Me^{n+}]$ in soln. according to the equation $\psi_1 \sim (RT/nF)\ln[Me^{n+}] + \text{const.}$, provided that $[Me^{n+}]$ exceeds a certain value, given by $[Me^{n+}][H_2O^+]^n \sim 1/y^{n-1}$, where y is the root of the equation $\varepsilon = 2dFy \sqrt{(n-1)RTD/2\pi n}\,\sqrt{y}$ (ε is the charge density and d the thickness of the Helmholtz double layer, and D is the dielect. const. of the solvent).

—G. B. H.

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FRUNKIN, A. N.

"Absorption and Oxidation Processes," by A. N. Frumkin, reported at the Fourth Annual Bakh Lecture, 17 March 1948 (Institute of Biochemistry imeni A. N. Bakh) 1951, 21 pp with illustrations.

Describes the characteristics of absorption processes in which oxygen molecules play a part. Reveiws the connection between absorption properties, redox potential, and the effect of oxidation on the properties of absorbents (carbon, etc.)

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Reply to N. I. Kobozev. A. N. Frumkin, Z. A. Iofa, and V. S. Bagotskii. *Zhur. Fiz. Khim.* 25, 1117-31(1951); cf. preceding abstr.—Kobozev's theory of H overvoltage rests on the assumptions that the discharge, $H_3O^+ + e \rightarrow H_a + H_2O$, is rapid and the slow step on cathodes with high η is the desorption of at. H: $H_a \rightarrow H$. The 1st assumption is known to be incorrect (F., *C.A.* 44, 6742*f*). The 2nd is discussed. Attempts to detect at. H near the cathode by means of WO_3 have failed (B. and I., *C.A.* 41, 3701*h*), and although polymerization can be initiated by cathodic evolution of H, Parravano's work (*C.A.* 45, 5068*e*) makes it probable that this reaction starts at the surface and that it is propagated through the vol. of the soln. not by at. H but by an org. radical. From the theoretical standpoint, desorption of at. H is ruled out because, at a c.d. of 0.1 amp./sq. cm. with η = 1.3 v., a calcn. shows that the surface coverage θ is $1.8.10^{-11}$; then the velocity of desorption is $0.8.10^{-10}$ mol./sq. cm. sec., which corresponds to $0.8.10^{-8}$ amp./sq. cm. Rough calcns. show that electrochem. desorption, $H_a + H_3O^+ + e \rightarrow H_2 + H_2O$; or recombination, $2H_a \rightarrow H_2$, are much more rapid processes than $H_a \rightarrow H$. Kobozev's position is definitely outdated.

Michel Boudart

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CA

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Determination of the kinetics of adsorption of organic substances by a.-c. measurements of the capacity and the conductivity at the boundary: electrode-solution. A. N. Frumkin and V. I. Melik-Gaikazyan (Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 77, 855-8(1951).—At a metal/soln. interface with a potential difference φ, ϵ = charge per unit surface area of the soln. side of the double layer, Γ = adsorbed amt. per sq. cm., the c.d. is $i = C_t\partial\varphi/\partial t + \Gamma i'$, where C_t = true electrode capacity at the given const. Γ, and $i' = (\partial\epsilon/\partial\Gamma)_\varphi(\partial\Gamma/\partial t)$. At zero frequency $i' = (\partial\epsilon/\partial\Gamma)_\varphi(\partial\Gamma/\partial\varphi)_\epsilon(\partial\varphi/\partial t) = C_{i0}\partial\varphi/\partial t$, where C_{i0} is the addnl. capacity due to the change of Γ with φ on infinitely slow charging, i.e., depending on φ and the concn. c of the adsorbable substance in soln. At a finite rate of charging, Γ lags behind φ, and $\partial\Gamma/\partial t$ will depend on the kinetics of the adsorption. (1) If the rate of adsorption is detd. by diffusion, solution of the differential equation, with the boundary conditions, leads to the addnl. c.d. $i' = -C_i\,an \sin nt + \Pi_i a \cos nt$, where n = frequency of the a.c.; the addnl. capacity C_i is given by $C_i = C_{i0}[A + 2]/B$, with $A = (\partial\Gamma/\partial c)_\varphi\sqrt{(2n/D)}$ and $B = (A + 1)^2 + 1$, where D = diffusion coeff., and the addnl. cond. $\Pi_i = C_{i0}An/B$. The phase shift angle θ = arc tan(n/Π_i) varies from 90 to 45° with n varying from 0 to ∞. With the aid of Gibbs' formula for the surface tension, one has, further, $(\partial\Gamma/\partial c)_\varphi = (RT/c)(\partial\epsilon/\partial\Gamma)_\varphi^{-1}C_{i0}$, and, for $n(\sqrt{2n/D}) \gg 1$ $(\partial\Gamma/\partial c)_\varphi^{-1}$, finally, $C_i = (c/RT)(\partial\epsilon/\partial\Gamma)_\varphi^2\sqrt{D/2n}$. The capacity and cond., at high n, are detd. by the amt. of the adsorbable substance diffusing to and from the electrode, where the concn. is stationary. (2) If the adsorption process proper is slow as compared with the diffusion, the concn. in soln. remains const. In this case, $C_i = C_{i0}G$ and $\Pi_i = -C_{i0}Gn$, with $G = (\partial\Phi/\partial\Gamma)_{\varphi,c}/[n^2 + (\partial\Phi/\partial\Gamma)_{\varphi,c}^2]$. The phase angle θ varies from 90 to 0° with n varying from 0 to ∞. (3) The ratio C_i/C_{i0} as a function of n follows different curves, depending on whether diffusion or adsorption proper are rate-detg. Inhibition of the over-all adsorption process by diffusion is more marked at low n, whereas inhibition by adsorption proper is more marked at high n. Exptl. detns. of C_i/C_{i0} as a function of n, for BuOH, AmOH, and $C_6H_{13}OH$ on Hg, gave a curve corresponding to the case of the over-all rate entirely detd. by diffusion in soln., and, consequently, adsorption proper must be immeasurably fast. The correctness of the above derivation was further corroborated by the agreement of the value of $(\partial\Gamma/\partial c)_\varphi$ detd. from C_i and Π_i as functions of n, and from $(\partial\epsilon/\partial\Gamma)_\varphi$.

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Frumkin, A. N.

USSR.

The mechanism of the reduction of oxalic acid on a mercury electrode. G. M. Florianovich and A. N. Frumkin. *Doklady Akad. Nauk S.S.S.R.* 79, 997-1000(1951).—The relation of the potential φ at const. c.d., i, to the concn. of undissocd. $H_2C_2O_4$ and to the pH of the soln. was detd. The curves φ — log i had a slope = 120 mv. at pH <1.5 and 90-100 mv. at a pH 1.5-4. From the data, the conclusion was drawn that the first step, which detd. the rate of reduction, consisted in the union of an electron with a $H_2C_2O_4$ mol. The H of the acid mol. did not enter into this reaction.

J. Rovtar Leach

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A.N.

THE ELECTROREDUCTION OF ANIONS. A. N. Frumkin and G. M. Florianovich. Translated by Vera ~~N. Brewer~~ from Doklady Akad. Nauk S.S.S.R. 80, 907-10(1951). 6p. (AEC-tr-1984)

Results are presented from a study of the electroreduction of the anions $S_2O_8^{=}$, $Fe(CN)_6^{-3}$, $PtCl_6^{=}$, $PtCl_4^{=}$, $IrCl_6^{=}$, $RhCl_6^{=}$, and MnO_4^{-} on a mercury cathode. Results and theories governing the electroreduction of anions are discussed. (C.H.)

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, Aleksandr Naumovich, 1895-, redaktor; BAGOTSKIY, V.S.; IOFA, Z.A.; KABANOV, B.N.

[Kinetic energy in electrode processes] Kinetika elektrodnykh protsessov. [Pod red. A.N.Frumkina. Moskva] Izd-vo Moskovskogo universiteta, 1952. 318 p. (MLRA 6:7)

(Electrochemistry)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

"B. S. Yakobi's Studies on Electrolytic Precipitation of Metals," Izv. AN SSSR, Otd. tekh. nauk, No. 4, 1952

MIRA November 1952

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

"Meeting of the Department of Chemical Sciences," Vest Ak nauk SSSR, No 6, p. 112-115, Jun 1952.

At a session of the Dept Chem Sci concerned with the problem of electrochemistry, 4 reports were read, namely: "Reactions of Electrical Reduction and the Zero Points of Metals" by Acad A. N. Frumkin; "Diffusion Kinetics" by V. G. Levich; "Crystallochemistry of Complex Thiocyanates" by G. S. Zhdanov; and "Metallic Compounds" by I. I. Kornilov.

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

1. FRUMKIN, A. N.

2. USSR (600)

4. Metals

7. Reductive reactions and zero points of metals. Vest.Mosk.un. 7 no. 9, 1952.

9. Monthly List of Russian Accessions, Library of Congress, March 1953, Unclassified.

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

1. FRUMKIN, A. N. NESTERDVA, V. I.

2. USSR (600)

4. Platinum

7. Platinum electrode. Part 9. Adsorption of oxygens on platinized platinum on contact with molecular oxygen and on anodic polarization. Zhur. fiz. khim. 26 no. 8, 1952.

9. Monthly List of Russian Accessions, Library of Congress, ~~January~~ 1953. Unclassified.

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

USSR/Chemistry - Overvoltage Sep 52

The Effect of Surface-Active Agents on the Kinetics of the Discharge of Hydrogen Ions at the Mercury Electrode," N. V. Nikolayeva, A. N. Frumkin, and Z. A. Iofa, Moscow State U

Zhur Fiz Khim, Vol 26, No 9, pp 1326-1336

Investigated effect of sol surface-active agents (butyl alc, amyl alc, hexyl alc, heptyl alc, caproic acid) and the effect of insol long-chain compds (cetyl alc, palmitic acid, and myristic acid) on the magnitude of the H overvoltage at an Hg cathode in HCl, HBr, and H_2SO_4 of 2 N- 20 N concns. The surface-active

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agents increase the H overvoltage at the Hg electrode if the value of the cd and the magnitude of the overvoltage increase do not exceed a certain limit. With an increase in concn of org substances in soln, there is an increase of overvoltage and the range of potentials in which an effect on the H overvoltage is observed. The increase in overvoltage occurred only at those potentials where the mols of the surface-active agents were adsorbed. The effect of the org substances investigated on the magnitude of overvoltage was detd by the reduction in the rate of H ion discharge.

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N. - IOFA, Z. A. - BAGOTSKIY, V. A.

Overvoltage

N. I. Kobozev's adsorption theory of overvoltage. Zhur. fiz. khim. 26 no. 12, 1952

9. Monthly List of Russian Accessions, Library of Congress, May 1953. Unclassified.

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

USSR/Chemistry - Development Nov 52

"New Progress in Soviet Science: II Development of Electrochemistry," Acad A. N. Frumkin,

Priroda, Vol 41 No 11, pp 63-64

New possibilities in electrochemistry are due to close bond between science and industry. Prevention of corrosion was developed by G. V. Akimov, Corr-Mem Acad Sci USSR, N. D. Tomashev, and others; and a network of anti-corrosion stations was established by the Inst of Phys Chem, Acad Sci USSR. Author and associates (B. N. Kabanov, B. V. Ershler, P. D. Lukovtsev, S. D. Levin, and others) investigated electrochem processes by studying the structure of boundary between the metal and its melt.

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A.N.

62

Effect of Pressure on the Solubility of Molecular Hydrogen in the β-Phase of the System Palladium-Hydrogen. P. S. Permiaov, A. A. Orlov, and A. N. Frumkin (*Doklady Akad. Nauk S.S.S.R.*, 1952, 84, (4), 749–752).—[In Russian]. A Pd specimen was placed in a bomb of accurately known vol. (20 c.c.) which could be filled with H; an equal vol. of Ag was placed in a similar bomb of identical vol. The solubility of H in Pd ([H]/[Pd]) was then measured by comparing the amounts of free H in each system when under the same pressure (P), allowance being made for the change in vol. of the Pd on dissolving the H. The results are tabulated; using Pd wire 0·1 mm. in dia., as P increased from 1 to 700 atm. [H]/[Pd], in g.-atom H/g.-atom Pd, increased from 0·700 to 0·876 at 15° C.; and from 0·560 to 0·774 at 88° C. Using Pd black prepared by reduction of purified $(NH_4)_2PdCl_4$ with H at 150°–200° C., data obtained at temp. (T) of 195°–373° K. over the pressure range 0·0140–1700 atm. satisfied the relation: $\ln P = a + b[H]/[Pd]$. The values of the const. a and b agree well with those for specimens of Pd black obtained by reduction of $(NH_4)_2PdCl_4$ with hydrazine hydrochloride, but not with those for Pd wire. The const. can also be derived electrochem.; if ϕ is the electrode potential $[H]/[Pd] = a - q\phi = a + (RTq/2F)\ln P$, so that $b = RTq/2F$. Values of a and b calculated from the electrochem. data of Fedorova (Dissertation, Moscow Univ., 1948) agree well with the values obtained by solubility measurements at 273° and 200° K., but at 241° and 323° K. the agreement is less satisfactory. At low temp. the electrochem. method is probably the more accurate.—G. V. E. T.

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"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

Adsorption of Organic Substances and Electrode Processes. A. N. Frumkin (*Doklady Akad. Nauk S.S.S.R.*, 1952, 85, (2), 373-376).—[In Russian]. There are four different types of action of adsorbed substances on electrode processes at the Hg cathode: (1) In the absence of an adsorbed layer, the electrode process is determined by the rate of reaction and not by the conditions of supply of reacting substances. The adsorbed layer acts over the whole range of its existence; e.g. the discharge of H ions. (2) The electrochem. reaction in the absence of the adsorbed layer proceeds so rapidly that chem. polarization can be neglected in comparison with concentration polarization (e.g. the electrodeposition of Cu or Ag). (3) The limiting diffusion current to the Hg cathode is substantially increased by the tangential motion of the electrode surface (i.e. polarographic max.). (4) The penetration of the adsorbed layer by the reacting particles is hindered by the layer and an activation energy is required; e.g. the discharge of metal ions in the presence of particularly stable adsorbed layers. 22 ref.—G. V. E. T.

62

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

USSR/Chemistry - Electrochemistry, Electrodes

21 Sep 52

"The Relationship Between the Electroreduction of Anions and the Position of the Points of Neutral Charge of the Electrode," N.V. Nikolayeva, N.S. Shapiro, and Acad A. N. Frumkin, Moscow State U im M. V. Lomonosov

DAN SSSR, Vol 86, No 3, pp 581-583

Data obtained on the reduction of anions in Cd and Pb electrodes confirm the usefulness of the theory of delayed discharge in explaining the process of anion reduction on these metals. These data also show that by detg the relationship between the intensity of current during the rduction of anions and the potential of the dil soln, the neutral point of the metal may be detd.

PA 247T15

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

✓ Kinetics of electrode processes and phenomena at the metal-solution interface. A. N. Frumkin. *Trudy Soveshchaniya Elektrokhim., Akademiya Nauk SSSR, Otdel. Khim. Nauk* 1950, 21-46(1953).—A comprehensive and crit. review of electrode kinetics with special emphasis on Russian contributions. 101 refs.

R. D. Misch

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.; OBRUCHEVA, A. D.

Electrochemistry

B. S. Yakobi's works in the field of chemical sources of current. Elektrichestvo No. 2, 1953.

Monthly List of Russian Accessions, Library of Congress, June 1953, Unclassified.

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A.N.

Chem Abs. v48
1-25-54
Electrochemistry

History of development of electrochemistry in Russia in the nineteenth century. A. N. Frumkin. *Uspekhi Khim.* 22, 355–74(1953).—Historical review with 68 references. G. M. Kosolapoff

2
Chem

5-6-54

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FRUMKIN, A. N.

USSR/Chemistry - Electrochemistry Feb 53

"Investigation of the System Palladium-Hydrogen by the Electrochemical Method," A.I. Fedorova and A.N. Frumkin, Moscow State U

Zhur Fiz Khim, Vol 27, No 2, pp 247-260

By measuring the relation of the potential to the quantity of current passed, the equilibrium pressures of H for the system Pd-H, at various temps, in the regions of phase transition and uniform β-phases were detd. It was discovered that in the region of β-phases, there is a linear

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relationship between the ratio $\frac{[H]}{[Pd]}$ and the log of the pressure of H and that the differential heat of soln of H in this area linearly diminishes with an increase in this ratio. The indicated relationship was verified up to the contents of H corresponding to $\frac{[H]}{[Pd]} = 0.72$ at 20.0° and $\frac{[H]}{[Pd]} = 0.82$ at -32.0°. The phenomena observed in connection with the removal of H from the system Pd-H in a stream of inert gas, were compared with the phenomena occurring in connection with its removal by anode polarization.

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FRUMKIN, A.N.

4

USSR

The catalytic generation of hydrogen on a mercury electrode in the presence of organic bases. A. N. Frumkin and R. P. Andreeva. *Doklady Akad. Nauk S.S.S.R.* 90, 417-20 (1953).—The action of certain alkaloids and substances contg. the SH group in lowering the H overvoltage on a Hg electrode is discussed. The decrease in the H overvoltage is ascribed to the adsorption of cations of the type BH^+ which form from the union of a neutral mol. B with a H^+. Curves are given for the overvoltage in *N* HCl in the presence of diphenylamine. J. Rovtar Leach

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

ROYKH, I.L.; RAFALOVICH, D.M.; FRUMKIN, A.N., akademik.

Photoactive particles emitted by metals during atmospheric corrosion. Dokl.AN SSSR 90 no.4:603-606 Je '53. (MLRA 6:5)

1. Akademiya Nauk SSSR (for Frumkin). (Photochemistry) (Corrosion and Anticorrosives)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

STRAZHESKO, D.N.; CHERVYATSOVA, L.L.; FRUMKIN, A.N., akademik.

Effect of active carbon on tautomeric conversion of acetone. Dokl.AN SSSR 90 no.4:607-610 Je '53. (MLRA 6:5)

1. Akademiya Nauk SSSR (for Frumkin). 2. Institut fizicheskoy khimii im. L.V. Pisarzhevskogo Akademii nauk Ukrainskoy SSR (for Starzheskiy, Chervyatsova). (Carbon, Activated) (Acetone)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

FORTUNATOV, A.V.; FINKEL'SETEYN, A.V.; FRUMKIN, A.N., akademik.

Mechanism of the process of electrical polishing of copper in phosphoric acid. Dokl.AN SSSR 90 no.5:823-826 Je '53. (MLRA 6:5)

1. Akademiya nauk SSSR (for Frumkin). (Grinding and polishing) (Copper)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

BARELKO, Ye.V.; KABANOV, B.N.; FRUMKIN, A.N., akademik.

Passivation and activation of magnesium in alkaline solution. Dokl. AN SSSR 90 no.6:1059-1062 Je '53. (MLRA 6:6)

1. Institut fizicheskoy khimii Akademii nauk SSSR. 2. Akademiya nauk SSSR (for Frumkin). (Magnesium) (Electrochemistry)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

KUL'KOVA, N.V.; KUZNETS, Z.D.; TEMKIN, M.I.; FRUMKIN, A.N., akademik.

Exchange of oxygen isotopes between carbon monoxide and carbon dioxide on a ferro-oxidic catalyst. Dokl. AN SSSR 90 no.6:1067-1070 Je '53. (MLRA 6:6)

1. Akademiya nauk SSSR (for Frumkin).
(Oxides) (Carbon--Isotopes)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

MARKOVSKIY, L.Ya.; MAZUR, Z.N.; EL'KINA, S.I.; FRUMKIN, A.N., akademik.

Catalytic action of mineral additions in the formation of carbon bisulfide from elements. Dokl. AN SSSR 90 no.6:1071-1074 Je '53. (MLRA 6:6)

1. Gosudarstvennyy institut prikladnoy khimii Leningrada. 2. Akademiya nauk SSSR (for Frumkin). (Carbon bisulfide) (Catallysts)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

EL'PINER, I.Ye.; SUROVA, M.D.; FRUMKIN, A.N., akademik.

Effect of carbon tetrachloride on the decomposition of saccharose in a field of ultrasonic waves. Dokl. AN SSSR 90 no.6:1083-1086 Je '53. (MLRA 6:6)

1. Institut biologicheskoy fiziki Akademii nauk SSSR. 2. Akademiya nauk SSSR (for Frumkin). (Carbon tetrachloride) (Sucrose)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

LEVIN, A.I.; UKSHE, Ye.A.; FRUMKIN, A.N., akademik.

Variations of concentration in layers around electrodes of a copper pyrophosphate bath. Dokl. AN SSSR 91 no.1:119-122 Jl '53. (MLRA 6:6)

1. Ural'skiy politekhnicheskiy institut im. S.M.Kirova. 2. Akademiya nauk SSSR (for Frumkin). (Copper plating)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

SHCHUKAREV, S.A.; LILICH, L.S.; LATYSHEVA, V.A.; FRUMKIN, A.N., akademik.

Heat of reaction of zinc, copper, barium oxide hydrates with perchloric, nitric, and halogen hydracids. Dokl. AN SSSR 91 no.2:273-276 Jl '53. (MLRA 6:6)

1. Akademiya nauk SSSR (for Frumkin)
(Chemical reaction, Heat of) (Oxides) (Acids, Inorganic)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"

"APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6

KRASIL'SHCHIKOV, A.I.; ANTONOVA, L.G. ; FRUMKIN, A.N., akademik.

Study of the catalytic oxidation of hydrogen by means of the electrochemical method. Dokl.AN SSSR 91 no.2:291-293 Jl '53. (MLRA 6:6)

1. Akademiya nauk SSSR (for Frumkin). (Oxidation) (Hydrogen)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000513820006-6"