[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Structure of the Double Layer and Electrode Processes[1]

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The influence of the double layer structure on the kinetics of electrode processes is discussed for simple processes without and with specific adsorption of electrolyte and for processes with coupled chemical reaction. Interpretation of processes without chemical reaction rests on two fundamental ideas advanced by Frumkin and studied in detail by him and his school: (a) the double layer structure influences the effective difference of potential which favors the forward electrochemical reaction and hinders the backward reaction; (b) the effective concentrations of reactants, particularly for ions, are different from the bulk concentrations because of the double layer structure. Frumkin's quantitative treatment for processes without adsorption is discussed and additional equations are given in Appendix for fast processes. Application is made to reduction of iodate ion on mercury in alkaline solution. The analysis of processes with specific adsorption of electrolyte is based on Ershler's model of the double layer and on Grahame's treatment for the differences of potentials between inner and outer Helmholtz planes and solution. It is shown that interpretation of the salt effect based upon the shift of the point of zero charge is open to question. Application is made to the reduction of nitromethane on mercury in acidic iodide medium. The effect of iodide on current–potential characteristics is essentially accounted for by variation of the difference of potential between the inner Helmholtz plane and solution. The salt effect for processes with a coupled chemical reaction is explained by variation of the concentrations of reactants in the reaction layer. *Approximate* correction is possible when the thickness of the reaction layer is small in comparison with that of the double layer. Results are given for the current-step method and are applied to the discharge of $Cd(CN)_4^{--}$ on mercury. Implications are discussed: shift of half-wave potentials for irreversible polarographic waves, distortion of log i *vs.* E diagrams in kinetics and correction of transfer coefficients and exchange currents, inadvisability of control of ionic strength for z–z' electrolytes; effect of foreign electrolytes on the discharge of certain complex ions. A detailed bibliography is given.

The structure of the double layer is of importance in electrochemical kinetics for at least two reasons. (a) It influences the effective difference of potentials which favors and hinders the electrochemical reaction. (b) The effective concentrations of reacting species, particularly in the case of ions, are different from the "bulk" concentrations because of the double layer structure; and the rate of the electrode reaction is affected accordingly. The study of these two effects was progressively developed by Frumkin and his school mostly for the reduction of hydrogen ions,[3-10] the electrolytic oxidation of hydrogen,[11] the reduction of anions[12-17] and the reduction of oxygen.[18-19]

A few other authors applied these ideas. Bockris[20] and de Béthune[21] used them in investigations of hydrogen overvoltage. Lothe and Rogers[22] correlated the shifts of the point of zero charge and the half-wave potential for irreversible processes upon addition of a specifically adsorbed electrolyte. Gerischer[23] pointed out the necessity of correction for the double layer structure in a.c. electrolysis. Bigwood and Gierst[24] took into account double layer effects in a detailed polarographic study of the reduction of chromate ion. In a very recent thesis, which was received after completion of this work, Gierst[25] investigated the influence of the double layer structure on several polarographic and related processes.

Electrostatic influences in electrochemical kinetics were invoked by several investigators: Heyrovsky,[26] Krjukova,[27] Randles,[28] Laitinen and Onstott[29] (see also related papers[30-32]).

Two cases can be distinguished in double layer effects according to whether or not there is specific adsorption. Furthermore, the electrochemical reaction can be preceded or followed by chemical reactions. Only simple electrode processes without

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(3) A. N. Frumkin, *Z. physik. Chem.*, **A164**, 121 (1933); *Acta Physicochim. U.R.S.S.*, **6**, 502 (1937); **7**, 475 (1937).

(4) S. Levina and V. Zarinskii, *ibid.*, **6**, 491 (1937); **7**, 485 (1937); *Zhur. Fiz. Khim.*, **10**, 586 (1937).

(5) A. N. Frumkin, *Disc. Faraday Soc.*, **1**, 57 (1947).

(6) P. D. Lukovtsev, *Zhur. Fiz. Khim.*, **21**, 589 (1947).

(7) P. Lukovtsev and S. Levina, *ibid.*, **21**, 599 (1947).

(8) N. Meiman, *ibid.*, **22**, 1454 (1948).

(9) V. S. Bagotskii, *ibid.*, **22**, 1466 (1948).

(10) A. N. Frumkin, *ibid.*, **24**, 244 (1950); see detailed bibliography.

(11) A. N. Frumkin and E. A. Aikazyan, *Doklady Akad. Nauk, S.S.S.R.*, **100**, 315 (1955).

(12) A. N. Frumkin, "Couche double, Electrocapillarité, Surtension," Actualités scientifiques et industrielles, No. 373, Herman et Cie, Paris, 1936.

(13) M. A. Vorsina and A. N. Frumkin, *Zhur. Fiz. Khim.*, **17**, 295 (1943).

(14) A. N. Frumkin and G. M. Florianovich, *Doklady Akad. Nauk, S.S.S.R.*, **80**, 907 (1951).

(15) T. V. Kalish and A. N. Frumkin, *Zhur. Fiz. Khim.*, **28**, 473 (1954).

(16) G. M. Florianovich and A. N. Frumkin, *ibid.*, **29**, 1827 (1955), see this paper in particular for most complete treatment.

(17) A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955); see detailed bibliography in this review.

(18) V. S. Bagotskii and I. E. Yablokova, *Zhur. Fiz. Khim.*, **26**, 1663 (1953).

(19) For a general review see A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa and B. N. Kabanov, "Kinetics of Electrode Processes," Moscow, University Press, Moscow, 1952.

(20) (a) J. O'M. Bockris, Ch. VII in "Electrical Phenomena at Interfaces," J. A. V. Butler, Editor, Methuen and Co., London, 1951, p. 183. (b) see review in J. O'M. Bockris, Ch. IV in "Modern Aspects of Electrochemistry," J. O'M. Bockris, Editor, Butterworths Scientific Publications, London, 1954, pp. 205–208.

(21) A. J. de Béthune, THIS JOURNAL, **71**, 1556 (1949).

(22) J. J. Lothe and L. B. Rogers, *J. Electrochem. Soc.*, **101**, 258 (1954).

(23) H. Gerischer, *Z. physik. Chem.*, **202**, 293, 302 (1953).

(24) A. Bigwood and L. Gierst, article in "Contributi Teorici e Sperimentali di Polarografia," Vol. III, Suppl. A, *Ricerca Sci.*, 1957, pp. 62–78.

(25) L. Gierst, "Cinétique d'approche et réactions d'électrodes irréversibles," thèse d'agrégation, University of Brussels, 1958.

(26) J. Heyrovsky, *Disc. Faraday Soc.*, **1**, 212 (1947).

(27) T. A. Krjukova, *Doklady Akad. Nauk, S.S.S.R.*, **65**, 517 (1949).

(28) J. E. Randles and K. W. Sommerton, *Trans. Faraday Soc.*, **48**, 957 (1952).

(29) H. A. Laitinen and E. I. Onstott, THIS JOURNAL, **72**, 4565 (1950).

(30) P. Kivalo and H. A. Laitinen, *ibid.*, **77**, 5205 (1955), and references therein to other investigators.

(31) P. Kivalo, *J. Phys. Chem.*, **61**, 1126 (1957).

(32) A. N. Frumkin and N. V. Nikolajeva, *J. Chem. Phys.*, **26**, 1552 (1957).

kinetic complications in the absence of specific adsorption were considered in detail by previous investigators except for Gierst[25] who also studied processes with coupled chemical reactions. Different possible processes will be discussed.

Simple Electrode Processes without Specific Adsorption

Fundamentals, Current–Potential Characteristics.—The following treatment, which is not our original contribution, is given because a simple and general discussion is not readily available. The model of Fig. 1A for the double layer is satisfactory in the absence of specific adsorption. The double layer is composed to two parts: the diffuse double layer and the Helmholtz double layer between the metal and the plane of closest approach. The structure of the double layer has an influence on the current–potential characteristic for an electrode process involving a single rate-determining step for two reasons: (a) the effective concentrations of reacting species must be taken in the plane of closest approach, and (b) the differences of potentials,[33] $\phi_H - \phi_S$, must be subtracted from the electrode potential. Cathodic reactions involving a rate-determining step with n_a electrons will be considered because fundamental results can be expressed with a minimum of algebra. The more complicated case of fast reactions is treated in the Appendix. Thus, one has for the cathodic current density (a similar equation can be written for the backward reaction)

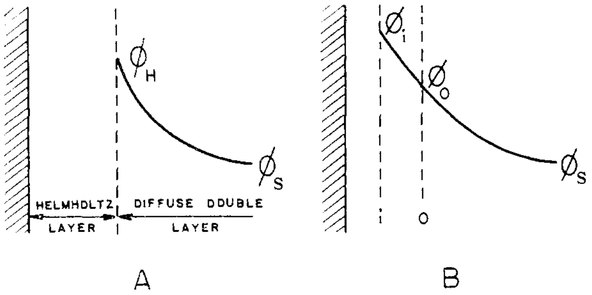

Fig. 1.—Models for the double layer at a metal-electrolyte interface: A, without specific adsorption; B, with specific adsorption.

$$i = kC^* \exp\left[-\frac{\alpha n_a FE}{RT}\right] \exp\left[\frac{\alpha n_a F(\phi_H - \phi_S)}{RT}\right] \quad (1)$$

where k is a proportionality constant, C^* is the concentration of reactant in the Helmholtz plane, α the transfer coefficient, E the usual electrode potential (European convention) and R, T and F have their usual significance.

Note that the potential E is *not* referred to the point of zero charge E_z in eq. 1. In the absence of specific adsorption E_z is independent of the electrolyte concentration and the introduction of E_z offers no particular advantage. In the case of specific adsorption, the current still varies exponentially with potential as a first approximation but eq. 1 is not applicable, and an interpretation based on the shift of the point of zero charge with electrolyte concentration may be open to question as will be pointed out below.

For an ion of valence z, the concentration C^* of reactants in the Helmholtz plane is

$$C^* = C_S \exp\left[-\frac{zF(\phi_H - \phi_S)}{RT}\right] \quad (2)$$

where z is taken with its sign and C_S is the concentration outside the double layer (more rigorously in the region of solution where variations of concentration due to the double layer structure become negligible). If the reactant is a neutral species *which is not adsorbed* one has approximately $C^* \approx C_S$. Variations of the concentration of a neutral substance resulting from the electrical field in the double layer could be treated, in principle, on a thermodynamic basis,[34] the electrical field strength being calculated from double layer theory. This effect will not be considered here.

It follows from eq. 1 and 2 that, at constant current density, the shift ΔE in electrode potential corresponding to a change $\Delta(\phi_H - \phi_S)$ is

$$\Delta E = \frac{(\alpha n_a - z)}{\alpha n_a} \Delta(\phi_H - \phi_S) \quad (3)$$

if α is constant. If $z = 0$, $\Delta E = \Delta(\phi_H - \phi_S)$, and the change of potential is entirely caused by variation of the difference of potentials across the diffuse double layer. Equation 3 holds regardless of the cause of the change in $\phi_H - \phi_S$. For instance, $\phi_H - \phi_S$ can be changed by addition of a foreign electrolyte which is not reduced or oxidized in the range of potentials being considered.

If α varies, one has at constant current density

$$(\alpha E - \alpha' E')n_a = (\alpha n_a - z)(\phi_H - \phi_S)_E - (\alpha' n_a - z)(\phi_H - \phi_S)_{E'} \quad (4)$$

and the shift of potential readily is obtained.

Equations 3 and 4 also give the shift of half-wave potential for irreversible polarographic waves provided that the diffusion current does not vary appreciably (constant current density at $E_{1/2}$) upon variation of the electrolyte concentration.

Calculation of $(\phi_H - \phi_S)$.—The difference $(\phi_H - \phi_S)$ is such that the sum of the charges on the metal and in the diffuse double layer is equal to zero (see Frumkin).[10] Thus

$$K_i[(E - E_z) - (\phi_H - \phi_S)] = \pm \left\{\frac{RT\epsilon}{2\pi} \Sigma C_i^S \left[\exp\left(-\frac{z_i F(\phi_H - \phi_S)}{RT}\right) - 1\right]\right\}^{1/2} \quad (5)$$

where K_i is the integral capacity of the Helmholtz double layer, E_z the electrode potential at the point of zero charge, ϵ the dielectric constant[35] (assumed to be constant in the double layer), and C_i the bulk concentration of ion i of valence z_i (with its sign) in moles cm.$^{-3}$. The right-hand member in eq. 3 is taken from the classical Gouy–Chapman theory.[36]

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[33] The difference $\phi_H - \phi_S$ is noted as ψ in the Russian literature, and the electrode potential or the difference between the electrode potential and the potential at the point of zero charge are designated by φ. These notations are not used here because ψ and ϕ (not φ) generally designate outer and inner potentials, respectively.

[34] E. A. Guggenheim, "Thermodynamics," 3rd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, pp. 410–416.

[35] Saturation of the dielectric can be neglected as a first approximation.

[36] (a) For a review see, for instance, D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947); (b) also, R. Parsons, Chap. 3 in ref. 21, pp. 144–148.

If only z–z electrolytes are present, eq. 5 reduces to

$$K_i[(E - E_z) - (\phi_H - \phi_S)] = \left(\frac{2RT\epsilon C_t}{\pi}\right)^{1/2} \sinh\left[\frac{|z|\ F(\phi_H - \phi_S)}{2RT}\right] \quad (6)$$

where $|z|$ is now taken in absolute value, and C_t is the sum of the electrolyte concentrations.

Variations of $\phi_H - \phi_S$ with $E - E_z$ are shown in Fig. 2 for different molar concentrations of a 1–1 electrolyte and for the constant value, $K_i = 20$ microfarads. cm.$^{-2}$. (K_i actually varies somewhat with E in the range considered.) A similar diagram is given by Frumkin, *et al.*[37]

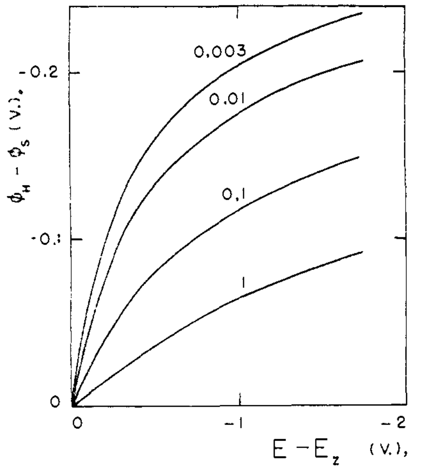

Fig. 2.—Variations of $\phi_H - \phi_S$ with $E - E_z$ for different molar concentration of a 1-1 electrolyte. See data in text.

It is seen from Fig. 2 that one can easily change ($\phi_H - \phi_S$) by 0.1 volt by variation of the electrolyte concentration, and consequently the change ΔE of eq. 3 can be quite pronounced.

When $|\phi_H - \phi_S| << |E - E_z|$, *i.e.*, at potentials not near the point of zero charge, and $|\phi_H - \phi_S| > 0.05$ volt, eq. 6 yields *approximately* for a given E

$$\phi_H - \phi_S = \pm \frac{RT}{|z|F} \ln C_t + \text{constant} \quad (7)$$

where the constant can be written in an explicit form from eq. 6, and the positive and negative signs hold, respectively, for the cathodic and anodic ranges of potential as referred to the point of zero charge. Equation 7 is useful because it readily gives the dependence of $\phi_H - \phi_S$ on C_t, but the more rigorous eq. 6 (or eq. 5 for z–z' electrolytes) must generally be applied.

Experimental Study for the Reduction of Iodate Ion.—Iodate ion is reduced in alkaline solution (pH > 12) on mercury at potentials (for a given current density) which are independent of pH. At 10^{-5}–10^{-4} amp. cm.$^{-2}$ potentials are in the range −1.0 to −1.2 volts (*vs.* S.C.E.), *i.e.*, outside the range of specific adsorption of the anions I^-, IO_3^-, OH^-. The effect of electrolytes on the reduction of iodate was previously studied in this Laboratory under polarographic conditions by application of the treatment of irreversible waves.[38] Results were explained on the assumption that cations reduce the electrostatic repulsion of iodate ions by the electrode.

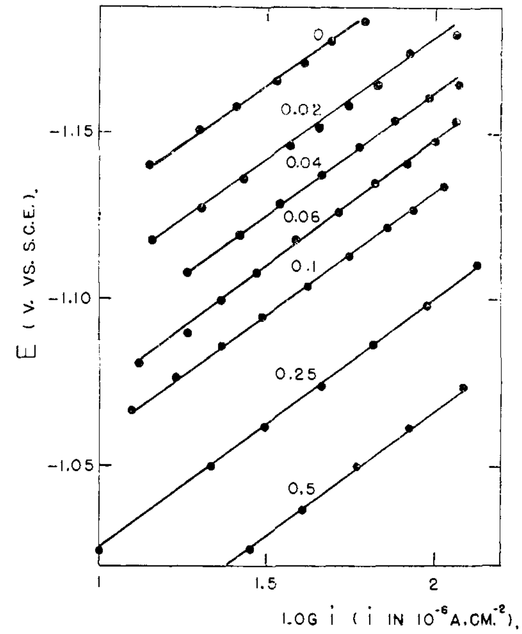

Fig. 3.—E *versus* log i plot for the reduction of 5×10^{-3} M KIO_3 in 2×10^{-2} M KOH with varying molar concentrations of KCl at 30°.

Linear plots of E *versus* log i (i, instantaneous current at the end of drop life) were obtained (Fig. 3) with a dropping mercury electrode in the absence of practically any concentration polarization ($i < 0.01 i_d$). Plots of log i *vs.* E were shifted toward less negative potentials upon the addition of potassium chloride. The product, $\alpha n_a = 0.81$, was independent of electrolyte concentration and in good agreement with the value, $\alpha n_a = 0.77 \pm 0.02$, previously obtained by polarography. Similar results were obtained with lithium chloride and potassium sulfate.

Experimental and calculated shifts are compared in Table I. The agreement is good for potassium and lithium chloride but not entirely satisfactory for potassium sulfate. Anyhow, it is concluded that changes in the double layer structure upon the addition of electrolyte essentially account for the salt effect in the reduction of iodate on mercury in alkaline media.

Approximate values of the shift ΔE calculated from eq. 7 are also listed in Table I to indicate the approximation achieved by this equation, especially for large changes in electrolyte concentration. It was assumed in this calculation that the constant of eq. 7 is independent of potential over the interval ΔE .

Data used in these computations and not previously quoted were as follows: $T = 303.1$; $\epsilon = 79$. The integral capacity K_i hardly varied between −1.0 and −1.2 volts (*vs.* S.C.E.), and consequently the K_i's at −1.1 volts (*vs.* S.C.E.) were used. The following values in units, microfarads. cm.$^{-2}$, were determined and additional ones were interpolated. For KCl series: 16.4 (no KCl added), 16.7 (0.02 M KCl), 19.6 (0.5 M KCl). For LiCl: 16.0 (no LiCl added), 16.6 (0.02 M), 20.4 (0.5 M). For K_2SO_4: 16.5 (no K_2SO_4 added), 17 (0.02 M), 18.8 (0.5 M). The point of zero charge in the absence of specific adsorption, $E_z = -0.45$ volt *versus* S.C.E., was used in all calculations. The shift $\Delta E_{\text{calcd.}}$ varies only by a few millivolts even when E_2 is changed by as much as 0.05 volt.

Liquid junction potentials were quite negligible. For KCl series: −2.5 mv. without addition of KCl; −1.1 mv. for the 0.5 M KCl solution. For the K_2SO_4 series: +3.9 mv. for the 0.5 M solution. No evaluation was made for LiCl. The minus sign indicates that the liquid junction potential was positive from the reference electrode to the dropping mercury electrode.

Simple Electrode Process with Specific Adsorption

Fundamentals.—The following discussion is based on a model of the double layer (Fig. 1B) with

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(37) Ref. 19, p. 17.

(38) P. Delahay and C. C. Mattax, THIS JOURNAL, **76**, 5314 (1954). See ref. therein for the polarography of iodate.

inner and outer Helmholtz planes (for review see ref. 36). The inner plane is the locus of adsorbed ions. The outer plane corresponds to the closest approach to the electrode outside the range of adsorption forces. As in the case of no specific adsorption, corrections in the rate equation should be made for the concentration of the reducible (or oxidizable) species and for the effective difference of potentials. However, two difficulties arise: (a) The plane for which the difference of inner potentials, $\phi - \phi_S$, is needed must be properly selected; (b) the corresponding difference of potentials cannot be calculated directly by the Gouy-Chapman theory.

If the substance being reduced or oxidized is an anion, which is adsorbed much in the same way as the anion of the foreign electrolyte, interpretation may quite safely rest on the difference $\phi_i - \phi_S$. In other cases an *a priori* choice of $\phi - \phi_S$ is not possible. The magnitude of the effect of a foreign electrolyte on kinetic parameters, however, may give an indication of the difference $\phi - \phi_S$ which must be considered.

Variations of $\phi - \phi_S$ upon addition of electrolyte cannot be simply equated to the shift of the point of zero charge. It is possible that in some cases the shift of the line E *vs.* log i for the reduction or oxidation of an uncharged particle is approximately equal to the shift of the point of zero charge, but this conclusion cannot be drawn *a priori*. In this respect, it should be noted that the relation, $\Delta(\phi_i - \phi_S) = \Delta E_z$, does *not* hold, E_z being the point of zero charge. This equality which was thought valid, leads to an incorrect dependence of the point of zero charge on the activity of electrolyte.[39-42] This is the reason why the point of zero charge is not introduced in eq. 1.

A method for the evaluation of $\phi_i - \phi_S$ and $\phi_0 - \phi_S$ was reported recently by Grahame[43] by extension of ideas first developed by Esin and Shikov[40] and improved by Ershler.[41] The analysis takes into account the discreteness of adsorbed ions arranged in a hexagonal array. Grahame applied the treatment to potassium iodide at concentrations between 0.025 and 1 M (see Fig. 4 for some of his results). By the use of such data it is possible to interpret, to a certain extent, the effect of electrolytes on the kinetics of electrode reactions as will now be shown.

The following interpretation is not complicated by variation of the electrode coverage for the adsorbed anion because, as pointed out by Ershler,[41] this coverage is relatively small (< 0.2) even for high electrolyte concentrations. Hence, the concentration C^* in eq. 1 for *a neutral species* is essentially independent of the coverage for the specifically adsorbed anion.

Experimental Study for the Reduction of Nitromethane.—The effect of iodide ion on the kinetics of the reduction of nitromethane was studied under polarographic conditions.

Nitromethane was selected for the following reasons: (a) its polarography has been studied[44]; (b) it is reduced in acid solution at potentials for which values of $\phi_i - \phi_S$ and $\phi_0 - \phi_S$ are given by Grahame; (c) nitromethane does not affect, within experimental error, the electrocapillary curve of iodide and consequently it is not strongly adsorbed on mercury; (d) the solubility of nitromethane in water is sufficiently high.

Irreversible waves for nitromethane were analyzed by the Koutecky method.[45] Results were expressed in terms of a global rate constant k' defined by $i = k'C_S$, C_S being the concentration of nitromethane outside the double layer (compare with eqs. 1 and 2).

Values of $k' \tau^{1/2}/D^{1/2}$ (τ drop time, D diffusion coefficient of nitromethane) were directly deduced from the ratio i/i_d of the instantaneous current at the end of drop life to the instantaneous diffusion current, and the corresponding (k')'s were then calculated ($\tau = 4.2$ sec., within 5% along the wave; $D = 1.66 \times 10^{-5}$ cm.$^{-2}$sec.$^{-1}$, practically independent of the iodide concentration). The rather linear plots of log k' *vs.* E which were obtained (Fig. 5) were shifted toward more cathodic potentials upon the addition of iodide. This shift is in the opposite direction of the one observed for the reduction of iodate upon the addition of electrolyte (Fig. 3). The slope of the lines in Fig. 5 varied somewhat with the iodide concentration, and consequently the experimental shift ΔE_{exp} between the 0.1 M line and any other one depends on the value of k'. Comparison for $k' = 10^{-2.8}$ cm.sec.$^{-1}$, *i.e.*, in the middle of the range in Fig. 5, was made between ΔE_{exp} and $\Delta(\phi_0 - \phi_S)$, $\Delta(\phi_i - \phi_S)$, and the shift ΔE_z of the point of zero charge. Values of $\Delta(\phi_0 - \phi_S)$, $\Delta(\phi_i - \phi_S)$ and ΔE_{exp} are hardly different from those in Fig. 6 if the extreme values of k' in Fig. 5 are used. The liquid junction potential was evaluated at 2.2 mv. for 0.1 M KI and 0.7 mv. for 1 M KI, the significance of sign being the same as for the case of iodate.

It is seen from Fig. 6 that ΔE_{exp} is not very different from $\Delta(\phi_i - \phi_S)$ and that ΔE_{exp} is in complete disagreement with $\Delta(\phi_0 - \phi_S)$ (even the wrong sign) and ΔE_z. Thus, the correction of the electrode potential for $\Delta(\phi_i - \phi_S)$ essentially accounts for the effect of the double layer in this particular case. An interpretation based on the shift of the point of zero charge would lead to values of ΔE_{exp} which are much too large.

A word of caution is in order in the interpretation of the above results. Firstly, values of $\Delta(\phi_i - \phi_S)$ and $\Delta(\phi_0 - \phi_S)$ calculated by Grahame[43] cannot be verified directly by experiment (although conclusions derived from these calculations are verified experimentally). Secondly, the kinetics of the nitromethane reduction were interpreted in a formal manner on the assumption that the reduction rate is proportional to the nitromethane concentration. This relation leads to a linear plot of log k' *vs.* E (Fig. 5) which is essentially obeyed experimentally but, nevertheless, there may be kinetic complications.

Electrode Processes with Coupled Chemical Reaction

We consider processes in which the electrochemical reaction is preceded or followed by a chemical reaction.[46] The double layer structure has not been considered in previous analysis of such processes, and particles have been treated as points. Thus, it has generally been assumed that concentrations are independent of the distance from the electrode before electrolysis. Modifications of existing theories would be very involved if the double layer structure were rigorously taken into account. However, a simple interpretation which accounts for experimental data obtained so far can be developed on the assumption that the double layer thickness is either small or large in

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(39) O. A. Esin and B. F. Markov, *Acta Physicochim. U.R.S.S.*, **10**, 236 (1943).

(40) O. A. Esin and V. M. Shikov, *Zhur. fiz. Khim.*, **17**, 236 (1943).

(41) B. V. Ershler, *ibid.*, **20**, 679 (1946).

(42) Review of R. Parsons, ref. 21, pp. 159–161.

(43) D. C. Grahame, Technical Reports to the Office of Naval Research, Nos. 1 and 5 (second series), Contract N-onr-2309 (1), 1957; *Z. Elektrochem.*, **62**, 264 (1958).

(44) F. Petru, *Collection Czechoslovak Chem. Communs.*, **12**, 620 (1947).

(45) J. Koutecky, *ibid.*, **18**, 597 (1953).

(46) For a review see for instance P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954.

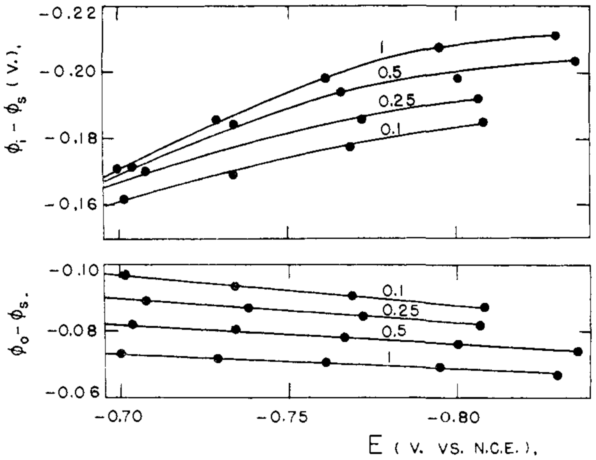

Fig. 4.—Differences of potentials in the double layer in the case of specific adsorption. Data for 25° and for mercury and potassium iodide at different molar concentrations according to Grahame.[43]

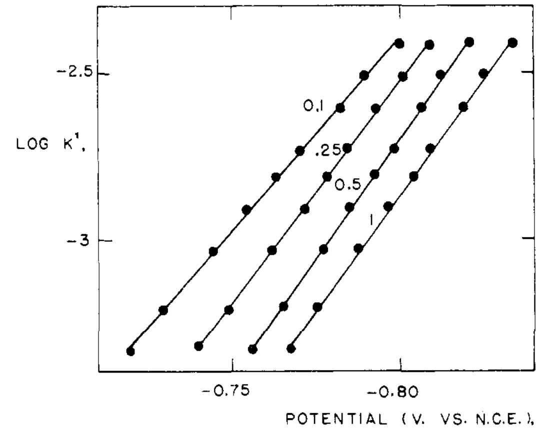

Fig. 5.—Analysis of nitromethane polarographic waves obtained at 25°. Solution composition: 1.2×10^{-3} *M* nitromethane, 2.1×10^{-2} *M* HI, and varying amounts of KI to make up the total molar iodide concentration indicated in each line.

comparison with the reaction layer thickness. In the first case the double layer structure is quite unimportant; in the second case there is a definite effect of the double layer. A similar approach was developed independently by Gierst.[25] The simple approach will be discussed for the particular process $Z \rightleftarrows O + n$, e $= R$ in which Z is not reduced or oxidized, but the analysis can be transposed to other types of reactions. Only results for the current-step method will be discussed because of their direct verification from existing data. Extension to the potential-step method and to polarography is immediate.

The transition time τ_k for the process $Z \rightleftarrows O + n$, e $= R$ under the usual conditions of the current-step method is such that [47]

$$i\tau_k^{1/2} = i\tau_d^{1/2} - \frac{\pi^{1/2}}{2K(k_f + k_b)^{1/2}}\, i \tag{8}$$

where k_f and k_b are the formal rate constants for $Z \rightleftarrows O$; i is the current density; K the equilibrium

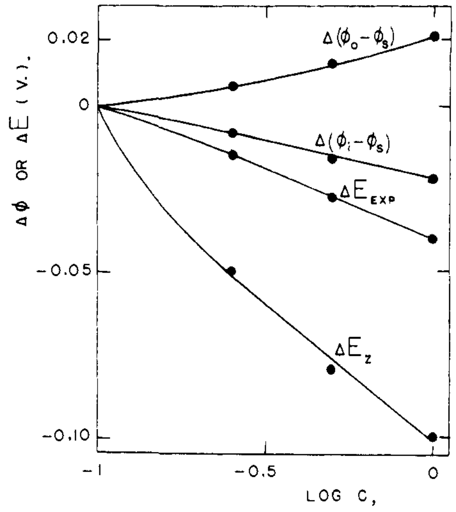

Fig. 6.—Effects of iodide on the kinetics of the nitromethane reduction and certain properties of the double layer. See data and notations in text.

constant for this reaction; and τ_d the transition time that would be measured if Z were reduced directly, all other conditions being the same. The product $i\tau_d^{1/2}$ is independent of current density. It follows from eq. 8 that a plot of $i\tau_k^{1/2}$ against I is linear. The formal rate constants k_f and k_b can be deduced from this plot provided that K is known.

The reaction layer thickness for the above process is $\mu = D^{1/2}/k_b^{1/2}$, D being the common value of the diffusion coefficients for Z and O (assumed to be equal). For example, $\mu \approx 2 \times 10^{-7}$ cm. for $D = 5 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ and $k_b = 10^8$ sec.$^{-1}$. The thickness of the diffuse double layer is somewhat larger than this value of μ, at least for fairly dilute electrolytes. In the absence of specific adsorption, one can then assume, as a first approximation, that the reaction $Z \rightleftarrows O$ occurs mostly in a layer in which concentrations of ions can be corrected on the basis of eq. 2. The salt effect on the kinetics of the reaction proper (variation of activities) is neglected in such a correction. In the case of specific adsorption, correction is more delicate because of the difficulty in the selection of the proper value of $\phi - \phi_S$ (see above).

By noting that the formal k's in eq. 8 are the products of rate constants k' by the exponential factor in eq. 2, one obtains for the slope of the $i\tau^{1/2}$ *versus* i line

$$\theta = -\frac{\pi^{1/2}}{2K\left\{k'_f \exp\left[-\frac{z_Z F(\phi_H - \phi_S)}{RT}\right] + k'_b \exp\left[-\frac{z_O F(\phi_H - \phi_S)}{RT}\right]\right\}^{1/2}} \tag{9}$$

where z_Z and z_O are the valences of ions Z and O with their sign, respectively. When $K << 1$, the term is k'_f can be neglected.

A similar equation can be written for a pseudo-first-order process $Z + Y \rightleftarrows O + n$, e $= R$ when Y is present in large excess and is not reduced or oxidized. The foregoing correction can also be applied to the plot of $i_d t^{1/2}$ *versus* i_d (i_d, diffusion currents) used by Ruetschi[48] for the study of kinetic currents in polarography.

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(47) P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

(48) P. Ruetschi, *Z. physik. Chem.*, *N.F.*, **5**, 323 (1955).

The correction for the double layer structure depends on the valence of the species that are involved. Thus, the corrective terms cancel out for the pseudo-first-order dissociation of a weak acid in presence of a large excess of anion.

The validity of the above correction was verified for the discharge of $Cd(CN)_4^{--}$ in presence of a large excess of cyanide. The following interpretations of the discharge of this ion have been given. Gierst and Juliard[49] inferred on the basis of plots of $i\tau^{1/2}$ against i that the discharge of $Cd(CN)_4^{--}$ on cadmium amalgam is preceded by a chemical reaction. Gerischer[50] identified this reaction as $Cd(CN)_4^{--} = Cd(CN)_3^{--} + CN^-$ and calculated the corresponding rate constants (large excess of CN^-) by application of eq. 8. Polarographic studies based on the same general interpretation were reported recently by Koryta.[51] Gierst[52] also expressed the idea that the $i\tau^{1/2}$ *versus* i plots could be interpreted on the basis of electrostatic repulsions much in the same way as the reduction of certain anions ($S_2O_8^{--}$). Randles[53] in a recent brief abstract seems to agree with this view. Very recently Gierst[25] reached the same conclusion we did,[54] namely, that experimental observations are accounted for by dissociation to $Cd(CN)_3^-$ but that a correction for the double layer structure must be introduced.

In view of Gierst's recent publication[25] details will not be given here. It suffices to note that by writing the slope for the pseudo-first-order dissociation of $Cd(CN)_4^{--}$ and by making the correction[55] of eq. 2, $\phi_H - \phi_S$ being taken from eq. 7, one can show that $1/|\theta|$, for a given potassium cyanide concentration, is proportional to the total concentration of cyanide and the added 1-1 foreign electrolyte. This relation is verified for the data of Gierst and Juliard.[48] Equation 7 is approximate, and a more refined calculation based on eq. 5 is possible. However, the model used in the correction hardly justifies this refinement.

Because of the relative uncertainty about concentrations in the reaction layer, caution is in order in the quotation of rate constants for dissociation of $Cd(CN)_4^{--}$ into $Cd(CN)_3^-$.

Implications and Conclusions

In the absence of specific adsorption and complexation, the effect of foreign electrolytes on the kinetics of electrode reactions seems to be primarily due to variations in the structure of the double layer. Agreement between theory and experiment is good.

Interpretation of the salt effect is more uncertain in the case of specific adsorption, but the order of magnitude of the effect can be interpreted on the basis of the Ershler model of the double layer. A simple interpretation based on the shift of the point of zero charge upon addition of a specifically adsorbed electrolyte is probably open to question in most cases.

Generalization of the results reported here suggests that Frumkin's interpretation of the salt effect in overvoltage phenomena can be extended to processes with specific adsorption. Thus, for processes without or with specific adsorption *the effective difference of potential which favors and/or hinders the electrode reaction is obtained by subtracting from the experimental electrode potential the difference of potential between the plane of closest approach and solution.* In the absence of specific adsorption, the plane of closest approach is the Helmholtz plane; in the case of specific adsorption the plane of closest approach is the inner Helmholtz plane. This generalization is *merely suggested* since it rests so far on detailed analysis of a single case.

The established practice of controlling the ionic strength, which is inspired from the theory of electrolytes, does not seem justified in electrochemical kinetics. One should rather control the valence z and the concentration of foreign electrolyte (preferably only one electrolyte). This point should be kept in mind in the preparation of buffers. Double layer effects are minimized when concentrated electrolytes (1 M for 1-1 electrolytes) are used.

The differences of potentials across the diffuse double layer and between inner and outer Helmholtz planes vary with the electrode potential, and consequently plots of log i *versus* E are distorted. Distortion should be particularly pronounced in the vicinity of the point of zero charge (Fig. 2) for low concentrations of electrolyte (< 0.1 M). Exchange currents and values of αn_a should be corrected accordingly.

Application of these ideas is suggested to the interpretation of the many empirical studies of the shift of half-wave potentials for irreversible polarographic waves upon addition of foreign electrolytes.[56] Another application would be the study of the effect of foreign electrolytes on the exchange current for fast electrode processes as determined by relaxation methods (see Appendix). In the discharge of certain metal ions it might be possible to separate the double layer effect from the influence of complexation upon addition of electrolyte.

Experimental

Experimental methods followed conventional practice. Current-potential curves were recorded with a Sargent polarograph model XXI, the pen-and-ink recorder of which had been replaced by a faster recorder (1.2 seconds full scale). Currents were measured at the end of drop life. Temperature was within ±0.1°. Differential capacities of the double layer were measured with the bridge previously described.[57] The bridge was balanced at the end of drop life.

Acknowledgment.—The support of the Office of Naval Research is gratefully acknowledged.

Appendix

Exchange Current in the Absence of Specific Adsorption.—The exchange current will be derived for processes of the type O + n e = R where O and R are soluble species. The derivation follows the one previously given[58] except that correction for the double layer is now introduced for processes without specific adsorption.

$$i = nF\left\{\begin{array}{l} C_Ok^0{}_f \exp\left[-\dfrac{\alpha nFE}{RT}\right] \exp\left[\dfrac{F(\alpha n - z_O)(\phi_H - \phi_S)}{RT}\right] \\ - C_Rk^0{}_h \exp\left[\dfrac{(1-\alpha)nFE}{RT}\right] \exp\left[-\dfrac{F[(1-\alpha)n + z_R](\phi_H - \phi_S)}{RT}\right] \end{array}\right\} \quad (10)$$

If $n = n_a$ (see eq. 1), the current density for a net cathodic process may be calculated according to equation (10), where C_O and C_R are the concentrations in the region of solution where variations of concentration due to the double

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(49) L. Gierst and A. Juliard, *Proc. Intern. Comm. Thermodynam. and Kinet.*, 2nd meeting, Tamburini, Milan, 1950, pp. 117; *J. Phys. Chem.*, **57**, 701 (1953).

(50) H. Gerischer, *Z. physik. Chem.*, *N.F.*, **2**, 79 (1954).

(51) J. Koryta, *Z. Elektrochem.*, **61**, 423 (1957).

(52) L. Gierst, *ibid.*, **59**, 784 (1955).

(53) J. E. B. Randles, *Trans. Faraday Soc.*, **53**, 1527 (1957).

(54) P. Delahay and C. Weis, paper presented at the national meeting, Electrochemical Society, New York, N. Y., April, 1958; see booklet of extended abstracts.

(55) This method of correction is permissible since μ is small enough.

(56) See Gierst[24,25] for some applications.

(57) P. Delahay and I. Trachtenberg, THIS JOURNAL, **79**, 2355 (1957).

(58) T. Berzins and P. Delahay, *ibid.*, **77**, 6448 (1955); see previous work of other investigators quoted therein.

layer structure (*not* due to concentration polarization) can be neglected; the k^0's are rate constants at some reference potential, for instance at $E = 0$ volt *versus* the normal hydrogen electrode; and the z's are the valences of O and R.

At the equilibrium potential, $E = E_e$, $i = 0$ and there is no concentration polarization. Hence, $C_O = C^0_O$ and $C_R = C^0_R$, where the C^0's are the bulk concentrations. By noting that $C^0_O/C^0_R = \exp [(nF/RT)(E_e - E_0)]$, where E_0 is the formal potential for $O + n e = R$, one can write the quantity

$$nFC^0_O k^0_f \exp \left[-\frac{\alpha nFE_e}{RT} \right] \exp \left[\frac{(\alpha n - z_O)F(\phi_H - \phi_S)}{RT} \right]$$

in the form

$$i_O = nFC^0{}_O{}^{(1-\alpha)}C^0{}_R{}^{\alpha}k_s \exp \left[\frac{(\alpha n - z_O)F(\phi_H - \phi_S)}{RT} \right] \tag{11}$$

with k_s, the rate constant at the formal potential E^0, given by

$$k_s = k^0_f \exp (\alpha nFE^0/RT) = k_b{}^0 \exp [(1 - \alpha)nFE^0/RT] \tag{12}$$

The exchange current density i_0 can also be written in terms of only C^0_O or C^0_R by noting that $C^0_O/C^0_R = \exp [(nF/RT)(E_e - E^0)]$.

The current-potential characteristic

$$i = i_0 \left\{ \frac{C_O}{C^0_O} \exp \left[-\frac{\alpha nF(E - E_e)}{RT} \right] - \frac{C_R}{C^0_R} \exp \left[\frac{(1 - \alpha)nF(E - E_e)}{RT} \right] \right\} \tag{13}$$

has the same form as the one previously given except that the exchange current density i_0 now depends on the double layer structure because of the term in $(\phi_H - \phi_S)$. This term would probably account for the salt effect in the absence of specific adsorption. Values of k_s should be corrected accordingly.

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED SHIFTS ΔE FOR REDUCTION OF 5×10^{-3} *M* IODATE IN 2×10^{-2} *M* HYDROXIDE WITH VARYING AMOUNT OF ELECTROLYTE AT 30°

C_{salt}, mole l.$^{-1}$	E_{exp}, v. *vs.* S.C.E.	ΔE_{exp}, v.	$\Delta E_{calcd.}$, rigorous, v.	$\Delta E_{calcd.}$, approximate (eq. 7), v.
		$KIO_3 + KOH + KCl$[a]		
0.00	−1.173	...	...	...
.02	−1.149	0.022	0.030	0.034
.04	−1.135	.039	.047	.055
.06	−1.119	.054	.060	.071
.10	−1.104	.069	.078	.094
.25	−1.073	.102	.111	.140
.50	−1.039	.136	.133	.177
		$LiIO_3 + LiOH + LiCl$[b]		
0.00	−1.151	...	...	...
.02	−1.125	0.026	0.025	0.034
.04	−1.109	.042	.042	.055
.06	−1.097	.054	.054	.071
.10	−1.079	.072	.071	.094
.25	−1.037	.114	.103	.140
.50	−1.004	.147	.127	.177
		$KIO_3 + KOH + K_2SO_4$[c]		
0.00	−1.157	...	...	...
.02	−1.127	0.030	0.047	0.056
.04	−1.101	.056	.072	.084
.06	−1.087	.070	.087	.103
.10	−1.070	.087	.102	.122
.25	−1.042	.115	.142	.175
.50	−1.018	.139	.169	.214

[a] At 40 microamp. cm.$^{-2}$. [b] At 27 microamp. cm.$^{-2}$. [c] Same as b.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Radiolysis of Simple Ketones[1]

BY P. AUSLOOS AND J. F. PAULSON

RECEIVED MARCH 24, 1958

The liquid and vapor phase radiolysis of acetone, methyl ethyl ketone and diethyl ketone has been investigated briefly. The effect of temperature and scavengers on the *G*-values of the volatile products has been interpreted on the basis of known radical processes. In the case of acetone it has been shown that at least 85% of the methyl radicals are thermalized before abstracting a hydrogen atom from acetone. In the liquid phase recombination products were found to be present in appreciable amounts and were not removed by iodine or DPPH at concentrations up to 2.5×10^{-2} mole/l.

This investigation was undertaken in connection with recent studies on the liquid phase photolysis of simple ketones.[2,3] Although the photolysis results are of some help in interpreting certain features of the radiolysis studies, it is obvious that they do not contribute to the explanation of phenomena related to ion processes and track effects.

In this work only the volatile products were determined quantitatively and no attempt has been made to interpret certain minor products such as C_2H_2, C_3H_4, C_3H_6, . . ., which were formed in the vapor and liquid phase radiolyses of the ketones and which have also been detected in the radiolyses of alcohols,[4] ethers[5] and esters.[6] It may be expected that small fractions of the major products are formed by processes analogous to those responsible for these unexplained products.

Experimental

Irradiation.—The liquids were irradiated in 10 cc. Pyrex volumetric flasks with flat bottoms. In all experiments 2

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(2) R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955)

(3) P. Ausloos, *ibid.*, **36**, 400 (1958).

(4) W. R. McDonnell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

(5) A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

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