

THE THEORY OF REDOXOKINETIC EFFECT AND A GENERAL METHOD FOR THE DETERMINATION OF "a" OF ABSOLUTE REACTION RATES

BY K. S. G. DOSS* AND H. P. AGARWAL†

(*Indian Institute of Sugar Technology, Kanpur, India*)

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1. INTRODUCTION

WHEN two platinum electrodes dipped in an aqueous solution are connected to a source of alternating current, it is found that a d.c. potential is developed at each of the electrodes. This d.c. potential can be measured with reference to a third platinum electrode of large area dipped in the same solution. This phenomenon which is caused by the kinetic factors controlling oxidation and reduction reactions at the electrodes has been termed the "Redoxokinetic Effect." The experimental set-up for the study of the phenomenon and some of the results obtained have been already published.^{1,2} It is the object of the present work to formulate a theory to explain quantitatively the phenomenon. An allied problem has been tackled by Randles.³ His procedure has been modified in the present work, taking into account the redoxokinetic effect.

2. THEORETICAL

Consider a microelectrode dipped in a mixture of an oxidant and a reductant, e.g., ferrous and ferric ions in equal proportions and in small concentrations (of the order of a few millimoles per litre). Let the concentration of each be C moles per c.cm. The solution also contains a supporting indifferent electrolyte at a high concentration so as to avoid the migration effects. Let this electrode be subjected to the action of a small alternating electric field with the help of another platinum electrode dipped in the solution. A third dummy electrode of large area is also kept in solution with a view to use it as a reference electrode for the measurements of the potentials. We may now consider the reaction occurring at the microelectrode due to the electric field which can be represented by the equation:—



* Professor of Sugar Chemistry, Indian Institute of Sugar Technology, Kanpur.

† Assistant Professor of Chemistry, D. A. V. College, Kanpur.

Since no current is passing through the dummy electrode, the reaction (1) is in equilibrium at this electrode, we shall take the potential of the dummy electrode arbitrarily as zero. The potential v , of the microelectrode with reference to the dummy electrode is given by the equation:—

$$v = V \cos \omega t + \psi, \quad (2)$$

where the first term is contributed directly by the applied a.c. field and ψ is the redoxokinetic potential developed. The alternating current flowing through the system can be denoted by

$$i = I \cos (\omega t + \phi). \quad (3)$$

(It is to be noted in this connection that there will be no d.c. component in the current as a condenser has been included in series with the cell while applying the alternating potential and an electron tube measuring instrument is used to measure the d.c. developed.)

As a result of this current there will presumably be a harmonic vibration in the concentrations of M^{m+} and $M^{(m-n)+}$ close to the interface, which will spread into the nearby solution. For the concentration C_1 , of the reductant we may write,

$$C_1 = C + \delta C_1 \quad (4)$$

and close to the interface,

$$C_1^\circ = C + \delta C_1^\circ, \quad (5)$$

where

$$\delta C_1^\circ = \Delta C_1^\circ \cos (\omega t + \theta), \quad (6)$$

where ΔC_1° is the amplitude of variation of C_1 , close to the interface and θ is the phase angle relative to that of the alternating potential at the microelectrode. Concentration near the interface and not the concentration in the adsorption layer is to be taken into account. The amount in the adsorption layer proper is small and the concentration may be extremely high or low; large changes in concentration in this layer can also be expected due to the passage of the current. But the effective concentration in the adsorption layer is defined by the concentration in the bulk, *i.e.*, near the interface. ΔC_1° represents the fluctuation in this region. A general expression for $\delta C_{1x,t}$ can be obtained by applying Fick's Law of diffusion:

$$\frac{\partial C_1}{\partial t} = D_1 \cdot \frac{\partial^2 C_1}{\partial x^2}, \quad (7)$$

where x is the distance from the electrode surface (regarded as planar) and D_1 is the diffusion coefficient of the reductant.

For the boundary condition given by equation (6) at $x=0$ this gives

$$\delta C_{1x,t} = \Delta C_1^\circ e^{-\sqrt{\omega/2D_1} \cdot x} \cos(\omega t - \sqrt{\omega/2D_1} \cdot x + \phi). \quad (8)$$

This equation represents a diffusion wave of length $2\pi\sqrt{2D_1/\omega}$ and whose amplitude declines exponentially with distance from the interface (compare the solution of corresponding problem in thermal conduction (Carslaw, *Conduction of Heat in Solids*, 1921, p. 47). Applying Faraday's law the current flowing (taking a positive value of i corresponding to the reduction reaction) is given by

$$i = -nFAD_1 \left(\frac{\partial (\delta C_1)}{\partial x} \right)_{x=0}, \quad (9)$$

where F is the Faraday and A is the area of the electrode.

Combining equations (8) and (9), we get

$$i = nFA \Delta C_1^\circ \sqrt{\omega D_1} \cos\left(\omega t + \theta + \frac{\pi}{4}\right). \quad (10)$$

Comparing equation (10) and (3) we get

$$I = nFA \Delta C_1^\circ \sqrt{\omega D_1}; \phi = \theta + \frac{\pi}{4}. \quad (11)$$

Comparison of equation (10) with the corresponding expression based on the diffusion of the oxidant shows that

$$\frac{\Delta C_1^\circ}{\Delta C_2^\circ} = \sqrt{\frac{D_2}{D_1}},$$

where subscript 2 indicates quantities appertaining to the oxidant. Since D_2 is generally approximately equal to D_1 we shall assume that

$$\Delta C_2^\circ = -\Delta C_1^\circ \quad (12)$$

the minus sign indicating that they are 180° out of phase. Having assumed that $D_1 \approx D_2$, the subscript on D will be dropped.

Let us now apply the theory of Absolute reaction rates⁴ for computing the current. When the micro-electrode is subject to the action of a potential v , a fraction of this potential favours the reduction process and the fraction $(1 - a)$ hinders the oxidation process. The sign of v is taken as positive when it is cathodic. The cathodic current i_c is, therefore, given by the equation

$$i_c = nFA k_2 C_2^\circ e^{avnF/RT}, \quad (13)$$

where A is the area of the electrode, k_2 is the rate constant ($\text{cm.}^3/\text{sec.}$) for the reduction reaction. Similarly the anodic current i_a is given by

$$i_a = nFA k_1 C_1^\circ e^{-(1-a)vnF/RT}, \quad (14)$$

where k_1 is the rate constant for the anodic reaction.

Hence the net cathodic current comes out to be

$$i = nFA \left[k_2 C_2^\circ e^{\alpha v n F / RT} - k_1 C_1^\circ e^{-(1-\alpha) v n F / RT} \right]. \quad (15)$$

Since at $v = 0$ the $i = 0$ and also

$$C_1^\circ = C_2^\circ, \text{ we can write}$$

$$k_1 = k_2 = k \text{ (say)} \quad (16)$$

Further, since in general $C_1^\circ = C + \delta C_1^\circ$ and $C_2^\circ = C - \delta C_1^\circ$, we get,

$$i = nFAk \left[(C - \delta C_1^\circ) e^{\alpha v n F / RT} - (C + \delta C_1^\circ) e^{-(1-\alpha) v n F / RT} \right] \quad (17)$$

For small values of v , taking the first approximation for the exponential term we get

$$i = nFAkC \left[\frac{vnF}{RT} - \frac{2\delta C_1^\circ}{C} - (2\alpha - 1) \cdot \frac{\delta C_1^\circ}{C} \cdot \frac{vnF}{RT} \right]. \quad (18)$$

Since the net current passing through the system (when subjected to the alternating field) is zero, we get

$$\int_{t=0}^{t=2\pi/\omega} idt = 0 \quad (19)$$

Combining equations (2), (16), (18) and (19),

we get,

$$\int_{t=0}^{t=2\pi/\omega} nFAkC \left[\frac{VnF}{RT} \cos \omega t + \frac{\psi nF}{RT} - \frac{2\Delta C_1^\circ}{C} \cos(\omega t + \theta) - \frac{VnF}{RT} \cos(\omega t + \theta) - \frac{\Delta C_1^\circ}{C} (2\alpha - 1) \cdot \frac{\psi nF}{RT} \cos(\omega t + \theta) \right] dt = 0. \quad (20)$$

Integrating, we get,

$$\psi = \frac{2\alpha - 1}{2} \cdot V \cdot \frac{\Delta C_1^\circ}{C} \cos \theta. \quad (21)$$

Equation (21) contains the term $\frac{\Delta C_1^\circ}{C} \cos \theta$ which can be evaluated as follows:

Differentiating equation (18) we get,

$$\frac{di}{dt} = 2nFAkC \left[\frac{nF}{2RT} \cdot \frac{dv}{dt} - \frac{1}{C} \frac{d(\delta C_1^\circ)}{dt} - \frac{2\alpha - 1}{2} \cdot \frac{nF}{CRT} \cdot \frac{d(v\delta C_1^\circ)}{dt} \right]$$

Since $\alpha \approx 0.5$ (as seen experimentally later), we get,

$$\frac{di}{dt} = 2nFAkC \left[\frac{nF}{2RT} \cdot \frac{dv}{dt} - \frac{1}{C} \cdot \frac{d(\delta C_1^\circ)}{dt} \right] \quad (22)$$

Combining (22), (2) and (6), we get,

$$\frac{di}{dt} = 2nFAkC \left[\frac{nF}{2RT} \omega V \sin \omega t + \frac{\Delta C_1^\circ}{C} \omega \sin(\omega t + \theta) \right] \quad (23)$$

Similarly, differentiating equation (10), we get,

$$\frac{di}{dt} = nFA\Delta C_1^\circ \sqrt{\frac{\omega D}{2}} [\omega \sin(\omega t + \theta) + \omega \cos(\omega t + \theta)] \quad (24)$$

Expanding equations (23) and (24) and equating coefficients of $\cos \omega t$ gives,

$$-\cot \theta = 1 + 2k \sqrt{\frac{2}{\omega D}} \quad (25)$$

Similarly, equating coefficients of $\sin \omega t$, and combining the result with equation (25), we get,

$$\Delta C_4^\circ = -\frac{kCnFV}{RT} \sqrt{\frac{2}{\omega D}} \sin \theta \quad (26)$$

Combining (21), (25) and (26), we get,

$$\psi = (a - .5) \cdot \frac{V^2 nF}{2RT} \frac{2 + \frac{1}{k} \sqrt{\frac{\omega D}{2}}}{2 + \frac{1}{k^2} \frac{\omega D}{2} + \frac{2}{k} \sqrt{\frac{\omega D}{2}}} \quad (27)$$

Let us consider two limiting cases:

$$\text{If } \frac{1}{k} \sqrt{\frac{\omega D}{2}} \ll 2, \quad \psi = \frac{V^2 nF}{2RT} (a - .5) \quad (28)$$

$$\text{If } \frac{1}{k} \sqrt{\frac{\omega D}{2}} \gg 2, \quad \psi = \frac{V^2 nF}{2RT} (a - .5) \cdot k \cdot \sqrt{\frac{2}{\omega D}} \quad (29)$$

The following general conclusions can be drawn from the above:—

- $\psi \propto V^2$ when ω is constant.
- At sufficiently low frequencies, ψ is independent of frequency.
- At higher frequencies, ψ varies inversely proportional to the square-root of frequency.
- At very high frequencies ψ becomes zero.

The most striking aspect of these results is that under conditions corresponding equation (28) a can be measured, by measuring ψ at known values of V .

3. EXPERIMENTAL

In order to test the theory, it is necessary to measure the redoxokinetic potential at low a.c. fields (not greater than c.a. 15 mv. (r.m.s.). All the

data so far obtained were at much higher a.c. fields. So experiments were specially conducted at low a.c. fields. One of the important features of our apparatus was that the potential measuring device did not draw any appreciable current from the system. This was achieved by combining the pH meter and sensitive galvanometer (L & N) No. 2420. For our present purpose, it was necessary to increase the sensitiveness a hundred-fold or more by using the highly sensitive galvanometer (L & N No. 2239 B). But it was found that the pH meter did not maintain the stability to the necessary degree. So, the pH meter was discarded and the highly sensitive galvanometer was used directly as the null instrument.

The circuit diagram used is given in Fig. 1. The alternating current is supplied by a transformer AB and the current is controlled by the variable resistance R_1 . The electrolytic cell contains three electrodes E_1 , E_2 and R. E_1 and E_2 conduct the alternating current through the cell. R is the

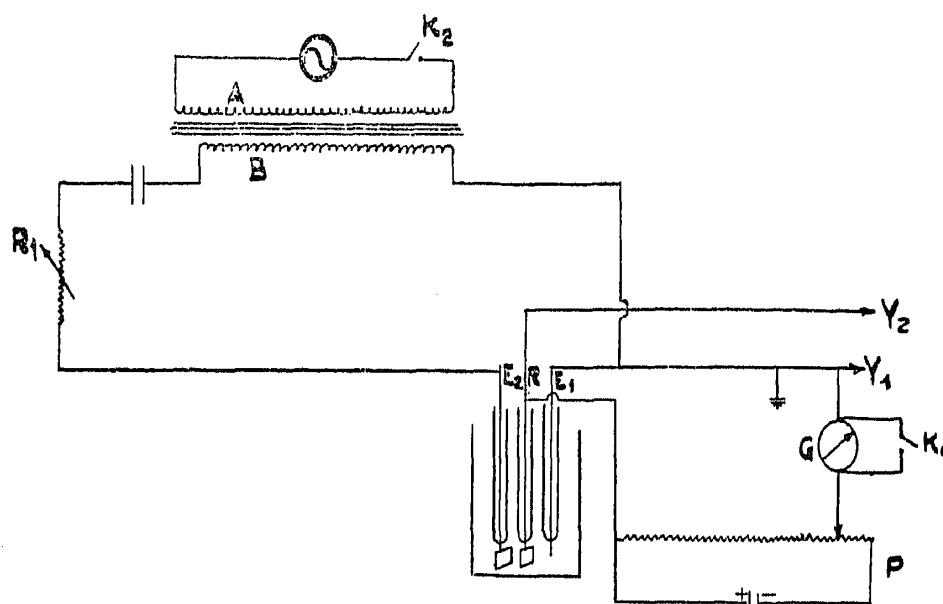


FIG. 1

reference electrode, with reference to which the redoxokinetic potential developed at E_1 , (the microelectrode) is measured. At E_2 the potential developed is small as it is a large electrode, and is not normally measured. The a.c. potential existing between E and R is measured by means of the oscillograph. The d.c. potential developed (redoxokinetic potential ψ) between E_1 and R is measured by the potentiometer P, making use of Leeds and Northrope galvanometer [sensitivity: 1 millimeter = $0.416 \mu V$ (at a distance of 4 metres) and resistance = 1182 ohms] as a null instrument. The cell contained ferrous-ferric mixture each at a concentration of 0.005 M. The supporting electrolyte used was 1.0 M sulphuric acid. The solution in the cell was covered with liquid paraffin so as to protect the layer from atmo-

spheric oxidation. The above system was left for twenty-four hours so as to allow it to acquire equilibrium. The key K_2 in the primary of the transformer was used for making a.c. on and off.

Some experiments were also tried by merely taking ferric-ferrous mixture each having concentration M/4 as the electrolyte. To avoid iR drop, the reference electrode consisted of a helical spiral placed round the fine electrode E_1 . The results obtained are given in Figs. 2 and 3, in which ψ has been plotted against V^2 .

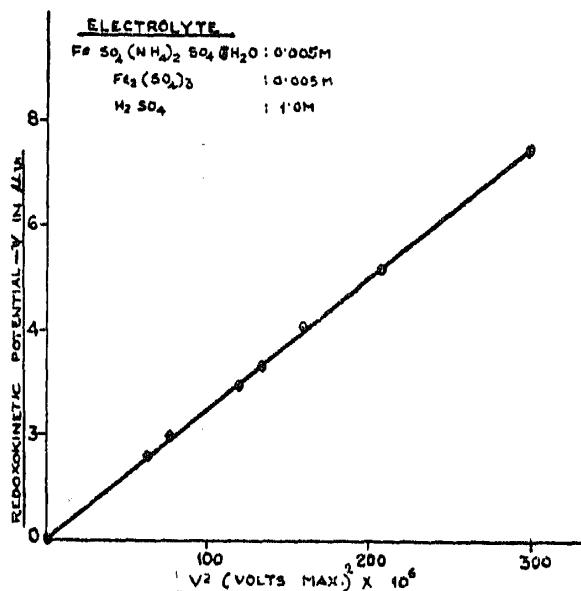
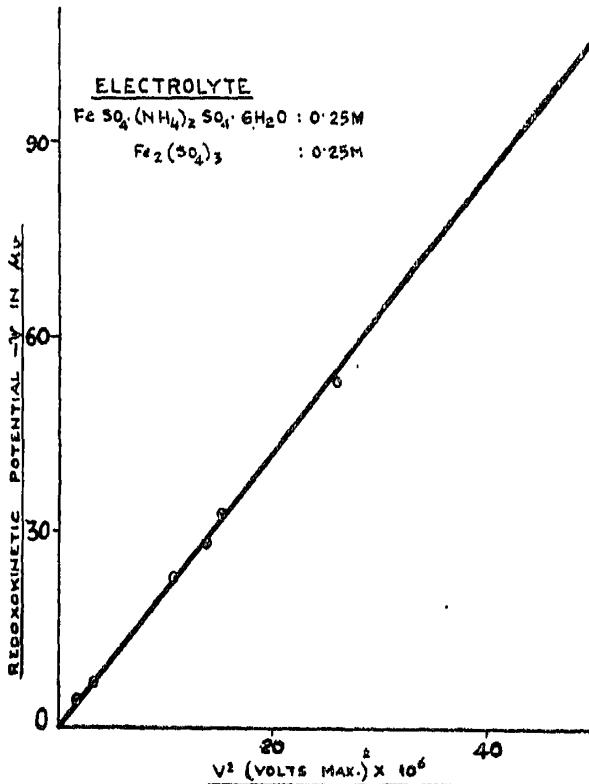


FIG. 2



4. DISCUSSION

An examination of Fig. 2 shows that the magnitude of the redoxokinetic potential is proportional to the square of the a.c. field at the electrode. This is in agreement with the prediction contained in the theoretical equation (27). Further experiments were done with a view to find out the effect of frequency on the system. In these experiments the transformer was replaced by a B.S.R. oscillation type L. 50. No detailed results are indicated here as the change in frequency from 12.5 cycles to 10,000 cycles per sec. did not produce any appreciable change in the redoxokinetic potential. Even this negative result however, is of interest in that it indicates that we are dealing with a system which satisfies equation (28). Applying this equation we get

$$\alpha = 0.5 + \frac{2\psi RT}{V^2 nF}$$

$$\text{If } n = 1 \text{ and } T = 303^\circ \text{ K, } \alpha = 0.5 - \frac{0.052 \psi}{V^2}$$

The value of α comes out to be 0.4987 ± 0.0001 .

It is of interest to note that the proportionality between ψ and V^2 also holds for the other system investigated, containing no supporting electrolyte, but having higher concentrations (0.25 molar each) of ferrous and ferric salts. Assuming the formulation to be applicable to this case also, the value of α comes out to be as low as 0.39. The exact significance of this result is a matter for further investigation.

It is to be noted that we have based our formulations on concentrations and not activities and in this regard the α contains in it a function relating to the activity co-efficients, though it is expected that the magnitude of the function will be nearly unity due to mutual cancellation of the different terms.

The values of " α " given in this paper are only tentative and illustrative of procedure as the effect of resistance of the system on the value is under investigation, as well as that of the previous history of the platinum electrode.

5. CONCLUSION

The discovery of the redoxokinetic effect and its theoretical formulation has thus led to a general method for the quantitative determination of the value of α for the first time after the working out of the theory of absolute reaction rates by Glasstone, Laidler, Eyring and others. Though we have described here a system dealing with redox potentials, it can equally well

be applicable to metal solution junction by employing electrodes of the type used by Randles.³ It is indeed likely that the new effect may throw further light on other aspects of electrode kinetics.

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7. SUMMARY

The theory of the redoxokinetic effect has been formulated for small a.c. fields. One interesting result coming out of the theory is that the redoxokinetic potential is proportional to the square of the a.c. field. Experiments have been done with the ferrous-ferric system which confirm the above theoretical result. From the observed values of the redoxokinetic potential it has been possible for the first time to get a general method for the determination of "a" a factor introduced in the theory of Absolute reaction rates as applied to electrode processes. The magnitude of this quantity comes out to be 0.4987 ± 0.0001 for ferrous-ferric system (both 0.005 M) containing 1.0 M sulphuric acid as the supporting electrolyte. The corresponding value for the ferrous-ferric system (each 0.25 M) without any supporting electrolyte has been found to be 0.39, which is comparatively low. The exact significance of the latter result needs further investigation. The values of "a" given herein are tentative and illustrative of procedure.

8. REFERENCES

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