

Frequency Dependence of the Capacity of a Diffuse Double Layer

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Frequency Dependence of the Capacity of a Diffuse Double Layer

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The capacity of a diffuse double layer is calculated to be inversely proportional to the square root of the frequency at frequencies high compared with the reciprocal of the relaxation time of the ionic atmosphere. This dependence is observed experimentally with inert electrodes in very dilute solutions, but at considerably lower frequencies. The observed capacity is probably concerned with phenomena at the immediate vicinity of the electrode rather than the diffuse double layer.

IN measurements of conductance¹ or dielectric constants²⁻⁴ of solutions containing ions, using inert electrodes, account must be taken of the polarization capacity at the electrode surface. For solutions of electrolytes such as potassium chloride of the order of 10^{-4} *M*, with smooth or sand-blasted platinum electrodes, the A.C. polarization capacity has often been found to be proportional to the inverse square root of the frequency;¹⁻³ although this relation fails¹⁻⁴ below frequencies of 25 kc for solutions with conductances of the order of 10^{-4} ohm⁻¹ cm⁻¹, and the deviations appear to be particularly marked in the case of hydrogen ions.⁵

A theory of polarization capacity was given by Warburg,⁶ who assumed that electrolysis occurred, and treated the diffusion of the products of hydrolysis away from the electrodes. Although this theory predicts the correct frequency dependence within a certain frequency range, it seems of dubious applicability to measurements at very low potentials, where perceptible electrolysis cannot be expected to occur.

A phenomenological theory by Fricke⁷ showed that, if the polarization voltage followed a transient decay with time of the form $V_0 t^{-1/2}$, the polarization capacity measured with an alternating potential should be proportional to the inverse square root of the frequency. However,

no physical interpretation of this decay relationship was offered.

More recent treatments of the differential polarization capacity (as measured with alternating current) at inert electrodes in dilute solutions of electrolytes have considered it as equivalent to two condensers in series, one representing an adsorbed layer of ions and the other a diffuse double layer.^{8,9} While the magnitude of the former capacity cannot be predicted,⁹ the latter has at low frequencies the well-known value¹⁰ $D\kappa/4\pi$, where D is the dielectric constant and κ the Debye-Hückel parameter (for a uni-univalent electrolyte $(8\pi e^2 n/DkT)^{1/2}$, e being the electronic charge, n the number of each ionic species per cc, k Boltzmann's constant, and T the absolute temperature).

If the potential across the diffuse double layer is removed, the charge due to unequal concentrations of positive and negative ions decays as the inequality of concentration is destroyed by diffusion. Under an alternating potential, this picture leads to a dispersion of the polarization capacity, which falls to zero at frequencies too high to permit changes in ion distribution within the period of alternation. The expected form of this dispersion has been calculated, to determine whether the observed frequency dependence of the polarization capacity can be explained on this basis.

We follow the treatment given by Falkenhagen¹¹ for relaxation of the ionic atmosphere,

¹ G. Jones and S. M. Christian, *J. Am. Chem. Soc.* **57**, 272 (1935).

² J. L. Oncley, *J. Am. Chem. Soc.* **60**, 1115 (1938).

³ J. D. Ferry and J. L. Oncley, *J. Am. Chem. Soc.* **63**, 272 (1941).

⁴ T. M. Shaw, *J. Chem. Phys.* **10**, 609 (1942).

⁵ W. G. Smiley and A. K. Smith, *J. Am. Chem. Soc.* **64**, 624 (1942).

⁶ Warburg, *Ann. Phys.* **6**, 125 (1901).

⁷ H. Fricke, *Phil. Mag.* (7) **14**, 310 (1932).

⁸ M. A. Vorsina and A. N. Frumkin, *Compt. rend. Acad. Sci. U.R.S.S.*, **24**, 918 (1939).

⁹ D. C. Grahame, *J. Am. Chem. Soc.* **68**, 301 (1946).

¹⁰ G. Gouy, *Ann. Chim. phys.* [7] **29**, 145 (1903).

¹¹ H. Falkenhagen, *Electrolytes* (Oxford University Press, Oxford, 1934), p. 176.

but treat a diffuse double layer at a plane surface instead of a spherical atmosphere around a single ion. Neglecting interionic effects, we obtain the differential equation (for a uni-univalent electrolyte with ions of equal mobility, *e.g.*, potassium chloride)

$$\partial f / \partial \tau = \partial^2 f / \partial s^2 - f(s, \tau).$$

Here $f\epsilon$ is the momentary excess charge density due to inequality of ionic concentrations, $s = \kappa x$ where x is the distance from the electrode surface, $\tau = t/\Theta$ where t is time and $\Theta = \rho/kT\kappa^2$, and ρ is the frictional constant for the ions (the force required to move an ion through the solvent at unit velocity).

The solution of this equation for the disappearance of net charge following removal of potential is

$$f = \frac{S}{(\pi)^{1/2}} e^{-\sigma} \int_{(\tau)^{1/2} - \sigma/2(\tau)^{1/2}}^{\infty} e^{-x^2} dx$$

where $S = -D\psi_a\kappa^2/4\pi\epsilon$, ψ_a being the potential between $x=a$ (the closest approach of an ion to the surface) and $x=\infty$, and $\sigma = \kappa(x-a)$. The excess charge per unit area throughout the diffuse double layer is

$$(\epsilon/\kappa) \int_0^{\infty} f d\sigma,$$

and the time derivative of this gives the current. Thus the transient current is

$$i_t = [S\epsilon/\kappa\Theta(\pi)^{1/2}] \partial/\partial \tau \int_0^{\infty} e^{-\sigma} \int_{(\tau)^{1/2} - \sigma/2(\tau)^{1/2}}^{\infty} e^{-x^2} dx d\sigma$$

$$= -(D\psi_a\kappa\epsilon^{-\tau}/8\pi\Theta) [1 + 1/(\pi\tau)^{1/2}].$$

According to the principle of superposition, the steady-state current produced by an alternating potential of the form $\psi = \psi_a \sin \theta \tau$ (where $\theta \tau = \omega t$, ω being the circular frequency) is

$$(D\kappa\theta\psi_a/8\pi\Theta) \left[\cos \theta \tau \int_0^{\infty} e^{-u} [1 + 1/(\pi u)^{1/2}] \cos \theta u du \right. \\ \left. + \sin \theta \tau \int_0^{\infty} e^{-u} [1 + 1/(\pi u)^{1/2}] \sin \theta u du \right].$$

To calculate the apparent capacity, C , we are interested only in the quadrature component,

which is $\omega C \psi_a \cos \theta \tau$. Equating the coefficients of $\cos \theta \tau$ in the last two expressions, we obtain

$$C = (D\kappa/8\pi) \left[\int_0^{\infty} e^{-u} \cos \theta u du \right. \\ \left. + \int_0^{\infty} [e^{-u}/(\pi u)^{1/2}] \cos \theta u du \right] \\ = (D\kappa/8\pi) \left\{ \frac{1}{1 + \theta^2} + \frac{1}{\sqrt{2}} \left[\frac{(\theta^2 + 1)^{1/2} + 1}{\theta^2 + 1} \right] \right\}.$$

At high frequencies ($\theta \gg 1$) this becomes

$$(D\kappa/8\pi) [1/(2\theta)^{1/2}] = [D(kT)^{1/2} \kappa^2 / 8\sqrt{2\pi}(\rho)^{1/2}] / \omega^{1/2},$$

giving the experimentally observed proportionality to the inverse square root of frequency. For low frequencies ($\theta \ll 1$), it reduces properly to $D\kappa/4\pi$.

For $10^{-4} M$ potassium chloride in water at 25°C , Θ , the relaxation time of the ionic atmosphere, is about 0.3×10^{-6} sec., so that according to the theory proportionality to $\omega^{-1/2}$ should be observed only for frequencies over 10^6 cycles; while at lower frequencies the capacities should be smaller than those calculated from the $\omega^{-1/2}$ law. Actually the observed deviations from the $\omega^{-1/2}$ law are in the right direction but appear at much lower frequencies, about 2×10^4 cycles.

The proportionality of polarization capacity to electrolyte concentration (measured by κ^2) predicted by the theory is roughly confirmed in potassium chloride solutions from 1.3 to $2.7 \times 10^{-4} M$, using electrodes of sand-blasted platinum.

For $10^{-4} M$ potassium chloride, the theory predicts that the polarization capacity at 25 kc should be less than 1 percent smaller than the maximum, or Gouy capacity, $D\kappa/4\pi = 2.3 \mu\text{f}/\text{cm}^2$. Experimental values obtained in connection with previously reported studies³ range from 0.1 to $1.0 \mu\text{f}/\text{cm}^2$, depending on the electrodes used and their previous history. In a frequency range where the capacity follows the $\omega^{-1/2}$ law, the absolute value should be much less than the maximum value $D\kappa/4\pi$. However, the actual surface of sand-blasted metal is probably much greater than the geometrical surface, so that comparisons of absolute values of capacity are of doubtful significance.

Thus the dependence upon frequency and concentration of the capacity of a diffuse double layer is the same as that observed experimentally for the polarization capacity. However, the frequency range in which dispersion occurs would be expected to be higher by about two decades than that observed. The discrepancy might conceivably be attributed to a higher effective vis-

cosity in the diffuse double layer, but this does not seem reasonable for a layer of thickness 300Å, which is the value of $1/\kappa$ at this concentration. It appears likely that the observed effects cannot be explained in terms of the diffuse double layer; they may involve slow processes in the immediate vicinity of the electrodes, such as adsorption and desorption of the ions.

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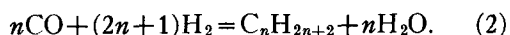
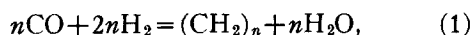
JULY, 1948

Thermodynamic Calculations Concerning the Possible Participation of the Carbides of Iron as Intermediate in Fischer-Tropsch Synthesis*

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(Received April 19, 1948)

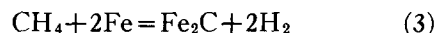
SINCE the discovery of the synthesis of hydrocarbons from carbon monoxide and hydrogen over iron catalysts, the suggestion has often been made that one of the iron carbides is an intermediate in the reactions:



Some evidence has been cited for the carbide being an intermediate;¹ other evidence has argued rather strongly against it.² During the past year we have obtained equilibrium data that enable us to conclude that the reduction of Fe_2C ³⁻⁵ by hydrogen at pressures up to ten atmospheres can form only negligible amounts of monoolefins in the temperature range 227 to 327°C. Furthermore, the formation of appreciable partial pressures of normal paraffin hydrocarbons for which n is greater than six by the reduction of Fe_2C is thermodynamically impossible at a hydrogen pressure of one atmosphere or less in the temperature range 227 to 327°C, and at as high as ten atmospheres pressure of hydrogen at

about 327°C. Accordingly, since it is well known that both at atmospheric pressure and at pressures of about ten atmospheres large partial pressures of monoolefins and of higher hydrocarbons are built up at temperatures as high as 300 to 330°C, it follows that these are formed by some mechanism other than the reduction of bulk Fe_2C .

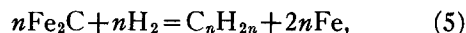
The free energy change ΔF for the reaction



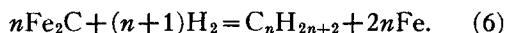
has been found to be 9.014 kcal. at 327°C and is estimated by extrapolation to be 11.91 kcal. at 227°C. It follows from the known free energies of formation of CH_4 ⁶ at 327 and 227°C (−5.490 and −7.841 kcal. per mole, respectively) for the reaction



that the ΔF value is 3.542 kcal. at 327° and 4.070 kcal. at 227°C. From these data and the known free energies of formation of the various hydrocarbons⁶ one can calculate the equilibrium constants for the reactions



and



Plots of the logarithm of the equilibrium con-

* Contribution from Gulf Research and Development Company's Multiple Fellowship, Mellon Institute, Pittsburgh, Pennsylvania.

¹ Ya. T. Eidus, *Bull. de l'Académie des Sciences de l'U.R.S.S. classe des sciences chimiques*, p. 447 (1946).

² Kummer, DeWitt, and Emmett, *J. Am. Chem. Soc.* (to be published).

³ Hägg, *Zeits. f. Krist.* **89**, 92 (1934).

⁴ Jacks, *Nature* **158**, 60 (1946).

⁵ Bahr and Jesson, *Ber.* **66**, 1238 (1933).

⁶ American Petroleum Institute, Research Project 44, National Bureau of Standards.