

where $v_{0,M}$ is the volume of the hypothetical liquid at 0°K. Table 2 shows the closeness of the values of c_0 calculated from Eqns. (12) and (13).

The calculated values of c_0 and published values of the density ρ_0 of the substances at 0°K¹⁴ have been used to find their adiabatic compressibilities β_0 at 0°K. Comparison of values for c_0 and β_0 with those for $c_{20^\circ\text{C}}$ and $\beta_{20^\circ\text{C}}$ shows that the compressibility of the hypothetical substance at 0°K, taken as that of the molecules, constitutes about 14–20% of the compressibility of the liquid at 20°C. This indicates that, although the compressibility of the molecules cannot be regarded as infinitesimal, intermolecular interactions play the main part in the compressibility of a liquid, being responsible for about 80% of the total at 20°C.

The velocity of sound in a liquid is more dependent than the compressibility on the properties of its molecules, as follows from an examination of the relation between c and β . On the assumption that the volume V of a liquid consists of the volume V_0 actually occupied by the molecules and the so-called free volume V_f , we can write

$$c \propto \sqrt{\frac{V}{\beta}} = \sqrt{\frac{V_0 + V_f}{\beta_0 + \beta_f}}, \quad (14)$$

where β_0 is the compressibility of the molecules and β_f the compressibility due to intermolecular interaction. Comparison of the volumes of liquids at 0°K with the volumes at 20°C given in Table 2 shows that at the latter temperature the molecules themselves are responsible for about 70%, and the free space for about 30%, of the volume of the liquid.

Thus the numerator in the expression under the square root sign in the formula (14) depends mainly on intramolecular properties, while the denominator, as noted above, is determined by intermolecular properties. Hence it can be concluded that the velocity of sound in a liquid depends to a considerable extent on intramolecular properties, owing on the one hand to the finite compressibility of the molecules and on the other to the great effect of the size of the molecules on the speed of sound.

SUMMARY

1. The link between the velocity of sound and the van der Waals constant b , the properties of the molecular speed of sound, regularities in the variation of the velocity of sound in binary mixtures, and also rough calculations of the velocity in polymer molecules indicate that the velocity of sound depends not only on intermolecular interactions but also on the properties of the molecules themselves.
2. Calculation of the compressibility of diatomic molecules and simple organic molecules indicates that the compressibility of liquids is determined mainly by intermolecular interactions.
3. The velocity of sound depends on the density and the molecular volume of a liquid, and since the latter is determined in liquids near the crystallisation temperature mainly by the actual volume of the molecules, the speed of sound in a liquid must be regarded as to some extent an intramolecular property of the substance.

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OVERPOTENTIAL OF THE ANODIC EVOLUTION OF CHLORINE ON GRAPHITE. II. KINETIC RELATIONS IN VARIOUS POTENTIAL RANGES

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In Part I¹ we have studied the effect of the acidity of the solution on the anodic overpotential accompanying the evolution of chlorine on graphite. We have established that the overpotential is lower at low than at high pH values, and that the cause of the increase in overpotential is retardation of the evolution of chlorine by the simultaneous evolution of oxygen. The present paper discusses additional results on the kinetics of chlorine evolution on graphite. Experiments were carried out by the technique described in Part I.¹

Fig. 1 shows a typical polarisation curve, obtained in strongly acid solution (after preliminary anodic treatment under conditions of oxygen evolution). The shape of the curve is noteworthy: it represents the intersection of two Tafel straight lines with the slope of one of them almost double that of the other (as the equilibrium potential is approached, divergence from the semilogarithmic relationship is observed, as was to be expected). The constant b is about 120 mV for the lower part of the curve, and 200–240 mV for the other part. Hence the true values of the slope — see Eqn. (3') of Part I¹ — are respectively 60 and 100–120 mV. The whole polarisation curve, from the lowest measured current density to the point of inflection, is well represented by Eqn. (3) of Part I with $b = 60$ mV. If, however, b is taken as 110 mV, very considerable deviation from experiment will be given at low current densities by the calculation (broken curve in Fig. 1). Thus the region of low slope cannot be a consequence of the well-known slow increase of the polarisation curve due to porosity of the electrode².

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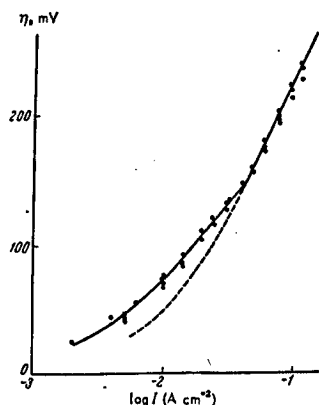


Fig. 1. Typical polarisation curve (explanation in text).

Experimental errors, in particular the effect of any impurities present, likewise provide no explanation of the presence of a sharp inflection. The latter hypothesis is contradicted by the fact that the overpotential is unaffected by many repeated electrolytic purifications of the solution, as also by vigorous stirring, although this would considerably increase the supply of the hypothetical impurities to the surface. This latter fact indicates also the absence of any substantial concentration polarisation.

In order to judge the mechanism of the electrode process, it is useful to determine the number of electrons λ involved in the slow stage. This has been found from data at high and low current densities by means of Eqns. (3)–(4) of Part I. Fig. 2 illustrates the linear relation between η and I near the equilibrium potential. We have found for strongly acid chloride solutions the values of λ 0.92, 0.83, and 0.83 (3 N Cl⁻ + 2 N H⁺); and 0.92, 0.97, 0.92, 0.99, 0.91, 1.17, and 0.98 (4.4 N Cl⁻ + 1.5 N H⁺). A feature of a porous electrode is that the value of λ is extremely sensitive to errors in the determination of I_0 and $d\eta/dI$, since it is inversely proportional to their square. In view of this, the experimental value of λ can be regarded as practically 1. This result makes mechanisms involving slow recombination and electrochemical desorption improbable. The value $\lambda = 1$ is consistent with slow discharge (with removal of chlorine by recombination) or breakdown of some kind of surface complexes, in which one chlorine atom is involved. In the latter case the constant $b = 60$ mV.

Slow discharge can give $b = 60$ mV in cases in which $\alpha = 1$. The theoretical feasibility of such a process has

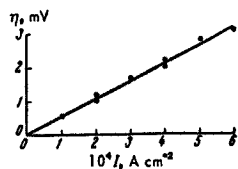


Fig. 2. Overpotential at low current densities.

been shown previously by one of us for the cathodic evolution of hydrogen³. The chief distinguishing feature of this process, termed barrierless discharge, is that the activation energy and the heat of the reaction are equal: in other words, the potential-energy curve does not show the usual activation barrier.

The theory of barrierless discharge leads to the conclusion that the overpotential is independent of the composition of the solution, in particular of the ψ_1 potential³. The effect of the latter on overpotential is due to two factors, the effect on the surface concentration of dischargeable ions and the effect on the potential drop in the dense part of the double layer⁴. The first factor usually predominates, since the potential drop in the double layer is multiplied by the coefficient α , which is less than unity. For barrierless discharge $\alpha = 1$, and this produces exact balancing of the two opposing effects.

In order to verify the corresponding relations for chlorine evolution, we have made a series of experiments with the same electrode in a strongly acid solution of sodium chloride alone and in solutions having the same acid and chloride concentrations but with additions of SO₄²⁻ (0.2 M) and Fe³⁺ (0.1 M), the results being plotted in Fig. 3. In the region in which the curves slope steeply the effect of solution composition is shown extremely clearly: sulphate retards the discharge of the Cl⁻ ion, whereas iron accelerates it; thus the situation corresponds to the expected ψ_1 effects for ordinary slow discharge. In the region with $b_{app} = 120$ mV ($b_{true} = 60$ mV), however, the curves for the solutions with and without additives practically coincide, as was to be expected for barrierless discharge[†].

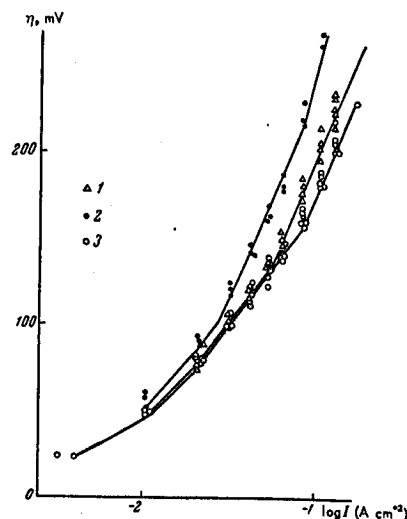


Fig. 3. Effects of added sulphate and iron(III) ions on overpotential in solution containing 4.4 N Cl⁻ + 1.5 N H⁺: 1) no addition; 2) 0.2 M Na₂SO₄; 3) 0.1 M FeCl₃.

[†] Experimental points are plotted directly in Fig. 3. In this case no correction has been made for the difference in electrical conductivities¹, since it is extremely small (~1 mV).

Fig. 4 shows polarisation curves in a solution containing $4.4 \text{ N Cl}^- + 1.5 \text{ N H}^+$ at different temperatures. Comparison with results in Part I¹ indicates that all these curves relate to the pH region before the start of oxygen evolution, and are therefore comparable with one another. As can be seen, the shape of the polarisation curve is maintained.

It is interesting that the overpotential corresponding to the point of inflection varies little with rise in temperature. This fact is well explained by the hypothesis of a transition from barrierless to ordinary discharge: the point of inflection then represents the point at which the activation energy of ordinary discharge becomes equal to the heat of reaction, i.e. the activation energy of barrierless discharge, and therefore the reaction velocity in the vicinity of the point of inflection, both somewhat above it and somewhat below it, shows almost the same temperature dependence. Consequently the overpotential corresponding to the inflection is almost independent of temperature. If, however, the inflection is attributed to transition from the slow breakdown of surface complexes to slow discharge (or electrochemical desorption), there are no grounds for expecting equality of the activation energies, and therefore the overpotential at the inflection can be independent of temperature only as a result of their fortuitous identity. These considerations compel us to regard the process of breakdown of surface compounds as less probable than barrierless discharge, but further work is required before the question can be finally settled.

Our results on the kinetics of chlorine evolution at a graphite anode agree well with the regularities of barrierless discharge. However, this explanation can be objected to on the grounds of the energy data. As noted above, the chief characteristic of barrierless discharge is equality of the activation energy and the heat of discharge. Since activation energy is essentially positive, it is clear that a barrierless process is possible only if the act of discharge involves the absorption of heat. This requires that the final product of discharge — an adsorbed chlorine atom — should be located at a fairly high energy level, i.e. that the adsorption of chlorine on graphite should be accompanied by the absorption (or comparatively slight evolution) of heat.

The energy of the Cl-Cl bond is 57 kcal, while the average value for the C-Cl bond is about 73 kcal.⁷ Hence the adsorption of chlorine should have been accompanied by a considerable evolution of heat, about 90 kcal mole⁻¹, which is inconsistent with the hypothesis of barrierless discharge. However, there are no grounds for accepting such a high heat of adsorption of chlorine. In contact with air, graphite is almost completely covered with chemisorbed oxygen⁸⁻¹⁰. Even if a C-Cl bond is formed under these conditions, there is nevertheless no doubt that its energy will be considerably diminished by the adsorption of oxygen at neighbouring

† The latter is a possible condition, since the energy level of the Cl^- ion in the double layer is probably rather lower than the level of Cl_2 owing to specific adsorption of this ion. The mechanism of the process is, of course, determined by the true form of the potential-energy surface, and not by the artificial construction required for calculation of the real activation energy. Therefore the "ideal" activation energy⁵, which may be positive with a rather higher energy of adsorption of chlorine, is to be considered provided that the latent equilibrium heat of the electrode process is positive. Judging from the entropy of Cl_2 and the conventional value of the entropy of Cl^- ,⁶ the latent heat of discharge is probably positive and of the order of a few kilocalories per mole.

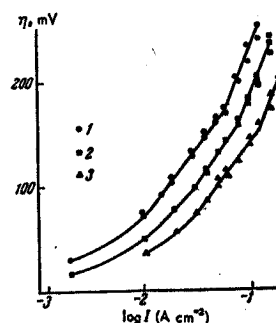


Fig. 4. Polarisation curves at different temperatures ($^{\circ}\text{C}$): 1) 25; 2) 40; 3) 60.

sites. Keyes and Marshall¹¹ found that the initial heat of adsorption of Cl_2 on previously degassed active charcoal is 31.9 kcal mole⁻¹, which is considerably below the above estimate. There is no doubt that the technique of degassing adopted in this work¹¹ did not permit the complete removal of adsorbed oxygen (this is noted by the authors themselves). The presence of oxygen on the carbon surface led to a considerable decrease in the adsorption energy in comparison with that to be expected from the bond energies; on the other hand, there is no doubt that in the experiments of Keyes and Marshall the surface coverage with oxygen was considerably less than with graphite specimens which have been oxidised in the air or anodically, and therefore a considerably lower heat of adsorption of chlorine can be expected under the conditions of our experiments.

The above considerations show that endothermic discharge of the Cl^- ion is extremely probable in the vicinity of the equilibrium potential, i.e. that a process of barrierless discharge is in principle feasible. In order to test this conclusion, a series of experiments was undertaken on the cathodic reduction of surface oxides on graphite. If the above hypothesis is correct, removal of even part of the oxygen from the surface should result in a diminution of the energy of bonding of the adsorbed chlorine, and thus lower the overpotential. It has already been noted¹ that very careful reduction of the surface produces a considerable decrease in overpotential (Fig. 2 of Part I, curves 4 and 9). Fig. 5 reproduces polarisation curves obtained at an electrode which has been subjected to more thorough reduction. A considerable diminution in overpotential is observed, and the mechanism of chlorine evolution has probably changed: instead of a (true) slope of 60 mV, the polarisation curves have a slope of 30–40 mV, i.e. values of b corresponding to slow recombination or electrochemical desorption. If removal of adsorbed chlorine has actually become the slow stage, this implies such a great acceleration of the discharge process that it has ceased to determine the rate of the overall process.

Many repetitions of the above experiments always gave the same result. They clearly show the great effect of

§ We have not made a special study of the mechanism of the process at a cathodically reduced surface. Determination of λ gave the not very reproducible results 0.81, 0.54, 0.65, and 0.76. According to Frumkin¹² values of λ smaller than unity can be observed with slow electrochemical desorption if its rate constant is of the same order as that of ionisation.

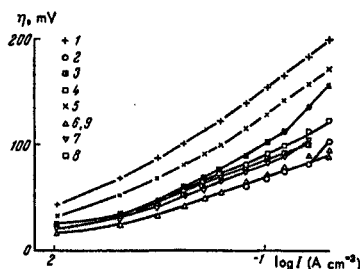


Fig. 5. Effect of cathodic reduction of graphite surface on chlorine overpotential in strongly acid chloride solution. Curves obtained on the same electrode after: 1) prolonged operation in weakly acid solution; 2) cathodic reduction at 0.3 A cm^{-2} (quantity of electricity passed 600 C cm^{-2}); 3) lying in air for 12 h (the same after 60 h); 4) anodic oxidation in weakly acid solution at 0.06 A cm^{-2} (150 C cm^{-2}); 5) anodic oxidation at 0.12 A cm^{-2} (1300 C cm^{-2}); 6) cathodic reduction at 0.3 A cm^{-2} (500 C cm^{-2}); 7) 4 days' operation in strongly acid solution; 8) as (7), after 10 days; 9) cathodic reduction at 0.3 A cm^{-2} ($20\,000 \text{ C cm}^{-2}$).

surface oxides on the bonding energy of adsorbed chlorine, and thereby confirm the above explanation of the possibility of the appearance of barrierless discharge of chlorine at a graphite anode.

It is interesting that the polarisation curves obtained on cathodically reduced graphite change very little (the overpotential increased slowly) after the graphite had been allowed to stand in air. It is obvious that we had not obtained a graphite surface free from oxygen by cathodic reduction followed by anodic treatment in an aqueous solution. Therefore keeping the electrode in air had little effect. However, after anodic treatment of such an electrode in a weakly acid solution, i.e. under conditions of definite oxygen evolution, its surface is again oxidised, and the polarisation curves return to the initial level.

The energy of adsorption of chlorine can in principle be affected by, apart from oxygen and probably to a lesser extent, other specifically adsorbed species, for example anions (a similar effect has been observed by Kolotyrkin and his coworkers¹³). This probably explains the slight increase in overpotential, of the order of the experimental error, on the lower part of the curve in the presence of sulphate (Fig. 3). It must again be noted that this effect lies on the borderline of the experimental error, and cannot be regarded as firmly established. In any case, the difference in overpotential in solutions with and without sulphate is considerably smaller before than after the inflection, which is consistent with the concept of a transition from barrierless to normal discharge.

We have not made a detailed study of the mechanism of chlorine evolution at low acidities, i.e. under conditions of simultaneous oxygen evolution. It must be noted that, even at considerably higher temperatures, when oxygen evolution is intensified, its fraction of the total current does not usually exceed a few per cent. We can therefore regard the measured current as in effect equal to the chlorine evolution current.

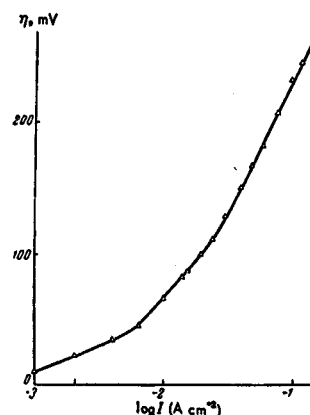


Fig. 6. Polarisation curve in $3 \text{ N Cl}^- + 0.1 \text{ N H}^+$.

Since at high pH values the surface of the electrode gradually increases during operation, it becomes difficult to find relatively small effects, such as that of SO_4^{2-} on the overpotential. In the present work we have therefore confined ourselves to determining polarisation curves and evaluating λ solely in a weakly acid solution of sodium chloride alone. The polarisation curves are similar in character to those for strongly acid solutions (Fig. 6). The values of λ are also close to unity (0.91, 1.06). It may therefore be supposed that simultaneous evolution of oxygen, while increasing the chlorine overpotential, has no significant effect on the mechanism of chlorine evolution.

SUMMARY

A study has been made of the overpotential of chlorine evolution in solutions of differing acidity. The polarisation curves obtained in strongly acid solutions comprise two sections with different true values, about 60 and 110 mV, of the constant b . The most probable mechanisms of chlorine evolution are respectively slow barrierless discharge and normal slow discharge. The situation is probably similar in weakly acid solutions, the only difference lying in a higher overpotential.

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THEORY OF THE DYNAMIC ADSORPTION LAYER OF MOVING SPHERICAL PARTICLES. II. THEORY OF THE DYNAMIC ADSORPTION LAYER OF A BUBBLE (DROP) AT A REYNOLDS NUMBER $Re \ll 1$ IN THE PRESENCE OF STRONG RETARDATION OF THE SURFACE

S. S. Dukhin and M. V. Buikov

The principles of the theory of the dynamic adsorption layer, and in particular the theory of the adsorption layer of drops and bubbles developed by Frumkin and Levich¹, are considered in the present paper. The description of the reciprocal effect of the adsorption layer on the motion of the drop surface encounters considerable difficulties². Levich² gives only a semiquantitative description of the problem based on the assumption of a sinusoidal distribution of velocity on the surface of the particle without taking into account the changes in the diffusional flux along such particles.

Deryagin and one of us³ proposed an approximate method of treating this problem when the surface is strongly retarded. It is not restricted to conditions at $Re \gg 1$, being applicable also if $Re \ll 1$; the latter case, which is discussed in the present paper, has the advantage that the result can be obtained in an explicit form whilst for $Re \gg 1$ so far only approximate results have been obtained³.

The generality of Frumkin and Levich's treatment¹ is restricted by the condition that the absolute and relative changes in the extent of adsorption along the drop surface are small. The generality of our treatment will be restricted only by the condition that the absolute change in the extent of adsorption for which a certain deviation of the shape of the drop from the spherical may be ignored is small. For this purpose, it is convenient to use the spherical system of coordinates with the origin located at the centre of the bubble and the Θ axis oriented in opposition to the direction of the stream. As before³, the case of strong retardation is understood to apply when the local

velocities of the bubble surface $v_\Theta(a, \Theta)$ with a radius a are much smaller than its velocity as a whole (u_0) relative to the medium:

$$v_\Theta(a, \Theta) \ll u_0. \quad (1)$$

Condition (1) makes it possible to apply the method of successive approximations for the calculation of the velocity, concentration, and adsorption fields. Since the velocity of the stream relative to the bubble is much greater than the velocity of the surface of the latter, the following boundary condition may be adopted as a first approximation:

$$v_\Theta(a, \Theta) = 0. \quad (2)$$

This is identical with the boundary condition for viscous flow past a rigid sphere. With this approximation the distribution of velocities when $Re \ll 1$ is expressed by Stokes' formula $\vec{v}(r, \Theta) = \vec{u}(r, \Theta)$. When the Stokes distribution of velocity $\vec{u}(r, \Theta)$ is known, it is easy to calculate the viscous stresses acting upon the surface of the sphere and the surface tension gradient which counterbalances them:

$$\frac{1}{a} \frac{d\sigma}{d\Theta} = \eta \left(\frac{1}{a} \frac{\partial u_r}{\partial \Theta} + \frac{\partial u_\Theta}{\partial r} - \frac{u_\Theta}{r} \right)_{r=a} = \frac{3}{2} \eta u_0 \sin \Theta. \quad (3)$$

Hence on the assumption of adsorption equilibrium, whose attainment is favoured by the retardation of the surface, it follows that

$$\frac{\partial c}{\partial \Theta}(a, \Theta) = \frac{3}{2} \eta \left(\frac{\partial \sigma}{\partial c} \right)^{-1} u_0 \sin \Theta, \quad (4)$$

where $c(a, \Theta)$ characterises the distribution of concentration along the surface. On integrating both sides of the equation and assuming that there is a linear relation between the local values of the extent of adsorption $\Gamma(\Theta)$ and $c(a, \Theta)$, we obtain the distribution $c(a, \Theta)$ and the extent of adsorption $\Gamma(\Theta)$ on the strongly retarded surface of a bubble, with a precision limited by the unknown constant $\delta c \delta \Gamma = \delta c \Gamma_0 / c_0$:

$$c(a, \Theta) = c_0 + \delta c - \frac{3}{2} \eta u_0 \left(\frac{\partial \sigma}{\partial c} \right)^{-1} \cos \Theta, \quad (5)$$

$$\Gamma(a, \Theta) = \Gamma_0 + \delta \Gamma - \frac{3}{2} \eta u_0 \left(\frac{\partial \sigma}{\partial \Gamma} \right) \cos \Theta, \quad (6)$$

where Γ_0 is the equilibrium value of the extent of adsorption on the stationary surface when the bulk concentration is c_0 .

Since the diffusion coefficient D in a liquid is greater than the kinematic viscosity ν by several powers of ten, conditions are possible³ in which the Peclet number $Pe = au/D$ is much greater than unity although $Re = au/\nu \ll 1$. Bearing in mind that, when $Pe \gg 1$, a boundary diffusion layer forms³ and that, when the retardation is very pronounced, it is possible to employ the Stokes velocity field, the equation for convective diffusion when $Re \ll 1$ and $Pe \gg 1$ may be transformed as follows³:

$$\left(\frac{\partial c}{\partial t} \right)_* = \frac{\partial}{\partial \psi} \left(r \psi \frac{\partial c}{\partial \psi} \right)_*, \quad (7)$$

where

$$t = \frac{Da^2 \sqrt{3} u_0}{2} f(\Theta) \quad (8)$$

$$f(\Theta) = \Theta - \frac{\sin 2\Theta}{2}, \quad (8')$$

and the stream function ψ within the limits of the boundary diffusion layer may be represented by $\psi = \frac{1}{4} u_0 y^2 \sin^2 \Theta$, $y = r - a$ being the distance of a given point from the surface of the bubble.