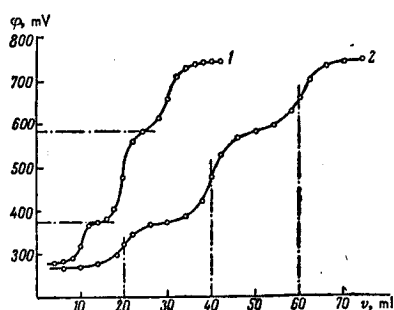




Curves for the potentiometric titration of tartaric acid with 0.5 M hydrogen peroxide in the presence of ferrous sulphate at 16°: 1) 5 ml of 1 M tartaric acid + 5 ml of 0.2 M FeSO_4 ; 2) 10 ml of 1 M tartaric acid + 10 ml of 0.2 M FeSO_4 .

containing the tartaric acid and the ferrous sulphate was introduced into the vessel and mixed by means of a magnetic stirrer. The molar ratio of tartaric acid to ferrous sulphate was varied from 100:1 to 4:1. Experiments were carried out at 2°, 16°, and 30°.

After each portion of oxidant had been introduced, the fall in potential with time was followed. The next portion was introduced only after the potential had remained constant for 15–20 min. In this way a curve was obtained for the variation of potential with volume of oxidant introduced.

The diagram shows curves for the potentiometric titration of 5 and 10 ml of 1 M tartaric acid with 0.5 M hydrogen peroxide. The curve can be seen to comprise several steps, corresponding to stages of oxidation.

Straight lines drawn at each stage through the point of inflection parallel to the ordinate axis cut off equal intercepts on the abscissa axis, the size of such intercepts showing that at each step one molecule of hydrogen peroxide is used up for each molecule of tartaric acid. Thus we are dealing with the stepwise oxidation of tartaric acid, with the splitting off of two hydrogen atoms or the addition of one oxygen atom at each stage. This suggests that the first stage involves the conversion of tartaric acid to dihydroxymaleic acid. The second stage corresponds to oxidation of dihydroxymaleic to dioxosuccinic acid or the hemialdehyde of mesoxalic acid. Mesoxalic acid itself or glyoxylic acid is formed at the third stage.

TABLE. Formation potentials and transition potentials (on standard hydrogen scale) for the stepwise oxidation of tartaric acid.

t, °C	Potentials at first stage		Potentials at second stage		Potentials at third stage	
	formation	transition	formation	transition	formation	transition
2	—	330	380	470	580	665
16	270–280	320	375	480	585	660
30	260–270	310	375	475	580	660

With reversible systems the potential at which half the reducing agent has been oxidised usually represents the standard redox potential of the system. Since we have been investigating systems in which irreversible reactions predominate, these potentials must be termed under our conditions "formation potentials" to avoid misunderstanding. The potential at which a given stage of oxidation is completed and the following one begins we shall denote by the term "transition potential". It has been established that, under the conditions of our investigations, the transition potentials and the formation potentials for each stage remain practically constant. The Table lists such potentials for each stage in the oxidation of tartaric acid with hydrogen peroxide in the presence of ferrous sulphate.

Certain fluctuations in these values, especially for the first stage, can be explained by the fact that these processes are irreversible, and the kinetic factor is involved to some extent, especially at low temperatures.

SUMMARY

1. A potentiometric investigation has been made of the oxidation of tartaric acid with hydrogen peroxide in the presence of ferrous sulphate as catalyst. The stepwise character of the oxidation has been established.
2. The formation potentials of the products at each stage and the transition potentials between one stage and another have been determined.
3. It has been shown that, in the oxidation of tartaric acid, a definite redox potential of the medium corresponds to the formation of a definite oxidation product.

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THEORY OF POLYELECTROLYTE SOLUTIONS. I. LOW DEGREES OF IONISATION

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Theoretical work on the electrostatic properties of polymeric macroions in solutions of ordinary electrolytes at low degrees of ionisation ($\alpha \ll 0.1$) has been based on the hypothesis that the surface charge of the macroions is uniform¹⁻³. At low degrees of ionisation, however, the charges produced by dissociation at individual units in the

macroions may be separated from one another by distances exceeding the diameter of the ionic atmosphere. Therefore the interaction between different charges on the macroion is small. However, the electrostatic interaction between isolated charges and the surrounding electrolyte becomes substantial. The interaction between different macroions is disregarded because of their low concentration. The concentration of the electrolyte is assumed to be such that the Debye-Hückel theory is applicable.

Distribution of Potential at the Surface of a Macroion

Let us suppose that the macroion has the form of a tightly packed ball with the charges situated in the surface region, which is true in the initial stages of the dissociation of a polymeric molecule in solution. The macroion is considerably larger than the ions of the electrolyte, and therefore the problem can be solved on the assumption that the interface between the polymer and the electrolyte solution is planar. The discrete charge attached to the inside of the polymer surface is assumed to be distributed in the form of a grid with the mean distance between the charges $d > 2/\kappa$, where $1/\kappa$ is the radius of the ionic atmosphere. To this approximation the problem reduces to the determination of the distribution of potential in a system containing a charge q at the polymer surface, without taking account of the effect of neighbouring charges. Strictly speaking, the charge q extends in space, but we shall assume that it is a point charge and that it is situated, not at the interface, but at a certain depth h inside the polymer. The latter assumption is introduced for convenience in the calculations. In the final formulae the value of h will be made equal to zero, and we shall obtain a result for the case of a surface point charge. The polymer molecule (on the left in Fig.1) is represented by a dielectric with dielectric constant ϵ_1 . The electrolyte solution, on the right-hand side, is a medium with dielectric constant ϵ_2 . The origin of the coordinate system is chosen to be the point on the interface at which the charge q is located. The positive direction of the z axis is taken to be the direction into the electrolyte solution. The xy plane is the polymer-electrolyte interface (Fig.1).

The distribution of potential in region I is described by Poisson's equation:

$$\Delta\psi = -\frac{4\pi}{\epsilon_1} q \delta(x) \delta(y) \delta(z+h), \quad (1)$$

while that in region II is represented by the equation

$$\Delta\psi = -\frac{4\pi}{\epsilon_2} \rho, \quad (2)$$

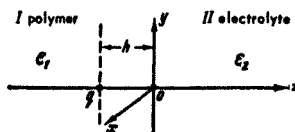


Fig.1.

where ρ is the charge density in the electrolyte, which has a Boltzmann distribution:

$$\rho = \sum_{i=1}^S |e| n_i z_i \exp\left(-\frac{z_i |e| \psi}{kT}\right), \quad (3)$$

n_i being the number of ions of a given type in unit volume, z_i their valency, and S the number of types of ions.

We can linearise Eqn. (2), since with a small charge q the potential satisfies the relation $|z_i e \psi / kT| \ll 1$. As a result, we obtain from Eqn. (2)

$$\Delta\psi - \kappa^2 \psi = 0, \quad (4)$$

where

$$\kappa^2 = \frac{4\pi e^2}{\epsilon_2 k T} \sum_{i=1}^S n_i z_i^2. \quad (5)$$

The constant arising in the linearisation is neglected, since the number of gegenions formed by dissociation of the macromolecule is negligible compared with the number of ions of the ordinary electrolyte. In this way the problem was reduced to finding solutions to Eqns. (4) and (1), for the ranges $-\infty < z \leq 0$ and $0 \leq z < \infty$ respectively, with the boundary conditions

$$\psi|_{z=0} = \psi|_{z=0}; \quad \epsilon_1 \frac{\partial \psi}{\partial z} \Big|_{z=0} = \epsilon_2 \frac{\partial \psi}{\partial z} \Big|_{z=0}; \quad \psi|_{z=\infty} = \psi|_{z=-\infty} = 0. \quad (6)$$

Solutions to Eqns. (1) and (4) satisfying the boundary conditions (6) are of the form

$$\varphi = \frac{q}{\pi} \iint_{-\infty}^{\infty} \frac{\exp[i(k_1 x + k_2 y) - (\sqrt{\kappa^2 + k_1^2 + k_2^2}) z - (\sqrt{k_1^2 + k_2^2}) h]}{\epsilon_2 \sqrt{\kappa^2 + k_1^2 + k_2^2} + \epsilon_1 \sqrt{k_1^2 + k_2^2}} dk_1 dk_2 \quad (7)$$

(for $0 \leq z < \infty$);

$$\psi = \frac{q}{\epsilon_1 \pi} \iint_{-\infty}^{\infty} \frac{[\epsilon_2 \sqrt{k^2 + \kappa^2} \operatorname{sh}(kh) + \epsilon_1 k \operatorname{ch}(kh)] dk_1 dk_2}{[\epsilon_2 \sqrt{k^2 + \kappa^2} + \epsilon_1 k] k \exp[-i(k_1 x + k_2 y) - kz]} \quad (8)$$

(for $-\infty < z \leq -h$);

$$\psi = \frac{q}{\epsilon_1 \pi} \iint_{-\infty}^{\infty} \frac{[\epsilon_1 k \operatorname{ch}(ks) - \epsilon_2 \sqrt{k^2 + \kappa^2} \operatorname{sh}(ks)] dk_1 dk_2}{[\epsilon_2 \sqrt{k^2 + \kappa^2} + \epsilon_1 k] k \exp[-i(k_1 x + k_2 y) + kh]} \quad (9)$$

(for $-h \leq z \leq 0$), where $k = \sqrt{k_1^2 + k_2^2}$.

The detailed derivation of the solutions (7)–(9) is given at the end of the paper. For the case of a surface charge, when $h \rightarrow 0$, solution (7) acquires a simpler form:

$$\varphi = \frac{q}{\pi} \iint_{-\infty}^{\infty} \frac{\exp[-\sqrt{\kappa^2 + k^2} + i(k_1 x + k_2 y)]}{\epsilon_2 \sqrt{\kappa^2 + k^2} + \epsilon_1 k} dk_1 dk_2. \quad (10)$$

Solution (10) thus obtained satisfies the condition of the electrical neutrality of the polymer-electrolyte system as a whole. Actually, the total charge in the double layer is obtained by simple integration of the charge density over the volume occupied by the right-hand half of the space in Fig.1, and should equal $-q$:

$$\int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z) dx dy dz = -q. \quad (11)$$

The correctness of this equation is readily confirmed by expressing ρ in terms of φ and carrying out the integration.

† Sh = sinh, ch = cosh (Ed. of Translation).

It can be shown that integral (10) can be computed approximately, but with a high degree of accuracy, within the limits of the double layer, when $z \ll \kappa^{-1}$, the result being to a first approximation spherically symmetrical. Actually, as will be shown later, integral (10) can be reduced to the following form:

$$\varphi(\rho, z) = 2q \int_0^\infty \frac{I_0(\sqrt{\lambda^2 - \kappa^2} \rho) \exp(-\lambda z)}{\epsilon_1 \sqrt{\lambda^2 - \kappa^2} + \epsilon_2 \lambda} \lambda d\lambda, \quad (12)$$

where $\lambda^2 = \kappa^2 + k^2$, $\rho = \sqrt{x^2 + y^2}$, and I_0 is the Bessel function of zero order. Let us investigate the behaviour of the function

$$f(\lambda) = \lambda / (\epsilon_1 \sqrt{\lambda^2 - \kappa^2} + \epsilon_2 \lambda)$$

when λ changes from κ to higher values. When $\lambda = \kappa$, we obtain $f(\lambda) = 1/\epsilon_2$; when $\lambda \gg \kappa$, we obtain $f(\lambda) = 1/(\epsilon_1 + \epsilon_2)$. When $\epsilon_1 \approx \epsilon_2$ the function $f(\lambda)$ changes only by a factor of 2 for an immense range of values of λ . The function $f(\lambda)$ is multiplied under the integral sign by the function $\exp(-\lambda z)$, which diminishes rapidly when $\lambda \approx 1/z \gg \kappa$. Thus integral (12) can be simplified by taking out the mean value of the function $f(\lambda)$ which varies only slightly. Over the range between κ and ∞ this mean value can be equated, with a high degree of accuracy, to the value of $f(\lambda)$ at $\lambda \gg \kappa$, because the range of values where this inequality holds is considerably greater than that where $\lambda \approx \kappa$. The function $I_0 \sqrt{\lambda^2 - \kappa^2} \rho$, which alternates in sign, is left inside the integral. Integral (12) thus becomes

$$\varphi(\rho, z) = \frac{2q}{\epsilon_1 + \epsilon_2} \int_0^\infty I_0(\sqrt{\lambda^2 - \kappa^2} \rho) \exp(-\lambda z) d\lambda. \quad (13)$$

The resulting integral is evaluated exactly⁵, and as a result we obtain

$$\varphi(\rho, z) = 2q/\epsilon_1 + \epsilon_2 \left[\frac{\exp(-\kappa r)}{r} \right], \quad (14)$$

where $r = \sqrt{\rho^2 + z^2}$.

Thus to a first approximation the result is spherically symmetrical, the deviations from spherical symmetry proving insignificant. If $\kappa = 0$, i.e. if no electrolyte is present, the result for φ is identical with the well-known value of the potential of a point charge at the boundary between two media having different dielectric constants ϵ_1 and ϵ_2 .⁶

Electrostatic Free Energy and Activity Coefficients

The electrostatic free energy of a real polyelectrolyte solution is defined by the difference between the total free energy of the solution and the free energy of the same solution in the absence of electrostatic interaction between the species, when the ions carry no charge at all. The expression for the change in free energy of the electrolyte when the charge on the macroion changes from 0 to q is then of the form⁴

$$F = \nu \int_0^q \Psi_0 dq, \quad (15)$$

where ν is the number of charges on the macroion, and Ψ_0 is the potential at the surface of the macroion. Expression (15) was obtained on the basis of a strictly statistical consideration of the system at potentials which are low in

comparison with kT/e . The total electrostatic free energy of unit volume of a system comprising macroions and ordinary electrolyte is

$$\Phi = n_p F + \Phi_0, \quad (16)$$

where n_p is the number of macroions in unit volume, and

$$\Phi_0 = - \sum_{i=1}^S n_i z_i^2 e^2 \kappa / 3D \quad (17)$$

is the electrostatic free energy of unit volume of ordinary electrolyte containing no macroions, calculated on the basis of the Debye-Hückel approximation. On replacing Ψ_0 in Eqn. (15) by the value of the potential produced by the ionic atmosphere at the location of the point charge q and integrating, we obtain

$$F = - \frac{\nu q^2 \kappa}{2\epsilon},$$

where

$$\epsilon = \frac{\epsilon_1 + \epsilon_2}{2}. \quad (18)$$

On substituting in Eqn. (16) for F from (18) and for Φ_0 from (17) we obtain

$$\Phi = - \frac{n_p \nu q^2 \kappa}{2\epsilon} - \frac{\sum_{i=1}^S n_i z_i^2 e^2 \kappa}{3\epsilon_2}. \quad (19)$$

To determine the activity coefficient of ions of a given kind we use the standard relation

$$\ln \gamma_k = \frac{1}{kT} \frac{\partial \Phi}{\partial n_k}. \quad (20)$$

Substituting in Eqn. (20) for Φ from (19) and remembering that κ depends on n_k in accordance with Eqn. (5), we obtain

$$kT \ln \gamma_k = - n_p \nu q^2 \kappa^2 / 4\epsilon - \sum_{i=1}^S n_i z_i^2 e^2 \kappa / 2\epsilon_2. \quad (21)$$

Eqn. (21) simplifies for the case of a uni-univalent electrolyte, where $z_i = 1$. To obtain an expression which is more convenient for comparing with experimental data we introduce instead of n_p and n_i the corresponding concentrations c_p of the polymer in monomoles [moles of the corresponding monomer? (Ed. of Translation)] per litre and c_i of free microions in moles per litre. As a result we obtain

$$kT \ln \gamma_k = - \frac{\alpha_p q^2 \kappa}{\sum_{i=1}^S c_i 4\epsilon} - \frac{e^2 \kappa}{2\epsilon_2}. \quad (22)$$

Strength of Interaction between Charges on the Surface of a Polymeric Molecule

Let us estimate the repulsive forces between neighbouring charges on the surface of a polymeric molecule. In contrast to the above treatment, we take into account the presence of a second charge q_2 . The distance between the charges is d (see Fig. 2). The distribution of potential in region I is described by the equation

$$\Delta \Psi = - \frac{4\pi}{\epsilon_1} [q_1 \delta(x) \delta(y) \delta(z+h) + q_2 \delta(x-d) \delta(y) \delta(z+h)]. \quad (23)$$

In region II Eqn. (2) is retained. Eqn. (23) is linear, and its solution results from the superposition of two solutions corresponding to the first and second terms on the

Eqn. (VIII). They are readily computed from Eqns. (IX) and (XII). The following expressions are then obtained for the Fourier components of the potential:

$$\psi_k(z) = \frac{q [e_2 \sqrt{k^2 + x^2} \operatorname{sh}(kh) + e_1 k \operatorname{ch}(kh)] \exp(kz)}{\pi e_1 k (e_2 \sqrt{k^2 + x^2} + e_1 k)} \quad (\text{XVI})$$

(when $-\infty < z \leq -h$);

$$\psi_k(z) = \frac{q [e_1 k \operatorname{ch}(kz) - e_2 \sqrt{k^2 + x^2} \operatorname{sh} kx] \exp(-kh)}{\pi e_1 k (e_2 \sqrt{k^2 + x^2} + e_1 k)} \quad (\text{XVII})$$

(when $-h \leq z < 0$).

We must remember that the charge q is located at the point $(0, 0, -h)$. The solutions thus obtained satisfy boundary conditions (VII) and (XII), as is easily verified by direct substitution.

Integral (10) can be somewhat simplified. We introduce the notation $k_1 x + k_2 y = \bar{k} \rho = k \rho \cos \beta$. We make the ρ axis a polar axis in the plane of the vector $\bar{k}$. Then $dk_1 dk_2 = k dk d\beta$, and integral (10) can be written in the form

$$\varphi(\rho, z) = \frac{q}{\pi} \int_0^\pi \int_{-\infty}^\infty \frac{\exp(-\sqrt{x^2 + k^2} z + i k \rho \cos \beta)}{(e_1 k + e_2 \sqrt{x^2 + k^2})} k dk d\beta.$$

Using the integral form of the zero-order Bessel function,

$$I_0(k, \rho) = \frac{1}{2\pi} \int_{-\pi}^\pi \exp(i k \rho \cos \beta) d\beta,$$

we obtain

$$\varphi(\rho, z) = 2q \int_0^\infty I_0(k\rho) \frac{\exp(-\sqrt{x^2 + k^2} z)}{e_1 k + e_2 \sqrt{x^2 + k^2}} k dk.$$

SUMMARY

1. The distribution of potential at the surface of a polymeric molecule surrounded by an electrolyte solution is obtained in the form of an integral, the value of which is calculated with a good degree of approximation. The formula obtained proves to be correct also in the absence of an external electrolyte.
2. The free energy of a system consisting of a polymer molecule surrounded by an electrolyte solution is calculated.
3. The ionic activity coefficients of the electrolyte are determined taking into account the effect of surface charges on the polymer molecule.
4. An estimate of the force of interaction between neighbouring charges on the surface of a polymer molecule shows that such interaction begins to play an important part if the distance between the surface charges becomes equal to the mean radius of the diffuse double layer surrounding them.

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MISCELLANY

TECHNIQUE OF INVESTIGATING INTERNAL STRESSES IN ELECTROLYTIC COATINGS

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At present different workers express differently the internal stresses in electrolytic coatings, which makes comparison difficult or impossible. In consequence the material suitable for generalisation accumulates very slowly, despite the expansion of research.

The following forms are used: relative units, *i. e.* the deflection h of the end of the cathode plate in mm;¹ as curves of $h = f(x)$, where x is the thickness of the deposit¹; and as curves of $\sigma_m = f(x)$ and $\sigma_t = f(x)$,²⁻⁵ where σ_m and σ_t are the mean and true internal stresses acting in a transverse section of the coating.

The use of relative units is the least satisfactory. The author has previously shown⁶ that the deflection h of the bottom end of the cathode is a function of the following quantities:

$$h = f(\sigma, \Delta t, E_1, E_2, l^2, t^2), \quad (1)$$

where σ is the internal stress, Δt the thickness of the deposit, E_2 the elasticity modulus of the deposit, E_1 the elasticity modulus of the cathode, and l and t are the length and thickness of the cathode plate. It follows that all the parameters of Eqn. (1) must be fixed if values of h obtained in different experiments are to be comparable. Thus any value of h quoted without a specification of all these parameters is indeterminate.

If it is required to investigate the effect of the basic cathode material on the internal stresses, then to obtain comparable values of h the rigidities of the base layers must be kept equal, *i. e.* $E_1 I_1 = E_2 I_2$, where E_1 and E_2 are the elasticity moduli of the cathode-plate materials and I_1 and I_2 the moments of inertia of the cathode cross-sections. If this condition is not fulfilled, the relative units cannot be compared with one another.

The presentation of experimental results as curves of $h = f(x)$ (curve *a* in Figure) is essentially the same as presentation in relative units. Without a knowledge of the rigidity and length of the cathode plate, nothing definite can be said about the values of internal stress shown on graph *a*.

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