THE EFFECTS OF ULTRASONIC WAVES ON ELECTROLYTES AND ELECTRODE PROCESSES

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When acoustic waves are propagated through a medium, the particles of the medium are subjected to periodic accelerations and compressions. The pressure changes take place under practically adiabatic conditions, even in the range of ultrasonic (inaudible) frequencies, *viz.*, above about 20 kilocycles/sec. Hence temperature fluctuations also occur. It is the changes in velocity, pressure, and temperature which cause the effects of acoustic waves on the properties of the medium and on reactions taking place therein.

In this Review the medium is restricted to simple ionic solutions. Acoustic effects in colloidal solutions, which have been reviewed by Sollner,[1] are largely omitted. Experimental procedures are not discussed since these have been covered in recent monographs.[2] The subject of sound absorption [3] is specifically excluded.

It will be clear from what follows that ultrasonic waves produce many interesting effects on electrolytes and electrode reactions. Although some of these have been known for over 15 years, there is a striking paucity of data on them.

(1) Compressibility

(1.1) **Compressibility from Acoustic Velocity.**—The velocity of sound u in a fluid is related to its adiabatic compressibility, $\beta_s = -(\partial V/\partial P)_s/V$, by the equation

$$u^2 = 1/\beta_s d \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where d is the density of the fluid. If the specific heat at constant pressure C_P is known, then the isothermal compressibility, $\beta = -(\partial V/\partial P)_T/V$, can be calculated from the thermodynamic formula

$$\beta = k\beta_s = \beta_s + \alpha^2 T/C_P d \quad . \quad . \quad . \quad . \quad (2)$$

where $k = C_P/C_V$ is the ratio of the specific heats and $\alpha = (\partial V/\partial T)_P/V$ is the coefficient of (cubic) thermal expansion. Conversely, where isothermal compressibility data are available, sound velocities yield specific heats.

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[1] Sollner, *Chem. Reviews*, 1944, **34**, 371 ; see also Alexander, " Colloid Chemistry, Theoretical and Applied ", Vol. 5, p. 337, Reinhold Publishing Corp., New York, 1944.

[2] Bergmann, " Der Ultraschall und Seine Anwendung in Wissenschaft und Technik ", 5th edn., S. Hirzel Verlag, Zurich, 1949 ; Carlin, " Ultrasonics ", McGraw-Hill Book Co., Inc., N.Y., 1949 ; Richardson, " Ultrasonic Physics ", Elsevier Press, Inc., Houston, 1952 ; Vigoureux, " Ultrasonics ", Chapman and Hall Ltd., London, 1950.

[3] Markham, Beyer, and Lindsay, *Rev. Mod. Physics*, 1951, **23**, 353.

The determination of ultrasonic velocity is the most accurate method of obtaining compressibilities of dilute solutions at atmospheric pressure. Velocity measurements are greatly simplified at high frequencies, since small samples of electrolytes are sufficient and reflections from the walls of the container can be made negligible. A resonance method is generally used, wherein standing waves are produced in a column of the solution and the wave-length evaluated. Precise velocity measurements may be made with the acoustic interferometer, developed by Pierce [4] for gases and by Hubbard and Loomis [5] for liquids. With this device absolute velocities accurate to 0·06% are claimed.[6] Greater relative precision is obtainable [7] by an optical method, originated by Debye and Sears [8] and independently by Lucas and Biquard.[9] The optical method depends upon the fact that the passage of ultrasonic waves through a liquid sets up periodic density variations. The latter act as an optical grating, which can be used to diffract a light beam or can be made directly visible.

(1.2) **Comparison of the Ultrasonic and Piezometric Methods.**—Compressibility data from ultrasonic measurements on aqueous solutions have been shown to be in good agreement with direct piezometric determinations. Although the latter are high pressure measurements, accurate compressibilities at atmospheric pressure may be computed from them by invoking the concept of "effective pressure" introduced by Gibson.[10] This concept follows from Tammann's hypothesis,[11] that at constant temperature the water in a given solution behaves as does the same weight of pure water under a constant effective pressure, P_e, in addition to the external pressure. The pressure–volume relationship of pure water, and of many other pure substances, is given by Tait's equation

$$-\partial v_0/\partial P = 0{\cdot}4343C/(B + P) \quad . \quad . \quad . \quad (3)$$

where B and C are positive constants and v_0 is the specific volume of the substance. With Tammann's hypothesis the Tait equation, applied to the water within a solution which is under a total pressure $P_e + P$, takes the form

$$-\partial v_1/\partial P = 0{\cdot}4343C/(B + P_e + P) \, . \quad . \quad . \quad (4)$$

where v_1 is the specific volume of the water in the solution, and the constants C and B have the same values as in equation (3) for pure water. The specific volume of the solution is given by

$$v = x_1v_1 + x_2v_2 \quad . \quad . \quad . \quad . \quad (5)$$

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[4] *Proc. Amer. Acad. Arts Sci.*, 1925, **60**, 271.

[5] *Nature*, 1927, **120**, 189 ; *Phil. Mag.*, 1928, **5**, 1177 ; *J. Opt. Soc. Amer.*, 1928, **17**, 295.

[6] Freyer, *J. Amer. Chem. Soc.*, 1931, **53**, 1313.

[7] Bachem, *Z. Physik*, 1936, **101**, 541 ; Falkenhagen and Bachem, *Z. Elektrochem.*, 1935, **41**, 570 ; Szalay, *Physikal. Z.*, 1934, **35**, 639.

[8] Debye, *ibid.*, 1932, **33**, 849 ; Debye and Sears, *Proc. Nat. Acad. Sci.*, 1932, **18**, 409.

[9] *Compt. rend.*, 1932, **194**, 2132 ; **195**, 121 ; *J. Phys. Radium*, 1932, **3**, 464.

[10] *J. Amer. Chem. Soc.*, 1934, **56**, 4, 865.

[11] *Z. physikal. Chem.*, 1893, **11**, 676.

where x denotes the weight fraction and v_2 the partial specific volume of the dissolved salt. Substitution for v_1 in equation (4) leads to the Tait–Gibson equation :

$$\beta v = \frac{0{\cdot}4343 x_1 C}{B + P_e + P} - x_2 \frac{\partial v_2}{\partial P} \quad . \quad . \quad . \qquad (6)$$

or, in integrated form,

$$(v)_P - (v)_{P_{\text{at.}}} = - x_1 C \log_{10}\left(\frac{B + P_e + P}{B + P_e + P_{\text{at.}}}\right) + x_2\{(v_2)_P - (v_2)_{P_{\text{at.}}}\} \quad . \qquad (7)$$

where $P_{\text{at.}}$ is atmospheric pressure. At moderate concentrations and pressures the terms containing v_2 are negligible.

Isothermal compressibilities at 25° and 1 bar, computed by two independent methods : (i) *ultrasonic,* (ii) *piezometric*

Concn., %	$10^6\beta$ (bar^{-1})							
	NaCl		KCl		KBr		KI	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
6 . .	40·4	40·6	41·7	41·8	43·5	43·2	44·3	44·3
10	37·5	37·6	39·4	39·5	41·9	41·7		
16	33·4	33·2	36·2	36·3			41·7	41·7
20	31·0	30·7	34·2	34·3	38·4	38·1		
24 . . .	28·8	28·4	32·4	32·4				
30 . . .					34·8	34·6	38·0	37·8
40					31·4	31·1		
45							33·7	33·4

Using equation (7), Gibson [12] determined P_e for various alkali halide solutions from a single compression of each solution to 1000 bars, and then calculated β at 1 bar from equation (6). His data are compared in the Table with those computed from Freyer's ultrasonic velocity measurements.[6] The excellent agreement shown by these entirely independent sets of data contributes strong support for the Tait–Gibson equation and the concept of effective pressure.

(1.3) **Correlation with the Debye–Hückel Theory.**—Acoustic velocity and compressibility data may also be correlated with the interionic attraction theory of electrolytes. For solutions of a single salt, the Debye–Hückel limiting law [13] evaluates the partial molal free energy of the dissolved salt, $\bar{G}_2 = (\partial G/\partial n_2)_{T,\,P}$, at a very low but finite molarity c as

$$\bar{G}_2 - \bar{G}_2^0 = \nu \boldsymbol{R} T \log_e c - A D^{-\frac{3}{2}} T^{-\frac{1}{2}} (\Sigma\, \nu_i z_i^2)^{\frac{3}{2}} c^{\frac{1}{2}} \quad . \quad . \qquad (8)$$

where $A = (\pi \varepsilon^6 \boldsymbol{N}^3/10^3 \boldsymbol{k})^{\frac{1}{2}}$ and $\bar{G}_2^0$ is a function of temperature and pressure only ; $\nu = \Sigma\, \nu_i$ where ν_i is the number of ions of the ith species per molecule ; z_i is the valency of the ion, D the dielectric constant, ε the electronic charge, $\boldsymbol{N}$ Avogadro's number, and $\boldsymbol{k}$ Boltzmann's constant. From this

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[12] *J. Amer. Chem. Soc.*, 1935, **57**, 284.

[13] *Physikal. Z.*, 1923, **24**, 185.

equation the partial molal volume of the dissolved salt, $\overline{V}_2 = (\partial G_2/\partial P)_T$, becomes[14]

$$V_2 - \overline{V}{}_2^0 = \sigma_V c^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\sigma_V = \frac{A}{2}\,\frac{(\Sigma\, \nu_i z_i^2)^{\frac{3}{2}}}{D^{\frac{3}{2}}T^{\frac{1}{2}}}\left(\frac{3}{D}\,\frac{\partial D}{\partial P} - \beta\right)$$

The partial molal compressibility of the dissolved salt, $\overline{K}_2 = -\,\partial V_2/\partial P$, is then evaluated[15] to be

$$\overline{K}_2 - \overline{K}{}_2^0 = \sigma_K c^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (10)$$

where

$$\sigma_K = \frac{A}{4}\,\frac{(\Sigma\, \nu_i z_i^2)^{\frac{3}{2}}}{D^{\frac{3}{2}}T^{\frac{1}{2}}}\left\{\beta^2 + 2\frac{\partial\beta}{\partial P} - \frac{6\beta}{D}\frac{\partial D}{\partial P} + 15\left(\frac{1}{D}\,\frac{\partial D}{\partial P}\right)^2 - \frac{6}{D}\,\frac{\partial^2 D}{\partial P^2}\right\}$$

For direct comparison with experimental determinations it is more convenient to use the corresponding apparent molal quantities. The apparent molal volume of the dissolved salt, ϕ_V, is defined by

$$\phi_V = (V - n_1\overline{V}_0)/n_2 \quad . \quad . \quad . \quad . \quad (11)$$

where n_1 and n_2 are the numbers of moles of solvent and solute respectively, V is the volume of the solution, and $\overline{V}_0$ the molal volume of pure solvent. It follows from this definition that

$$\partial(n_2\phi_V)/\partial n_2 = \overline{V}_2 \quad . \quad . \quad . \quad . \quad (12)$$

which may be applied to extremely dilute solutions as

$$\partial(c\phi_V)/\partial c = \overline{V}_2 \quad . \quad . \quad . \quad . \quad (13)$$

or, in integrated form,

$$\phi_V = \frac{1}{c}\int_0^c \overline{V}_2 . \mathrm{d}c \quad . \quad . \quad . \quad . \quad (14)$$

Substitution for $\overline{V}_2$ from equation (9) yields

$$\phi_V - \phi_V^0 = S_V c^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (15)$$

where $S_V = \frac{2}{3}\sigma_V$. Similarly, the apparent molal compressibility, defined as

$$\phi_K = -\,\partial\phi_V/\partial P = (\beta V - n_1\beta_0 V_0)/n_2 \quad . \quad . \quad (16)$$

where subscript zero denotes pure solvent, obeys the equation

$$\phi_K - \phi_K^0 = S_K c^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (17)$$

where $S_K = \frac{2}{3}\sigma_K$.

Equation (15) may be rewritten in terms of density, whence[16]

$$d - d_0 = ac - bc^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (18)$$

where $a = 10^{-3}(M_2 - d_0\phi_V^0)$ and $b = 10^{-3}d_0S_V$; M_2 is the molecular weight of the solute. A similar expression for compressibility is obtained upon combining equations (15) and (17), *viz.*[17]

$$\beta - \beta_0 = -fc + gc^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (19)$$

where $f = 10^{-3}(\beta_0\phi_V^0 - \phi_K^0)$ and $g = 10^{-3}(S_K - \beta_0 S_V)$.

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[14] See Redlich, *Naturwiss.*, 1931, **19,** 251; Redlich and Rosenfeld, *Z. physikal. Chem.*, 1931, *A*, **155,** 65.

[15] Gucker, *Chem. Reviews*, 1933, **13,** 111.

[16] Root, *J. Amer. Chem. Soc.*, 1933, **55,** 850.

[17] Gucker, *ibid.*, p. 2709.

Since all these equations have been derived from the limiting Debye–Hückel law, they apply only to extremely dilute solutions. For such solutions, the relationship $u^2 = k/\beta d$ may be utilised in the form

$$-2\frac{\Delta u}{u_0} = \frac{\Delta d}{d_0} + \frac{\Delta\beta}{\beta_0} \quad . \quad . \quad . \quad . \quad (20)$$

where $\Delta u = u - u_0$, etc. Substitution for Δd and $\Delta\beta$ from equations (18) and (19) gives the acoustic velocity as a function of concentration only :[18]

$$u - u_0 = hc - jc^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (21)$$

where

$$h = \frac{u_0}{2}\left(\frac{f}{\beta_0} - \frac{a}{d_0}\right) = \frac{u_0}{2000}\left(2\phi_V^0 - \frac{\phi_K^0}{\beta_0} - \frac{M_2}{d_0}\right)$$

and

$$j = \frac{u_0}{2}\left(\frac{g}{\beta_0} - \frac{b}{d_0}\right) = \frac{u_0}{2000}\left(\frac{S_K}{\beta_0} - 2S_V\right)$$

For a given solvent at fixed temperature the limiting slopes S_V and S_K, which characterise the linear relationships between the apparent molal quantities and the square root of the concentration, are constants for all salts of the same valency type. Hence the limiting slopes of the plots $\Delta d/c$–$c^{\frac{1}{2}}$, $\Delta\beta/c$–$c^{\frac{1}{2}}$, and $\Delta u/c$–$c^{\frac{1}{2}}$ are also constants for all salts of a given valency type.

Experimentally, the determination of any one of the five functions ϕ_V, ϕ_K, $\Delta d/c$, $\Delta\beta/c$, and $\Delta u/c$ at high dilution with sufficient accuracy to test the theoretical limiting slope is difficult. Some success has been achieved with density measurements ; the results obtained for strong electrolytes tend to support the interionic attraction theory.[19] The measurement of ultrasonic velocity or compressibility in very dilute solutions with the precision required to test the limiting theory has not yet been accomplished. A striking result is obtained when the experimental values of any one of the above functions are plotted against the square root of the concentration. A linear relationship is observed in each case,[20] extending over wide concentration ranges and down to relatively low concentrations. The coefficients of these empirical relationships differ from the theoretical values given by equations (15), (17), (18), (19), and (21). Furthermore the slopes of the observed lines are not constants for salts of the same valency type. No adequate explanation of these facts has appeared.

In the case of the apparent molal compressibility the empirical square-root relationship, first observed by Gucker [15, 17] at high concentrations, has been found to hold within experimental error down to 0·03 molar, the lowest concentration studied.[7] The same relationship has been observed for some

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[18] Barnartt, *J. Chem. Phys.*, 1952, **20**, 278.

[19] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd edn., p. 254, Reinhold Publishing Corp., New York, 1950.

[20] Barnartt, ref. (18) ; Gucker, ref. (17) ; Masson, *Phil. Mag.*, 1929, **8**, 218 ; Root, ref. (16).

60 strong electrolytes.[21] * In most instances the adiabatic compressibility data determined from ultrasonic velocities were used without conversion to isothermal compressibilities, since neither the linearity nor the slopes of the square-root plots are appreciably affected by this substitution.[24]

(1.4) **Solvation from Compressibility Data.**—Compressibility data may be correlated with the degree of solvation of dissolved salts. The correlation is based on the assumption that the water molecules in the immediate vicinity of an ion have modified physical properties, similar to those of pure water under high pressure. An ion may be considered to be surrounded by one or two (or possibly several) shells of bound water molecules which are under such high pressure as to be virtually incompressible. As a first approximation, the water of hydration about one ion is conceived as a sphere at the boundary of which the compressibility falls abruptly from that of pure water down to zero. It follows then, if n_i is the number of moles of incompressible solvent in the solution, that

$$\beta = -\frac{1}{V}\frac{\partial}{\partial P}\{\bar{V}_0(n_1 - n_i)\} = (n_1 - n_i)\frac{\beta_0\bar{V}_0}{V} \quad . \quad . \quad (22)$$

and therefore

$$s = \frac{n_i}{n_2} = \frac{n_1}{n_2}\left(1 - \frac{\beta V}{\beta_0 n_1 \bar{V}_0}\right) = -\frac{\phi_K}{\beta_0 \bar{V}_0} \quad . \quad . \quad . \quad (23)$$

where s is the solvation expressed in moles of solvent per mole of solute.

The study of solvation in this manner originated with Passynski,[25] who used the following modification of equation (23) :

$$s = (n_1/n_2)(1 - \beta/\beta_0) \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Solvation numbers calculated from equation (24) decrease slowly with increasing concentration,[25, 25a] and are qualitatively in harmony with Bernal and Fowler's theory of ionic hydration.[26]

(1.5) **Solutions of More than One Salt.**—Measurements of ultrasonic velocity in solutions containing more than one salt have been confined to sea water. These measurements are important for oceanic depth studies and for sonar ranging. In an investigation of a synthetic sea water containing 7 salts, Weissler and Del Grosso [23] found that the contributions of

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[21] Bachem ; Falkenhagen and Bachem, ref. (7) ; Giacomini and Pesce, *Ric. Sci.*, 1940, **11,** 605 ; Gucker, refs. (15), (17) ; Lunden, *Svensk Chem. Tidskr.*, 1941, **53,** 86 ; *Z. physikal. Chem.*, 1943, **192,** 345 ; Prozorov, *J. Phys. Chem. U.S.S.R.*, 1940, **14,** 384, 391.

[22] Krishnamurty, *Current Sci. India*, 1950, **19,** 87 ; *J. Sci. Ind. Res. India*, 1950, **9,** *B*, 215 ; Prakash, Saxena, and Srivastava, *Nature*, 1951, **168,** 522.

[23] Weissler and Del Grosso, *J. Acoust. Soc. Amer.*, 1951, **23,** 219 ; Lunden, ref. 21.

[24] Bachem, ref. (7).

[25] *Acta Physicochim. U.R.S.S.*, 1938, **8,** 385.

[25a] Giacomini and Pesce, ref. 21.

[26] *J. Chem. Phys.*, 1933, **1,** 515.

* Recent reports from India [22] present data on alkali halide solutions which do not obey this relationship. The ultrasonic velocity measurements, however, exhibit concentration dependence quite different from that shown by the more accurate measurements of other authors,[7, 21, 23] and must be tentatively considered as unreliable.

each salt to the sound velocity and compressibility of the solution were additive. Thus, from the data on simple solutions of each of the seven salts, the increments $(u - u_0)$ and $(\beta - \beta_0)$ were obtained at the same concentration as that at which the individual salt is present in sea water. Then the velocity and compressibility for the sea water were calculated by summing up the increments and combining the sums with the corresponding value for distilled water. The calculated values agreed with the measured values within experimental error (0·1%).

(2) Conductivity

Since the conductivity of an electrolyte varies with temperature and pressure, the passage of ultrasonic waves is accompanied by periodic conductance changes. The change in conductivity of an electrolyte, $d\kappa$, brought about by a small adiabatic compression may be written

$$d\kappa/\kappa = \gamma \, dP + \delta \, dT \quad . \quad . \quad . \quad . \quad (25)$$

where $\gamma = (1/\kappa)(\partial\kappa/\partial P)$ is the pressure coefficient and $\delta = (1/\kappa)(\partial\kappa/\partial T)$ the temperature coefficient of conductivity. Substitution for dT from the general thermodynamic relationship

$$(\partial T/\partial P)_S = \alpha T/C_P d \quad . \quad . \quad . \quad . \quad (26)$$

leads to the equation

$$d\kappa/\kappa = (\gamma + \delta\alpha T/C_P d)dP \quad . \quad . \quad . \quad (27)$$

If the amplitude of the conductance change produced by an acoustic wave be measured in an electrolyte whose coefficients γ and δ are known from static measurements, the pressure amplitude of the wave may be computed by means of equation (27). From the pressure amplitude p, the sound intensity I is computed from

$$I = p^2/2ud \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where I is the average energy flow per sq. cm. per second. Thus the measurement of the conductance changes in an electrolyte may be used to determine acoustic intensity. Conversely, if the intensity is also evaluated experimentally, then the pressure coefficient of conductivity may be calculated for electrolytes whose temperature coefficients are known.

The conductance effect was first studied by Fox, Herzfeld, and Rock.[27] In their method a filament of constant alternating current, of frequency f_1, is passed between the ends of two fine wire electrodes brought close together. The current filament is arranged perpendicular to the direction of a travelling ultrasonic wave, and may be made essentially small in comparison with the wave-length if the acoustic frequency f_0 is not too high. Under these conditions two side bands of frequency $(f_0 + f_1)$ and $(f_0 - f_1)$ are produced with a voltage that depends upon the conductance changes. Measurements of the side-band voltages for sodium chloride and copper sulphate solutions showed satisfactory agreement with the voltages calculated from the known conductivity coefficients.

A method of measuring the conductivity effect employing stationary

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[27] *Phys. Review*, 1946, **70**, 329.

acoustic waves has been described by Lichter and Khaikin.[28] A constant alternating current having the same frequency as the sound wave is applied to fine wire electrodes situated in a pressure antinode of the standing wave. Location of the electrodes in a velocity node eliminates possible complications from velocity variations. A phase difference is maintained between the applied voltage and the sound wave. The phase displacement produces a rectified voltage which is a measure of the conductivity fluctuations. Electrode polarisation is minimised by changing the sign of the rectified voltage periodically. This is accomplished by changing the phase of the applied voltage to the opposite phase f' times per second, where $f' \ll f_0$. With this method the pressure coefficient γ was determined at 20° for 0·005M-silver nitrate solution, for which the temperature coefficient δ was known. Then, γ being assumed to be independent of temperature, δ was determined ultrasonically over the temperature range 5—60°. These values of δ agreed with those from static measurements within experimental error.

Recently, Krishnamurty [28a] announced that the conductivities of nitrate solutions, as measured by the usual Kohlrausch method, decrease when the solution is subjected to ultrasonic vibrations. Conductance changes as high as 20% were reported for an ultrasonic frequency of 2·51 megacycles/sec. at an unspecified intensity. In addition, the passage of current through each solution was accompanied by an increase in the velocity of ultrasonic waves in it, and consequently by a decrease in its compressibility. These effects merit confirmation.

(3) Space Charge (the Debye Effect)

In 1933 Debye [29] predicted that ultrasonic waves create space charge in electrolytic solutions. The space charge arises because the ions, owing to their inertia, lag behind the solvent in the sound field. Since the positive and negative ions will usually move with different velocities, the electrical potential at a given point in the irradiated solution will acquire an alternating component having the same frequency as the acoustic wave.

Debye derived the magnitude of the effect to a first approximation, specifically omitting diffusion and interionic attraction as being second-order considerations. The force on an ion in a plane ultrasonic wave was considered to comprise an electrical force resulting from the space charge and a frictional force resulting from the difference in velocity of the ion and the surrounding liquid. The equation of motion is then

$$e_i X - \rho_i(v_i - v_0) = m_i \mathrm{d}v_i/\mathrm{d}t \quad . \quad . \quad . \quad (29)$$

where e_i, ρ_i, v_i, and m_i are respectively the charge, friction constant, velocity, and mass of the ion ; v_0 is the velocity of the solvent ; and X is the electric field intensity. Combination of this equation with the equation of continuity and Poisson's equation leads to the following general solution : [29]

$$E = \frac{m_H}{\varepsilon} u a_0 \frac{\Sigma\,(\nu_i z_i M_i/\rho_i)}{\Sigma\,(\nu_i z_i^2/\rho_i)} \, \frac{4\pi\kappa/D\omega}{\{1 + (4\pi\kappa/D\omega)^2\}^{\frac{1}{2}}} \quad . \quad . \quad (30)$$

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[28] *J. Exp. Theor. Phys. U.S.S.R.*, 1948, **18,** 651.

[28a] *J. Sci. Ind. Res. India*, 1951, **10,** *B*, 149.

[29] *J. Chem. Phys.*, 1933, **1,** 13.

Here E is the amplitude of the potential oscillations, m_H the mass of the hydrogen atom, a_0 the velocity amplitude of the solvent, κ the conductivity of the solution in electrostatic units, D the dielectric constant of the solvent, M_i the effective gram-ionic weight of the ion, and $\omega/2\pi$ the frequency.

If the frequency is not too high, the expression on the extreme right can be made equal to unity. Under these conditions equation (30), applied to an aqueous solution of a uni-univalent salt, reduces to

$$E = 1{\cdot}4 \times 10^{-7} a_0 \frac{M_+/\rho_+ - M_-/\rho_-}{1/\rho_+ + 1/\rho_-} \text{ volt} \quad . \quad . \quad (31)$$

Thus the Debye effect provides a measure of the relative masses of ions, and hence their degree of solvation. With a solution of known ionic masses the effect may be used to determine a_0, from which the acoustic intensity may be calculated by the equation

$$I = \tfrac{1}{2} u d a_0^2 \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The order of magnitude of E may be revealed by putting $\rho_+ = \rho_-$ and $M_+ - M_- = 15$, whence E becomes 10^{-6} volt per unit velocity amplitude.

Oka [30] extended the derivation to include interionic attraction by adding terms to equation (29) for the electrophoretic force and the force of relaxation. The added forces, however, applied only to dilute solutions and represented small corrections. Hermans [31] pointed out that equation (29) fails to show that the space charge must disappear when the densities of the ions and solvent are equal. He remedied this by taking into consideration the force on the ion resulting from the pressure gradient in the acoustic wave. The equation of motion then becomes

$$e_i X - \rho_i(v_i - v_0) = m_i \mathrm{d}v_i/\mathrm{d}t - V_i d_0 \mathrm{d}v_0/\mathrm{d}t \quad . \quad . \quad (33)$$

where V_i is the volume of the ion and d_0 the density of the solvent.

Bugosh, Yeager, and Hovorka [32] extended the calculations to include not only this pressure-gradient term, but also the forces resulting from diffusion and interionic attraction. The extended solution has only theoretical interest at the present time, however, since experimental evidence for the Debye effect is as yet qualitative. Yeager, Bugosh, Hovorka, and McCarthy [33] first demonstrated the existence of the effect in simple electrolytes, utilising a stationary ultrasonic field. The apparatus used did not permit determination of the velocity amplitude within the test solution, hence comparison of the data with the predictions of equation (31) was not possible. In agreement with theory, however, the measured alternating potentials were found to be roughly independent of concentration for dilute uni-univalent electrolytes, and to vary with the electrolyte used.

With the standing-wave technique elaborate screening precautions are necessary to prevent electromagnetic coupling between the high-frequency source and the detecting cell. This complication can be minimised by the

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[30] *Proc. Phys. Math. Soc. Japan*, 1933, **15**, 413.

[31] *Phil. Mag.*, 1938, **25**, 426.

[32] *J. Chem. Phys.*, 1947, **15**, 592.

[33] *Ibid.*, 1949, **17**, 411.

use of pulse-modulated ultrasonic waves,[34] whereby the acoustical effects are separated in time from electromagnetic coupling and are measured under essentially free-field conditions. A potential amplitude of 5 microvolts per unit velocity amplitude has been obtained recently by the pulse method in 0·005M-potassium chloride solution.[35] From equation (31), this corresponds to a mass difference between the potassium and chloride ions of 70, or approximately $4H_2O$ per mole of potassium ion on the basis of Bernal and Fowler's conclusion [26] that the chloride ion is not hydrated. This result may be compared with the values 6—$7H_2O$ from compressibility data [25] and $2H_2O$ from ionic-activity data.[36]

Hermans [31] and independently Rutgers [37] pointed out that the Debye effect should be much larger in colloidal solutions, where the positive and negative ions exhibit greater differences in mass. Approximate theoretical treatments for this case have been presented by Hermans [31, 38] and by Enderby.[39] Both theories assume that the vibration potentials in colloidal solutions arise primarily from periodic distortion of the double layer around each colloidal particle, and that the relative motions of small positive and negative ions contribute very little. The distortion occurs because the heavy colloidal particle moves more slowly than the ionic charges outside it. The resulting asymmetric charge distribution is equivalent to a dipole situated at the centre of the particle. The potential differences developed by the acoustic wave may be computed by summing up the dipole moments of all the particles. Hermans's derivation predicts that potential amplitudes of the order of a volt should be attainable.[38] Much smaller potentials are indicated by Enderby's theory.

The following simple formula for estimating the potential amplitude in colloidal solutions has been given by Vidts : [40]

$$E = ua_0D\zeta m/4\pi\kappa\eta \quad . \quad . \quad . \quad . \quad (34)$$

where ζ is the electrokinetic potential of the colloidal particles, m their mass per c.c., and η the viscosity. The first measurements reported, for a silver iodide sol,[40, 41] indicated potential amplitudes two orders of magnitude smaller than those predicted by equation (34). More recent measurements in a colloidal arsenic trisulphide solution,[42] however, gave an amplitude of 1·5 mv as compared with 7 mv calculated from the formula.

(4) Effects on Electrode Potentials

(4.1) **Unpolarised Electrodes.**—When an unpolarised electrode is subjected to acoustic vibrations, the electrode potential should acquire an

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[34] Hunter, *Proc. Phys. Soc.*, 1950, *B*, **63,** 58 ; Yeager, Bugosh, and Hovorka, *ibid.*, 1951, *B*, **64,** 83.

[35] Yeager, Dietrick, Bugosh, and Hovorka, *J. Acoust. Soc. Amer.*, 1951, **23,** 627.

[36] Stokes and Robinson, *J. Amer. Chem. Soc.*, 1948, **70,** 1870.

[37] *Physica,* 1938, **5,** 46.

[38] *Phil. Mag.*, 1938, **26,** 674.

[39] *Proc. Roy. Soc.*, 1951, *A*, **207,** 329.

[40] *Bull. Acad. roy. Belg.*, Classe sci., 1945, No. 3, p. 5.

[41] Rutgers, *Nature*, 1946, **157,** 74.

[42] Rutgers and Vidts, *ibid.*, 1950, **165,** 108.

alternating component resulting from the periodic compressions. Where the electrode is composed of condensed phases only, the alternating component should be very small. Moriguchi [43] observed no change in the potential of copper electrodes in dilute copper sulphate solution upon irradiation with ultrasonics. Schmid and Ehret [44] confirmed this observation, and also noted no change of potential for nickel electrodes in nickel chloride solution. These workers, however, did not attempt to reveal small alternating components.

The potential of a gas electrode is much more sensitive to compression, and in this case an appreciable temperature variation will occur in the gas phase if the compression is adiabatic. Schmid and Ehret [44] reported that the potential of a hydrogen electrode in dilute sulphuric acid became indefinite to ± 5 mv in the presence of ultrasonics. Again no attempt was made to reveal an alternating component.

A theoretical derivation of the alternating component has been given recently by Yeager and Hovorka [45, 46] for the hydrogen electrode. If it is assumed that the irradiated electrode is reversible, the change in electrode potential may be evaluated by thermodynamics. The added acoustical pressure in the gas phase, P_a, produces a change in potential given by the general equation

$$\Delta E = \frac{RT}{zF} \log_e \frac{P_g + P_a}{P_g} \quad . \quad . \quad . \quad . \quad (35)$$

where P_g is the time average of the gas pressure and F the Faraday of electricity. With the restriction of low acoustic intensity, so that P_a is a small fraction of P_g, the approximation $\log_e (1 + P_a/P_g) = P_a/P_g$ may be applied to equation (35) to give

$$\Delta E = RTP_a/zFP_g \quad . \quad . \quad . \quad . \quad (36)$$

or

$$E = RTp/zFP_g \quad . \quad . \quad . \quad . \quad (37)$$

where E is the potential amplitude and p the pressure amplitude. At low audio-frequencies, where the thickness of the gas film is small compared with the wave-length, the acoustic compressions in the gas phase may be almost isothermal, in which case the potential amplitude would approach the value given by equation (37).

At higher frequencies the compressions would be practically adiabatic and, providing the electrode behaves reversibly, the potential amplitude is readily shown [45] to be approximately

$$E = \frac{RTp}{zFP_g}(S/C_P - 1) \quad . \quad . \quad . \quad . \quad (38)$$

where S is the molar entropy of the gas and C_P its molar heat capacity at constant pressure. Yeager and Hovorka [46] have expressed doubt whether gas electrodes can remain reversible at ultrasonic or even at the upper audio-frequencies. They proposed a kinetic treatment, and developed a

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[43] *J. Chem. Soc. Japan*, 1934, **55**, 749.

[44] *Z. Elektrochem.*, 1937, **43**, 597.

[45] *J. Chem. Phys.*, 1949, **17**, 416.

[46] *J. Electrochem. Soc.*, 1951, **98**, 14.

general equation for the hydrogen electrode which is applicable to both unpolarised and polarised electrodes and which reduces to equation (37) at low frequencies.

This electrode effect, like the conductivity and Debye effects, may prove useful for the absolute measurement of acoustic intensity in liquids, and consequently for exploring complex ultrasonic fields. All three effects do not have a characteristic frequency, as the usual crystal gauges do. They have the further advantage that the electrolyte surrounding the electrodes may be selected so that its characteristic acoustic impedance (*ud*) is nearly equal to that of the irradiated liquid. Since the electrodes may be made small in comparison with the wave-length, reflection of the wave at the measuring instrument can be avoided.

(4.2) **Polarised Electrodes.**—In the case of electrodes polarised by current flow, pronounced depolarising effects can be produced by the application of ultrasonic waves. Acoustic agitation is particularly violent at a liquid–solid interface.[47] At the electrode surface, therefore, the concentration changes in the diffusion layer are reduced and the products of electrolysis largely removed.

From a study of the electrolysis of copper sulphate solution with copper electrodes, Moriguchi [43] concluded that the diffusion layer at each electrode was eliminated by irradiation with ultrasonics. With ordinary stirring the plot of current through the cell against applied voltage deviated considerably from linearity (Ohm's law). When ultrasonic waves were substituted for the stirring, however, a linear plot was obtained, indicating that polarisation was eliminated at both anode and cathode. It is possible, however, that appreciable polarisation remained if it were approximately proportional to the current density.

Where one of the products of electrolysis is a coating over the surface of the electrode, ultrasonics may give rise to considerable depolarisation by removing the coating. The surface layer tends to be disrupted and dispersed colloidally in the liquid, especially when it is brittle or does not adhere tenaciously to the substrate.[48] The mechanism whereby the coating is torn off probably involves cavitation, the periodic formation and collapse of cavities, which occurs most readily at interfaces.[48, 49]

Depolarisation by removal of a coating from the electrode surface was first demonstrated by Moriguchi,[50] using smooth platinum electrodes for the electrolysis of aqueous solutions. Ordinarily the liberation of hydrogen and oxygen at smooth platinum electrodes requires approximately 1·7 volts. When the anode was irradiated with ultrasonics, the voltage required at moderate current densities was reduced to about 1·2, which is close to the equilibrium value for the oxygen and hydrogen electrodes. Most of this depolarisation resulted from the removal of an anodic coating (presumably

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[47] Richards, *J. Amer. Chem. Soc.*, 1929, **51,** 1724 ; Richards and Loomis, *ibid.*, 1927, **49,** 3086.

[48] Söllner, *Trans. Faraday Soc.*, 1938, **34,** 1170.

[49] Bondy and Söllner, *ibid.*, 1935, **31,** 835.

[50] *J. Chem. Soc. Japan*, 1934, **55,** 751.

platinum oxide) which was found to be dispersed in the electrolyte. At relatively high current densities the anodic film was not all removed and the marked depolarisation no longer occurred.

Several other examples of ultrasonic action on electrode coatings have been described by Schmid and Ehret.[50a] The formation of an anodic coating on lead in sodium carbonate solution is retarded. On aluminum anodes in sodium sulphate solution, on the other hand, the anodic film forms more rapidly in the presence of ultrasonics ; however, a thinner film and decreased polarisation are obtained. The grey layer that passivates iron in concentrated sulphuric acid is removed, and the iron continues to dissolve as long as the ultrasonic waves are applied. The reactivation of passive chromium in concentrated hydrochloric acid occurs much more rapidly. In concentrated nitric acid, the passivity of chromium is not affected by ultrasonics but that of iron is quickly destroyed. Roll [51] has shown that the passivating film which causes pronounced polarisation of silver anodes in cyanide plating solutions at relatively low current densities does not form in an ultrasonic field until much higher current densities are applied.

In intense ultrasonic fields marked depolarisation occurs at gas electrodes, even in the absence of surface coatings on the electrodes. At constant current density there exists generally an intensity above which depolarisation suddenly increases. Similarly, at constant intensity there exists a current density above which the depolarising action rapidly diminishes. Figs. 1 and 2 taken from Schmid and Ehret's data [44] show typical curves obtained for hydrogen evolution at nickel cathodes in 0·2M-sodium sulphate solution (pH 4·2) with an acoustic frequency of 284 kilocycles/sec. Curves similar to that of Fig. 1 were obtained for hydrogen deposition from sodium sulphate solution on eight other metal electrodes. Anodic deposition of chlorine on platinum from hydrochloric acid solution also gave the same type of curve. In all cases a hissing noise characteristic of cavitation began at the intensity at which the potential jumped. That the jump in potential is produced by the cavitation was later confirmed by Polotskii and Filippov,[52] who reproduced the potential jump for both hydrogen and chlorine liberation when cavitation was brought about by superheated steam.

Fig. 2 shows that the pronounced depolarisation disappears at relatively high current densities. This behaviour was also observed by Piontelli [53] for hydrogen deposition from several other electrolytes. According to Schmid and Ehret,[44] the depolarisation mechanism is a mechanical one. When cavitation occurs, the gas being deposited at the electrode is drawn into the cavities and the gas pressure at the electrode decreases. At low current densities where the gas is liberated very slowly, the gas pressure at the electrode may be reduced considerably below atmospheric pressure, and the electrode polarisation may become negative when based upon the equilibrium potential for one atmosphere pressure (see Fig. 2). At high current densities only part of the liberated gas is removed by cavitation.

[50a] *Z. Elektrochem.*, 1937, **43**, 408.

[51] *Z. Metallk.*, 1950, **41**, 413.

[52] *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 193.

[53] Piontelli, *Atti Accad. Lincei*, Classe sci. fis. mat. nat., 1938, **27**, 357, 581.

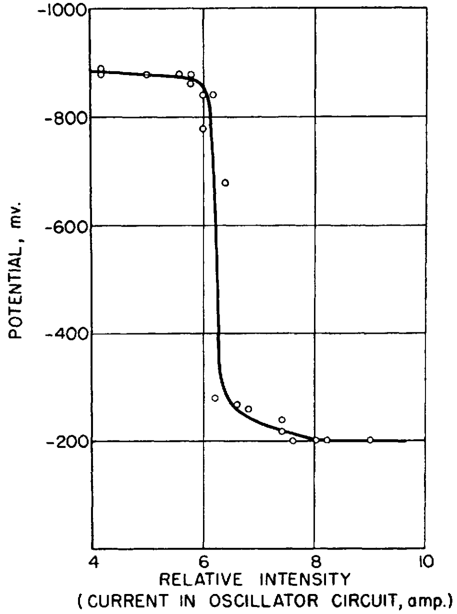

FIG. 1

Effect of ultrasonic intensity on hydrogen deposition potential at 2·5 *milliamp./cm.*^{2} *(from Schmid and Ehret,* Z. Elektrochem., 1937, **43**, 597).

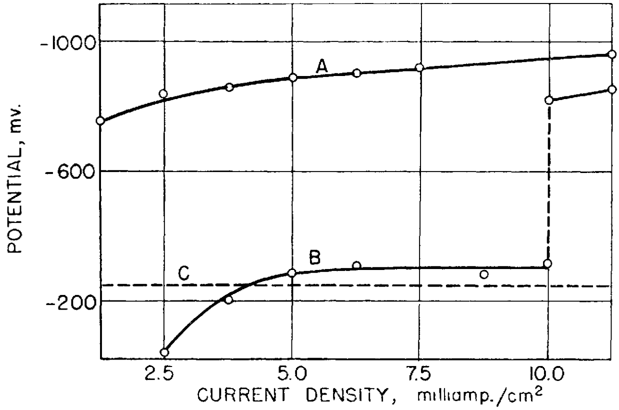

FIG. 2

Variation of hydrogen deposition potential with current density : A—*in the presence of strong agitation ;* B—*in the presence of intense ultrasonics ;* C—*equilibrium potential at hydrogen pressure of* 1 *atm. (from Schmid and Ehret*, loc. cit.).

This mechanism is in accord with the observations that the acoustic intensity required to produce the potential jump increases with current density, and that the potential jump is practically independent of the nature of the cathode metal.

Limited data on the anodic deposition of oxygen indicate somewhat different behaviour in an ultrasonic field. Schmid and Ehret,[44] using a platinum anode in 0·2M-sodium sulphate solution, found no sudden potential jump, rather a gradual depolarisation with increasing ultrasonic intensity. In this case the mechanism is complicated by oxidation of the platinum surface.[53]

Depolarisation at relatively low acoustic intensities, where cavitation is absent, has been studied by Roll.[51, 54] During the simultaneous deposition of hydrogen with nickel, with silver, and with copper, the depolarising action of ultrasonics was similar to that of strong agitation. This was true also for anodic dissolution of silver in the argentocyanide plating bath. For copper dissolution in the acid sulphate bath, neither ultrasonics nor agitation produced any appreciable change in polarisation. The acoustic depolarisation is greatly dependent upon the frequency. At a given acoustic intensity level, the cathodic depolarisation during nickel deposition was found to increase with decreasing frequency.[55]

The presence of an alternating component in the potential of a polarised gas electrode subjected to acoustic vibrations was demonstrated by Nikitin [56] at audible frequencies and by Yeager, Bugosh, Hovorka, and McCarthy [33] at ultrasonic frequencies. A theoretical treatment of this effect has been given for the hydrogen electrode by Yeager and Hovorka.[46]

Pulse techniques have been used recently to measure the alternating component for polarised hydrogen electrodes.[57] The following results were obtained.[58] With platinised platinum in dilute hydrochloric acid or sodium sulphate solutions, the potential amplitude increased linearly with the polarising current at low current densities, but at higher current densities the curves exhibited regions of almost constant amplitude. The amplitude was practically independent of the electrode metal, although with platinised platinum the alternating component was steadiest with respect to rapid time fluctuations. At a given current density the amplitude was an increasing, but not a linear, function of ultrasonic intensity. Measurements in sodium sulphate solutions of different concentrations indicated that the amplitude is roughly inversely proportional to the conductivity of the solution.

(5) Electrodeposition

Since ultrasonic waves change the polarisation of electrodes at which metals and hydrogen are liberated, they can influence the current efficiency of metal deposition, the grain growth of the depositing metal, the composition of alloy deposits, and other important factors in electroplating. In addition, the purity of the deposit can be increased. It was pointed out by Kelsen,[59] who first proposed the use of ultrasonics in electroplating, that suspended

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[54] *Z. Metallk.*, 1950, **41,** 339.

[55] Roll and Schrag, *ibid.*, 1951, **42,** 197.

[56] *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4,** 309; 1936, [2], **2,** 67; *J. Gen. Chem. U.S.S.R.*, 1936, **6,** 1393, 1401; 1940, **10,** 97.

[57] Yeager, Bugosh, Dietrick, and Hovorka, *J. Acoust. Soc. Amer.*, 1950, **22,** 686.

[58] Yeager, Personal communication.

[59] Austrian Patent 121,986 (1931); *Chem. Abs.*, 1931, **25,** 2926.

impurities in the electrolyte would not adhere to the electrode, since the relatively massive electrode will not follow the movements of the particles. He stated also that the hydrogen content of the metal could be reduced in some cases by preventing the deposition of unstable metal-hydrogen alloys.

A patent by Dutt [60] claimed that metals such as aluminum and magnesium may be electrodeposited from aqueous solutions in an ultrasonic field. However, Schmid and Ehret [50a] did not succeed in depositing aluminum or magnesium by the method described in the patent, and from the action of ultrasonics on the deposition potential of hydrogen at magnesium electrodes [44] they concluded that the electrodeposition of magnesium from aqueous solution appears unlikely. On the other hand, these workers demonstrated that metal deposition can indeed be promoted by an intense ultrasonic field. Thus a uniform nickel deposit was obtained from a nickel sulphate solution under conditions that fail to yield nickel in the absence of ultrasonics.[44]

In the electrodeposition of metals at high current densities where hydrogen is co-deposited, the agitating action of ultrasonic waves should increase the current efficiency of metal deposition just as ordinary stirring does. This effect has been demonstrated in the deposition of chromium from chromic acid solution,[61] of nickel [54, 55] and copper [51] from sulphate solution and of silver from cyanide solution.[51] The current efficiency increases continuously as the ultrasonic intensity is raised.[51,54] According to Roll,[54] the agitating action is unusually violent because the motion of the hydrogen bubbles at the electrode surface is speeded up by the acoustic field. In support of this mechanism he found that air bubbles in aqueous glycerol rise more rapidly when irradiated with ultrasonics.[51]

For metal deposition at low current densities and relatively high current efficiencies, the influence of ultrasonics on current efficiency cannot be explained by agitation. A reduction in current efficiency has been reported for zinc,[62] nickel,[54, 55] and copper [51, 62] plating from sulphate solutions, and for silver plating from nitrate solutions.[63] The decrease in current efficiency may be only an apparent one, however, resulting from colloidal dispersion of part of the electrodeposited metal. Such dispersion is likely to occur if the deposit does not adhere strongly to the substrate [64] or if it consists of fine-grained aggregates having poor cohesion,[63] particularly at acoustic intensities above cavitation levels.[65] Ultrasonic waves do not disperse solid substances of high cohesion, such as glass and ductile metals [48] and large-grained electrodeposits.[63]

The dispersion of cathodically deposited metal by ultrasonic irradiation during electrolysis is an effective method for the preparation of very finely

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[60] F.P. 749,007 (1933); *Chem. Abs*, 1933, **27**, 5657.

[61] Müller and Kuss, *Helv. Chim. Acta*, 1950, **33**, 217.

[62] Rummel and Schmitt, *Korrosion u. Metallschutz*, 1942, **19**, 101.

[63] Levi, *Ric. Sci.*, 1949, **19**, 887.

[64] Claus, *Z. tech. Physik*, 1935, **16**, 80.

[65] Roll, *Z. Metallk.*, 1951, **42**, 271.

divided metal. The method originated with Claus,[64, 66] who showed that the degree of dispersion obtained depends upon several factors. A smooth electrode surface, low cathode current density, high acoustic energy, and high frequency all favour finer particle size. The most suitable cathode materials are those to which the depositing metal adheres poorly. Practically all metals which separate out electrolytically can be dispersed.[67] This method should find use in the preparation of metal powders, sols, catalysts, etc.

In the case of electrodeposits which are not dispersed, the action of ultrasonics on grain growth is the resultant of two opposing tendencies. The violent agitation in the solution decreases the cathode polarisation and therefore promotes the growth of large grains. On the other hand, the mechanical vibrations may induce prolific nucleation in the depositing metal, as they do during the solidification of metallic melts.[68] Rummel and Schmitt [62] noted an increase in the grain size of copper deposits from an acid sulphate bath exposed to ultrasonics. On the other hand, Levi [63] found that silver crystals in deposits from irradiated silver nitrate solutions were invariably very fine. Greater hardness and tensile strength of electrodeposited copper and nickel [61] and increased hardness of chromium deposits [61, 69] have been produced by ultrasonics. This is indirect evidence for refinement of grain size in these deposits, since reduced grain size generally increases the hardness and tensile strength of electroplated metals.[70]

The influence of an acoustic field on grain growth should increase as the intensity of the field is increased. This has been demonstrated by Roll [71] with nickel plating. The current-density range for bright nickel plating from a sulphate solution was shifted to continuously increasing current densities as the intensity was raised. For example, the maximum current density for bright deposits, which was 3 milliamp./cm.^{2} in the unstirred solution and 9 milliamp./cm.^{2} with agitation, was raised to 10 and 43 milliamp./cm.^{2}, respectively, with ultrasonic intensities of 0·02 and 0·3 watt/cm.^{2}. Frequency is also an important factor. Müller and Kuss [61] reported that the acoustic effects on copper, nickel, and chromium electrodeposits diminished with an increase in frequency from 16 to 320 kilocycles/sec. They also made the interesting observation that brass deposits had higher zinc content when plated in the presence of ultrasonics.

In general, the effects described above refer to electrodes situated perpendicular to the direction of propagation of the sound. An interesting phenomenon was observed by Young and Kersten [72] when electroplating

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[66] *Z. tech. Physik*, 1935, **16**, 202.

[67] Claus and Schmidt, *Kolloid-Beih.*, 1936, **45**, 41.

[68] Schmid and Ehret, *Z. Elektrochem.*, 1937, **43**, 869 ; Schmid and Roll, *ibid.*, 1939, **45**, 769 ; Sokoloff, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 939.

[69] Ishiguro and Haramai, *J. Centr. Aeronaut. Res. Inst.*, 1944, No. 3, 201 ; *Chem. Abs.*, 1948, **42**, 1515.

[70] Blum and Hogaboom, " Principles of Electroplating and Electroforming ", 3rd edn., p. 66, McGraw-Hill Book Co., Inc., New York, 1949.

[71] *Z. Metallk.*, 1951, **42**, 238.

[72] *J. Chem. Phys.*, 1936, **4**, 426.

metals on a cathode whose surface was parallel to the acoustic beam. Rippled deposits were obtained from several plating baths. The distance between ripples was equal to half the ultrasonic wave-length. Other investigators have also observed this phenomenon.[55, 62] Young and Kersten interpreted their results as indicating that stationary waves were set up, and that the metal ions were relatively more concentrated in layers 0·5 wave-length apart. According to the Debye effect, the periodic changes in ion concentration and the potential differences arising therefrom would be minute—too small to cause gross ripples in the deposit. It is more probable that the ripples result from the depolarising action of the acoustic field, which can vary considerably from the nodal positions to the antinodes.

In the process of concentrating deuterium by preferential electrodeposition of hydrogen, it has been shown that ultrasonic vibrations increase the efficiency of separation.[73] The explanation of this effect is based upon the assumption that some of the deuterium evolved at the cathode is not discharged directly, but is liberated by reactions such as

$$H_2 + HDO \rightleftharpoons HD + H_2O,$$

which are catalysed by the electrode surface. The longer the discharged hydrogen remains in contact with the cathode, the greater the quantity of deuterium liberated. Ultrasonic agitation speedily removes the discharged hydrogen from the electrode surface and therefore diminishes deuterium evolution.

[73] Mason, Biddick, and Boyd, *J. Chem. Phys.*, 1951, **19**, 1551.