Electrolytic Methods for Measuring Water Velocities

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A convection-controlled mass transfer process in which the rate of mass transfer results in an electrical signal should have certain advantages as the working principle for a velocity- and turbulence-measuring device. The velocity can be read at a remote place as a calibrated electrical signal. Compensation for phase shift and amplitude attenuation of a fluctuating signal should be small because the measuring probe would have no capacity for the transferred quantity. In water, such processes are possible whenever electrolysis occurs under conditions of *concentration polarization*, and they exist in relatively uncomplicated form as the *limiting currents* of polarographic analysis. The investigation reported here was intended as a survey and evaluation of electrolytic methods for measuring water velocities.

The series of experiments that was performed showed that a working instrument could be designed on the principle of convection-controlled electrolysis, but that the chemical reactions involved were unreliable for consistent trouble-free results. Practical instruments appear to be possible only after long development and considerable study of chemical mechanisms.

EXAMPLE SYSTEM

A variation of an experiment in polarography (*2*, *7*) illustrates what happens when the mass transfer rate controls an electrolytic reaction and shows how the phenomenon can be used to measure velocities. The cell components shown in Figure 1 are (*a*) a platinum *indicator* electrode, (*b*) a silver and silver chloride *reference* electrode (S.S.C.E.) immersed in saturated potassium chloride and in contact with the electrolyte through an agar plug, and (*c*) an aqueous electrolyte of 0.1 M potassium chloride containing naturally dissolved oxygen as the electroactive species. The cell is attached to a polarograph instrument that can vary the potential of the indicator electrode with respect to the reference electrode. The current flow through the cell is read on a suitable recorder.

The electrolyte is now made to flow past the indicator electrode at various velocities v_0, and the curves of current vs. voltage are plotted as shown in Figure 2. The current *plateaus* are called *limiting currents*. The existence of limiting currents and the fact that different curves are plotted for different values of v_0 are evidences of a convection-controlled electrochemical reaction. Current values at constant voltage are obviously a measure of velocity at nearly every voltage setting at which finite currents are realized. Voltage values at constant current are also a measure of velocity when the constant current is not a limiting current.

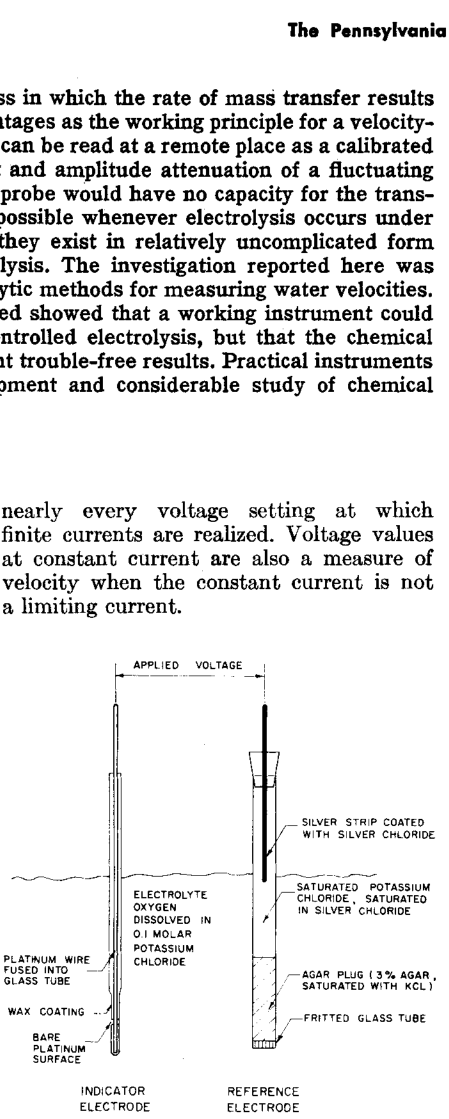

Fig. 1. Electrolysis cell which can be used for velocity measurements.

The random current fluctuations shown in Figure 2 probably resulted from turbulence in the test medium. The electrolyte was contained in a plastic basin, which was rotated at various speeds (*5*). The cylindrical electrode was immersed near the outer circumference with its axis perpendicular to the flow. The probe traveled in its own wake and detected the turbulence of this wake, the eccentricity of the rotating system, and the stirring action of the reference electrode, which was also immersed in the electrolyte. Figure 2 is a direct copy of the chart record taken on a Leeds and Northrup Electro-chemograph, type *E*, which applied a voltage change at a constant rate. The voltage scale is also a time scale, and the recorder gave a time record within the limits of its response rate.

EFFECT OF MASS TRANSFER ON THE OVER-ALL RATE OF ELECTROLYSIS

A brief discussion of electrochemical reactions and associated rate phenomena is necessary to explain Figure 2.

As the potential of the probe was brought into a range where dissolved oxygen was reduced to hydrogen peroxide (and possibly to water), the current increased exponentially with increasing negative potential. (There may be evidence in Figure 2 that the reaction occurred in two steps, the second reaction beginning at a slightly different potential.) When the reaction rate was sufficiently high to reduce the concentration of oxygen next to the surface to a value negligibly small compared with the ambient concentration, the curve exhibited constant current over a range of potentials between −0.65 and −0.85 volt.

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*Supplementary material has been deposited as document 5714 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

TABLE 1. EXPERIMENTAL CONDITIONS FOR THE CURVES SHOWN IN FIGURE 3

	Electroactive Species		Electrolyte		Probe						
Curve (Fig. 3)	Type	Concentration	Type	Temperature, °C.	Type	Diameter, mm.	Length, mm.	Base, mm.	Height, mm.	Applied voltage vs. S.S.C.E.	Cell resistance, ohms
1	$Fe(CN)_6^{-3}$	$1.994 \times 10^{-3}M$	$1.0M$ KCl	25	Cyl.	4.432	4.736			0.00	< 500
2	O_2 (dissolved)	Saturated by air at 732 mm. Hg	$0.1M$ KCl	25	Cyl.	0.449	5.310			−0.75	< 500
3	O_2 (dissolved)	Saturated by air at 737 mm. Hg	Sea water	25	Cyl.	0.449	5.310			−0.95	—
4	$Fe(CN)_6^{-3}$	$2.057 \times 10^{-3}M$	$1.0M$ KCl	25	Pencil			1.19	2.04	0.00	< 300
5	O_2 (dissolved)	Saturated by air at 737 mm. Hg	$0.1M$ KCl	25	Pencil			1.21	1.41	−0.75	400
6	$Fe(CN)_6^{-3}$	$2.003 \times 10^{-3}M$	$1.0M$ KCl	25	Pencil			1.19	2.04	−2.00	12,000*
7	O_2 (dissolved)	Saturated by air at 736 mm. Hg	$0.1M$ KCl	25	Pencil			1.21	1.41	−0.95	< 800
8	O_2 (dissolved)	Saturated by air at 734 mm. Hg	$0.5M$ Na_3PO_4	33–34	Pencil (mercury plated)			1.19	2.04	−0.81	1,000

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*Total resistance in cell circuit containing an oscillograph in parallel with the resistance.

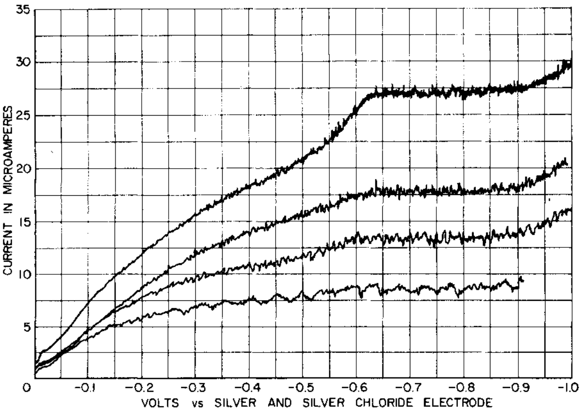

Fig. 2. Effect of applied voltage on electrolytic currents at four flow velocities.

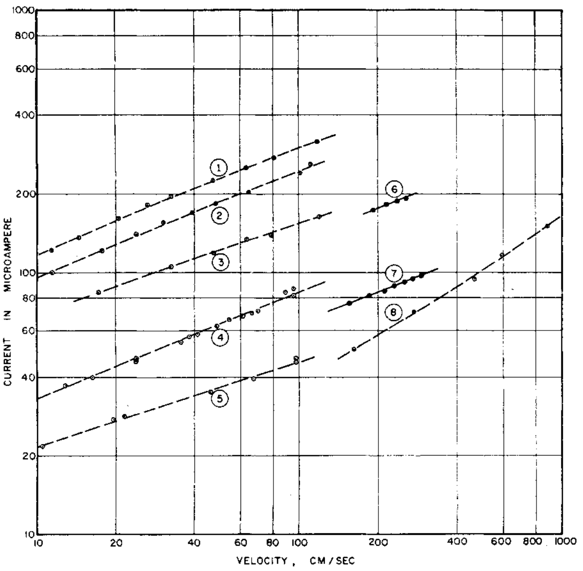

Fig. 3. Limiting current vs. velocity for a variety of experimental conditions.

In the region of constant current, where the reaction rate did not depend on the reaction constant but on the rate at which dissolved oxygen could be brought to the surface by convection and diffusion, the current was not affected by changes in the applied voltage. Finally, when a potential was reached at which hydrogen was evolved, the current again rose exponentially with increasing negative potential.

The over-all rate of electrolysis, as measured by the electric current, depends on three interrelated processes which occur in series (*5*, *10*): (1) mass transfer of reactants to the electrode surface, (2) electrochemical reaction, and (3) mass transfer of reaction products from the electrode surface. Diffusional rate equations can be written for processes 1 and 3. A chemical rate equation can be written for process 2. An over-all rate equation, of the form of Figure 2, results when the unknown surface concentrations of reactants and products are eliminated from the three equations (*5*, *10*).

When only the oxidized form of the electroactive species is contained in the main flow and when limiting current conditions are reached, the rate equation reduces to a form which involves only mass transfer by convection and diffusion

$$I_l L/nFA_i C_{Ox0} D_{Ox} = N_{Sh}(Lv_0/\nu, \nu/D_{Ox}) \qquad (1)$$

POSSIBLE ELECTROLYTIC REACTIONS FOR MEASURING WATER VELOCITIES

Because dissolved oxygen is contained in nearly all natural water, much of the attention of this survey was devoted to the use of the oxygen reaction. In principle, an electrolytic probe operating with oxygen currents can be used in fresh waters if sufficient potential is applied to overcome the high electrical resistance of the cell. Boyer and Lonsdale's device (*1*) for measuring low water velocities appears to have worked on such a principle. Here the negative potentials of the probe were relatively small and the currents were not limiting currents.

Sea water contains a ready-made "indifferent" electrolyte; therefore, the oxygen current can be observed directly with applied potentials in the same range as those of laboratory experiments.

In test facilities a noncorrosive electrolyte, such as sodium phosphate, might be added to the water to decrease the cell resistance and to create chemical con-

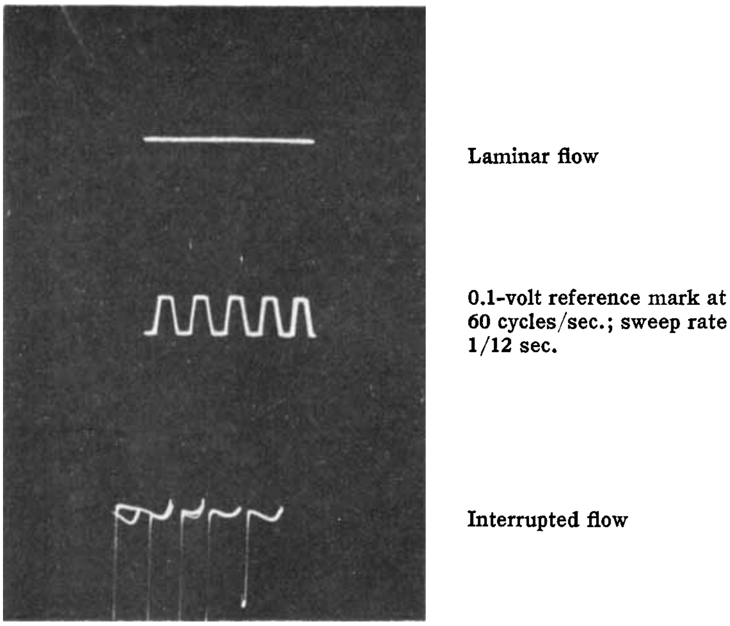

Fig. 4. Oscillograph record of the response of an electrolytic probe; average limiting current = 170 μa., resistance across oscillograph = 12,000 ohms.

ditions that stabilize the oxygen current readings.

Only a few other substances, notably the ferricyanide ion, can be used as the electroactive species in the presence of dissolved oxygen. Suitable ions for such conditions give limiting currents at potentials that are less negative than those for the oxygen reaction. Such ions may be desirable in test waters because the chemical reaction can be simpler and the applied potentials are less likely to evolve hydrogen.

When the test water is deoxygenated, a very large number of electrolytic reactions (*7*) can, in principle, be applied to give electric currents that are a measure of water velocity.

EXPERIMENTAL APPARATUS

Three types of flow systems were used to obtain the experimental data for the curves shown in Figure 3. The experimental conditions for these data are listed in Table 1.

In system 1, described in reference (*5*), the indicator electrode was immersed in a rotating basin of electrolyte.

In system 2, probes were mounted in the free-liquid jet issuing from a 0.50-cm. nozzle at the bottom of a 10-cm.-diameter glass tube. A flow free from turbulence was obtained by allowing the liquid to drain from a height of about 60 cm.

In system 3, probes were mounted in a free-liquid jet issuing from a 3-in.-diameter, sharp-edged orifice. To obtain data at high velocities a 300-gallon circulating system was constructed. The liquid jet was deflected by a cone into a 3-ft.-diameter by 5-ft.-deep tank and returned overhead through a 450-gal./min. pump into an 8-ft.-long, 18-in.-diameter standpipe containing two bundles of flow-straightening tubes. The orifice was located at the bottom of this standpipe. Both the probe and the reference electrode were mounted in the free jet.

In principle many types of probes and electrodes can be used for velocity measurements. In the experiments reported here platinum was used as the indicator electrode material, and the S.S.C.E. (silver and silver chloride reference electrode) shown in Figure 1 was used as the anode. Short platinum wires were fused into the ends of narrow glass tubes to form cylindrical probes, the ends of which were ground to form a "pencil point" of platinum on the end of a glass cone. In the case of the 300-gal. system a special mount to hold the indicator probe and a deceleration tube to protect the reference electrode were constructed.

EXPERIMENTAL RESULTS

Figure 3 shows typical plots of measured current vs. velocity for a variety of experimental conditions in which the applied voltage appeared to be in a range of limiting currents. In every case the current is a function of the velocity and does not appear to have a well-defined form, being about the ½ power of the velocity.

The probes were extremely sensitive to low velocities and could measure flows of 1 cm./sec. to two significant figures. Although no velocities greater than 9 meters/sec. were measured, there seemed to be no upper limit to the velocity which could be measured.

The shorter the period of time in which the data were obtained, the more consistently the points fell on a single curve; for example, the data for curves 6 and 7 were taken within 2 min. and show no scatter. Data taken over periods of hours show scatter, and, if the data were rerun after a period of days, another curve would be obtained that would be displaced from the original curve.

Curve 3 was obtained with a sample of sea water. Since curves 2 and 3 were taken with the same probe under nearly equivalent chemical conditions, they should be nearly alike. The large difference in current between these two curves could have been caused by the gradual masking of active surface area by contaminating materials in the sea water. Indeed, the limiting currents in this case showed a gradual decrease with time.

Flow system 2 was constructed to show the stability of the current and to indicate the time response of the probe. A 12,000-ohm resistor was placed in series with the cell and in parallel with an oscillograph. A glass stirring rod with six short spokes or knobs on its end was rotated at 600 rev./min. so that the knobs would pass through the edge of the jeb and interrupt or disturb the flow. Figure 4 shows the results of this experiment. The undisturbed flow had a turbulence intensity of less than 0.5%, and the probe easily responded to a 60 cycles/sec. disturbance. The data showed fine scale variations in the disturbance to frequencies at least ten times that of the major frequency. No attempt was made to determine the phase lag or attenuation of the fluctuating signal.

CHEMICAL ASPECTS

The time sensitivity of the calibration of an electrolytic probe appears to depend upon the fraction of the geometric surface area that is actively engaged in the chemical reaction and the nature of the chemical reaction itself (as characterized by changes in the values of the standard-reaction potential and rate constant). Surface reactions such as these are notably fickle and have a memory for their previous history and chemical experiences. Moreover, there is always the possibility that additional reactions will appear and confuse the situation.

Figure 5 represents a convenient basis for discussing the chemical aspects of an electrolytic-velocity meter.

Figure 5*a* shows the current-voltage curve when a ferricyanide ion is the electroactive species. The curve is cleanly drawn, has a well-defined limiting current, and is in accord with theory. The limiting current at 0.0 volt was found to be proportional to ion concentration over a wide range (the chemical test for a true limiting current), but the velocity dependence of the limiting current (curve 4, Figure 3) did not follow exactly the ½-power relationship expected from theory (*4*) and from experimental correlations.

Figure 5*b* shows the current-voltage curve for oxygen of the air dissolved in 0.1M potassium chloride. The oxygen reaction

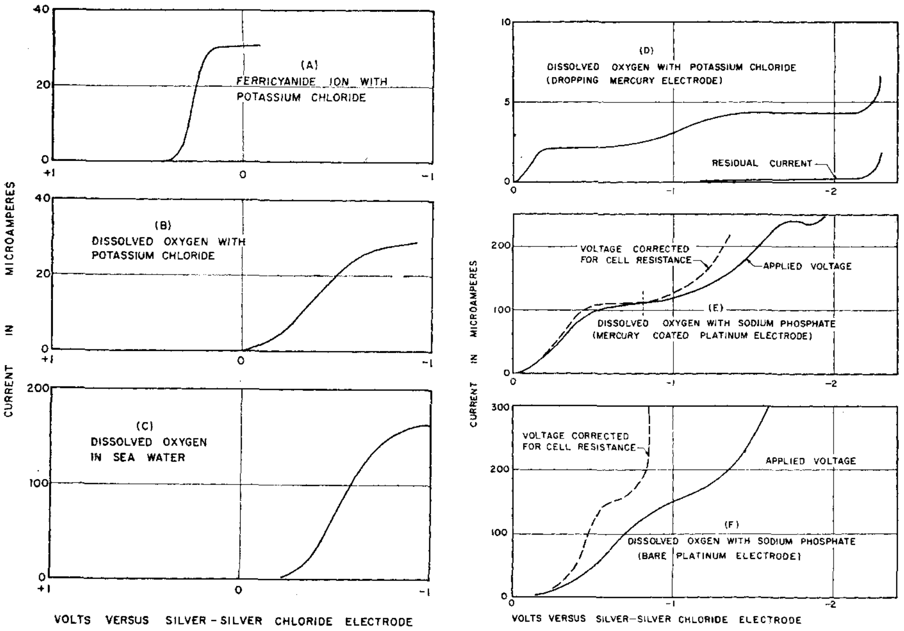

Fig. 5. Current-voltage curves.

occurs at a higher negative potential than does the ferricyanide reaction and would have appeared as an added step on Figure 5*a* had more negative voltages been explored. Figure 5*b* was taken with a newly made probe. After several days of use the limiting-current plateau would disappear and could be restored only by such drastic chemical treatment as soaking the probe in nitric acid and evolving hydrogen from its surface.

Figure 5*c* shows a similar curve for oxygen dissolved in a sample of sea water. Unaccountably the voltage at which the wave appears has become more negative, indicating a change in the nature of the reaction. The limiting currents, which were much less than would be expected from a completely active surface, gradually decreased with time.

Figure 5*d* shows the chemical features of the oxygen reactions in terms of the current-voltage curve of a dropping mercury electrode where the electrode surface is always a newly created liquid surface. The curve shown is an average of the saw-tooth curve drawn by the recorder. Two reactions are involved. The first reaction has been interpreted (*7*) as a two-electron reaction in which dissolved-oxygen molecules are converted to hydrogen peroxide; the second reaction has been interpreted as a four-electron reduction of oxygen molecules to two molecules of water. It should be noted that the second limiting current is nearly twice the first limiting current and that the current rises again only at a relatively high negative potential (−2.2 volts vs. the S.S.C.E.). The final current rise is due to the reduction of potassium ion to form potassium amalgam.

Figure 5*d* shows the so-called "residual current." When the electrolyte is deoxygenated, a small current of a few tenths of a microampere may appear at voltages where hydrogen evolution does not occur. These currents are attributed, in part, to capacity and double-layer effects, and they should be subtracted from an apparent limiting current to obtain a true limit current.

Figure 5*e* shows the current-voltage curves for oxygen of the air dissolved in sodium-phosphate electrolyte taken with a mercury-coated, platinum electrode. It appears that a two-electron oxygen reaction occurred but at a larger negative potential than in the case of Figure 5*d*. Higher in the curve there is a discontinuity at a voltage where a four-electron reaction should be expected. When an attempt was made to repeat the data of Figure 5*e*, which was taken with a newly plated probe, current values were found to be much less, the dip disappeared, and hydrogen was evolved at less negative potentials. To establish current-velocity curve 8 of Figure 3, the applied voltage on the platinum probe, newly electroplated with mercury, was always kept less negative than −0.9 volt.

Figure 5*e* also indicates the effect of cell resistance at relatively high-current levels. The current-voltage curve is stretched out along the abscissa, and the region of limiting currents is less apparent.

Figure 5*f* shows the current-voltage curve for the newly ground and polished probe of Figure 5*e* before it was mercury coated. Apparently a convection-controlled oxygen reaction occurred, but the limiting current was poorly defined. Comparisons with the limiting currents of curve 8 of Figure 3 and consideration of relative velocities indicated that the reaction required four electrons for each oxygen molecule* and occurred at a surprisingly low negative potential. Although the resistance of the cell (2,500 ohms) was not known accurately enough to plot the exact electrode potentials, the onset of the hydrogen reaction has moved to less negative potentials, overcoming much of the effect of the oxygen reaction.

Evolution of hydrogen by electrolytic decomposition of water is a major difficulty to be resolved in the application of electrolysis to velocity measurement. Ordinary dirt and contaminants appear to promote hydrogen evolution, and the reaction itself is unpredictable. Since the oxygen reaction concerns recent studies of cathodic corrosion protection, and since the hydrogen reaction continues to receive much attention from electrochemists interested in hydrogen overvoltage, there is some hope for eventual understanding and control of both reactions.

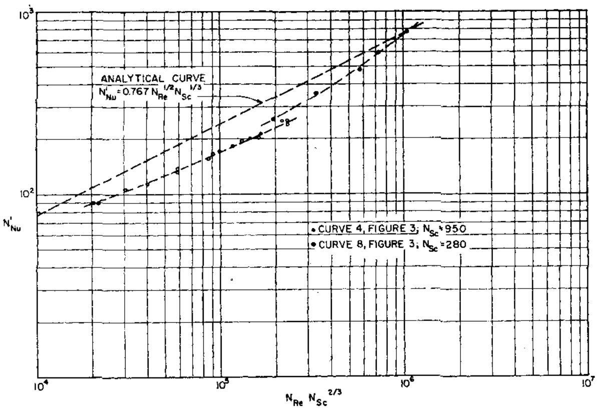

Fig. 6. Mass transfer to conical probe. Comparison with theory.

MASS TRANSFER RATES: COMPARISON WITH THEORY

Limiting current can be predicted by transfer correlations. In many recent research investigations (such as those in references *3* and *8*) the limiting current has been used to measure mass transfer rates and to establish correlations, one type of which is given in functional form by Equation (1). The chief difficulties associated with establishing or using a generalized correlation lie in the paucity of data on diffusivities and in the marked effect of small temperature variations on viscosity and diffusivity.†

Figure 6 is a generalized plot of curves

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*A possible explanation of this unusual result is that the dissolved oxygen first undergoes a two-electron electrolytic reaction forming hydrogen peroxide. The hydrogen peroxide then undergoes a further reaction forming water and oxygen. Since one out of every two oxygen molecules reappears in the second reaction, the over-all result is a four-electron transfer.

†Diffusivity and oxygen-solubility values used for correlation were taken from references *6* and *7*.

4 and 8 of Figure 3. Here the characteristic dimension of the electrode surface is taken to be the slant height of the platinum cone. The theoretical solution for a laminar boundary layer (*4*) is superimposed. While theory predicts the proper order of magnitude of the limiting current under most conditions, the agreement is not very good. Similar correlations of the other curves shown in Figure 3 are in as much agreement with theory and independent correlation as Figure 6. Reasons for disagreement are numerous and beyond the scope of the limited experimental results obtained. As a ½-power relationship between current and velocity would have permitted the circuitry of hot-wire anemometers to be directly applicable to the analysis of fluctuating currents, it was particularly disappointing that this simple relationship did not exist.

EVALUATION

Beyond purely chemical limitations, which require further study, there are other factors to be considered in evaluating the practical potentialities of electrolytic flow meters.

In water the active area of a useful probe will have to be about 10^{-2} to 10^{-3} sq. cm. to prevent dirt particles from making serious changes in calibration. An increase in size is also dictated by a need for mechanical strength sufficient to withstand the hydrodynamic forces. Turbulence-scale measurements would, of course, be limited to the size of the probe, and frequency measurements would be limited to a value equal to the flow velocity divided by the size of the probe.

It is natural to compare the response of an electrolytic probe to the response of a hot-wire probe which has been successfully adapted to measurements in water by Ling and Hubbard (*9*). They developed a wedge-shaped probe of glass thinly coated with a platinum resistance element. The active area is sufficiently large (1 mm. wide with a slant height of 0.2 mm. on each side) to satisfy the requirement for an area of such size that calibration would not be destroyed by a few dirt particles. The platinum coating is thin enough (a few angstrom units) to give rapid response to fluctuating velocities, and the temperature of the film is always well below the boiling point of the water. The construction is sturdy enough to withstand hydrodynamic forces at velocities as high as 80 ft./sec., and resistance of the probe is about 5 ohms.

The hot-film probe can also be used as an electrolytic probe. As designed, it works on a heat transfer principle. As an electrolytic probe it would work on a mass transfer principle. A comparison of performance can be predicted by considering the Nusselt number and the mass-transfer number N_{Sh} for a thin wedge at various values of the Reynolds, Prandtl, and Schmidt numbers. Such a comparison under normal operating conditions leads to several conclusions.

The hot-film anemometer gives mean currents measured in milliamperes; the electrolytic instrument with an oxygen current gives mean currents of only tens and hundreds of microamperes.

Because electrical dissipation into heat is proportional to I^2 and because the rate of electrolysis is proportional to I, the the hot-film anemometer gives a mean current that is proportional to the ¼ power of the velocity, and the electrolytic instrument gives a mean current that is approximately proportional to the ½ power of the velocity.

Fluctuations in velocity give $dI/I = (\frac{1}{4})\ dv_0/v_0$ in the case of the hot-film anemometer, and $dI/I = (\frac{1}{2})\ dv_0/v_0$ in the case of the electrolytic instrument.

A rough comparison of the ability to respond to fluctuations in convection conditions can be obtained by comparing the product of the thermal diffusivity of the fluid and the ⅔ power of the Prandtl number with the product of the diffusivity of the electroactive species and the ⅔ power of the Schmidt number. A larger value indicates a better response rate. The value for the hot-film anemometer is about 5×10^{-3} sq. cm./sec.; the value for the comparable electrolytic instrument using the oxygen reaction is about 1.5×10^{-3} sq. cm./sec. The hot-film anemometer also has a response lag because of the thermal capacity of the film and the glass wedge; the electrolytic instrument is not subject to a similar kind of response lag because it has no capacity for the transferred component.

It is not possible to make a complete comparison between the response rates of the two probes. It is probable, however, that the response rates are comparable for the smallest size of probe and that the response rate of the electrolytic probe becomes relatively much better as the bulk of the probe is increased.

On the basis of survey experiments, it appears that applications of electrolysis to the problem of measuring water velocities can be made, but practical success will require a development comparable to that which was needed for the hot-wire anemometer. Because of the many chemical unknowns, further chemical studies would be required for a full evaluation of the electrolytic method and for its successful development into a practical velocity meter.

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NOTATION

A_i = interfacial area of electrode
C_{Ox_0} = main-stream concentration of oxidized form of electroactive species
ΔC = concentration difference of electroactive species across the transfer path
D = diffusivity
D_{Ox} = diffusivity of oxidized form of electroactive species
F = Faraday's constant = 96,500 amp. sec./g. equivalent
I_1 = limiting current
L = characteristic dimension of electrode surface
n = number of electrons involved in reduction of each molecule or ion of electroactive species
N_{Sh} = Sherwood number, mass transfer number analogous to Nusselt number for heat transfer: $N_{Sh} = r_{ai}L/\Delta CD = N_{Sh}(N_{Re}, N_{Sc})$
N_{Re} = Reynolds number; $N_{Re} \equiv Lv_0/\nu$
N_{Sc} = Schmidt number; $N_{Sc} \equiv \nu/D$
r_{ai} = average rate of mass transfer (or rate of reaction) of electroactive species/unit area of electrode interface
v_0 = flow velocity
ν = kinematic viscosity

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