DYNAMICS OF THE DOUBLE LAYER AT THE POLARIZABLE MERCURY-ELECTROLYTE INTERFACE

by

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I. INTRODUCTION

The investigations of electrical phenomena associated with interfaces date back to the early experiments in the nineteen hundreds on streaming potentials and electrocapillarity. Due to the complexity of the electrical double layers at the interfaces, there still seems to be some confusion regarding the exact mechanisms involved in producing the observed voltage and current.

Background

During the study of surface electrical phenomena Ueda et al. at Kyoto University in Japan discovered a phenomena which they called the U-effect. This study was first reported in Japanese journals[1] and was later reported in an English journal[2] in 1957.

In these papers the U-effect has been classified as two separate effects: U-effect I and U-effect II. The former was produced by the periodic relative movement of an electrolyte in a glass capillary with respect to the capillary walls through which electrodes were inserted. A fine glass rod fixed to a stationary external support was also inserted into one end of the capillary to impede the liquid from following the motion of the oscillating capillary wall, particularly at lower frequencies. The mechanical disturbance of the electrical double layer formed between glass and electrolyte produced an alternating voltage of the same waveform and frequency as that of the original vibration. This effect was studied with dilute salt solutions (10^{-3} to 10^{-6} N), at frequencies from 60 c/s. to 13.5 kc/s. and the observed

a.c. potentials ranged from 10^{-4} to 10^{-3} volt. The U-effect II was produced by a fast periodic vibration of a glass capillary in which alternate drops of mercury and electrolyte (1N HCl), forming about forty interfaces, had been sealed with electrodes in the end drops of mercury. The voltage was suggested to be caused by the distortion of the double layer between the mercury electrolyte interface when the capillary was accelerated. The double layer was considered to be similar to a condenser with the distortion of the interface changing its area, while the charge remained constant. This resulted in a voltage at the ends which added in series from the many interfaces. This effect was studied at frequencies from .5 to 15 kc/sec. with amplitudes of the order of 10^{-3} mm. The output voltage ranged from 10 to 70 mV. and was found to be proportional to the amplitude of vibration at constant frequencies and proportional to the square of the frequency at constant amplitude. The output voltage was also found to be a linear function of the number of interfaces.

In 1954, Elliot et al.[3] reported a practical application of U-effect II in ballistocardiography. They constructed capillary tubes containing fifty to eighty interfaces between 1N sulfuric acid and mercury and reported that the output voltage was proportional to the acceleration, being linear from 0 to .015g. No data has been given of this study. The output voltage for a given acceleration was found to be constant for a period of eight months and increased with a decrease in the capillary diameter.

A further experimental and theoretical investigation of the U-effect II was carried out by Fain et al.[4] One-and-two-interface sealed capillary tubes of .07 cm. internal diameter and approximately one inch long were used in the investigation. An air gap was intentionally introduced at one end of the tubes. The output voltage was found to be linearly dependent on the amplitude of the tube motion, with the upper limit for the linear region being dependent upon the frequency. They reported that the output voltage versus the frequency curve passed through the origin and had a definite peak at some frequency (between 400 to 800 c/s.), which they called the resonance frequency. Above this resonance frequency the output dropped rapidly to a fairly stable value. The resonance frequency was reported to vary from tube to tube with the variation attributed to the changes in the physical structure (length of the mercury drop and the volume of air introduced) of the tubes. No quantitative study was done for the individual dependence of the output voltage on either of these variables. The dependence of the internal output impedence of the tube upon the frequency of vibration was studied. It was found to decrease exponentially with the increase in frequency. The theoretical treatment of the U-effect II by Fain et al.[4] was based upon the area changes of a capacitor whose charge remained fixed, as was the theoretical treatment by Ueda et al.[2].

A new effect called U-effect III was reported by Podolsky et al.[5] and it was thought to be caused by the relative motion between the drops and the capillary wall. The effect was explained as follows:

"The flow pattern causes an effective expansion of the forward interface and an effective contraction of the rear interface. As a result, a double layer distribution of charge which is uniform when there is no relative motion between the drop and the capillary becomes non-uniform when the drop moves. At the forward end the effective expansion leads to a reduction of the dipole moment density over the interface, at the rear interface the effective contraction causes an increase of the dipole moment density there. The field of the non-uniform dipole moment distribution leads to an observable output voltage." This effect was studied in capillaries ranging from 5 to 50 cm. in length and up to 1.5 mm. in diameter. Various lengths of mercury drops ranging from two to ten in number were used to form the interfaces with 1N sulfuric acid. The output voltage was found to be linearly dependent upon the amplitude of the relative drop motion. The output voltage for constant amplitude of the tube was proportional to the square of the frequency, in the range of 0 to 500 cps. The short circuit current was measured to be independent of the proportions of the constituent drops and thus independent of the amount of mercury in the tube. By considering the electrical equivalent circuit for the tube, they constructed a theory which gave output voltages that were independent of the number of interfaces. Figazewski et al.[6] gave an improved version of this electrical equivalent circuit. They presented a two-terminal form of the electrical equivalent circuit which reflected the electrical and mechanical properties of these electrocapillary transducers.

Statement of the Problem

When a mercury drop is in contact with the electrolyte inside a capillary tube, there exists a double layer* having equilibrium dipole moment density over each end of the mercury drop. When the capillary is shaken, the mercury drop is distorted; and as a result, each end now has a different dipole moment density. This results in an emf across the probes at the two ends of the capillary tube.

According to Ueda et al.[2] and Fain et al.[4] the output voltage is due to the changes in the area of the mercury electrolyte interfaces. On the other hand Podolsky et al.[5] claim that the differences in the charge density at the ends of the mercury slugs, provoked by the movement with respect to the capillary surface, play a decisive role especially at low frequencies. They described two processes for the double layer to return to equilibrium after a disturbance:

1. mercurous ions are transferred across the interface at some rate K.
2. dipoles diffuse over the drop from one face to the other with some characteristic diffusion rate λ.

It has been found[4,5] that the longer the mercury drop the greater the output voltage, for short enough drops. This would tend to indicate that the dipole diffusion over the drop is of some importance. If this rate of diffusion is approximately the same order of magnitude as the transfer rate of mercurous ions across the interface, then making

*An explanation of the formation of the double layer is given in Appendix A.

the drop longer would increase the effective number of excess dipoles at one end relative to the other, thus producing a greater output voltage. This suggested that an experimental study was required to see the relative importance of the mechanisms described above. Also, according to Podolsky et al.[5], the output voltage depends on the amount of mercury but is independent of the number of the interfaces, and this is in direct contradiction with the findings of Ueda et al.[2] and Fain et al.[4] They[5] also claimed that the U-effect III gave rise to a potential of opposite polarity to the U-effect II. The investigation reported herein was carried out in an attempt to resolve all the above mentioned controversies.

II. EXPERIMENTAL TECHNIQUES

An apparatus was designed to give the mercury electrolyte interfaces a finite displacement inside the capillary tube, instead of oscillating them as was done in the past. The investigation was carried out on single mercury drops of varying lengths, at room temperature.

Preparation of Tubes

The pyrex glass capillary tubes, henceforth called tubes, were of precision bore and had their internal diameters varying from .5 to 1.5 mm. At both ends of the tube, pyrex glass cups of .7 cm. internal diameter were attached which gave the tube a shape of a dumb-bell with open ends as shown in Fig. 1. The tubes were cleaned by drawing boiling nitric acid through them, then rinsed with equilibrium water[7] and dried in vacuum. The electrolyte used was 1N perchloric acid, since it was found to give a higher output voltage than sulfuric acid of the same concentration. Perchloric acid (from Fisher Scientific Co.) was diluted with equilibrium water in order to avoid contamination with organic and other impurities. Triple distilled mercury (from Bethlehem Apparatus Co.) was used throughout the experiment. The tubes were filled with a single mercury drop and electrolyte on either side. Teflon pistons were put into the glass cups to make the whole system rigid. Care was taken to prevent any air from entering the tube. Platinum electrodes (gauge 22), across which the voltage was obtained, were sealed in the tube as shown in Fig. 1.

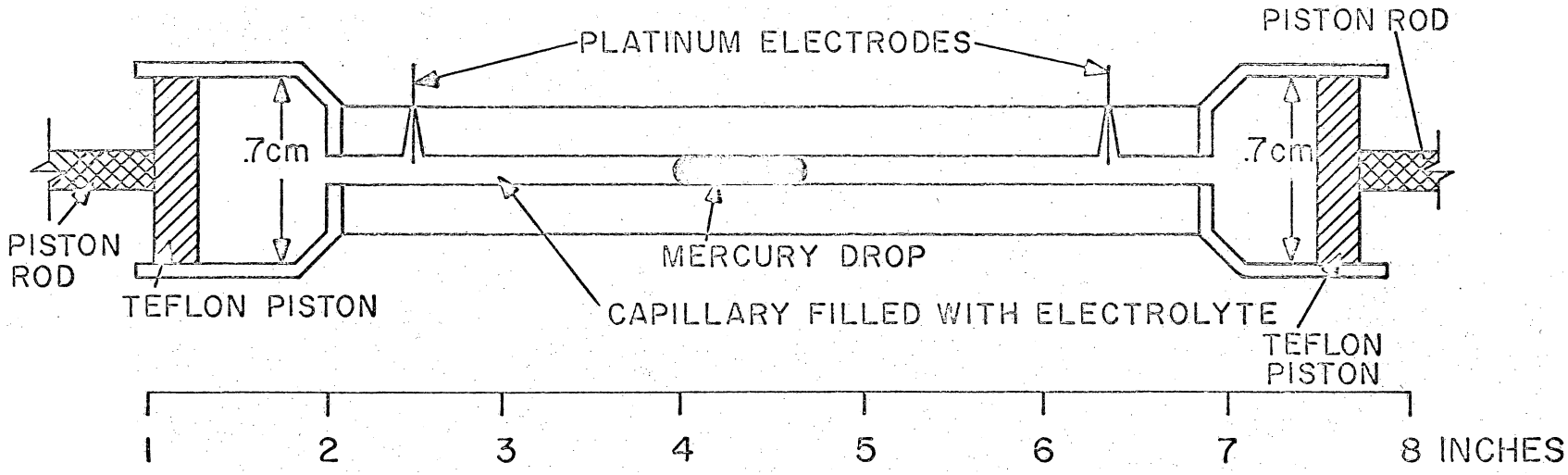

Fig. 1. Glass capillary tube in the shape of a dumb-bell.

Apparatus

Fig. 2 shows the design of the apparatus used for accelerating the drops. The tube was fastened to the bottom by clamps A and the piston rods were attached to the carriage C. This carriage was driven against an air pressure of about 70 lbs/sq.in. by the rotation of a screw. The screw in turn was rotated by dropping a hammer with a mass attached to it from different heights on to a sponge. This caused the piston to move in such a way that when one piston moved to the right, the other piston moved to the right also, so that the mercury electrolyte system moved as a rigid body. By dropping the hammer from different heights and with different mass attached to it, the drop could be accelerated to achieve different maximum velocities*. This displacement of the mercury drop was read by the use of a travelling microscope. The air pressure served to cushion the mercury electrolyte system when it came to an abrupt stop and thus prevented the mercury drop from breaking up. When the mercury drop moved relative to the tube an output voltage was obtained across two platinum leads, and was displayed on an oscilloscope (Tektronics Model 7490). This suggested that a constant voltage might be obtained as long as the drop moved relative to the tube. In order to obtain this, an experiment was devised in which the mercury electrolyte interfaces were made to flow at constant velocity. Teflon spaghetti tubes, hereafter called tubes, with internal diameters varying from .5 to 1.7 mm. and about 2 meters

*The mechanics of the apparatus and the methods for measuring the acceleration and velocity are described in Appendix B.

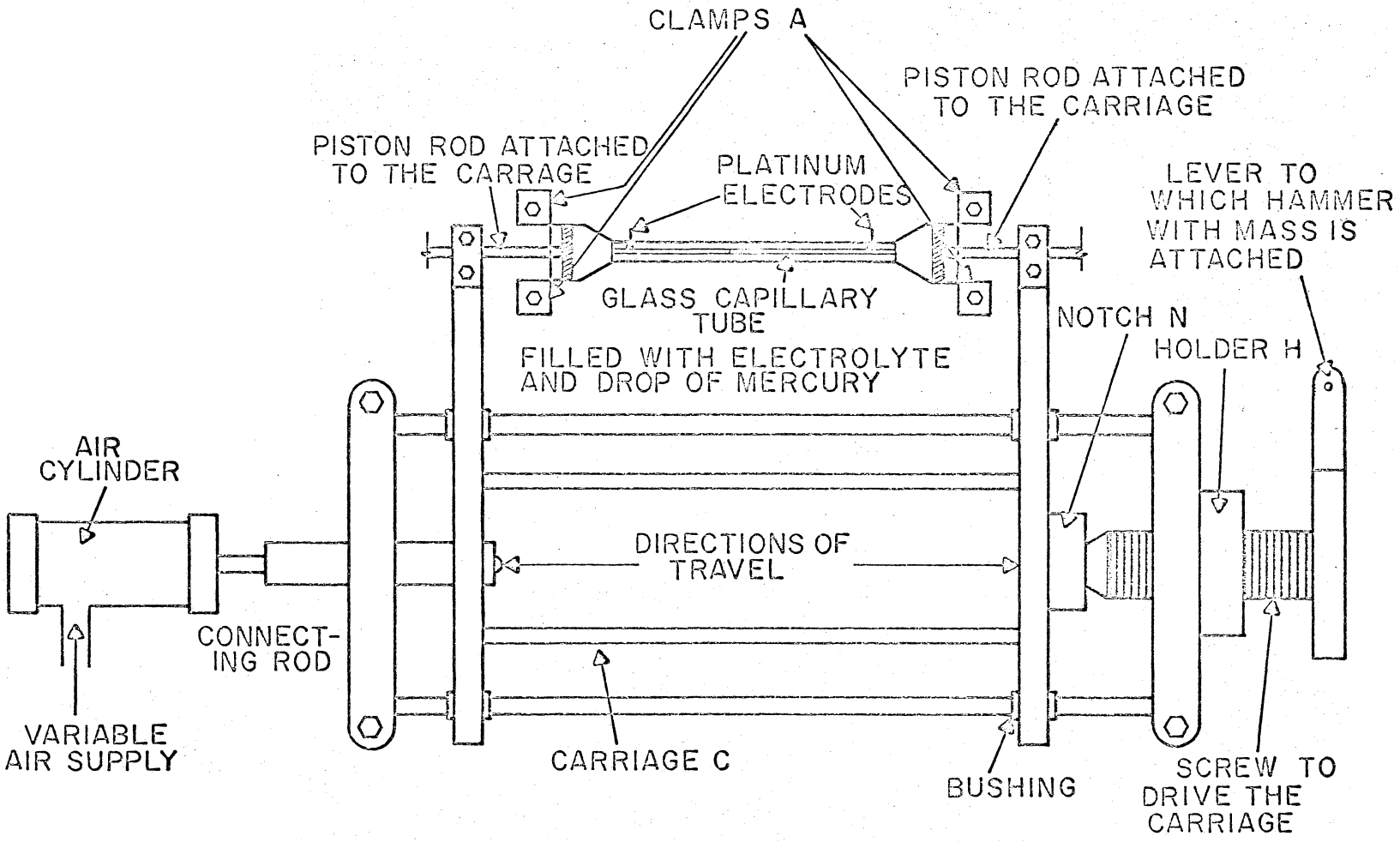

Fig. 2. Top view of the apparatus for giving the mercury drop a constant acceleration.

long were wound around a cardboard drum as shown in Fig. 3. The glass cup at the top and the tube were filled with electrolyte (1N $HClO_4$) and a single drop of mercury was injected from the side at point P, by means of a syringe. The stop cock was opened, allowing the liquid to be discharged at a constant rate. Output voltages were obtained across the platinum leads sealed to the tubes and were recorded on a strip chart recorder (Esterline Angus Model L11025). By varying the rate of discharge and the length of the mercury drop, different output voltages were obtained as long as the mercury drop moved between the platinum electrodes. The length of the mercury drop and the velocity with which it moved was measured by attaching electronic timers to the tube. Current measurements were made by directly connecting the platinum electrodes to a microammeter (Hallmark Standard Inc. Model HDC43). The internal impedence of the tube was very high (order of $10^4\Omega$) as compared to the impedence of the microammeter (order of 10Ω) and hence these currents are short circuit currents.

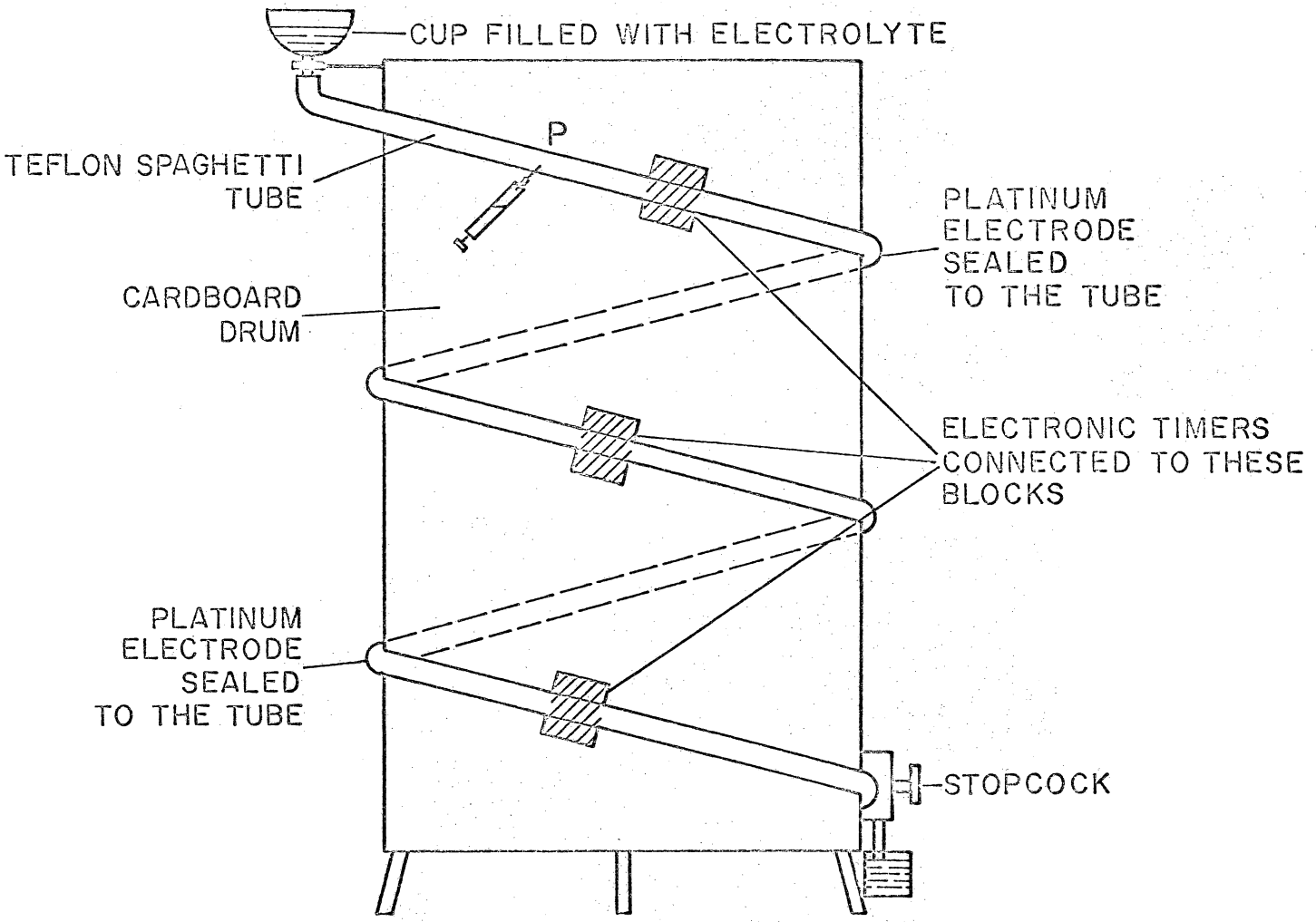

Fig. 3. Apparatus for moving the mercury drop with constant velocity.

III. EXPERIMENTAL RESULTS

Constant Acceleration Measurements

It was observed that as long as the mercury drop in the tube moved relative to the tube, an output voltage was observed. The output voltage increased as the drop was accelerated up to a certain maximum velocity and then decayed exponentially when the drop came to an abrupt stop. This output voltage was photographed as displayed on the scope and a typical trace is shown in Fig. 4.

The decay constant τ was obtained by fitting the decay part of this curve to the equation

$$V = V_o e^{-t/\tau}$$

where V is the output voltage at some time t and V_o is the maximum output voltage for t=0. The polarity of the output voltage was positive in the direction of motion of the drop.

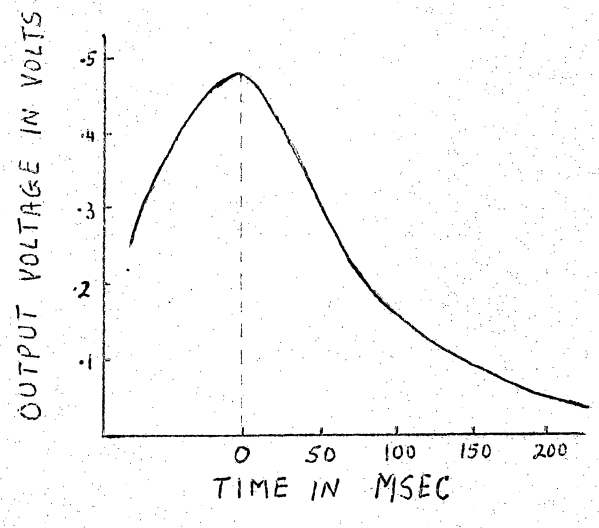

Fig. 4. Trace of the output voltage when a constantly accelerated drop is brought to a sudden stop.

In Figs. 5a to 5c, the maximum output voltage as read on the photograph is plotted against the maximum velocity to which the drop was accelerated; for different diameter tubes. The plot shows that the output voltage increases with the velocity and saturates at high velocities. The output voltage was also found generally to increase with the length of the drop. (For a 2 cm drop the output voltage was found to decrease in all the tubes.) For the same drop the output voltage decreased with the increase in the tube diameter.

In Figs. 6a to 6c, the decay constant is plotted against the maximum velocity, for different diameter tubes. The plots show that the decay constant initially decreases as the drop velocity increases up to a certain value (depending on the drop length), and then increases with further increase in velocity. In the 1.5 mm. diameter tube, for drops longer than 1 cm., the decay constant was found only to increase with the velocity. In all the above curves, the acceleration of the drop was not the same for each drop length but varied within about 23%.

Figs. 7a and 7b show plots of the maximum output voltage against the maximum velocity of the drop for fixed accelerations (within 4%). These plots show that the output voltage increases with the velocity but decreases with increasing acceleration, suggesting that the velocity and the acceleration could be producing opposite effects.

Fig. 8 is a plot of the decay constant versus the velocity of the drop for fixed accelerations (within 4%). It shows that the dependence of the decay constant on the velocity is also opposite to that

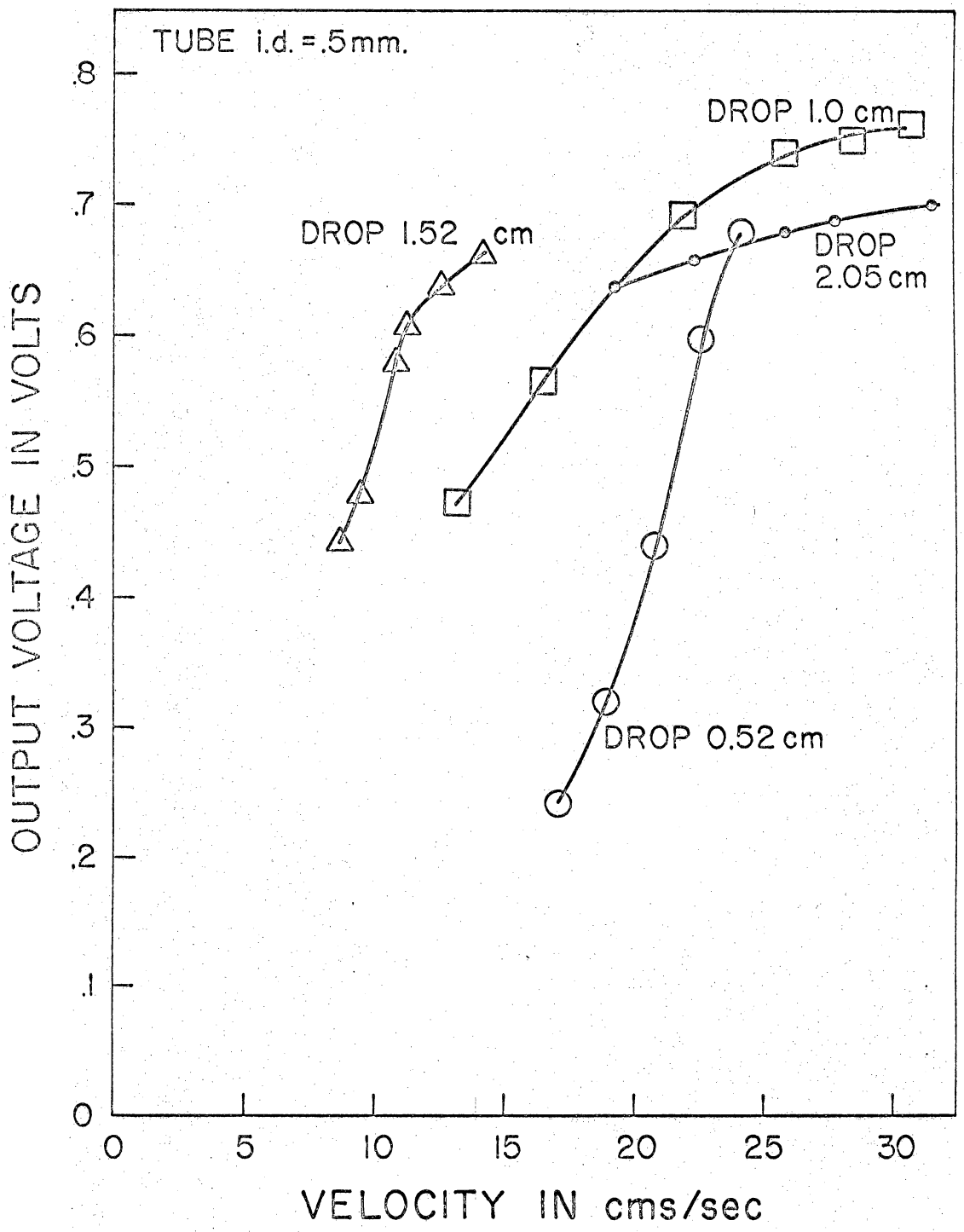

Fig. 5a. Dependence of the output voltage of different drop lengths on velocity.

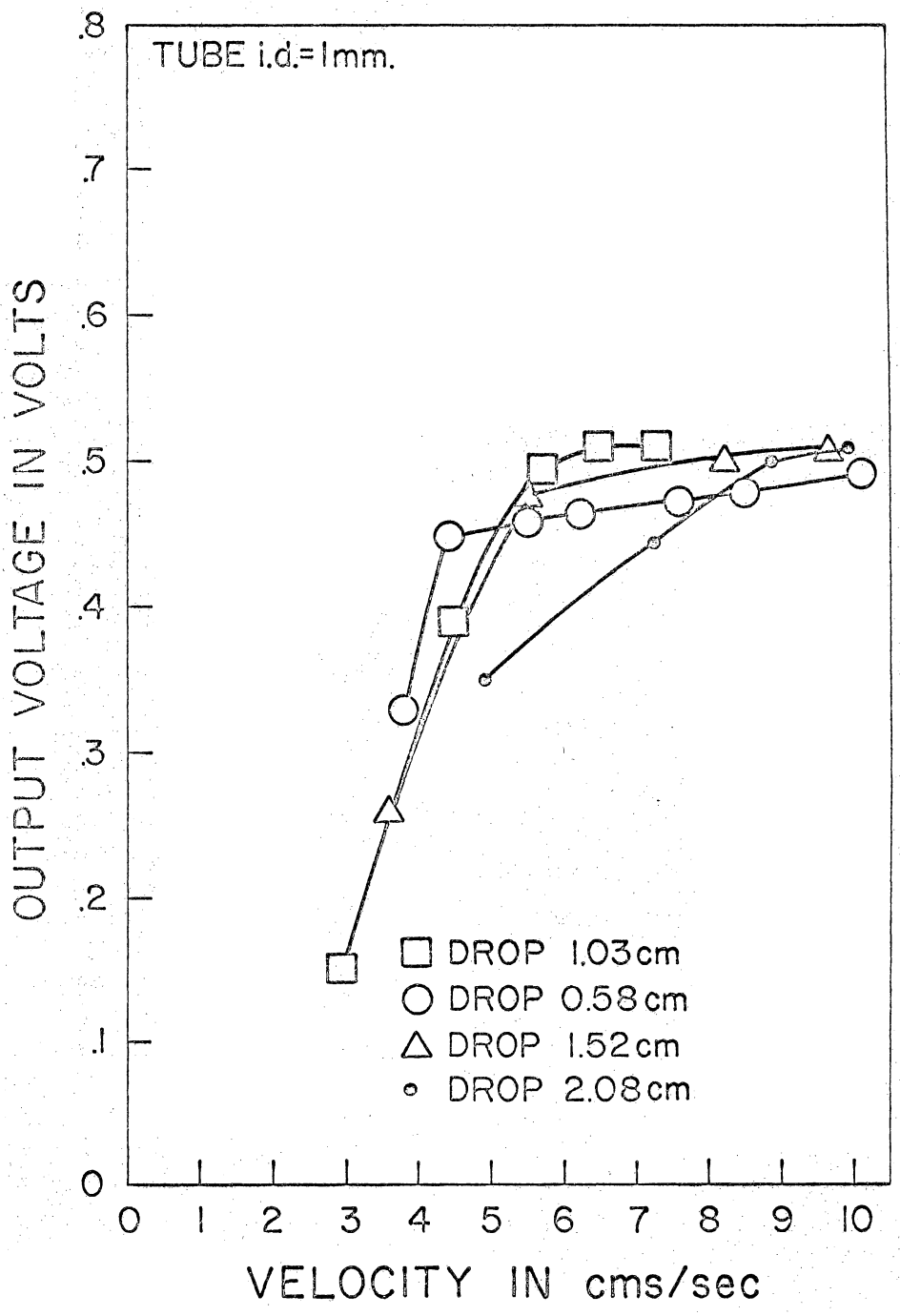

Fig. 5b. Dependence of the output voltage of different drop lengths on velocity.

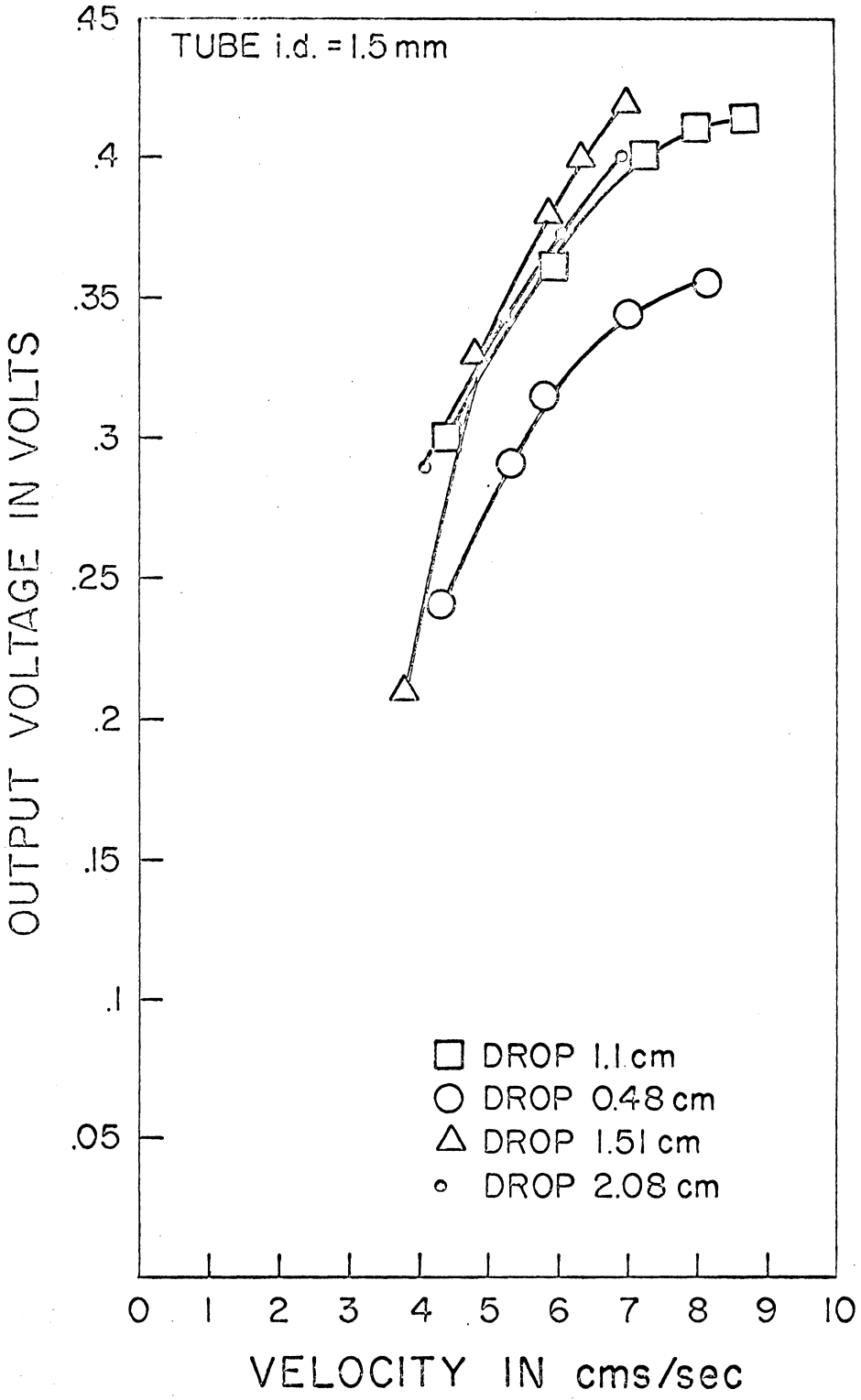

Fig. 5c. Dependence of the output voltage of different drop lengths on velocity.

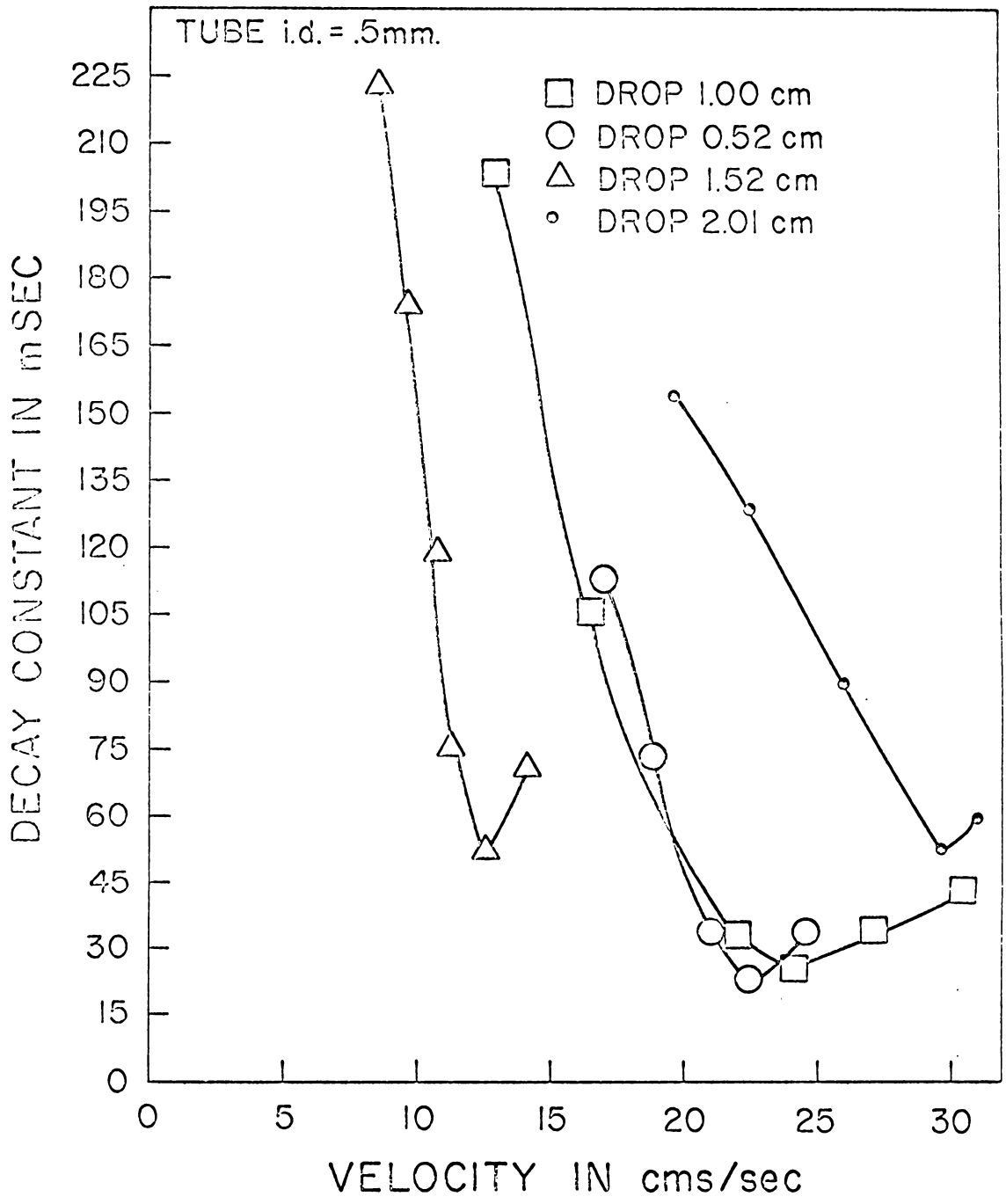

Fig. 6a. Dependence of the decay constants of different drop lengths on the velocity.

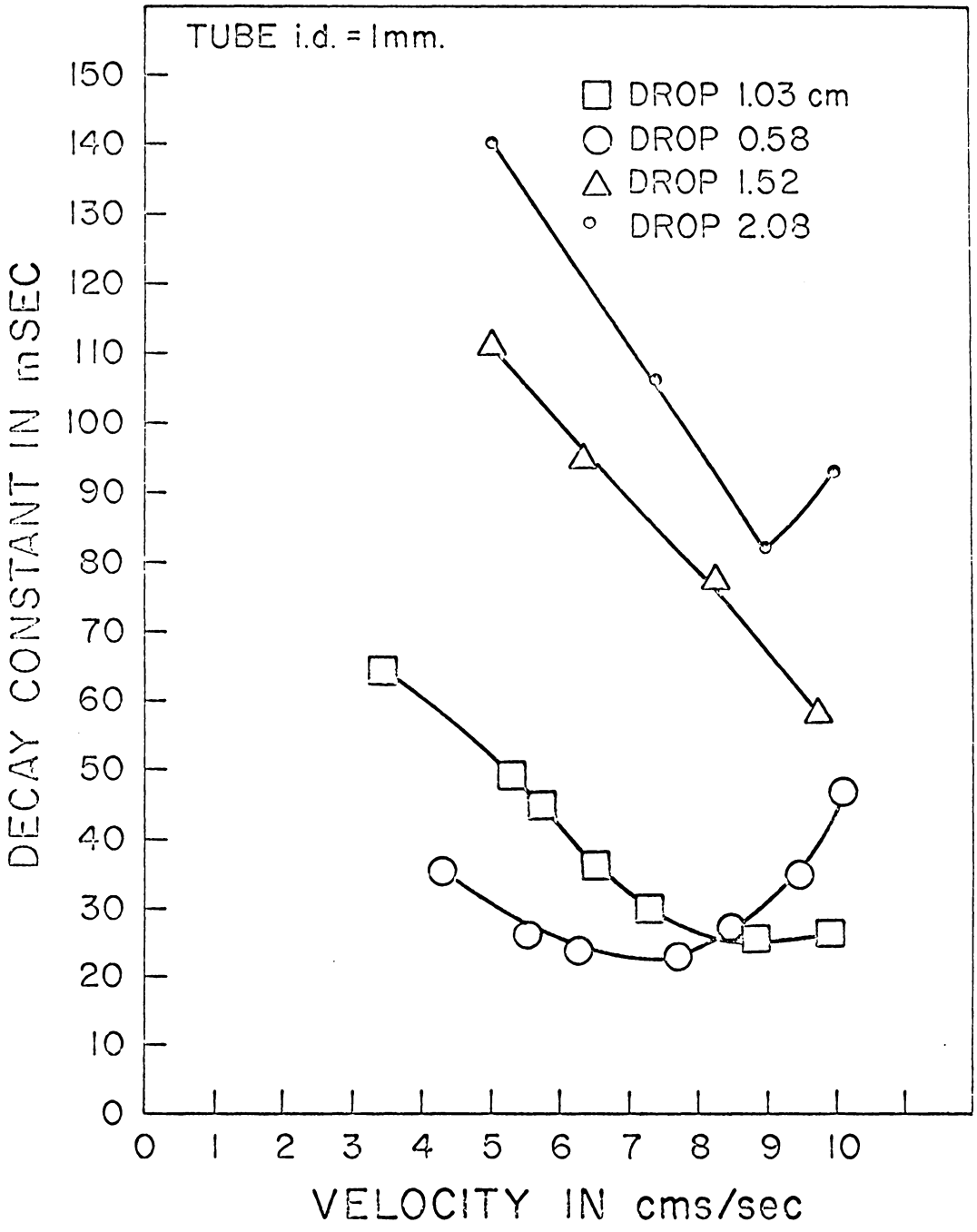

Fig. 6b. Dependence of the decay constants of different drop lengths on the velocity.

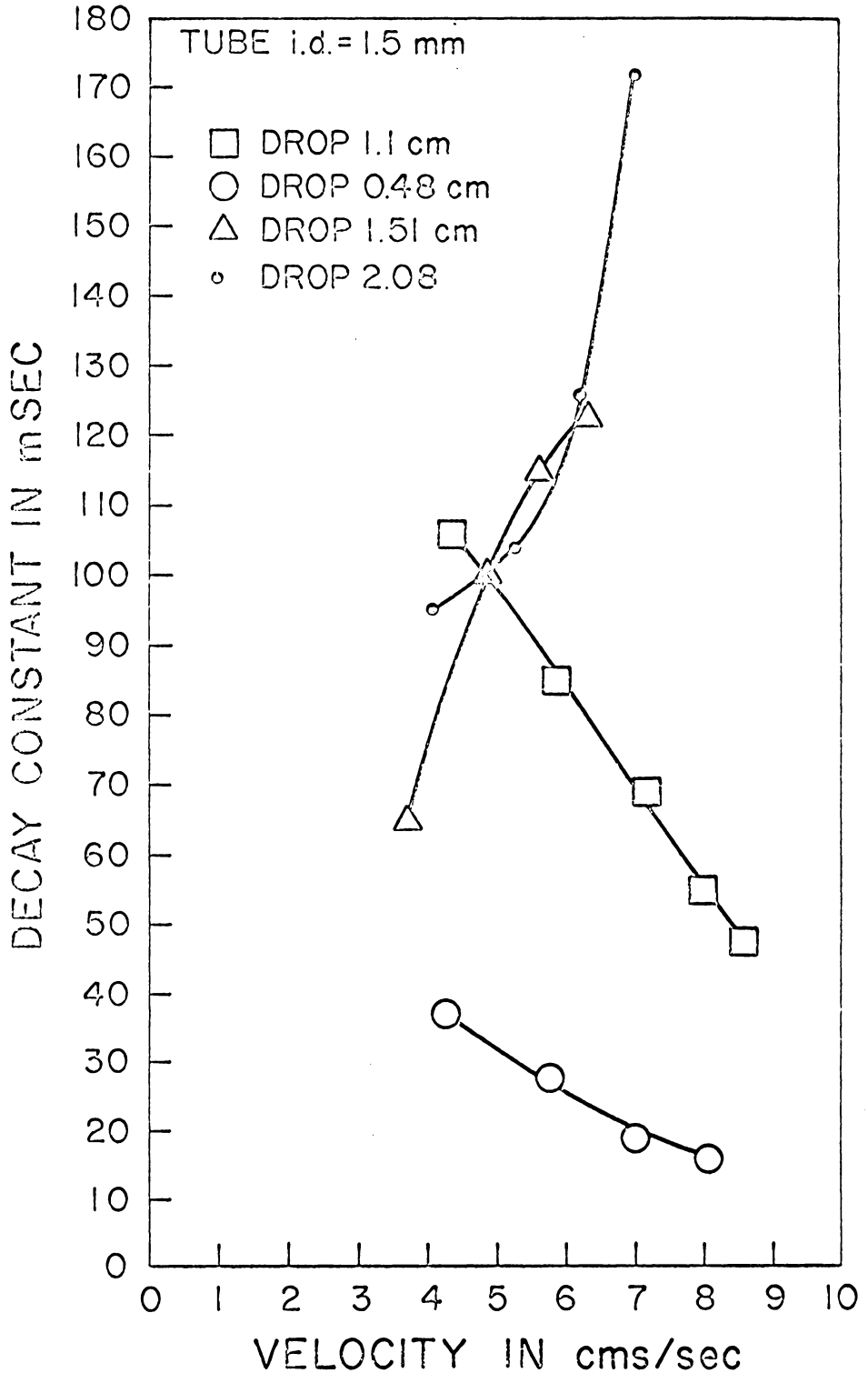

Fig. 6c. Dependence of the decay constants of different drop lengths on the velocity.

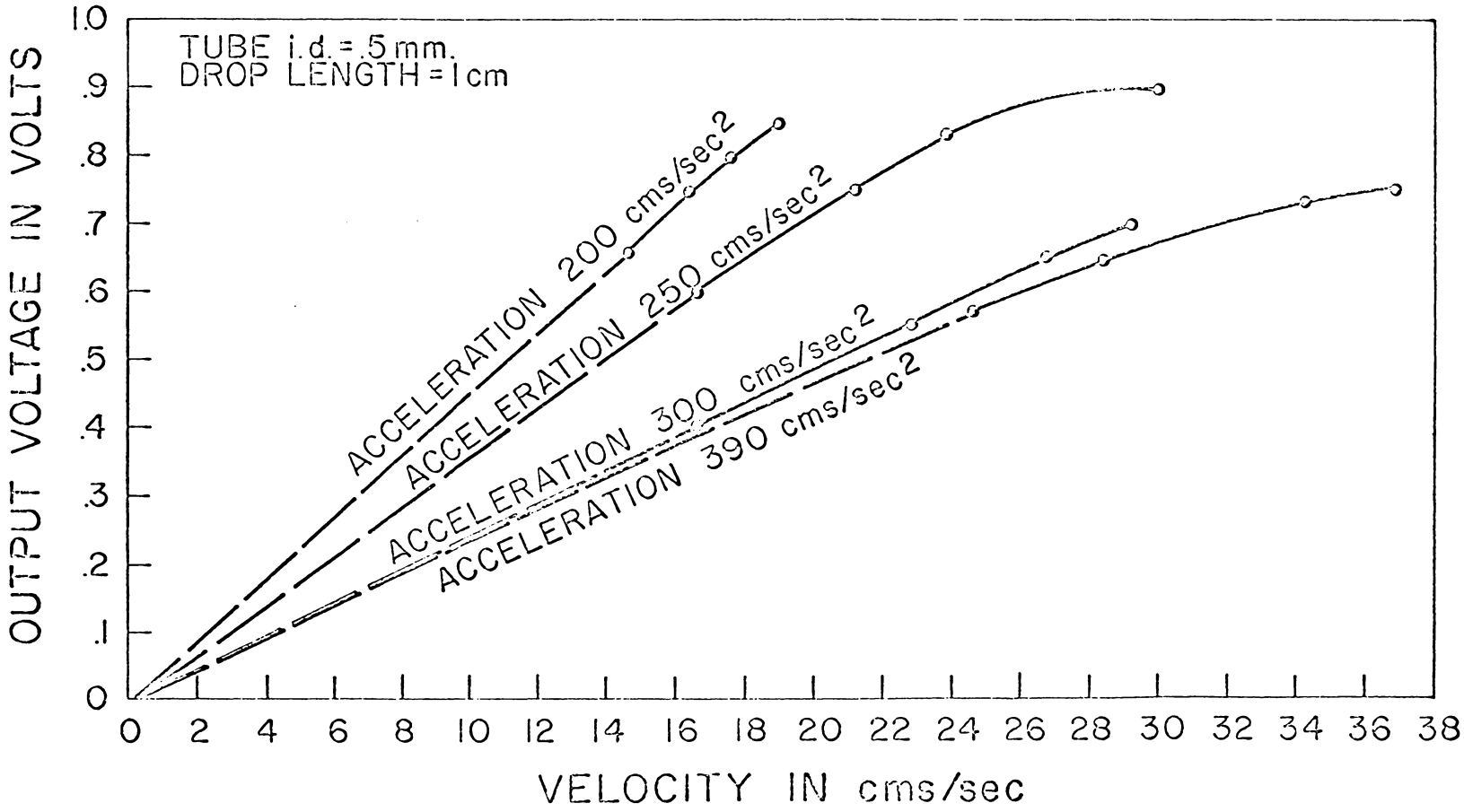

Fig. 7a. Dependence of the output voltage of 1 cm. drop on the velocity (for fixed acceleration).

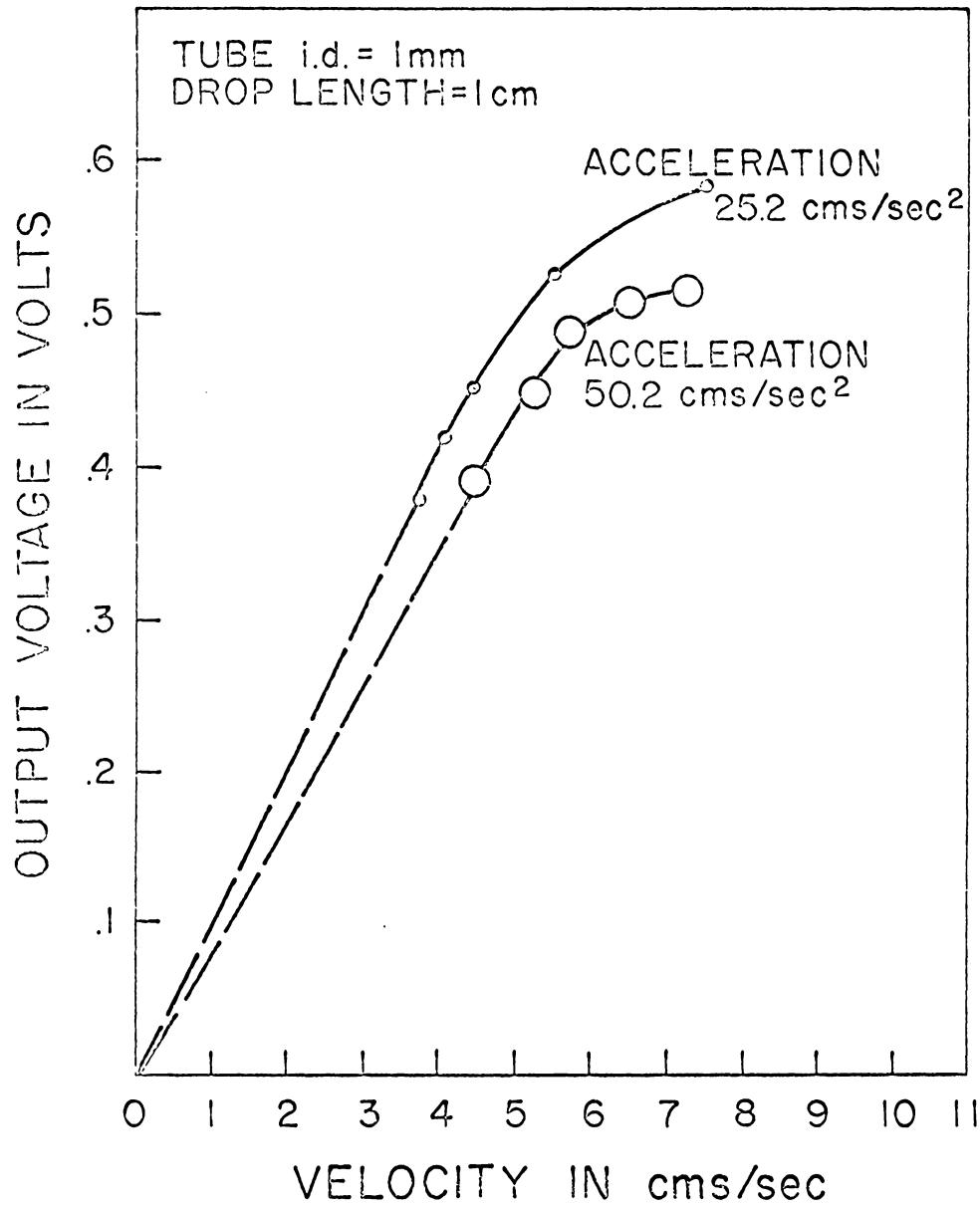

Fig. 7b. Dependence of the output voltage of 1 cm. drop on the velocity (for fixed acceleration).

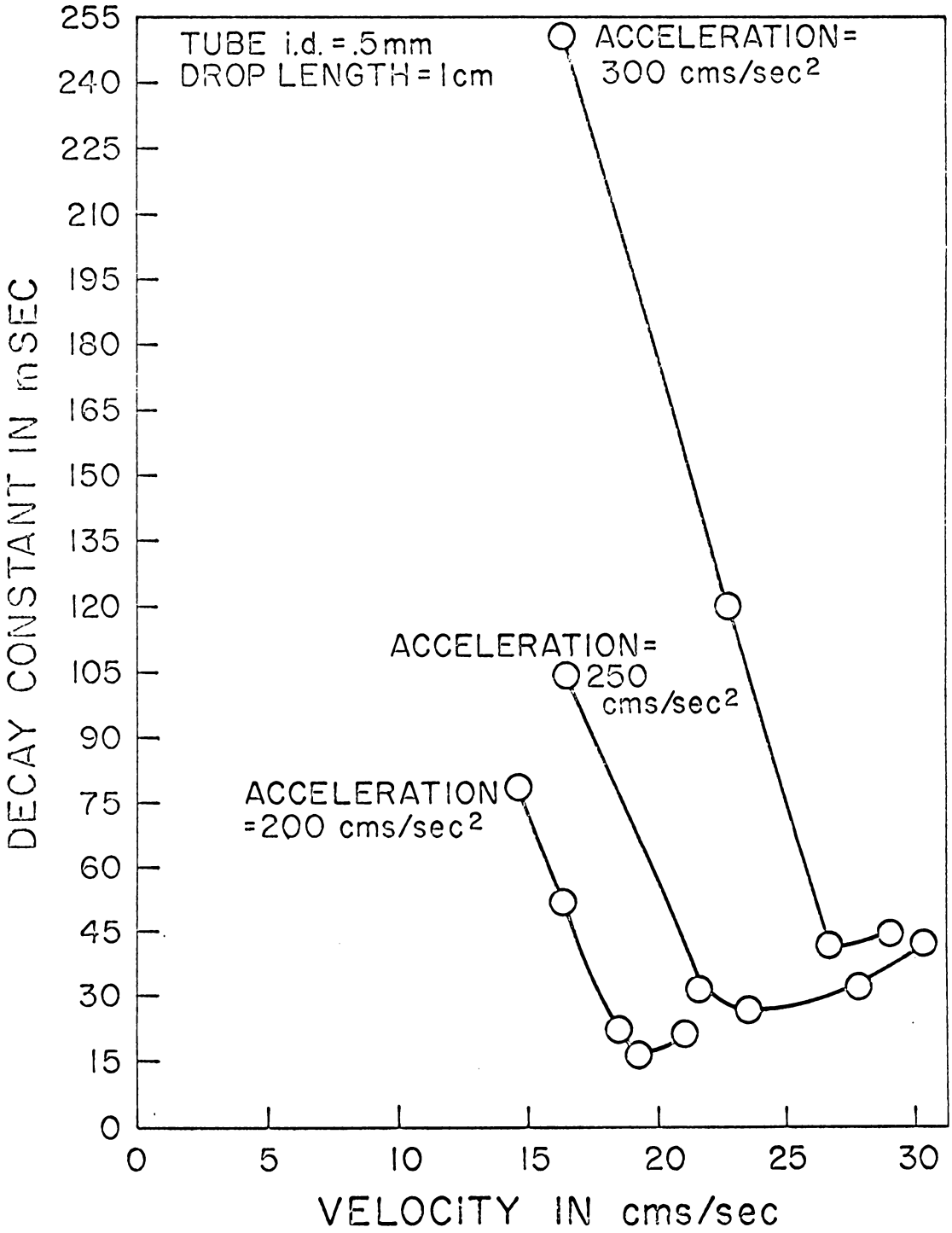

Fig. 8. Dependence of the decay constant of a 1 cm. drop on the velocity (for fixed accelerations).

of the acceleration.

Constant Velocity Measurements

For the constant velocity experiment, it was observed that in this case also, the output voltage was obtained as long as the drop moved relative to the tube. This output voltage was displayed on a strip chart recorder and a typical trace is shown in Fig. 9.

Part A is the streaming potential with only the electrolyte flowing in the tube. The mercury drop was then injected into the tube and as soon as it touched the top electrode the polarity changed as at B; then decayed and remained constant as in part C as long as the drop moved. When the mercury drop reached the bottom electrode the polarity again reversed as at D; and then decayed with a large decay constant to the value of the streaming potential (part E).

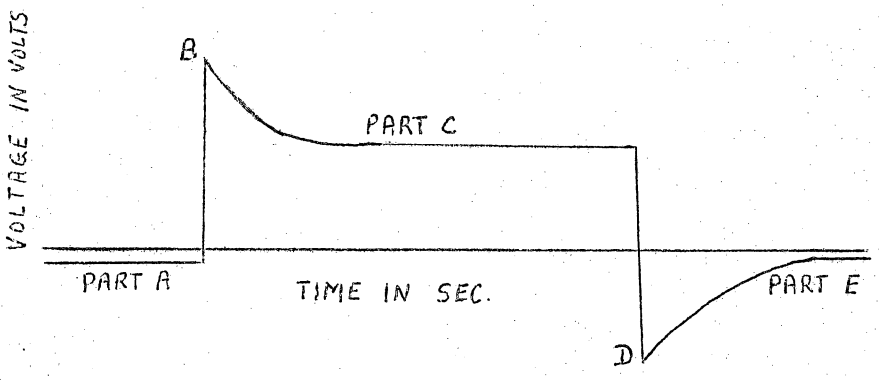

Fig. 9. Trace of the output voltage for constant velocity experiment.

In Figs. 10a to 10c, the output voltage is plotted against the drop length for different constant velocities. The plot shows that the output voltage initially increases as the drop length increases and then saturates for very long drops. The output voltage also increases with the increase in the velocity of the drop; but decreases with the increase in the tube diameter. The polarity of the output voltage was positive in the direction the drop moved, which agrees with our previous experiment.

Current measurements were made by short circuiting the platinum electrodes with a microammeter. In Fig. 11, the short circuit current is plotted against the drop length for different velocities of the drops. The current is found to decrease with the increase in the tube diameter. For 1.5 mm. diameter tube, the short circuit current was less than .02μ A. for drops as long as 3 cm. Since the currents are in the microampere range while the potentials are fractions of a volt, it indicates that the tube is not a good energy source (like a battery) but it can serve as a transducer for converting mechanical disturbances to electric potentials.

Other Facts of Interest

Several facts were noted which were not followed with quantitative measurements, but which are perhaps worthy of comment.

Drop Given a Constant Acceleration. When this part of the experiment was initially performed with a single mercury drop, the output voltages were high and the decay constants were small. Repeating the experiment after twenty four hours gave small output voltages (aging

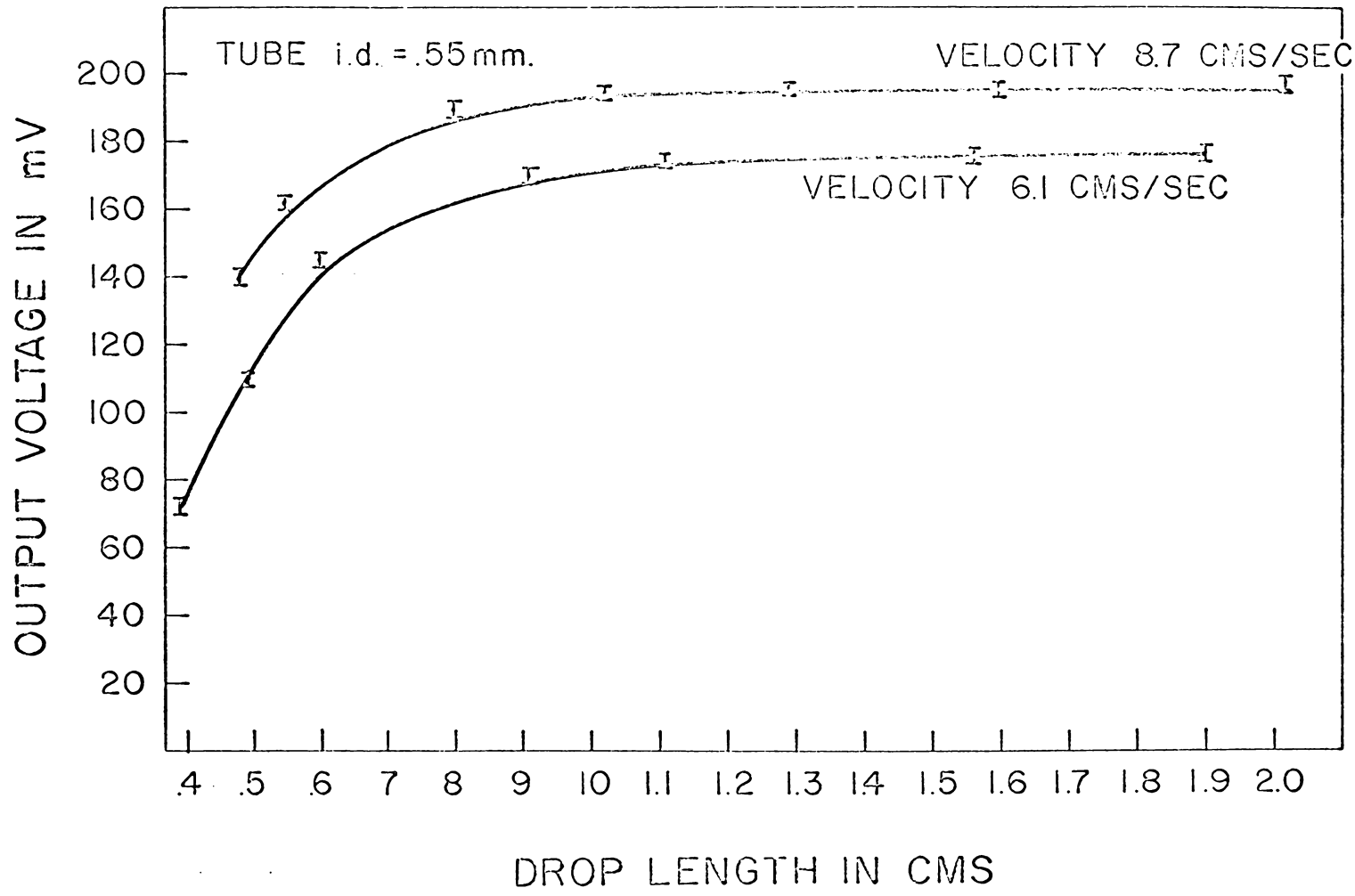

Fig. 10a. Dependence of the output voltage on the length of drop for constant velocity motion.

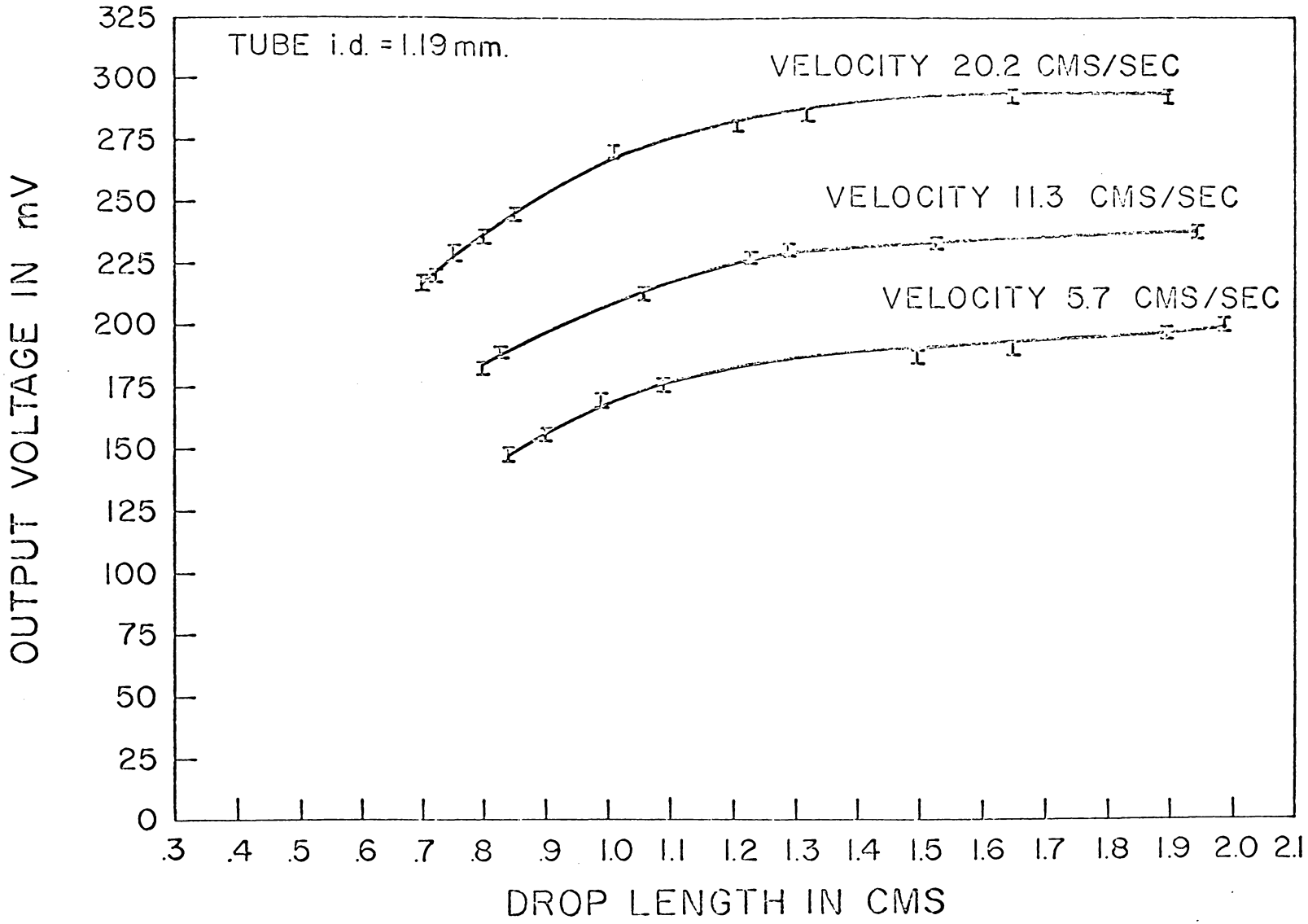

Fig. 10b. Dependence of the output voltage on the length of drop for constant velocity motion.

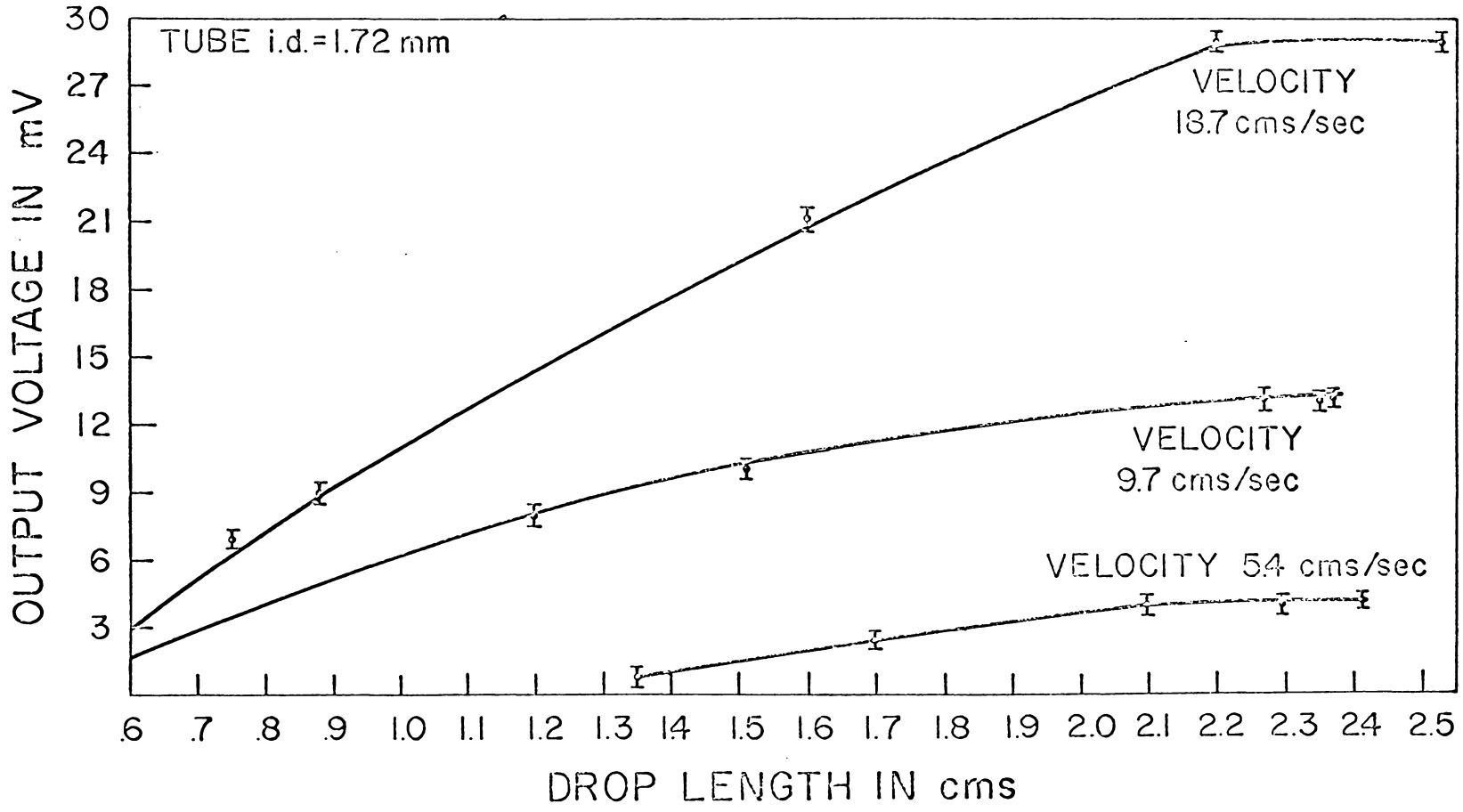

Fig. 10c. Dependence of the output voltage on the length of drop for constant velocity motion.

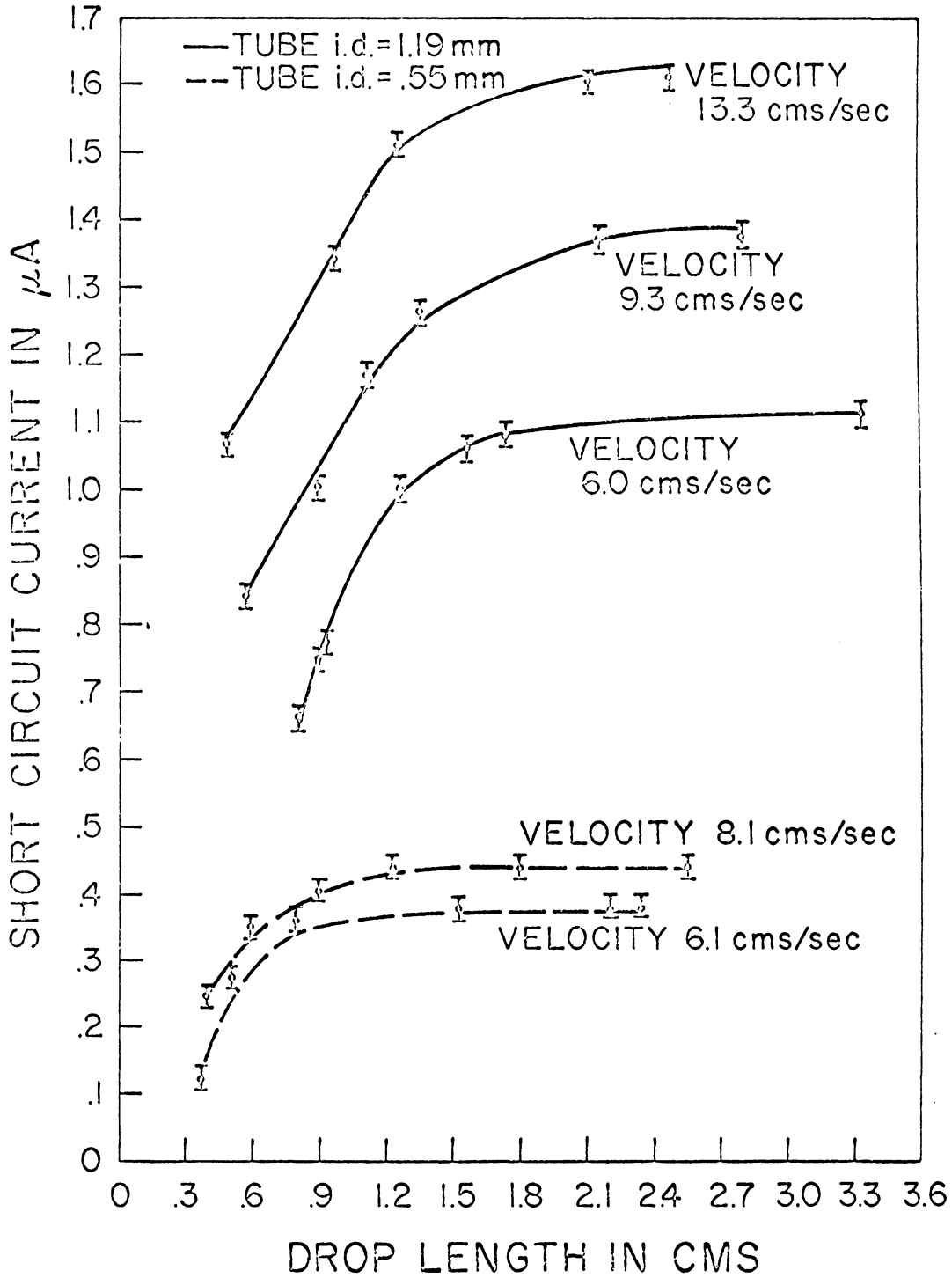

Fig. 11. Dependence of the short circuit current on the length of drop moving with constant velocity.

process described by Fain et al.[4] and Kuskevics[10]) and long decay constants. However by moving the drop to and fro in the tube, the original readings were obtained. This suggests that the double layer may get contaminated when the interface remains stationary for a long time, and perhaps, this contamination was removed by moving the drops in the tube.

The output voltage was found to increase and the decay constant was found to decrease with the increase in the number of the drops in the tube. Also, decreasing the concentration of the electrolyte decreased the output voltage, for the same drop.

Drop Moving with Constant Velocity. It was observed that the output voltage which was obtained when a mercury drop moved down the tube was reduced to zero, when the drop was stopped between the electrodes.

Also, increasing the number of drops in the tube increased the output voltage and current. When initially two drops were introduced in the tube, a high output voltage was obtained. During the travel down the tube the drops got joined and formed a single drop. This caused the output voltage to drop to less than half of the original value. This indicates that also for the constant velocity experiment, the output voltage depends on the number of interfaces and (for large enough drops) not on the size of the mercury drop.

IV. THEORY

Shape of The Interface For No Flow

Consider a drop of mercury in a capillary tube of radius a, with electrolyte on either side as shown in Fig. 12. Choose an axially symmetric cylindrical coordinate system such that at z=0, r=a and any point on the interface has coordinates $(r(z),\phi,z)$. The curvature of a liquid-liquid interface at any point is given by Rayleigh's formula in terms of the pressure difference across the interface at that point (cf. Appendix C):

$$\Delta p_o = p-p' = \gamma\left(\frac{1}{r(\dot{r}^2+1)^{\frac{1}{2}}} - \frac{\ddot{r}}{(\dot{r}^2+1)^{3/2}}\right)$$

where p and p' are the pressures on the concave and convex sides of the interface respectively at that point, γ is the surface tension in dynes/cm, r is a function of z and $\dot{r}$ denotes the derivative of r with respect to z.

The equation for the surface can thus be written as

$$\alpha \equiv \frac{\Delta p_o}{\gamma} = \frac{1}{r(r^2+1)^{\frac{1}{2}}} - \frac{\ddot{r}}{(\dot{r}^2+1)^{3/2}} = \frac{1}{r\dot{r}}\frac{d}{dz}\left\{\frac{r}{(\dot{r}^2+1)^{\frac{1}{2}}}\right\}$$

and can be integrated by choosing that at z=0, $\dot{r}$=0 which gives[11]

$$r(z) = \frac{2}{\alpha}\,(1-\alpha^2 z^2/4)^{\frac{1}{2}}$$

This equation requires the interface to be in the form of a hemisphere, making zero contact angle with the glass tube, since at z=0, $r=a=\frac{2}{\alpha}$.

The contact angle which a mercury-electrolyte (fluid-fluid) interface makes with glass is not necessarily zero but may have a finite

value[13,14]. For capillary tubes having small radii (less than 0.7mm), the contact angle can be assumed to be determined by the radius of curvature of the interface and the radius of the capillary tube. The geometry of Fig. 13 gives

$$\cos\theta = \frac{dz}{(1+\dot{r}^2)^{\frac{1}{2}}dz}\Bigg|_{z=0} = \frac{1}{(1+\dot{r}^2)^{\frac{1}{2}}}\Bigg|_{z=0} \text{ or } \dot{r}\Big|_{z=0} = -\tan\theta$$

By defining the value of z at r=0 to be z_o (where $\dot{r}= -\infty$), the above equation of the interface can be integrated to give

$$r(z) = \frac{2}{\alpha}\{1-(1+\frac{\alpha}{2}(z-z_o))^2\}^{\frac{1}{2}}$$

In terms of the contact angle θ, the last equation can be written as

$$r(z) = \frac{a}{\cos\theta}\{1-(\sin + \frac{z}{a}\cos\theta)^2\}^{\frac{1}{2}} \qquad (2)$$

Equation 2 indicates that for a stationary drop in a capillary tube, the front as well as the back interface is a part of a sphere of radius $a/\cos\theta$ which makes an angle of contact θ with the glass capillary. By applying the boundary condition that at z=0, r=a, to Equation 2, we get

$$a = \frac{2}{\alpha}\cos\theta$$

Using this value of a, the equation of the surface, (Equation 1) can be written as

$$\Delta p_o = \frac{2\gamma}{a}\cos\theta \qquad (3)$$

The surface area of the interface is

$$A = \frac{2\pi a^2(1-\sin\theta)}{\cos^2\theta}$$

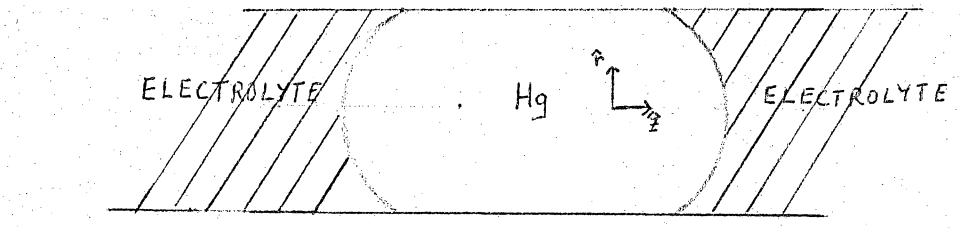

Fig. 12. Mercury-electrolyte interfaces in a capillary tube.

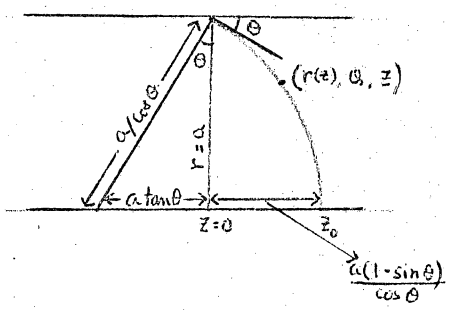

Fig. 13. Part of a mercury-electrolyte interface.

Shape of the Front and Back Interface for a Moving Drop

For a drop moving with constant velocity we have attempted to construct a theory by assuming that each interface behaves independently of the other and that we can neglect the contribution to the force due to viscosity from the radial velocity terms since they are small as compared to the contribution from the axial velocity terms.

The forces of viscosity which act at both ends of the moving drop can be determined by considering an annular ring which consists of the surface material of the interface and has a radius r(z). The force due to viscosity on a cylinder of radius r is

$$F_z(r) = 2\pi r(\eta_e \ell_e + \eta_m \ell_m) \frac{\partial v_z}{\partial r}$$

where η_e and η_m are the viscosities of the electrolyte and mercury respectively, ℓ_e and ℓ_m are the lengths of the electrolyte column and mercury drop respectively and, assuming laminar flow, v_z is the velocity in the z direction given by Poiseuille's equation

$$v_z = v_o(1 - \frac{r^2}{a^2})$$

where v_o is the velocity at the center of the tube of radius a.

The force due to viscosity on the annular ring is then approximately

$$F_z(r + dr) - F_z(r) = \frac{\partial F_z}{\partial r} dr$$

or

$$\frac{\partial F_z}{\partial r} dr = [2\pi(\eta_e \ell_e + \eta_m \ell_m) (\frac{\partial v_z}{\partial r} + \frac{r\partial^2 v_z}{\partial r^2})]dr$$

By using Poiseuille's equation the above equation becomes:

$$\frac{\partial F_z}{\partial r}\, dr = -8\pi(\eta_e \ell_e + \eta_m \ell_m)\, \frac{v_o}{a^2}\, r\dot{r}dz$$

It has been shown in Appendix C that the force balance on the annulus of a stationary drop is

$$\Delta p_o 2\pi r\dot{r}dz = \gamma\left[\frac{\dot{r}}{(1+\dot{r}^2)^{\frac{1}{2}}} - \frac{r\dot{r}\ddot{r}}{(1+\dot{r}^2)^{3/2}}\right]$$

For a drop moving with constant velocity, by including the viscosity term to the above equation, we get

$$\Delta p_o 2\pi r\dot{r}dz - 8\pi(\overline{\eta\ell})\, \frac{v_o}{a^2}\, r\dot{r}dz = \gamma\left[\frac{\dot{r}}{(1+r^2)^{\frac{1}{2}}} - \frac{r\dot{r}\ddot{r}}{(1+r^2)^{3/2}}\right] 2\pi dz$$

which gives

$$\Delta p_o - \frac{4\overline{\eta\ell}v_o}{a^2} = \gamma\left[\frac{1}{r(1+r^2)^{\frac{1}{2}}} - \frac{\ddot{r}}{(1+r^2)^{3/2}}\right]$$

where the negative sign is chosen since the polarity was positive in the direction of motion and $\overline{\eta\ell} = (\eta_e \ell_e + \eta_m \ell_m)$

This equation shows that an interface moving with constant velocity remains spherical in shape but now α is velocity dependent and is given as

$$\alpha(v_o) = \frac{1}{\gamma}\left[\Delta p_o - \frac{\overline{\eta\ell}v_o}{a^2}\right]$$

The forces due to viscosities of the fluids cause the two ends of the moving drop to make different contact angles with the glass tube. At any point on the front interface the new pressure difference Δp_f is

$$\Delta p_f = \frac{2\gamma}{a} \cos\theta_{fv} = \Delta p_o - 4\frac{(\eta_e \ell_e + \eta_m \ell_m)}{a} \frac{v_o}{a} \tag{4}$$

and on the back interface the new pressure difference Δp_b, is

$$\Delta p_b = \frac{2\gamma}{a} \cos\theta_{bv} = \Delta p_o + 4\frac{(\eta_e \eta_e + \eta_m \ell_m)}{a} \frac{v_o}{a} \tag{5}$$

where θ_{fv} and θ_{bv} are the contact angles of the front and back interface respectively. From Equation 3 for the value of Δp_o, Equations 4 and 5 become

$$\cos\theta_{fv} = \cos\theta - \frac{2\overline{\eta\ell}}{\gamma} \frac{v_o}{a} \tag{6}$$

and

$$\cos\theta_{bv} = \cos\theta + \frac{2\overline{\eta\ell}}{\gamma} \frac{v_o}{a} \tag{7}$$

Equations 6 and 7 show that for a drop moving with constant velocity, the contact angle at the front end increases while at the back end, the contact angle decreases. In other words the front interface flattens and the back interface bulges out.

At some value of velocity v_o, say v_{ox}, the contact angle at the back end of the drop will become zero, that is, the back interface will become hemispherical in shape.

For velocities greater than v_{ox}, the back end will not bulge out

any further because it must remain spherical in shape within our approximation but the front end will keep on flattening until it becomes a circular disc. Thus v_{ox} is the velocity at which one could expect a change over from the behavior which reflects both ends of the mercury drop deforming (for $v_o<v_{ox}$) to only one end deforming ($v_o>v_{ox}$).

By applying the condition that when $\theta_{bv}=0$, $v_o=v_{ox}$, Equation 7 gives

$$v_{ox} = \frac{\gamma a}{2\eta\ell} (1-\cos\theta)$$

The experimental velocity v is one half of the velocity v_o, so the above equation becomes

$$v_x = \frac{v_{ox}}{2} = \frac{\gamma a}{4\eta\ell} (1-\cos\theta) \tag{8}$$

This equation can be used for calculating the contact angle θ for a stationary drop, if v_x is experimentally determined. The contact angles θ_{fv} and θ_{bv} of the moving drop can be determined in terms of v/v_x from Equations 6 and 7 as

$$\cos\theta_{fv} = \cos\theta - \frac{v}{v_x} (1-\cos\theta) \tag{9}$$

and

$$\cos\theta_{bv} = \cos\theta + \frac{v}{v_x} (1-\cos\theta) \tag{10}$$

We assume the output voltage E across a moving mercury drop is due to the difference in the dipole moment densities at each end because

of the distortions of the surface areas of these ends. Implicit in this assumption is that the total number of dipoles across the double layer do not change during the deformation of the surfaces. The output voltage across the drop is

$$E = \frac{qh}{K\varepsilon_o}\left(\frac{1}{A_f} - \frac{1}{A_b}\right) \tag{11}$$

where q is the charge on the double layer, h is the distance across the double layer, K is the dielectric constant of the medium between the double layer, ε_o is the permittivity of free space and A_f and A_b are the surface areas of the front and back ends of the mercury drop. The maximum output voltage across the moving drop occurs when the back end becomes a hemisphere having surface area $2\pi a^2$ and the front end becomes a circular disc having surface area πa^2

$$E_{max} = \frac{qh}{K\varepsilon_o(2\pi a^2)}$$

Thus for a drop moving with constant velocity the output voltage across the drop is

$$E_v = E_{max}\left(\frac{2\pi a^2}{A_{fv}} - \frac{2\pi a^2}{A_{bv}}\right) \tag{12}$$

where the surface areas of the front and the back ends in terms of the respective contact angles θ_{fv} and θ_{bv} are

$$\frac{1}{A_{fv}} = \frac{\cos^2\theta_{fv}}{2\pi a^2(1-\sin\theta_{fv})}$$

and

$$\frac{1}{A_{bv}} = \frac{\cos^2\theta_{bv}}{2\pi a^2(1-\sin\theta_{bv})}$$

For different ratios of v/v_x the contact angles θ_{fv} and θ_{bv} can be determined from Equations 9 and 10 and these values when used in Equation 12 give the output voltage E_v, across a drop moving with constant velocity.

However, for a mercury drop moving with constant acceleration a phenomenological approach can be used to obtain the surface areas of the front and the back ends of the moving drop.

Rivers[11] has shown that when a capillary tube containing a mercury drop having electrolyte at both ends is acted on by a small force for a short time such that this force does not cause any relative motion between the drop and the capillary wall, the effect of this force is to distort the surface areas of the front and the back ends of the drop. Using perturbation theory he has obtained the surface area of the back end, S', to be

$$S' = S(1 + \frac{1}{6} a^2 (\frac{\rho_m - \rho_e}{\gamma})A)$$

where S is the surface area of the stationary (unperturbed drop), a is the radius of the capillary tube, ρ_m and ρ_e are the densities of mercury and electrolyte respectively, γ is the surface tension of mercury and A is the acceleration given to the capillary tube.

This approach can be used to obtain the surface area of a drop moving with constant acceleration by assuming that the force causing the acceleration also causes a small perturbation to the surface areas of the drop moving with constant velocity (zero acceleration). This makes the front end to have a surface area

$$A_{fA} = A_{fv'} [1 + Ca^2 \frac{(\rho_m - \rho_e)}{\gamma} A]$$

and the back end to have a surface area

$$A_{bA} = A_{bv'} [1 - Ca^2 \frac{(\rho_m - \rho_e)}{\gamma} A]$$

where C is a constant, A is the acceleration given to the drop and $A_{fv'}$ and $A_{bv'}$ are the surface areas of the front and the back ends for a drop moving with constant velocity, but with v_x replaced by v_t (cf. analysis section), when the velocity is not constant. The output voltage across a drop moving with constant acceleration is obtained by replacing A_f and A_b in Equation 11 by A_{fA} and A_{bA}. This gives

$$E_A = E_{max}\left[\frac{2\pi a^2}{A_{fv'}[1 + Ca^2 \frac{(\rho_m - \rho_e)}{\gamma} A]} - \frac{2\pi a^2}{A_{bv'}[1 - Ca^2 \frac{(\rho_m - \rho_e)}{\gamma} A]} \right] \quad (13)$$

For finite acceleration and zero relative velocity the above equation gives small output voltages (U-effect II) as compared to the output voltage for a drop moving with constant acceleration and having a finite velocity with respect to the capillary tube (U-effect III). The dependence of the output voltage on acceleration is opposite to that of velocity and hence U-effect II has an opposite polarity to U-effect III[5].

The physical significance of E_{max} is that it is the potential difference across a single hemispherical interface.

V. ANALYSIS

Dependence of the Output Voltage on Various Parameters

The output voltage E was found to be a function of the acceleration (a) of the mercury drop, the velocity (v) with which the mercury drop moved, the length (l) of the drop and the radius (r) of the tube,

$$E = f(a,v,l,r)$$

Since in our theory the force per unit area P (due to viscosity) on the outermost annulus of the mercury-electrolyte interface is proportional to v/r, and the output voltage E is proportional to P, we are motivated to study the dependence of the product Er on the velocity of the drop. The plots of the output voltage versus the velocity for a 1 cm. drop having fixed accelerations in different diameter tubes are given in Figs. 7a and 7b. These curves were transfered on to a single plot by reducing the velocities and the accelerations of the drop in different diameter tubes with the use of the equation

$$A_1 x_1 = A_2 x_2$$

where A_1 and A_2 are the cross-sectional areas of two different diameter tubes, and x_1 and x_2 are the velocities or accelerations of the mercury drop in these two tubes respectively.

Fig. 14 shows the plots of the product $E_A r$ against the reduced velocity (all on 1 mm. diameter). In these plots the points for the same acceleration in two different diameter tubes, all fell on the same curve. Also, points for 1 cm. and 2 cm. drops having the same

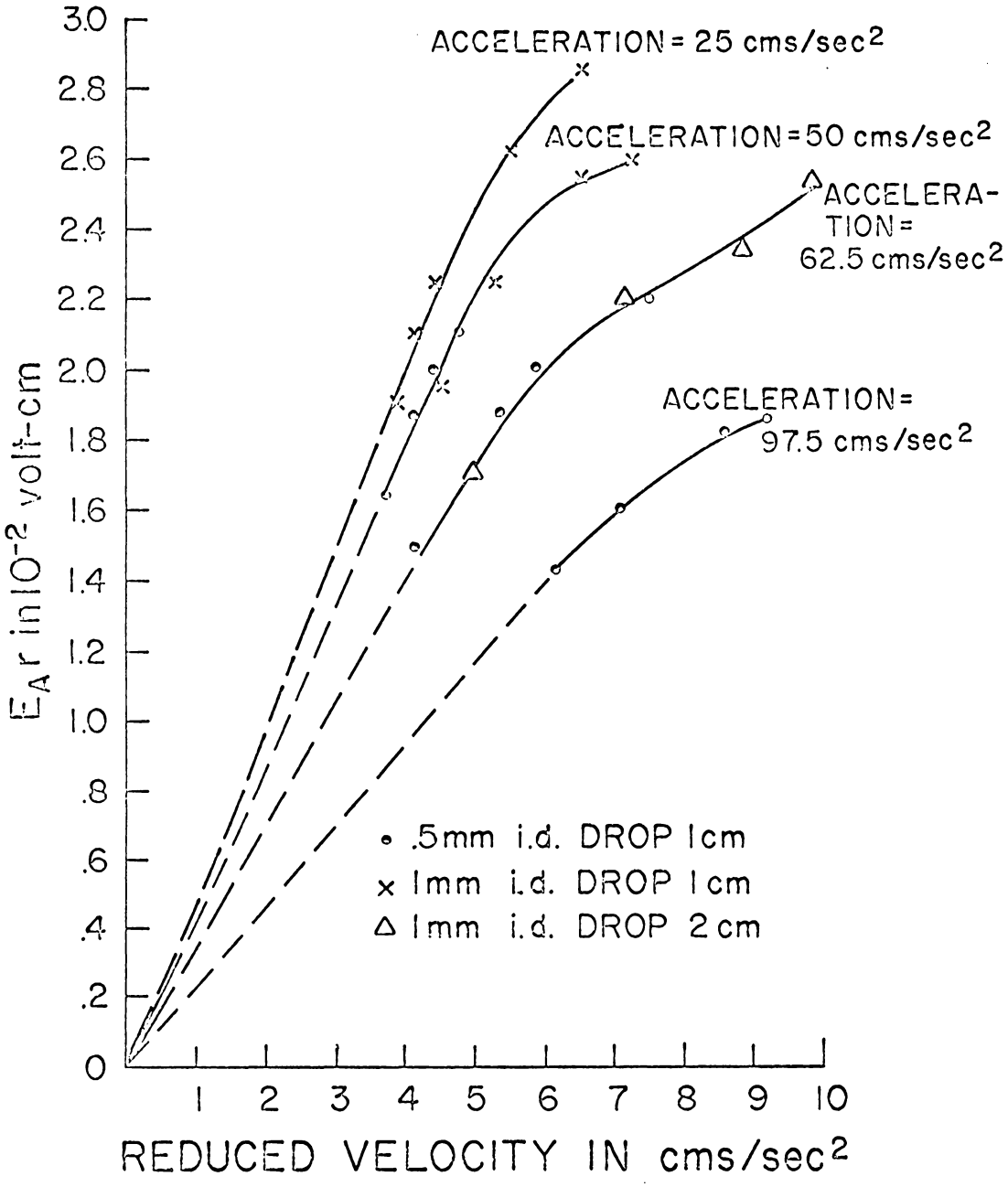

Fig. 14. Dependence of $E_A r$ on reduced velocity.

acceleration fell on one curve. The curves were extrapolated to the origin since for zero velocity the output voltage (due to U-effect II) is very small (less than .05V). Each curve shows a "knee" at some velocity v_t which is called the velocity of the cross-over point.

Fig. 15 is a plot of velocity v_t against the acceleration of the drop. The curve is a straight line which does not pass through the origin, since at zero acceleration, the velocity is constant. The velocity at which the decay constants change direction (Fig. 8), when plotted against the acceleration, fell on this curve (within the limits of experimental error). The value of the intercept on the velocity axis of this curve (v_x the velocity of zero acceleration) was substituted in Eq. 8 to find the stationary contact angle θ. Using typical values of γ=375 dynes/cm, a=.05 cm, η_e=1 cp, η_m=1.5 cp, ℓ_m=1 cm and ℓ_e=12 cm the contact angle θ was calculated to be 29°. The contact angle which a mercury-air interface makes with a glass wall is 40°[13]. Since we have mercury-electrolyte interfaces in capillaries having small diameters we should expect a greater curvature of the interface, and hence an angle of 29° is reasonable.

This value of θ and the values of E_A, v and v_t from Fig. 15 were used in Equation 13 to evaluate the parameters E_{max} and C which are given in Table I. The agreement of the values of E_{max} for accelerations of 25 and 50 cms/sec^2 only and not for higher accelerations suggests that Equation 13 may only be valid for small accelerations. Fig. 16 is a plot of the output voltage E_A versus v/v_t for different accelerations obtained by using the theoretical expression (Equation 13).

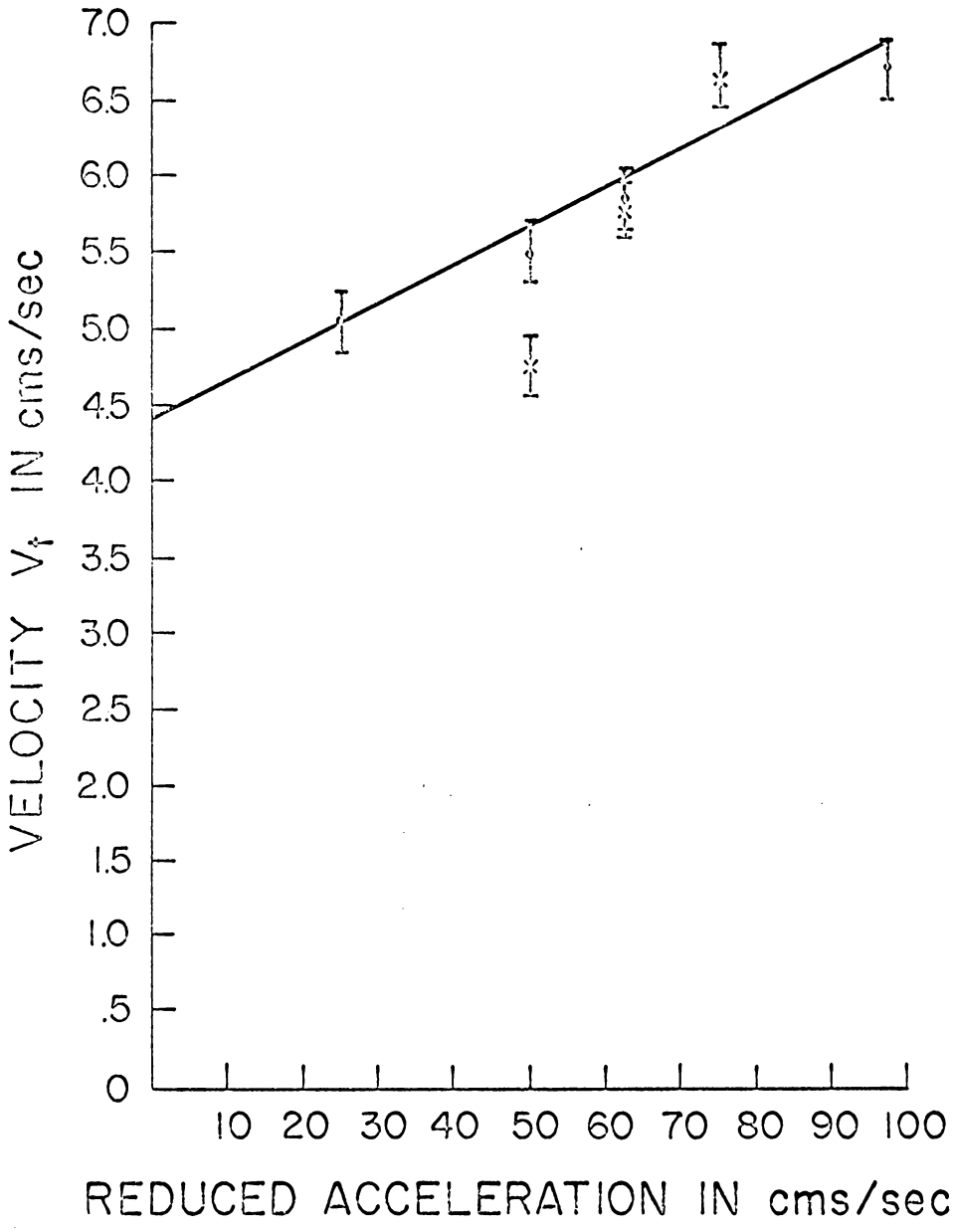

Fig. 15. Dependence of velocity v_t on reduced acceleration.

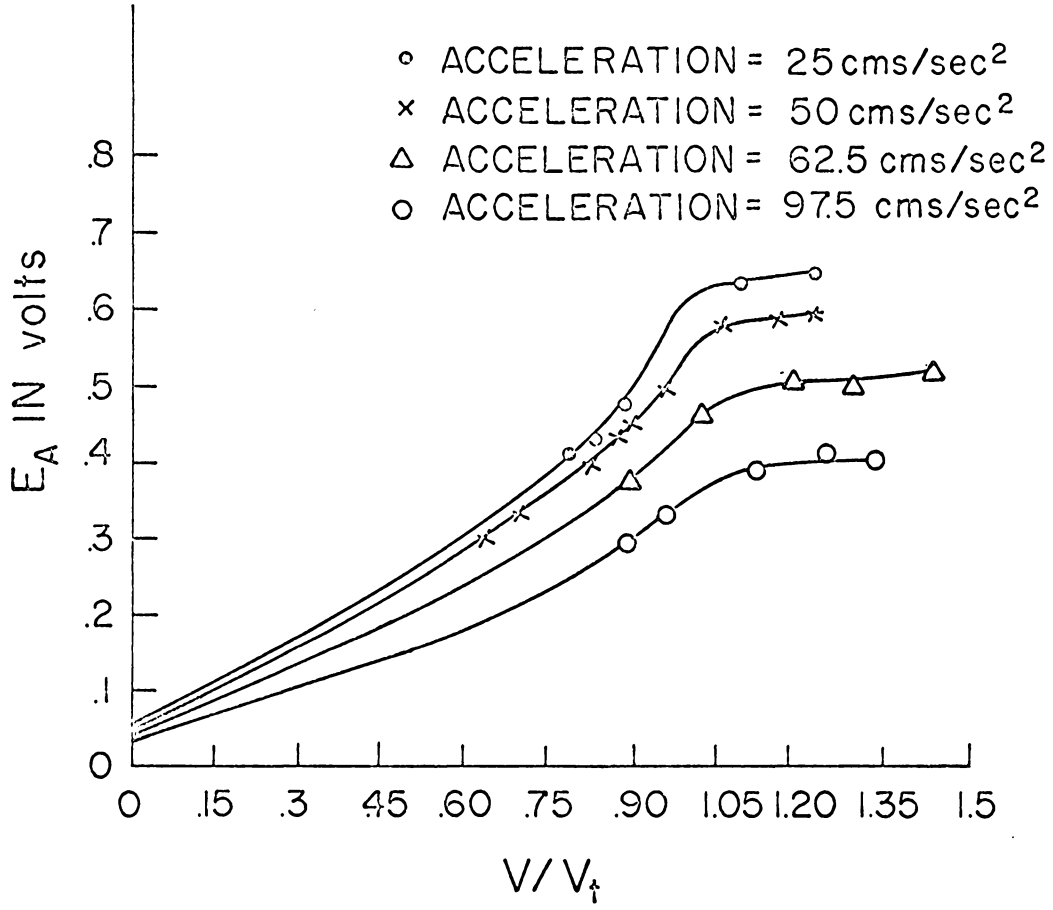

Fig. 16 . Theoretical plots of E_A versus v/v_t.

The points on the curves are the data points from the respective experimental curves (Fig. 14).

For drops moving with constant velocity, the plots of the output voltage versus the drop length were found to fit exponential curves.

Fig. 17 shows the plot of the experimentally determined $E_v r$ versus the reduced velocity (all on 1 mm.). For a 1 cm. drop having different constant velocities using the value of v_o from Fig. 15, the surface areas of the front and the back ends of the moving mercury drop were calculated. These values were used in Equation 12 to find E_{max} which would make Equation 12 (theoretical curve) fit the experimental curve (Fig. 17). The value of E_{max} obtained in this way was .35V. The difference between the E_{max} from the constant velocity and constant acceleration experiments could be due to neglecting interface distortion effects due to gravity in the constant velocity experiment. Since E_{max} is the potential difference across a single hemispherical interface our experiment suggests a method for measuring the potential difference across a single liquid-liquid interface.

Contradictions to the Theory of Podolsky et al.

According to Podolsky et al.[5], the double layer returns to equilibrium after a disturbance, by transferring mercurous ions across the interface and by diffusing the dipoles along the length of the drop from one end to the other. If this were true, then replacing the mercury drop in the tube by a solid metal slug should give a comparable output voltage. However, when our experiments were repeated with a slug of platinum and other metals, the output voltages obtained were less than 1 mV. This suggests that the changes in the areas of the

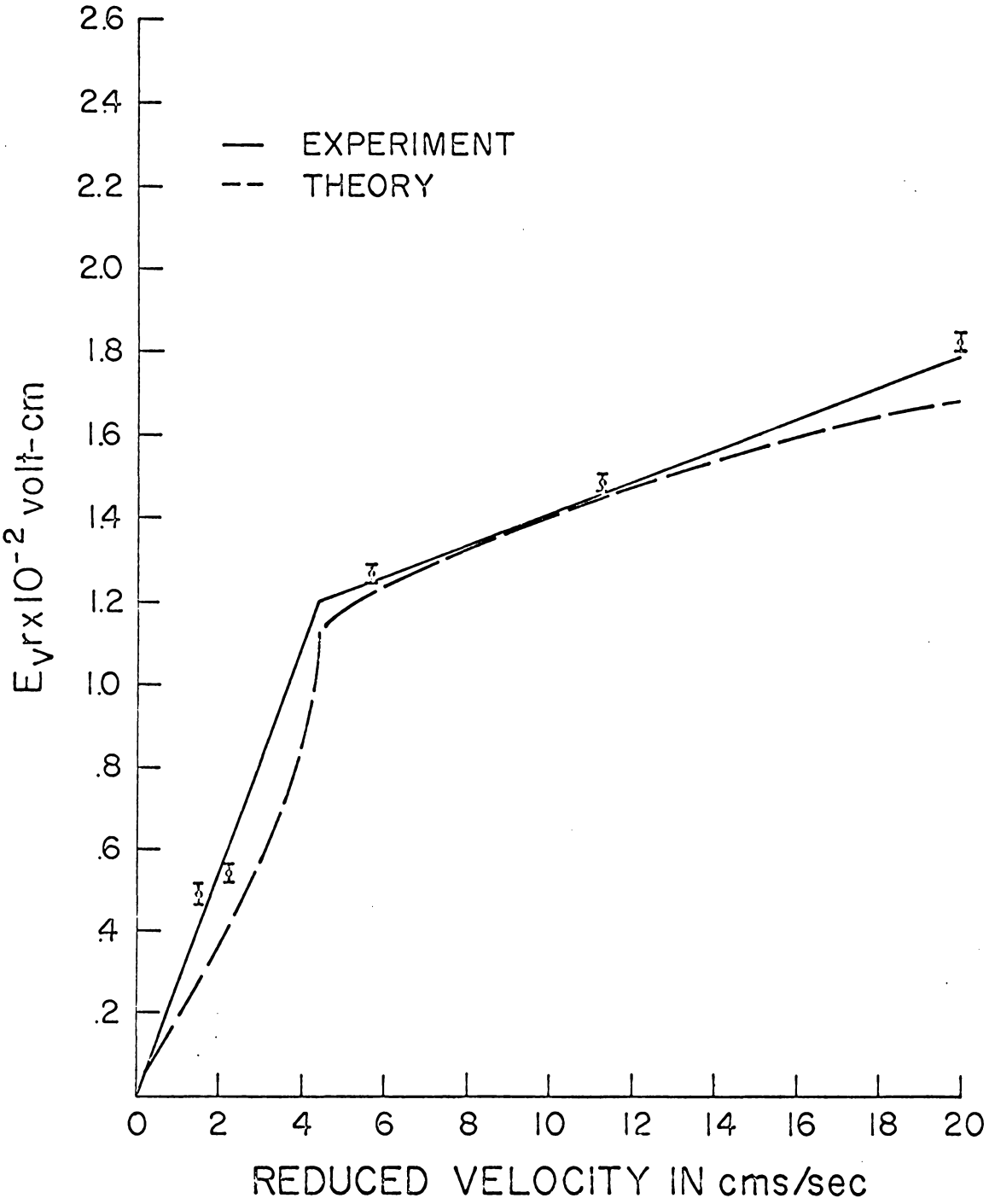

Fig. 17. Plot of $E_v r$ versus reduced velocity.

two ends of the mercury drop caused the observed output voltages.

According to Rivers[11], for a drop moving with constant velocity the available output across the tube shortly reduces to zero. For our constant velocity experiment, output voltages were obtained as long as the drop moved relative to the tube.

The decay constants that were obtained for our experiment in which the drop was accelerated and brought to a sudden stop, were of the order of milliseconds. Now since the transfer of mercurous ions across the interface (formation dissociation process described by Rivers[11]) is of the order of microsecond and the diffusion process is relatively slow (of the order of 10 seconds); the theory of Podolsky et al.[5] cannot account for teh decay constants observed in our experiments.

If chemical reaction was occuring when the drop moved with respect to the tube, then this should give rise to a large current (in the milliampere range). However, the largest current observed for our constant velocity experiment was in the microampere range.

According to Rivers[11], for a mercury drop moving along the capillary with a velocity v, a quantity of charge moves out of the interface and is turned under in a newly formed cylindrical region of the drop. This contradicts Rose[12], who states that for a fluid-fluid interface moving along a horizontal tube, no relative tangential motion can occur in the interface region and the moving interface will have a constant curvature throughout.

Error Analysis

The reproducibility of the experiments were within twelve percent.

The glass and teflon capillary tubes were of precision bore and a small (negligible) error was introduced by doing measurements in different tubes. However, there was a 6% error in determining the velocity and the acceleration of the mercury drop, and a 3% error in reading the maximum output voltage from the photographs. The rest of the error (3%) could be due to the chemistry of the problem (organic and other impurities in the electrolyte and prepering the tubes in atmosphere instead of vaccuum).

Table I. Computed Values of E_{max} and C for Drop Having Different Constant Accelerations

Acceleration cm/sec^2	E_{max} Volt	C
25	.7221	6.318
50	.7059	5.320
67.5	.6008	4.016
97.5	.4820	3.394

Suggestions for Future Experiments

The experiments described herein suggest a dynamical method of measuring the output voltage across a single interface which could help in understanding the basic mechanism of the formation of the double layer across an interface.

More experimental work is required in order to find the dependence of the output voltage on large accelerations of the drop. The problem of taking gravity into account for the constant velocity experiment could be avoided by making the drop move with constant velocity in long horizontal tubes by means of an electronically controlled driving force.

For drops given a constant acceleration and then brought to an abrupt stop, the decay constants could be studied by considering the excited modes of the two ends of the moving drop. The decay constants being in the millisecond range suggests that mechanical distortions (changes in the surface areas) play a very significant role.

Also the dependence of the output voltage on the number of interfaces and the electrolyte concentration should be studied so that a transducer which would give an optimum output for a given mechanical disturbance, can be designed.

VI. CONCLUSIONS

It has been shown that the two electrokinetic phenomena, U-effect II and U-effect III, are essentially the manifestation of the same effect, namely, that the distortions of the surface areas of the ends of the moving mercury drop cause the output voltage across the drop. The output voltage is proportional to the acceleration and velocity of the moving drop and does not depend on the relative displacement between the drop and the capillary wall.

The polarity of the output voltage for a moving drop was positive in the direction the drop moved.

A phenomenological equation was derived for the dependence of the output voltage on the acceleration and velocity. For zero relative velocity and non-zero acceleration between mercury and glass this equation gave small output voltages (U-effect II) as compared to the output voltage for a drop having a constant acceleration and moving with finite velocity. The dependence of the output voltage on the velocity of the drop is opposite to that of the acceleration.

By considering a model for the changes in the surface areas of the ends of the moving drop we have suggested a method for measuring the potential difference across a single liquid-liquid interface. Since the potential difference across a single interface cannot be measured, our experiment gives an indirect means of obtaining this potential difference by dynamic method, and this could be very valuable in understanding the double layers across interfaces and in electrochemistry.

APPENDIX A

Electrical Double Layer at Interfaces

The electrical double layer is an array of charged particles and oriented dipoles which is thought to exist at every interface. For metal electrolyte interface the double layer may consist of a layer of electrons on the metal, a layer of neutral water molecules (some adsorbed ions may exist in this layer), and a diffuse layer consisting of an ionic atmosphere in which ions of one sign are in excess of their normal concentrations whereas those of the other sign are in defect. This atmosphere of abnormal concentration of ions falls off rapidly with distance from the surface.

The study of interfaces is mostly done with mercury-solution interface because, mercury being a liquid, its surface is readily cleaned, it is free from mechanical strains and its interfacial tension is readily measured. In addition, mercury is distinguished by its low chemical activity and high 'hydrogen overvoltage'. The latter property prevents the reduction of the solvent to form hydrogen, until large potentials are applied across the interface. That is why a mercury-electrolyte interface is called a polarizable interface. An ideal polarizable interface behaves like an electrical condenser without leakage. Its capacity arises from the fact that charges may approach or recede from the interface, though they do not cross it. For all practical purposes, the electrical behaviour of a polarizable interface (mercury-electrolyte interface) can be compared to that of a capacitor and resistor in parallel, connected to a source of potential

difference E, as shown in Fig. A.1. The resistance is very high (practically no charges can leak across this double layer); and so the capacitor charges up to the value of the potential difference put out by the source.

Formation of the Double Layer

The exact mechanism for the formation of double layers at interfaces is still not well understood. Several explanations exist, and one of the possibilities for the formation of the double layerat the mercury-perchloric acid interface is as follows: When a drop of mercury is brought in contact with perchloric acid, mercurous ions will leave the mercury and go in solution since the heat of solvation is released in this process. This leads to a charge seperation (residual electrons on the mercury surface and hydrated mercurous ions in the solution) between the two phases. The charge on the metal produces a preferantial orientation of the water dipoles. The majority of sites on an electrode surface are occupied by water molecules[8]. The hydrated mercurous ions will be replaced by hydronium (H_3O^+) ions because the system has a lower potential energy for this configuration. Thus an electrical double layer is formed which consists of electrons on the surface of the metal and hydronium ions on the solution side with a layer of oriented water molecules between them. The possibility of salt formation $Hg_2(ClO_4)_2$ is ruled out because no heat is released in this process. Transfer of mercurous ions from metal to the solution will continue until a potential is built up which would prevent any further transfer of the ions. Since mercury has a high hydrogen

overvoltage the hydronium ions cannot be reduced to form hydrogen.

It was experimentally observed that when a mercury electrode was introduced in a bath of perchloric acid a potential difference was established on a time scale of microsecond. The trace of such a curve is shown in Fig. A.2. Grahame[9] has ststed that ionic equilibrium in the solution is attained in a matter of microsecond, and this is in agreement with our experimental result (Fig. A.2).

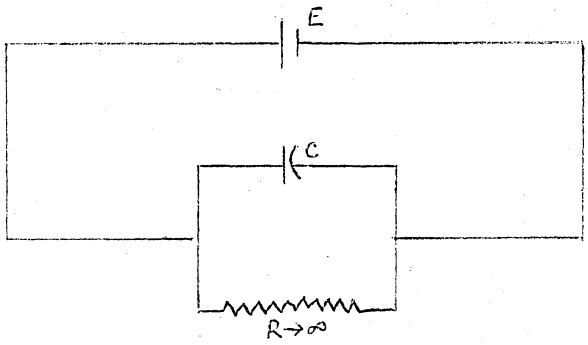

Fig. A.1. Equivalent circuit of a polarizable interface.

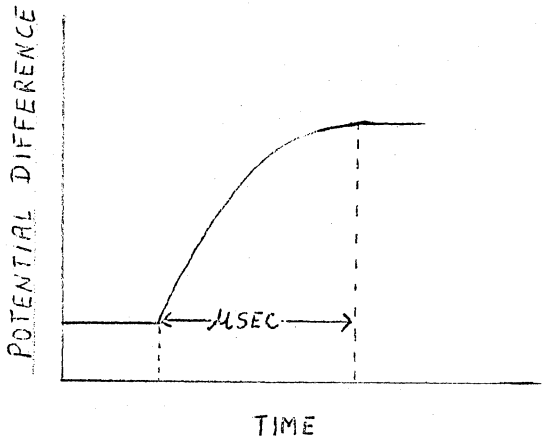

Fig. A.2. Trace of the potential difference when mercury and electrolyte phases are brought together.

APPENDIX B

Mechanics of the Apparatus.

The equation for the velocity of the carriage C can be determined by considering seperately the linear motion of the carriage, and the linear motion and the angular rotation of the screw, lever arm and the hammer with mass attached to it.

a) Linear Motion of the Carriage

The forces acting on the carriage are shown in Fig. B.1. Newton's equation for the motion of the carriage of mass m_c having velocity v is

$$m_c \frac{dv}{dt} = F_s - F_{ap} - f \qquad (1)$$

where F_s is the force exerted by the screw on the carriage, F_{ap} is the force due to the air pressure, and f is the frictional force. This frictional force f consists of two terms:

1) the friction due to the carriage sliding on the bars, given by $\mu_{kc} m_c g$, where μ_{kc} is the coefficient of sliding friction.
2) the friction between the teflon pistons and glass given by bv, where b is a constant.

Hence, Equation 1 becomes

$$m_c \frac{dv}{dt} = F_s - F_{ap} - \mu_{kc} m_c g - bv \qquad (A)$$

b) Linear Motion of the Screw, Lever Arm and Hammer with Mass Attached To It.

The linear acceleration of the screw x_s is given by the equation

$$(m_s+m_A+m_H+m)\ddot{x}_s = N_H-F_c' \tag{2}$$

where m_s is the mass of the screw, m_A is the mass of the lever arm, m_H is the mass of the hammer, m is the mass attached to the hammer, N_H is the force exerted by the screw threads of the holder H, and F_c' is the force exerted by the carriage on the screw.

But, by Newton's third law, the force exerted by the carriage on the screw is equal and opposite to the force F_s exerted by the screw on the carriage, and thus Equation 2 becomes

$$(m_s+m_A+m_H+m)\ddot{x}_s = N_H-F_s \tag{B}$$

c) Angular Rotation of the Screw, Lever Arm and Hammer with Mass Attached To It

Fig. B.2 shows the cross section of the screw of radius R_s with the lever arm and hammer with mass attached to it. The equation of motion for the angular acceleration $\ddot{\theta}$ of this screw assuming R_A and α remain constant is

$$[I_s+m_A(R_A/2)^2+(m+m_H)R_A^2]\ddot{\theta} = (m+m_H)gR_A\sin\alpha + m_Ag(R_A/2)\sin\alpha-\Gamma_i \tag{C}$$

where I_s is the moment of inertia of the screw, R_A is the length of the lever arm, α is the angle between the lever arm and the hammer,

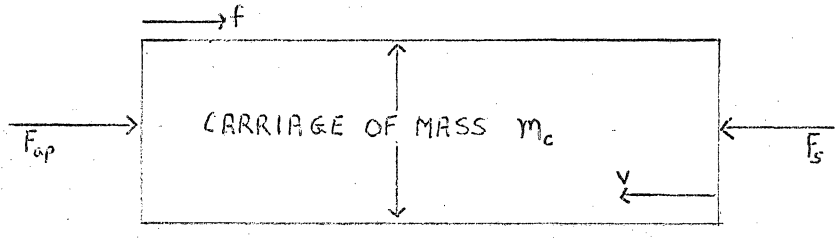

Fig. B.1. Forces acting on carriage of mass m_c.

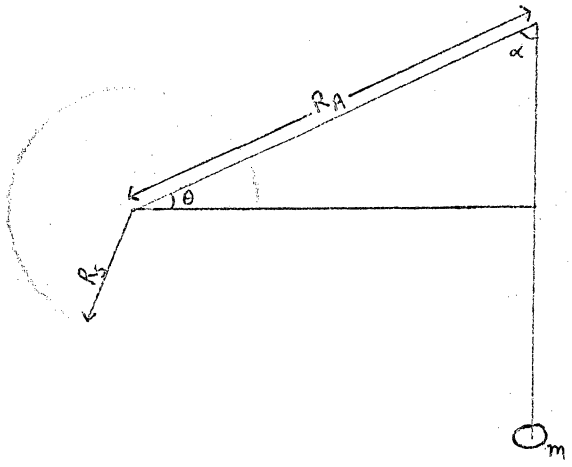

Fig. B.3. Front cross-sectional view of the apparatus.

and Γ_i is given as

$$\Gamma_i = \mu_{kh} R_s N_H + \mu_{kn} r_{eff} F_s \tag{3}$$

where μ_{kh} is the coefficient of sliding friction of the screw in the holder H, μ_{kn} is the coefficient of sliding friction of the screw in the notch N, and r_{eff} is the effective radius of the part of the screw that is in the notch N.

The acceleration of the carriage is equal to the linear acceleration of the screw which in turn is related to the angular acceleration of the screw by the pitch p, so that

$$\frac{dv}{dt} = \ddot{x}_s = p\ddot{\theta} \tag{4}$$

Using this relation, Equations A, B and C can be combined to give the equation of motion of the carriage C as

$$\{\frac{1}{p}[I_s + m_A(R_A/2)^2 + (m+m_H)R_A^2] + \mu_{kh}R_s(m_s+m_A+m_H+m) + \mu_{kc}r_{eff}m_c\}\frac{dv}{dt} = \{(m+m_H)gR_A\sin\alpha$$

$$+ m_A g(R_A/2)\sin\alpha - \mu_{kh}R_s(F_{ap}+\mu_{kc}m_c g) - \mu_{kc}r_{eff}(F_{ap}+\mu_{kc}m_c g)\} - \mu_{kh}R_s bv \tag{D}$$

or

$$\frac{dv}{dt} = \frac{K}{m_{eff}} - \frac{\mu_{kh}R_s bv}{m_{eff}} \tag{E}$$

where m_{eff} is the curly bracket on the left hand side of Equation D and K is the curly bracket on the right hand side of Equation D.

Now K and m_{eff} are of the order of 10^6 and $\mu_{kh}R_s bv$ is of the order of 10. The second term on the right hand side of Equation E is

very small (since m_{eff} is very large) compared to $\mu_{kh} R_s bv$ and hence can be neglected. Thus,

$$\frac{dv}{dt} = \frac{K}{m_{eff}} = a \text{ (constant)} \qquad (F)$$

where a is the acceleration of the carriage.

Equation F was experimentally verified as follows: In Equation D the only variables are the mass m attached to the hammer, the length R_A of the lever arm and angle α which this lever arm makes with the hammer. By keeping R_A and α fixed and varying m, the acceleration of the carriage can be varied. This was done experimentally and Table B.1 shows the values obtained for the acceleration of the carriage with different mass m attached to the hammer.

For the evaluation of Equation F, r_{eff} was obtained from Equation D, by applying the condition for no turning of the screw. For this case Equation D becomes

$$0 = (m+m_A)gR_A\sin\alpha + m_A g(R_A/2) - \mu'_{sh} R_s (F_{ap} + \mu'_{sc} m_c g) - \mu'_{sc} r_{eff} (F_{ap} + \mu'_{sc} m_c g)$$

from which r_{eff} can be found. In the above equation μ'_s are the coefficients of static friction. The agreement between the values obtained from the experiment and from the evaluation of Equation F (theory) is also shown in Table B.1.

Thus the acceleration of the carriage can be kept constant by attaching the same mass to the hammer, while the velocity of the carriage can be varied by letting the hammer fall from different heights (this would change the time of fall), for fixed values of R_A and α.

Since the pistons were attached to the carriage they would move with the same velocity v as that of the carriage while the mercury drop in the capillary would have a velocity v_m given by:

$$v_m A_m = vA$$

where A_m is the cross-sectional area of the capillary and A is the cross-sectional area of the glass cups.

For evaluating Equation E the following values were used:

I_s=16.01 gm-cm^2	Moment of inertia of the screw
m_s=142 gms	Mass of the screw
R_s=.475 cm	Radius of the screw
p=.15/2π	Pitch of the screw threads
m_c=416 gms	Mass of the carriage including pistons
m_H=528 gms	Mass of the hammer without weights
m_A=68 gms	Mass of the lever arm
F_{ap}=6.705x10^6 dynes	Force due to air pressure of 70 lbs./sq.in.
R_p=.375 cm	Radius of teflon pistons
A_p=.44/cm^2	Cross-sectional area of teflon pistons
R_c=.665 cm	Radius of air cylinder
A_c=1.389 cm^2	Cross-sectional area of air cylinder
μ_{kc}=1.4	Coefficient of sliding friction for Al. on Al.
μ'_{sc}=1.05	Coefficient of static friction for Al. on Al.
μ_{kh}=.44	Coefficient of sliding friction for steel in brass
μ'_{sh}=.51	Coefficient of static friction for steel in brass
μ_{kn}=.44	Coefficient of sliding friction for steel in brass
r_{eff}=.0785 cm	Effective radius of screw in notch N

Table B.1. Values of Acceleration of Carriage and Mass Attached to Hammer

Mass	Acceleration of Carriage in cm/sec^2	
m in gms	Experiment	Theory
87	1.77	1.915
174	1.85	2.04
261	2.01	2.15
348	2.15	2.28
439	2.30	2.305
530	2.41	2.46

Method for Measuring the Velocity and the Acceleration of the Mercury Drop

Two metal flags were attached to the hammer. These flags were made to pass through slits in wooden blocks to which a light pipe and a photo diode were inserted in the holes at either sides. When the flags pass by the holes they would block the light and change the resistance of the photo diode which in turn would trigger electronic timers. The first flag was used to start one electronic timer at the instant the hammer was released from some height and to stop the timer at the instant the hammer came to a stop. Thus, this timer measured the time it took the hammer to drop. Another timer was used to measure the time it took a second flag (.5 cm. in breadth) to pass the hole, just before the hammer came to a stop. This gave the instanteneous (maximum) velocity of the hammer, just before it came to a stop. This velocity of the hammer was related to the maximum velocity of the mercury drop by a coupling constant k; which is the ratio of the distance the hammer moved to the distance the drop moved. Thus, by knowing the velocity of the drop and the time it travelled, the acceleration was computed using Equation F.

APPENDIX C

In order to derive the curvature of a stationary liquid-liquid interface inside a glass capillary tube we choose an axially symmetric cylindrical coordinate system $(r(z),\phi,z)$ as shown in Fig. C.1. A unit tangent vector to the interface is

$$\hat{T} = \frac{\dot{r}\hat{r}+\hat{z}}{(1+\dot{r}^2)^{\frac{1}{2}}}$$

and a unit normal vector is

$$\hat{n} = \frac{\dot{r}\hat{z}-\hat{r}}{(1+\dot{r}^2)^{\frac{1}{2}}}$$

Consider an annular ring of radius $r(z)$ which consists of the surface material of the interface. The area of the annulus (Fig. C.1) is

$$dA = 2\pi r(1+\dot{r}^2)^{\frac{1}{2}}dz$$

The component of the force due to the pressure difference Δp_o across the interface in the z direction is

$$F_z = \Delta p_o \hat{n}\cdot\hat{z}dA$$

Since the components of this force in the radial direction cancel out, the total force F_p due to the pressure difference across the interface is

$$F_p = \Delta p_o \frac{\dot{r}}{(1+r^2)^{\frac{1}{2}}} 2\pi r(1+r^2)^{\frac{1}{2}}dz = 2\pi\Delta p_o r\dot{r}dz \qquad (1)$$

For a stationary fluid-fluid interface this force due to pressure difference must equal to the force due to surface tension. The forces of

surface tension in the z direction on the annulus are obtained by considering the forces on the edges at $r(z\pm dz/2)$ and $z\pm dz/2$. The directions of these forces are along the tangent vectors $\hat{T}(z\pm dz/2)$ as shown in Fig. C.2. The total force due to surface tension in the z direction is

$$F_{ST} = \hat{T}(z+dz/2)\cdot\hat{z}2\pi r(z+dz/2)\gamma - \hat{T}(z-dz/2)\cdot\hat{z}2\pi r(z-dz/2)\gamma$$

Expanding T(z dz/2) and r(z dz/2) in the above equation in a Taylor series about z gives the total force due to the surface tension as

$$F_{ST} = \left(\frac{1}{(1+\dot{r}^2)^{\frac{1}{2}}} - \frac{\dot{r}\ddot{r}}{(1+\dot{r}^2)^{3/2}}\frac{dz}{2}\right)2\pi\gamma\left(r+\dot{r}\frac{dz}{2}\right) - \left(\frac{1}{(1+\dot{r}^2)^{\frac{1}{2}}} + \frac{\dot{r}r}{(1+\dot{r}^2)^{3/2}}\frac{dz}{2}\right)2\pi\gamma\left(r-\dot{r}\frac{dz}{2}\right)$$

or

$$F_{ST} = 2\pi\gamma dz\left(\frac{\dot{r}}{(1+\dot{r}^2)^{\frac{1}{2}}} - \frac{r\dot{r}\ddot{r}}{(1+\dot{r}^2)^{3/2}}\right) \qquad (2)$$

Equating equations 1 and 2 gives

$$\Delta p_o 2\pi r\dot{r}dz = 2\pi\gamma dz\left(\frac{\dot{r}}{(1+\dot{r}^2)^{\frac{1}{2}}} - \frac{r\dot{r}r}{(1+\dot{r}^2)^{3/2}}\right)$$

from which

$$\Delta p_o = \gamma\left(\frac{1}{r(1+\dot{r}^2)^{\frac{1}{2}}} - \frac{\ddot{r}}{(1+\dot{r}^2)^{3/2}}\right)$$

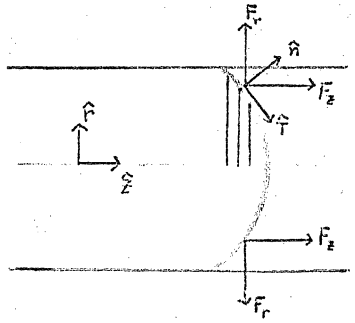

Fig. C.1. Geometry of a mercury-electrolyte interface.

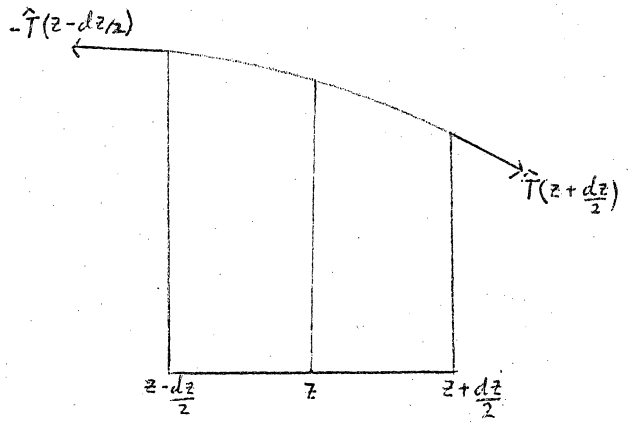

Fig. C.2. Tangential forces on the annulus of interface.

APPENDIX D

The data for the constant acceleration experiment is given in Tables D.1 to D.5 and for the constant velocity experiment in Tables D.6 to D.10. The symbols used in these data are as follows:

i.d. - Internal diameter of the capillary tube

τ - Decay constant computed by using exponential fit

Comp. - Output voltage computed by using exponential fit

Pict. - Maximum output voltage as read from the photograph

M.Vel. - Maximum velocity to which the drop was accelerated

T.F. - Time of fall of the hammer

Acc. - Acceleration of the mercury drop

Disp. - Displacement of the mercury drop

Vol. - Volume of the mercury drop assuming hemispherical ends

S.A. - Surface area of the mercury drop assuming hemispherical ends

k - Coupling constant which is the ratio of the distance the hammer moved to the distance the drop moved

s.p. - Streaming potential due to the flow of electrolyte only

TABLE D1. DATA FOR THE CONSTANT ACCELERATION EXPERIMENT

Tube i.d.=.5mm.	τ m.sec.	Comp. Volt	Pict. Volt	M.Vel. cm/sec	T.F. sec.	Acc. cm/sec^2	Disp. cm
Drop 0.52 cm	111.28	.213	.24	17.21	.0557	308.97	.45
Vol=$9.87 \times 10^{-4} cm^3$	74.68	.292	.32	18.95	.0572	331.45	.53
S.A.=$7.95 \times 10^{-2} cm^2$	34.36	.464	.44	20.76	.0542	382.48	.57
k=1.911	23.13	.617	.60	22.55	.0672	335.54	.74
	33.62	.707	.68	24.20	.0679	356.33	.80
Drop 1.00 cm	203.87	.468	.47	12.97	.0473	274.29	.27
Vol=$19.30 \times 10^{-4} cm^3$	106.38	.577	.565	16.58	.0673	246.28	.54
S.A.=$15.7 \times 10^{-2} cm^2$	33.54	.662	.69	21.50	.0777	279.95	.84
k=1.795	25.71	.723	.74	25.79	.0827	311.59	.99
	33.10	.760	.75	27.30	.0988	276.20	1.30
	42.57	.781	.76	30.50	.1081	282.12	1.56
Drop 1.52 cm	223.46	.450	.44	8.53	.0814	104.76	.31
Vol=$29.51 \times 10^{-4} cm^3$	175.65	.478	.48	9.51	.0888	107.13	.40
S.A.=$24.1 \times 10^{-2} cm^2$	119.74	.593	.58	10.69	.1043	102.45	.57
k=1.835	76.51	.622	.61	11.12	.1162	95.65	.68
	51.86	.648	.64	12.47	.1364	91.41	.83
	70.37	.679	.66	13.95	.1712	81.47	1.07
Drop 2.00 cm	154.75	.631	.64	19.62	.0659	297.55	.60
Vol=$39.15 \times 10^{-4} cm^3$	129.80	.649	.66	22.91	.0753	298.69	.83
S.A.=$31.5 \times 10^{-2} cm^2$	90.55	.679	.68	25.94	.1002	258.87	1.30
k=1.633	52.79	.707	.69	27.83	.1012	274.98	1.53
	59.41	.711	.70	31.89	.1633	195.21	2.68

TABLE D2. DATA FOR THE CONSTANT ACCELERATION EXPERIMENT

Tube i.d.=1mm.	τ m.sec.	Comp. Volt	Pict. Volt	M.Vel. cm/sec	T.F. sec.	Acc. cm/sec^2	Disp. cm
Drop 0.58 cm	-	.295	.33	3.89	.0679	57.22	.15
Vol=$42.3x10^{-4}cm^3$	35.71	.465	.45	4.39	.0799	54.94	.17
S.A.=$17.5x10^{-2}cm^2$	25.75	.529	.46	5.55	.0942	58.88	.27
k=5.813	24.11	.530	.465	6.25	.1053	59.35	.34
	23.20	.522	.47	7.69	.1568	49.02	.59
	27.51	.487	.48	8.53	.1683	50.68	.70
	35.54	-	-	9.57	.1811	52.83	.87
	47.73	.507	.49	10.16	.1681	60.41	.84
Drop 1.03 cm	-	.151	.15	2.95	.0654	45.10	.11
Vol=$76.5x10^{-4}cm^3$	64.60	-	-	3.39	.0746	45.44	.12
S.A.=$32.1x10^{-2}cm^2$	-	.401	.39	4.50	.0819	54.90	.19
k=5.303	49.07	-	-	5.30	.0848	62.47	.24
	45.23	.513	.49	5.70	.1006	56.62	.30
	36.93	.538	.51	6.52	.1313	49.62	.41
	30.20	.541	.51	7.32	.1238	59.08	.44
	25.56	-	-	8.86	.1447	61.23	.63
	26.13	-	-	9.94	.1550	64.09	.74
Drop 1.52 cm	-	.255	.26	3.61	.0603	59.78	.10
Vol=$116.2x10^{-4}cm^3$	112.53	-	-	5.06	.0801	63.16	.19
S.A.=$48.9x10^{-2}cm^2$	-	.422	.48	5.49	.0863	63.57	.26
k=5.58	79.28	.516	.50	8.27	.1514	54.60	.64
	58.82	.537	.51	9.73	.1546	62.90	.73
Drop 2.08 cm	140.72	.309	.35	4.89	.0731	66.81	.06
Vol=$156.4x10^{-3}cm^3$	106.95	.431	.44	7.36	.0974	75.50	.09
S.A.=$64.8x10^{-2}cm^2$	82.64	.504	.50	8.94	.1763	61.09	.13
k=5.63	93.11	.516	.51	9.90	.1582	62.55	.16

TABLE D3. DATA FOR THE CONSTANT ACCELERATION EXPERIMENT

Tube i.d.=1.5mm	τ m.sec.	Comp. Volt	Pict. Volt	M.Vel. cm/sec	T.F. sec.	Acc. cm/sec^2	Disp. cm
Drop 0.48 cm	37.06	.255	.24	4.32	.0609	70.968	.11
Vol=$78.5 \times 10^{-4} cm^3$	-	.318	.29	5.33	.0757	70.44	.19
S.A.=$22.8 \times 10^{-2} cm^2$	28.35	.361	.31	5.87	.0906	64.83	.27
k=10.381	19.23	.315	.34	7.06	.1057	66.62	.34
	16.21	.322	.35	8.10	.1329	60.96	.49
Drop 1.1 cm	106.47	.326	.30	4.48	.1113	40.30	.26
Vol=$185.4 \times 10^{-4} cm^3$	75.24	.380	.36	5.92	.1308	45.26	.36
S.A.=$51.82 \times 10^{-2} cm^2$	70.07	.420	.40	7.22	.1502	48.08	.52
k=10.536	55.86	.446	.41	8.00	.2034	39.33	.78
	47.10	.411	.41	8.64	.2827	30.57	1.10
Drop 1.51 cm	65.48	.211	.21	3.78	.0631	59.91	.10
Vol=$256.8 \times 10^{-4} cm^3$	100.73	.325	.33	4.85	.0737	65.85	.20
S.A.=$71.1 \times 10^{-2} cm^2$	115.38	.363	.38	5.69	.0844	67.50	.26
k=10.616	123.83	.387	.40	6.32	.1024	61.68	.31
	-	.396	.42	6.99	.1130	61.84	.37
Drop 2.08 cm	95.60	.274	.29	4.15	.0818	50.81	.15
Vol=$360.5 \times 10^{-4} cm^3$	104.72	.307	.33	5.30	.0936	56.64	.23
S.A.=$98.1 \times 10^{-2} cm^2$	126.72	.351	.37	6.15	.1067	57.64	.31
k=10.588	172.98	.386	.40	6.99	.1114	62.73	.37

TABLE D4. DATA FOR FIXED ACCELERATIONS

Tube i.d.=.5mm	τ m.sec.	Comp. Volt	Pict. Volt	M.Vel. cm/sec	T.F. sec.	Acc. cm/sec^2	Disp. cm
Drop 1 cm	80.71	.602	.66	14.85	.0727	204.09	.55
Vol=$19.307 \times 10^{-4} cm^3$	52.83	.731	.75	16.32	.0795	205.12	.64
S.A.=$15.7 \times 10^{-2} cm^2$	22.57	.791	.80	17.65	.0893	197.61	.80
k=1.863	18.31	.867	.85	19.00	.0976	194.52	.92
	21.03	-	-	20.23	.1004	201.36	1.03
Drop 1 cm	105.73	.570	.60	16.50	.0673	246.28	.49
Vol=$19.307 \times 10^{-4} cm^3$	32.37	.743	.75	21.27	.0847	250.95	.85
S.A.=$15.7 \times 10^{-2} cm^2$	27.09	.822	.83	23.70	.0943	253.59	1.01
k=1.831	33.74	-	-	28.03	.1112	252.03	1.43
	42.60	.911	.90	30.60	.1218	251.20	1.72
Drop 1 cm	253.50	.417	.40	16.60	.0556	298.52	.43
Vol=$19.307 \times 10^{-4} cm^3$	122.78	.571	.55	22.99	.0750	306.39	.72
S.A.=$15.7 \times 10^{-2} cm^2$	41.63	.666	.65	26.83	.0929	291.29	1.27
k=1.913	43.30	.692	.69	29.27	.0959	305.14	1.38
Drop 1 cm	-	.541	.57	24.61	.0621	395.71	.68
Vol=$19.307 \times 10^{-4} cm^3$	-	.582	.64	28.47	.0740	384.81	.96
S.A.=$15.7 \times 10^{-2} cm^2$	-	.625	.73	34.37	.0876	392.12	1.35
k=1.890	-	.637	.74	36.91	.0953	387.26	1.70

TABLE D5. DATA FOR FIXED ACCELERATIONS

Tube i.d.=1 mm	Comp. Volt	Pict. Volt	M.Vel. cm/sec	T.F. sec.	Acc. cm/sec^2	Disp. cm
Drop 1 cm	.405	.38	3.88	.1465	26.48	.27
Vol=$75.91 \times 10^{-4} cm^3$	.455	.42	4.06	.1578	25.72	.315
S.A.=$31.4 \times 10^{-2} cm^2$	.478	.45	4.39	.1723	25.47	.36
k=5.731	.525	.52	5.50	.2101	26.17	.57
	.581	.58	7.50	.2892	25.93	1.11
Drop 1 cm	.432	.39	4.56	.0895	50.91	.20
Vol=$75.91 \times 10^{-4} cm^3$	.518	.45	5.30	.1047	50.60	.27
S.A.=$31.4 \times 10^{-2} cm^2$	.510	.49	5.75	.1119	51.37	.32
k=5.385	.589	.51	6.53	.1275	51.18	.416
	.588	.52	7.32	.1448	50.53	.530
Drop 2 cm	.306	.32	5.02	.0793	63.23	.20
Vol=$75.91 \times 10^{-4} cm^3$	.344	.45	7.23	.1148	62.95	.41
S.A.=$31.4 \times 10^{-2} cm^2$	.491	.50	8.94	.1412	63.31	.63
k=5.480	.530	.51	9.94	.1577	63.01	.78

TABLE D6. DATA FOR CONSTANT VELOCITY

Tube i.d.=.5 mm
Distance between the probes=223 cm

Velocity Time sec	Drop Time sec	Drop Velocity cm/sec	Drop Length cm	Output Voltage m.V.	S.P. m.V.
25.691	.055	8.68	.477	140	-3
25.661	.065	8.69	.565	162	-2
25.780	.095	8.65	.821	190	-2
25.661	.123	8.69	1.07	195	-1
25.632	.149	8.70	1.29	195	-5
25.602	.183	8.71	1.60	195	-1
25.632	.232	8.70	2.02	198	-3
37.232	.064	6.07	.39	72	-3
37.232	.080	6.07	.49	110	-2
36.677	.098	6.08	.60	147	-1
36.497	.150	6.11	.92	170	-5
36.319	.180	6.14	1.11	174	-3
36.398	.254	6.13	1.56	174	-2
36.084	.307	6.18	1.90	175	-2

TABLE D7. DATA FOR CONSTANT VELOCITY

Tube i.d.=1.19 cm
Distance between the probes=198.5 cm

Velocity Time sec	Drop Time sec	Drop Velocity cm/sec	Drop Length cm	Output Voltage m.V.	S.P. m.V.
34.947	.147	5.68	.84	148	-3
34.642	.157	5.73	.90	155	-2
34.885	.173	5.69	.99	167	-1
34.885	.191	5.69	1.09	175	-4
34.763	.262	5.71	1.50	197	-5
34.763	.288	5.71	1.65	192	-4
34.824	.333	5.70	1.90	198	-3
34.824	.349	5.70	1.99	200	-3
17.504	.070	11.34	.8	182	-3
17.504	.073	11.32	.83	190	-3
17.535	.093	11.28	1.06	213	-2
17.550	.108	11.31	1.23	227	-1
17.550	.114	11.31	1.29	230	-3
17.566	.136	11.30	1.54	232	-2
17.535	.171	11.32	1.94	237	-1
9.763	.034	20.33	.7	215	-5
9.836	.035	20.18	.72	220	-3
9.831	.037	20.19	.75	230	-2
9.773	.039	20.31	.80	235	-1
9.797	.041	20.26	.85	245	-3
9.836	.050	20.18	1.02	270	-3
9.773	.059	20.31	1.21	280	-3
9.821	.065	20.21	1.32	285	-2
9.797	.081	20.26	1.65	292	-1
9.841	.094	20.17	1.9	292	-3

TABLE D8. DATA FOR CONSTANT VELOCITY

Tube i.d.=1.72 mm
Distance between the probes=194 cm

Velocity Time sec	Drop Time sec	Drop Velocity cm/sec	Drop Length cm	Output Voltage m.V.	S.P. m.V.
19.897	.061	9.75	.6	1.9	-3
21.248	.131	9.13	1.2	8	-2
20.145	.156	9.63	1.51	10	+3
19.517	.228	9.94	2.27	13	+3
21.225	.257	9.14	2.35	13	-3
19.715	.240	9.84	2.37	13	-4
Distance between the probes=198.5 cm					
10.491	.032	18.92	.60	3	-2
10.718	.040	18.52	.75	7	-3
10.552	.046	18.81	.88	9	+2
10.469	.055	18.96	1.06	21	-3
10.782	.119	18.41	2.20	28	+2
10.436	.133	19.02	2.53	29	-3
35.573	.241	5.58	1.35	.5	-1
39.463	.337	5.03	1.70	2.7	-1
38.099	.403	5.21	2.10	4	+3
35.446	.410	5.60	2.30	4	+2
36.556	.445	5.43	2.42	4	+2

TABLE D9. DATA FOR THE SHORT CIRCUIT CURRENT

Tube i.d.=.5 mm
Distance between the probes=223 cm

Velocity Time sec	Drop Time sec	Drop Velocity cm/sec	Drop Length cm	Current μA
37.478	.062	5.95	.369	.12
36.142	.080	6.17	.495	.28
37.353	.120	5.97	.72	.36
37.416	.256	5.96	1.53	.37
35.794	.361	6.23	2.25	.37
35.909	.373	6.21	2.32	.37
27.599	.053	8.08	.43	.24
27.429	.073	8.13	.60	.35
27.633	.111	8.07	.90	.40
27.463	.151	8.12	1.23	.44
27.429	.221	8.13	1.80	.44
26.932	.311	8.28	2.58	.44

TABLE D10. DATA FOR THE SHORT CIRCUIT CURRENT

Tube i.d.=1.19 mm
Distance between the probes=198.5 cm

Velocity Time sec	Drop Time sec	Drop Velocity cm/sec	Drop Length cm	Current μA
14.736	.038	13.47	.52	1.06
14.617	.067	13.58	.92	1.34
15.060	.094	13.18	1.25	1.51
15.049	.159	13.19	2.10	1.60
15.026	.186	13.21	2.46	1.61
32.594	.141	6.09	.86	.66
33.473	.150	5.93	.89	.73
33.028	.153	6.01	.92	.77
33.028	.209	6.01	1.26	.99
33.028	.262	6.01	1.58	1.06
33.417	.287	5.94	1.73	1.08
32.973	.555	6.02	3.34	1.11
21.139	.061	9.39	.58	.83
21.275	.096	9.33	.9	1.0
21.413	.116	9.27	1.08	1.16
21.482	.145	9.24	1.34	1.26
21.505	.237	9.23	2.19	1.36
21.321	.299	9.31	2.79	1.37

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DYNAMICS OF THE DOUBLE LAYER AT THE POLARIZABLE MERCURY-ELECTROLYTE INTERFACE

by

Soli S. Bamji

ABSTRACT

An experimental method of indirectly measuring the potential difference across a single mercury-electrolyte interface is suggested. By choosing a model for the moving electrolyte-mercury-electrolyte system, the maximum output voltage (which is mathematically the potential difference across a single interface) is obtained when the back end of the moving mercury drop becomesaa hemisphere and the front end becomes a flat circular disc. It has been shown that the U-effect II and the U-effect III are essentially the manifestations of the same effect namely, that the output voltage is due to the distortion of the surface areas of the two ends of the moving mercury drop while the number of dipoles across each interface remains fixed. The output voltage has been found to be dependent on the velocity and the acceleration of the mercury drop and not on the relative displacement of this drop with respect to the capillary wall. The dependence of the output voltage on the acceleration of the mercury drop is opposite to that of the velocity.