Stable, Unstable and Metastable Charged Droplets[1]

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ABSTRACT

Experiments with charged water droplets show the existence of the metastable states predicted by Cahn as well as the well-known unstable state predicted by Lord Rayleigh. The charge lost at metastability is completely recovered with time, whereas the charge lost at instability is only partially recovered. The recovery of charge may be a space-charge effect, or it may be a result of electrification that accompanies the exchange of water vapor.

1. Introduction

The exchange of matter between a solid or liquid and its environment, or between two phases of the same substance has often been found to be accompanied by electrification. Such exchange takes place in the formation of precipitation by the Bergeron mechanism, the growth of ice particles at the expense of cloud droplets. Workman and Reynolds (1950) suggested that the accompanying electrification is the source of thunderstorm electricity. Charge measurements on ice particles in partially glaciated clouds by MacCready and Takeuchi (MacCready and Baughman, 1968), Latham and Stow (1969), and Berg and Gaukler (1968a) support this view. The electrification accompanying the evaporation of water droplets has been studied by Mühleisen (1959), Dubois (1963) and Berg and George (1967). Mühleisen associated this effect with the stability of fogs.

One might expect droplets growing in precipitating warm tropical clouds, e.g., tropical thunderstorm clouds, to be charged to an extent comparable to that of growing ice particles in cold clouds, but charge measurements in tropical rain clouds are not available. Droplets in nonprecipitating cold liquid clouds are comparatively weakly charged, however.

Even the largest drop charges are usually negligible second-order effects in the overall thermodynamics of the exchange process. But they may not be negligible with respect to the kinetics and the mechanisms of the exchange. Matters of special concern here are instability and metastability of strongly charged drops, and their role in the exchange of charge and mass with the environment.

The study of these secondary effects requires experimental techniques of great sensitivity and resolution, or the choice of experimental conditions that enhance them. We have combined these two approaches. Strongly charged droplets of 100–250 μ in diameter were suspended in a non-uniform ac field and observed through a microscope, visually and photographically, and by high-speed photography. Size and charge were measured accurately and at a high resolution in time.

2. Instability and metastability of charged drops

When a charged drop shrinks by evaporation, it loses relatively more mass than charge; eventually, it becomes unstable with respect to its spherical shape and suddenly gives off charge so as to regain stability. This effect has been studied by Lord Rayleigh (1945) and more recently by Doyle *et al.* (1964), Berg and George (1967) and Abbas and Latham (1967). Before it becomes unstable, the drop may become metastable with respect to its size. This effect has been studied theoretically by Cahn (1962). We find that, under certain experimental conditions, the metastable state may be converted into an unstable state, presumably as a result of a small disturbance. A brief review of the theoretical background may help to define nomenclature and symbols and to clarify concepts.

Lord Rayleigh derived the frequencies of vibration of a charged drop of diameter d, charge q and surface tension γ. When the frequency is zero, the drop deforms proportionally to time. This occurs when

$$\frac{q^2}{2\pi\gamma d^3}=\frac{n+1}{2},\quad n=1,2,3,\cdots. \tag{1}$$

The integer n is the order of the harmonic. In particular, for $n=1$, the fundamental is

$$\frac{q^2}{2\pi\gamma d^3}=1. \tag{2}$$

On the other hand, Lord Kelvin has treated the effect of charge upon the effective surface tension γ' of a

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drop and derived the formula

$$\gamma' = \gamma - \frac{q^2}{2\pi d^3}. \tag{3}$$

When $\gamma' = 0$, the spherical shape is unstable, and (3) and (2) are identical.

Putting

$$s = \frac{q^2}{2\pi\gamma d^3}, \tag{4}$$

we obtain

$$s = \frac{n+1}{2}, \quad n = 1,2,3,\cdots \tag{5}$$

from (1) and

$$s = \frac{\gamma - \gamma'}{\gamma} \tag{6}$$

from (3). In both cases the drop is stable for $s<1$ and unstable for $s=1$. Eq. (5) also gives successive instabilities in steps of $\frac{1}{2}$ in the value of s with intermediate regions of stability.

A different approach was taken by Cahn, who related metastability to the energy of the drop as compared to that of a number of equal spherical fragments. Metastability with respect to fragmentation occurs when

$$s = \frac{1}{2}\,\frac{m - m^{\frac{2}{3}}}{m^{\frac{2}{3}} - 1}, \quad m = 1,2,3,\cdots, \tag{7}$$

m denoting the number of fragments. The values of s calculated from this formula are listed in Table 1. In contrast to (5) and (6), (7) gives metastability for $s<1$. Thus, one may say, a drop is unstable with respect to its spherical shape for $s=1$, but it may be metastable with respect to its size for $s<1$. Of course, a metastable state may be turned into an unstable state by the slightest disturbance, and there may be little practical difference between a metastable and an unstable state.

There is a remarkable resemblance between (5) and (7), namely, that the values of s form sequences of approximately the same ratios. This is brought out by the values of $12s$ in Table 1. They are half-integers within 1 or 2%. Consequently, the mere ratios in the sequence of s values as determined experimentally do not distinguish between the theories of Lord Rayleigh and Cahn. When a charged drop shrinks by evaporation, it becomes metastable at the values of $s<1$ given by Eq. (7), and it becomes unstable according to Eqs. (5) and (6) at $s=1$ whereupon s does not increase further. If the experiment is conducted under conditions such as to make the metastable drop unstable, the drop will become unstable for $s<1$ according to (7).

TABLE 1. Values of s calculated from Eq. (7) for various values of m.

m	1	2	3	4	5	6	7
s	0.250	0.347	0.425	0.494	0.536	0.588	0.628
$12s$	3.0	4.15	5.10	5.93	6.44	7.05	7.54
m	8	9	10	11	12	13	14
s	0.667	0.701	0.736	0.766	0.798	0.830	0.854
$12s$	8.00	8.42	8.85	9.19	9.56	9.96	10.25
m	15	16	17	18	19	20	25
s	0.878	0.902	0.924	0.946	0.970	0.992	1.087
$12s$	10.53	10.82	11.08	11.35	11.63	11.90	13.04
m	30	35	40	45			
s	1.173	1.250	1.323	1.387			
$12s$	14.07	15.00	15.88	16.64			

The instability is easily recognized when a droplet is suspended in an electric field by a sudden decrease in q/m. There is a considerable loss of charge, but often there is only a small loss of mass. The phenomenon bears no resemblance to instability of suspension, from which it is easily distinguished.

We have used Eq. (2) for the calculation of q, knowing γ and d, in the calibration of our suspension field (Berg and George, 1967). The results were quite reproducible. Abbas and Latham (1967) determined q and d independently as functions of time and calculated the corresponding values of s. The plot of s vs time rose gradually to $s=1$, then fell suddenly to some lower value, then increased again to $s=1$, etc., so that the plot had a saw-tooth shape for successive instabilities. The data presented here are in agreement with those results in some cases, but in other cases apparent instabilities, corresponding to metastabilities, occurred for values of $s<1$.

Whereas electrostatic instability has been verified experimentally by many investigators, metastability has apparently not been observed previously, and the results reported here apparently furnish the first experimental verification of Cahn's theory.

3. Experimental technique

The experimental technique used in this work has been used in several investigations with minor modifications (Berg and George, 1967; Berg and Gaukler, 1968a, 1969a; Berg *et al.*, 1969). The earliest of those papers gave a general description of its theory and practice. It was demonstrated in Toronto (Berg and Gaukler, 1968b) and at the New York meeting of the American Association of Physics Teachers in 1969 (Berg and Gaukler, 1969b).

A charged particle is suspended in a non-uniform ac field of 60 Hz. It thereby oscillates along the vertical axes of symmetry. The position and the amplitude depend upon the charge to mass ratio, q/m, the applied voltage V_{ac}, and the geometry of the field. This latter factor is determined empirically by the use of an unstable droplet, the charge of which is calculated from Eq. (2). Thus,

$$\frac{q}{d^3} = \frac{k_{\text{ac}}}{V_{\text{ac}}}. \tag{8}$$

As a suspended droplet evaporates, V_{ac} may be reduced gradually to hold the droplet in a fixed position at a fixed amplitude. V_{ac} is recorded for convenience and for rapid and accurate measurement. Size measurements are made by high-speed photography. An almost uniform dc field may be superimposed upon the ac field and used to lift the suspended droplet to the center of symmetry of the ac field. At this point the ac field is close to zero, but it still provides horizontal containment and a vertical restoring force so that the droplet can be held stationary. The ac voltage has then no other effect upon the suspension and

$$\frac{q}{d^3}=\frac{k_{dc}}{V_{dc}}, \tag{9}$$

where V_{dc} is the applied dc voltage. Size measurements are made by photography. Even when using the ac voltage for measurement it is convenient to lift the suspended droplet to the midpoint in order to suppress the oscillation and to bring the droplet entirely within the field of view of the high-speed camera or to permit the use of a still camera.

Eq. (8) holds exactly for a large droplets only, above 80 μ. For smaller droplets the aerodynamic drag causes a damping and a phase angle φ between the oscillations of the field and the particle. Then V_{ac} should be replaced by $V_{ac}\cos\varphi$. Although $\cos\varphi$ can be calculated, (9) is preferably used for accurate measurements with small droplets. Droplets so small that $\cos\varphi=0$, or where motion is aperiodic, cannot be suspended and do not experience a net force in the ac field. This is sometimes an advantage as compared to a dc field.

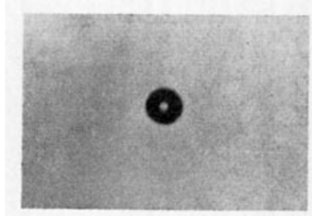

FIG. 1. Photograph of a 30μ water droplet taken with a still camera at a magnification of 80.

In order to illustrate the quality of the photographs used for size measurements, a reproduction of a photograph of a 30 μ water droplet taken with a still camera is shown in Fig. 1. The optical system, shown in Fig. 2, provides Koehler illumination with a minimum of stray light and a maximum of contrast. There is one microscope along the optical axis for shadow photography of the droplet, as in Fig. 1, and one microscope at a right angle for visual observation.

Two types of suspension chamber were used. The one shown in Fig. 3 was sealed and permitted the use of filtered air in the chamber. It had spherical electrodes inside a cylindrical electrode. The chamber shown in Fig. 4 was open and had ring-shaped electrodes. It was used for comparatively large droplets.

The charged droplets were produced by growing a drop on the tip of a hypodermic needle and tearing off

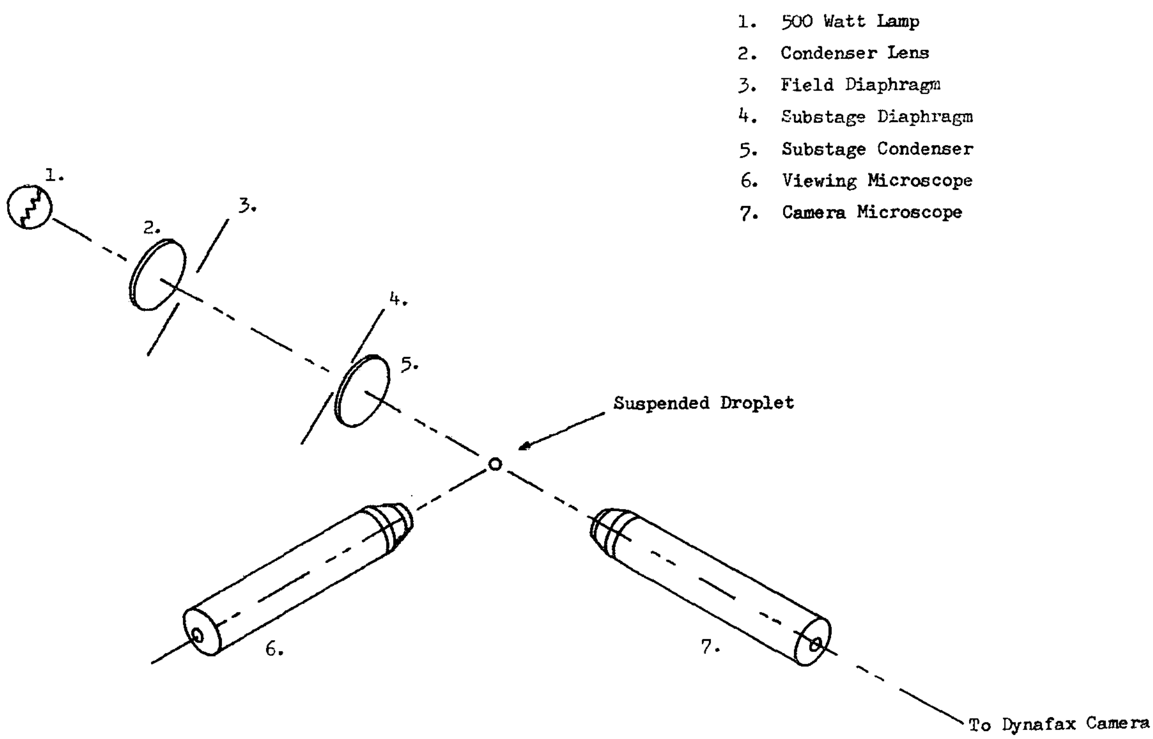

FIG. 2. The optical system for photography in shadow illumination and for observation in scattered light.

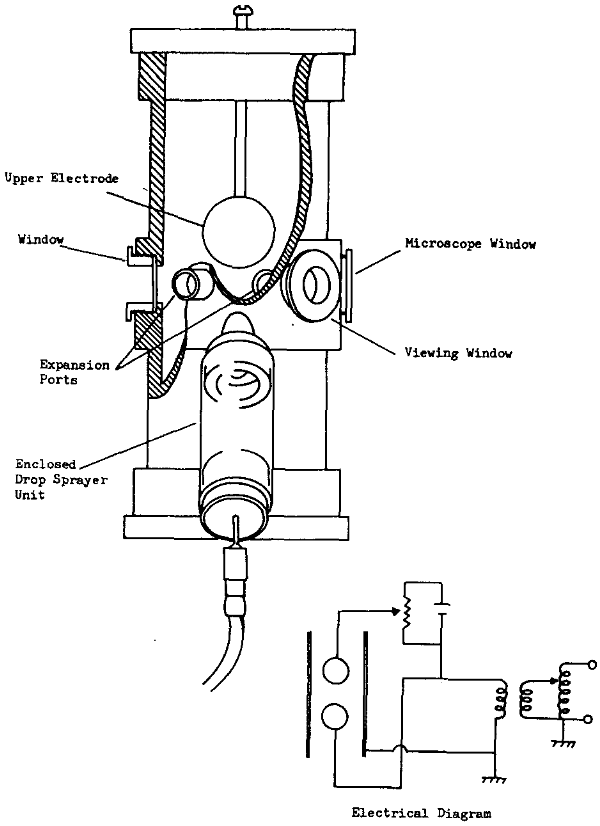

FIG. 3. Sealed suspension chamber with spherical electrodes.

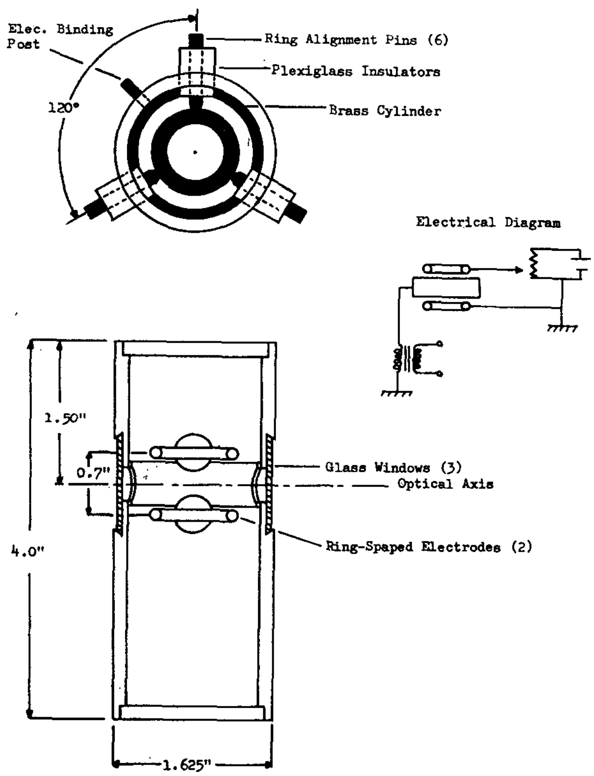

FIG. 4. Open suspension chamber with ring-shaped electrodes.

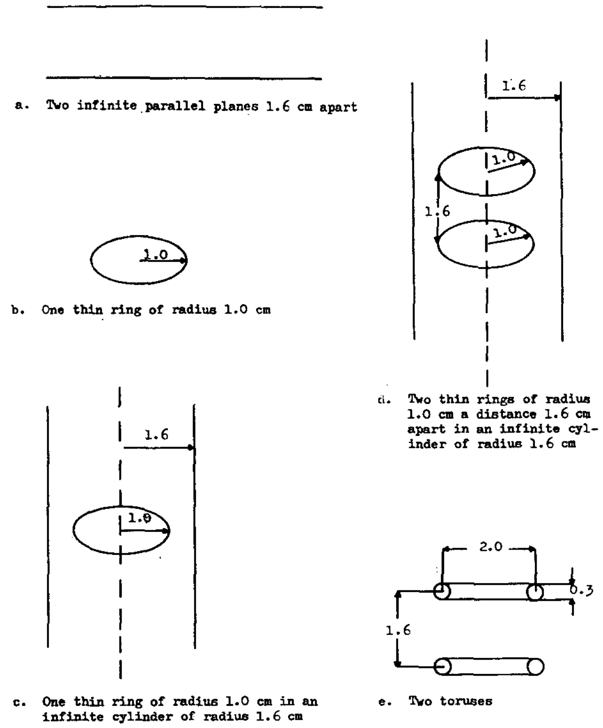

FIG. 5. Electrode configurations from which k_{dc} was calculated.

droplets by means of a field applied between it and a ring-shaped electrode. They were thrown into the chamber by the field.

Plotting $V_{ac}^{\frac{2}{3}}$ or $V_{dc}^{\frac{2}{3}}$ and d^2 vs time, two straight lines are obtained under suitable conditions, and the values of V_{ac} or V_{dc} and d at the first instability can be determined by extrapolation. By using these data inserted in Eqs. (8) or (9), the calibration value of k_{ac} or k_{dc} can be determined. The values for the chamber shown in Fig. 4 were $k_{ac}=1.27\times10^7$ and $k_{dc}=3.52\times10^5$, when q is in esu, d in cm, and V in volts.

It is conceivable that the droplets used in this calibration were not unstable but metastable. In order to check this point, we have calculated the value of k_{dc} for the electrode configurations shown in Fig. 5. The results are listed in Table 2. We also conducted an experiment in which two disks were inserted to cover the two rings and then withdrawn while the dc voltage was adjusted so as to maintain a particle suspended at the midpoint. The two values of V_{dc} with and without

TABLE 2. Calculated values of k_{dc}.

	k_{dc}
Two infinite planes 1.6 cm apart	2.5×10^5
One thin ring	4.0×10^5
One thin ring in infinite cylinder	3.0×10^5
Two thin rings in infinite cylinder	2.5×10^5
Two thick rings (toruses)	3.3×10^5
Experiment with and without disks	3.4×10^5
Comparison with spherical electrodes	3.5×10^5

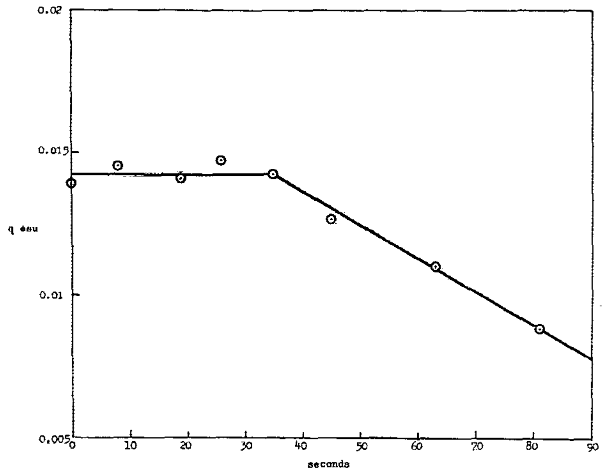

Fig. 6. Plot of q vs time for a drop suspended in clean air after charging at 3500 V.

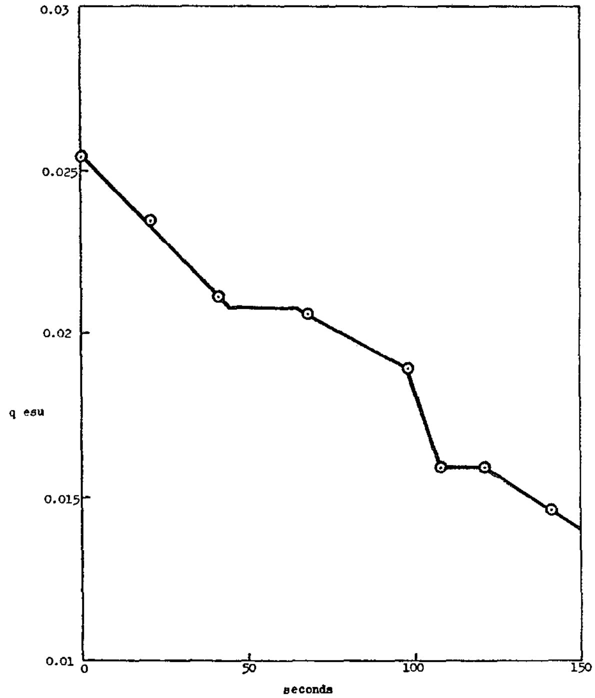

Fig. 8. Plot of q vs time for a drop suspended in laboratory air after charging at 5000 V.

disks were 19 and 26 V dc, respectively. The ratio of values of k_{dc} for parallel plates and rings was thus $26/19=1.37$. Assuming that $k_{dc}=2.5\times10^5$ for the disks as well as for parallel plates, we thus obtain $k_{dc}=3.4\times10^5$ for the rings. The calculated values of k_{dc} vary remarkably little with the electrode configuration. Finally, the value for k_{dc} for this chamber was compared with that for the chamber with spherical electrodes. The calculations support the value of k_{dc} obtained experimentally.

The size and the mass-to-charge ratio of the droplet can be selected within certain limits depending upon the choice of charging voltage and suspension (or catching) voltage, and the mode of injection of the droplet. In order to be caught in the suspension field, a droplet must have a small enough velocity. For this reason, large droplets cannot be caught when injected at a 45° angle (Fig. 3); they do not slow down rapidly enough. But large droplets can be caught when injected vertically (Fig. 4), provided they reach their apex at the level of suspension. Thus, the size of the suspended droplet may be varied by varying the distance of flight of the droplet before suspension. It is noteworthy that the velocity of the droplet also depends upon the charging voltage. The droplets were selected so as to show clearly the effects under study. The results reported previously (Berg and George, 1967) were obtained with smaller droplets, having diameters $\leqslant 100\,\mu$.

There are several differences between small and large droplets. Droplets $>200\,\mu$ occasionally split into 2, 3 or even 4 approximately equal fragments at the instant they became caught by the suspension field. This observation lends support to the basic postulate of Cahn's theory of metastability. The metastable droplet

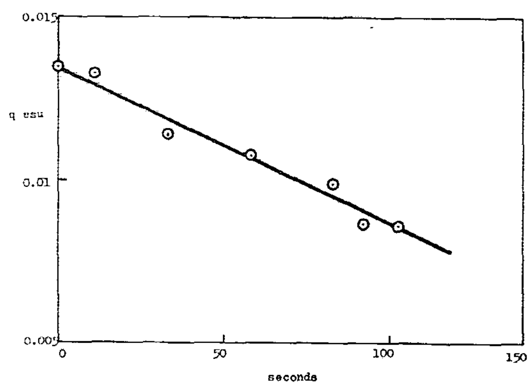

Fig. 7. Plot of q vs time for a drop suspended in laboratory air after charging at 3500 V.

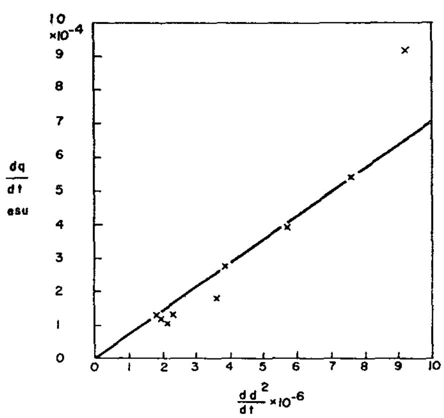

Fig. 9. Relation between rates of loss of mass and loss of charge for droplets suspended in filtered air. The initial size was $\sim150\,\mu$ for this droplet.

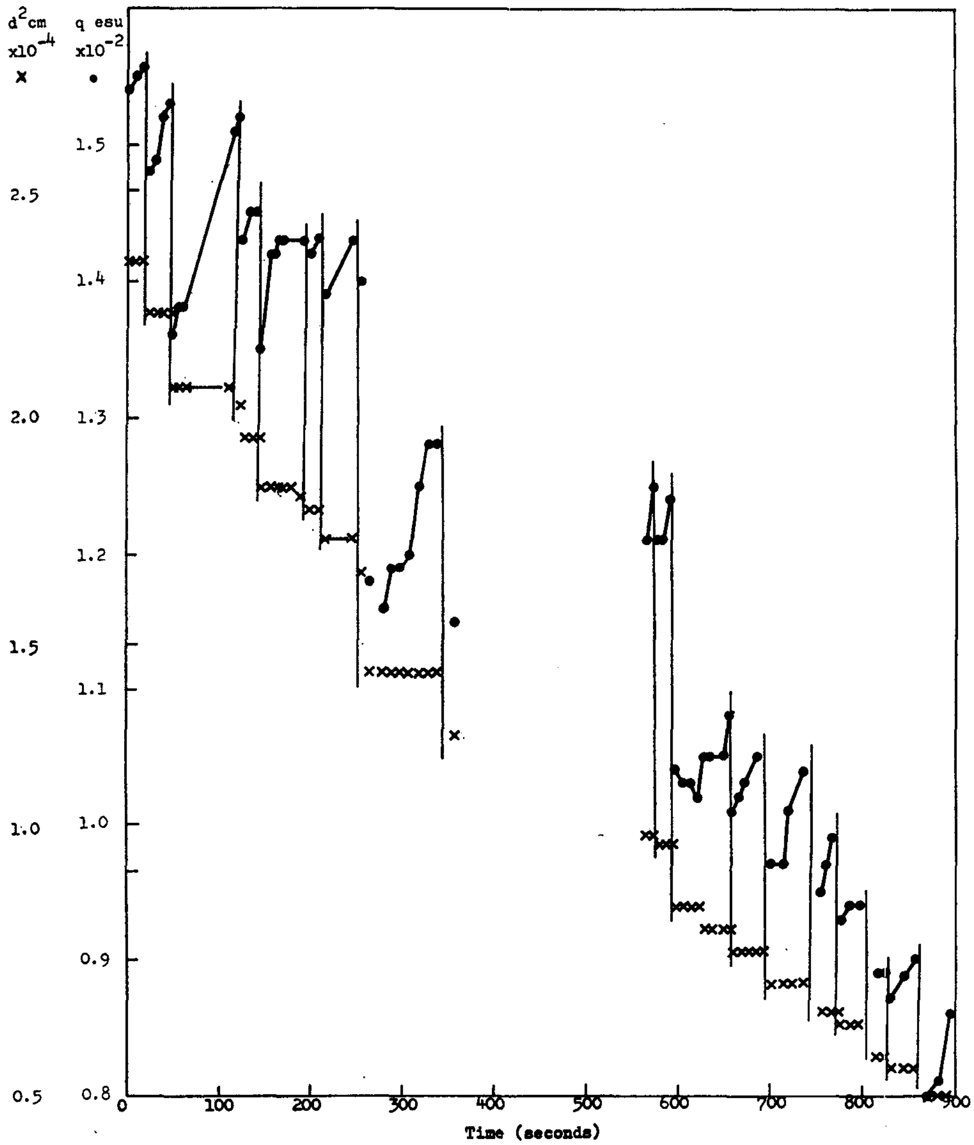

FIG. 10. Time variation of charge q and diameter square d^2 for a charged droplet suspended between spherical electrodes.

was presumably rendered unstable by the shock it experienced when suddenly caught by the field. But in no case did we observe this type of fragmentation of a suspended droplet in the course of its evaporation. Unstable droplets usually give off very little mass, and in contrast to Doyle *et al.* (1964), we have never seen ejected droplets under these circumstances. Only at a slight supersaturation of water vapor in the suspension chamber could a shower of tiny droplets be observed (Berg and George, 1967). Other differences between small and large droplets were revealed by the data.

Ordinary laboratory air contains charged dust particles in abundance. A small, say 15 μ, solid particle cannot therefore be suspended for more than a few minutes in a stream of such air. But it can be suspended indefinitely in filtered air (Berg and Gaukler, 1969a). Strongly charged droplets, 100 μ or more in diameter, are much less affected by small dust particles, but it appears that impinging dust particles would disturb the surface of the droplet. The dust also produces condensate droplets that occasionally, though rarely, collide with the suspended droplet. Such collision and coalescence produces remarkably extensive disturbances of the surface. A note on this effect is under preparation.[2] In view of these circumstances one may expect some differences in the behavior of suspended droplets in clean and dirty air. It is noteworthy that large droplets are more succeptable to surface disturbances

[2] G. Jennings: Coalescence of colliding falling water drops (to be published).

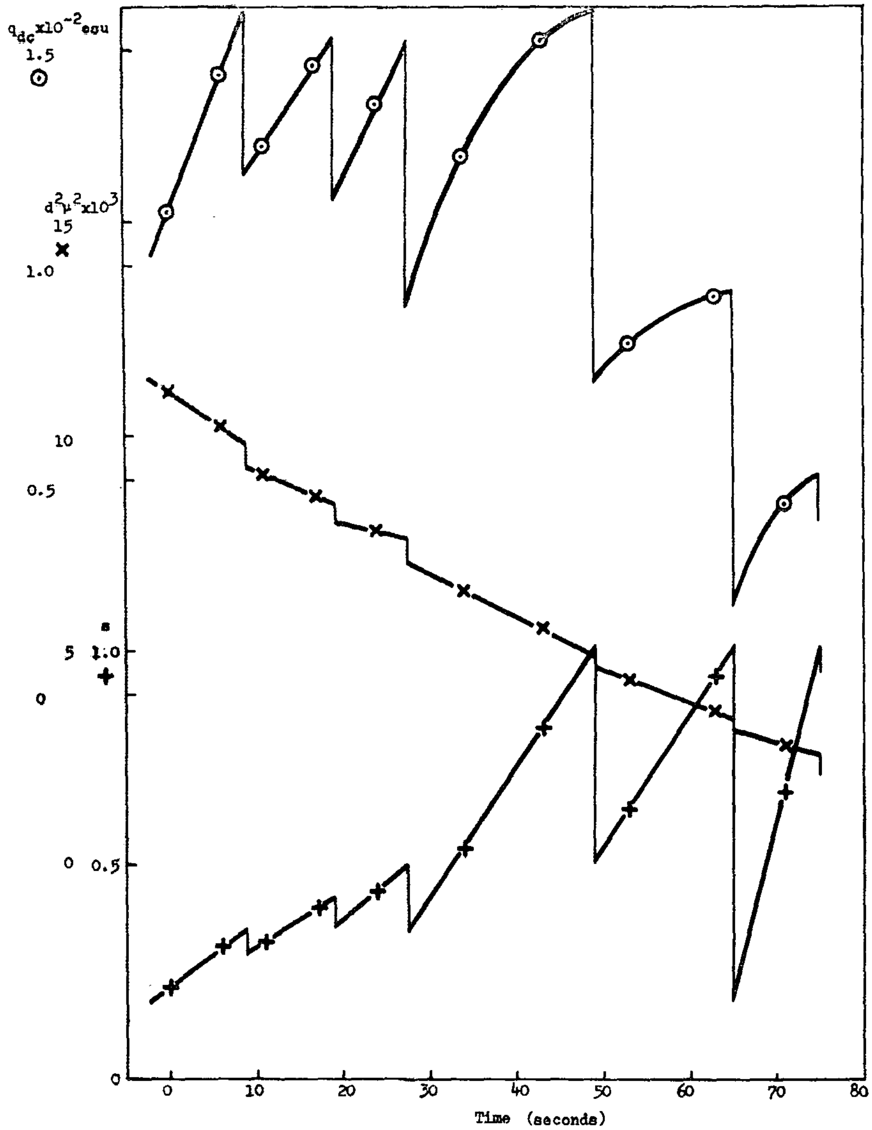

FIG. 11. Plots of q, d^2 and s vs time for a droplet suspended in the dc field and contained by a weak ac field. The last three instabilities at $s=1$ were seen by the observer and recognized as real instabilities. The values of s at the first three instabilities are 0.25, 0.43 and 0.50. The suspension chamber was that shown in Fig. 4.

than are small droplets as a consequence of their lesser rigidity.

In order to maintain reproducible conditions of slow evaporation, the humidity in the suspension chamber was held close to saturation by means of a pool of water in the chamber.

4. Experimental results

The experimental results varied with the conditions as just described. Small droplets, with diameters $\leqslant 100\,\mu$ apparently lost no charge, only mass, until they became unstable according to Eq. (2). The plots of d^2 and $V^{\frac{2}{3}}$ were linear. However, the spread of the data was sometimes far in excess of the error of measurement. Large droplets, $150\,\mu$ and more, lost substantial fractions of their charges under some circumstances. There was usually an initial rapid loss of charge that is not always reflected by the data. Time zero was taken arbitrarily after checking the droplet for its main characteristics, especially the probable time of instability. The most conspicuous difference between small and large droplets was the occasional splitting of the large droplets when caught in the suspension field. Intermediate size droplets had intermediate type characteristics. A few illustrative sets of data were presented previously (Berg and George, 1967). Figs. 6–8 show plots of q vs time for intermediate and large droplets.

These plots cannot be represented by straight lines.

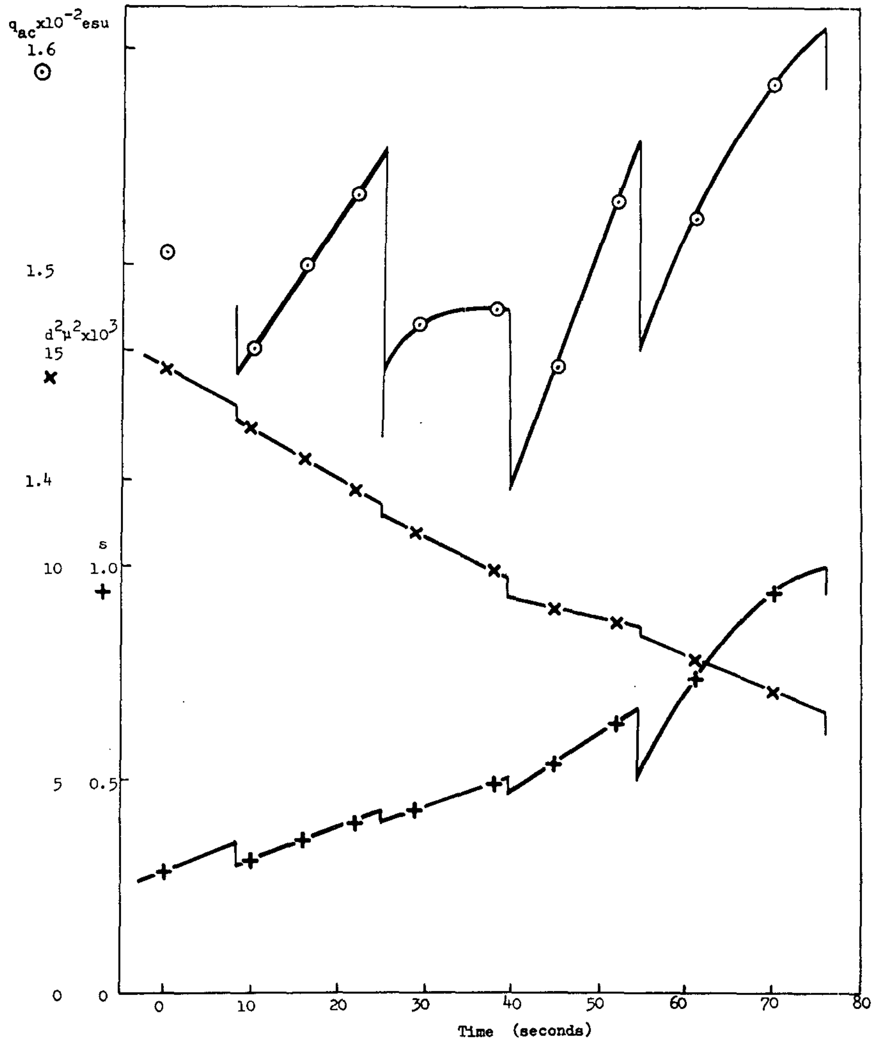

FIG. 12. Plots of q, d^2, and s vs time for a droplet suspended in the ac field with an intermittent dc field. The last instability at $s=1$ was seen by the observer and recognized as a real instability. The values of s at the preceding instabilities are 0.35, 0.43, 0.50 and 0.67. The suspension chamber was that shown in Fig. 4.

Nevertheless, the data obtained with droplets suspended in filtered air permit the definition of an average rate of loss of charge as the slope of the straight line that best matches the data. This does not apply to droplets suspended in unfiltered laboratory air. The value of dq/dt was determined for a large number of droplets, some large but most of intermediate size. Correlations among dq/dt, dd^2/dt, q and d were sought, but the only correlation found was one between the first two quantities, shown in Fig. 9.

These data were obtained with the suspension chamber shown in Fig. 3, using the high-speed camera (Dynafax) for size determinations. The camera was running at a low framing rate, say 500 frames $\sec^{-1}$, and a few frames were exposed at a time. Some twelve pictures could be taken without serious double exposure. The Dynafax has the advantage of a very short exposure time, so that it is not necessary to hold the droplet perfectly stationary. Furthermore, the pictures can be taken at very short intervals. However, it is well possible to use a still camera, as shown by the photograph in Fig. 1, and this has the advantage that a larger number of pictures can be taken, provided the event has a sufficient duration. Data obtained in this manner are shown in Fig. 10. The break in the data sequence occurred when a new film was put into the camera.

The plots in Fig. 10 explain the apparent spread of the data in Figs. 6–8. In order to follow the event, it is necessary to have a sufficient resolution in time.

Experiments were then conducted with the suspension chamber shown in Fig. 4, using the Dynafax camera. Figs. 11 and 12 show typical plots of q, d^2 and s. The droplets used in these experiments were all large.

5. Discussion

The results show that the loss of mass and the loss of charge occur in intermediate bursts. The corresponding values of s may be unity or less than unity. The data also show that such a sudden loss of charge is followed by a gradual recovery of charge, the recovery being complete, or almost complete, for $s<1$ and only partial for $s=1$. Thus, instabilities occurred according to Lord Rayleigh's Eq. (2) and also according to Cahn's Eq. (7), but there were occasional additional instabilities for s values smaller than those given by (7).

Doyle *et al.* and Abbas and Latham used a uniform dc field for the suspension of charged droplets. Our experience with that technique is that only comparatively small droplets can be suspended. Small droplets rarely show instability for $s<1$, and our observations agree in this respect with those of Doyle *et al.* and Abbas and Latham. Only the largest droplets showed instabilities for $s<1$.

The data of Doyle *et al.* show the partial recovery after an instability at $s=1$, although this is not explicitly mentioned in their paper. The data by Abbas and Latham do not show this effect. The almost complete recovery after an instability at $s<1$ is not detectable when the droplet is suspended in a uniform dc field because the technique has inadequate accuracy and resolution.

The recovery of charge could be explained in a variety of ways. The trivial explanation of exchange with a space charge does not seem to explain why the recovery is complete for $s<1$ and partial for $s=1$. As already pointed out, the exchange of mass with the environment is accompanied by electrification. This effect seems to be reversible. Reference may be given to a recent paper on this subject (Berg and Gaukler, 1969a). Accordingly, one may expect a temporary reversible disturbance of a metastable droplet to be accompanied by a temporary reversible change in charge. An irreversible change in mass may correspondingly be accompanied by an irreversible change in charge as shown in Fig. 9.

The data presented here do not permit conclusions with respect to the electrification mechanism. We think, however, that the mechanism is probably similar to the electrochemical mechanism previously proposed for electrification in the exchange of water vapor with a solid and in the freezing of water (Berg and Gaukler, 1969a), and in the friction of glass against glass (Berg and Gaukler, 1969c). This exchange should then involve not only water vapor but also other gaseous constituents of the air. There should then also be more or less pronounced effects of salts dissolved in the water. These effects are yet to be investigated.

The agreement of the data with Cahn's theory may be significant. It should be pointed out, however, that Hickman *et al.* (1952a,b, 1954) and Kingdon (1963) have found intermittent evaporation from large flat liquid surfaces in vacuo or under some dry gas.

6. Conclusions

The results presented and discussed here show that apparent instabilities may occur at charges smaller than those given by Lord Rayleigh's criterion and indicate that they are the metastabilities predicted by Cahn's theory. The results show that the exchange of vapor between a charged droplet and its environment is accompanied by electrification, and that this process is reversible. These observations seem to bear upon warm thunderstorm clouds and other warm rain clouds.

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