SOME PROPERTIES OF MERCURY DROPLETS IMPORTANT IN ELECTRONIC CHARGE MEASUREMENTS.

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INTRODUCTION.

THE work described below was incidental to additional investigation of the correction to Stokes's formula in gases,[1] using mercury spheres. Mercury has the advantage of being easily obtained in the form of small drops by several different methods; it is a liquid and therefore sphericity is assured;[2] its density and viscosity are known and are nearly constant at room temperature. In earlier work mercury spheres had been abandoned on account of the high reflecting power of their surfaces and the consequent difficulty experienced in obtaining a definite image under a microscope when the radius is only a few wave-lengths of light.[3] The method finally devised, and described below, removes this difficulty completely, and permits measurement of the radius of such spheres with a probable error of one or two per cent., and without systematic errors of comparable amount. The homogenity of such mercury droplets, and the constancy of their mass, form, and density have been matters of dispute,[4] so it seemed proper to investigate these properties, if possible, with the aid of the measuring device already constructed. The experiments show that constancy of mass is incompatible with the continued purity of the material in a gas, and that hitherto neglected chemical properties of the metal profoundly modify its behavior in this state of subdivision without correspondingly important changes in the appearance of the drops.

EXPERIMENTS.

Small spheres in a wide range of suitable sizes were deposited on a steel spring from the mercury vapor carried by a light puff of dry air sent across the surface of freshly distilled and nearly boiling mercury. The

[1] L. W. McKeehan, PHYS. REV. (1), 32, 341, March, 1911.

[2] J. Perrin suggests however, that vibrations of the surface may be caused by unbalanced molecular impacts. C. R., 152, 1165, May, 1911.

[3] J. Zeleny and L. W. McKeehan, PHYS. REV. (1), 30, 535, May, 1910.

[4] A. Schidlof and A. Karpowicz, C. R., 158, 1992, June, 1914; Ph. ZS., 16, 42, Feb., 1915; F. Ehrenhaft, Ph. ZS., 16, 227, June, 1915; 228, Aug., 1915; A. Schidlof, Ph. ZS., 16, 372, Oct., 1915.

spring was snapped against the surface of a glass plate rotating under a measuring microscope; and this plate could be enclosed if desired during the remainder of an experiment.

A microscope plate micrometer,[1] was used in measuring the spheres, one centimeter on its scale corresponding to about 7.5×10^{-6} cm. on the object measured. The accuracy of a single setting on a fixed mark is approximately 3×10^{-6} cm. Incandescent lamps with frosted globes were placed on each side of the microscope in the lower focal plane; *i. e.*, in a horizontal plane through the drop, and about 20 cm. from the axis of the microscope. When a sphere is brought to the center of the field by rotating the glass plate, the two reflected images of these lamps formed by the spherical mercury mirror appear as point source diffraction patterns against the dark background of the sphere itself. When the central disc of each pattern is as well-defined as possible, and the outer fringes are correspondingly inconspicuous, the distance between centers is measured, the width of the platinum cross-hair (0.0006 cm.) being so chosen that it can be seen clearly against the bright disc. Experiment shows that a variation in focus sufficient to make the central disc insignificant in luminosity in comparison with the first diffraction band (a variation that could not remain unnoticed in practice) does not affect the distance between the centers of the patterns whereas the same variation in focus blurs the apparent outline of the sphere enough to render impossible any measurement of its diameter by the usual method. The lateral illumination is varied by iris diaphragms or condensing lenses, or by moving the lamps along guides provided for that purpose, to give patterns of suitable brightness with spheres of different sizes. A diffuse illumination of the background makes the work less fatiguing to the eye without increasing the difficulty of making settings. A measurement, in the following paragraphs, means the average of ten consecutively measured diameters (twenty settings of the cross-hair) taken alternately in opposite directions to eliminate temperature drift across the field. This was otherwise reduced to a negligible amount by leaving all lights burning continuously for several days, the temperature attained being about 26° C. The large number of settings chosen minimizes the effect of accidental displacements due to jarring of the apparatus during a measurement. These sometimes occur, since the glass disc is turned magnetically and held at any position merely by the slight friction of its pivot, but the whole apparatus is much more rigidly constructed than that previously used, and disturbances due to tremors of the supporting pier, formerly so troublesome, are no longer observed.

[1] J. Zeleny and L. W. McKeehan, PHYS. REV. (1), 32, 530, May, 1911.

The measurement above described gives the quantity $a_1\sqrt{2}$, where a_1 is the radius of the spherical mirror. Calculation shows that the deviation from sphericity is negligible.[1] A correction is, however, necessary if we wish to know the radius, a, of the sphere before it settled upon the glass plate, since the sphere of radius a_1 lacks a segment whose volume depends upon the angle of contact, α, between mercury and glass. This need only be known approximately to give a quite accurately, and the surface force is so great in comparison with the gravitational force that we may assume this angle constant even when the truncated sphere changes volume rapidly. If $\alpha = 148°$, $a = 0.93\ a_1$, and would be still smaller if α were less.[2] Since contamination of surface reduces α, the rates of decrease in radius observed below are, if anything, too small.

Measurements have been repeated at intervals on about fifty spheres, made in fifteen lots, the time of making and of each measurement being recorded. The same sphere was under observation for as long as ten days. Continuous diminution in size occurred in every case, but the rate of decrease in radius ($-da/dt$) may be very different for different spheres of the same age and radius. Each sphere shows a variation in the rate of decrease that depends upon the age and the previous history of the sphere.

Spheres exposed to either dry or moist air for from one to forty-eight hours reach a final stage in which the rate of decrease in radius is to first approximations independent of time and inversely as the radius, between $a = 10^{-4}$ cm., and $a = 10^{-3}$ cm. The value of $-da/dt$ for $a = 4 \times 10^{-4}$ cm. is about 1.4×10^{-10} cm./sec.[3]

The initial value of $-da/dt$ may be only a little greater than the value in the final stage, or many times greater (as high as 1.5×10^{-8} cm./sec. in one case). In the former case the final stage is reached in a short time, in the latter case the time required to reach the final stage is the longer the greater the value of a. The initial rate appears not to depend upon a, but the larger spheres are more uniform in their behavior than the smaller ones. The total decrease in a before the final stage is reached varies from 10 to 50 per cent., the *maximum* per cent. of decrease being greater for the smaller spheres. The variation of a with the time is shown for typical spheres in Fig. 1.

Spheres surrounded by an atmosphere of illuminating gas (carbon

[1] F. Bashforth and J. C. Adams, Capillary Action, Camb. Univ. Press, 1883.

[2] O. W. Silvey does not mention such a correction. Its value in his experiments would be difficult to estimate since the spheres were supported for measurement on oiled steel needles. PHYS. REV. (2), 7, 87 and 106, Jan., 1916.

[3] A similar law for the evaporation of iodine spherules was found by H. W. Morse, Amer. Acad. Proc., 45, 363, April, 1910.

monoxide and hydrogen) immediately after being formed in air showed the same initial peculiarities and about the same range in the initial values of $-da/dt$ as spheres left in air, but the later stages are entirely

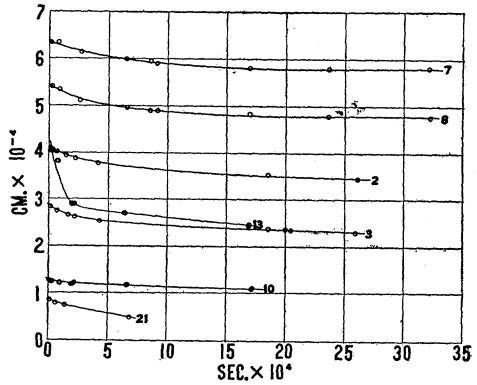

Fig. 1.

Spheres in air. Curves 2, 3, 7, 8, 21, are typical. Curve 10 shows a low initial rate of decrease. Curve 13 shows a high initial rate of decrease.

different, as shown in Fig. 2. If the initial rate is high it changes very little with time until the radius is less than 5×10^{-5} cm. Beyond this point the measurements cannot be carried with the intensity of illumination so far employed, but the rate must finally decrease, for the particle remains visible longer than it would if the initial rate were maintained to the end. If air is admitted during the period of rapid decrease the subsequent behavior is like that of a new sphere. If the initial rate of decrease is low it rises to a value of the same order as the initial rate for the class last mentioned, remains constant at this high value for a time, and finally sinks again to a low value. The last effect may or may not occur before the sphere is too small to measure, and is easiest to

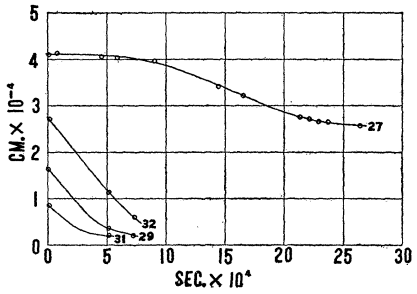

Fig. 2.

Spheres in illuminating gas. Curves 29, 31, 32, are typical. Curve 27 shows a low initial rate of decrease.

detect in the case of spheres originally of large size. If resolution of the image is still possible when it occurs the surface is seen to be roughened, the appearance being similar to that of an orange peel, and the reflecting power is greatly reduced.

Effects similar to those last described are also observed when spheres that have reached the final stage in air are then kept in illuminating gas for a further period of time. If such spheres are treated with a drop of

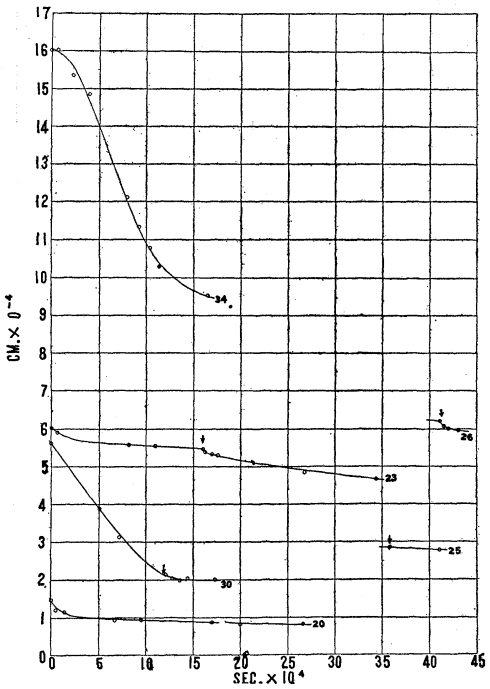

Fig. 3.

Miscellaneous effects. Curve 20 is typical for a sphere kept in air. Curve 23 shows effect of washing with alcohol at time marked with arrow, sphere kept in air. Curve 25 shows effect (negligible) of washing with water at time marked with arrow, sphere kept in air. Curve 26 shows effect of washing with water at time marked with arrow, sphere kept in air. Curve 30 shows effect of replacing illuminating gas by air at time marked with arrow. Curve 34 shows effect of replacing air by illuminating gas at time zero (sphere was an old one).

water or alcohol (the volume of such a drop will be at least 10^{12} times that of the mercury) which is then allowed to evaporate, the rate of decrease is either unaffected or it is increased. If the latter is the case the subsequent behavior in air is like that of a new sphere. Fig. 3 shows examples of these effects.

The rate is little, if at all, affected by a moderate velocity of circulation

of the surrounding air or other gas, or by illuminating the sphere only occasionally instead of continuously.

Spheres made and measured in illuminating gas showed a high rate of decrease but finally became dirty and distorted. Similar experiments in carbon dioxide show the latter effect occurring sooner.

By condensing a great number of spheres directly upon the glass plate it was found possible to supersaturate an atmosphere of carbon dioxide with mercury vapor to such an extent that the larger spheres grew slowly while the smaller spheres decreased. In a particular experiment the radius of spheres in (unstable) equilibrium with the vapor was 1.1×10^{-4} cm.

Discussion of Results.

The rate of evaporation from a clean mercury surface at the average temperature of experiment is more than sufficient to account for the maximum rate of decrease observed.[1] Since circulation of the gas was found to have little effect upon the rate it may be assumed that diffusion of the vapor is able to keep its partial pressure in the neighborhood of an isolated sphere of the size used very far below the saturation pressure.

This is additionally probable because the curvature of the surface of such a sphere is so great that it would evaporate readily even in an atmosphere saturated with respect to a plane surface. The presence of even a thin layer of gas not sharing the general circulation would explain the low maximum rate of evaporation here noted (less than one per cent. of the theoretical maximum in a perfect vacuum). Since Knudsen[2] found that the maximum rate persisted for less than four seconds even in the best vacuum it seems reasonable, however, to attribute the discrepancy mainly to contamination of the surface, especially since the still lower rates obtained are evidently due to this cause. On account of the protection afforded by the glass plate the rates of decrease observed are no doubt somewhat smaller than they would be for freely falling spheres of the same mass (of actual radius a).

The contamination that occurs in air is inferred to be a thin but coherent and translucent layer of mercuric oxide,[3] which may be removed mechanically by a liquid or chemically by a reducing atmosphere such as illuminating gas.[4] The latter also naturally prevents the formation of the oxide on a clean sphere. Even if the removal is incomplete the coherence of the oxide layer is destroyed and fresh surface is exposed.

[1] M. Knudsen, Ann. d. Phys., 47, 697, Aug., 1915.

[2] Loc. cit.

[3] G. B. Taylor and G. A. Hulett predict the formation of this oxide at room temperatures. Journ. Phys. Chem., 17, 565, Oct., 1913.

[4] L. Moser and O. Schmid, ZS. Anal. Chem., 53, 217, 1914.

The appearance of dirt on the surface at a later stage suggests that the formation of a carbonate accompanies the reduction. The oxide layer formed on the smaller spheres is apparently more porous than that formed on the larger ones. This may be due to the greater fractional decrease in area and consequent more frequent disturbance of the layer for the same rate of decrease in radius in the former case. Spectroscopic examination of the reflected light is suggested as an independent method of investigating these points.

The experiments of A. Schidlof and A. Karpowicz[1] agree very well with the explanation offered above, the persistence of evaporation in nitrogen but not in air being particularly striking. The experiments of F. Ehrenhaft[2] show no less strikingly the effect of the oxide layer that was certainly formed under his experimental conditions.

The alterations in surface observed would have an effect upon the correction to Stokes's formula that might well be different in the case of different drops as prepared by condensation from vapor. This variation would make electronic charge determinations especially erratic for very small spheres, where the correction to Stokes's formula is large. Atomization should prove a more reliable method for obtaining initial uniformity, but it seems clear that sufficient purity of surface is a good deal harder to get and to keep than has hitherto been realized.

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[1] Loc. cit.
[2] Loc. cit.