26 sq. m., respectively,[20] for powders I and II. On the basis of these areas, the surface concentration of oxygen at $-78.5°$ is 0.21×10^{15} and 0.16×10^{15} molecules per sq. cm. which is virtually identical with that on the foil. The fact that the oxygen held on the foil so strongly at $-183°$ that it could not be pumped off at temperature was also present on the surface at a concentration of 0.16×10^{15} molecules per sq. cm. suggests, though it does not prove, that the sites which hold oxygen so strongly at $-183°$ are the same upon which activated adsorption occurs at $-78.5°$.

It is interesting to note that if one assumes that the activated adsorption at $-78°$ represents the formation of a silver oxide complex on the surface, the number of sites is about equal to the observed number of molecules sorbed. Thus, on this basis, each oxygen molecule would be associated with 4 atoms of the silver on the surface. The X-ray diffraction patterns indicate that as a first approximation the silver grains are so arranged that the (110) planes lie on the surface, and since, on this plane, four silver atoms occupy an area of about 46 sq. Å., the concentration of groups of sites of four silver atoms is about 0.22×10^{15} per sq. cm., which corresponds very well with the observed concentration of oxygen sorbed at $-78°$, and to the concentration of oxygen held so tightly at $-183°$ that it cannot be removed by pumping at temperature.

(20) Assuming that the cross section of an oxygen molecule in a complete monolayer is 12 sq. Å.

Summary

The adsorption of hydrogen, nitrogen, argon, carbon monoxide, carbon dioxide and oxygen at pressures up to 0.1 cm. on a substantially plane, reduced surface of silver has been measured over the temperature range -195 to $20°$. Hydrogen is not measurably sorbed at any temperature; argon, nitrogen and carbon monoxide are sorbed at -195 and $-183°$ but not at -78 or $20°$. Carbon dioxide is not sorbed at $20°$ but at $-78°$ is sorbed to the slight extent of 6 cu. mm. at a pressure of 0.02 cm. The adsorption is in each case instantaneous and reversible. Oxygen is sorbed at -195 and $-183°$ and although most of the gas appears to be held by van der Waals forces some part of it cannot be removed by pumping at temperature. At -78 and $20°$ there is activated adsorption of oxygen. All the isotherms are of the type observed in a plane surface of other metals, and are satisfactorily represented by the Langmuir equation. The values of V_s as derived from the slope of the $p/v - p$ isotherm, correspond to a surface only partially covered, the coverage varying from about 20 to 90% of a close-packed monolayer.

Force–area curves are derived by two different methods, with results which differ significantly. The adsorption of oxygen on smooth silver is compared with the adsorption of oxygen on finely-divided silver as reported by Benton and Drake.

The Attachment and Detachment of Dropping Mercury under Various Conditions

BY I. M. KOLTHOFF AND G. J. KAHAN

Although the mercury–water interfacial tension is little affected by dissolved non-capillary active electrolytes in the aqueous phase, it has been found by several workers that the drop time of mercury from a glass capillary into air-saturated water can be quite different from that into electrolyte solutions. For example, J. Heyrovský reports[1] that his capillary had a drop time of six to eight seconds in distilled water and of three seconds in electrolyte solutions. On the other

hand, Kolthoff and Lingane[2] mention that with their capillary the drop times in water and in 0.1 M potassium chloride were hardly different. It is not stated whether the water used was air-free.

In our experiments we found that the drop time of an electrically disconnected capillary in air-containing water was badly reproducible and, as a rule, much larger than in 0.1 M salt solutions. Slight deviations from the vertical in the position of the capillary resulted in large variations of the drop time, whereas no such effect was found in not

(1) J. Heyrovský, in W. Böttger, "Physikalische Methoden der analytischen Chemie," Vol. II, Akadem. Verlagsges, Leipzig, 1936, p. 276.

(2) I. M. Kolthoff and J. J. Lingane, Chem. Rev., 24, 26 (1939).

Capillary 1.—Drop in distilled water; picture 1.

Capillary 1.—Drop in 0.1 M KCl; picture 2.

Capillary 2.—Drop in distilled water at intermediate stage of its life; picture 3.

Capillary 2.—Drop in distilled water ·at last stage of its life; picture 4.

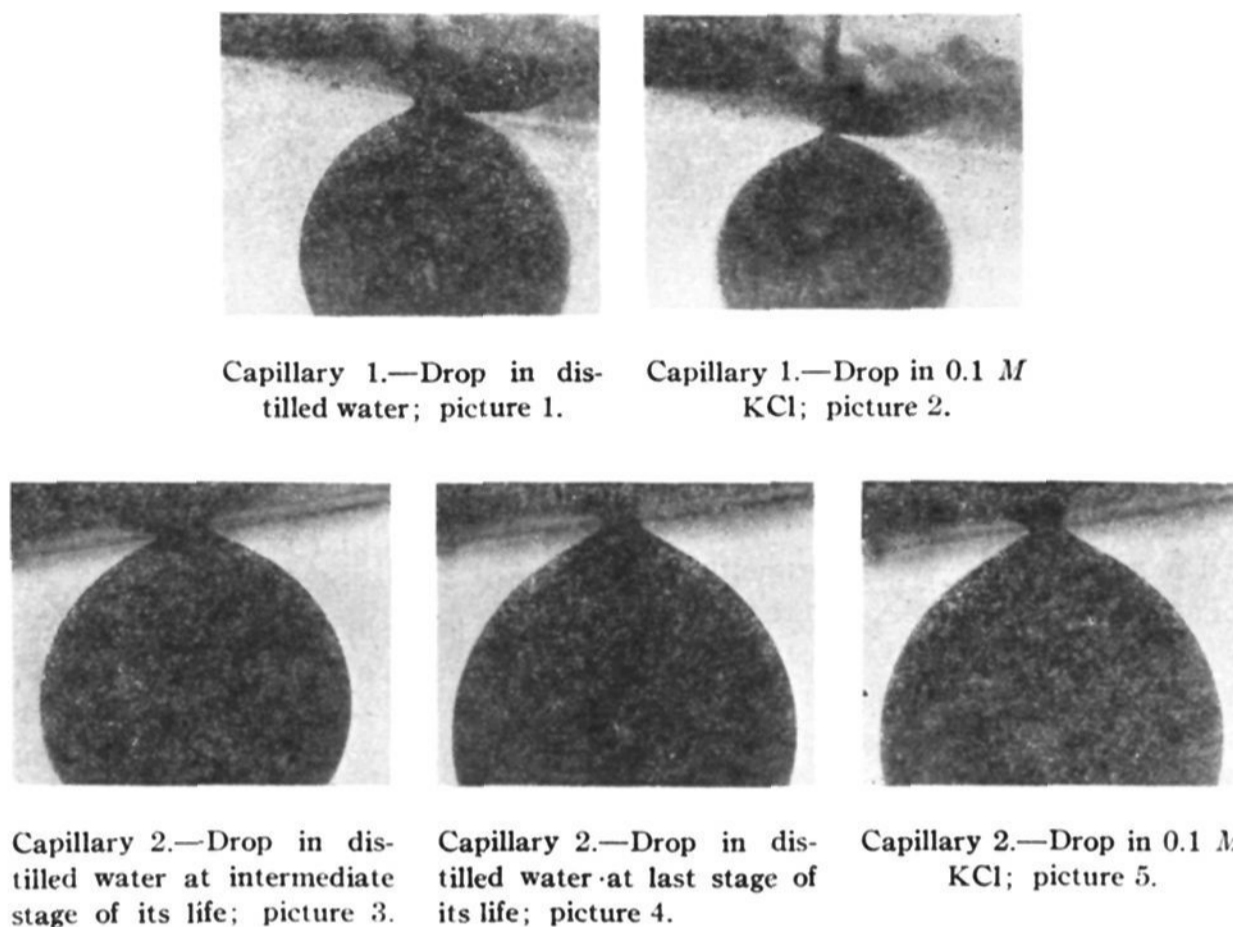Capillary 2.—Drop in 0.1 M KCl; picture 5.

Fig. 1.

too dilute electrolyte solutions. By slightly changing the angle of inclination it was sometimes possible to obtain the same drop time in air-containing water as in electrolyte solutions, the agreement being merely accidental and not readily reproducible. Moreover, it was found that the ratio $t_{H_2O}/t_{0.1 M KCl}$ of an electrically disconnected capillary in air-saturated solutions depended greatly upon the properties of the capillary. A ratio of the order to 2 to 3 was found with capillaries of small diameter and small length, while wider capillaries with greater length gave ratios close to 1.

The present study attempted to find the reason for the large erratic drop time found in air-containing water when narrow, short capillaries were used. Microscopic observation of the drops revealed that in case of an abnormally large drop time the drop of mercury remained attached to the glass during its life-time (Fig. 1). Pictures 1 and 2 were obtained with capillary no. 1 which was short and had a small diameter. Picture 1 shows the drop of mercury in air-saturated water just before it fell. Picture 2 was made with the same capillary but in 0.1 M potassium chloride solution. In distilled water the drop touched the glass and it was larger than in 0.1 M potassium chloride solutions. In the electrolyte solution the

drop did not touch the glass, but was suspended symmetrically from the bore of the capillary. In air-containing distilled water it hung sideways from the glass. The area of glass touched by the mercury depended upon the inclination of the capillary, and upon small irregularities of the glass surface. The short capillary (no. 1) delivered 1.62 mg. of mercury per second in 0.1 M potassium chloride solution without electrical connection. The drop time of this capillary was 2.5 seconds in 0.1 M potassium chloride solution and was of the order of three and one-half to four seconds in air-saturated distilled water.

In 0.1 M potassium chloride solution the drop time is approximately given by the equation

$$mgt = 2\pi r\sigma \qquad (1)$$

in which m is the mass of mercury that flows from the capillary per second, g is the acceleration due to gravity, t is the drop time, r is the radius of the bore of the capillary and σ is the interfacial tension between mercury and the solution. Experimental data which demonstrate the validity of the expression[1] are found in Kolthoff and Lingane.[3] When the drop is attached to the glass, this equation does not hold. Here not only the mercury-solution interfacial tension but also the mercury-

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 68.

glass interfacial tension contribute to the support of the drop. The drop weight is greater under these conditions than when the drop is not attached to the glass.

Pictures 3, 4 and 5 were obtained with capillary no. 2, which had a wide bore, a length of 20 cm. and a drop time of three seconds in 0.1 M potassium chloride. The dropping mercury was always electrically disconnected unless otherwise stated. Picture 3 in Fig. 1 was taken when the mercury was dropping into air-saturated water. At the moment when the picture was taken the mercury was attached to the glass. At a later stage during the life of the drop the weight became large enough to detach it from the glass, but the force resulting from the interfacial tension between the mercury and the solution kept the drop suspended. Equation (1) was found to hold approximately, even though the drop was attached to the glass during part of the time. After the drop became detached from the glass its appearance and characteristics became closely similar to that of the drop formed in 0.1 M potassium chloride (pictures 4 and 5, Fig. 1). The ratio of the drop time in water and 0.1 M potassium chloride solution was close to unity.

In order to find the factors which are responsible for the attachment or detachment of the mercury to the glass experiments were carried out with water or aqueous solutions from which the air had been displaced by hydrogen. The capillary used (no. 3) had approximately the same characteristics as capillary no. 1. It was found that in the absence of oxygen the drop time of the electrically disconnected capillary in water was normal and close to the drop time in 0.1 M potassium chloride solutions. However, when connection was made with a pool of mercury in the bottom of the cell, the drop time in water became abnormally large and the drop became attached to the glass during its lifetime. When a positive potential was applied to the dropping mercury electrode, the drop time increased, whereas it decreased upon application of a negative potential. When the current became zero or cathodic, the drop time became normal. A normal drop time was accompanied by detachment of the drop from the glass. Some typical data are found in Table I.

In air-free 0.001 M potassium chloride solution, the results were qualitatively the same as in distilled water, but the drop times were smaller (see Fig. 2).

Table I

Mercury Dropping into Air-free Distilled Water Saturated with Hydrogen (Capillary No. 3)

E, applied volts	i, microamp.	t, seconds	Microscopic observation
Not connected	..	5.5	Detached
+0.8	−1.5	13.2	Attached
+ .5	−0.5	13.5	Attached
+ .1	− .1	13.5	Attached
.0	− .03	11.9	Attached
− .1	− .02	8.5	Attached
− .2	− .005	7.4	Attached
− .3	.000	5.5	Detaching
− .4	+ .01	5.5	Detached
− .5	+ .02	5.5	Detached
− .7	+ .04	5.5	Detached
−1.0	+ .06	5.2	Detached
−1.5	+ .16	4.6	Detached

When the experiments were carried out in air-free 0.001 M potassium iodide solution no abnormalities were observed. The drop remained detached at all applied voltages as it did in 0.1 M potassium chloride solution.

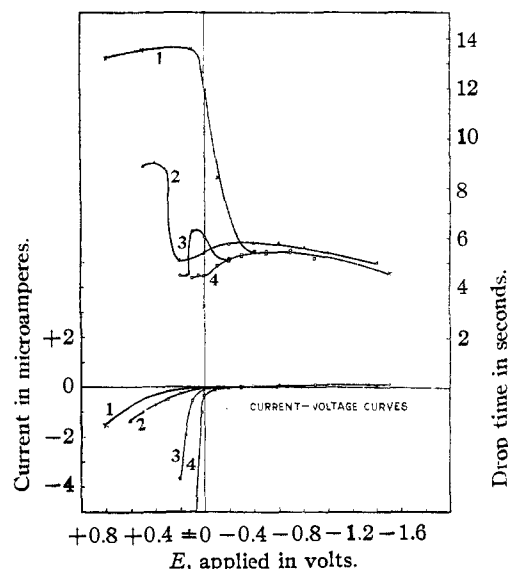+0.8　+0.4　±0　−0.4　−0.8　−1.2　−1.6
E, applied in volts.

Fig. 2.—Drop times (upper part) and currents (lower parts) at various applied voltages in different solutions—Capillary 3, mercury pool in cell as reference electrode: Curve 1 in distilled water; 2, in 10^{-5} M lanthanum chloride; 3, in 10^{-3} M potassium chloride; 4, in 0.1 M potassium chloride.

A normal behavior, the same as in 0.1 M potassium chloride was observed in 5×10^{-5} M thorium nitrate solutions at all applied voltages.

In 10^{-5} M thorium nitrate and in 10^{-5} M lanthanum chloride a normal behavior was found at an applied voltage of zero or upon cathodic polarization. When the dropping mercury electrode was anodically polarized, the drop time be-

came abnormally large in these solutions and the drop remained attached to the glass. The data for 10^{-5} M lanthanum chloride are given in Table II.

TABLE II

MERCURY DROPPING INTO AIR-FREE 10^{-5} M LANTHANUM CHLORIDE SATURATED WITH HYDROGEN (CAPILLARY No. 3)

E, applied volts	i, microamp.	t, seconds	Microscopic observation
Disconnected	..	5.8	Detached
+0.5	−0.95	8.9	Attached
+ .4	− .68	9.0	Attached
+ .3	− .50	8.5	Attached
+ .2	− .26	5.1	Detached
.0	− .13	5.4	Detached
− .2	− .08	5.8	Detached
− .4	− .04	5.8	Detached
− .6	− .02	5.8	Detached
− .8	+ .03	5.6	Detached
−1.0	+ .06	5.4	Detached
−1.4	+ .10	5.0	Detached

Discussion

From the fact that the drop time of the electrically disconnected mercury in air-free water was normal but became abnormal upon connection with the mercury pool, it was concluded that normal or abnormal drop time, accompanied by detachment or attachment of the drop of mercury to the glass depended upon the interaction of the double layers at the glass and mercury interfaces. Glass in contact with distilled water acquires a negative charge and the sign of its electrokinetic potential is negative. In distilled water the electric field of the electrokinetic potential extends relatively far beyond the layer of liquid firmly attached to the glass. Electrically disconnected mercury dropping into pure air-free water is uncharged and there is no electrokinetic potential at the mercury–water interface. However, when the dropping mercury is electrically connected with the mercury pool at the bottom of the cell, it acquires a positive charge and the electrokinetic potential is positive. Again the electrokinetic field at the mercury–water interface extends far beyond the liquid layer firmly attached to the mercury surface. Thus when the glass with its firmly adhering water layer and the mercury with its adhering water layer come together, the negative field around the glass attracts the positive field around the mercury, and the drop remains attached to the glass.

This explanation is substantiated by several of the experiments described. In 0.1 M or more concentrated electrolyte solutions the double layers are compressed and do not extend beyond the firmly adhering liquid films. Detachment results.

In 0.001 M potassium iodide solutions there is a strong adsorption of iodide ions on the mercury and a negative instead of a positive electrokinetic potential at the mercury results.[4] In this case the two double layers have the same sign; they repel one another and detachment results.

In 5×10^{-5} M thorium nitrate the electrokinetic potential of the glass is positive. At the positive side of the isoelectric point of the mercury the sign of the double layer is also positive. The double layers at the glass and mercury surfaces repel each other and the drop remains detached.

At first glance one might expect that on the negative side of its isoelectric point the mercury in the thorium nitrate solution would become attached to the glass. However, the tetravalent thorium ions compress the negative double layer around the mercury so much that the electric intensity outside the attached liquid film is zero.

Not explained are the facts that the drops of anodically polarized mercury become attached to the glass in 10^{-5} M lanthanum chloride and 10^{-5} M thorium nitrate.

In the experimental part it was shown that the electrically disconnected mercury becomes attached to the glass when it is dropping into air-saturated water. Under these conditions the mercury is no longer electrically neutral. By the adsorption of oxygen it acquires a positive charge. Hence, there again results interaction between the negative field close to the glass and the positive field close to the mercury, leading to attachment.

In the above we have considered the interaction between the two liquid films as the primary cause of the attachment. Whether there is an aqueous film between the attached mercury and the glass or whether the liquid is squeezed out cannot be answered on the basis of our experiments. In view of the experiments of Frumkin, et al.,[5] one could expect that such a film between the attached drop and the glass should exist.

In order to avoid the abnormal effects described in this paper it is recommended that the characteristics of a capillary—drop time and mass of mercury per second—always be determined in

(4) For a detailed picture of the potential curves in iodide see I. M. Kolthoff and J. J. Lingane, "Polarography," p. 99.

(5) A. Frumkin, A. Gorodetzkaja, B. Kabanow and N. Nekrassow. *Physik. Z. Sowjetunion*, **1**, 255 (1932); B. Derjaguin and M. Kussakow, *Acta Physicochim.*, **10**, 25 (1939).

0.1 M electrolyte solutions and not in distilled water.

Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled us to carry out this investigation.

Summary

1. When electrically disconnected mercury drops into air-saturated water or when mercury connected with a pool of mercury drops into air-free water an abnormally large drop time is found.

The drop of mercury remains attached to the glass. The abnormal behavior becomes more pronounced the smaller is the bore of the capillary.

The results obtained with an abnormally dropping capillary are badly reproducible and depend greatly on the degree of inclination of the capillary.

2. The abnormal behavior has been interpreted on the basis of interaction between the electric double layers at the glass and at the mercury–aqueous phase interfaces.

Studies in Stereochemistry. II. Steric Strains as a Factor in the Relative Stability of Some Etherates of Boron Fluoride

By Herbert C. Brown and Richard M. Adams[1]

Modern physical techniques for studying gaseous molecules have contributed much information regarding molecular configurations.[2,3] In the main, these later results have confirmed those of the early workers in stereochemistry who drew their conclusions from isomer number and chemical reactions. In many instances, however, detailed data on atomic dimensions and valence angles and the careful study of small irregularities in the physical and chemical properties of substances has made possible some interesting extensions of the classical principles of stereochemistry.

One recent extension of this kind is based on evidence that steric interference between two groups may weaken considerably the bond joining the groups. To illustrate, the per cent. dissociation of the tetraaryldialkylethanes and the dixanthyldialkylethanes increases with increasing size of the alkyl group[4]; and the ortho methyl groups of sym-tetraphenyldi-o-tolylethane increase the dissociation into free radicals more than do the methyl groups of the corresponding meta or para derivatives (25% vs. 5%).[5]

Unfortunately, these examples are not entirely satisfactory. The molecules are large and complicated; moreover, interpretation of the results is made particularly hazardous by the fact that resonance plays an important part in the dissociation of such ethane derivatives. It would be highly desirable to have more substantial evidence of this same effect in simpler molecules in which resonance is not important. Recently, such examples of unmistakable weakening of bonds by steric strains have been found.[6] A study of the relative stability of some coördination compounds of borine, boron fluoride and trimethylboron with amines revealed that trimethylamine is a stronger base (in the generalized Lewis sense[7]) than pyridine toward the acids hydrogen chloride, borine and boron fluoride, but that the reverse is true when trimethylboron is used as the reference acid.

This "anomalous" result is apparently due to steric strains, for molecular models reveal that in the compounds studied considerable steric interference is to be expected only in trimethylamine-trimethylboron.[8,9]

There are reasons to believe that such steric strains are more common than has been supposed

(1) This paper is taken from a dissertation submitted by Richard M. Adams to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Master of Science.

(2) Stuart, "Molekülstruktur," Julius Springer, Berlin, 1934.

(3) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

(4) Conant and Bigelow, This Journal, **50**, 2041 (1928); Conant, Small and Sloan, ibid., **48**, 1743 (1926).

(5) Marvel, Mueller, Himel and Kaplan, ibid., **61**, 2777 (1939).

(6) Brown, Schlesinger and Cardon, ibid., **64**, 325 (1942).

(7) Lewis, J. Franklin Inst., **226**, 293 (1938).

(8) For a discussion of the nomenclature used for these coördination compounds, see Davidson and Brown, This Journal, **64**, 316 (1942), footnote 11.

(9) It was pointed out that steric strains present in trimethylamine-trimethylboron must be duplicated in its isostere, hexamethylethane, since the dimensions and configurations of the two molecules are almost identical.[4] It is of considerable interest that in a recent electron-diffraction study of this hydrocarbon, Bauer and Beach [ibid., **64**, 1142 (1942)] find evidence that the central C–C bond is stretched (1.58 vs. 1.54 Å.).