however, an oxygen molecule reaches an active center and is adsorbed, it is activated so that it is able to react with the ethylene which reaches it. Mere adsorption is not sufficient, otherwise the silica gel itself would be an active catalyst. Because of their higher energy content the primary products of oxidation are likely to be very reactive whether they are dihydroxyethylene or formaldehyde. Furthermore, as indicated in the tables, the temperature of the catalysts is often higher than that of the bath in which they are immersed. This indicates that the temperature at which the reaction takes place may be very much higher than that indicated, so that successive collisions with oxygen molecules result in complete oxidation. Otherwise intermediate products of oxidation should be detected when the rate of streaming through the catalyst was increased.

Conclusion

1. Metallized silica gels actively promote the oxidation of ethylene, beginning to be effective at about 100°.
2. The catalysts are so active that no intermediate products of oxidation are detected.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE GAYLEY CHEMICAL LABORATORY, LAFAYETTE COLLEGE]

THE FLUIDITY OF MERCURY[1,2]

BY EUGENE C. BINGHAM AND THEODORE R. THOMPSON

RECEIVED JUNE 25, 1928 PUBLISHED NOVEMBER 6, 1928

Tammann and Hinnüber[3] have raised the question whether the viscosity of a liquid is trustworthy when it is measured in a tube that is not thoroughly wetted by the liquid. They claim to have found the viscosity of mercury in an amalgamated copper capillary to be 4.931 ± 78 *cp* at 13.5° instead of 1.609 *cp* for mercury in glass. Whether one accepts their explanation of the phenomenon based on "slippage," or not, the discrepancy of over 200% is quite beyond experimental error and demands investigation.

1. The hypothesis of slippage is, of course, not new. It has often been offered to account for results which at the time seemed inexplicable, but on further investigation it has always been found that some factor has been overlooked which has made this explanation unnecessary. On the other hand, the fair agreement among the results of different investigators using widely different forms of viscometers and shearing stresses constitutes what may be fairly regarded as proof that slippage is certainly not

---

[1] In memory of Ira Remsen.

[2] Part of Master's Degree "Thesis" of Theodore R. Thompson.

[3] Tammann and Hinnüber, *Z. anorg. Chem.*, **167**, 230 (1927).

a very important factor in the flow of mercury over glass. As the subject has been discussed elsewhere,[4] repetition here is unnecessary. We propose to inquire whether there is not some other explanation for the phenomenon other than the one suggested by Tammann and Hinnüber.

2. S. Erk[5] has already suggested as an alternative explanation that the walls of metal capillaries are perhaps not as smooth as those of glass capillaries, so that the flow is not perfectly linear. Erk has shown that in the steel capillary used by Tammann and Hinnüber the velocity of flow was so high that according to the Reynold's criterion turbulence should have been expected. The weak points in this explanation are, first, that the decrease in fluidity was not marked in the steel capillary and not very marked in the copper capillary until after thorough amalgamation; and, second, that the apparent fluidity in the amalgamated copper capillary steadily decreased for several days. It is not obvious why thorough amalgamation should increase the turbulence nor why the turbulence should not reach its maximum value at once.

3. The most obvious explanation is that the copper or something derived from the copper has decreased the fluidity of the mercury. This hypothesis has been considered by Tammann and Hinnüber and rejected because copper is only soluble to 0.0032% at 15° and at this dilution the fluidity is lowered not over 0.3%. We have confirmed this, finding that the fluidity at 20° of a saturated solution of copper was 63.9 rhes,[6] as compared with 64.2 for pure mercury. The method of preparation was intentionally such that the solution would contain the impurities derived from the copper but the solution was passed through chamois skin before measurement in order to remove any suspended particles. The difference obtained is only a little more than experimental error.

4. E. von Schweidler[7] claimed to have prepared a solution of copper in mercury containing 0.5% of copper with the low fluidity of 61.7. This may have been a suspension of colloidal copper, mercury or oxide, but whatever its nature it is worth considering whether suspended material could have caused the actual reduction in apparent fluidity noted by Tammann and Hinnüber. This difficulty can be largely overcome by the cleaning out of the viscometer and the use of clean mercury, but we have proved that the fluidity is not restored to that obtained in a glass capillary, so that this explanation is inadequate.

5. Even if the copper does not dissolve to any extent in the mercury, it is possible that the mercury diffuses into the copper and causes it to expand, thus partially filling the capillary. However, the measurements

---

[4] Bingham, "Fluidity and Plasticity," pp. 29–35.

[5] S. Erk, *Z. Physik*, **47**, 886 (1928).

[6] Reciprocal *poises*.

[7] E. von Schweidler, *Wied-Sitzb.*, [2A] **104**, 273 (1895).

of the diameter of the amalgamated tube made by Tammann and Hinnüber give no evidence of a decrease in diameter.

6. Copper is slightly soluble in mercury and the solution is very fluid, as already pointed out. In a saturated solution it is to be expected that the small crystals of copper would be dissolved to promote the growth of large crystals. It is therefore possible that after amalgamation there is a progressive alteration in the surface which would in time result in a pronounced change in the *effective* radius of the capillary. Since the copper taken away at one place is deposited at another, the average radius measured by Tammann and Hinnüber would not be affected, but the "constant" of the capillary should change. We have found as a matter of fact that after removing the mercury from the amalgamated capillary of a viscometer by heating in a stream of hydrogen, the constant of the viscometer as determined with pure water decreased from 4.94 to 4.79 × 10^{-7}, which is roughly 3.0%.

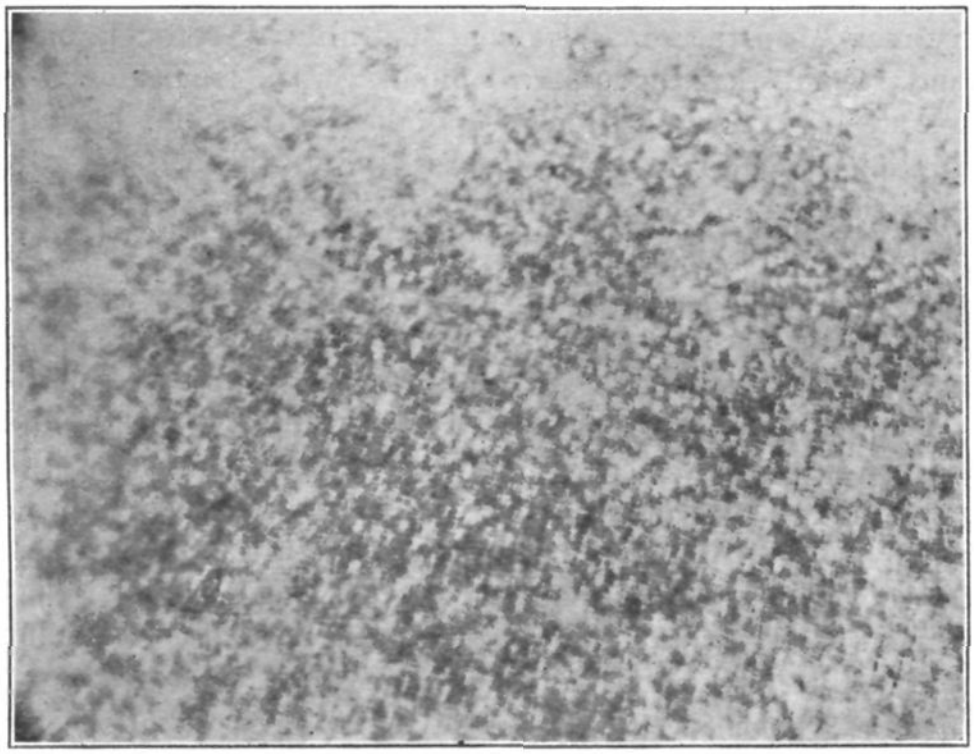

Fig. 1.—Surface after fifteen minutes.

Before amalgamation the apparent fluidity of the mercury as measured at different pressures in the copper capillary at 20° was 62.2 rhes and after twenty-four hours 62.1 rhes. We obtained in a glass capillary at 20° the fluidity of 64.3 rhes. The apparent fluidity in the copper capillary is therefore 3.3% lower than when measured in a glass capillary but it does not change rapidly with the time. Tammann and Hinnüber obtained a value 22.3% lower than the value as measured in glass. Perhaps the difference is due to partial but unequal amalgamation.

After thorough amalgamation the apparent fluidity decreased steadily but there was no evidence that it was tending toward a constant value until after ten hours it had fallen to 20% of its original value, when the experiment was discontinued. Repeating the experiment with a smaller capillary, the flow after a time ceased altogether. Tammann and Hinnüber observed that the time of flow increased for a period of five days, but on somewhat scanty evidence they assumed that the time of flow will reach a constant value. However, even if the time of flow does become constant, this fact would not prove that the fluidity of the mercury was tending toward a constant value, for it might be the capillary and not the mercury which is changing. Slippage is supposed to help the flow so that the final value of Tammann and Hinnüber should be a minimum, but our value of about 12.5 rhes is considerably lower than their value of 20.3 rhes, and it is not the minimum value.

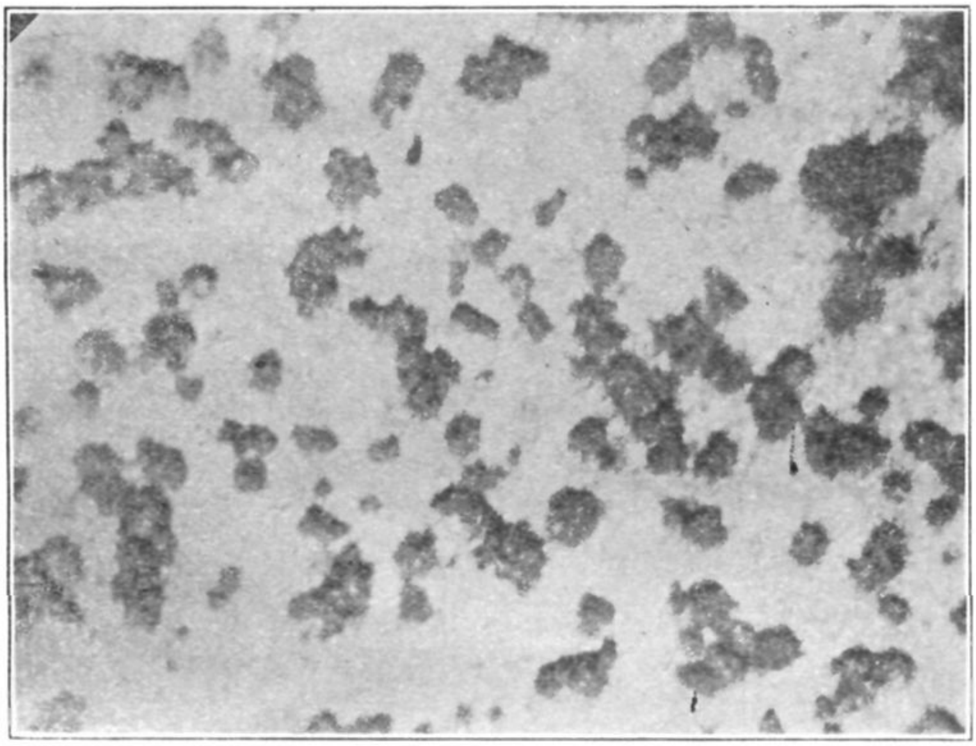

Fig. 2.—Surface after forty-two hours.

It appeared possible to prove quite conclusively that recrystallization of the copper does take place on the walls of the capillary and that it is sufficient to explain any decrease in apparent fluidity. To do this, pieces of copper were smoothly polished, amalgamated for a few seconds with mercurous nitrate and then bathed in metallic mercury for different periods of time, after which the mercury was driven off by heat in an atmosphere of hydrogen. It will be seen from Fig. 1 that the etching of the surface is quite marked after only fifteen minutes, large isolated crystals stand out prominently from the surface at the end of two days, Fig. 2, and at the end of two weeks, Fig. 3, large crystals appear to cover the entire surface. Some of the crystals were as much as 0.5 mm. above the surface, which is about twice the diameter of one of the capillaries which we used. A section made at right angles to the surface showed the irregular surface very well.

It is not necessary, however, to use any elaborate technique to show the effect, for a smooth piece of copper amalgamated for more than a few hours shows to the unaided eye a rough sandy appearance. We assume that this recrystallization has been noticed repeatedly heretofore but we are unable as yet to give any references.

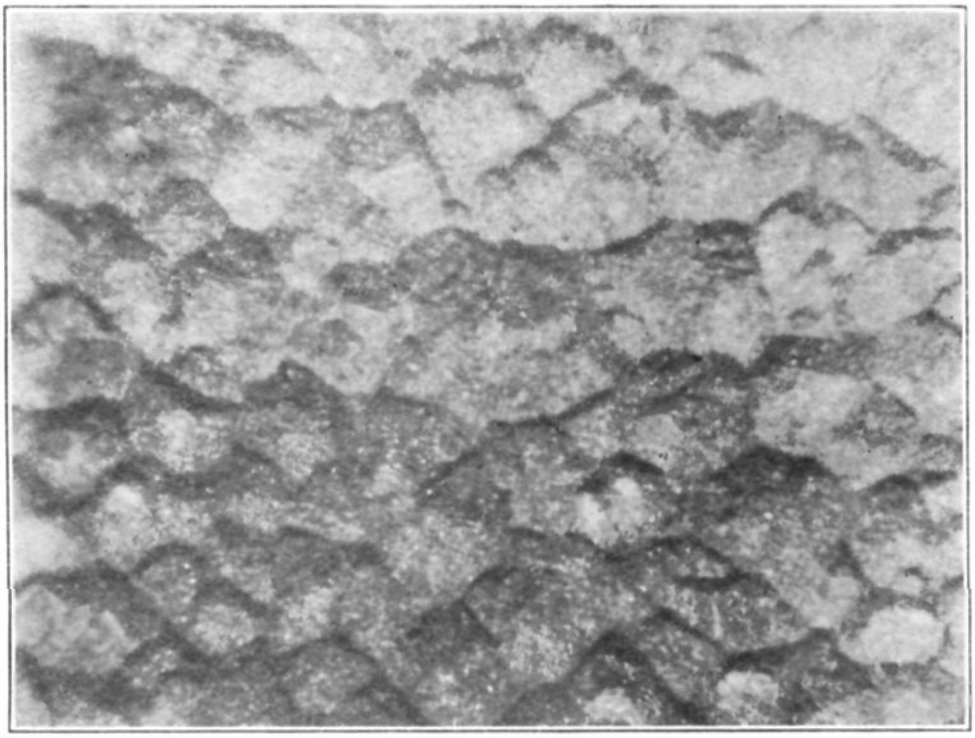

Fig. 3.—Surface after two weeks.

We therefore reaffirm the earlier conclusion that there is no positive evidence of slippage of mercury in a glass tube, and we reach the new conclusion that the fluidity of mercury measured in a copper tube is unreliable, particularly when the copper is wetted by the mercury.

TABLE I

THE FLUIDITY OF MERCURY MEASURED IN A GLASS CAPILLARY

Capillary No. 1.23; $C = 1.994 \times 10^{-7}$; $C' = 0.018$; $h' = 0.15$ cm.

Temp., °C.	Time of efflux	Fluidity, rhes	Av. earlier fluidity, Erk	Temp., °C.	Time of efflux	Fluidity, rhes	Av. earlier fluidity, Erk
0	254.5	59.4	59.3	60	211.8	72.9	73.2
10	244.0	62.1	61.9	70	207.3	74.9	75.1
20	237.0	64.3	64.8	80	203.2	76.7	77.0
30	228.9	66.8	66.7	90	199.3	78.5	78.9
40	223.4	68.6	69.0	100	196.0	80.0	80.6
50	216.9	71.0	71.1				

The fluidity of mercury from 0 to 100° was determined as an incidental part of this investigation, using glass capillary No. 1.23. The values are a little higher at low temperatures than the mean values of earlier experimenters given by Erk,[5] and our values are somewhat lower than theirs at 40° and above. This slight change does not alter the conclusion that mercury is different from all other liquids yet studied in that its fluidity temperature curve is concave toward the temperature axis.

Summary

1. The suspicion that mercury exhibits slippage while flowing over unwet surfaces such as glass appears to be unfounded.

2. The fluidity of mercury from 0 to 100°, measured in a glass capillary viscometer with attention to recent corrections, was found to be not inconsistent with earlier determinations.

3. The rate of flow of mercury through a narrow copper capillary is irregular but decreases with time, particularly when the tube is well amalgamated. The values of the fluidity are quite untrustworthy. The effect is the indirect result of the very slight solubility of copper in mercury. Differential solubility of the crystals causes large crystals to build up on the surface of the capillary which interfere with the flow.

EASTON, PENNSYLVANIA

[CONTRIBUTION FROM HILLSIDE LABORATORY]

THE COLOR OF IODINE SOLUTIONS[1]

BY FREDERICK H. GETMAN

RECEIVED JULY 2, 1928 PUBLISHED NOVEMBER 6, 1928

The dependence of the color of solutions of free iodine upon the nature of the solvent has been the subject of numerous investigations, but notwithstanding the thoroughness of these studies the problem of the exact composition of iodine solutions yet remains to be solved completely.

As a result of their study of colors of iodine solutions, Gauthier and Charpy[2] concluded that four different colors may be distinguished, depending upon the nature of the solvent, as follows: (1) violet, as in chloroform; (2) red, as in ethylene bromide; (3) reddish-brown, as in toluene; (4) brown, as in ethyl alcohol. Although a number of solvents were found to conform to this classification, no satisfactory relation between the properties of the solvents and the colors of the solutions was discovered. Subsequent investigations by Rigollot[3] and by Krüss and Thiele[4] failed to establish any satisfactory connection between the chemical

---

[1] In memory of Ira Remsen.

[2] Gauthier and Charpy, *Compt. rend.*, **110**, 1890; **111**, 645 (1890).

[3] Rigollot, *ibid.*, **112**, 38 (1891).

[4] Krüss and Thiele, *Z. anorg. Chem.*, **7**, 25 (1894).