TABLE III (*continued*).

Substance.	Visibility.	Substance.	Visibility
orange G	0	rubin	0
orcein	0	safranine (alcohol)	0
phloxin red	0	scarlet red	0
phosphin 3 R	0	solid green	0
ponceau PR	0	sudan III	0
pyronine	0	tropaeolin	0
rapid filter yellow	0	tropaeolin-*o*-resorcine yellow	0
rapid filter green I	0	trypan blue	2
resorcine fuchsine	0	trypan red	1
rosanilin acetate	0	uranin (fluorescent)	2
rose bengale	0		

Summary.

An extended search for a substance which might be available for application in animal experiment (relatively soluble), and at the same time capable of emitting fluorescent rays in the mid-ultra-violet region of the spectrum under the influence of the X-ray, has revealed only sodium bromide as possessing these qualities. Many organic chemical compounds fluoresce brightly in the visible region of the spectrum and a moderate number of them give fluorescence which is capable of blackening the photographic plate.

It has been shown that there are solids, liquids, gases and certain solutions which fluoresce. The phenomenon is not limited to any physical state. The nature of the fluorescence excited in any material, both as to intensity and quality is independent of the quality of the exciting X-rays and dependent on their energy alone.

I wish to express my appreciation to Dr. Paul Lewis for the very considerable interest which he has taken in this problem.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORIES OF THE UNIVERSITY OF CAPE TOWN.]

HYDROGEN OVERVOLTAGE.

Criticism of the Papers by MacInnes, Adler and Contieri.[1]

BY EDGAR NEWBERY.

Received June 1, 1920.

In these papers the authors appear dissatisfied with the explanations so far proposed for the influence of the physical condition of the electrode surface on hydrogen overvoltage, and they have carried out certain experiments and restated in a modified form the theory of Möller to account for these changes. Unfortunately, their method of experiment and also certain vital parts of their reasoning are open to most serious objections. It is to be feared that these objections are of such a nature

---

[1] THIS JOURNAL, 41, 194 and 2013 (1919).

as to invalidate completely the whole work so far as its original purpose is concerned. A few of these objections will be pointed out in the present criticism, but many others could be given if needed.

1. The definition of overvoltage given at the commencement of the first paper is quite incorrect. The potential of an electrode at which molecular hydrogen is being formed from hydrogen ions depends not only upon the overvoltage but also upon the applied E. M. F., the resistance of the electrolyte, and especially upon the transfer resistance.

Overvoltage is of necessity an *active* voltage or electromotive force, capable of doing work after all external sources of E. M. F. have been removed. Transfer resistance is a purely *passive* or frictional force which entirely ceases when the external E. M. F. is interrupted. These 2 forces work in the same direction during the passage of the current; but directly this current is interrupted, overvoltage alone exists and may then be measured. Although overvoltage and transfer resistance occur together in this way, they are mutually independent and frequently vary in opposite directions.

A fairly full account of the behavior of transfer resistance is given in the *Transactions of the Faraday Society*, **15**, Part I, 1919, under the title "The Resistance of an Electrolytic Cell." It will there be seen that when hydrogen is being liberated, transfer resistance is greatest at low current-densities. In the work under discussion, extremely low current-densities were employed, but these current-densities were just sufficient to liberate visible bubbles of gas. The electrodes must, therefore, have been saturated with gas; and the authors, apparently without knowing it, have chosen ideal conditions for obtaining the highest possible transfer resistances. Since the surface area of the electrode used was very small (no definite data are given), the transfer resistance at the electrode must have amounted to at least 1000 ohms, and may have been 100,000 ohms. Under these conditions, therefore, the effect of overvoltage is negligible and the whole work of the authors has consisted in measuring, not overvoltage, but the excess potential required to overcome transfer resistance.

(2) The authors are under some misapprehension as to the true overvoltage of platinum. They state (p. 194) that "a polished platinum electrode may show an overvoltage as high as 0.1 volt, whereas for platinized platinum it is nearly zero." This statement is incorrect. Platinum has 4 overvoltages corresponding to 4 states of valence, 0, 8, 4 and 2. These overvoltages are approximately 0.0, 0.18, 0.45 and 0.65 volt respectively, and are shown by both polished and platinized platinum, the only difference between the two being the greater care and time required to make the latter show the higher overvoltages. The "raison d'etre" of their work (*viz.*, the difficulty of explaining the supposed in-

fluence of physical condition of the electrode upon overvoltage) appears, therefore, to be non-existent.

(3) In evolving their theory, the authors appear to look upon the electrode as something in the nature of a spongy mass exuding gas through its pores, and lose sight of the fact that this gas has first to penetrate through the layer of adhering molecules before it can give up its electric charge to the electrode. The fact that this molecular layer cannot be seen with the microscope is, of course, no evidence whatever against its existence, and the well known sudden rush of current rapidly falling to nearly zero when an E. M. F. is first applied to a fresh electrode should have led the authors to suspect the presence of such a gas film. The formation of bubbles is then due to the gradual creeping together of this surface gas, and this process in certainly affected by surface conditions but has nothing to do with overvoltage.

(4) The proposed theory is quite unable to account for the dependence of overvoltage upon valence; the sudden rapid changes shown by a metal such as iridium from one definite and constant overvoltage to another equally definite and constant; the remarkably constant overvoltage shown by a metal such as thallium under the greatest variations of current density and time; the high "metal overvoltages" shown by iron, nickel and cobalt during electrolytic deposition from solutions of their salts; passivity, permanent and periodic; valve action; and many other electrode phenomena, all of which are readily accounted for by the hydride and higher oxide theory.

(5) The effect of external pressure upon true overvoltage is almost zero, no appreciable change being produced by pressures of 100 atmospheres or more of hydrogen or oxygen.[1] The effects observed by the authors are, therefore, due to changes of transfer resistance and as such are of considerable interest.

Many more objections could be stated, but sufficient has been said to show that this theory as it stands is quite untenable. If it is borne in mind that overvoltage in their experimental work is a negligible quantity and that transfer resistance is the main quantity which is being measured, many interesting points may be observed. The fluctuations of potential due to escape of bubbles are among these, and are evidently due to changes in the state of strain and tenuity of the molecular gas film which is the prime cause of transfer resistance. It is, however, unnecessary to use such small electrodes and sensitive galvanometers to observe these phenomena, since they are easily studied with electrodes of one sq. cm. area and a milliammeter. Polished surfaces show the phenomena best and also show a different effect when placed horizontally from that observed when held vertically. Mercury in particular shows

---

[1] *J. Chem. Soc.*, **105**, 2428 (1914).

the effect in a very marked manner even when fairly high current densities are used, and if the authors have access to an oscillograph (which the present writer has not), it is hoped they will utilize it in further experiments on this subject. These effects were observed by the present writer in 1914, when engaged on the preliminary work on overvoltage, but were then considered (perhaps wrongly) to be of insufficient importance for discussion. They may be explained as follows.

The gas bubbles grow in size by continually attracting smaller bubbles, dragging them against considerable frictional forces over the surface of the electrode. These large bubbles, therefore, produce a condition of lateral strain in the gas film on the surface, increasing its tenuity and hence diminishing its opposition to the entrance of new ions from the solution, in other words, lowering the transfer resistance. The attractive power of the bubble, and hence the diminution of transfer resistance, will therefore vary with the radius of the bubble. Directly the bubble breaks away, this surface strain is released, the surface film rapidly thickens and thus increases the transfer resistance until a new bubble forms, when the process is repeated. The gas nucleus left behind is probably attached to some projecting point on the electrode surface, and the absence of such points accounts for the intensification of the phenomena in the case of mercury.

The equation which the authors deduce

$$FE = \frac{3RT}{2pr}\gamma,$$

showing the relation between transfer resistance, bubble-radius, and external pressure, is very interesting, and when rightly applied may perhaps afford a mathematical basis for explaining the behavior of transfer resistance. The reason why its application is less successful with metals other than platinum is evidently due to the disturbing effect of true overvoltage which will be quite appreciable with most other metals. This can fortunately be eliminated by determining the overvoltage directly with the aid of a rotating commutator, and this commutator may be short-circuited by means of a plug key when the excess potential due to overvoltage plus transfer resistance is to be measured. If this is done, the equation will probably represent the facts with very fair accuracy in all cases, even where high current densities and high-overvoltage metals are used.

The effect of change of pressure on transfer resistance described by the authors is also a matter of considerable interest. The assumption that p is accurately represented by the external atmospheric pressure is, however, somewhat doubtful. In the case of very small bubbles, it may be far from true, since the electrostatic and surface tension forces present may greatly increase the actual value of p. At the same time, since the radii only of the larger bubbles just on the point of escaping were measured, the value of p for these is probably not far removed from that for the external pressure. It is quite possible that the observations on the increase of efficiency of metal deposition at low pressures may find important technical applications.

It is hoped that the authors will continue their investigations along these lines, taking the precaution to eliminate overvoltage effects by the introduction of a rotating commutator as already suggested.

Cape Town, South Africa.

[Contribution from the Gayley Chemical and Metallurgical Laboratory of Lafayette College.]

FLUIDITIES AND SPECIFIC VOLUMES OF MIXTURES OF BENZYL BENZOATE AND BENZENE. XXIX.

By Eugene C. Bingham and Landon A. Sarver.

Received July 15, 1919.

Introduction.

Evidence has been accumulating to prove that the old hypothesis that viscosities are additive is quite untenable. At the same time there is both theoretical and experimental proof that fluidities are additive. The decision as to whether one or the other or neither of these properties is additive is of course absolutely imperative before fluidity can come into use for solving physical chemical problems. Since fluidity is very well suited to solve many such problems, it seems strange to the uninitiated that the fundamental decision has been arrived at so late. The reason, however, is not far to seek. To test the hypothesis that fluidities are additive, it would be most natural and easy to measure the fluidities of mixtures of 2 pure inert liquids. The difficulty comes in finding liquids which are "inert," *i. e.*, individually non-associated as well as without tendency to combine with each other.

We have more or less satisfactory methods for determining when a given liquid is non-associated, but we are unable to predict with certainty when loose combinations may be formed; much less are we able to explain the nature of the "molecular compounds."

It is this complication of "variables" which has hitherto rendered the problem of their separation insoluble. One procedure is that advocated by Bingham of seeking evidence outside of mixtures of liquids in suspensions and pure liquids, which seems to speak more unequivocally in favor of the view that fluidities are additive. If this course is pursued and we boldly maintain that fluidities are additive the number of variables is at once reduced and it becomes possible to calculate the associa-