3. The heat of combination of iodine and ethyl acetate is calculated to be 3060 cal.

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

ON A PHENOMENON OBSERVED IN THE ACTION OF HYDROCHLORIC ACID ON VERY DILUTE ALKALI AMALGAMS.

BY GEORGE MCPHAIL SMITH.

Received October 14, 1908.

In the action of solutions on the amalgams of the alkali metals, especially during the decomposition of the latter with hydrochloric acid, preparatory to their analysis, the writer has often observed that, just before the evolution of hydrogen slows up, a characteristic cloud of minute gas bubbles is suddenly liberated from the surface of the amalgam, and that at the same time the amalgam suddenly shrinks together.

A series of electromotive measurements, which was published in a previous paper,[1] was preceded by two other series of experiments, which were considered less suitable for publication in that connection. The first of these throws light on the phenomenon referred to, and is the subject of the present paper.

The apparatus employed consisted of a vertically disposed glass tube, A, 11.8 cm. in length, with an internal diameter of 1.28 cm., which was held in position by a clamp. A small glass tube, B, carrying a short, platinized platinum wire, and partially filled with mercury, was inserted in the mouth of the larger tube, where it was held by means of a cork. The arrangement will be understood at a glance from Fig. 1. The voltmeter used was a Weston standard direct-reading instrument, with a range of 5 volts, divided into 150 equal parts.

The amalgams employed contained very close to 1 mg. atomic weight of amalgamated metal in 100 grams, and, unless otherwise stated, the hydrochloric acid was 0.1 normal.

Before starting the series, 2 cc. of mercury were run into the tube from a burette, and then 9 cc. of 0.1 normal hydrochloric acid, also from a burette, were added. A mark was made on the tube at the line of demarcation between the mercury and the solution, and also a line at the upper meniscus of the solution. In the subsequent experiments the same volumes of amalgam and solution were always used, the marks serving as guides. The circuit was closed in every case by inserting the cork bearing the platinum electrode, immediately after the addition of the hydrochloric acid.

With the combination Hg/N/10HCl/Pt, no perceptible deflection of the needle was observed on closing the circuit.

In the case of the alkali amalgams, there was at first a fairly uniform

---

[1] *Z. anorg. Chem.*, 58, 381 (1908).

evolution of hydrogen, accompanied by a gradual fall of potential. After a short time, however, the voltage began to fluctuate, and then fell suddenly. The sudden fall was accompanied by the characteristic expulsion

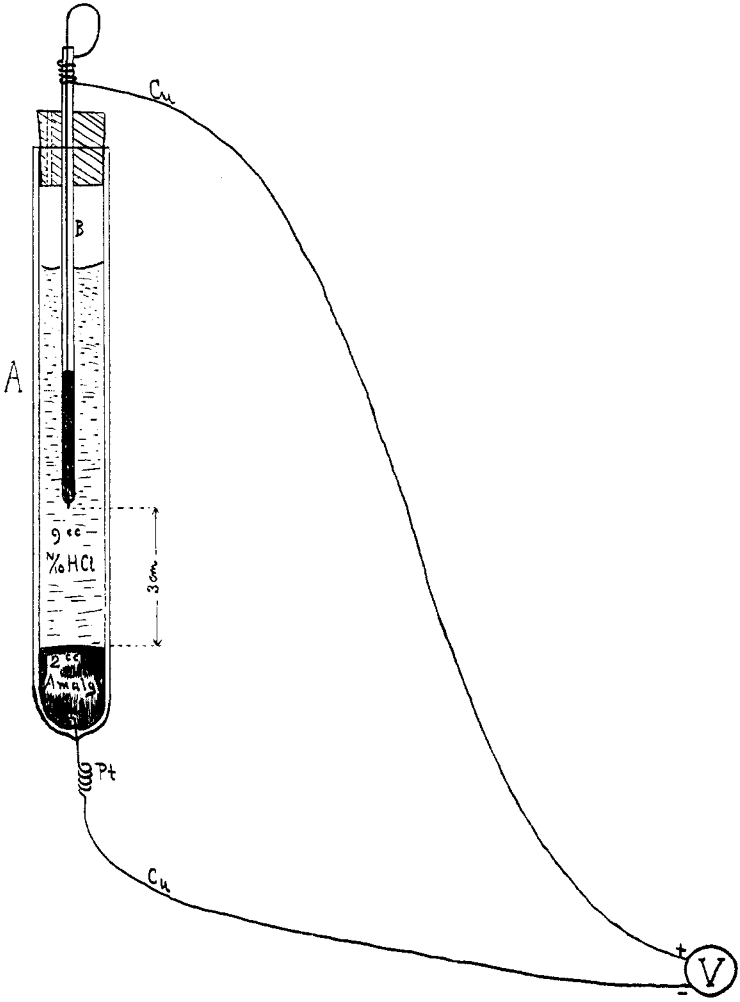

Fig. 1.

of a cloud of exceedingly minute hydrogen bubbles, which rendered the solution opaque for the time being. Simultaneously, the surface of the amalgam became more convex, and resembled more closely that of pure mercury. After this the potential continued to drop gradually, and, in most cases, a second sudden fall took place simultaneously with the rise of a large gas bubble from the surface of the amalgam, where it had gradually accumulated.

TABLE I.

→

Combination: 2 cc. 0.128% Cs amalgam | 9 cc. N/10 HCl | Pt. ($t = 20°–24°$.)

Minutes.	I.	II.	III.	Mean.	Remarks.
0	25.0	24.0	25.0	25.0	Evolution of H uniform and not very fast. Needle oscillated a little (maximum about 1/30 volt). Bubbles rose fast enough to keep the solution well stirred.
0.5	23.0	22.0	20.0	22.0	
1	22.0	21.0	20.0	21.0	
1.5	21.5	20.2	21.0	21.2	
2	20.5	21.3	19.5	21.1	
2.5	20.8	20.5	20.0	20.4	Here evolution of hydrogen gradually accelerated.
3	19.0	20.0	20.0	19.7	
3.5	17.5 }e	18.0	20.0	19.0	
4	11.0 }	17.0 }e	18.0 }e	17.5 }e	Here sudden evolution of cloud of H; voltage fell in at most 5 seconds.
4.5	10.0	11.0 }	10.0 }	10.6 }	
5	9.5	9.8	9.5	9.8	Evolution of hydrogen much slower; bubbles larger, and tended to adhere to surface of amalgam, and consolidate. In I and II large bubble rose between 6 and 7 minutes. After this bubbles reformed, and voltage again rose a little.
6	7.5	7.3	8.0	7.6	
7	1.4	3.0	5.5	3.3	
8	1.8	2.0	3.2	2.3	
9	1.8	2.7	2.5	2.3	
10	1.8	2.3	1.8	2.0	
15	1.5	1.8	1.4	1.6	
20	1.1	1.3	1.1	1.2	

TABLE II.

→

Combination: 2 cc. amalgam | 9 cc. N/10 HCl | Pt. ($t = 20°–24°$.)

Minutes.	Cs.	Rb.	K.	Na.	Li.	Ba.	Sr.	Ca.
0	25.0	27.0	33.0	32.0	33.0	22	25	15
0.5	20.0	25.0	31.2	30.5	30.5			12
1	20.0	25.0	30.2	30.0	30.3	15	16.5–17.5	11
1.5	21.0	24.5	29.7	29.5	30.2			
2	19.5	23.8	29.2	28.8	29.5	14–15	16–17	10–10.5
2.5	20.0	23.0 }e	28.7	28.0	27.5			
3	20.0	14.5 }	27.8	27.3	26.3	14–15	15–16	10
3.5	20.0	12.8	26.0 }e	25.8	24.7			
4	18.0 }e	11.5	18.8 }	24.0 }e	22.5 }e	13.5–14	16–16	9.5
4.5	10.0 }	10.8	17.0	16.7 }	13.6 }			
5	9.5	10.0	16.0	16.0	12.7	13.5–14	15	9.8–10
5.5	9.0	9.5	15.4	14.9	11.1			
6	8.0	3.5	14.0	13.7	8.2	13.5–14	14–15	8.7–9
6.5	7.8	3.4	13.5	12.4	6.0			
7	5.5	3.5	12.2	11.0	4.7			8.7–9
8	3.2	3.5	9.0	7.8	3.8	12–13	14–15	8.5
10	1.8	3.4	7.3	5.3	2.3	11	13–14	7.3
15	1.4	3.2	4.8	3.1	0.8	9–11	13–15	6.0
20	1.1	3.1	2.3	1.6	0.8	9–12	10–11	4.5
21.5						9.5–10.5	9–10 }e	4.6
22						9.5–10.5 }e	7 }	4.2
23						8 }	6–7	4.2
24						6–8	7–5	4.1
25						5	6–7	4.1

The experiments performed with caesium amalgam are given in detail in Table I. In Table II are given the results of one of the three experiments performed with each amalgam. In all cases the point at which the sudden evolution of minute hydrogen bubbles took place is marked *e*. The potentials are given in 1/30 volts, just as they were read from the voltmeter.

The experiments performed with alkali earth amalgams containing 1 mg. atomic weight of amalgamated metal in 100 grams are also given in Table II, although the phenomena under discussion are very much less pronounced in their case.

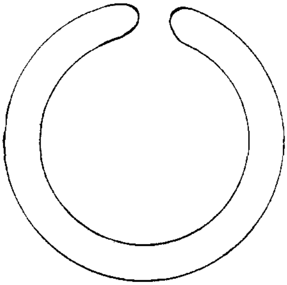

Fig. 2.

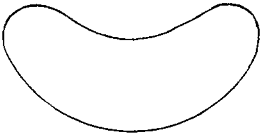

Fig. 3.

From the manner in which the alkali amalgams shrink together, it appears that the phenomena, marked *e* in the tables, are closely related to sudden changes in the surface tension of the amalgams. That such changes do take place at this point is clearly shown by the fact that, if enough dilute alkali amalgam (*e. g.*, 0.3 per cent. K-amalgam) is introduced into a small beaker to assume the shape indicated in Fig. 2, and an excess of 0.2 normal hydrochloric acid is then added, the amalgam at first gives off hydrogen at a moderate rate, in the form of distinguishable bubbles; after a few minutes the rate of evolution becomes faster, the surface of the amalgam begins to pulsate, and a few seconds later the characteristic cloud of minute bubbles is suddenly liberated; at the same time, the amalgam suddenly shrinks to the form indicated in Fig 3.

Finally, the potentials at which the phenomena under discussion take place appear to be fairly constants under varied conditions. This is brought out in Table III.

TABLE III.

Minutes.	2 cc. Li amalgam | 9 cc. N/5 HCl | Pt.	2 cc. Li amalgam | 9 cc. N/10 HCl | Pt.	1 cc. Li amalgam | 9 cc. N/10 HCl | Pt.
0	32	33.0	28.0
0.5	25	30.5	25.0
1	24	30.3	23.5
1.5	23 ⎫ *e*	30.2	21.0 ⎫ *e*
2	12 ⎭	29.5	9.0 ⎭
2.5	10	27.5	
3	9	26.3	
3.5		24.7	
4		25.5 ⎫ *e*	
4.5		13.6 ⎭	
5		12.7	

Summary.

It is shown in this paper that in the decomposition of the alkali amalgams by means of hydrochloric acid, a point is reached at which there is a sudden increase in the surface tension of the amalgams, and that this increase in surface tension is accompanied by the sudden evolution of a cloud of minute hydrogen bubbles, and by a sudden decrease in the solution pressure of the amalgams.

CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS,
URBANA ILL., Oct. 10, 1908.

COLORIMETRIC DETERMINATION OF DISSOLVED OXYGEN IN WATER.

G. B. FRANKFORTER, G. W. WALKER AND A. D. WILHOIT.

Received October 17, 1908.

Dissolved oxygen is becoming an important factor in the regular sanitary analysis of water. The amount of free oxygen will frequently enable the analyst to diagnose the sample with accuracy. If a sample of water contains less than the normal amount of dissolved oxygen, one may conclude that the water has, during its recent history, contained a considerable quantity of organic matter or some other reducing reagent like iron or perhaps that it has come from some deep underground current where it has been excluded from the air for a long time as in the case of very deep wells.

While the variation in the amount of dissolved oxygen is not so great as the variation in the amount of some of the other sanitary constituents in water, it is nearly always sufficient to enable one to draw a pretty definite conclusion as to the source and history of the sample. From a large number of analyses of water from a great many different sources, we have found that the volume of oxygen usually lies between 1 and 7.5 cc. per liter. In extreme cases, we have found samples to vary from a trace to 10 cc. per liter. In many of the artesian wells we have found the oxygen to run as low as 0.3 cc. per liter. Samples from the iron mines of Northern Minnesota frequently contain only a mere trace, while samples from some of the peat bog springs do not contain even a trace. On the contrary, the water from the Mississippi river as it flows over the St. Anthony Falls in winter, contains as high as 10.6 cc. per liter, while the same water, collected just below the inlet of a large sewer, contained only 3.2 cc. per liter. Samples from the iron springs of the northern part of this state and from peat bogs, rarely ever contain more than a trace of oxygen.

In the beginning of this work, various methods of determining oxygen were used. The boiling out method was first tried and the Reichardt and Tenax apparatuses were tested. The results, on the whole, were