

state," in which the concentrations of bromine, bromide, and acid remain constant in a single experiment.

2. At the steady state the rate of decomposition of the peroxide in the dark at 25° in sulfuric acid solutions above 0.2 *N* is represented by (Equation 7),  $-d(\text{H}_2\text{O}_2)/dt = 0.0140 (\text{H}_2\text{O}_2)(\text{acid})(\text{bromide})$ .

3. At the steady state the following functional relation has been demonstrated to hold for sulfuric acid concentrations below normal (Equation 13):  $R = (\text{Br}_2)/(\text{acid})^2(\text{bromide})^2 = 0.20$ . The value of *R* increases slightly with decreasing temperature, but decreases to a very small value when the reaction mixture is exposed to sunlight.

4. Definite evidence that the catalysis is completely accounted for by the two compensating reactions is obtained by measuring the rate of each at a distance from the steady state. The results obtained agree closely with those predicted from the steady-state data and the assumption of a kinetic (or rate-determining) mechanism involving hypobromous acid (Equations 8 to 12). The ratio of the specific reaction rates of the two reactions is equal to *R*, and at the steady state each reaction accounts for half the peroxide decomposed.

5. The possibility of choosing catalysts by means of free-energy data is discussed and some examples are given.

6. A method is described for the volumetric determination of hydrogen peroxide in the presence of bromide.

BERKELEY, CALIFORNIA

---

## NOTES

**The Collodion Membrane for Liquid Junctions.**—Investigators in the measurement of hydrogen-ion concentrations by the electromotive-force method have greatly felt the need of an effective simple device which will prevent the mechanical intermixing of one liquid into another at the liquid junctions in the system being measured. In this respect, the authors believe that they have made an improvement by the use of a collodion membrane. It should be borne in mind, however, that this type of junction is applicable only to those solutions to whose ions the collodion membrane is equally permeable, because if the membrane is not equally permeable, then, as shown by the work of Loeb,<sup>1</sup> the effect known as the Donnan equilibrium leads to high potential values at the membrane.

The collodion membrane is made simply by dipping the siphon tube of the electrode vessel several times into a small test-tube of collodion (18 g. of ether per oz. (31 g.); 27% alcohol, U. S. P. IX) and exposing it to the air until a solid membrane is formed at the end of the siphon tube. It is best to expose the collodion solution at first to the air for a short

<sup>1</sup> Loeb, "Proteins and the Theory of Colloidal Behavior." McGraw-Hill Book Co., New York, 1922. Chap. VIII.

while in order to evaporate some of the ether before dipping in the tube. The thickened collodion solution will then by the further evaporation of ether prevent a bubble of air from entering the gooseneck of the electrode vessel and thus increasing the resistance of the system. In order to test the membrane at any time, the stopcock of the siphon tube is opened; if no liquid drops appear at the end of the tube, the membrane has been satisfactorily made. With this device careful adjustment of the levels of the solutions in the several vessels is not necessary, for no potassium chloride will siphon into the solution whose hydrogen-ion concentration is to be measured. The authors have made over a hundred measurements on various solutions of hydrochloric, acetic, monochloro-acetic and oxalic acids with saturated potassium chloride solution as salt bridge, and in no case did they obtain a test for either potassium ion or chloride ion with the collodion membrane.

It is customary practice to accept the final value in all e.m.f. determinations when the resultant e.m.f. value is constant for an hour or more. Experience has shown that the drift in the contact potential has caused considerable uncertainty in the final value. With the collodion membrane this drift is greatly retarded, as evidenced by the constancy (within  $\pm 0.2$  mv.) of the final observed values after the hydrogen electrodes have become thoroughly saturated with hydrogen.

The following observed values show the constancy of the measurements on acetic acid.

SYSTEM: Hg-HgCl SAT. KCl-SAT. KCl-SAT. KCl-HX-H <sub>2</sub> Pt						
Temp. 25° C. $\pm$ .01°						
Start H <sub>2</sub> at 2:10 P. M.	Min.	For collodion Membrane	Start H <sub>2</sub> at 3:30 P. M.	Min.	For Cotton Plugs	3.0 M CH <sub>3</sub> COOH
2:46	36	0.3608	4:13	43	0.3622	
2:59	49	.3608	4:34	64	.3615	
3:26	66	.3607	4:48	78	.3616	
3:31	81	.3607	4:55	85	.3611	
3:38	88	.3608	5:06	96	.3618	

CONTRIBUTION FROM THE  
CHEMICAL LABORATORIES OF  
COLUMBIA UNIVERSITY, No. 403

NEW YORK, N. Y.  
Received February 17, 1923

HAROLD A. FALES  
MORTIMER J. STAMMELMAN

**A Simplified Method of Writing "Electronic" Formulas.**—The current methods of writing or printing "electronic" formulas, besides lacking uniformity, are open to other objections. The formulas in use are often cumbersome and difficult to write and to interpret due to the possible confusion of the valence sign with the negative sign, and the notation for the very low difference of polarity present in methane with the same notation used to indicate ionization.