These results show that the liquid junction formed by the confluence of the 2 streams gives exactly the same and just as constant a potential as does the one-way flow of a single electrolyte. However, the stirred junctions formed here were not constant and in general gave lower potentials than the flowing junctions, whereas in the previous arrangement higher results were obtained.

Summary.

The above experiments have shown:

1. That liquid junctions formed between the bearing surfaces of ground glass stoppers, in gelatin diaphragms and in parchment paper diaphragms, with 0.1 *N* hydrogen chloride and potassium chloride solutions are not constant and reproducible to closer than 0.2 or 0.4 of a millivolt.
2. That parchment diaphragms with stirring give somewhat more constant results.
3. That fresh junctions in tubes of 5 mm. bore give potentials reproducible in 0.1 *N* solutions to about ±0.03–0.06 millivolt when oscillations of the electrolyte are prevented, but that with *N* solutions variations of ±0.3 millivolt occur.
4. That stirred junctions sometimes give very constant potentials, but these are quite different from that produced by a "flowing" junction and, moreover, they differ, depending on the mode of stirring, etc.
5. That a "flowing" junction, obtained simply by having an upward current of the heavier electrolyte meet a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with *N* solutions, gives potentials constant and reproducible to ±0.01 of a millivolt.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA.]

THE REACTION BETWEEN HYDROCHLORIC ACID AND POTASSIUM PERMANGANATE.

BY F. P. VENABLE AND D. H. JACKSON.

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On account of its convenience and ease of regulation, the reaction between hydrochloric acid and potassium permanganate has become the usual one for the preparation of chlorine for laboratory purposes. On looking over the text-books one finds some confusion of thought, some misstatements, and a certain amount of evasion of the facts involved. The equation given for this reaction in most of the text-books is

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

In others it is represented as an oxidation of the hydrochloric acid

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

By some the only statement made is that the reactions are quite complicated, and it is also stated that, whether the reaction is between hydrochloric acid and permanganate or manganese dioxide, enough molecules of the acid must be used to furnish hydrogen to combine with all of the oxygen of the oxidizing agent.

The following investigation was undertaken to explain certain observations made during the use of this method for class and laboratory purposes, and, if possible, to clear up the confusion in which the matter stands.

When conc. hydrochloric acid is allowed to drop upon solid permanganate chlorine is evolved and a brown-black mass is formed. On further careful addition a point is reached where this brown-black mass settles out from a colorless liquid and no permanganate is left. This takes place when half the amount of hydrochloric acid called for in the above equation has been added. The brown substance, dried and weighed, is converted quantitatively into Mn_3O_4 by ignition and is, therefore, manganese dioxide.

Following these observations quantitative experiments were carried out in which the amounts of permanganate and acid used were those called for in the equation

$$2KMnO_4 + 8HCl \longrightarrow 2KCl + 2MnO_2 + 4H_2O + 6Cl,$$

and the manganese dioxide and chlorine were determined.

		I.	II.	III.		I.	II.	III.
Theoretical, %..........	MnO_2	1.10	2.88	2.39;	Cl	1.35	3.53	3.16
Found, %..............	MnO_2	1.102	2.85	2.36;	Cl	1.34	3.47	3.18

When the permanganate is used in excess, all over the theoretical amount is left unchanged. When an excess of acid is used the brown-black dioxide is first formed, then dissolved, and so much of the acid enters into the reaction as is indicated in the equation

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

Changes in color show that there are intermediate reactions. A green solution is obtained under certain conditions indicating the presence of manganese tetrachloride. For the second stage of the reaction application of heat is necessary. This equation was also tested quantitatively, giving the following results:

		I.	II.	III.		I.	II.	III.
Theoretical, %............	HCl	4.68	3.69	3.69;	Cl	2.83	2.25	2.25
Found, %................	HCl	4.71	3.67	3.66;	Cl	2.81	2.21	2.23

Experiments were then carried out in which dry hydrogen chloride was passed at room temperature over the permanganate placed in a boat in a glass tube. So long as the permanganate was in excess only the dioxide was formed. The reaction is exothermic and the water formed was vaporized and condensed on the sides of the glass tube. On continuing the passage of the hydrogen chloride after all the permanganate had been acted upon a white crust of manganese chloride and potassium chloride appeared on the dioxide. The presence of the potassium chloride formed before this was doubtless obscured by the dioxide.

It is evident then that there are two reactions taking place in sequence, first, that represented by the equation

$$2KMnO_4 + 8HCl \longrightarrow 2KCl + 2MnO_2 + 4H_2O + 3Cl_2,$$

and following that, in case excess of acid is used, the reaction

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2.$$

Similar experiments were carried out with potassium permanganate and hydrogen bromide and analogous results obtained. It was noted that hydrobromic acid reacted at a dilution of 0.00154 N, whereas no reaction with hydrochloric acid at a dilution beyond 0.002 N took place, 50 cc. of the acid being used in each case.

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THE IONIZATION AND ACTIVITY OF LARGELY IONIZED SUBSTANCES.[1]

BY ARTHUR A. NOYES AND DUNCAN A. MACINNES.

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In applications of the ionic theory of solutions it is customary to employ, in accordance with the original hypothesis of Arrhenius, as a measure of the degree of ionization of salts, acids, and bases, the ratio of the equivalent conductance of the substance at any given concentration to the limiting value of the equivalent conductance as the concentration approaches zero, where the ionization may be assumed to be complete.

This assumption, however, is not a necessary conclusion from the fundamental theory of ionic conduction. According to this theory, the equivalent conductance Λ (which is by definition the quantity of electricity which under a potential difference of one volt passes per second between electrodes of indefinite extent one centimeter apart, between which is placed that quantity of solution which contains one equivalent weight of the ionizing substance) is for a uni-univalent substance given by the expression, $\Lambda = \gamma \mathrm{F}(\mathrm{U}^+ + \mathrm{U}^-)$, in which γ is the fraction of the substance ionized (equal in this case to the number of equivalents of each ion present in the solution), F the quantity of electricity (96500 coulombs) associated

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[1] Read before the National Academy of Science, November 10, 1919.