No.	Wt. sample.	I absorbed.	Calc. for W″.	Calc. for W‴.	Calc. for W⁗.
1	0.1007	0.138	0.174	0.131	.....
2	0.1008	0.131	0.174	0.131	.....
3	0.1016	0.089	.....	0.132	0.088
4	0.1009	0.167	0.174	0.131	.....

Summary.

1. The action of chlorine on tungsten metal to form hexachloride is catalyzed to a remarkable degree by the presence of a small amount of platinum black.

2. Tungsten forms the compound $W_6Cl_{12}.2HCl.9H_2O$, resembling the molybdenum derivative $Mo_3Cl_6.HCl.4H_2O$, prepared by Rosenheim and Kohn.

3. The alkaline solution of the preceding compound oxidizes readily and from the solution stable hydrates of trivalent and quadrivalent tungsten were obtained.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE LABORATORY FOR CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

THE EFFECT OF PRESSURE UPON THE POTENTIAL OF THE HYDROGEN ELECTRODE.

BY N. EDWARD LOOMIS AND S. F. ACREE.

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In the previous work by the authors,[1] by Desha,[2] Myers,[3] and by Clarke,[4] it was shown how to make hydrogen and calomel electrodes which can be read to a few millionths of a volt. It was further found that by using a large number of hydrogen and calomel electrodes in batteries to reduce errors, by thoroughly saturating the acid solutions and electrodes with hydrogen before connecting the systems, by using a saturated (4.12 *N*) solution of potassium chloride to annul the contact potential as completely as possible, and by using wide connecting tubes and large fresh contact surfaces, and keeping the barometric pressure constant, it is possible to reproduce readings in a given series to close to 0.00001 volt. Recent investigations of our own and by others[5] have shown that these methods must be adhered to closely for work of the highest precision and accuracy.

The two greatest sources of uncertainty in this work are contact potential and the potential of the hydrogen electrode when incompletely saturated, and, because of these, high reproducibility of readings does not mean corresponding high accuracy. We, therefore, devised,[6] in 1910–11,

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[1] *Am. Chem. J.*, **46**, 585, 621 (1911); Loomis, *J. Phys. Chem.*, **19**, 660 (1915).

[2] *Am. Chem. J.*, **46**, 638, 641, 643, 647 (1911).

[3] *Ibid.*, **50**, 396 (1913).

[4] *J. Phys. Chem.*, **20**, 243 (1916).

[5] Clarke and Lubs, *J. Biol. Chem.*, **25**, 479; Ellis, THIS JOURNAL, **38**, 737 (1916).

[6] *Am. Chem. J.*, **46**, 585, especially Dissertation, J. H. U., p. 29, 609. footnote.

an automatic pressure regulating device involving a Fuess normal barometer and electrical equipment for measuring the e. m. f. while keeping the hydrogen at normal and any other desired pressure while it passes through the system. Because of other work, however, we have not yet been able to take up all the problem outlined of studying the effect of hydrogen pressure on the e. m. f. at different temperatures, of measuring the rate of establishment of the gaseous and electrical equilibrium within the electrodes of different materials having different kinds of surfaces in order to study constant and especially *changing* solutions, and especially the problem of studying the mechanism of the establishment of the equilibrium between the molecules, atoms, and ions of hydrogen in and at the different kinds of electrodes. This last phase of the problem is also being studied by Prof. Edward Bennett and one of us in our investigations on the conductivities of solutions. Especial attention will be given to the well-known facts that between 100° and 180° hydrogen dissolves in palladium as hydrogen atoms[1] up to about 400 mm. and above this pressure chiefly as H_2 to the extent of about 900 volumes. Platinum black[2] dissolves about 100 volumes oxygen and 110 volumes of hydrogen up to 300 mm. and above this pressure up to 4–5 atmospheres. The volume absorbed is practically constant for hydrogen but increases 8.5 volumes for oxygen. This last point may be significant in connection with the fact that the hydrogen-oxygen cell gives only 1.08 volts instead of 1.23. Experiments will be performed at 1–3000 mm. at different temperatures to see whether at the critical pressures discussed above, 300 mm. and 400 mm., there is any break in the e. m. f.-pressure-temperature relation should involve $(P - 300)$ and $(P - 400)$ instead of P.[3] This effect of pressure on the electromotive force must be considered all the more important because of such work as that of Harris[4] in which he found that in hydrogen gas the negative charge is associated with 1, 3 and 6 molecules of hydrogen and that the positive charge is associated with 9 molecules of hydrogen. A discussion of all of these relations will be found in another article.

When the work of Loomis and of Myers was carefully considered the data seemed to fit in best with the barometric corrections deduced from the formula $E = RT/nF \log n\ H_2/H'_2$, in which n was chosen as unity for the balance of the hydrogen ions. But the corrections were so small, and were so masked by such other errors as contact potential that it was shown that the same average values were obtained whether a barometric correction was applied or not. In view of these uncertainties and the fact that no one else had had occasion to work with the precision requiring

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[1] Hoitsema, *Z. physik. Chem.*, **17**, 1 (1895).

[2] *Ibid.*, **19**, 25 (1896).

[3] *Z. physik. Chem.*, **17**, 1 (1895).

[4] *Phil. Mag.*, **31**, 339 (1916).

the solution of this problem, it seemed desirable[1] to get direct evidence on the effect of wider variations of pressure upon the potential of the hydrogen electrode, especially in the chain

$$H_2—Pt—0.1\ N\ HCl—0.1\ N\ KCl—Hg_2Cl_2—Hg$$

upon which most of the work had been done. The experiments described in this article show that the corrections in the data of Loomis and Myers obtained by the use of the above equation are double the values now found, as has been pointed out by Loomis.[2] When the proper corrections are applied to all our data there are no changes in the general averages because, as pointed out before,[3] the average barometric pressure in Baltimore is practically 760 mm. The same average value 0.4272 is obtained for the data of Myers and Clarke as we obtained in the present study of the electromotive force on the hydrogen electrode in 0.1 N hydrochloric acid against calomel in 0.1 N KCl.

This work, therefore, shows that the absorbed molecular hydrogen in the electrode is proportional to the $^1/_2$ power of the hydrogen pressure or that the absorbed molecular gas gives hydrogen atoms in accordance with the equations $H_2 = K \times 2H$, and $H^+ = K' \times H$, either condition leading to the equation $E = RT/2F \log n\ p_1/p_2$, as discussed in another paper. Our work, therefore, harmonizes with that of Czepinski,[4] Haber and Foster,[5] Lewis and Rupert,[6] and of Ellis,[7] who recently made one direct measurement of the effect of pressure on the hydrogen electrode.

The method used in obtaining the results given in this paper was to measure the hydrogen electrode in 0.1 N hydrochloric acid against the calomel electrode in 0.1 N KCl with no intermediate solution, first at barometric pressure and then at increased or decreased pressure. The arrangement of the solutions was such that increase in pressure caused very slight shifting of the solutions. Contact between the two solutions was made in a wide tube as in all our other work and as recommended since by Cummings and Gilchrist,[8] and by Clarke and Lubs.[9] In order to get constant potentials it was found necessary to renew the surface of contact between the two electrolytes at each set of readings. All measurements were made at 25°.

The apparatus used in making the measurements was the same as

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[1] *Am. Chem. J.*, **46**, 585, 609, footnote.

[2] *J. Phys. Chem.*, **19**, 663 (1915).

[3] *Am. Chem. J.*, **46**, 626 (1911), footnote.

[4] *Z. anorg. Chem.*, **30**, 1 (1902).

[5] *Ibid.*, **51**, 289 (1906).

[6] THIS JOURNAL, **33**, 299 (1911).

[7] *Ibid.*, **38**, 737 (1916).

[8] *Trans. Faraday Soc.*, **9**, 174 (1913).

[9] *J. Biol. Chem.*, **25**, 491 (1916).

that which has already been described in previous papers from our laboratory.

One experiment is described in detail to illustrate the method in which the measurements were carried out.

8.40 A.M.	E. M. F. experiment started.	8.40 A.M.	E. M. F. experiment started.
9.16	0.42583	Increased pressure to atmospheric + 40 mm.	
9.35	0.42634	10.19	0.42701
9.43	0.42642	10.26	0.42717
9.54	0.42654	10.36	0.42721
9.56	0.42652	10.40	0.42722
Bar. (corrected) = 735 mm.		Pressure = 735 + 40.	

Corresponding to an increase in pressure of 40 mm. there is an increase in potential of 0.42722 — 0.42652 = 0.00070.

In calculating the change in potential of the hydrogen electrode from the equation

$$E = \frac{RT}{2F} \log n \frac{p_1}{p_2} = \frac{0.05915}{2} \log_{10} \frac{p_1}{p_2},$$

it has seemed more logical[1] to use for p_1 and p_2 not the total pressures of the system but the partial pressures of the hydrogen, *viz.*, the total pressures minus the vapor pressure of the water solution, practically the same as that of pure water for dilute solutions. There is a difference[2] of only a few hundred thousandths of a volt in the two ways of calculating and our results are not sufficiently accurate to indicate which method of calculation gives the better results.

Applying the equation to this experiment we have

$$E = \frac{0.05915}{2} \log_{10} \frac{775 - 24}{735 - 24} = 0.00070.$$

In this case there is perfect agreement between the measured and theoretical values.

To indicate the steadiness of the electromotive force of the system this same experiment may be followed somewhat further. After the measurement at 775 mm. had been made the pressure upon the system was increased to 789 and then allowed to fall to the original pressure of 735 again. The reading at 789 was 0.42749 at 11.09 A.M. The pressure was released and the subsequent readings were as follows:

Time	11.17	11.26	11.34	11.41	11.45	11.48	11.54
E. m. f.	0.42683	0.42654	0.42647	0.42645	0.42648	0.42651	0.42653

It will be noted that the last two readings are practically identical with those two hours earlier at the same pressure.

The following table summarizes the results which were obtained in eigh-

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[1] Loomis and Acree, *Am. Chem. J.*, 46, 610 (1911), footnote. Ellis and Clarke and Lubs have now adopted this method.

[2] Loomis and Acree, *Am. Chem. J.*, 46, 610 (1911), footnote.

teen similar experiments. The readings at different time periods are omitted and only the final e. m. fs. obtained at equilibrium are given.

Pressure Change.		Difference of Potential.	
Meas.	Corr. for vapor tens.	Meas.	Calc. $(RT/2F \log_n p_1/p_2)$.
743.5–785.	719.5–761.5	+0.00099	+0.00073*
740 –778	716 –754	+0.00053	+0.00066*
778 –742	754 –718	—0.00067	—0.00063
742 –788	718 –764	+0.00075	+0.00080
788 –742	764 –718	—0.00076	—0.00080
742 –794	718 –770	+0.00086	+0.00092
739 –760	715 –736	+0.00043	+0.00037
760 –738.5	736 –714.5	—0.00046	—0.00038
733.5–763	709.5–739	+0.00052	+0.00052
735 –775	711 –751	+0.00070	+0.00070
775 –789	751 –765	+0.00027	+0.00024
789 –735	765 –711	—0.00096	—0.00094
735 –785	711 –761	+0.00097	+0.00087*
785 –734.5	761 –710.5	—0.00090	—0.00088
734.5–780.5	710.5–756.5	+0.00078	+0.00081
734.5–809.5	710.5–785.5	+0.00125	+0.00129
735 –794.5	711 –770.5	+0.00119	+0.00103*
794.5–733.5	770.5–709.5	—0.00121	—0.00106*

The first two experiments are to be considered as preliminary ones. The poorer agreement in these is probably due to the fact that fresh surfaces of contact between the two solutions were neglected. The lack of agreement in the fifth from the last is probably due to incomplete saturation or to a change in the potential of the calomel cell, possibly due to shaking, as indicated by the fact that when the pressure was released the electrode failed to come back to its original value by an amount very close to the difference between the theoretical and measured values. In the two final experiments the temperature of the bath varied. But even in these experiments the changes in e. m. f. obtained are much closer to the theory than to double this amount. These experiments marked * are omitted from the final average. For the remaining determinations the average change in potential per mm. change in pressure is 0.00001751; that calculated is 0.00001746, a variation of 0.29%.

This series of experiments also gave opportunity for further measurements of the potential of the system

$$H_2\text{–Pt–}0.1\ N\ \text{HCl–}0.1\ N\ \text{KCl–}Hg_2Cl_2\text{–Hg}.$$

The average values of previous measurements of this system by Bjerrum (1) Loomis and Acree (2), and Myers and Acree (3) are 0.4273, 0.4269 and 0.4273, respectively, after correcting for barometric pressure, for the vapor tension of the solution at the hydrogen electrode, and for the present voltage of the Weston cell, and the average is 0.4272. For a more complete summary of these measurements see Loomis and Meacham in an article soon to be published. The following table gives the measured voltage of five experiments with the above system at 25° with corrections for the potential of the calomel cell, for the barometric pressure, and for the vapor tension of the solution, and the final corrected voltage. The corrections for the potential of the calomel cell were determined as usual in our laboratory by comparing the working electrode with the mean of a large battery containing ten other electrodes. The couplets in the first column give the e. m. f. observed at first under atmospheric conditions and again at this pressure after having subjected the system to the increased pressure.

	Corrections.			
Meas. E. M. F.	Cal. cell.	Bar.	Vap. T.	Corrected. E. M. F.
0.42636	+0.00013	+0.00031	+0.00040	0.42720
0.42635	+0.00013	+0.00031	+0.00040	0.42719
0.42661	—0.00013	+0.00036	+0.00040	0.42724
0.42658	—0.00013	+0.00036	+0.00040	0.42722
0.42652	—0.00009	+0.00042	+0.00040	0.42725
0.42653	—0.00009	+0.00042	+0.00040	0.42726
0.42645	—0.00001	+0.00042	+0.00040	0.42726
0.42609	+0.00035	+0.00039	+0.00040	0.42723
			Average,	0.42723

Conclusions.

1. Experiments on the influence of the partial pressure of hydrogen on the potential of the hydrogen electrode show that near atmospheric pressure the changes can be expressed by the formula $E = RT/2F \log n\ H_2/H'_2$, in which H_2 and H'_2 are the partial pressures. The average change in potential found is 0.00001751 volt per millimeter which is only 0.3% larger than the value 0.00001746 volt calculated by the use of the above formula.

2. Five experiments on the system

$$H_2\text{–Pt–0.1 } N \text{ HCl–0.1 KCl–}Hg_2Cl_2\text{–Hg}$$

gave the potential 0.42723 ± 3, which is in very close agreement with the average of our earlier values and with those of Bjerrum, namely, 0.4272.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

STUDIES IN THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES. V. INVESTIGATIONS ON THE USE OF THE VREELAND OSCILLATOR AND OTHER SOURCES OF CURRENT FOR CONDUCTIVITY MEASUREMENTS.[1]

BY W. A. TAYLOR AND S. F. ACREE.

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As the measurement of the true electrical conductivities of solutions

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[1] Robertson and Acree, *J. Phys. Chem.*, **19**, 381 (1915); Taylor and Curtis, *Phys. Rev.*, **6**, 61 (1915); Taylor, *Science*, **42**, 388 (1915). We are indebted to the Carnegie Institution of Washington for aid in this work.