

3. The method is shorter, more convenient, and requires less oversight than that involving the use of sulfur dioxide, and the results are fully as accurate as those obtained by the latter process.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 145]

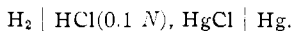
## THE EFFECT OF HYDROGEN PRESSURE ON THE ELECTRO- MOTIVE FORCE OF A HYDROGEN-CALOMEL CELL. I

BY WILLIAM R. HAINSWORTH AND DUNCAN A. MACINNES

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### Introduction

This investigation is concerned with the effect of pressure of gaseous hydrogen on the potential of a cell consisting of a hydrogen electrode and a calomel electrode, both in 0.1 *N* hydrochloric acid, *i. e.*, a cell of the type



The main interest of the experiments is, of course, the effect of varying the hydrogen pressure on the potential of a reversible hydrogen electrode. In a series of investigations, the results of which have appeared in *THIS JOURNAL*, one of the authors, with his associates, has endeavored to explain the irreversible overvoltage effects occurring when hydrogen gas is formed from its ions. It became evident during these researches that equilibrium measurements, such as will be described below, are essential for a more complete knowledge of the phenomena of hydrogen overvoltage. A discussion of this relation will be reserved for another paper. The measurements are, however, of interest outside of this connection.

Lewis and Randall,<sup>1</sup> Loomis and Acree<sup>2</sup> and Ellis<sup>3</sup> have studied the effect of pressure on a reversible hydrogen electrode. They found that the usual equation

$$\Delta E = \frac{RT}{2F} \ln p \quad (1)$$

(in which  $\Delta E$  is the change of the e.m.f. of the cell produced by changing the pressure from 1 atmosphere to  $p$  atmospheres) is applicable within the experimental error. The range of Ellis' experiments was, however, only from 1 to 1.5 atmospheres and this was considerably greater than the ranges of pressures covered by the other investigators. In this research the pressure range was extended to 400 atmospheres.

This article will discuss the apparatus used for the measurements,

<sup>1</sup> Lewis and Randall, *THIS JOURNAL*, **36**, 1969 (1914).

<sup>2</sup> Loomis and Acree, *ibid.*, **38**, 2391 (1916).

<sup>3</sup> Ellis, *ibid.*, **38**, 737 (1916).

the experimental results, and also a more complete expression than Equation 1 for the change of e.m.f. with pressure, and one which is applicable to higher pressures.

### The Apparatus

The apparatus consisted of (a) the hydrogen-calomel cell, contained in a steel bomb, and (b) the equipment for obtaining and measuring high pressures of hydrogen, and of controlling the passage of the gas through the cell.

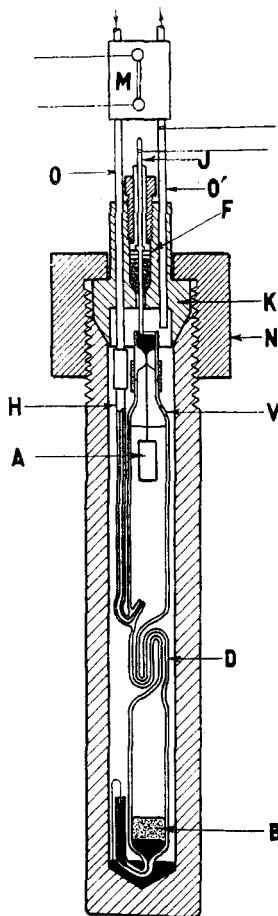


Fig. 1.

(a) **The Cell.**—The cell consisted, as is stated above, of a hydrogen electrode and a calomel electrode in 0.1 *N* hydrochloric acid. The hydrogen electrode, A in Fig. 1, was made of pure platinum gauze platinized according to the directions of Kohlrausch and Holborn.<sup>4</sup> Hydrogen passed into the cell and over the electrode through the tube H, and out through a small hole in the cell wall at V. The lower half of the cell held the calomel electrode B,<sup>5</sup> connection being made with the mercury by means of a platinum wire sealed through the glass of the cell wall. The bends in the glass tubing (at D in the figure) between the two half-cells served to prevent finely divided platinum from falling into the calomel, and to lengthen the path of diffusion for the calomel in solution, thus protecting the platinum electrode from the poisoning effect of the mercury salt. Contact was made with the calomel electrode by connecting, as shown, to mercury in the bottom of the bomb. The hydrogen electrode was connected by means of a mercury cup to a steel rod, J, passing through a specially designed insulating pressure joint, F. It was necessary to make several of these joints before one was obtained which would not give a galvanometer deflection with a potential across the insulation. Hard rubber insulators with mica washers were finally successful.

**The Bomb.**—The bomb consisted of a piece of 37mm. hexagonal, cold-rolled steel, 25 cm. long, bored with a 19mm. drill, and internally beveled to 60° at the top. The plug K closing the bomb and holding the insulating joint was beveled to 59.5° at the base, and was held in place with a lock nut, N, as shown. The copper tubing O and O' which was used to lead the hydrogen in and out of the cell was fastened with silver solder through holes in the plug. Connection to the potentiometer was made by wires to the insulated steel rod and to one of the copper tubes.

<sup>4</sup> Kohlrausch and Holborn, "Leitvermögen der Electrolyte," Teubner, Leipzig, 1898, p. 9.

<sup>5</sup> The mercurous chloride for the calomel electrode was precipitated from mercurous nitrate solution and was washed repeatedly with distilled water, followed by 0.1 *N* HCl solution. A saturated solution was then obtained by agitating the calomel in 0.1 *N* HCl for several days, at approximately 25°.

An annoying difficulty, during the early experiments, was that surges of gas would occur which would blow all the solution out of the upper half of the cell. These surges were largely due to the fact that the operator could not tell the rate of formation of hydrogen bubbles in the cell. Control was made possible by placing a simple microphone at the point M. This consisted of a light carbon pencil between two carbon supports, to which were connected a single dry cell and a telephone receiver. With this arrangement the breaking loose of each bubble was distinctly audible. At the higher pressures (above 100 atmospheres) this device decreased in sensitiveness for some reason that we have not been able to discover. However, regulation at these pressures was easier, as the differences were smaller between the successive pressures in the cell and those in the hydrogen reservoir.

(b) **The Apparatus for Obtaining and Measuring Hydrogen at Different Pressures.**  
—The apparatus as a whole is shown diagrammatically in Fig. 2. The flow of hydrogen from the tank A (at a maximum pressure of 120 atmospheres) was controlled by the tank

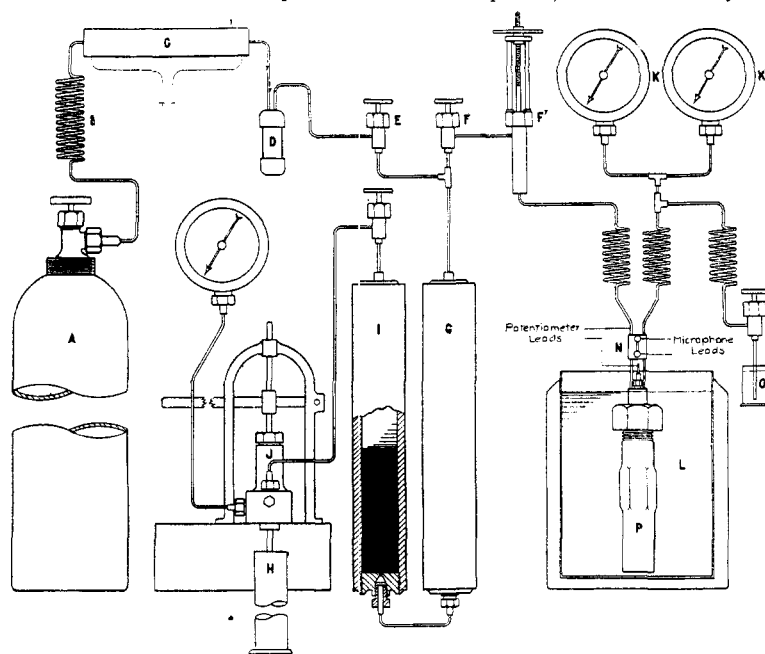


Fig. 2.

valve and the capillary copper tubing B. Traces of oxygen, in the (electrolytic) tank hydrogen, were removed by passage over platinized asbestos, maintained at  $110^{\circ}$  in the chamber C. The water formed was condensed in the drip pot D, which also served to saturate the hydrogen with water vapor at approximately  $25^{\circ}$ . The gas then passed through the needle valve E, either to the cell, through the controlling valves F and F' and the capillary tubing, or into the cylinder G, for further compression.

The higher pressures (above 120 atmospheres) were obtained by first displacing the mercury in G by hydrogen at the tank pressure, with valves F and F' closed, and then closing E and forcing oil from the graduated container H into the cylinder I, by means of the Cailletet hydraulic pump J. Care was taken to allow no oil to get into the gas chamber over the mercury, as it is probable that, if it should, frothing would result when the pressure was decreased, filling the copper tubing and other parts of the apparatus with

oil. The levels of mercury and oil were controlled by watching the amounts of oil remaining in H, and also by noting the pressures registered by the pump gage. The gas, at the higher pressure, was allowed to pass through the valves F and F', and through the cell (keeping the valve E closed) after which it escaped through the capillary tubing and the outlet valve into the atmosphere at O.

The pressures in the cell were determined by the gages K and K'. Two Crosby hydrostatic gages, and a special hydrostatic test gage, reading to 1500, 6000 and 8000 pounds per square inch, respectively, were used in various combinations, different gages, or combinations for comparison, being of service at different ranges of pressure. These gages were calibrated against a standard piston and weight apparatus such as is described by Keyes and Brownlee.<sup>6</sup> The latter gage had previously been tested against a mercury column. A slight inaccuracy in the hydrostatic gages probably developed during use, due to strain of the metal parts. It seems likely that this was the principal source of experimental errors in this work. The comparison of several series of measurements indicates that this error did not lead to uncertainties of over 0.2 mv. in the calculated potentials of the cell. However, the investigation is now being carried to higher pressures with a piston and weight apparatus (such as was used in calibrating the gages) for measuring the pressures.

The bomb P, containing the cell, was placed in a thermostat, kept at  $25^{\circ} \pm 0.1^{\circ}$ . The temperature was measured on a thermometer which had been calibrated by the Bureau of Standards. Kerosene was used in the thermostat, instead of water, to prevent rusting of the steel bomb, and to provide additional insulation.

A Leeds and Northrup potentiometer, which was carefully calibrated during the course of this work, was used to measure the e.m.f. of the cell. The standard cell used was compared, at intervals, with another standard cell which had recently been calibrated by the Bureau of Standards.

**Details of Manipulation.**—The following procedure was adopted in obtaining the experimental data. The lower half of the cell was filled (with the aid of suction) by introducing pure mercury, solid calomel and 0.1 *N* hydrochloric acid saturated with calomel. After rinsing the upper half of the cell several times with pure 0.1 *N* hydrochloric acid and nearly filling with this solution, the platinized platinum electrode, which had been washed with acid of the same concentration, was inserted. The upper half of the cell was then saturated with hydrogen at atmospheric pressure, and, if the cell potential was within 0.1 millivolt of 0.3990,<sup>7</sup> at  $25^{\circ}$ , corrected to one atmosphere of hydrogen and exactly 0.1 *N* hydrochloric acid, it was placed in the bomb, and the cone joint tightened. The hydrogen pressure was then increased. At intervals the pressure was held constant by a manipulation of the valves, which allowed a small amount

<sup>6</sup> Keyes and Brownlee, "The Thermodynamic Properties of Ammonia," Wiley and Sons, 1916, p. 10.

<sup>7</sup> Other than work on standard cells, the combination:  $H_2$  (1 atm.) HCl (0.1*N*), HgCl|Hg at  $25^{\circ}$  has received more attention than any other cell. Lewis, Brighton, and Sebastian, [THIS JOURNAL, 39, 2257 (1917)], give a summary of the values found by different investigators. Their experimental value is 0.3989. The other values are: Lewis and Randall 0.3990, Harned 0.3991, Loomis and Meacham 0.3988, Ellis 0.3989. All these values have been corrected for the vapor pressure of water. This correction, however, soon becomes negligible when the pressure is raised above 1 atmosphere.

of hydrogen to pass through the cell until a constant e.m.f. was obtained. Half an hour after reaching a constant pressure a constant potential (within 0.02 mv.) was observed, and this did not change further as long as the pressure was held at that point. After reaching the maximum pressure for a series, potential measurements were made while lowering the pressure, which was reduced so slowly that substantial equilibrium was maintained throughout.

### Experimental Data

Four successful "runs," or series of measurements, were made. These will be called Expts. 1, 2, 3, and 4, respectively. In Expt. 1 the maximum pressure obtainable was that of the tank of hydrogen A (Fig. 2) since the mercury pump I, G, had not yet been installed. Expt. 2 was a repetition of Expt. 1, except that measurements were made only at 1 atmosphere and at the maximum tank pressure.

For Expt. 3, the mercury pump was added to the apparatus and readings at higher pressures than the tank pressure were obtained. The range, however, did not extend as high as was anticipated due to a leak which developed in one of the gages.

In Expt. 4 a maximum of 406 atmospheres was reached. After obtaining this maximum the pressure was very slowly reduced to that of the atmosphere, substantial equilibrium being attained at all points down to about 2 atmospheres.

It was found in every case except Expt. 2 that on reducing the pressure to about 3 atmospheres, bubbles formed in the bent tube connecting the two halves of the cell. This broke the electrical circuit. The effect was undoubtedly due to the diffusion of dissolved hydrogen into the tubes and its appearance as the gas phase at low pressures. In Expt. 2, however, the time elapsing between the initial and final reading was made a minimum, thus reducing this diffusion, and no bubbles formed. In this experiment, the "return" value of the e.m.f. agrees within 0.1 mv. with the initial value. An examination of the agreement of the values obtained while increasing and decreasing the pressure shows, with certainty, that equally good agreement in the other three experiments would have been found if the return measurements below 3 atmospheres could have been made.

The results of the four experiments are summarized in Table I. In the first column is given the number of the experiment. The letter *I* indicates that increases of pressure were made before and after the measurements recorded, *D* represents measurements with corresponding decreases of pressure, and *M* the maximum pressure of the particular experiment. The "return" value obtained in Expt. 2 is represented by *2R* in the table.

Expts. 2, 3 and 4 were made with 0.0993 *N* acid in the cell. A cor-

rection of  $-0.0004$  v. was necessary for these experiments to bring all the measurements to a basis of exactly  $0.1 N$ . This small correction can be obtained, without any error, from a consideration of the activities of hydrochloric acid at the concentrations involved. The measurements for Expt. 1 were made with exactly  $0.1 N$  acid. The values for the e.m.f. as given in Table I include this correction and, for the initial determination of each series, the usual corrections for the difference between one atmosphere and the barometer reading, and also for the vapor pressure of the solution.

TABLE I  
MEASUREMENTS OF THE CELL  $\text{H}_2 | \text{HCl} (0.1 N), \text{HgCl}_2 | \text{Hg}$  AT  $25^\circ$  AND AT DIFFERENT PRESSURES

Expt.	<i>P</i> Atm.	E.m.f.	Expt.	<i>P</i> Atm.	E.m.f.	Expt.	<i>P</i> Atm.	E.m.f.
1	1	0.3990	4 <i>D</i>	23.1	0.4392	4 <i>D</i>	122.2	0.4611
2	1	0.3990	4 <i>D</i>	24.0	0.4396	3 <i>D</i>	169.8	0.4654
3	1	0.3990	1 <i>I</i>	43.2	0.4472	3 <i>M</i>	199.6	0.4677
4	1	0.3990	1 <i>I</i>	76.5	0.4547	4 <i>I</i>	209.6	0.4683
2 <i>R</i>	1	0.3991	3 <i>I</i>	85.4	0.4563	4 <i>D</i>	216.8	0.4690
4 <i>D</i>	2.2	0.4091	4 <i>D</i>	89.6	0.4568	4 <i>D</i>	268.5	0.4720
4 <i>D</i>	2.9	0.4127	1 <i>I</i>	95.8	0.4577	4 <i>I</i>	281.1	0.4725
4 <i>D</i>	7.6	0.4251	2 <i>M</i>	106.7	0.4594	4 <i>I</i>	337.2	0.4751
1 <i>I</i>	16.3	0.4348	1 <i>M</i>	112.0	0.4604	4 <i>M</i>	406.2	0.4779

### Theoretical Discussion

If we apply the first law of thermodynamics to a reversible process which includes an electrical work term,  $EdC$ , in which  $E$  is the electromotive force, and  $C$  the current (coulombs) and substitute the relation,  $dQ = TdS$  between the heat absorbed,  $Q$ , the entropy  $S$  and the absolute temperature  $T$ , we obtain,

$$dU = TdS - pdV - EdC \quad (2)$$

in which  $U$ ,  $p$  and  $V$  are the total energy, the pressure and the volume, respectively.

The thermodynamic potential  $F_p$ ,<sup>8</sup> for which  $p$  and  $T$  are the independent variables, is defined by the relation,

$$F_p = U - TS + pV \quad (3)$$

Differentiating and substituting in (2) we have

$$dF_p = Vdp - SdT - EdC \quad (4)$$

At a constant temperature, the following reciprocal relation between the differential quantities holds, if  $dF_p$  is a total differential

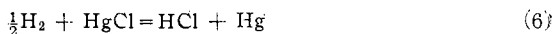
$$\left(\frac{\partial E}{\partial P}\right)_{C,T} = -\left(\frac{\partial V}{\partial C}\right)_{P,T} \quad (5)$$

<sup>8</sup> This is the free energy as used by G. N. Lewis [THIS JOURNAL, 35, 1 (1913)] but not as defined by Helmholtz. In the process of the cell we are considering, it is the electrical work,  $nEC$ , when the cell operates at constant pressure.

In a cell operating at constant pressure and temperature the change of volume is determined by the chemical reaction occurring, and is dependent only on the amount of current passing through the cell. For that reason  $\left(\frac{\partial V}{\partial C}\right)_{P,T} = \frac{\Delta V}{F}$  in which  $\Delta V$  is the change of volume during the passage of  $F$  faradays. Equation 5, therefore, becomes

$$\left(\frac{\partial E}{\partial p}\right)_{C,T} = -\frac{\Delta V}{F} \quad (5a)$$

When the cell,  $\text{H}_2|\text{HCl} (0.1 N), \text{HgCl}|\text{Hg}$ , operates, the reaction



takes place. Equation 5a shows that the e.m.f. of the cell increases with increasing pressure on the system if the volume decreases when the above reaction proceeds, and *vice versa*.

If we allow the cell to operate reversibly at constant pressure and temperature until one faraday of electricity passes, the following total volume change,  $\Delta V$ , occurs,

$$\Delta V = (\bar{V}_{\text{HCl}} + V_{\text{Hg}}) - (\frac{1}{2}V_{\text{H}_2} + V_{\text{HgCl}}), \quad (7)$$

in which  $\bar{V}_{\text{HCl}}$  represents the partial molal volume of hydrochloric acid in a 0.1  $N$  hydrochloric acid solution, and the remaining terms are the molal volumes of the substances indicated by the corresponding subscripts. In order to integrate Equation 5a it is necessary to express the separate terms in Equation 7 as functions of the pressure. These terms will be considered separately in the following paragraphs.

**The Molal Volume of Hydrogen,  $V_{\text{H}_2}$ , as a Function of the Pressure.**—The most important term in Equation 7 is, of course, the volume of gaseous hydrogen. Several equations of state were investigated with regard to their agreement with the existing data on the pressure-volume relations for this gas. The Keyes<sup>9</sup> equation of state was found to be nearest in agreement with the existing experimental data under the conditions of our experiments. The Keyes equation is generally given in the form

$$P = \frac{RT}{v - \delta} - \frac{A}{(V - l)^2} \quad (8)$$

in which  $\delta = \beta e^{-\alpha/v}$  and  $\alpha, \beta, A$  and  $l$ , are characteristic constants. For hydrogen, when  $V = \text{cc. per g.}$ ;  $\alpha = 2.898, \beta = 9.619, A = 3.91 \times 10^4, l = 1.18$  and  $R = 40.72$ . Using the above data, the  $pV$  product, obtained by assuming values of  $V$  and solving for  $p$ , was plotted against  $p$ , and the following equation obtained for hydrogen at 25°,

$$pV = 298.1 R (1 + 0.00057p - 1 \times 10^{-8} p^2). \quad (9)$$

Equation 9 is in satisfactory agreement with the interpolated values

<sup>9</sup> Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); *THIS JOURNAL*, **46**, 589 (1919).

obtained from the experimentally determined  $pV$  products at  $0^\circ$  and  $100^\circ$ . Although the values obtained by Amagat<sup>10</sup> and Holborn<sup>11</sup> are slightly higher, for pressures over 200 atmospheres, than those given by Equation 8, the Keyes equation is in good agreement, over a large pressure and temperature range, with the data obtained by Witkowski,<sup>12</sup> and by Onnes and Braek.<sup>13</sup> For this reason Equation 9 was chosen in preference to an empirical equation based on experimental determinations of the  $pV$  product, interpolated between  $0^\circ$  and  $100^\circ$  approximately. There are no data recorded for  $25^\circ$ .

**The Partial Molal Volume,  $V_{\text{HCl}}$  of Hydrochloric Acid.**—To evaluate  $\bar{V}_{\text{HCl}}$ , the partial molal volume<sup>14</sup> of hydrochloric acid, the following expression for the volume of the solution at any concentration and pressure can be used,

$$V = \frac{1000 + CM}{D_0} (1 - \alpha p) \quad (10)$$

in which  $C$  is the weight concentration, (moles per 1000 g. of water),  $M$  the equivalent weight of hydrochloric acid,  $D_0$  the density of the solution at atmospheric pressure, and  $\alpha$  is the compressibility of the solution.

Then,

$$\left(\frac{\partial V}{\partial C}\right)_p = \bar{V}_{\text{HCl}} = \frac{D_0 M - (1000 + CM) \frac{dD_0}{dC}}{D_0^2} (1 - \alpha p). \quad (11)$$

In order to evaluate  $dD_0/dC$  it is necessary to make use of density determinations of hydrochloric acid solutions, a series of which are given (for  $25^\circ$ ) in Table II.

TABLE II

HCl Conc.	$d_4^{25}$	Observer Ref.	HCl Conc.	$d_4^{25}$	Observer Ref.
		Landolt-Börnstein			
0.0000	0.997071	"Tabellen"	0.1000	0.99886	16
0.0050	0.997140	15	0.1004	0.9989	17
0.0100	0.997224	15	0.3376	1.0031	17
0.0200	0.997405	15	0.5000	1.00591	16
0.0400	0.997779	15	0.5095	1.0059	17
0.1000	0.998868	15			

A plot of these data is almost exactly a straight line and gives for the

<sup>10</sup> Amagat, *Ann. chim. phys.*, [6] **29**, 68 and 505 (1893).

<sup>11</sup> Holborn, *Ann. Physik.*, **63**, 674 (1920).

<sup>12</sup> Witkowski, (1905), from Landolt and Börnstein, "Tabellen."

<sup>13</sup> Onnes and Braek, *Versl. Amsterdam*, **30**, 411 (1907).

<sup>14</sup> This is the change of volume which would occur if one mol of HCl gas were added to an infinite volume of a solution of the substance at the given concentration.

<sup>15</sup> Ansdell, *Chem. News*, **41**, 75 (1880).

<sup>16</sup> C. E. Ruby, private communication.

<sup>17</sup> Ellis, *THIS JOURNAL*, **38**, 737 (1916).



slope,  $\frac{\Delta D_0}{\Delta C}$ , the value 0.0175 which may, in this case, be set equal to  $\frac{dD_0}{dC}$ . If we make the assumption that  $\alpha$  is equal to the compressibility of water, which has a mean value of  $44 \times 10^{-6}$  between 1 and 400 atmospheres, then Equation 11 reduces to

$$\bar{V}_{\text{HCl}} = 18.89 - 8.3 \times 10^{-4} p \quad (12)$$

for a 0.1 N hydrochloric acid solution. This ignores a possible change of the partial molar volume due to solubility of the hydrogen gas by which the pressure is applied. This point will be referred to later.

**The Molal Volumes of Mercury and Calomel.**—From the density data of Thiesen, Scheel and Sell<sup>18</sup> the molar volume of mercury was found to be 14.82 at 25°. A simple computation shows that the compressibility of mercury, in the pressure range of our experiments, can be neglected, the effect of a pressure of 400 atmospheres leading to a correction of only 0.005 mv. on the computed potential of the cell.

The density of solid calomel was redetermined for this investigation. Three determinations gave, respectively, 7.155, 7.153 and 7.152, having an average value of 7.153 at 25° referred to water at 4°. This is concordant with the value, 7.151, given by Timofejew.<sup>19</sup> Using the mean value of the density we obtain 33.00 cc. for the molal volume of calomel. The compressibility of calomel has apparently not been determined, but it must be of the same order of magnitude as that of mercury or smaller. Further, since mercury and calomel are on opposite sides of the equation for the reaction occurring in the cell, the resultant effect of the compressibilities of these substances must be smaller than the effect of either one.

**The Equation for the Change of Potential with Pressure.**—When we substitute the values of the specific volumes obtained in the foregoing paragraphs into Equation 7 we obtain for the change of volume when one equivalent of current passes through the cell, at the pressure  $p$ , the following expression.

$$\begin{aligned} \Delta V &= (18.89 - 8.3 \times 10^{-4} p + 14.82) - \\ &\quad \left[ 33.00 + 12230 \left( \frac{1}{p} + 0.00057 - 1 \times 10^{-8} p \right) \right] \\ &= - \frac{12230}{p} - 6.26 - 7.1 \times 10^{-4} p \end{aligned}$$

This gives, on substituting in Equation 5a,

$$\Delta E = \frac{0.1013}{F} \int_1^p \left( \frac{12230}{p} + 6.26 + 7.1 \times 10^{-4} p \right) dp$$

<sup>18</sup> Thiesen, Scheel and Sell, *Wiss. Abh. P.T.R.*, **2**, 184 (1895).

<sup>19</sup> Timofejew, *Z. physik. Chem.*, **78**, 299 (1911).

and integrating between the limits  $p$  and 1 we obtain

$$\Delta E = 0.02958 \log p + 6.56 \times 10^{-6} (p-1) + 3.7 \times 10^{-10} (p^2 - 1) \quad (13)$$

This appears to be the most complete thermodynamic treatment that can be obtained using the available experimental data. As stated above, it does not include effects due to the change of volume of the acid solution due to the solubility of the hydrogen. It will be noted that the first term of this equation follows directly from the expression  $RT/2F \cdot \ln p$  of Equation 1, and that the other terms are of appreciable magnitude only at comparatively high pressures.

The data of Table I are represented graphically in Fig. 3. Curve 1 of that figure is the result of plotting the observed voltages against the logarithm of the pressure in atmospheres. Up to 100 atmospheres

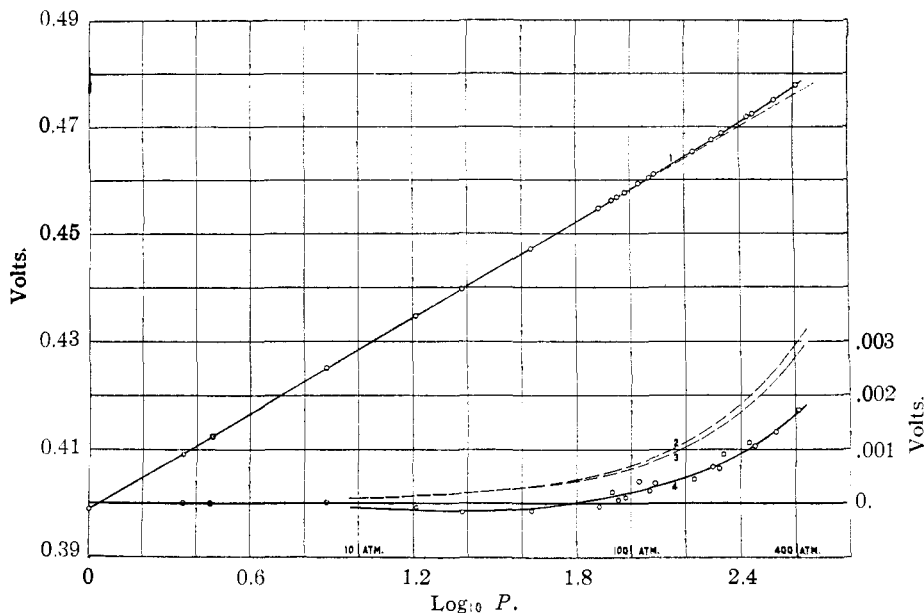


Fig. 3.

this is a straight line, within the experimental error, the slope of which is exactly,  $0.02958 (= 2.303RT/2F)$  required by Equation 1. However, above 100 atmospheres there is a slight but definite divergence from this linear relation. The dotted line is a prolongation of the straight line below 100 atmospheres. A straight line throughout the range of the measurements would result, of course, if the hydrogen were a perfect gas and if the compressibilities of the other substances entering into the reaction of the cell were negligible or compensating.

In Curve 4 the divergences, from the simple logarithmic relation, are plotted on a much larger scale. The base line corresponds to no divergence

from the expression  $\Delta E = RT/2F \cdot \ln p$ . It will be noted that at the highest pressure this divergence is nearly 2 mv.

Curve 3 is a plot of e.m.f. values computed from Equation 13 and plotted in the same manner as Curve 4 for the observed results. It will be seen that the observed and computed values deviate from each other by about one millivolt at the highest pressure. A summary of observed and computed values, for round pressures, is given in Table III. It would appear, then, that the thermodynamic theory as outlined above is not quite

TABLE III

Pressure Atms.	$\Delta E$ obs. Volts	$\Delta E$ from Equation 13	Divergence
50	0.0504	0.0506	0.0002
100	0.0594	0.0598	0.0004
200	0.0688	0.0694	0.0006
300	0.0745	0.0753	0.0008
400	0.0787	0.0797	0.0010

sufficient to account for the experimental measurements at high pressures. It seems very probable that the solubility of the gaseous hydrogen can produce volume changes, resulting in a different variation of the partial volume of hydrochloric acid,  $\bar{V}_{\text{HCl}}$ , with the pressure from that given by Equation 12. It was with the hope of finding such a change of "environment" that this investigation was begun.

Curve 2 represents the deviation which is to be expected from the failure of hydrogen to obey the perfect gas law and was obtained from Equation 9. It will be noted that the deviation from this source is slightly greater than the summation, given by Equation 13, *i. e.*, the other terms of that equation nearly compensate each other.

Work is now in progress to extend the measurements to considerably higher pressures with a modified and improved apparatus. An independent study of the effect of pressure on the partial volume of hydrochloric acid, and the effect of the dissolved hydrogen at different pressures on that quantity is also being investigated.

We are indebted to Prof. F. G. Keyes for invaluable advice and assistance during the progress of this research.

### Summary

The variation, with pressure of hydrogen, of the potential of the cell:  $\text{H}_2|\text{HCl} (0.1 N), \text{HgCl}|\text{Hg}$  at  $25^\circ$ , has been measured up to 400 atmospheres.

The thermodynamic theory of this change of e.m.f. has been investigated.

At the higher pressures a correction, probably due to the solubility

of hydrogen, is necessary. This correction is at present under investigation.

The study of the variation of the potential of the cell with pressure is being extended to higher pressures.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF Breslau]

## NITROSYL SELENIC ACID

BY JULIUS MEYER AND WALTER WAGNER

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Since selenic acid, in many respects, is similar to sulfuric acid, it is to be expected that it would give with nitrous acid an anhydrous compound corresponding to nitrosyl sulfuric acid,  $\text{SO}_2(\text{OH})(\text{ONO})$ . Victor Lenher and J. H. Mathews,<sup>1</sup> by treating selenic acid of the strength of about 83% with liquid nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) at a temperature obtained by the use of solid carbon dioxide, have prepared dinitrosyl selenic acid  $\text{SeO}_2(\text{ONO})_2$  which is stable below  $-13^\circ$  and which is described as an easily decomposable compound of blue color. Previous to our experiments, the mononitrosyl compound had not been described.

The existence of a new compound between selenic and nitrous acid can be shown by dissolving solid sodium nitrite in ice-cold selenic acid of about 95% strength. The salt dissolves without evolution of gas and without change in color of the liquid. On diluting the solution with water, red oxides of nitrogen are evolved in large amounts, a behavior resembling the decomposition of "lead chamber crystals" by water.

In order to prepare nitrosyl selenic acid we brought together, in absence of water, liquid nitrogen trioxide ( $\text{N}_2\text{O}_3$ ) and selenic acid prepared by the method of Meyer and Moldenhauer.<sup>2</sup> While sulfur dioxide reacts readily with nitric acid to form nitrosyl sulfuric acid, selenium dioxide in our experience does not react similarly.

In order to prepare nitrosyl selenic acid, liquid nitrogen trioxide is poured into 100% selenic acid, the former being in great excess. The greater part of the excess of the nitrogen trioxide is evaporated from the white crystalline mass by vigorous stirring, after which the last trace of excess of the oxides of nitrogen is removed by spreading the crystals on a porous plate and evaporating, at as low a temperature as possible, in a vacuum desiccator. The white crystals can be preserved in dry, sealed tubes, but decompose when warmed, with an evolution of the red oxides of nitrogen. Moisture decomposes the crystals with a similar evolution and the solution when treated with barium chloride yields barium selenate. The crystals irritate the skin.

<sup>1</sup> Lenher and Mathews, *THIS JOURNAL*, **28**, 516 (1906).

<sup>2</sup> Meyer and Moldenhauer, *Z. anorg. Chem.*, **116**, 193 (1921).