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THE EFFECT OF HYDROGEN PRESSURE ON THE ELECTROMOTIVE FORCE OF A HYDROGEN-CALOMEL CELL.

II. THE FUGACITY OF HYDROGEN AND HYDROGEN ION AT PRESSURES TO 1000 ATMOSPHERES

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In an earlier paper[1] a description was given of a preliminary set of measurements on the electromotive force of the cell: H_2 | HCl (0.1 *N*), HgCl | Hg, over a pressure range of from 1 to 400 atmospheres. The experience thus gained led us to the conclusion that if the work were to be extended to still higher pressures a number of changes in the apparatus and procedure would be advisable. These changes have been carried out and have made higher accuracy in the measurements possible. We have, further, been led to revise somewhat our conclusions as to the effect of pressure on the potential of the cell.

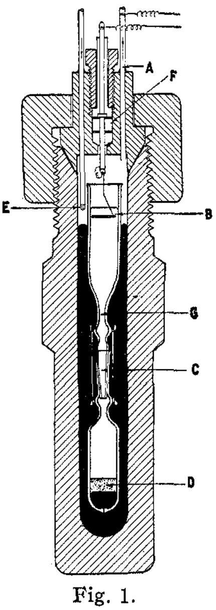

Fig. 1.

The chief alterations in the apparatus are: (*a*) the substitution of an absolute piston gage for the hydrostatic gages; (*b*) elimination of the bubbling of hydrogen through the solution, and (*c*) modifications of the design of the cell.

The Cell

The cell as used in this series of measurements is shown occupying its place in the bomb, in Fig. 1.

The arrangement differs from that of our previous work in that the hydrogen was not bubbled through the solution, but was simply caused to exert its pressure on the surface of the electrolyte. In order that the platinized platinum electrode could come to equilibrium with the hydrogen in a reasonable time, it was made into a disk, B, which hung in a horizontal position just under the surface of the electrolyte. The disk was, in turn, supported by a platinum wire which hooked over another wire of the same material, allowing the disk to swing freely. The agitation of the thermostat transmitted a vibratory motion to the electrode, which agitated the electrolyte. A very fine platinum wire spiral was attached to the hook and to its support to give a definite metallic connection between the two without interfering with the swinging motion of the electrode. The cell was of new design and consisted of two parts held together by a ground-glass joint, C, which was held in place, as shown, by rubber bands. The lower portion held the calomel-mercury electrode, D, and was filled with electrolyte which was saturated with calomel. The upper half of the cell was filled with calomel-free acid. A plug of glass wool at G prevented calomel-bearing acid from reaching the platinized platinum electrode, and kept particles of platinum black out of the calomel. The glass wool was,

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[1] Hainsworth and MacInnes, THIS JOURNAL, **44**, 1021 (1922).

however, omitted in some experiments without any apparent effect. The cell was supported in a metal stand, not shown in the figure. Finally, the free space in the bomb was filled with mercury. This served to connect the calomel electrode with the bomb, to which one terminal of the potentiometer was fastened, and also reduced the work of the compresser by decreasing the volume of hydrogen.

Hydrogen from the compressing apparatus was led into the bomb through the tube E which was bent parallel to the surface of the mercury in order to prevent splashing of the latter due to sudden rushes of gas. The tube A served as an outlet through which hydrogen could be passed to sweep out the air in the free space in the bomb and through which, with the aid of a needle valve, the pressure could be slowly lowered.

The Bomb

The bomb used was substantially as described in the previous communication. Some modifications were, however, made on the insulating joint F. The insulated conductor was a steel rod on which a steel ring was soldered to keep the rod from being forced out by pressure. The packing nut pressed against a hard rubber bushing under which was placed, in turn, a mica washer, a soft rubber packing, another mica washer, and a hard rubber bushing.

The Pressure Measurements

The main improvement over our earlier work consists in the substitution of a piston gage for the dial gages. This gage consisted of a steel piston of 3mm. diameter, fitting within about 0.00005 cm. in a steel cylinder. The pressure on the piston was directly measured by placing weights on a scale pan which it supported. Since the design of a gage very similar in construction has been outlined by Smith and Taylor[2] in a recent number of THIS JOURNAL, the description will not be repeated. The calibration of the gage against a mercury column was also carried out as described by these authors. The pressures above 100 atmospheres were obtained in this work in the same way as in that already reported. The purification of the hydrogen and the measurement of the potentials of the cell were also carried out as described in the previous communication.

The Experimental Results

The results of this series of measurements, which are given in Table I, are uniformly higher than those reported in our last series. The difference undoubtedly lies in the hydrostatic gages used in the earlier work and about which some doubt was expressed in our last paper. It now seems probable that, due to the fact that the calibration of the gages against a piston gage was not made under exactly the conditions of the experiments, the gages gave too high pressure readings. In the calibration the gages were held at each pressure for a short time only, whereas when measuring the pressure in the bomb the gages were held at the same reading for a day or more giving them time in which the moving parts could overcome any hysteresis that might be present. Our experience seems to show that

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[2] Smith and Taylor, THIS JOURNAL, 45, 2109 (1923). See also Keyes, Smith and Joubert, *J. Math. Phys.*, Mass. Inst. Tech., 1, 194 (1922).

the hydrostatic gages are quite unreliable for accurate work. On this account we wish the data in Table I, which were all obtained with an absolute piston gage, to supersede those in our earlier paper.

Table I

Measurements of the Cell: $H_2 \mid HCl\ (0.1\ N),\ HgCl \mid Hg$, at 25°, and at Different Pressures

Pressure Atmospheres	E.m.f. Volts	Pressure Atmospheres	E.m.f. Volts
1.0	0.3990	701.8	0.4891
37.8	.4456	717.8	.4899
51.6	.4496	731.8	.4893
110.2	.4596	754.4	.4903
204.7	.4683	862.2	.4932
386.6	.4784	893.9	.4938
439.3	.4804	974.5	.4963
556.8	.4844	1035.2	.4975
568.8	.4850	...	...

Discussion

In our previous communication the thermodynamic equation

$$\left(\frac{\mathrm{d}E}{\mathrm{d}p}\right)_{C,T} = \frac{\Delta V}{F} \tag{1}$$

was derived. In this equation E, p, F and ΔV are, respectively, the e.m.f. of a cell, the pressure, the faraday, and the total volume change due to the reaction occurring when one faraday passes through the cell. For the cell under consideration, in which the reaction is

$${}^1/_2H_2 + HgCl = HCl\ (0.1\ N) + Hg \tag{2}$$

the total volume change is equal to

$$\Delta V = (\overline{V}_{HCl} + V_{Hg}) - ({}^1/_2V_{H_2} + V_{HgCl}) \tag{3}$$

Here $\overline{V}_{HCl}$ represents the partial molal volume of hydrochloric acid in a 0.1 N solution and the remaining terms are the molal volumes of the substances indicated by the corresponding subscripts. In order to integrate Equation 1 it is necessary to express each term of Equation 3 as a function of the pressure. The only terms which require any discussion are V_{H_2} and $\overline{V}_{HCl}$. For the former, since no compressibility data are available for 25°, a series of values of the pV product were computed from Keyes' equation[3] for hydrogen,

$$p = \frac{40.72\ T}{V - 9.619\ e^{(-2.898/v)}} - \frac{3.91 \times 10^{-4}}{(V - 1.18)^2}$$

in which p is the pressure in atmospheres and V is the volume in cc. per g. This equation agrees within the limit of error with the available data for this gas at 0°, 100° and 200° and up to 1000 atmospheres. These pV products were found to be represented by the empirical equation

$$pV = RT(1 + 0.000537\ p + 3.5 \times 10^{-8}\ p^2) \tag{4}$$

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[3] Keyes, *Proc. Nat. Acad. Sci.*, **3,** 323 (1917); This Journal, **41,** 589 (1919).

which is slightly different from the equation for the same purpose given in our previous paper. (Because of its complex form Keyes' equation cannot be used directly for the integration.) The values of $\overline{V}_{HCl}$ can be computed from density data. However, one effect which does not seem possible of computation or independent measurement is that of dissolved hydrogen, at the higher pressures, upon this term. This will be discussed below. Aside from this effect, integration of Equation 1 yields

$$\Delta E = 0.02958 \log p + 6.12 \times 10^{-6} (p - 1) + 6.6 \times 10^{-10} (p^2 - 1) \qquad (5)$$

For the details of this integration the reader is referred to the previous paper.

In Fig. 2, the measured electromotive force of the cell is plotted in Curve A against the logarithm of the pressure. Curve B is a plot of Equation 5

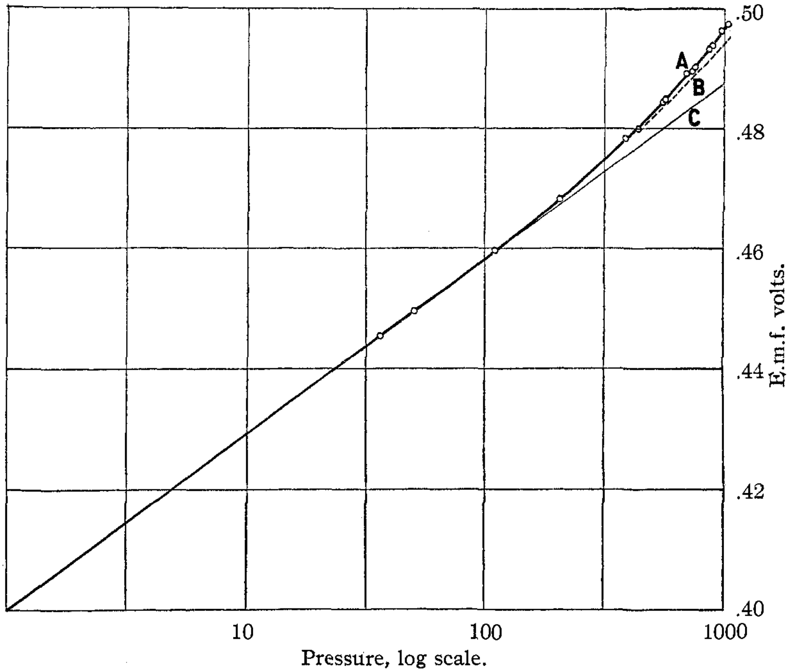

Fig. 2.

which, it will be noted, differs from the plot of the measured e.m.f.'s only at the higher pressures. The straight line, C, represents the equation $\Delta E' = 0.02958 \log p$, which would be followed if hydrogen were a perfect gas and the compressibilities of the other substances negligible or compensating.

The deviation from this "perfect gas behavior" is given as ordinates on a much larger scale against the pressures as abscissas in Fig. 3. Here, Curve A is a plot of values of $1000(\Delta E - 0.02958 \log p)$ in which ΔE is the measured increase of potential of the cell produced by the pressure p. Curve B is a corresponding plot of the last two terms of Equation 5. The two curves are in agreement, within the experimental error, at the lower pressures, but fall apart steadily, the deviation reaching a maximum of 2.3 mv. at 1000 atmospheres. This appears to be a real effect, almost certainly due to the increased solubility of hydrogen in the electrolyte at the higher pressures. It can be interpreted, from a thermodynamic standpoint, as has been done above, as an effect of the presence of dissolved hydrogen on the partial molal volume of hydrochloric acid. The deviation can also be looked upon as a change of hydrochloric acid as an ionizing medium produced by the presence of the gas.

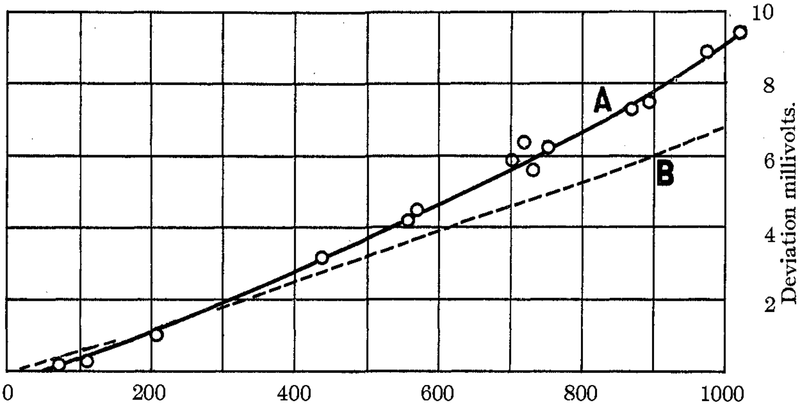

Fig. 3.

The main object of this investigation has been to study the relation of the apparent fugacity[4] of the hydrogen at a hydrogen electrode to its pressure. From a study of the electrolytic evolution of the gas it has appeared probable that at high pressures this fugacity would be higher than the pressure. This apparent fugacity may be computed from the relation, $\Delta E = \frac{RT}{2F} \log f'$, in which ΔE is the measured increase of potential of the cell produced by hydrogen pressure over the value at one atmosphere and f' the corresponding fugacity, the value of the latter being taken as unity for hydrogen at one atmosphere. The apparent change of fugacity of hydrogen can be considered, with but little error, as a combination of the effects on the constituents of the reaction, $H^+ = {}^1/_2H_2$ since, in the first place, by far the greater part of the total change of e.m.f. with pressure is due to the properties of the hydrogen gas, and also the thermodynamic environment of the hydrogen ion is disturbed by the presence of dissolved hydrogen. The calomel electrode, on the other hand,

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 190.

is affected only by direct pressure, and the effect of the pressure on its e.m.f. is relatively small. As the data given in Table I and Figs. 2 and 3 show that the e.m.f. of the cell increases somewhat more rapidly than would be expected from the properties of the hydrogen gas alone, it is evident that the relative fugacity of the hydrogen ions (or the activity to which it is proportional) must decrease with pressure. As the activities of all the reacting substances increase with the pressure, this decrease of the activity of the hydrogen ion is relative to the activity *at the same total pressure.* The computed values of the apparent change of fugacity of hydrogen for a series of pressures, are given in Table II. In this table are also given (*a*) values of the actual fugacity of hydrogen, computed from the formula, $RT \log f = \int V dp$ using Equation 4 for the integration, and (*b*) values of the relative activity of hydrogen ion obtained with the aid of the equation, $\Delta' E = RT \log (1/a)$, in which $\Delta' E$ is the difference between the experimentally determined e.m.f.'s of the cell at each pressure, and that computed from Equation 5. Physically, $\Delta' E$ is the potential of a cell without transference in which the hydrogen ion in one half-cell is modified by the presence of dissolved hydrogen, and the other half-cell is assumed to be free from dissolved hydrogen, but at the same total pressure of the gas. It will be seen that at the highest pressure the apparent change of fugacity is *more than double the corresponding pressure.* This means, of course, that if the perfect gas laws were used for a computation of the effect of pressure on a hydrogen electrode at 1000 atmospheres, the error would be over 100%. Of this difference about three-fourths is due, at this pressure, to the deviation of hydrogen from the perfect gas law, and the remaining portion depends upon a relative decrease of the fugacity, or activity, of the hydrogen ions in the electrolyte. It will be seen that a comparatively small decrease of this activity, namely, 8.9%, will account for the potentials observed. This change of activity can readily be accounted for by the presence of dissolved hydrogen.

TABLE II

FUGACITIES OF HYDROGEN AND RELATIVE ACTIVITIES OF HYDROGEN ION

Pressure Atm.	Apparent fugacity of hydrogen Atm.	Actual fugacity of hydrogen Atm.	Relative activity of hydrogen ion
500	665.0	656.8	0.996
600	866.6	832.7	.981
700	1103.0	1027.3	.954
800	1361.0	1243.5	.946
900	1654.0	1479.0	.931
1000	2040.0	1737.5	.912

A rough calculation of the concentration of hydrogen dissolved in the electrolyte at 1000 atmospheres is of interest in this connection. The data of Timofejew[5] and of Geffcken[6] give the solubility of hydrogen in 0.1 *N* hydrochloric acid as 0.00158 g. per liter at 1 atm. and 25°. Multiplying this by the fugacity (1737 atm.), we obtain 2.74 g. or 1.36 moles per liter for the desired concentration. This assumes, of course, the validity of a modified form of Henry's law. It seems probable that this concentration of hydrogen is sufficient to affect the activity of hydrogen ion to the extent observed. The dissolved hydrogen reduces the mole fraction of the acid by 2.4%.

It also seems quite probable that effects similar to that just described, that is, the change of the activity of the electrolyte of a cell by the solubility of the material, or materials, reacting at an electrode, is more common than is generally supposed, and may influence the results of e.m.f. measurements under normal conditions, particularly when the electrolytes are dilute.

A factor which has been left out of the discussion is the liquid junction that must exist between the electrolyte, in which hydrogen is dissolved, and the hydrogen-free electrolyte, since the ions in the two solutions have different activities, and the two ions of the electrolyte have different mobilities. The effect of this junction is to reduce the deviations as given in Table II and Fig. 3, that is, the deviations at the electrode are larger than those stated, the cell measurements giving, of course, the net effect of the potentials present. It does not appear possible to compute this liquid-junction potential with any accuracy, but its value at 1000 atmospheres is probably of the order of a millivolt, and its sign, as has been said, is in the direction to reduce the apparent deviation.

It is hoped in the future to extend this investigation to pressures much higher than those reached during the experiments described in this communication.

Summary

The measurements of the effect of hydrogen pressure on the e.m.f. of the cell, $H_2 \mid 0.1\ N\ HCl, HgCl \mid Hg$, as described in a previous paper, have been carried to 1000 atmospheres with improved apparatus and increased accuracy. At the highest pressure the apparent fugacity is 100% higher than the pressure. Of this difference between fugacity and pressure, about three-fourths is due to the departure of hydrogen from the perfect gas laws and one-fourth is due to a decrease in the relative activity of the hydrogen ion, due presumably to the solubility of the hydrogen.

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[5] Timofejew, *Z. physik. Chem.*, **6**, 141 (1890).

[6] Geffcken, *ibid.*, **49**, 257 (1904).