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IX. *The Carbon Cell.*
By W. H. PATTERSON, *B.Sc.**

IN two publications, Haber and Bruner † have given reasons for considering that the so-called Jacques Carbon Cell is in reality an oxy-hydrogen battery.

This cell consists of an iron and a carbon pole in molten caustic soda.

Iron, as Liebenow and Strasser ‡ have already shown, is in molten caustic at first active and of base potential. After some time, however, such iron becomes coated with an oxide skin and then functions as an air electrode; the small quantities of manganate which are always present acting as oxygen carriers.

On the other hand, the carbon develops hydrogen by a slow reaction with the molten alkali, which forms the source of potential of the carbon electrode.

The reaction is according to the equation:—



Water, according to Le Blanc and Brode, is retained by molten sodium hydroxide with great pertinacity.

The slower the reaction the less the hydrogen is able to charge up the carbon dipping into the molten alkali, because the manganate and ferrite contained in it, as well as the air surrounding its upper surface, are striving to remove the hydrogen, thereby making the potential approach the value for air.

If there results, however, carbon monoxide from the action of the oxidizing substances contained, the formation of hydrogen is increased, because carbon monoxide reacts rapidly and completely with molten caustic soda, forming carbonate and hydrogen.

The author has made some experiments in order to establish this interpretation of the Carbon Cell. First of all, it was shown that there is a slow production of hydrogen if carbon and sodium hydroxide are maintained at 350° C. in an atmosphere of nitrogen. On the other hand, the measurements of Haber and Bruner on the potential of hydrogen in molten sodium hydroxide were repeated. In the various experiments, the alkali was contained in a large silver crucible

* Communicated by the Author.

† Haber & Bruner, *Zeit. f. Electroch.* vol. x. p. 697 (1904); also vol. v. p. 78 (1906).

‡ Liebenow & Strasser, *Zeit. f. Electroch.* p. 353 (1897, Feb.).

heated by a small Bunsen flame; temperatures were determined thermoelectrically. After the method of Haber and Bruner, hydrogen was led into the molten alkali through a platinum tube, and the E.M.F. of this tube measured by the compensation method against a N/10 electrode. In other experiments, the hydrogen was produced by throwing into the molten alkali a little formate and using a platinum wire as electrode. In both cases a value near to that of Haber and Bruner, *i. e.* -1.5 volt, was attained without perceptible temperature coefficient.

Experiments were then carried out on the oxy-hydrogen combination, with sodium hydroxide as electrolyte, in order better to establish its dependence on the temperature.

Haber and Bruner, in the latter communication, have calculated this potential thermodynamically from water-vapour dissociation at high temperature, with the assumption that the molten alkali is in equilibrium with the water-vapour of the air, the latter having an average tension of 0.031 atmos. The calculation rests on the integration of the Helmholtz formula for the free energy:—

$$A = Q_v + T \frac{\delta A}{\delta T},$$

which is integrated in the form

$$\frac{dA}{dT} = - \frac{Q_v}{T^2}.$$

By help of the well-known value of the reaction-heat of the formation of water-vapour from its elements and from the data found by Langen for the mean specific heat of the gases taking part in the reaction, the integral becomes

$$\begin{aligned} *A &= 57084 - 2.976 \times \log_e T + 0.00125T^2 \\ &\quad - 4.56 \times T \times \log \frac{p_{H_2O}}{p_{H_2} \times p_{O_2}} + \text{const.} \times T. \end{aligned}$$

The constant of this expression follows from the measurements carried out by Nernst and Wartenberg on the dissociation of water-vapour. It amounts to 7.6 . In the equation, T denotes the absolute temperature, and p the partial pressure of the gases. The free energy A is calculated in small calories.

* For further information relative to the above calculation *cf.* English edition of Prof. Haber's 'Thermodynamics of Technical Gas Reactions' (Longmans, Green & Co., 1907).

The values of the E.M.F. of the cell are derived from those of A by dividing with 2F, *i. e.* 46220.

The following numbers are those obtained :—

° C.	E.M.F. (in volts).	
327	1.096—0.059	$\log \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}}$
427	1.068—0.069	” ”
527	1.039—0.079	” ”
627	1.010—0.089	” ”

Taking with Haber and Bruner,

$$p_{H_2O} = 0.031,$$

$$p_{H_2} = 0.969,$$

$$p_{O_2} = 0.2,$$

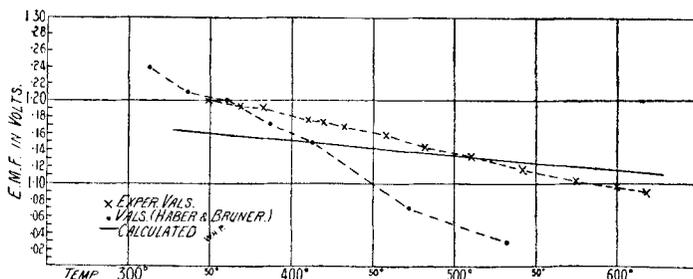
it follows—

$$\log \frac{p_{H_2O}}{p_{H_2} p_{O_2}^{\frac{1}{2}}} = -1.1455 ;$$

so there is obtained for the E.M.F.

° C.	E.M.F. (in volts).
327	1.164 *
427	1.147
527	1.129
627	1.112

These figures are plotted in the accompanying diagram.



* No stress is laid on the absolute value of the third decimal place ; as it has a relative value, however, the last figure is given here and subsequently in smaller type.

The values of Haber and Bruner are marked by points; they are above the curve at low temperatures and beneath it at high temperatures.

The reason for the high values at low temperatures can be understood, the molten alkali, according to Le Blanc and Brode, being at this range of temperature hygroscopic. The values at higher temperatures Haber and Bruner themselves regard as uncertain, their method seeming unfit to yield more exact results.

In order to obtain better values the author tried to find electrodes which would, by insertion in molten alkali, behave as hydrogen and as air-electrodes respectively, so that the difference of potential between them would give at once the E.M.F. of the oxy-hydrogen cell looked for.

It seemed probable that palladium saturated with hydrogen might be used as a hydrogen electrode. Palladium wires were charged, either in dilute sulphuric acid or dilute alkali, dried and inserted. Such wires develop hydrogen rapidly, but the amount of gas cathodically incorporated with the wire is so far above the amount which is in equilibrium with hydrogen under atmospheric pressure, at the high temperature of the molten alkali, that an excess of E.M.F. amounting to some centivolts is brought about. Of course the supercharge only lasts for a very short time, the hydrogen being driven off rapidly and the E.M.F. falling slowly; finally it reaches the value of the air electrode. There was no marked break in this fall of potential at the value belonging to that in equilibrium with hydrogen at atmospheric pressure. Hydrogenized palladium was therefore not suitable as a hydrogen electrode. Iron was tried, a metal which, as previously shown by Haber and Bruner, gives a value very near to that of hydrogen gas. The difficulty which ensues from the iron becoming too rapidly passive was overcome by coating the iron wires used with electrolytic iron, after the method of Classen, from a solution containing ferrous oxalate or from a solution containing ammonium chloride. Such wires show the hydrogen potential and for a longer time.

The possibilities with regard to the air electrode were more numerous. Silver, platinum, palladium, nickel, and iron were tried. Wires of these metals, after insertion into molten alkali, all showed the air-potential—the iron and nickel of course after some time—necessary to let them become passive. There is possibly a slight deviation in the case of palladium which, being probably slightly attacked by

the alkali, shows some inclination to deviate towards the hydrogen value.

Combinations consisting of such electrically coated iron wires, acting as a hydrogen electrode, and platinum, functioning as the air electrode, were finally found to be the best arrangement for measuring the temperature coefficient of the cell.

The following figures were thus arrived at (values plotted on diagram as curve with crosses).

Temp. ..	348°	369°	382°	410°	420°	432°	458°
E.M.F. . .	1·201	1·198	1·191	1·176	1·174	1·168	1·159
Temp. ..	482°	510°	542°	575°	600°	618°	
E.M.F. . .	1·144	1·132	1·118	1·103	1·096	1·090	

The results are in agreement with those which Haber and Bruner obtained by their different methods of working up to about 400°; above this the values are higher than those of Haber and Bruner, and are in closer proximity with theory.

In connexion with this, it was thought that perhaps addition of sodium oxide (Na_2O) could render the molten alkali free from water, and therefore change the E.M.F. of the cell, which, as a consequence of theory, would thereby be increased. This plan, however, did not bring about the desired result. Adding a little oxide did not cause a marked change; on the other hand, if all the associated water was eliminated, the iron, even coated electrolytically, quickly assumed the passive state.

The influence of associated water is more marked with potassium hydroxide. Caustic potash freshly melted, thereby containing relatively much water, gives rise to values which are much smaller than those obtained from caustic potash which has been kept molten for a long time and is therefore poorer in water.

This influence of water is easily misleading. The presence of water always causes iron to remain longer active and the hydrogenized palladium to retain its charge. Thus it is easier to work with molten alkali containing water, but the results may be several centivolts too low, the equilibrium pressure of the water-vapour above the molten alkali being in excess of the atmospheric vapour-pressure to some extent.

Caustic potash, moreover, from which water has been eliminated by prolonged heating, causes iron to become much more rapidly passive than does caustic soda.

The following values, in the case of caustic potash, were,
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however, obtained with the same arrangement, *i. e.* electrolytic iron against platinum.

Temp.	405°	410°	425°	480°
E.M.F.	1.18 ₂	1.18 ₀	1.17 ₀	1.13 ₃

On comparing these numbers with those obtained from sodium hydroxide, it is seen that the difference is not very great.

The above results are in close agreement with those found by Haber and his co-workers Fleischmann and Foster * concerning the oxy-hydrogen cell with glass and porcelain as electrolyte. In especial between 340° and 575° C. the same thermodynamical expressions have been confirmed with these gas-cells (described by Haber in *Zeit. f. Electrochem.* 1906, No. 24).

It seems rather interesting that such distinct cases as the Carbon Cell and the dissociation of water-vapour at high temperatures are governed by the same thermodynamic relation; that is to say, they are both consequences of the free energy of the formation of water-vapour from its elements, the amount of which is found to be almost identical with the results of experiments described and quoted above.

In conclusion the author wishes to acknowledge his obligations to Professor Haber for kind assistance and advice.

Karlsruhe, Chem. Techn. Institut
der Hochschule, July 1906.

X. *Notices respecting New Books.*

The Royal Society, Or, Science in the State and in the Schools.

By Sir WILLIAM HUGGINS, K.C.B., O.M., D.C.L., LL.D., Sc.D.,
F.R.S., &c. With twenty-five illustrations. London: Methuen
& Co. 1906. Pp. xvi+132.

THIS sumptuously printed and beautifully illustrated volume deserves to be widely circulated, not so much, perhaps, on account of its intrinsic artistic value, as by reason of the weighty matters of national importance with which it deals. It is practically a plea, by its distinguished author, for the wider recognition of the claims of Science by the State, the responsible public, and the schools. The bulk of the subject-matter has been taken from Sir William Huggins's Presidential Addresses. The introductory part contains an interesting sketch of the early history of the Royal

* *Zeit. f. anorgan. Chem.* vol. li. pp. 245 & 289 (1906).