centration of catalyst is not particularly marked. It may be noted that the change of coefficient with temperature is not so great with sulfate as with chloride, the results for the former agreeing substantially with those of von Bertalan, who found $K_{40}/K_{30} = 3.2$ and $K_{30}/K_{20} = 3.3$.

In the columns E_1 and E_2 are shown the "critical increments" of the reaction according to the radiation hypothesis, calculated[17] from the expression $\frac{d \log K}{dT} = \frac{E}{RT^2}$. The mean value of the critical increment is 23,960 cals. per mole of hydrogen peroxide decomposed; this, when substituted in the expression $E = Nh\nu$ gives 2.5×10^{14} for the frequency of the active radiation, the wave length of which would therefore be 1.2×10^{-4} cm. $= 1.2\mu$.

Summary

1. This paper is a continuation of a former study of the catalytic decomposition of hydrogen peroxide by ferric salts. The existence of an intermediate compound, H_2FeO_4, previously suggested, has been confirmed by a spectroscopic examination of the reaction mixture.

2. The free energy of formation of ferrate ion, FeO_4^{--}, is shown to be in the neighborhood of —140,000 cals. Free-energy relationships show that the ferrous-ferric ion intermediate reactions postulated by von Bertalan are improbable.

3. The catalytic effect of ferrous salts is shown to be due solely to the fact that they are oxidized first to ferric salts.

4. The molecules of ferric salt, as well as the ions, appear to exert catalytic activity. It is possible that there are two molecular forms of differing activity.

5. The temperature coefficient of the reaction shows the "critical increment" of the reaction to be 23,960 cals., the frequency of the active radiation 2.5×10^{14}, and its wave length 1.2μ.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A WATER-JACKETED HYDROGEN ELECTRODE

BY HENRY S. SIMMS

RECEIVED MAY 21, 1923

A hydrogen electrode cell has been designed to give rapid and accurate results and at the same time offer greater convenience in manipulation when working with certain fluids, than other types of cells. The results have been sufficiently satisfactory to warrant publication of a description of the cell.

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[17] For the methods of these calculations, see among others, Daniels and Johnston, THIS JOURNAL, **43**, 53, 72 (1921).

Description of Cell

This cell is kept at constant temperature by means of a water jacket through which water from a thermostatic bath is circulated. It has a 3-bore, 4-way stopcock which performs all the functions required. This stopcock is bored as shown in Fig. 1. The three bores do not intersect. Bore *c* is used in both Position III and Position IV. In order that both ends of Bore *c* may coincide with the opening of the arm for the salt bridge, this opening of the arm must be elliptical in shape. The cell may be constructed of either Pyrex or ordinary glass.

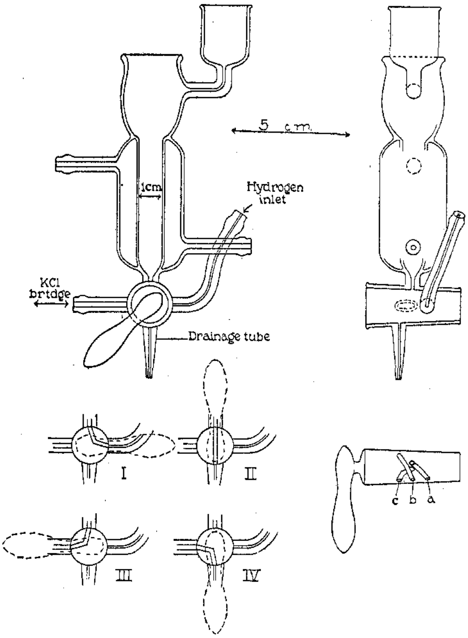

Fig. 1.—The water-jacketed hydrogen electrode cell. In Position I, Bore *a* connects the source of hydrogen with the cell; in Position II, Bore *b* connects the cell with the drainage tube; in Position III, Bore *c* connects the cell with the salt bridge; in Position IV, Bore *c* connects the salt bridge with the drainage tube. Order of manipulation: I, II, IV, III

The Platinum Electrode is a spiral of platinized platinum wire sealed into a glass tube passing through a rubber stopper to the bottom of the cell. The tube contains mercury in order to make contact. The stopper has a supplementary hole for the escape of hydrogen. Readings are taken with the electrode entirely immersed. The spiral serves, furthermore, to break up the bubbles of hydrogen, thus promoting rapid saturation. The electrodes are frequently changed and re-platinized. A fresh electrode must be saturated for a much longer period before the first reading is made. When not in use, the cell is kept filled with distilled water.

The Calomel Cell is constructed with a water jacket and has a platinum wire sealed into the bottom and a mercury contact. In it are placed mercury, calomel and mercury, and a solution saturated with both potassium chloride and calomel. It is filled to the top and when the stopper is introduced the excess solution is forced out of the tube (which contains a loose plug of cotton), thus eliminating all air bubbles.

The Salt Bridge is "closed," that is, not open to the atmosphere's pressure. When the liquid junction is formed there can be no flow of liquid. Saturated potassium chloride solution is used to eliminate liquid junction potential and, for convenience, is colored with α-azurine G. A reservoir (D) of this solution is kept at constant level by means of a glass tube connected with an inverted bottle of potassium chloride solution on a shelf above the apparatus, and is connected to the bridge by means of a stopcock (E) which is kept closed by an elastic band attached to a glass hook fused to the stopcock handle. One liter of potassium chloride solution will serve as a supply for a year.

The Hydrogen, which is supplied from a tank with a reducing valve, is passed through water and then through a coil in the constant-temperature bath, from which it is brought to the electrode by means of Tube J. The pressure of the hydrogen is regulated to about 6–7 mm. of mercury. This gives an even flow of small bubbles when the stopcock (in Position I) is partly opened.

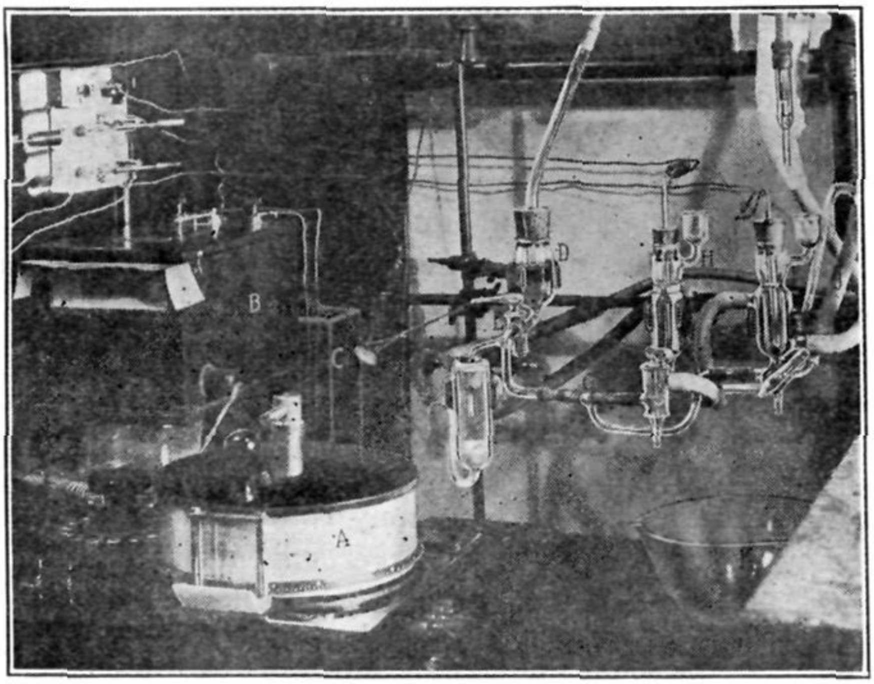

Fig. 2.—Hydrogen-ion apparatus. A. Potentiometer. B. Galvanometer. C. Storage battery, single cell. D. Constant level reservoir of saturated potassium chloride solution. E. Self-closing stopcock connecting the potassium chloride reservoir with the salt bridge. F. Water-jacketed calomel cell. G. Salt bridge. H. Hydrogen electrode cell (of a different type than described in this article). I. *Hydrogen electrode cell* described in this article. J. Hydrogen gas supply. K. Dish to collect drainage. L. Automatic nipple for distilled water supply

Water Circulation from the bath through the cells is accomplished by means of an "air lift" which is merely a siphon system through the cells into which air is injected to raise the water back up to the bath. It is not essential for the functioning of the air lift that the bath be at a higher level than the cells. If the bath were on the same level as (or even below) the cells, the water after passing through them could be carried down to the floor and then raised to the bath by means of the air lift, thus circulating the water.

Manipulation

The hydrogen electrode cell has but a single stopcock which performs the following functions. *First,* in Position I, it allows hydrogen to be bubbled through the apparatus (for three minutes). *Second,* in Position II, it permits a few drops of solution to drain, and thus remove all bubbles of hydrogen.[1] *Third,* it is swung around (to the left) to Position IV, connecting the salt bridge with the drainage tube. Here no liquid can flow until Stopcock E is opened. Hence the stopcock of the cell is left open in Position IV while the operator reaches with the same hand to open Stopcock E, permitting a few drops of potassium chloride solution to drain. Thereafter it is necessary merely to release the Stopcock E, since it closes automatically. This procedure has filled Bore *c* of the cell stopcock with potassium chloride solution. *Fourth,* it is then turned to Position III, thus forming the liquid junction, and a reading is taken. If another reading is desired, the stopcock is turned to Position II, where a few drops of solution are allowed to drain, and then turned to Position I, where the saturation with hydrogen is continued.

Discussion

This cell has the following advantages.

1. Its temperature may be accurately controlled without interfering with its manipulation. It may be more conveniently handled than is the case with cells placed in an air or oil thermostat.
2. The temperature of the cell is maintained with such constancy that a solution which is much colder or much warmer than the cell will be brought to the desired temperature during the three minutes required for saturation. Thus, a solution may be taken from the refrigerator and introduced directly into the cell without being previously warmed.
3. One stopcock performs all the functions required, thus preventing accidental passage of gas into the salt bridge or of potassium chloride solution into the cell.
4. The closed bridge prevents mechanical agitation when the liquid junction is formed.
5. The liquid junction is only 6 mm. from the platinum electrode, thus permitting accurate readings even with solutions of low conductivity.
6. One to two cc. of solution is sufficient for 2 to 6 consecutive readings.

Accuracy.—Bubbling with hydrogen for three minutes gives readings

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[1] In case the drainage of the solution (in Position II) is stopped by bubbles, the hole in the rubber stopper is closed with the forefinger of the left hand, while the fleshy portion of the right thumb is gently pressed on the filling cup of the cell. The pressure created will start the flow of liquid.

which do not change more than 0.1 to 0.2 millivolt even after two hours' bubbling. Readings are reproducible to 0.01 *P*H.

The fact that the whole system is not at the same temperature should produce no appreciable error, since the liquid junction is at practically the same temperature as the electrodes and no potential can be produced by temperature variations in the bridge.

The "open stopcock" junction is subject to the usual errors.

Summary

A simple water-jacketed hydrogen electrode cell of the bubbling type is described which is accurately maintained at constant temperature with water from a bath, circulated by means of an air lift.

It gives accurate readings reproducible to 0.01 *P*H with 1 or 2 cc. of solution after three minutes' saturation with hydrogen, even with solutions of low conductivity.

It has a single stopcock which performs separately the following functions: It permits (1) bubbling of hydrogen gas through the solution; (2) drainage of solution; (3) drainage of potassium chloride solution from the salt bridge; (4) formation of liquid junction.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE FREE ENERGY OF MERCURIDES

BY ROSCOE H. GERKE

RECEIVED MAY 26, 1923

Alloys and metallic compounds are important classes of substances for which there are few free-energy data. It is the purpose of this paper to collect available data on metallic compounds and solid solutions containing mercury, and incidentally point out that the method of calculating these quantities involves the use of partial molal free energy. Hitherto, the concept of partial molal free energy has not been used to split up the free energy of formation of a compound from its constituent elements into two parts, as has been done in this paper. In the case of the mercurides and other metallic compounds, it will be seen that the free energy of formation of the compound from its elements is equal to the sum of the separate free-energy changes which the elements undergo in the formation of the compound.

In the case of sodium mercuride, $NaHg_5$, the partial molal free energy $\bar{F}_2$,[1] of the sodium in the compound is measured by the electromotive force of the galvanic cell, Na(s) | Na^+ | Na in Hg + $NaHg_5$(s). The chemical equa-

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[1] The notation employed is that of Lewis and Randall, THIS JOURNAL, **43**, 233 (1921).