

III. The melting point of gallium was found by 2 methods to be 29.75° C. on the international hydrogen scale.

IV. The density of the purest gallium was found to be 5.904 and that of liquid gallium 6.095, both at the melting point. The expansion on solidification (0.00531 cc. per g.) was proved not to be due to impurities.

V. The cubic coefficient of expansion of solid gallium was found to be about 0.000055. Hence the density of the solid at 20° is 5.907, and its atomic volume 11.85.

VI. The compressibility of solid gallium was found to be 0.0000020 and that of the liquid about twice as great.

VII. The surface tension of liquid gallium in carbon dioxide at 30° was found to be 36.54 mg./mm. In control experiments with the same apparatus, that of mercury at the same temperature was found to be 44.06.

VIII. The latent heat of fusion calculated from the Clapeyron equation and the change of melting point with pressure was found to be 19.04 calories per g. at 173 megabars pressure; that is, the melting point is lowered 0.00207° by the increase of pressure of one atmosphere.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 128.]

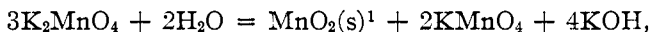
THE EQUILIBRIUM CONDITIONS OF THE REACTION BETWEEN MANGANATE, PERMANGANATE AND MANGANESE DIOXIDE.

BY CHARLES E. RUBY.

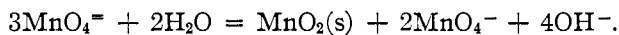
Received December 6, 1920.

I. Introduction.

The immediate object of this research was to study the equilibrium conditions of the reaction



or more properly, those of the corresponding ionic reaction:



The ultimate purpose in view was to derive from the equilibrium constant of this reaction, by combining it with the fairly well known electrode-potential of the reaction $\text{MnO}_4^{\ominus} + \oplus = \text{MnO}_4^{\ominus}$, the electrode-potential of the reaction $\text{MnO}_2(\text{s}) + 4\text{OH}^{\ominus} + 2\oplus = \text{MnO}_4^{\ominus} + 2\text{H}_2\text{O}$, and of other related reactions, thus contributing to our knowledge of the quantitative relations between the different stages of oxidation of manganese.

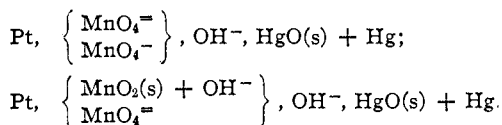
This research was undertaken at the suggestion of Prof. A. A. Noyes, and was carried out with the aid of a grant made to him by the Carnegie

¹ A formula followed by (s) denotes that the substance is present as a solid phase.

Institution of Washington. I desire to express my indebtedness for this financial assistance and for his valuable advice in relation to the experimental work and the preparation of this article for publication. I wish also to acknowledge the assistance which was afforded me by the preliminary work which had been done upon this equilibrium in this laboratory by Mr. C. E. Linscott.

2. Previous Investigations.

An investigation of the equilibrium of the reaction under consideration was undertaken by Sackur and Tagener;¹ but, on account of the difficulty of securing sufficiently accurate results, they abandoned the attempt and turned their attention to the study of voltaic cells in which took place the electronic reactions of which this reaction is the resultant. Namely, they measured the electromotive force of the cells



By combining the results with the electromotive force of the cell $\text{Hg} + \text{HgO(s)}, \text{OH}^{\ominus}, \text{H}_2$ (1 atm.),² they obtained -0.61 volt for the molal electrode-potential of $\text{MnO}_4^{\ominus} + \oplus = \text{MnO}_4^{\ominus}$, and -0.50 volt for that of $\text{MnO}_2(\text{s}) + 4\text{OH}^{\ominus} + 2\oplus = \text{MnO}_4^{\ominus} + 2\text{H}_2\text{O}$, both referred to the molal hydrogen electrode.

The value of the first of these 2 potentials seems fairly reliable. The correction (0.005 volt) for the liquid-potential involved in the cells was small, and the alkali hydroxide concentrations were not excessive (0.8 — 1.5 *M*).

The value (-0.50 volt) of the electrode-potential of $\text{MnO}_2(\text{s}) + 4\text{OH}^{\ominus} + 2\oplus = \text{MnO}_4^{\ominus} + 2\text{H}_2\text{O}$ obtained by Sackur and Tagener can, however, be regarded only as a first approximation; for the cells did not in general give reproducible results, the hydroxide concentrations were very large (4 to 10 *M*), and the correction for the liquid potential was very uncertain. It was with the hope of obtaining a more reliable value of this molal electrode-potential that the present research was undertaken.

3. Preparation of the Substances and Solutions.

The potassium hydroxide solution was prepared at first by the decomposition of potassium amalgam; but the large concentration (10 *N*) required necessitated the repeated use of a very large amount of mercury, during which the alkali unavoidably became carbonated to a slight extent. The potassium hydroxide actually employed was therefore prepared in the following manner. A 12 *N* solution of potassium hydroxide was made from the purest commercial product; and its carbonate content was approximately determined. A slight excess of solid barium hydroxide was added, and the mixture was

¹ Sackur and Tagener, *Z. Elektrochem.*, **18**, 718 (1915).

² Auerbach, *ibid.*, **18**, 13 (1912).

allowed to stand for several days in a warm place with frequent shaking. It was then filtered through asbestos out of contact with the atmosphere. The barium content was then accurately determined, an equivalent quantity of anhydrous potassium sulfate was added, and the solution was again allowed to stand for several days and finally filtered. The resulting solution yielded no precipitate with potassium sulfate or with barium chloride. Chlorides were also absent, which is essential to the success of one of the analytical methods employed.

The potassium permanganate was purified by twice recrystallizing a pure commercial product. Two solutions of it were prepared. One, used in the equilibrium experiments, containing 0.05 mol. per liter of permanganate, was made by simply dissolving the recrystallized salt in water. The other, used in the analysis of the equilibrium mixtures, containing 0.01 mol. of permanganate per liter, was prepared as described by McBride.¹

The potassium manganate was made by the decomposition of potassium permanganate by heating with potassium hydroxide solution in the following way. One hundred and six g. (equal to $\frac{2}{3}$ mol.) of potassium permanganate was placed in a Pyrex flask, provided with fittings which enabled the solution to be introduced and maintained for a period of time without contact with the atmosphere. Into this flask 526 g. of a 39.36% potassium hydroxide solution (equal to $3\frac{2}{3}$ mols.) was introduced and the apparatus was allowed to stand for 2 days in a hot closet at a temperature of 80° to 90°. Oxygen was evolved slowly, but continuously. At the end of the second day, the flask was cooled, and the solid material was carefully removed as quickly as possible, and allowed to drain in a device which protected it from the carbon dioxide in the air. Finally, the material was dried over sulfuric acid in a vacuum. Thus prepared, the material contained some potassium hydroxide and some manganese dioxide, but it was free from chloride and carbonate.

A stock solution of the potassium manganate was made by dissolving 0.075 mol. in a liter of 1.2 *M* potassium hydroxide solution. Upon standing, this stock solution gradually assumed a purple color and deposited manganese dioxide; but the decomposition, even after several months, did not amount to more than 50%.

The manganese dioxide was prepared by the action of hydrogen peroxide upon a cold solution of potassium permanganate. The precipitated material was washed many times with conductivity water to remove the alkali and the excess of hydrogen peroxide, whereby it acquired a tendency to pass into the colloidal state. It was finally suspended in 1.2 *N* potassium hydroxide solution. Analysis of the moist material showed that it contained approximately 3% less oxygen than the theoretical amount corresponding to the manganese in the compound MnO_2 . This deficit in oxygen did not affect the final equilibrium, for the oxide was converted into manganese dioxide in the equilibrium experiments by the long contact with the solution of manganate and permanganate.

The other materials required in the investigation were standard solutions of sulfuric acid and of potassium hydroxide, a saturated aqueous solution of sulfurous acid, a 3% solution of hydrogen peroxide, a standard solution of ferrous sulfate in sulfuric acid, nitric acid solutions, solid sodium oxalate, solid sodium bismuthate, and an alcoholic solution of methyl red.

4. The Methods of Analysis of the Equilibrium Mixtures.

The plan adopted for determining the concentrations of manganate and permanganate in the equilibrium mixtures consisted: (1) in adding one weighed portion of the mixture to an excess of a known solution of ferrous sulfate containing sulfuric acid and titrating the excess of ferrous salt with standard permanganate; and (2) in subjecting another weighed

¹ McBride, *THIS JOURNAL*, **34**, 393-416 (1912).

portion of the mixture to the process described by Blum,¹ which consists in reducing the manganese in the acidified mixture with sulfurous acid, reoxidizing it to permanganate with sodium bismuthate, and determining the permanganate as usual with ferrous sulfate. The first of these determinations gave results concordant within 0.05%, and the second of these determinations results concordant within 0.5%.

The first of these determinations gives a value A of the number of oxidation-equivalents per 1000 g. of solution which is equal to $4x + 5y$, and the second of these determinations leads to a value B equal to $5x + 5y$, where x denotes the number of formula-weights of potassium manganate, and y the number of formula-weights of potassium permanganate, per 1000 g. of solution. The value of x and y are therefore found by the equation $x = B - A$, and $y = A - 4/5 B$. The large multiplication of errors introduced by this indirect calculation and the fairly large experimental error (0.5%) in the experimental determination of B produce an error of several per cent. in the values of x and y , and a still larger error in the quantity y^2/x^3 which occurs in the expression for the equilibrium-constant K of the reaction.

The potassium hydroxide in the equilibrium mixture was determined by adding to a weighed sample 3% hydrogen peroxide solution till the manganate and permanganate were reduced to manganese dioxide, adding an excess of standard sulfuric acid, filtering the solution rapidly through asbestos, and titrating back the excess of acid. A correction was applied to this determination for the acidic material present as impurity in the hydrogen peroxide solution, and the alkali produced by the decomposition of the manganate and permanganate was of course subtracted from the amount of acid present. This procedure gave results accurate to 0.5%.

5. Preparation of the Equilibrium Mixtures.

The reaction vessels consisted of Pyrex tubes about 4 cm. in diameter and 16 cm. in length, of 200 cc. capacity. They were found to be remarkably resistant to the alkali, showing only slight corrosion of the glass after several months' contact with 0.4–0.8 *N* potassium hydroxide. The tubes had a short side-arm at one end, for convenience in filling and emptying them. After the tube was charged with the reaction mixture, the side arm was sealed with a blast-lamp.

The tubes were placed in a horizontal position along the shaft of a rotating apparatus within a thermostat kept at a temperature of $45^\circ \pm 0.1^\circ$. They were rotated for periods varying from one week to 4 months. The tubes were opened, and the contents were rapidly filtered through perforated crucibles containing asbestos into dry flasks. No considerable pressure was ever found upon opening the tubes, showing that little, if any, oxygen had been produced by the decomposition. Portions of the filtrate

¹ Blum, *THIS JOURNAL*, 34, 1379–1398 (1912).

were drawn out with a pipet, weighed, and analyzed as described in the preceding section of this article.

The reaction mixtures for approaching equilibrium from the manganate side were made up by diluting 50 cc. of the stock solution with 100 cc. of liquid consisting in different experiments of various volumes of water and of 1.2 *N* potassium hydroxide solution. This procedure yielded mixtures which were at the start from 0.01 to 0.025 formal in potassium manganate, from 0.0–0.01 formal in permanganate (arising from previous decomposition of the manganate), and varying from 0.4 to 0.8 formal in potassium hydroxide.

The reaction mixtures for approaching equilibrium from the permanganate side were prepared by diluting 50 cc. of the stock 0.05 formal permanganate solution with 100 cc. of a mixture consisting in different experiments of various volumes of water and of 1.2 *N* potassium hydroxide solution containing in suspension manganese dioxide in at least 5 times the quantity required for complete reaction. This procedure yielded mixtures which were at the start about 0.016 formal in permanganate and varying from 0.4 to 0.8 formal in the hydroxide.

6. Results of the Equilibrium Measurements.

Table I shows, in the second, third, and fourth columns, the composition of the equilibrium mixtures that were obtained in the separate experiments.

The table contains, in the fifth column, the corresponding equilibrium constants calculated by the expression $(\text{MnO}_4^-)^2(\text{OH}^-)^4/(\text{MnO}_4^=)^3$ under the assumption that the 3 substances are completely ionized. (This is equivalent to the assumptions that the ionizations (or activity-coefficients) of the univalent 2 substances potassium permanganate and potassium hydroxide are equal and that the square of these ionizations (or activity-coefficients) is equal to the ionization (or activity-coefficient) of the univalent salt potassium manganate—assumptions which are probably not very far from the truth). The values of the constant obtained from the experiments in which the equilibrium was approached from the manganate side are indicated by an asterisk. The constants without an asterisk were obtained from experiments in which the equilibrium was approached from the permanganate side.

In the last column of the table are given the true densities at 45° of the equilibrium mixtures. These densities will enable the weight-concentrations to be converted to volume-concentrations, in case this is desirable for any purpose.

It will be noted that the mean value (51.6) of the constants from the experiments in which the equilibrium was approached from the permanganate side agrees substantially with the mean value (54.6) from the experiments in which the equilibrium was approached from the opposite

side. This shows that in general equilibrium conditions were attained. Therefore the average of these 2 mean values, namely 53 may, in spite of the large deviations of the separate values, be regarded as a fairly close approximation to the true equilibrium constant.

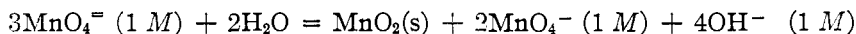
TABLE I.—COMPOSITION OF THE EQUILIBRIUM MIXTURES AND THE EQUILIBRIUM-CONSTANTS AT 45°.

Expt.	Millimols per 1000 g. of water.			Equil. const.	Density at 45°.
	KMnO ₄ .	K ₂ MnO ₄ .	KOH.		
1.....	11.48	3.29	375.4	73.5	1.013
2.....	7.04	4.17	584.8	79.7	1.024
3.....	7.71	4.95	474.0	25.0	1.019
4.....	13.60	4.34	389.5	52.2	1.014
5.....	8.13	4.34	380.5	16.9	1.014
6.....	11.26	10.13	606.0	16.1	1.027
7.....	7.53	4.37	582.5	78.6	1.024
8.....	7.07	3.22	484.0	81.9	1.019
9.....	16.14	4.94	452.8	82.0*	1.018
10.....	15.67	4.08	446.5	90.4*	1.017
11.....	13.38	7.38	559.0	43.5*	1.023
12.....	13.65	6.77	534.1	48.8*	1.022
13.....	15.11	4.78	444.0	81.0*	1.017
14.....	14.84	5.16	446.0	63.4*	1.017
15.....	11.47	5.27	472.0	44.5*	1.019
16.....	12.07	8.69	604.0	29.5*	1.030
17.....	6.51	7.39	802.3	43.8	1.034
18.....	8.88	11.27	809.0	23.5*	1.038
19.....	5.30	6.26	804.4	48.1	1.038
20.....	9.56	9.94	805.0	39.3*	1.037

Means $\left\{ \begin{array}{l} 51.6 \\ 54.6^* \end{array} \right.$

7. Computation of the Electrode-Potentials.

From the value of the equilibrium constant K the free-energy decrease $-\Delta F$ attending the reaction

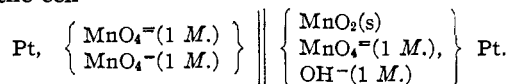


may be calculated by the expression

$$-\Delta F = RT \log K = 8.316 \times 318.1 \times 2.303 \log_{10} 53.$$

This free energy decrease is thus found to be 10,500 joules.

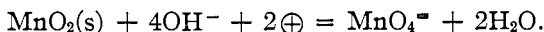
Now this reaction takes place when 2 faradays (193,000 coulombs) pass through the cell



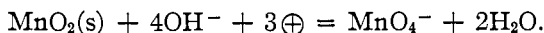
Therefore, the electromotive force of this cell at 45° is 10500/193000, or +0.0545 volt.

The electromotive force \mathcal{E} of this cell is the difference between the

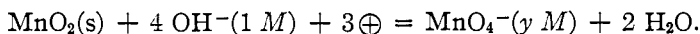
molal electrode potentials \bar{E}_1 and \bar{E}_2 of the 2 half-cells of which it is composed; that is, $E = \bar{E}_1 - \bar{E}_2$. Assuming that the electromotive force of the cell is substantially the same at 25° as at 45° , we may substitute for E the value $+0.054$ and for \bar{E}_1 the value -0.61 found at 25° by Sackur and Tagener. We thus find for \bar{E}_2 the value -0.664 . This is the molal electrode-potential, referred to the molal hydrogen electrode of the reaction,



From this manganate molal electrode-potential may be derived one for permanganate; namely, that corresponding to the reaction:



This may be done with the aid of the following considerations. The manganate molal electrode-potential must be equal to the electrode-potential corresponding to the change in state,

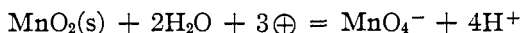


where the quantity γ is that concentration of MnO_4^- which is in equilibrium with one molal MnO_4^{\ominus} , 1 molal OH^- , and solid MnO_2 . The concentration γ is for this case, however, simply equal to the square-root of the value 53 of the equilibrium-constant of the reaction studied in this research, namely, equal to 7.3. This electrode-potential E is, moreover, related to the desired molal electrode-potential \bar{E}_1' (where the MnO_4^- and OH^- are both at a concentration one molal) in the way expressed by the equation

$$\bar{E}_1' = E + \frac{RT}{nF} \log \gamma = -0.664 + \frac{0.0591}{3} \log_{10} \gamma.$$

The molal electrode-potential for permanganate in presence of hydroxidation is therefore -0.647 volt.

From this molal electrode-potential (\bar{E}_1'), that (\bar{E}_2') of the reaction



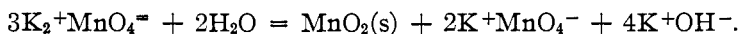
can be similarly derived by the equation

$$\bar{E}_2' = \bar{E}_1' + \frac{RT}{nF} \log (\text{H}^+)^4 = -0.647 + \frac{0.0591}{3} \log_{10} (0.81 \times 10^{-14})^4,$$

where (H^+) represents the H^+ concentration¹ in a solution one molal in OH^- ion, and n is the number of faradays (3) of electricity passing when 4 mols of H^+ are produced. The molal electrode-potential for permanganate in presence of hydrogen ion is thus found to be -1.757 volts.

8. Summary.

In this article a method has been described for determining the equilibrium-conditions of the reaction



¹ Lewis and Randall, *THIS JOURNAL*, 36, 1979 (1914).

The results of measurements made at 45° have been presented in detail (in Table I). The equilibrium-constant, as given by the expression $(\text{MnO}_4^-)^2(\text{OH}^-)^4/(\text{MnO}_4^{\equiv})^3$, these ion-concentrations being calculated under the assumption that all the substances are completely ionized (or that their ionizations compensate each other), was found to have the value 53 at 45°. The corresponding free-energy decrease attending the reaction as above written is 10,500 joules, and the electromotive force of a cell in which it takes place is +0.054 volt.

Regarding this electromotive force as having the same value at 25°, and combining it with the molal electrode-potential (−0.61 volt) of $\text{MnO}_4^{\equiv} + \oplus = \text{MnO}_4^-$ as determined by Sackur and Tagener, the following molal electrode-potentials at 25° were derived.



CAMBRIDGE 39, MASS.

NOTES.

[CONTRIBUTION FROM BEDFORD COLLEGE, UNIVERSITY OF LONDON.]

Cottrell's Ebullioscopic Apparatus.—In a recent number of this JOURNAL Cottrell¹ described a modification of the Beckmann method of determining the molecular weight of substances in solution by measuring the elevation of the boiling point. This method was used in a slightly modified form by Read and Washburn² for a specific purpose and found to fulfil the demands made upon it excellently. The new method has very much to recommend it, particularly in the greater ease and rapidity with which results may be obtained and also in the accuracy of those results. The apparatus is much less sensitive to small air currents than the original Beckmann apparatus. When put into the hands of students, however, it suffers from one drawback, namely its relatively complicated structure. The permanent attachment of the pump to the inner jacket, makes this portion of the apparatus very fragile in the hands of students with the consequence that breakage or considerable loss of time is the result when it requires cleaning.

Experience with the Cottrell apparatus in the hands of a junior class in experimental physical chemistry has shown that the following slight alterations in the method of fitting up the various parts of the apparatus make it more serviceable in relatively inexperienced hands, and since the changes are all in the direction of saving time and preventing breakage they may be of use to others.

¹ Cottrell, THIS JOURNAL, 41, 721–729 (1919).

² Read and Washburn, *ibid.*, 41, 729–741 (1919).