of mixtures amount in some cases to more than 7%. Curves presenting the equivalent conductances of the mixtures as functions of their relative compositions show all modes of behavior, and any equation advanced to account quantitatively for the equivalent conductances of such mixtures must be of a power greater than linear.

The relative viscosities of the mixtures of these electrolytes are consistently less than values computed by the rule of mixtures from the relative viscosities of pure solutions of their constituent electrolytes, save in the cases of the most dilute mixtures studied, where the differences between the measured and computed values are negligible. The presentation of the relative-viscosity data in terms of its reciprocal, the relative fluidity, is less satisfactory.

The values of the $\Lambda\eta$ products of the mixtures of these electrolytes of the concentrations of 0.5 *M* and 1.0 *M* can be computed by the alligative formula somewhat more exactly than can the equivalent conductances of the same mixtures. For concentrations of greater magnitude, the data are not sufficiently accurate to warrant making such calculations.

CAMBRIDGE 39, MASSACHUSETTS

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

THE MANGANESE DIOXIDE-PERMANGANATE ELECTRODE

BY D. J. BROWN AND RALPH F. TEFFT

RECEIVED JULY 27, 1925 PUBLISHED MAY 5, 1926

The values in the literature for the potential of the manganese dioxide-permanganate electrode differ by more than 0.1 volt. Inglis[1] has been the only person to measure directly the potentials of the manganese dioxide-permanganate electrode in acid solutions with any degree of accuracy. His measurements are consistent to within a few millivolts, but the error is probably somewhat greater than this. Inglis prepared the manganese dioxide by plating it on platinum electrodes which were then electrolyzed as anodes in sulfuric acid. He does not state the nature of the electrolyte from which the manganese dioxide was prepared, but it was probably a solution of some manganous salt. Neither does he give details concerning the applied potential or the current density during the electrolysis. Attempts by the authors to prepare pure manganese dioxide electrolytically failed. Analyses showed that the product, even after being dried at 300°, did not have the oxidizing power of an equal weight of manganese dioxide. Small variations in the conditions used in preparing the electrodes by this method also produced a large deviation in the observed potential. On the basis of a number of preliminary measurements made in this Laboratory

---

[1] Inglis, *Z. Elektrochem.*, 9, 226 (1903).

the authors believe that the consistency of Inglis' results was due to his using the same conditions each time in preparing the electrodes.

Ruby[2] calculated the potential of the manganese dioxide-permanganate electrode in acid solution from values which he obtained for the equilibrium constant at 45° of manganate, permanganate and manganese dioxide together with the results of Sackur and Taegener[3] for the alkaline manganate-permanganate electrode. He gives a value of 1.757 volts, but this is probably very much in error. The value given by Sackur and Taegener for the potential of the alkaline manganate-permanganate electrode can by no means be assumed to hold for infinite dilution since it was obtained from measurements in 1.5 M potassium hydroxide.

The authors have studied this electrode in perchloric acid solution in an attempt to determine the potential more accurately. The cell H_2, $HClO_4$ (m_1); $HClO_4$ (m_2), $KMnO_4$ (m_3), MnO_2 was investigated at 25°. The electrode reaction involved is as follows: $MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$. We may write the following equation for the observed potential of the electrode: $E = E^0 + (0.05915/3) \log (a_{MnO_4^-})(a_{H^+})^4$, which is equivalent to $(0.05915/3) \log (\gamma_{MnO_4^-}) = [E-(0.5915/3) \log (c_{KMnO_4})(a_{H^+})^4]-E^0$. E^0 is then evaluated by plotting the quantity in parentheses ($E^{0\prime}$) against the square root of the concentration of the permanganate and extrapolating to zero concentration where $E^{0\prime} \equiv E^0$.

Schuhmann[4] has shown that the activity coefficients of perchloric acid are the same as the activity coefficients of hydrochloric acid up to 1.1 M. Therefore, the values of the mean activity coefficients of hydrochloric acid as determined by Scatchard[5] were taken as the activity coefficients of the hydrogen ion in perchloric acid.

When the concentration of the perchloric acid was the same throughout the cell the liquid-junction potential was disregarded, for the effect of this potential is eliminated in the extrapolation to zero permanganate concentration. In other cases the following approximation formula was used to evaluate the liquid junction potential: $E = (t_+ - t_-)0.05915 \log (a_{\pm 1}/a_{\pm 2})$. The same values of the transference numbers of perchloric acid were assumed to hold at 25° and finite concentrations as at 18° and infinite dilution.

Experimental Part

Conductivity water was used for all solutions. Pure potassium permanganate was prepared by recrystallization of the best grade salt and the purified salt was kept in the dark. Perchloric acid solutions were prepared by dilution of the best commercial acid. Manganese dioxide was prepared by heating manganous nitrate in the electrode vessel at 160° for several days and treating the product with nitric acid several times in the

---

[2] Ruby, THIS JOURNAL, **43**, 300 (1921).

[3] Sackur and Taegener, *Z. Elektrochem.*, **18**, 721 (1912).

[4] Schuhmann, THIS JOURNAL, **46**, 58 (1924).

[5] Scatchard, *ibid.*, **47**, 641 (1925).

course of the heating. Several samples of manganese dioxide prepared in this way were found to be more than 99% pure.

All potentials were measured at 25° with a Leeds and Northrup Type K potentiometer in conjunction with a Leeds and Northrup Type 2500 galvanometer. All observations were made in a room lighted only by red lights.

The reaction cell consisted of two Ostwald hydrogen electrodes filled with perchloric acid solution and connected through a central chamber to a manganese dioxide-permanganate electrode. In all cases this central chamber contained the same solution as did the hydrogen electrodes.

The manganese dioxide-permanganate electrode was simply a large test-tube in the bottom of which a platinum conducting wire was sealed. A glass tube was sealed on the outside at this point and filled with mercury to provide electrical contact. This vessel was connected to the perchloric acid chamber by means of a siphon tube provided with a stopcock. It was found necessary to bend the end of this siphon tube upwards at the point of contact to prevent mixing due to a slight difference in density of the two solutions. Since these cells were under observation for several days at a time, it was necessary to keep all stopcocks closed as much as possible to eliminate diffusion effects.

The two hydrogen electrodes were supplied with hydrogen from independent sources. It was hoped that the accuracy of the electrodes could be checked in this way. One electrode was supplied with hydrogen prepared from C.P. hydrochloric acid and C.P. zinc while the hydrogen for the other electrode was prepared from C.P. hydrochloric acid and C.P. aluminum. The gas in each case was passed through sodium hydroxide solution and finally through a gas absorption tube filled with conductivity water. The hydrogen prepared from the zinc was passed through a solution of silver sulfate before the final washing to remove any trace of arsine. Apparently this method of checking the accuracy of the hydrogen electrodes was quite satisfactory.

When a newly prepared manganese dioxide electrode is first filled with the permanganate-perchloric acid solution the potential rises rapidly until a maximum is reached, usually within eight or ten hours, and then begins to fall off approaching a limiting value after several weeks. The initial rise of about 30 or 40 millivolts may be due to adsorption of permanganate or hydrogen ion from the solution and the fall, which is about 15 or 25 mv., may be due to the saturation of the solution with manganese dioxide. Analyses of the solutions indicated that this drop in the potential was not due to decomposition of the permanganate. In every case this final value was assumed to be the true value.

To show that the activity of the hydrogen ion affects the potential in accordance with the equation given above, it is only necessary to study the effect of changing the acid concentration on the potential of the manganese dioxide-permanganate electrode. Table I shows the results of measurements made on this basis. The concentration of the perchloric acid in the hydrogen electrode was maintained constant at 0.0250 M. The concentration of the permanganate was 0.00250 M. The corrected potentials given in the last column of Table I when plotted against the logarithm of the hydrogen-ion activity gave a straight line whose slope was 0.079 as predicted by the equation.

TABLE I

EFFECT OF ACIDITY ON MANGANESE DIOXIDE-0.00250 M POTASSIUM PERMANGANATE

Concn. of $HClO_4$, M	E obs.	E, liq. junc.	E, corr.
0.250	1.535	+0.037	1.572
.0250	1.498	.000	1.498
.00250	1.458	− .038	1.420

With the perchloric acid at a constant concentration of 0.0250 M throughout the cell and varying permanganate concentration the results given in Table II were obtained. The values given in the third column are corrected for the activity of the hydrogen ion in both electrodes. By plotting these corrected potentials against the square root of the permanganate concentrations and extrapolating to zero concentration a value of 1.585 volts is obtained for the oxidation potential of the manganese dioxide-permanganate electrode in normal hydrogen ion. To correct for the presence of the perchloric acid it is logical to assume that in so low a concentration the activity coefficient of the permanganate ion is the same as the mean activity coefficient of potassium chloride in a solution whose ionic strength is 0.0250. Then the oxidation potential becomes $1.585 - (0.05915/3) \log 0.853 = 1.586$ volts, which is probably correct to within 1 mv. The value of the mean activity coefficient of potassium chloride used here was obtained by interpolation from the values given by Scatchard.[6]

TABLE II

EFFECT OF PERMANGANATE IN 0.0250 M $HClO_4$ THROUGHOUT THE CELL

Concn. of $KMnO_4$, M	E, obs., v.	$E^{0'}$
0.0237	1.5114±0.9 mv.	1.5762
.00237	1.4975± .5	1.5821
.000237	1.4799± .1	1.5841

Activity coefficients calculated from these data are very much smaller than those determined by other methods. This may be due to variations in the activity of the hydrogen-ion and the liquid junction potential with varying permanganate concentration.

Summary

A value of 1.586 volts has been obtained for the oxidation potential of the reaction $MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$ from measurements in perchloric acid solutions.

---

[6] Ref. 5, p. 648.

The change in concentration of the acid was found to affect the potential exactly as predicted.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 87]

THE DYNAMIC MODEL OF THE CHEMICAL BOND AND ITS APPLICATION TO THE STRUCTURE OF BENZENE

BY LINUS PAULING[1]

RECEIVED SEPTEMBER 14, 1925 PUBLISHED MAY 5, 1926

Introduction

The continued success of the Bohr atom has led all physicists except the most cautious to attribute a certain reality to the physical concept underlying the theory; namely, that the atom is composed of electrons rotating in stable orbits about the positive nucleus. The determination of these stable orbits can be made, in those cases that are simple enough to permit mathematical treatment, by the application of the principles of the quantum theory, thus verifying the correctness of the dynamic atom, since the quantum theory has been widely used in the explanation of the most varied phenomena. Hence, in attempting to explain the chemical properties of substances on the basis of the structure of the atom it would seem desirable to assume the Bohr theory to be true, and to make only those changes and additions which are necessary and logical extensions of the theory. This was the procedure followed by Knorr,[2] who first suggested and supported the idea that in non-ionized molecules electrons are in motion in orbits about two atomic nuclei. Further evidence in support of Knorr's views has since become available.

The study of the structures of crystals has also provided valuable information regarding the nature of the chemical bond. In this paper the arguments in favor of the dynamic models of molecules are reviewed and crystal structure evidence is presented to show that in molecules or ions, atoms may have stable electronic arrangements other than those of the noble gases. Electronic structures of benzene and other aromatic compounds based on these conceptions are then suggested and briefly discussed.

The Electron-Orbit-Sharing Theory of Chemical Bonding

The Pairing of Electrons.—Lewis[3,4] has shown that electrons have a strong tendency to pair. In terms of the Bohr atom the pairing of elec-

---

[1] National Research Fellow.

[2] Knorr, *Z. anorg. allgem. Chem.*, **129**, 109 (1923).

[3] Lewis, THIS JOURNAL, **38**, 762 (1916).

[4] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 79.