ucts have been measured at several temperatures and from them heats of formation have been calculated by substitution in the Clausius–Clapeyron formula. The measurements were made by the method of evacuation and are therefore subject to errors due to incomplete attainment of equilibrium. These errors are probably not greater than about 1 mm. at the lower pressures and 3 or 4 mm. at the higher pressures. The logarithms of the vapor pressures plotted against the reciprocals of the absolute temperatures gave reasonable concordance with straight lines. Vapor pressures calculated from the equations of these lines, in which the constants are so chosen as to give the pressure in millimeters, agree with the measured values within the experimental error.

TABLE III

VAPOR PRESSURES OF SULFUR DIOXIDE ADDITION PRODUCTS AT VARIOUS TEMPERATURES

Equation: $\log P = a - b(1/T \times 10^4)$

Compound	Temp. range, °C.	*a*	*b*	Heat of formation, cal.
o-Toluidine	10.8–50.4	16.529	0.4419	20,200
m-Toluidine	8.0–25.0	19.190	.4970	22,600
p-Toluidine	10.3–29.9	19.234	.5265	24,100
Quinoline	22.5–47.6	18.478	.5016	22,900
n-Amylamine	20.0–58.3	3.4481	.0771	3,500
n-Heptylamine	20.0–50.0	5.6392	.1391	6,400

For the three cases in which the use of dibutyl ether as solvent was necessary, namely, *p*-toluidine, *n*-amylamine and *n*-heptylamine, it is clear that the added corrections make the calculated heats of formation less accurate. It appears that 1:1 compounds of sulfur dioxide with the three toluidines and with quinoline have heats of formation of the same order as that found for the aniline compound,[4] which is 19,630 cal.; the two aliphatic amines give heats of reaction very markedly less (3500 cal. and 6400 cal.). It does not appear possible at this time to correlate the heats of formation or the vapor pressures of the compounds with their structures.

Summary

Compound formation has been studied between sulfur dioxide gas and a number of aromatic and aliphatic amines; the composition of these bodies, determined by phase-rule methods, shows variations in the ratio sulfur dioxide: amine from 1:2 to 2:1, the 1:1 ratio predominating. Vapor tension measurements of the systems have been made at different temperatures, and the approximate heats of formation calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

The Oxidation Potential of the Alkaline Permanganate–Manganese Dioxide Electrode

BY LYLE V. ANDREWS AND D. J. BROWN

No direct measurement of the potential of the alkaline permanganate–manganese dioxide electrode has been made. Inglis[1] measured the electrode in acid solution from which the value in alkaline solution was calculated to be 0.52 volt. Sackur and Traegner[2] measured the two electrodes MnO_4^-–$MnO_4^{=}$ in 1.5–5.8 *m* alkali and $MnO_4^{=}$–MnO_2 in 4–10 *m* alkali against Hg–HgO in 0.8 *m* alkali and calculated the value of the alkaline permanganate–manganese dioxide electrode to be 0.54 volt. Ruby[3] determined the equilibrium concentration for the reaction $3MnO_4^{=} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$ and using Sackur and Traegner's value for the MnO_4^-–$MnO_4^{=}$ electrode, calculated the value of the alkaline permanganate–manganese dioxide electrode to be 0.647 volt. Schlesinger and Siems'[4] data for the reaction would give a slightly different value.

From the equilibrium relations for the reaction studied by Ruby and by Schlesinger and Siems, it is readily seen that the concentration of the manganate would decrease rapidly with dilution of the permanganate and hydroxide and in more diluted solutions the fraction of permanganate reduced by the manganese dioxide would be less than the experimental error in its effect on any observed potential. We believe more accurate values should be obtained in more diluted solutions than those previously used. A study from this point of view is presented in this paper.

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

[2] Sackur and Traegner, *ibid.*, **18**, 718 (1912).

[3] Ruby, THIS JOURNAL, **43**, 294 (1921).

[4] Schlesinger and Siems, *ibid.*, **46**, 1965 (1924).

The half cell Hg, HgO, KOH, which has a potential of 0.0988 volt[5] was used as a reference electrode. Then the cell reaction would be $2KMnO_4 + 3Hg + H_2O \rightleftharpoons 2MnO_2 + 3HgO + 2KOH$. When the concentrations of hydroxide and permanganate in solution are of the same molality

$$E_0 = E + \frac{0.0591}{3} \log \frac{\gamma_{KOH}}{\gamma_{KMnO_4} a_{H_2O}}$$

On dilution $E \doteq E_0$ since the values of γ and a_{H_2O} approach unity. Since the potassium hydroxide is of the same concentration throughout the cell, the actual value of the liquid junction potential may be very small and in the extrapolation to zero concentrations would be zero.

The potassium hydroxide and the alkaline mercury electrode were prepared by methods similar to those used by Ming Chow.[6] Conductivity water was used to prepare all reagents and solutions. The more diluted solutions of potassium hydroxide were prepared by diluting the analyzed solution using calibrated apparatus.

A very good grade of potassium permanganate was recrystallized from conductivity water, filtered and washed, using the crystals as a filter bed, and dried in a desiccator. This operation and all others involving permanganate, including the measurement of the electrodes, were carried out in a "dark room" lighted by light filtered through ruby glass.

A quantity of manganese dioxide was prepared[7] by heating manganous nitrate at 180°, followed by treatment with nitric acid. The product examined microscopically was found to be crystalline.[8] No detectable impurity except water was found to be present, but a large quantity of the powdered substance slowly decolorized a very dilute solution of potassium permanganate. When the manganese dioxide was refluxed with water, the filtrate reacted with very dilute alkaline permanganate. Attempts to purify manganese dioxide by refluxing with water were not satisfactory due to the formation of colloidal manganese dioxide. Analysis indicated 99.9% MnO_2. Manganese dioxide has a large adsorption capacity.[9] If this impurity can be reduced to a minimum, even if it reacts reversibly and rapidly, the determination of a true standard potential may be possible. Manganese dioxide that did not decolorize potassium permanganate was prepared by dipping platinum foil in a 15% solution of manganous nitrate, heating to 180° for two or three days with subsequent treatment of the manganese dioxide with nitric acid and finally oxidizing with a hot solution containing 30% nitric acid and 15% perchloric acid. When used in alkaline solution, the above electrode gave fluctuating values. This variation was observed especially when part of the deposit had left part of the platinum bare. We attributed this to polarization at the surface of the platinum.

In order to reduce the effects of any impurity or polarization to a minimum, very small amounts of manganese dioxide were deposited, as described in the preceding paragraph, directly on tips drawn on the side of a glass tube in the end of which was a piece of stiff platinum foil that had been thoroughly cleaned and ignited. The manganese dioxide was washed with potassium hydroxide of the same concentration that was to be used in the cell, then with water and finally dried. The electrode served as a stirrer. The electrode stirrer was trapped with vaseline to prevent the absorption of carbon dioxide by the potassium hydroxide. The mixture was stirred continuously except while the measurements were being made. Electrodes prepared at different temperatures from various concentrations of manganous nitrate gave reproducible results.

At least two reference half cells and two permanganate half cells were made for each series. Connections between the two half cells were made through a solution of the same constitution as the one in the mercury half cell. All measurements were made at 25 ± 0.1°. The laboratory standard cell was checked against two cells checked by the Bureau of Standards. A type K potentiometer was used. The observed values were

Molality of KOH and $KMnO_4$	E. m. f. of cell, mv.
0.1	+0.493 ± 1
.01	.489 ± 1
.002	.490 ± 1
.001	.489 ± 1

The positive value indicates that the reaction as represented by the chemical equation is spontaneous, or, in other words, the alkaline permanganate–manganese dioxide electrode as observed is positive.

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(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, p. 408, recalculated to data of Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

(6) Ming Chow, *ibid.*, **42**, 488 (1920).

(7) Brown and Tefft, *ibid.*, **48**, 1128 (1926).

(8) Ferrari, *Atti. accad. Lincei*, [6] **3**, 224 (1926); *C. A.*, **20**, 1926 (1926).

(9) Chattirji and Dhar, *Kolloid Z.*, **33**, 18 (1923).

The observed values for 0.1 molar solution were higher exactly as would be expected from the equilibrium constants of Ruby[3] and of Schlesinger and Siems.[4] For the more diluted solutions the effect of the reaction would be less than the experimental error. These latter values would indicate a value of 0.489 ± 0.001 volt for the cell and +0.588 ± 0.001 for E^0 for the half cell

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_{2(s)} + 4OH^-$$

The voltage of other half cells with the same components as indicated by the preceding chemical equation would be

$$E' = E_1^0 - \frac{0.0591}{3} \log \frac{a^4_{OH^-}}{a_{MnO_4^-}a^2_{H_2O}} = +0.588 - \frac{0.0591}{3} \log \frac{a^4_{OH^-}}{a_{MnO_4^-}a^2_{H_2O}}$$

For half cells represented by the chemical equation

$$MnO_4^- + e \rightleftharpoons MnO_4^{=}$$

$$E'' = E_2^0 - 0.0591 \log \frac{a_{MnO_4^{=}}}{a_{MnO_4^-}}$$

For the half cell represented by the chemical equation

$$MnO_4^{=} + 2H_2O + 2e \rightleftharpoons MnO_{2(s)} + 4OH^-$$

$$E''' = E_3^0 - \frac{0.0591}{2} \log \frac{a^4_{OH^-}}{a_{MnO_4^{=}}a^2_{H_2O}}$$

Using the equilibrium studied by Schlesinger and Siems[4] and assuming for dilute solutions that

$$\frac{[MnO_4^-]^2\,[OH^-]^4}{[MnO_4^{=}]^3} = 16 \pm 7$$

$a_{H_2O} \doteq 1$ and $a \doteq m$ of other components, the other values were calculated as follows

$$E''' - E' = 0 = E_3^0 - \frac{0.0591}{2} \log \frac{[OH^-]^4}{[MnO_4^{=}]} - \left(0.588 - \frac{0.0591}{3} \log \frac{[OH^-]^4}{[MnO_4^-]}\right)$$

$$E_3^0 - 0.588 = \frac{0.0591}{2} \log \frac{[OH^-]^4}{[MnO_4^-]} - \frac{0.0591}{3} \log \frac{[OH^-]^4}{[MnO_4^-]} = \frac{0.0591}{6} \log \frac{[OH^-]^4[MnO_4^-]^2}{[MnO_4^{=}]} = \frac{0.0591}{6} \log (16 \pm 7) = 0.012 \pm 0.002$$

$$E_3^0 = +0.600 \pm 0.003$$

$$E_2^0 = (3 \times 0.588) - (2 \times 0.600) = +0.564 \pm 0.003$$

The free energy changes for the half cells are

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2(s) + 4OH^-$$

$$\Delta F_1^0 = -0.588 \times 3 \times 23{,}070 = 40{,}600 \text{ cal.}$$

$$MnO_4^- + e \rightleftharpoons MnO_4^{=}$$

$$\Delta F_2^0 = -0.564 \times 1 \times 23{,}070 = 13{,}000 \text{ cal.}$$

$$MnO_4^{=} + 2H_2O + 3e \rightleftharpoons MnO_2(s) + 4OH^-$$

$$\Delta F_3^0 = -0.600 \times 2 \times 23{,}070 = 27{,}600 \text{ cal.}$$

Summary

The oxidation potential of the alkaline permanganate–manganese dioxide electrode has been determined and the oxidation potentials of related electrodes and the free energies have been calculated.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Specific Conductance of Some Dilute Solutions at 0 and 25°

BY CLYDE R. JOHNSON AND GEORGE A. HULETT

In searching for some easily and accurately reproducible systems for use in calibrating conductance cells in the dilute solution range, we have studied the properties of some difficultly soluble salts and measured the conductance of various dilute solutions.

Apparatus and Materials

Electrical Equipment.—Resistances were measured by the alternating current method. A Type A Vreeland oscillator furnished the current. All final measurements were made at a frequency of 1040 cycles per second, with the output adjusted to give a sharp minimum without heating effects. The bridge assembly comprised a Kohlrausch drum-wound slide-wire, a 6-dial 99,999.9-ohm resistance box, tunable telephones, and air condensers for balancing out capacity effects. The resistances were calibrated by the substitution method of Parker and Parker,[1] and were referred to the International ohm through resistances evaluated at the U. S. Bureau of Standards and the Reichsanstalt. The two d. c. calibrations (polarity reversed) agreed perfectly, and checked the three somewhat less precise a. c. calibrations to better than: (a) 0.01% between 100 and 10,000 ohms and (b) 0.1% over the entire range. The Kohlrausch wire was accurately calibrated between the ratios 1.00429 and 0.99625 and used only within this range.

Conductance Cells and Accessories.—The five cells were made of Pyrex glass, in the general form illustrated in Fig. 1. The roughened, unplatinized platinum electrodes were introduced by the device shown in the same figure. In making the cells the sequence of operations was such that all tungsten parts of the electrodes uncovered by glass were covered with platinum, which was burnt

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[1] Parker and Parker, THIS JOURNAL, **46**, 312 (1924).