arrangement in build is believed to favor practically complete removal of sorbed vapors at extremely low partial pressures while random arrangement may lead to conditions which result in retention.

4. The heats of the several sorption processes have been calculated from the free energy changes, and their temperature coefficients.

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The Potential of the Silver-Silver Iodate Electrode at 25°

BY J. N. PEARCE AND VERDA I. WIRTH

Any slightly soluble salt of a metal may form, potentially, a good electrode, provided the electrode is perfectly reversible and the metallic salt is stable in solution. The present paper gives briefly the results obtained from a study of the silver-silver iodate electrode.

Materials and Apparatus.—The silver crystals used in the preparation of the electrodes were formed by the electrolysis of a hot, concentrated solution of pure silver nitrate, using a platinum wire cathode and a pure silver anode, surrounded by a porous cup. A current of five to ten amperes gave uniform, well-defined crystals which were free from amorphous silver.

Silver iodate was prepared by adding a dilute solution of pure silver nitrate slowly and with rapid stirring to a large volume of a dilute solution of potassium iodate. The precipitate was washed free from excess salts and dissolved in a pure concentrated solution of ammonium hydroxide. The ammonia was allowed to evaporate spontaneously, leaving the iodate in the form of fine white crystals.[1] These were washed thoroughly and stored under conductivity water until used.

All other chemicals were carefully purified by approved methods. All solutions were made on the weight molal basis in conductivity water.

The experimental data recorded in the following tables are the mean potential values obtained from three to five cells, each containing three to five individual electrodes. While the calomel electrodes attained equilibrium quickly, the iodate electrodes required four or five days. The deviations of the potentials of the different electrodes in any single iodate half-cell did not exceed 0.05 mv., and the mean deviation of duplicate half-cells containing potassium iodate did not in any case exceed 0.2 mv.

The determination of the potentials of the iodate electrodes involved the measurement of electromotive forces of cells, with ion transference, of the type: Hg, Hg_2Cl_2, KCl (0.1 *m*), KIO_3 (0.1 *m*), $AgIO_3$, Ag. The half-cells were connected by a modified form of the Lamb and Larson[2] flowing junction device. The liquid junction potentials were calculated by means of the relation used by Lewis and Sargent,[3] namely

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(1) Greensfelder and Latimer, THIS JOURNAL, **53**, 3813 (1931).

(2) Lamb and Larson, *ibid.*, **42**, 239 (1920).

(3) Lewis and Sargent, *ibid.*, **31**, 363 (1909).

$$E_l = RT/nF \ln \lambda_1/\lambda_2$$

where λ_1 and λ_2 are the equivalent conductances of the chloride and iodate solutions at the same concentrations, respectively. This potential must be added to the potential of the cell with ion transference, E_t, to give the potential of the cell, E, without ion transference. Since data on the conductance of potassium iodate solutions[4] at 18° only are available, we have made the assumption that the ratio of the equivalent conductances of the two salt solutions is the same at 25° as at 18°. The validity of this assumption was affirmed by comparing the ratios of the conductances of potassium chloride solutions with those of potassium chlorate and bromate at the same two temperatures. The potential data thus obtained are collected in Table I. The solutions in all cells were under an atmosphere of pure nitrogen.

TABLE I

THE ELECTROMOTIVE FORCES OF CALOMEL–IODATE CELLS AT 25 ± 0.02°

m	0.20	0.10	0.05	0.01
E_t, volt	.0850	.0833	.0825	.0810
E_l, volt	.0096	.0087	.0082	.0075
E_{298}, volt	.0946	.0920	.0907	.0885

To calculate the potentials of the iodate electrodes in the given potassium iodate solutions it is only necessary to add the potentials of the calomel electrodes in the same concentrations of potassium chloride. The latter were calculated by means of the equation: $E = E^\circ - 0.05915 \log a_{\mathrm{Cl}^-}$, using for the potential of the electrode, Hg, Hg_2Cl_2, $Cl^-(a = 1)$, $E^\circ = 0.2676$ volt,[5] and the activity coefficients as obtained by Harned[6] for potassium chloride. The potentials of the calomel electrodes thus calculated are given in Table II. By adding these potentials to the total potentials, E_{298}, of the calomel–iodate cells, Table I, we obtain directly the potentials of the electrode: Ag,$AgIO_3$,$KIO_3(m)$, in the various concentrations of potassium iodate. These electrode potentials are given in the fifth column of Table II.

TABLE II

THE POTENTIALS OF THE CALOMEL AND SILVER IODATE ELECTRODES AT 25°

m	γ^6 KCl	γ^8 KIO_3	E_{298} Calomel	E_{298} Iodate	E°_{298} Iodate
0.20	0.712	...	0.3178	0.4124	...
.10	.764	0.692	.3336	.4256	0.3571
.05	.815	.765	.3498	.4405	.3567
.01	.899	.882	.3886	.4771	.3552

Two methods are available for calculating E° for the silver–silver iodate electrode. The potential E° is given by the equation

$$E = E^\circ - 0.05915 \log a_{\mathrm{IO}_3^-} \qquad (1)$$

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(4) "International Critical Tables," 1929, Vol. VI, pp. 234 and 252.

(5) *Ibid.*, 1929, Vol. VI, p. 332.

(6) Harned, THIS JOURNAL, **51**, 416 (1929).

Subtracting 0.05915 log $m_{IO_3^-}$ from both sides of (1), we obtain a modified form of a relation employed by Lewis and Randall[7]

$$0.05915 \log (a/m)_{IO_3^-} = E^\circ - (E + 0.05915 \log m_{IO_3^-})$$

The log a/m is equal to zero at infinite dilution and hence $E^\circ = (E + 0.05915 \log m_{IO_3^-})$. If we plot the quantity in parentheses against the square root of the molality, the intercept on the ordinate at $m = 0$ is equal to E°.

Since extrapolation is precarious in any case, and because of possible errors in determining the potential of the most dilute solution, which was the most difficult to obtain, we have calculated the potential, E°_{298}, by (1), using accepted values[8] for the activity coefficients of potassium iodate. The values of E°, which should be the same at all concentrations, are given in the last column of Table II. It is evident that the potential of the 0.01 m electrode is too low. Omitting this, we take as the most probable value of the potential of the Ag, $AgIO_3$, IO_3^-, ($a = 1$) electrode, $E^\circ_{298} = 0.3569$ volt.

Summary

The electromotive forces of a series of cells of the type: Hg,Hg_2Cl_2,KCl-(m),KIO_3,$AgIO_3$,Ag, have been measured at 25°. By combining these values with the potentials of the corresponding calomel electrodes, the potential of the Ag,$AgIO_3$,IO^- ($a = 1$) electrode is found to be, $E^\circ_{298} = 0.3569$ volt.

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(7) Lewis and Randall, "Thermodynamics," 1923, p. 334.

(8) Lewis and Randall, *ibid.*, p. 362.

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The Optical Properties of the Double Salt $(NH_4)_2SO_4 \cdot CaSO_4 \cdot 2H_2O$

BY ALBERT R. MERZ, JOHN O. HARDESTY AND STERLING B. HENDRICKS

During the course of an investigation of the hygroscopicities of mixtures of fertilizer salts not having common ions,[1] one of the solid phases obtained in the systems, $NH_4^+Ca^{++}NO_3^-SO_4^=$ and $NH_4^+Ca^{++}H_2PO_4^-SO_4^=$, was found to be a double salt of calcium and ammonium sulfates. Three double salts, in which the ratios of ammonium sulfate to calcium sulfate are 1:1, 1:2 and 1:5, respectively, have been reported in the literature. The double salt with the ratio 1:2 does not exist below 75°[2] and, as the vapor pressure measurements were carried out at 30°, it therefore remained to identify the salt as one of the other two compounds. Since the double salt with the ratio, 1:5, cannot exist, in the system $NH_4^+Ca^{++}SO_4^=$, in contact with solid ammonium sulfate,[2] gypsum was added to a saturated solution of ammonium sulfate which was then evaporated until considerable ammonium sulfate had crystallized and finally allowed to stand for several days. Microscopic examination of the solid phases disclosed both am-

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(1) A. R. Merz, W. H. Fry, J. O. Hardesty and J. R. Adams, *Ind. Eng. Chem.*, **25**, 136 (1933).

(2) J. D'Ans and O. Schreiner, *Z. anorg. Chem.*, **62**, 141 (1909).