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

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

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

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

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

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

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

LINCOLN, NEBRASKA RECEIVED OCTOBER 10, 1934

[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).

into the tungsten in the manner described by Hibben.[2] All of the cells were thoroughly steamed, washed and aged before calibration.

The cells were calibrated with solutions made by adding accurately weighed amounts of sodium or potassium chloride to weighed amounts of water of known specific conductance. All weighings were reduced to vacuum in the usual manner. The calibrated weights were referred to a set of Class M weights evaluated at the Bureau of Standards. Concentrations were reckoned in millimoles per liter of solution at 25°, using "I. C. T." data.

The cell calibrations were also checked by intercomparing the various cells over wide ranges of resistance at 0 and 25°, at three frequencies. Over large portions of the ranges studied the cell ratios were independent of temperature and frequency. The calibrations and intercomparisons extended systematically throughout the entire series of measurements, and showed that the cell constants did not change during this time.

Empirical corrections totalling about 0.02 ohm compensated for the electrodes and the wires connecting the cell into the bridge.

Thermostats.—During measurements the cells were sufficiently immersed in a twenty-gallon kerosine bath, kept at 25.000 ± 0.002°. The two thermometers used in the bath were compared with two other thermometers calibrated to 0.001°, at different times, at the Bureau of Standards. Measurements at 0° were made with the cells in a thermostat similar to that described by Parker and Parker.[1]

Reagents.—Sodium chloride and potassium chloride were crystallized seven and fifteen times, respectively, and fused in platinum in a current of dry nitrogen.

Minerals were broken up in a mortar and the clear crystals selected under a magnifying glass.

Lead, silver, magnesium, calcium, strontium and thallous nitrates; strontium and thallic chlorides; cadmium sulfate; and potassium fluoride, bromide, iodide, selenate, chromate and oxalate were prepared by two crystallizations of ordinary C. P. material, with centrifugal draining and rejection of head and tail fractions. Ten- to fifty-gram quantities of the difficultly soluble salts were synthesized from these reagents by double decomposition. In general, two equivalent dilute solutions of the reagents were added simultaneously, drop by drop, to a 200- to 500-cc. volume of water, rapidly stirred in a quartz dish at about 80°.

Strontium sulfate No. 1 was prepared from strontium nitrate; strontium sulfate No. 2 from the chloride. Thallous chloride was prepared by passing sulfur dioxide into a dilute solution of thallic chloride and separating the white fraction by crystallization from water. The thallous dichromate preparation differed from the chromate preparation only in that a small amount of nitric acid was present during the precipitation. Thallium and silver salts were protected from light.

After digestion and cooling the precipitates were washed to remove most of the mother liquor, and then washed with twenty to thirty 500-cc. portions of water over periods varying from one to twenty months. In addition, following the above treatment each strontium sulfate sample was dried, heated at 800°, thoroughly washed and finally subjected to five four-hour extractions with 700-cc. portions of boiling water stirred by a current of purified air.

SPECIFIC CONDUCTANCE OF $SrSO_4$ EXTRACTS AT 25° ($\times 10^6$)

Extract no.	1	2	3	4	5
$SrSO_4$ no. 1	114	125	106	119	114
$SrSO_4$ no. 2	146	146	120	140	148

Water.—Water was prepared by distilling 3-liter quantities of the ordinary distilled water of the laboratory without addition of reagents. Head and tail fractions were rejected and the middle fraction was condensed in block tin condensers and stored in platinum or quartz vessels.

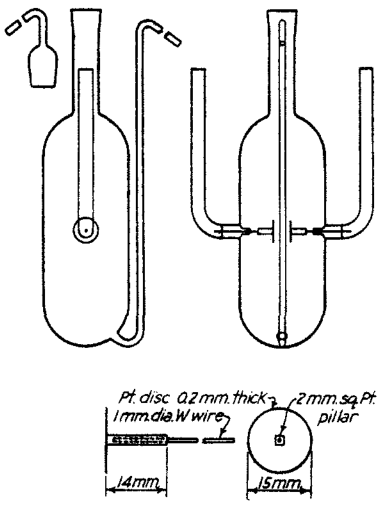

Fig. 1.—Typical cell and detail of electrodes.

Nitrogen.—Commercial tank nitrogen was passed in succession through Pyrex glass towers of beads containing concentrated sulfuric acid, 1:1 sodium hydroxide, and water; and finally rinsed in two 2-liter flasks half full of water.

When a slow current of this nitrogen was passed through the water its conductivity reached a minimum after a few hours, and then very slowly increased. Below are summarized some typical results obtained when nitrogen was passed through water samples continuously for several days. These results offer excellent qualitative and quantitative evidence regarding the purity of the water and nitrogen, the rate of solution of the Pyrex cells, and the precision of the experimental method.

Cell volume, cc.	Specific conductance of water $\times 10^6$ Minimum	Final	Time, hours
75	0.218	0.246	47
75	.136	.155	48
75	.266	.402	148
300	.218	.255	58
300	.236	.249	82
300	.242	.265	312

Experimental Method

For each measurement a 5- to 25-g. quantity of the difficultly soluble salt was placed in the bottom of a cell and washed with several portions of water;

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(2) Hibben, THIS JOURNAL, 50, 1118 (1928).

the cell was finally filled about nine-tenths full of water. Water from the same source was placed in a rinsed water-cell and the two cells were immersed in the bath and joined "in series," so that nitrogen could be bubbled first through the water-cell, then through the salt-cell, and allowed to escape into the air. In most cases the cells were filled at night and a slow current of nitrogen was started at once. On the following morning the temperature was adjusted to 25.000° and conductance measurements were made, with the nitrogen still passing, until the readings became constant or indicated that a sufficiently accurate extrapolation to zero change of conductance per minute could be made. The water in both cells was then changed and the experiment was repeated.

The data obtained in the experiments are summarized in Tables I and II.

TABLE I

SPECIFIC CONDUCTANCE OF SATURATED SOLUTIONS AT 25°

Solution	Spec. cond. $\times 10^6$ of Water κ_W	Solute (κ_S)	Solution	Spec. cond. $\times 10^6$ of Water (κ_W)	Solute (κ_S)
$PbBr_2$[a]	0.17	2405	SrF_2	0.22	224.0
Gypsum	.23	2210[b]		.18	224.8
	.22	2201	$SrSO_4$-2	.25	152.7
	.24	2189		.26	152.6
	.21	2182	$SrSO_4$-1	.3	147.3
$TlCl$[a]	.17	2159[b]		..	148
	.18	2156	CaF_2	.182	45.14[b]
Ag_2SeO_4	.135	596.04		.185	45.02
	.20	595.91		.219	45.00
	.15	595.96[b]	Aragonite	.47	39.2
PbF_2	.165	505.48		.50	39.3
	.440	505.50[b]	TlI	.165	36.62
MgF_2	.30	439.5		.440	36.59
	.32	439.7	$CdC_2O_4 \cdot 3H_2O$	.188	36.02
PbI_2-1	.25	433.3[b]		.217	36.07[b]
	.18	433.0		.291	35.90[b]
PbI_2-2[a]	.220	433.06	$Tl_2Cr_2O_7$	.209	35.21
	.224	433.01		.174	35.16
$TlBr$-1	.21	295.3[b]		.275	35.27[b]
	.179	295.20	Tl_2CrO_4	.173	20.27
$TlBr$-2[a]	.220	295.18		.176	20.08[b]
	.224	295.29		.135	20.06[b]
SrF_2	.13	223.7			

[a] Recrystallized from water. [b] Approached from supersaturated side.

TABLE II

SPECIFIC CONDUCTANCE OF SOLUTIONS AT 0 AND 25°

Solution	Millimoles / liter at 25°	Spec. cond. $\times 10^6$ (25°) Water (κ_W)	Solute (κ_S)	Spec. cond. $\times 10^6$ (0°) Water (κ_W)	Solute (κ_S)
KCl	19.967	0.20	2763		
KCl	9.982	.21	1410.1		
$NaCl$	10.005	.82	1185.1	0.39	634.0
KCl	5.004	.63	720.3	.28	393.4
$NaCl$	4.941	.83	598.1	.44	318.3
KCl	2.0013	.81	292.57	.43	160.1
$NaCl$	2.0029	.67	246.20	.36	131.0
KCl	1.0026	.690	147.69	.37	80.9
$NaCl$	1.0042	.691	124.59	.335	66.27
KCl	0.8010	.322	118.01		
KCl	.5796	.95	85.65	.47	46.9
$NaCl$	.6772	1.11	84.15	.56	44.8
KCl	.4005	0.331	59.33		
$NaCl$	.3159	.69	39.60	.35	21.04
KCl	.2372	1.16	35.24	.58	19.25

Discussion of Results

The results show that there is ample room for working out a practical method for calibrating conductance cells with saturated solutions of slightly soluble electrolytes. A number of the compounds studied, including the thallium salts, lead salts, silver selenate, and (possibly) cadmium oxalate, approach saturation equilibrium rapidly (hours) and form highly reproducible and constant conducting systems. These compounds can be prepared in the form of coarse particles or well-defined crystals and most of them can easily be recrystallized.

Others of the salts have properties which make it difficult or inconvenient to reproduce their saturated solutions accurately. Strontium sulfate, for example, exhibits a variable composition depending on the environment and conditions of precipitation, and even finely divided samples of the salt approach equilibrium very slowly (days). Similar statements apply to the alkaline-earth fluorides.

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Summary

Measurements of the conductance of various dilute solutions have been made at 0 and 25°. The results indicate that useful and convenient methods may be devised for calibrating conductance cells with saturated solutions of difficultly soluble salts.

PRINCETON, N. J. RECEIVED OCTOBER 16, 1934