chloride per 100 parts of water and per 100 parts of hydrochloric acid, respectively.

The following melting points were found for the salts.

$MCl_3.6H_2O$	Nd	Sa	Y	Yb
M. p., °C.	124	142–142.5	161–163	153–155

Summary

The solubilities of the hexahydrated trichlorides of yttrium, samarium and neodymium in water and in hydrochloric acid (d., 1.1051), and that of ytterbium in the latter solvent have been determined.

This work is being continued with other salts and solvents.

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[Contribution from the Wm. H. Chandler Chemical Laboratory of Lehigh University]

THE PREPARATION OF ELECTROLYTIC MERCUROUS CHLORIDE IN SATURATED POTASSIUM CHLORIDE FOR USE IN THE CALOMEL ELECTRODE

By Warren W. Ewing

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The use of single electrode potentials is becoming more and more important. This is especially true of the use of the hydrogen electrode potential in acidimetric titrations and in determinations of the hydrogen-ion concentration, as well as of the use of oxidation-reduction potentials in various electrometric determinations. The measurement of single electrode potentials involves the use of some standard half-cell of known potential. The calomel electrode in 0.1 *N*, in 1 *N* and in saturated potassium chloride solutions are the standard half-cells generally used. This article offers an electrolytic method of preparing calomel directly in a saturated potassium chloride solution. It eliminates the preparation of pure hydrochloric and nitric acids and the tedious washing and shaking processes involved in the other methods. It offers a reliable and dependable standard which is comparatively easy to prepare.

Preparation of Calomel

The calomel used in the electrodes described in this article was made electrolytically and directly in saturated potassium chloride solutions employing the apparatus shown in the figure.

A and B were battery jars 10 cm. in diameter. They were connected by means of salt bridges E 1 cm. in diameter. The ends of the bridges were covered with collodion membranes G which were made in the following manner. The ends were first covered with strong filter paper which was held in place by means of rubber bands. They were then dipped in a 4% collodion solution in a mixture of alcohol and ether. After a few seconds they were dipped again and the collodion was allowed to dry evenly. When it was dry enough to touch with the finger they were placed in a beaker of water and the solvents allowed to dissolve out. These bridges were filled, at F, with approximately *N* potassium chloride solution and sealed by means of glass plugs H. Generally two bridges were used in parallel in order to lessen the resistance, since otherwise the bridges became too hot before the run was finished. Larger tubes could of course be used. The stirrer was adjusted so that it scraped the surface of the mercury thus pushing aside the calomel as fast as it was formed, and keeping down the resistance. It was driven at the rate of 120 r.p.m. The current density used, 1.3 amperes per sq. dm., required 35 to 40 volts. Each run lasted from 20 to 30 minutes. Enough calomel was formed in this time to fill a half dozen electrodes. The surface of the mercury was covered with a layer of crystals of potassium chloride. These crystals were mixed with the calomel and finely divided mercury formed and together with the saturated potassium chloride solution used as the electrolyte, were used for filling the electrodes.

In a large number of runs no trace of copper was ever found in the saturated potassium chloride solutions. The diffusion of the cupric ion from the cathode to the anode compartment was prevented by the difference in levels of the solutions (see Fig. 1), the difference in densities and the direction of migration of the ions. Various types of membranes, such as gelatin and undried silica gel, were tried but of these the collodion membrane proved to be the only practical one. Hydrochloric acid and potassium chloride solutions were tried as electrolytes for the cathode compartment using platinum or mercury cathodes. Hydrochloric acid diffused somewhat into the bridge and the heat of conductance caused it to volatilize, forcing the electrolyte out of the bridge. The high migration velocity of hydroxyl ion and the solvent action of potassium hydroxide on collodion make the use of potassium chloride impractical. The low deposition potential of copper, the density of the saturated cupric chloride solution, and the plating out of the copper without the formation of objectionable compounds, make a saturated cupric chloride solution available.

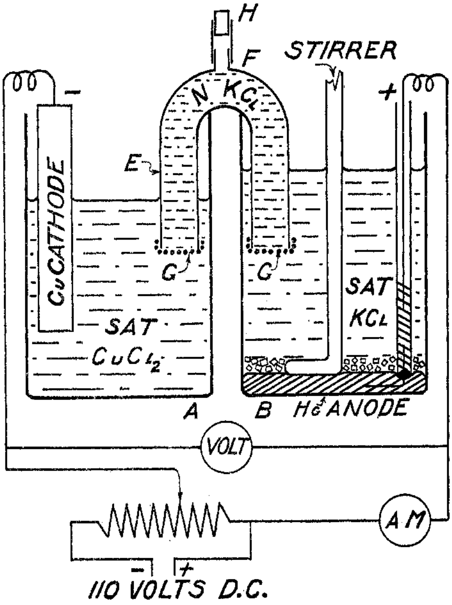

Fig. 1.

The *mercury* used was purified by spraying it through a 1.8-meter tower of 10% nitric acid several times and then distilling twice in a vacuum.

The *potassium chloride* was twice recrystallized from a C. P. material.

The *calomel* for the standard reference electrodes was made electrolytically as described by Hulett and Lipscomb.[1]

The electrodes were prepared by placing mercury in the *carefully dried* cell. Above this was placed the electrolytic calomel containing finely divided mercury and crystals of potassium chloride. More crystals of potassium chloride and the saturated potassium chloride solution were then added. The cells were kept for 48 hours at a constant temperature, within ± 0.02°, until equilibrium was reached, although the change was negligible after four hours. The potentials of these electrodes were measured against *N* calomel electrodes which were made at different times by electrolysis in hydrochloric acid. A beaker containing saturated potassium chloride solution was used as a bridge between the two solutions. A grounded equipotential shield was used.

Reproducibility of Electrodes

The experimental data were obtained by measuring the e.m.f. of cells of the following type: Hg + *HgCl*, HgCl in satd. KCl, HgCl in *N* KCl, *HgCl* + Hg. Table I gives the results obtained. Normal electrode No. 3 was made from electrolytic calomel, the hydrochloric acid being washed out with absolute alcohol and the alcohol being in turn washed out with *N* potassium chloride solution. Normal electrode No. 10 was made from another batch of electrolytic calomel in a similar manner except that the acid was washed out with water. Other normal electrodes were made

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Hg + *HgCl*, HgCl in satd. KCl, HgCl in *N* KCl, *HgCl* + Hg

	Against normal electrode No. 3			Against normal electrode No. 10		
Saturated electrode number	E.m.f. in volts	Period of observation Days	No. of readings	E.m.f. in volts	Period of observation Days	No. of readings
4a	0.03885 ± 0.00010	14	5			
4b	.03883 ± .00005	21	5	0.03877 ± 0.00005	10	5
4c	.03883 ± .00007	2	4			
6a	.03888 ± .00000	10	1			
6b	.03889 ± .00010	33	12	.03881 ± .00012	26	9
6c	.03894 ± .00000	1	1			
7a	.03888 ± .00000	1	1			
7b	.03889 ± .00000	1	1			
7c	.03885 ± .00010	20	9	.03881 ± .00007	11	7
8a	.03888 ± .00010	42	15	.03885 ± .00010	28	10
8b	.03888 ± .00000	2	2			
8c	.03889 ± .00001	2	2			
12	.03888 ± .00003	8	5	.03884 ± .00005	8	4
13	.03873 ± .00006	7	4	.03863 ± .00004	7	4
	Av., 0.03886 volts.			Av., 0.03879 volts.		

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[1] Hulett and Lipscomb, THIS JOURNAL, **38,** 22 (1916).

from time to time in order to check any change in the two standards. However, they remained constant throughout the period of this work.

The numeral in Col. 1 refers to the batch of calomel, the letter to the individual electrodes. Batch 4 was the same electrolytic calomel employed in making normal electrode No. 3 except that in this case the alcohol was washed out with saturated potassium chloride solution. The other batches of calomel were all made by the new method described in this article. In general the electrodes containing a given batch of calomel were prepared on different days. For example, Electrodes 4b and 4c were made three weeks after 4a was prepared, 4a having been broken at that time. A few individual saturated electrodes are not recorded, the results being obviously wrong. This usually was due to carelessness in cleaning and filling the cell. On emptying, cleaning and refilling the cell, accurate results were obtained. All batches of saturated potassium chloride calomel are recorded except No. 11, which gave abnormally low results (0.03845 volts) for some unexplained reason. Various readings on the same day are grouped as one reading.

(i)	Hg + *HgCl*,	HgCl in satd. KCl,		HgCl in *N* KCl, *HgCl* + Hg
(ii)			KCl (0.1 *M*),	HgCl in *N* KCl, *HgCl* + Hg
(iii)			KCl (0.1 *M*),	HgCl in *N* KCl
(iv)				HgCl in *N* KCl, *HgCl* + Hg
(v)		HgCl in satd. KCl,		HgCl in *N* KCl
(vi)	Hg + *HgCl*,	HgCl in satd. KCl		

The average of all these results gives as the e.m.f. of Cell i, 0.0388 volts at 25°. Fales and Mudge[2] find 0.0387 volt for this cell. Lewis, Brighton and Sebastian[3] give as the electrode potential of Combination ii, 0.2828 volt at 25°. This is referred to the normal hydrogen electrode, taking its value as zero. They call this combination the "normal calomel electrode." Fales and Vosburgh[4] give as the contact potential of Combination iii —0.0004 volt at 25°. Combining (ii) and (iii) gives as the electrode potential of (iv), 0.2832 volt. Fales and Mudge give as the contact potential of (v), 0.0002 volt at 25°. Combining (i), (iv) and (v) gives as the electrode potential of (vi) —0.2446 volt at 25°. This is the electrode potential of the saturated potassium chloride calomel electrode referred to the normal hydrogen electrode as zero. The negative sign before the voltage means that when the cell is producing electricity the positive current passes through the cell as written from right to left.

The temperature coefficient of our saturated potassium chloride calomel electrodes was determined by keeping the temperature of five of these electrodes constant at 30° and again at 20° for 48 hours and measuring

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[2] Fales and Mudge, This Journal, **42,** 2434 (1920).

[3] Lewis, Brighton and Sebastian, *ibid.*, **39,** 2245 (1917).

[4] Fales and Vosburgh, *ibid.*, **40,** 1291 (1918).

them against the normal calomel electrodes 3 and 10, which were kept at 25°. The electrodes were connected by means of a glass-tube salt-bridge 30 cm. long and 7 mm. in diameter having cotton plugs in the ends and filled with saturated potassium chloride solution. The average e.m.f. of these cells was 0.0377 volt at 30°, 0.0388 volt at 25° and 0.0398 volt at 20°. This gives as the electrode potential of these saturated calomel electrodes on the hydrogen scale —0.2457 volt at 30°, —0.2446 volt at 25°, and —0.2436 volt at 20°. This gives a temperature coefficient of 0.0002 volt per degree. Fales and Mudge obtained the same value.

Summary

A method of making electrolytic mercurous chloride directly in saturated potassium chloride is outlined.

The advantages of the method are that it gives a dependable quality of calomel mixed with finely divided mercury and it avoids tedious washing and shaking processes and the resultant uncertainties.

The e.m.f. of the cell, Hg + *HgCl*, HgCl in satd. KCl, HgCl in N KCl, *HgCl* + Hg is 0.0388 volt at 25°.

The electrode potential of the saturated potassium chloride calomel half-cell is —0.2446 volt at 25° on the hydrogen scale.

The temperature coefficient of the saturated potassium chloride calomel half-cell is 0.0002 volt per degree for the temperature range 20° to 30°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 161]

EQUILIBRIUM PRESSURES OF INDIVIDUAL GASES IN MIXTURES AND THE MASS-ACTION LAW FOR GASES

BY LOUIS J. GILLESPIE

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To a surprising degree the ordinary mass-action law, based on the properties of ideal gases, suffices for the treatment of measured gas equilibria. However, the recent work of Larson and Dodge[1] on the Haber equilibrium at high pressures has shown an important deviation from the consequences of the ideal-gas laws, namely, that the equilibrium constant, K_p, at any temperature is found to be a function of the pressure. In the absence of data to the contrary, we must now believe that K_p will vary if the concentrations are varied at constant temperature and pressure —in other words, that K_p is not strictly constant with respect to any change

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[1] Larson and Dodge, THIS JOURNAL, **45**, 2918 (1923); also a later paper by Larson, *ibid.*, **46**, 367 (1924).