[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Behavior of the Silver, Silver Chloride and the Mercury, Mercurous Chloride Electrodes at High Temperatures[1]

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In continuing the development of a high temperature reference electrode a series of measurements of the potential of the silver, silver chloride and the mercury, mercurous chloride electrode combination in hydrochloric acid has been made. The temperature was varied from 25 to 263° and the acid concentration from 0.01 to 1.0 *M*. The potentials obtained at given temperatures were compared with those predicted on the basis of thermodynamic calculations for this cell combination. Evidence for hydrolytic decomposition of calomel at low acid concentrations and high temperatures has been found.

Introduction

In previous work[3] the useful range of the silver, silver sulfate and the mercury, mercurous sulfate electrodes was established to 150° in the presence of 0.5 *M* sulfuric acid. For acid systems involving hydrochloric acid information was desired on the behavior of the analogous cell combination involving the chlorides of silver and mercury. Measurements were made up to 263° at hydrochloric acid concentrations of 0.01, 0.1, 0.5 and 1.0 *M*. The measured potentials were compared with those predicted on the basis of thermodynamic calculations.

Theoretical.—When the silver, silver chloride electrode is used in conjunction with the mercury, mercurous chloride electrode the cell reaction is

$$\mathrm{Ag} + {}^1/_2\mathrm{Hg_2Cl_2} \rightleftarrows \mathrm{AgCl} + \mathrm{Hg} \qquad (1)$$

If saturated electrodes are used, the potential for the cell combination, calculated from the ΔF for the reaction, should be +45.5 mv. at 25°. This means that the calomel electrode is 45.5 mv more noble than the silver chloride electrode at 25° and that the cell reaction proceeds according to equation 1. ΔS for the cell reaction at 25° is 7.8 e.u.,[4] hence $\mathrm{d}E/\mathrm{d}T$ (the temperature coefficient of the potential) is 0.34 mv./degree at 25°.

In order to evaluate the potential of the cell combination at higher temperatures it is necessary to derive an equation giving the ΔF of the cell reaction as a function of temperature. This can be done by integrating

$$\left(\frac{\partial \Delta F/T}{\partial T}\right)_{\mathrm{p}} = \frac{-\Delta H}{T^2} \qquad (2)$$

where $\Delta H = \Delta H^\circ + \int \Delta C_{\mathrm{p}}\,\mathrm{d}T$.

The equations giving C_{p} for each substance as a function of temperature are

$$C_{\mathrm{p}}(\mathrm{Ag})^5 = 5.09 + 2.04 \times 10^{-3}T + 0.36 \times 10^5T^{-2}$$

$$C_{\mathrm{p}}(\mathrm{Hg_2Cl_2})^5 = 22.10 + 7.4 \times 10^{-3}T$$

$$C_{\mathrm{p}}(\mathrm{AgCl})^5 = 14.88 + 1 \times 10^{-3}T - 2.7 \times 10^5T^{-2}$$

$$C_{\mathrm{p}}(\mathrm{Hg})^6 = 7.01 - 1.092 \times 10^{-3}T$$

Therefore

$$\Delta C_{\mathrm{p}} = 5.75 - 5.832 \times 10^{-3}T - 3.06 \times 10^5T^{-2}$$

and

$$\Delta H = -1206 + 5.75T - 2.92 \times 10^{-3}T^2 + 3.06 \times 10^5T^{-1} \qquad (3)$$

since ΔH = 1275 cal. at 25°.[7]

When equation 3 is substituted into equation 2 and the integration performed, equation 4 is obtained.

$$\Delta F = -1206 - 13.24T\log T + 2.92 \times 10^{-3}T^2 + 1.53 \times 10^5T^{-1} + 30.7T \qquad (4)$$

since ΔF = −1050 cal. at 25°.[7] Then E may be evaluated at any desired higher temperature since $E = -\Delta F/nF$.

It is possible that at high temperatures and at low concentrations of acid side reactions may occur which would produce potentials substantially different from those predicted by equation 1. Two possible side reactions might be

$$\mathrm{Hg_2Cl_2} \longrightarrow \mathrm{Hg} + \mathrm{HgCl_2} \qquad (5)$$

and

$$2\mathrm{Ag} + \mathrm{HgO} + 2\mathrm{HCl} \rightleftarrows \mathrm{Hg} + 2\mathrm{AgCl} + \mathrm{H_2O} \qquad (6)$$

The extent to which these or other similar side reactions might influence the potential would depend on the specific acid concentration and temperature used. If divalent mercury were present as indicated in equation 5 a maximum potential of 222 mv. would be developed. If the potential were determined by equation 6 a value of 703 mv. would be observed. In the latter case ΔS = 17.2 e.u. at 25°, hence $\mathrm{d}E/\mathrm{d}T$ = 0.37 mv./degree, which is approximately the same as the temperature coefficient of equation 1.

Experimental

The equipment used was essentially as described previously.[3] However, certain modifications were made to facilitate preparation and testing of the cell before its insertion into the steel bomb. Figure 1 is a schematic diagram of the electrode assembly.

The electrode container was made from a 180-ml. Pyrex tall-form beaker by removing the flared rim. It was fitted with a Teflon cover having holes to admit the glass tubes which served as electrode compartments.

The silver, silver chloride electrodes were contained in 10 mm. o.d. glass tubes which were drawn down to capillary size at the lower end and then bent up in the form of a U. The silver, silver chloride electrodes found useful at high temperatures were prepared as follows:

(a) Ag, AgCl Electrode No. 1.—A 30 mm. length of 18 gage platinum wire was flattened at one end to form a ribbon 10 mm. long and 2 mm. wide. The flat section of

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] On leave from Stetson University.

[3] M. H. Lietzke and R. W. Stoughton, THIS JOURNAL, **75**, 5226 (1953).

[4] K. K. Kelley, Bulletin 477, U. S. Department of the Interior, Bur. of Mines, U. S. Gov. Printing Office, Washington, D. C., 1950.

[5] K. K. Kelley, Bulletin 476, U. S. Department of the Interior, Bur. of Mines, U. S. Gov. Printing Office, Washington, D. C., 1949.

[6] Derived from data in T. B. Douglas, A. F. Ball and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **46**, 334 (1951).

[7] R. H. Gerke, THIS JOURNAL, **44**, 1684 (1922).

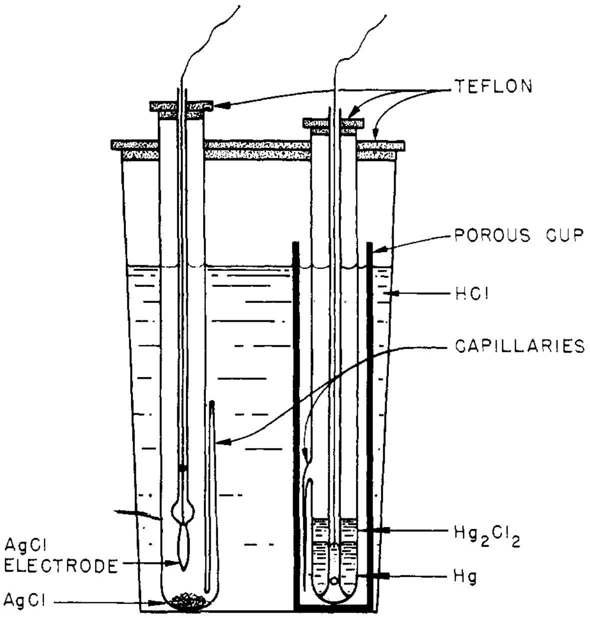

Fig. 1.—Schematic diagram of electrode assembly.

the wire was twisted into a spiral. The wire was then sealed into the end of an 85 mm. length of 3 mm. o.d. soft glass tubing so that only the spiral remained outside. The platinum spiral was then coated with spongy silver by immersing it repeatedly in a thick slurry of silver oxide in distilled water, followed each time by baking in a muffle at 450-500° for 20 minutes. Care was taken to cover all the platinum. After the final baking, which lasted at least one hour, the silver was dipped into a saturated solution of silver chloride in strong ammonium hydroxide solution and replaced in the muffle at 450-500°. Two such silver chloride coatings were generally used. Leads were attached to the platinum in the tube by inserting them along with a small amount of solder and flux and heating the glass tube to melt the solder.

(b) Ag, AgCl Electrode No. 2.—Preparation of the second type of Ag, AgCl electrode differed from the first only in the method for depositing the AgCl on the silver sponge. In this method the silver was dipped into a slurry of AgCl in 1 *M* HCl and heated to 250° in a bomb. Upon cooling AgCl was deposited on the silver in a form that was found to be active and stable for e.m.f. measurements. Since this method was more cumbersome and offered little advantage over the first, it was not extensively used in the present work.

The silver, silver chloride electrodes were inserted into the 10 mm. o.d. glass compartments described above and these were filled with hydrochloric acid solution of the desired concentration. A granule of silver chloride was placed in each electrode compartment to maintain saturation of the solution with respect to silver chloride and minimize removal of silver chloride from the electrode itself at the higher temperature.

The calomel cell container was made of 13 mm. o.d. Pyrex tubing. A tube of smaller diameter was sealed into the cell concentric with the larger tube. The smaller tube was perforated at the bottom so that mercury placed in the cell would come to the same level in both tubes. A thin layer of calomel and mercury paste covered the mercury in the annular region. A small capillary tube attached to the cell just above the paste line provided contact with the main body of solution. The calomel cell was placed in a porous alundum extraction thimble to isolate it from the silver, silver chloride electrodes. This arrangement delayed diffusion of Hg_2Cl_2 to the silver, silver chloride electrode which was apparently sensitive to traces of Hg_2Cl_2. The entire electrode assembly was filled with hydrochloric acid solution of the specified concentration.

As in the previous work electrical connection to the outside of the bomb was made by wires passing through crushable soapstone pressure glands. Since acid fumes from the solution in the bomb tend in time to make the soapstone fittings electrically conducting, a small plug of Teflon was placed immediately below the soapstone to prevent the fumes from diffusing into the packing. Prior to assembly of the bomb the leads passing through the bomb head were hard-soldered to the leads from the silver, silver chloride electrodes or dipped into the mercury in the center tube of the calomel electrode, respectively.

Both the bomb temperature and the cell e.m.f. values were measured with a Rubicon Portable Precision Potentiometer. The e.m.f. values were also measured with a vibrating reed electrometer and recorded on a Brown recording potentiometer so that it was easy to determine when cell equilibrium had been established at each temperature.

Results and Discussion

Figure 2 shows the potentials obtained with the silver, silver chloride electrode measured against the calomel electrode as a function of temperature and acid concentration. The potentials measured in 1 *M* HCl follow the values calculated for the reaction Ag + $^1/_2Hg_2Cl_2$ = AgCl + Hg up to about 240°. As the acid concentration was decreased the potentials became more positive than expected at the higher temperatures. Even in 1*M* HCl above 240° the observed potentials were more positive than those calculated.

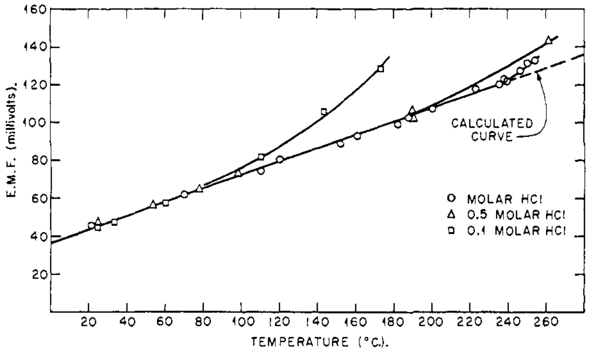

Fig. 2.—Potential of the Ag, AgCl and Hg, Hg_2Cl_2 electrode system as a function of temperature and acid concentration.

According to Mellor[8] calomel disproportionates slowly even at room temperature in contact with water as shown by equation 7

$$Hg_2Cl_2 \rightleftarrows Hg + HgCl_2 \qquad (7)$$

$HgCl_2$ hydrolyzes at room temperature to give an acid solution. At 80° in a sealed tube $HgCl_2 \cdot 3HgO$ is formed, while at 150° $HgCl_2 \cdot 4HgO$ is formed. Complete hydrolysis would give HgO and the electrode reaction would in the limit be given by equation 6. This reaction would give a potential of 703 mv. at 25° and a potential of 780 mv. at 250°. Hence the deviations in potential observed in the present work are consistent with a mechanism assuming hydrolysis at the higher temperatures and lower acid concentrations.

To check on the hydrolysis of Hg_2Cl_2 at high temperature and low acid concentration a small quantity of Hg_2Cl_2 and 0.01 *M* HCl was heated in a glass tube to 250°. After a short time the particles of Hg_2Cl_2 were coated with a layer of reddish-brown oxide. It is probable that as the temperature is raised the reaction given by equation 6 is

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[8] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., London, 1952.

TABLE I

TYPICAL POTENTIALS OBTAINED WITH THE Ag, AgCl AND THE Hg, Hg_2Cl_2 ELECTRODE SYSTEM AS A FUNCTION OF TEMPERATURE AND HCl CONCENTRATION

1 *M* HCl		0.5 *M* HCl		0.1 *M* HCl	
Temp., °C.	Pot., mv.	Temp., °C.	Pot., mv.	Temp., °C.	Pot., mv.
25	46	25	46	25	46
50	55	54	56	60	57
87	68	78	65	110	82
110	75	98	73	135	92
154	89	142	88	143	106
166	95	153	92	173	128
200	107	190	104		
235	120	263	143		
247	128				
254	133				

approached as a limit after perhaps several stages of basic salt formation.

The life of the electrode pair was comparatively short at temperatures above 200°. Of the two electrodes the calomel apparently deteriorated the more rapidly. This was due in part to loss of mercury and calomel from the cell compartment.

The electrode pair was also briefly studied in 1 *M* KCl solution and 0.01 *M* HCl. In 1 *M* KCl the electrodes showed the expected potential at 25° but became very erratic at temperatures above 70°. In 0.01 *M* HCl the electrode pair showed very erratic behavior. In two experiments no consistent potentials were obtained, even at 25°, and further work below 0.1 *M* HCl was postponed.

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The Beryllium–Citrate System. II. Ion-exchange Studies[1]

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Ion-exchange studies have been performed on mixtures composed of radiotracer concentrations of beryllium isotope, Be^7, in excess citrate at various *p*H's, 34° and $\mu = 0.15$ The results in the *p*H range 3-4 are explainable on the basis of the existence of three complexes, BeH_2Cit^+, $BeHCit^0$ and $BeCit^-$, the respective instability constants being 4×10^{-2}, 6×10^{-3} and 3×10^{-5}. The results above *p*H 4 suggest that polynuclear complexes begin to form above this *p*H. In slightly alkaline solution there exists a complex having a charge more negative than −1.

In this paper we have applied to the beryllium-citrate system the ion-exchange method originated by Schubert[2] for the study of complex ions and, of necessity, have elaborated upon the scope of the applicability of this technique.

Experimental

Materials.—The beryllium isotope, Be^7, was obtained from the Oak Ridge National Laboratory and was purified by the method of Toribara and Chen.[3]

The cation-exchange resin, Dowex 50, ammonium form, 40-60 mesh, was a preparation previously described.[4] Some of this resin was converted to the hydrogen form by shaking six times (1 to 4 hours each time) with 5 *M* HCl, washing with distilled water, and air-drying. The Dowex 1 resin, chloride form, was prepared by shaking a batch of the hydroxide form six times with 1 *M* HCl, washing with water and air-drying.

All other chemicals were C.P. grade.

Procedure.—Except for the experiments at *p*H 1.0 (see Table I), 28.0 ml. of each solution was prepared by mixing the indicated quantities (see Tables I and II) of beryllium isotope, citric acid and 5 ml. of 0.75 *M* NH_4ClO_4, diluting to *ca.* 25 ml. with water, adjusting to the indicated *p*H with a measured volume of 0.25 *M* NH_4OH, dissolving the amount of solid ammonium perchlorate calculated to give the desired ionic strength, μ, and then diluting to 28.0 ml. with water. A Beckman Model G *p*H meter was employed for the *p*H adjustments. A 20-ml. volume of each solution was added to the indicated amount of resin in a 50-ml. glass-stoppered erlenmeyer flask. The unused portion of each solution was used as a standard in the final counting procedure. Each stopper was sealed with paraffin and then wrapped tightly with parafilm. The flasks were shaken for three hours on a Boerner oscillating platform shaker in a constant-temperature room maintained at 34°. After being shaken, the solutions were decanted from the resin, and the *p*H's and relative beryllium concentrations were determined. The results of typical experiments were the same after overnight shaking, indicating that the three-hour shaking-time was sufficient to bring about equilibrium. The relative beryllium concentrations were determined by γ-ray counting as previously described.[4]

TABLE I

INVESTIGATION OF SIGN OF CHARGE ON BERYLLIUM–CITRATE COMPLEX AT 34°

		% of original Be left in aqueous phase after equilibration with			
		Cation-exchange resin[a]		Anion-exchange resin,[b] %	
*p*H	Total citrate, moles/l.	G. of resin	%		No resin, %
1.0	0	0.12	10	..	.....
1.0	0.10	.12	10	..	.....
3.0	0	.070	42	100	.....
3.0	.078	.070	61	100	.....
4.0	0	.20	20	100	.....
4.0	.012	.20	43	100	.....
4.6	0	.60	8	100	.....
4.6	.0089	.60	60	100	.....
7.0	0	.07	11	9	60[c], 19[d]
7.0	.01	3.0	98	89	100[d]
7.5	.07	0.14	99	12	100[d]
7.5	.0001	.8	96	..	95[d]
7.5	0-.0001	.8	(95 but not reproducible)		

[a] At *p*H 1.0; $\mu = 0.10$, hydrogen form of Dowex 50 resin used. At all other *p*H's: $\mu = 0.15$, ammonium form of Dowex 50 used. [b] 0.5 gram of Dowex 1, chloride form, used for each experiment. [c] Solution not centrifuged. [d] Solution centrifuged 15 minutes.

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[1] This publication is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York. Presented at the Gordon Research Conference on Ion Exchange, New Hampton, New Hampshire, July, 1954.

[2] J. Schubert, *J. Phys. Chem.*, **56**, 114 (1952). This paper has an extensive bibliography.

[3] T. Y. Toribara and P. S. Chen, Jr., *Anal. Chem.*, **24**, 539 (1952).

[4] I. Feldman and J. R. Havill, THIS JOURNAL, **74**, 2337 (1952).