character. Since they have the same type of chemical formula, the same crystal form and the same habit, cleavage and general optical properties, we consider that they constitute an isomorphous series.

The acid fluoride of copper has the same type of formula, but differs crystallographically.

From the original preparation of copper fluoride small crystals of the normal fluoride, $CuF_2.2H_2O$, were obtained, which were not good enough for measurement and which reverted unexpectedly to the acid fluoride on recrystallization from water.

The experimental work upon which this article is based was completed in May, 1918.

College of the City of New York,
New York, N. Y.

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[Contribution from the Department of Chemistry of Columbia University.
No. 332.]

# A STUDY OF THE SATURATED POTASSIUM CHLORIDE CALOMEL CELL.

By Harold A. Fales and William A. Mudge.

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The increasing use of the electromotive force method for hydrogen-ion measurements, and the variety of combinations employed, have intensified the desirability of devising a single combination which will not only minimize, as far as possible, the inherent errors of this important method, but will give, in addition, an improved technique for working over a wide range of temperature, 5–60°.

The combinations which have been used to the greatest extent are those employing either the 0.1 $N$ or $N$ calomel cell in conjunction with either the 0.1 $N$,[1] $N$,[2] 3.5 $N$,[3] or saturated[4] potassium chloride salt bridge.

In the use of such combinations the difficulties are two-fold: (*a*) those due to the changes in value of the contact potentials brought about by the interdiffusion of the respective solutions at their several junctions; and (*b*) those due to the change in value of the calomel cell resulting from the diffusion of the potassium chloride of the salt bridge into the more dilute solution of the salt in the calomel cell.

Fales and Vosburgh,[5] in a study of Planck's formula for contact poten-

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[1] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911); Myers and Acree, *ibid.*, 50, 398 (1913); Harned, This Journal, 37, 2475 (1915); Fales and Vosburgh, *ibid.*, 40, 1302 (1918).

[2] Ostwald. Ostwald-Luther, "Physico-chemische Messungen," 3rd Ed., p. 445.

[3] Bjerrum, *Z. physik. Chem.*, 53, 430 (1905); Fales and Nelson, This Journal, 37, 2781 (1915).

[4] Loomis and Acree, *loc. cit.*; Harned, *loc. cit.*; Fales and Vosburgh, *loc. cit.*

[5] This Journal, 40, 1291 (1918).

tials, deduced the value of zero for the contact potential 1.0 *M* HCl—sat. KCl, and 0.1 *M* HCl—sat. KCl at 25°.[1] Inferentially it follows that the same value of zero applies for concentrations of hydrochloric acid between 1.0 *M* and 0.1 *M*, and also for concentrations less than 0.1 *M*, *e. g.*, that the use of saturated potassium chloride in contact with concentrations of hydrochloric acid up to 1.0 *M* gives zero contact potential at 25°.[2]

The selection of the saturated salt bridge, therefore, minimizes difficulty *a*, but still leaves difficulty *b*, when 0.1 *M* or *M* calomel cells are used. The simple device of substituting the saturated potassium chloride calomel cell for the others will also remove difficulty *b*. In view of the above considerations the logical procedure is to use the saturated potassium-chloride calomel cell in conjunction with a saturated salt bridge, and thereby eliminate or minimize both difficulties.[3]

The purpose of the present investigation is therefore as follows: to study the applicability of the saturated potassium chloride calomel cell for use in systems of the type,

Combination (1) Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—$H_2$(Pt),[4]

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[1] According to Planck's formula, the values for the contact potential 1.0 *M* HCl-sat. KCl and 0.1 *M* HCl-sat. KCl at 25° are, respectively, 0.0170 and 0.0055 volt. The main argument that the values are each zero, as deduced by Fales and Vosburgh, is that the acceptance of this value leads to consistent results when taken in conjunction with the corresonding electrode potentials, and applied to the 28 combinations studied by them, whereas Planck's values lead to inconsistent results.

The matter of the exact value of contact potentials cannot, however, be considered as settled in its finality until (1) it is shown that no other set of values but the ones selected will give consistent results, or until (2) some method is devised by which either electrode potentials or contact potentials can be measured independently. The difficulty in dealing with individual electrode potentials, as has always been realized, is that there are always at least $n + 1$ potentials to be considered for every set of $n$ combinations chosen, that is to say, the experimental observations always give rise to a set of indeterminate equations; this indeterminateness of the problem was pointed out by Fales and Vosburgh (*loc. cit.*, p. 1304). For a further appreciation of the difficulties in this regard, see Lewis, Brighton and Sebastian, THIS JOURNAL, **39,** 2256 (1917).

[2] Loomis and Acree, *Am. Chem. J.*, **46,** 621 (1911), had previously inferred that the use of a saturated potassium chloride salt bridge would eliminate the contact potential between it and 0.1 *M* hydrochloric acid at 25°.

[3] Michaelis, it seems, was the first to propose the use of the saturated potassium chloride calomel cell in conjunction with a saturated salt bridge. In his monograph, "Die Wasserstoffionen-Konzentration," Julius Springer, Berlin, 1914, p. 150, he recommends this scheme, and gives figures for the combination:

$$\text{Hg–HgCl sat. KCl–sat. KCl–}\left\{\begin{matrix}0.1\ M\ \text{NaC}_2\text{H}_3\text{O}_2\\ 0.1\ M\ \text{HC}_2\text{H}_3\text{O}_2\end{matrix}\right\}\text{–H}_2\text{(Pt)}$$

for the temperature range 15–38° with the comment, however, that his values may be in error by 2 or 2.5 millivolts.

Fales and Ware, THIS JOURNAL, **41,** 487 (1919), used this combination, and provisionally gave the value of the electrode potential Hg–HgCl sat. KCl– as 0.5272 volt at 25°.

and to compare its use for such purposes with the 0.1 *M* and *M* potassium-chloride calomel cells respectively, throughout the temperature range 5–60°.

## Experimental.

**Water-baths, Potentiometer, and Galvanometer.**—Two baths, Nos. 1 and 2, were used; the former was controlled to within ±0.02°, and the latter to within ±0.01°. From Combination 8, Table IV, it will be seen that the difference in e. m. f. between any 5° is about 0.003 volt; this is equivalent to 0.000006 volt per 0.01°, and shows that both temperature regulations were well within the required precision.

The null method was employed and the e. m. f. determined by means of a Leeds and Northrup potentiometer and a D'Arsonval galvanometer. The latter had a sensibility of 280 megohms, a period of 2.5 seconds, and a total resistance of 444 ohms. A Weston cell was used as a primary standard of reference; it had been calibrated by the U. S. Bureau of Standards, checked against another standard cell in the department, and found to have a value of 1.0183 volts at 20°.

**Types of Cells.**—The calomel electrode described by Fales and Vosburgh,[1] and the bubbling hydrogen cell were used throughout the work.

**Making New Calomel Cells.**—At first the mercury and the calomel in a calomel cell were not removed from the cell when it was desired to make up a new cell; only the solution of 0.1 *M* or *M* potassium chloride above the calomel was replaced. In every case the value of the new cell was not appreciably different from the old value before the fresh potassium chloride solution had been added. One case is cited as an illustration: a 0.1 *M* calomel cell, $B_6$, was employed in Combination 6 and gave an observed value for the combination at 25° of 0.3934 volt (theory 0.4016 volt).[2] When the potassium chloride solution in the cell had been replaced by some fresh solution, the value of the combination was 0.3935 volt. The entire contents of the cell were then removed, the cell thoroughly cleaned and prepared again with all fresh materials. The resulting value of the combination was 0.4015 volt.

This would seem to indicate that whenever a new cell is prepared an entire change of materials must be effected if accurate values are desired. It is quite possible that there is an adsorption of the potassium chloride by the calomel, and this phenomenon would not be altered by a simple substitution of some fresh solution. This point would undoubtedly bear further investigation.

**Hydrogen Electrodes and Hydrogen.**—Platinum electrodes of plate form, 2 cm. long × 1 cm. wide × 0.025 cm. thick, platinized with plat-

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[1] THIS JOURNAL, **40**, 1305 (1918).

[2] This particular cell had shown a decrease in its e. m. f., due to diffusion into it of potassium chloride from the salt bridge; hence the low value of the combination.

inum black, were used. They were reblacked several times during the work, whenever any 2 gave a greater difference than 0.0002 volt.

Compressed hydrogen was used exclusively; it was passed successively through alkaline permanganate solution, alkaline pyrogallate solution, water, and cotton wool to purify it; then through a hydrochloric acid solution of the same concentration as that employed in the hydrogen cell; the rate of flow was about 2 or 3 bubbles per second.

**Liquid Junctions.**—The liquid junctions were made by dipping the ends of the siphon tubes of the component cells into a saturated solution of potassium chloride contained in a small beaker, the amounts of the solutions in all parts of a combination being so adjusted that all meniscuses were on the same level. At the beginning of the work small wooden plugs or toothpicks were used in the ends of the siphon tubes to prevent any mechanical mixing of the solutions. With these it was often found that duplicate measurements of a combination did not agree to a closer precision than ±0.0005 volt.[1] Investigation showed that this variation was due solely to the change in contact potential and not to any change in the value of the electrode potential; a conclusion which is confirmed by the fact that the loosening or tightening of the wooden plugs in the ends of the siphon tubes would cause an immediate change in the value of the combination. By using small cones of cotton wool fitted snugly, but not tightly, into the siphon tubes of all the cells of a combination, the present authors found that they could duplicate their results with ease at any time with a precision of ±0.0001 to ±0.0002 volt. This method was, therefore, adopted and the values reported in this work are, unless otherwise specified, those obtained by using cotton plugs.

With respect to the reproducibility which is thus gained by the use of cotton plugs, it is possible that the greater space between the fibers of the cotton than between the cells of the wood allows a more even and rapid diffusion of the 2 liquids to their point of juncture, with the result that contact is made through the plug when cotton is used, instead of around the plug as is the case when wood is used.[2]

[1] See the work of Fales and Vosburgh, *loc. cit.*, who used wooden plugs, and commented on the variability of measurements caused by the interdiffusion which occurs at liquid junctions.

[2] Attention must be called to the admirable and quite different "flowing junction" method of Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2254 (1917), and of Lamb and Larson, *ibid.*, **42**, 1229 (1920), for establishing constancy of contact conditions and insuring reproducibility of results. In view of the theoretical excellence of the "flowing junction" method, it would be of great service to the study of e. m. f. measurements to have all other methods critically compared with it. In the meantime it is certainly worth while to state that the L. B. and S. method allows duplication of results to be obtained within one or two minutes after making contact, and it would seem, therefore, to be particularly desirable for those combinations, where large contact potentials exist.

**Preparation of Materials and Solutions.**—Conductivity water was obtained by distilling ordinary distilled water through a block tin condenser from alkaline permanganate solution, and kept in Non-sol bottles. It was used throughout the work except for making saturated potassium chloride solution for the salt bridge, when ordinary distilled water was used. In order to prevent any contamination of the salt bridge it was renewed every 2 or 3 days with fresh solution.

The mercury employed in the preparation of the calomel cells was washed several times with nitric acid according to the method of Hildebrand,[1] then filtered through a clean dry towel, and finally distilled under reduced pressure with access of air as proposed by Hulett.[2]

But one lot of calomel was used, a commercial "c. p." grade; it was tested for iron and non-volatile residue and found satisfactory. A sufficient amount was put in a Non-sol bottle together with a little pure mercury and about 400 cc. of potassium chloride solution of the desired concentration; this mixture was then shaken intermittently for 2 days before being used.[3]

TABLE I.—SPECIFIC GRAVITIES AND DENSITIES OF SOLUTIONS.

| | (1.0 $M$ HCl). 1.022 $\underline{M}$ HCl[a] | | | (0.1 $M$ HCl) 0.1003 $\underline{M}$ HCl | | |
| --- | --- | --- | --- | --- | --- | --- |
| Temp. °. | Sp. gr. t°/t°. | Density t°/4°. | Mols per liter. | Sp. gr. t°/t°. | Density t°/4°. | Mols per liter. |
| 5....... | 1.0188 | 1.0188 | 1.004 | 1.0020 | 1.0020 | 0.1003 |
| 10....... | 1.0182 | 1.0179 | 1.003 | 1.0018 | 1.0015 | 0.1002 |
| 15....... | 1.0179 | 1.0170 | 1.002 | 1.0018 | 1.0010 | 0.1001 |
| 20....... | .... | .... | 1.000 | .... | .... | 0.1000 |
| 25....... | 1.0176 | 1.0146 | 0.999 | 1.0018 | 0.9990 | 0.0999 |
| 40....... | 1.0169 | 1.0091 | 0.993 | 1.0016 | 0.9939 | 0.0993 |
| 45....... | 1.0169 | 1.0071 | 0.991 | 1.0016 | 0.9920 | 0.0991 |
| 50....... | 1.0169 | 1.0049 | 0.989 | 1.0016 | 0.9898 | 0.0989 |
| 55....... | 1.0167 | 1.0023 | 0.987 | 1.0016 | 0.9875 | 0.0987 |
| 60....... | 1.0166 | 0.9997 | 0.984 | 1.0015 | 0.9848 | 0.0984 |
| | (1.0 $M$ KCl) 1.030 $\underline{M}$ KCl | | | (0.1 $M$ KCl) 0.1004 $\underline{M}$ KCl | | |
| 5....... | 1.0482 | 1.0482 | 1.004 | 1.0049 | 1.0049 | 0.1002 |
| 10....... | 1.0473 | 1.0470 | 1.003 | 1.0050 | 1.0047 | 0.1001 |
| 15....... | 1.0466 | 1.0457 | 1.002 | 1.0049 | 1.0040 | 0.1001 |
| 20....... | .... | .... | 1.000 | .... | .... | 0.1000 |
| 25....... | 1.0462 | 1.0431 | 0.999 | 1.0048 | 1.0019 | 0.0999 |
| 40....... | 1.0454 | 1.0374 | 0.993 | 1.0044 | 0.9967 | 0.0993 |
| 45....... | 1.0453 | 1.0352 | 0.991 | 1.0043 | 0.9946 | 0.0991 |
| 50....... | 1.0452 | 1.0329 | 0.989 | 1.0044 | 0.9925 | 0.0989 |
| 55....... | 1.0452 | 1.0304 | 0.986 | 1.0045 | 0.9902 | 0.0987 |
| 60....... | 1.0451 | 1.0277 | 0.984 | 1.0044 | 0.9877 | 0.0984 |

[a] By $\underline{M}$ is understood the No. of mols per 1000 g. of water. $M$ indicates true mols.

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[1] THIS JOURNAL, **31**, 933 (1909).

[2] *Z. physik. Chem.*, **33**, 611 (1900).

[3] Fales and Vosburgh, *loc. cit.*, used 3 lots of calomel: an imported, a domestic, and that prepared by the electrolytic method of Ellis, THIS JOURNAL, **38**, 740 (1916). They noticed no difference between cells prepared with any one of the 3 lots of calomel.

The various standard solutions employed in preparing the several cells were made up as described by Fales and Vosburgh. In order to extend the data given by those authors,[1] the specific gravities, densities and molar concentrations of the standard solutions are given above in Table I for temperatures not considered by them.

## Comparison of the Values of the Saturated Potassium Chloride Calome Cell with Potassium Chloride Calomel Cell of Different Concentrations, at 25°.

The starting point in the investigation was to study the system, Combination 2

$$\text{Hg—HgCl}xM\text{ KCl—sat. KCl—}0.1\ M\text{ HCl—H}_2\text{ (1 Atmos.) Pt, at } 25°,$$

where $x$ varies from 0.1 $M$ to saturation (4.12 $M$). The results are given in Table II.

TABLE II.—VALUES OF COMBINATION 2 AT 25°.

| Conc. KCl. | Av. obs. value of combination 2 (volt). | No. of detns. | Av. bar. reading (mm. Hg). | Av. corr. value[a] to 1 atmos. $H_2$ (volt). |
|---|---|---|---|---|
| 0.1 $M$ | 0.4016 ± 0.0002 | 39 | 759 | 0.4020 ± 0.0002 |
| 0.5 | 0.3642 ± 0.0001 | 8 | 761 | 0.3646 ± 0.0001 |
| 1.0 | 0.3479 ± 0.0002 | 90 | 760 | 0.3483 ± 0.0002 |
| 2.0 | 0.3321 ± 0.0001 | 8 | 760 | 0.3325 ± 0.0001 |
| 3.0 | 0.3209 ± 0.0001 | 8 | 760 | 0.3213 ± 0.0001 |
| Saturated | 0.3099 ± 0.0002 | 101 | 761 | 0.3103 ± 0.0002 |

[a] For correction of values to 1 atmos. $H_2$, see paragraphs headed "Correction for Barometric Pressure."

From the values given in the last column of Table II, the values of the several electrode potentials

$$\text{Hg—HgCl}xM\text{ KCl}$$

may be obtained by correcting for the small contact potentials existing between the saturated potassium chloride solution of the salt bridge and the less concentrated solution of the same salt in the calomel electrode. These values for the 0.1, 0.5, 1.0, 2.0 and 3.0 $M$ potassium chloride solutions in contact with the saturated salt bridge have been calculated from Nernst's formula,

$$E = RT\frac{u - v}{u + v}\log\frac{C_2}{C_1},$$

and found to be: 0.0006, 0.0003, 0.0002, 0.0002 and 0.0001 volt, respectively. Using these values and the value 0.5648 volt for the electrode potential, Hg—HgCl 1.0 $M$ KCl at 25°[2] we get as the values of the several electrode potentials the results given in Table III and expressed graphically in Fig. 1.

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[1] *Loc. cit.*, p. 1309. It is also desired to point out that the values for the several solutions at the temperatures of 15° and 18°, as given by F. and V., are incorrect due to an error in calculation.

[2] See Fales and Vosburgh, *loc. cit.*, for the selection of the value 0.5648 volt.

TABLE III.—ELECTRODE POTENTIALS OF SEVERAL POTASSIUM CHLORIDE CALOMEL CELLS AT 25°.

| Cell Hg-HgCl $xM$ KCl. | Electrode potential (volt). |
|---|---|
| 0.1 | 0.6177 |
| 0.5 | 0.5808 |
| 1.0 | 0.5648 |
| 2.0 | 0.5488 |
| 3.0 | 0.5377 |
| Sat. KCl | 0.5266 |

Relation of Pole Potential Difference to Concentration of KCl at 25°C.

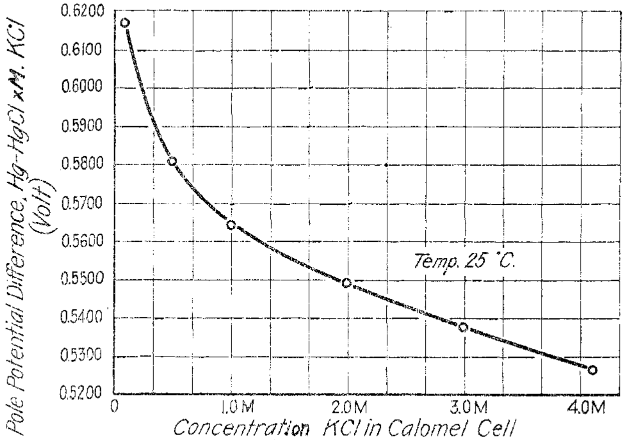

Fig. 1.

From Fig. 1 it can readily be seen that the e. m. f. of the calomel cell changes more rapidly when the concentration of the potassium chloride is more dilute. From this one consideration alone, neglecting for the moment the fact that the saturated cell would eliminate both the error due to diffusion and that due to the change of contact potential, it is obvious that the saturated potassium chloride calomel cell would be the safest cell to use.

## Correction for Barometric Pressure.

In order to obtain the absolute value of any combination in which a hydrogen cell is employed, it is necessary to determine the correction which must be applied to the electrode potential of the hydrogen cell on account of the barometric pressure and the temperature at which the measurement is made. In the combination

$$\mathrm{Hg}\underset{\xleftarrow{\ a\ }}{—}\mathrm{HgCl}\ xM\ \mathrm{KCl}—yM\ \mathrm{KCl}—zM\ \mathrm{HCl}\underset{\xrightarrow{\ b\ }}{—}\mathrm{H_2(Pt)}$$

if we decrease the pressure of the hydrogen, the value of $b$ will increase. Therefore, when the pressure of the hydrogen is less than one atmosphere the value of $b$ will be greater than the value which it has when the pressure of hydrogen is equal to one atmosphere, while the value of the whole combination will be correspondingly low because the electrode potentials *a* and *b* are oppositely directed. Consequently if we know the variation in *b*, we can apply the necessary correction by subtracting it from the electrode potential $2M$ HCl—$H_2$(Pt), or by adding it to the observed value of the combination.

Two standards of reference may be adopted: correction to one atmosphere of hydrogen; or correction to one atmosphere total pressure, *e. g.*, one atmosphere as indicated by the barometer.

### Correction to One Atmosphere of Hydrogen.

Assuming that the partial pressure of the hydrogen above the solution bathing the hydrogen electrode is equal to the observed barometric pressure less the vapor pressure of water,[1] and making the calculations according to the formula

$$E = \frac{RT}{2F \ln 1/P} \quad ^{2}$$

we obtain the graph given in Fig. 2, where the correction is plotted as a function of the observed barometric pressure.

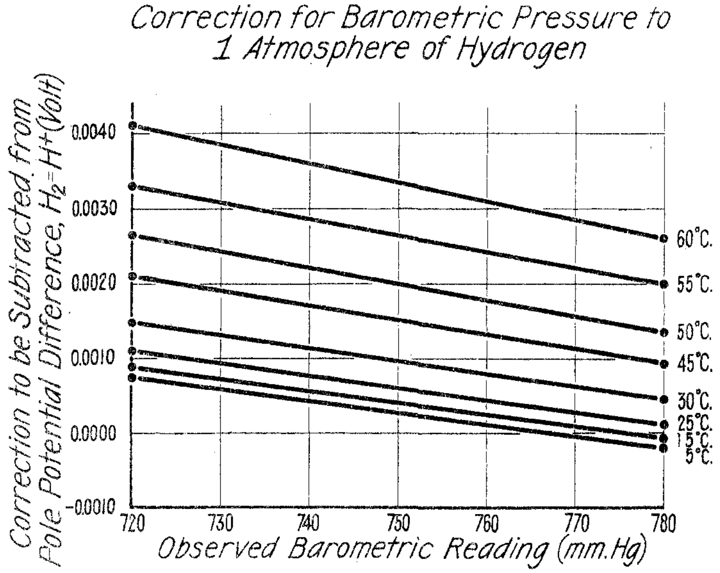

Fig. 2.

While this assumption holds for dilute solutions and temperatures around 25°, it is very probable that the relationship is different for con-

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[1] For concentrated solutions, this would not be strictly true, since the vapor pressure of concentrated solutions may depart considerably from that of water.

[2] See Harned, THIS JOURNAL, 37, 2465 (1915).

centrated solutions and high temperatures, say above 50°. It would seem a safer procedure, in general, therefore, to refer all measurements to one atmosphere total pressure.

### Correction to One Atmosphere Total Pressure.

In the present work the extreme barometric pressures observed over a period of 8 months were 755 mm.—770 mm., with an average of 762.5 mm. It can readily be seen that this deviation of about 10 mm. from the average would correspond to a correction which is less than the experimental error involved in the measurements of the systems. The authors, therefore, propose to neglect the correction when one atmosphere total pressure is used as a standard, and to employ it only when it shall be necessary to refer to one atmosphere of hydrogen, as in Table II, where the ultimate or absolute value of the different combinations was desired.

### Comparison of Cells at 30°, 35°, and 40°.

In order to compare the relative merits of the saturated, *M* and 0.1 *M* potassium chloride calomel cells, 3 of each type, which we shall, respectively designate "S," "A," and "B" were placed in a constant temperature bath along with three 0.1 *M* hydrochloric acid cells, "D." The calomel cells were not disturbed from day to day, but the hydrogen cells were removed from the bath after each day's measurements, thoroughly washed, and each platinum electrode allowed to stand overnight in distilled water. The next day the hydrogen cells were prepared with fresh acid. This procedure gave many duplicate determinations of the same calomel cell, and served to make the results more reliable. After the value of the various combinations had been obtained at any one temperature, the temperature of the bath was raised through an interval of 5°. It was originally intended to extend the measurements for all 3 calomel cells over the range of 25° to 60°, but it was soon plainly evident that the lack of merit of the *M* and 0.1 *M* calomel cells did not warrant the necessary time or labor.

Each cell in the bath was measured against the other 11, using a saturated potassium chloride salt bridge. This gave the following combinations.

(3) Hg—HgCl 0.1 *M* KCl—sat. KCl— sat. KCl HgCl—Hg,
(4) Hg—HgCl 1.0 *M* KCl—sat. KCl—sat. KCl HgCl—Hg,
(5) Hg—HgCl 0.1 *M* KCl—sat. KCl—1.0 *M* KCl HgCl—Hg
(6) Hg—HgCl 0.1 *M* KCl—sat. KCl—0.1 *M* HCl—$H_2$(Pt),
(7) Hg—HgCl 1.0 *M* KCl—sat. KCl—0.1 *M* HCl—$H_2$(Pt)
(8) Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—$H_2$(Pt)

The combinations were always kept at one temperature until observations of 2 successive days, with renewals of the hydrochloric acid in the hydrogen cells, did not differ from each other by more than the experimental error, ±0.0002 volt. Combination 8 was measured throughout the temperature range, 5° to 60°, but measurements of the other 5 combinations were abandoned at 40°. The results are given in Table IV, all observations being expressed in volts, and the values for Combinations 6, 7, and 8 being referred to one atmosphere total pressure.

TABLE IV.—THE e. m. f. OF THE SATURATED, *M*, AND 0.1 *M* POTASSIUM CHLORIDE CALOMEL CELLS AT 25–40°.[a]

| Temp. ° C. | No. of detns. | Time. Days. | Average bar. reading (mm. Hg). | Average e. m. f. (volt). |
|---|---|---|---|---|
| (3) Hg–HgCl 0.1 *M* KCl–sat. KCl–sat. KCl HgCl–Hg. | | | | |
| 25 | 36 | 4 | 760 | 0.0918 ± 0.0002 |
| 30 | 27 | 3 | 760 | 0.0904 ± 0.0034 |
| 35 | 9 | 1 | 761 | 0.0902 ± 0.0033 |
| 40 | 9 | 1 | 757 | 0.0759 ± 0.0149 |
| (4) Hg–HgCl 1.0 *M* KCl–sat. KCl–sat. KCl HgCl–Hg. | | | | |
| 25 | 36 | 6 | 760 | 0.0387 ± 0.0002 |
| 30 | 27 | 3 | 760 | 0.0397 ± 0.0005 |
| 35 | 6 | 1 | 761 | 0.0404 ± 0.0004 |
| 40 | 6 | 1 | 757 | 0.0386 ± 0.0022 |
| (5) Hg–HgCl 0.1 *M* KCl–sat. KCl–1.0 *M* KCl HgCl–Hg. | | | | |
| 25 | 28 | 4 | 760 | 0.0533 ± 0.0002 |
| 30 | 27 | 3 | 760 | 0.0508 ± 0.0035 |
| 35 | 9 | 1 | 761 | 0.0513 ± 0.0028 |
| 40 | 9 | 1 | 757 | 0.0407 ± 0.0148 |
| (6) Hg–HgCl 0.1 *M* KCl–sat. KCl–0.1 *M* HCl–$H_2$(Pt).[b] | | | | |
| 25 | 39 | 5 | 760 | 0.4016 ± 0.0002 |
| 30 | 27 | 3 | 760 | 0.3971 ± 0.0035 |
| 35 | 18 | 2 | 760 | 0.3967 ± 0.0031 |
| 40 | 27 | 3 | 756 | 0.3782 ± 0.0123 |
| (7) Hg–HgCl 1.0 *M* KCl–sat. KCl–0.1 *M* HCl–$H_2$(Pt).[c] | | | | |
| 25 | 90 | 10 | 759 | 0.3479 ± 0.0002 |
| 30 | 18 | 2 | 760 | 0.3462 ± 0.0005 |
| 35 | 18 | 2 | 760 | 0.3443 ± 0.0005 |
| 40 | 27 | 3 | 756 | 0.3411 ± 0.0029 |
| (8) Hg–HgCl sat. KCl–sat. KCl–0.1 *M* HCl–$H_2$(Pt). | | | | |
| 25 | 108 | 12 | 761 | 0.3099 ± 0.0002 |
| 30 | 27 | 3 | 760 | 0.3070 ± 0.0001 |
| 35 | 27 | 3 | 760 | 0.3042 ± 0.0001 |
| 40 | 36 | 4 | 756 | 0.3014 ± 0.0001 |
| 45 | 27 | 3 | 762 | 0.2996 ± 0.0002 |
| 50 | 27 | 3 | 758 | 0.2966 ± 0.0001 |
| 55 | 36 | 4 | 762 | 0.2942 ± 0.0002 |
| 60 | 18 | 2 | 763 | 0.2919 ± 0.0002 |

[a] The following individual cells were used: $B_7$, $B_8$, $B_9$; $A_4$, $A_5$, $A_7$; $S_1$, $S_2$, $S_3$, $S_4$; and $D_1$, $D_2$, $D_3$.

[b] For combination 6 at 25° and one atmos. $H_2$ the following values are reported in the literature: Fales and Vosburgh, THIS JOURNAL, **40,** 1314 (1918), 0.3991 volt; Bjerrum, *Z. physik. Chem.*, **53,** 430 (1905), 0.4012 volt; Harned, *loc. cit.*, 0.4000 volt; Myers and Acree, *Am. Chem. J.*, **50,** 411 (1913), 0.4012 volt.

[c] For combination 7 at 25° and one atmos. of $H_2$, Fales and Vosburgh, *loc. cit.*, found 0.3470 volt; Harned, *loc. cit.*, 0.3491 volt.

The results given in Table IV show that the *M* and 0.1 *M* potassium chloride calomel cells are entirely unreliable above 25° when used in conjunction with a saturated potassium chloride salt bridge. In every case the average deviation increases with temperature and is far greater than the experimental error, being 0.012–0.015 volt at 40°, and due as we shall show later, to the diffusion of the saturated solution from the salt bridge into the *M* or 0.1 *M* solution in the calomel cell. It is also evident that the saturated potassium chloride calomel cell shows marked superiority over the other 2 calomel cells for use under the above conditions.

## The System, Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—$H_2$(Pt), from 5° to 60°, Also Four Other Systems.

In order to test the saturated potassium chloride calomel cell further and to obtain its temperature coefficient, the saturated cells $S_1$ and $S_2$,[1] together with 8 new ones, $S_5$, $S_6$, ... $S_{12}$, were used in conjunction with four 0.1 *M* hydrochloric acid hydrogen cells, $D_1$, $D_2$, $D_3$, $D_4$, as follows the odd-numbered cells of each kind were placed in Bath 1, which was maintained at 25°, while the even-numbered cells were placed in Bath 2, which was varied from 5° to 60°. The saturated potassium chloride solution serving as a salt bridge in Bath 1 was connected to that serving in Bath 2, by means of a siphon tube of 0.5 cm. diameter; this tube contained saturated potassium chloride, and had its ends stopped with small cotton plugs, similar to those used in the ends of the siphon tubes of the component cells. Before any measurements were made, the platinum electrodes of the hydrogen cells were carefully blackened with platinum

Table V.

(8) Hg–HgCl sat. KCl–sat. KCl–0.1 *M* HCl–$H_2$(Pt).
5–60° 5–60°

| Temperature. | | | | | |
|---|---|---|---|---|---|
| Calomel. °. | Hydrogen. °. | No. of detns. | Time. Days. | Average bar. reading (mm. Hg). | Average e. m. f. 1 atmos. total pressure (volt). |
| 5 | 5 | 8 | 2 | 767 | 0.3183 ± 0.0001 |
| 10 | 10 | 6 | 3 | 765 | 0.3161 ± 0.0001 |
| 15 | 15 | 6 | 2 | 766 | 0.3143 ± 0.0001 |
| 20 | 20 | 8 | 2 | 764 | 0.3122 ± 0.0001 |
| 25 | 25 | 20 | 3 | 765 | 0.3100 ± 0.0001 |
| 30 | 30 | 4 | 1 | 770 | 0.3070 ± 0.0001 |
| 35 | 35 | 4 | 1 | 765 | 0.3043 ± 0.0001 |
| 40 | 40 | 4 | 1 | 770 | 0.3016 ± 0.0001 |
| 45 | 45 | 4 | 1 | 766 | 0.2997 ± 0.0002 |
| 50 | 50 | 4 | 1 | 755 | 0.2966 ± 0.0001 |
| 55 | 55 | 4 | 1 | 762 | 0.2942 ± 0.0002 |
| 60 | 60 | 4 | 1 | 762 | 0.2917 ± 0.0002 |

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[1] The 2 cells $S_1$ and $S_2$ had already been employed in obtaining the values given in Table IV; their further use was to give information as to their reliability for continued use after having been passed through the temperature range 25° to 60° and back again to 25°.

TABLE V (*continued*).

(9) $Hg–HgCl$ sat. $KCl$–sat. $KCl$–sat. $KCl$ $HgCl–Hg$,
5–60°   25°

| Temperature. | | | | | |
|---|---|---|---|---|---|
| Calomel. °. | Calomel. °. | No. of detns. | Time. Days. | Average bar. reading (mm. Hg). | Average e. m. f. 1 atmos. total pressure (volt). |
| 5 | 25 | 8 | 2 | 767 | 0.0042 ± 0.0001 |
| 10 | 25 | 8 | 3 | 765 | 0.0035 ± 0.0002 |
| 15 | 25 | 8 | 3 | 766 | 0.0025 ± 0.0001 |
| 20 | 25 | 8 | 2 | 764 | 0.0014 ± 0.0001 |
| 25 | 25 | 4 | 1 | 765 | 0.0001 ± 0.0001 |
| 30 | 25 | 4 | 1 | 770 | 0.0011 ± 0.0001 |
| 35 | 25 | 4 | 1 | 765 | 0.0023 ± 0.0001 |
| 40 | 25 | 4 | 1 | 770 | 0.0030 ± 0.0002 |
| 45 | 25 | 4 | 1 | 766 | 0.0040 ± 0.0001 |
| 50 | 25 | 4 | 1 | 755 | 0.0050 ± 0.0001 |
| 55 | 25 | 4 | 1 | 762 | 0.0059 ± 0.0001 |
| 60 | 25 | 4 | 1 | 762 | 0.0068 ± 0.0002 |

(10) $Hg–HgCl$ sat. $KCl$–sat. $KCl$–0.1 *M* $HCl–H_2(Pt)$,
5–60°   25°

| Calomel. °. | Hydrogen. °. | | | | |
|---|---|---|---|---|---|
| 5 | 25 | 8 | 2 | 767 | 0.3052 ± 0.0001 |
| 10 | 25 | 12 | 3 | 765 | 0.3061 ± 0.0002 |
| 15 | 25 | 8 | 2 | 766 | 0.3072 ± 0.0001 |
| 20 | 25 | 6 | 2 | 764 | 0.3086 ± 0.0001 |
| 25 | 25 | 20 | 3 | 765 | 0.3100 ± 0.0001 |
| 30 | 25 | 4 | 1 | 770 | 0.3111 ± 0.0001 |
| 35 | 25 | 4 | 1 | 765 | 0.3119 ± 0.0001 |
| 40 | 25 | 4 | 1 | 770 | 0.3129 ± 0.0001 |
| 45 | 25 | 4 | 1 | 766 | 0.3136 ± 0.0001 |
| 50 | 25 | 4 | 1 | 755 | 0.3142 ± 0.0001 |
| 55 | 25 | 4 | 1 | 762 | 0.3150 ± 0.0001 |
| 60 | 25 | 4 | 1 | 762 | 0.3162 ± 0.0002 |

(11) $(Pt)H_2$–0.1 *M* $HCl$–sat. $KCl$–0.1 *M* $HCl–H_2(Pt)$.
5–60°   25°

| Hydrogen. °. | Hydrogen. °. | | | | |
|---|---|---|---|---|---|
| 5 | 25 | 8 | 2 | 767 | 0.0122 ± 0.0001 |
| 10 | 25 | 8 | 3 | 765 | 0.0096 ± 0.0002 |
| 15 | 25 | 12 | 3 | 766 | 0.0066 ± 0.0001 |
| 20 | 25 | 8 | 2 | 764 | 0.0034 ± 0.0001 |
| 25 | 25 | 4 | 1 | 765 | 0.0001 ± 0.0001 |
| 30 | 25 | 4 | 1 | 770 | 0.0049 ± 0.0002 |
| 35 | 25 | 4 | 1 | 765 | 0.0087 ± 0.0001 |
| 40 | 25 | 4 | 1 | 770 | 0.0125 ± 0.0001 |
| 45 | 25 | 4 | 1 | 766 | 0.0146 ± 0.0001 |
| 50 | 25 | 4 | 1 | 755 | 0.0181 ± 0.0002 |
| 55 | 25 | 4 | 1 | 762 | 0.0216 ± 0.0002 |
| 60 | 25 | 4 | 1 | 762 | 0.0260 ± 0.0002 |

TABLE V (*continued*).

(12) Hg–HgCl sat. KCl–sat. KCl–0.1 $M$ HCl–$H_2$(Pt).

25° 5–60°

| Temperature. | | | | | |
|---|---|---|---|---|---|
| Hydrogen. °. | Calomel. °. | No. of detns. | Time. Days. | Average bar. reading (mm. Hg). | Average e. m. f. 1 atmos. total pressure (volt). |
| 5 | 25 | 8 | 2 | 767 | 0.3230 ± 0.0001 |
| 10 | 25 | 8 | 3 | 765 | 0.3194 ± 0.0001 |
| 15 | 25 | 8 | 2 | 766 | 0.3163 ± 0.0002 |
| 20 | 25 | 6 | 2 | 764 | 0.3128 ± 0.0002 |
| 25 | 25 | 20 | 3 | 765 | 0.3100 ± 0.0001 |
| 30 | 25 | 4 | 1 | 770 | 0.3070 ± 0.0002 |
| 35 | 25 | 4 | 1 | 765 | 0.3031 ± 0.0001 |
| 40 | 25 | 4 | 1 | 770 | 0.3003 ± 0.0002 |
| 45 | 25 | 4 | 1 | 766 | 0.2964 ± 0.0002 |
| 50 | 25 | 4 | 1 | 755 | 0.2926 ± 0.0002 |
| 55 | 25 | 4 | 1 | 762 | 0.2886 ± 0.0002 |
| 60 | 25 | 4 | 1 | 762 | 0.2842 ± 0.0002 |

black until, on subsequent trial, identical values were obtained when they were checked against a saturated calomel cell of known value. When the hydrogen cells containing these electrodes were measured against each other, there was no difference in e. m. f. Each cell in Bath 1 was measured against each cell in Bath 2, thus giving additional data for Combination 8 as well as data for 4 other combinations, namely, 9, 10, 11 and 12, as contained in Table V.

## The Electrode Potentials of the Calomel and Hydrogen Cells.

The value of the electrode potential Hg—HgCl 1.0 $M$ KCl at 18° is taken as the standard as adopted by Ostwald[1] with the value 0.5600 volt. This is equivalent to 0.5648 volt at 25°[2] and is the standard to which we shall refer all our calculations.

The value of the electrode potential Hg—HgCl sat. KCl is found in terms of the standard calomel cells by means of Combination 4 to be 0.5263 volt at 25°, by solving for $a$:

(4) Hg—HgCl 1.0 $M$ KCl—sat. KCl—sat. KCl HgCl—Hg; 0.0387 volt.

$\xleftarrow{0.5648}$ $\xleftarrow{0.0002}$ zero $\xrightarrow{a}$

Likewise the electrode potential Pt (1 atmos.) $H_2$—0.1 $M$ HCl is found in terms of the standard calomel cell to be 0.2167 volt at 25° by solving for $b$ in Combination 7:

(7) Hg—HgCl 1.0 $M$ KCl—sat. KCl—0.1 $M$ HCl—$H_2$(1 atmos.) Pt; 0.3483 volt.

$\xleftarrow{0.5648}$ $\xleftarrow{0.0002}$ zero $\xrightarrow{b}$

Also from Combination 8 at 25°:

(8) Hg—HgCl—sat. KCl—sat. KCl—0.1 $M$ HCl—$H_2$ (1 atmos.) Pt; 0.3103 volt.

$\xleftarrow{a}$ zero zero $\xrightarrow{0.2167}$

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[1] *Z. physik. Chem.*, **35**, 333 (1900).

[2] Fales and Vosburgh, THIS JOURNAL, **40**, 1300 (1918).

we obtain a second value, 0.5270 volt, for the electrode potential Hg—HgCl sat. KCl, by solving for *a*.

The value of the electrode potential Hg—HgCl 0.1 *M* KCl at 25° may be obtained from Combination 5, by solving for *c*:

(5) Hg—HgCl 0.1 *M* KCl—sat. KCl—1.0 *M* KCl HgCl—Hg; 0.0533 volt.
$\xleftarrow{c}$ $\xleftarrow{0.0006}$ $\xrightarrow{0.0002}$ $\xrightarrow{0.5648}$

It is found to be 0.6177 volt. Using this value in Combination 3

(3) Hg—HgCl 0.1 *M* KCl—sat. KCl—sat. KCl HgCl—Hg; 0.0918 volt.
$\xleftarrow{0.6177}$ $\xleftarrow{0.0006}$ zero $\xrightarrow{a}$

we obtain a third value for *a*, which is 0.5265 volt. Likewise using the same value for *c*, 0.6177 volt, in Combination 6, we find a second value of *b* which is 0.2163 volt:

(6) Hg—HgCl 0.1 *M* KCl—sat. KCl—0.1 *M* HCl—$H_2$ (1 atmos.) Pt; 0.4020 volt.
$\xleftarrow{0.6177}$ $\xleftarrow{0.0006}$ zero $\xrightarrow{b}$

By averaging the respective values we find that the value of the electrode potential Hg—HgCl sat. KCl is equal to 0.5266 ± 0.0003 volt at 25°, while that of Pt (1 atmos.) $H_2$—0.1 *M* HCl is equal to 0.2165 ± 0.0002 volt at the same temperature. These values, along with the value of the standard calomel cell of 0.5648 volt at 25°, were used for the calculation of the results given in Table III and Fig. 1.

## The Temperature Coefficient of the Saturated Potassium Chloride Calomel Cell.

From Combinations 9 and 10, Table V, it will be seen that the difference in e. m. f. for the saturated calomel cell between 5° and 60° is 0.0110 volt, and that the e. m. f. is sensibly a linear function of the temperature. Consequently the temperature coefficient of the cell is

$$\frac{0.0110}{55} = 0.00020 \text{ volt per degree C.}$$

This shows that the saturated calomel cell has a very small temperature coefficient.

## The Free Energy Change of the Several Systems.

In order to accomplish the change in state,

$$H_2 \text{ (1 atmos.)} + 2HgCl \rightleftarrows 2\,Hg \text{ (liquid)} + 2HCl$$

it is necessary that 2 faradays pass through the system. Therefore, the free energy decrease accompanying this reaction where the system is maintained at the constant temperature *t*, may be obtained by the use of the thermodynamic relationship,

$$(\Delta F)_t = 2\ (\text{e. m. f.})_t \times 96{,}500.$$

This is true for systems of the type represented by Combinations 8 and 11. When we have systems like Combinations 3, 4, or 5, the same change will be effected by the passage of one faraday so that we have for the decrease in free energy in such cases

$$(\Delta F)_t = (\text{e. m. f.})_t \times 96{,}500.$$

## Behavior of the Saturated Potassium Chloride Calomel Cell on Falling Temperature.

When the systems employing the saturated potassium chloride calomel cell were subjected to an increase in temperature, it was necessary to add a slight excess of solid potassium chloride to the solution of the salt in the cell in order to maintain the solution at the point of saturation. This was easily accomplished and caused no difficulty in technique, because of the construction of the calomel cell. However, the amount of salt necessary to produce a saturated solution at 60° was much greater than the amount needed for the lower temperatures. The result was that a considerable excess of the salt always crystallized out when the temperature was lowered. This excess of salt in the cell caused no variation in the observed e. m. f. of the system except when the temperature drop was from 30° to 25°. In this interval it was noticed for Combination 8 using cells $S_1$ and $S_2$ that the readings were about one millivolt high when the cells were being taken through the temperature cycle 25° to 60° a second time, and descending temperatures were being used. The precise values after dropping from 30° to 25° were 0.3114 and 0.3107 volt, respectively, whereas the initial values at the start of the cycle were 0.3100 and 0.3101 volt (theory 0.3100 volt). These values of 0.3114 and 0.3107 remained constant for 4 days. To see the effect of further cooling, followed by subsequent warming, the cells were cooled down to 15° for 5 minutes and then placed in the constant temperature bath at 25°. Two hours later both cells gave a value of 0.3104 volt. Four days later $S_1$ gave its original value of 0.3100 volt. In view of the fact that the solid phase of potassium chloride was always present during the changes in temperature, the variation in e. m. f. cannot be ascribed to supersaturation, but must be attributed to some other cause. On ascending temperatures no such variation was encountered.

## Variation in e. m. f. of the Molar and Tenth-molar Potassium Chloride Calomel Cells.

It has been noticed by several workers that the values of the *M* and 0.1 *M* calomel cells, when used in conjunction with a potassium chloride salt bridge of greater concentration than that employed in the calomel cell, varied from time to time. Richards and Archibald[1] described the decrease in potential as due to the formation of a complex mercuric ion by the interaction of the alkali chloride and the calomel. They also

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[1] Richards and Archibald, *Z. physik. Chem.*, **40**, 385 (1902).

offered a mathematical proof of their theory. Gewecke[1] almost simultaneously corroborated Richards' results. Loomis and Acree,[2] by careful preparation of materials, were able to obtain 0.1 *M* calomel cells that would remain constant for about 3 weeks and then change gradually. Ellis[3] observed a similar effect in his work, but offered no explanation. Loomis and Meacham[4] adopt the view of Richards. Fales and Vosburgh[5] ascribed the decrease to the diffusion of the saturated potassium chloride from the salt bridge into the more dilute solution in the calomel cell; they made an unsuccessful attempt to eliminate it by the use of a jelly salt bridge of agar agar. Lewis, Brighton and Sebastian[5] made frequent renewals of the liquid junction in a specially designed form of apparatus in order to overcome this gradual diffusion.

The present authors found no confirmation of Richards'[5] theory in their work; they are of the opinion that the decrease in value is due only to the diffusion of the saturated potassium chloride from the salt bridge into the *M* and 0.1 *M* potassium chloride solution in the cell, and offer the following evidence in support of this belief. After the e. m. f. of Combinations 6 and 7 had undergone a considerable decrease, they withdrew from each 0.1 *M* and *M* calomel cell employed, 10 cc. of its potassium chloride solution. Each portion was carefully withdrawn by means of a small pipet, diluted with water, aliquoted as necessary and then titrated with 0.01 *M* silver nitrate solution, using potassium chromate as indicator. In some cases, that part of the potassium chloride solution which was in the siphon tube of the cell was excluded, but no great difference was noticed in the chloride content, thus showing that the solution in the cell had practically a uniform concentration throughout.

Table VI gives the detailed information.

During their use, Cells $B_1$, $B_2$, $B_3$, and $A_3$ were allowed to stand in contact with a molar salt bridge with stopcocks closed. When a measurement was to be made the cells were transferred to a saturated potassium chloride salt bridge and the stopcocks opened. The other cells were kept in contact with a saturated bridge at all times, the stopcocks being closed except when a measurement was being made. It will be noticed that the original values of Cells $B_4$, $B_5$ and $B_6$ are somewhat lower than the accepted value for the 0.1 *M* calomel cell (0.4016 volt). This is probably due to the fact that diffusion had already begun since they had been in contact with the saturated salt bridge for 2 days before the initial measurements were made. The addition of methyl orange to the potassium chloride solution in the cells showed no trace of hydrochloric acid which

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[1] Gewecke, *ibid.*, 45, 685 (1903).

[2] Loomis and Acree, *Am. Chem. J.*, 46, 621 (1911).

[3] Ellis, THIS JOURNAL, 38, 737 (1916).

[4] Loomis and Meacham, *ibid.*, 38, 2312 (1916).

[5] *Loc. cit.*

might have diffused into the cell due to the salt bridge having become contaminated with acid from the hydrogen cell.

TABLE VI.—VARIATION IN E. M. F. OF THE TENTH MOLAR AND MOLAR CELLS DUE TO DIFFUSION.

| Cell. | Time in use (days). | Original value at 25°. 1 atmos. total pressure. | Final value at 25°. 1 atmos. total pressure. | Final conc. of KCl. *M*. |
|---|---|---|---|---|
| | | 0.1 *M* KCl. | | |
| $B_1$ | 16 | 0.4006 volt | 0.3884 volt | 0.197 |
| $B_2$ | 16 | 0.4006 | 0.3855 | 0.210 |
| $B_3$ | 16 | 0.4003 | 0.3912 | 0.186 |
| $B_4$ | 8 | 0.3989 | 0.3903 | 0.155 |
| $B_5$ | 8 | 0.3985 | 0.3921 | 0.138 |
| $B_6$ | 8 | 0.3994 | 0.3855 | 0.152 |
| $B_7$ | 19 | 0.4015 | 0.3824[a] | 0.170 |
| $B_8$ | 19 | 0.4015 | 0.3819[a] | 0.179 |
| $B_9$ | 19 | 0.4017 | 0.3585[a] | 0.657 |
| | | 1.0 *M* KCl. | | |
| $A_3$ | 16 | 0.3469 | 0.3458 | 1.106 |
| $A_4$ | 23 | 0.3479 | 0.3355[a] | 1.61 |
| $A_5$ | 23 | 0.3481 | 0.3390[a] | 1.44 |
| $A_7$ | 23 | 0.3474 | 0.3442[a] | 1.12 |

[a] The final values of these cells were measured at 40° as they were being used to compare the different kinds of cells.

In the case of Cell $B_9$ a very pronounced decrease in potential was noticed over a comparatively short period of time. At the start $B_9$ against $D_1$, $D_2$ and $D_3$ at 35° gave an average observed value of 0.3991 volt. Twenty-two hours later it gave an average of 0.3960 volt; 2.5 hours later its value had decreased to 0.3864 volt. The next day its value was 0.3843 volt. This shows a decrease in potential of 0.0100 volt in 2.5 hours following a decrease of about $^2/_3$ this amount during the previous day, and followed by a further decrease of about $^1/_3$ this amount during the next 24 hours. The cell was also measured against the *M* and saturated calomel cells, and they, in turn, against the hydrogen cells, in order that there might be no doubt in ascribing the drop in potential to the 0.1 *M* cell $B_9$. It should also be mentioned at this point that the diffusion of the saturated potassium chloride solution, from the salt bridge, into the more dilute solution in the calomel cell is greatly increased by a rise in temperature, as might be expected.

By comparing the final concentrations of the potassium chloride solutions withdrawn from the cells, as given in the last column of Table VI, with the theoretical concentrations of potassium chloride corresponding to the e. m. f. given in the fourth column of the same table, it is seen that the decrease in e. m. f. corresponds almost exactly to the increase in the concentration of the solution in the cell; see Fig. 3.

To further confirm the belief that the decrease in the e. m. f. of the cell is not due to the formation of a complex mercuric ion, 5 cc. of the potassium chloride solution from a 0.1 *M* cell, which had shown a decrease in potential due to diffusion, was made approximately 3 *M* with respect to hydrochloric acid, hydrogen sulfide passed into the solution, and the solution then allowed to stand for one hour in a stoppered bottle; no trace of a precipitate of mercuric sulfide was formed.

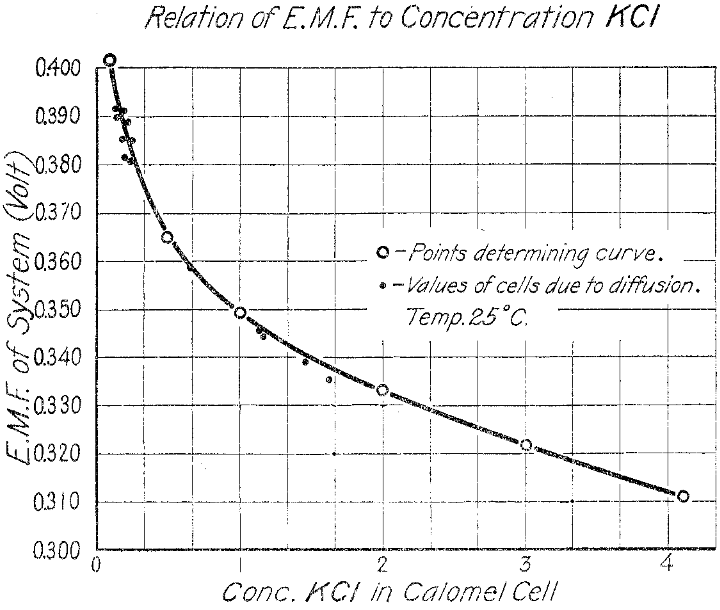

Fig. 3.

It is also to be remarked that the 0.1 *M* and *M* cells when used at 25° in conjunction with a saturated salt bridge were not found reliable over any great length of time, usually not longer than a week. Thus at 25° three 0.1 *M* cells decreased 0.1069 volt (average) after 12 days, while another 3 decreased 0.0016 volt (average) after 7 days; 3 molar cells decreased 0.0014 volt (average) after 15 days; another 3 decreased 0.0013 volt (average) after 6 days, and in the same time their average deviation increased from ±0.0002 to ±0.0006 volt.

### Diffusion of the Saturated Potassium Chloride Solution into the Tenth-molar Hydrochloric Acid Solution of the Hydrogen Cell.

So far mention has been made only of the diffusion of the saturated potassium chloride solution from the salt bridge into the calomel cell, an occurrence which happens when the concentration of the salt solution in the cell is less than that in the salt bridge. There is also a diffusion of the saturated potassium chloride solution from the salt bridge into the hydrochloric acid solution of the hydrogen cell, and it was to offset the effect of this as completely as possible, that the acid of this cell was renewed each day that new measurements were to be made. At 40° this diffusion is quite rapid, while at 55° to 60° it is so rapid that considerable difficulty was encountered in obtaining satisfactory measurements. The best procedure is to draw off the acid solution which is in the siphon tube just before a reading is to be made, then to lower the siphon tube of the cell into the salt bridge and measure the e. m. f. of the combination at once. At 50–60°, when it so happened that the cotton plug had not been fitted snugly enough into the end of the siphon tube, the reading of the potentiometer could be seen to change as much as a millivolt per minute during the first and second minutes in which the siphon tube had been immersed in the salt bridge. At 25°, however, the diffusion into the hydrogen cell is not rapid enough to prevent one from duplicating their values with ease.

## Superiority of the Saturated Potassium Chloride Calomel Cell.

With respect to the durability, accuracy and reproducibility of the saturated potassium chloride calomel cell, the following table, giving the history and measurements of 12 such cells, speaks for itself. Each value represents the average of 3 determinations, using Combination 8 at 25°.

TABLE VII.—HISTORY OF TWELVE SATURATED POTASSIUM CHLORIDE CALOMEL CELLS.

| Cell. | Time in use (days). | E. m. f. of combination 8 (1 atmos. total pressure). Initial Volt. | E. m. f. of combination 8 (1 atmos. total pressure). Final Volt. | Remarks. |
|---|---|---|---|---|
| $S_1$ | 147 | 0.3100 | 0.3101 | Carried around cycle 25–60° |
| $S_2$ | 147 | 0.3101 | 0.3103 | |
| $S_3$ | 71 | 0.3100 | 0.3009 | Destroyed to test KCl for acidity |
| $S_4$ | 143 | 0.3009 | 0.3104 | Carried around cycle 25–60° |
| $S_5$ | 20 | 0.3101 | 0.3102 | |
| $S_6$ | 20 | 0.3009 | 0.3100 | Kept at constant temperature 25° |
| $S_7$ | 8 | 0.3008 | 0.3008 | |
| $S_8$ | 8 | 0.3008 | 0.3007 | Carried around cycle 25–5° |
| $S_9$ | 8 | 0.3100 | 0.3100 | |
| $S_{10}$ | 8 | 0.3100 | 0.3009 | |
| $S_{11}$ | 8 | 0.3009 | 0.3009 | |
| $S_{12}$ | 8 | 0.3009 | 0.3009 | |
| | Average, | 0.3009 | 0.3100 | |

Cells $S_1$, $S_2$, $S_5$ and $S_7$ were used again around the temperature cycle 25–60°, and gave the following results:

| | | | |
|---|---|---|---|
| $S_1$ | 20 | 0.3101 | 0.3100 |
| $S_2$ | 20 | 0.3103 | 0.3104 |
| $S_5$ | 8 | 0.3102 | 0.3008 |
| $S_7$ | 8 | 0.3008 | 0.3008 |

## Conclusions.

1. The e. m. f. of the combination,

$$(8)\ \mathrm{Hg—HgCl\ sat.\ KCl—sat.\ KCl—0.1}\ M\ \mathrm{HCl—H_2(Pt)},$$

has been measured for the temperature range 5–60°, in intervals of 5°.

2. Taking the value of the normal calomel cell at 25° as 0.5648 volt, the value of the saturated potassium chloride calomel cell at 25° is 0.5266 volt. Its temperature coefficient is +0.00020 volt per degree rise in temperature for temperatures within the interval 5–60°.

3. The e. m. f. of the system,

(2) Hg—HgCl $xM$ KCl—sat. KCl—0.1 $M$ HCl—$H_2$ (1 atmos.) Pt,

at 25°, and the value of the electrode potential Hg—HgCl $xM$ KCl in the above system, where $x$ ranges from 0.1 $M$ to saturation (4.12 $M$), have been given.

4. The e. m. f. of the combinations,

(3) Hg—HgCl 0.1 $M$ KCl—sat. KCl—sat. KCl HgCl—Hg,
(4) Hg—HgCl 1.0 $M$ KCl—sat. KCl—sat. KCl HgCl—Hg,
(5) Hg—HgCl 0.1 $M$ KCl—sat. KCl—1.0 $M$ KCl HgCl—Hg,
(6) Hg—HgCl 0.1 $M$ KCl—sat. KCl—0.1 $M$ HCl—$H_2$(Pt),
(7) Hg—HgCl 1.0 $M$ KCl—sat. KCl—0.1 $M$ HCl—$H_2$(Pt),

have been measured for the temperature range 25–40°, in intervals of 5°, and it has been found that these combinations are quite unreliable above 25°, and only reliable at 25° for about one week.

5. It appears that the decrease in the e. m. f. of the 0.1 $M$ and $M$ potassium chloride calomel cells, when used in conjunction with a saturated salt bridge, is due to the diffusion of the concentrated solution of potassium chloride from the bridge into the cell, and not due to the formation of a complex ion as a result of the interaction of the calomel and the potassium chloride solution.

6. In preparing new calomel cells it is necessary to use all new materials, and not simply replace the potassium chloride solution.

7. The saturated potassium chloride calomel cell is the best cell for use in conjunction with a saturated salt bridge, because it has a very small temperature coefficient, is easily reproducible, can safely be used at temperatures from 5° to 60°, and can be relied upon for its constancy of value over long periods of time.

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