includes palladium as one of the outstanding examples of the importance of porosity in the absorption of hydrogen, especially in connection with catalytic problems. Reference should also be made to the recent observations of Alexejew, Afanassjew and Ostroumow,[24] who have investigated the effect of tension on the permeability of iron to electrolytic hydrogen, and from their results have drawn conclusions not dissimilar to those reached in earlier studies of the electrical conduction of palladium–hydrogen, iron–hydrogen, etc.,[22,25] to the effect that the highly absorbent metals display both lacunal and lattice occlusion. The evidence here presented, together with that of our preceding metallographic study,[4] demonstrates, however, that the lacunae concerned are not *inter*granular, as we were previously inclined to suppose, but are situated within the grains, upon the planes of slip.

Summary

Experiments by resistometric methods are described upon the facilities with which pure palladium foils absorb and evolve hydrogen, and the ways in which these facilities are influenced by factors which affect the physical state of the metal.

The factors studied include: time of decay; annealing temperature; rate of cooling; grain size; effect of air; deformation and its degree.

The effects of electrolytic charging and of charging from the gas are compared.

The results confirm and extend those of several earlier observers, and in addition yield the following facts.

Any variations in the metal not caused by mechanical deformation always affect the facilities of absorption and of evolution in the same sense.

Deformation affects, in general, both facilities, whether in like or in opposite senses being sometimes dependent upon its severity.

The rate of occlusion at atmospheric temperature and pressure is independent of time, for both worked and unworked metal.

The results are shown to confirm conclusions previously reached, that diffusion occurs primarily along slip-plane fissures, and only secondarily through the undisordered lattice.

FRICK CHEMICAL LABORATORY
PRINCETON, N. J.
RECEIVED JUNE 12, 1934

[24] D. Alexejew, P. Afanassjew and W. Ostroumow, *Z. Elektrochem.*, **40**, 92–98 (1934).

[25] D. P. Smith, *Z. Physik*, **69**, 253 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

A Thermodynamic Study of Liquid Potassium Amalgams[1]

BY MARION H. ARMBRUSTER[2] AND JAMES L. CRENSHAW

Introduction

The present study was undertaken to investigate the conditions under which the potassium amalgam electrode gives the most reproducible results in aqueous solutions. In a recent paper, Spencer[3] has compared the values for the activity coefficients of potassium chloride obtained by freezing point methods with those obtained by electromotive force measurements and has come to the conclusion that the amalgam electrode is not reliable. There is considerable evidence that electromotive force and freezing point methods agree,[4,5] but since the amalgams do react with aqueous solutions and are admittedly unreliable in dilute solutions, it seemed worth while to make a study of the conditions under which the only appreciable reaction is a reversible transfer of potassium from the amalgam to the solution.

The purpose of the present paper is to determine the effect of the following factors on the reproducibility of the potassium amalgam electrode: (1) the concentration of the amalgam; (2) the concentration of the potassium ion in the aqueous solution; (3) the form of dropping electrode and the rate of flow; and (4) temperature. If in a cell made up as follows

K (c_2) (amalgam)/KCl (solution)/K (c_1) (amalgam)[6,7]

the electrodes are reversible, the only reaction

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[1] This article is based upon the dissertation presented to the Faculty of the Graduate School of Bryn Mawr College by Marion H. Armbruster in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The complete dissertation is on file in the Bryn Mawr College Library.

[2] Helen Schaeffer Huff Memorial Research Fellow.

[3] Spencer, THIS JOURNAL, **54**, 4490 (1932).

[4] Young, *Chem. Rev.*, **13**, 103 (1933).

[5] Smith, THIS JOURNAL, **55**, 3279 (1933).

[6] Cells similar to this have been studied by Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933), using non-aqueous solutions and by

[7] Shibata, *J. Chem. Soc. Japan*, **52**, 352, 365 (1931), using a concentrated potassium hydroxide solution, but the influence of the various factors mentioned above was not investigated.

will be a transfer of potassium from one amalgam to the other. Then, if the free energy of transfer as calculated from the electromotive force measurements agrees with that obtained from freezing point or vapor pressure measurements of the same amalgams or from electromotive force measurements of the same amalgams in non-aqueous solutions of potassium salts in which the amalgams do not react with the electrolyte, it will indicate that the potassium amalgam electrode is reliable in aqueous solutions.

It also seemed desirable to measure a potassium amalgam electrode against the calomel and the silver–silver chloride electrode in potassium chloride solution of known concentration in order to recalculate the standard electrode potential of the potassium electrode without the uncertainty due to the liquid junctions which were present in the measurement of Lewis and Keyes.[8]

The solubility of potassium in mercury from 0 to 35° was also determined experimentally.

Experimental Technique[9]

Purification of Materials

Mercury.—All of the mercury was purified chemically and then twice distilled by Hulett's method.[10]

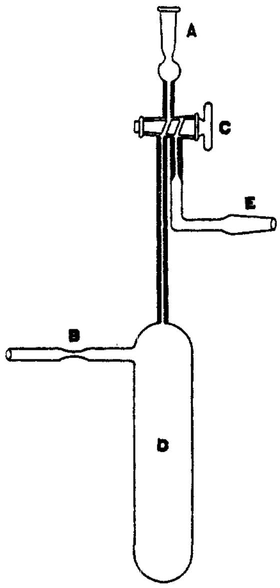

Fig. 1.

Hydrogen.—The hydrogen used in carrying out all of the operations was carefully purified, special precautions being taken to remove oxygen and water vapor.

Potassium Carbonate and Potassium Chloride.—These salts were purified by recrystallization of high-grade analyzed chemicals.

Amalgams

Preparation and Handling.—The amalgams were prepared by the electrolysis of a saturated solution of potassium carbonate using an ample mercury cathode and an anode of platinum foil. During the preparation the amalgam was stirred by bubbling a stream of pure nitrogen up through it. After preparation, the amalgam was filtered directly into the vessel shown in Fig. 1, which had been previously evacuated. This receptacle proved very convenient for handling the amalgams and for transferring them to any desired piece of apparatus *in vacuo*.

The amalgams thus prepared did not differ in appearance from pure mercury and remained unchanged however long they were kept.

Analysis.—The sample of amalgam was added to a slight excess of standard hydrochloric acid. When the extraction of potassium was complete, the excess of acid was titrated with barium hydroxide, using rosolic acid as indicator and stirring the solution with a current of carbon dioxide-free air. The mercury was then washed, dried in a vacuum desiccator and weighed.

Several duplicate analyses of the amalgams were always made. The accuracy of the analytical method may be seen from the data given under the solubility of potassium in mercury.

Electrolyte.—Much precaution was taken to have the electrolyte free of all dissolved air and well saturated with pure hydrogen.

Electrode Vessels.—The electrode vessels EE (Fig. 2) finally adopted for the flowing amalgams were somewhat similar to types previously used.[11,12] GG had ground seals which fitted into the ground seal A of the receptacle for a filling *in vacuo*. Before filling an electrode vessel with amalgam *in vacuo*, the capillary of the dropper H was filled with mercury through the bore of the stopcock, and the bore of the stopcock in the side-tube F was evacuated.

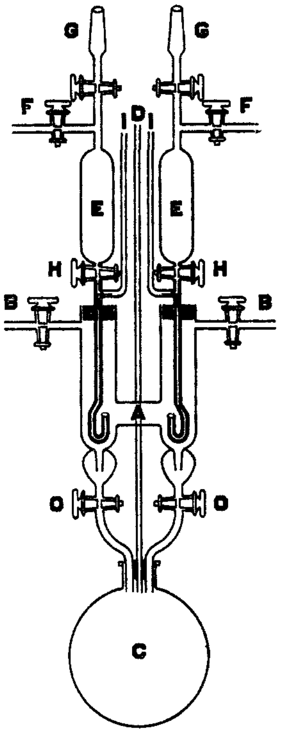

Fig. 2.

Besides electrode vessels with U-shaped droppers, electrode vessels with drawn-down capillary droppers, that is, jet droppers, were employed.

The Cell and its Manipulation.—The cell employed (Fig. 2) was very simple in design. By a proper manipulation of the stopcocks, all the air in the cell was replaced by hydrogen before the introduction of the air-free electrolyte. Hydrogen was also introduced above the amalgams in the electrode vessels. The hydrogen was sufficiently pure to allow the surface of the amalgams to remain bright during a run. After assemblage, the apparatus was lowered into a specially constructed, glass-walled thermostat, maintained at the desired temperature within ±0.01°.

In measurements for which flowing electrolyte was used, the method of procedure was the same except that the electrolyte was introduced by means of the side-tubes BB. In these cases, the electrolyte was previously boiled

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[8] Lewis and Keyes, This Journal, **34**, 119 (1912).

[9] A detailed description of the apparatus and method will be found in the dissertation by M. H. Armbruster, Bryn Mawr College, 1934.

[10] Hulett, *Phys. Rev.*, **21**, 388 (1905)

[11] Lewis and Kraus, This Journal, **32**, 1459 (1910).

[12] Scatchard and Tefft, *ibid.*, **52**, 2265 (1930).

out *in vacuo* and saturated with hydrogen in a flask provided with two tubes bearing stopcocks. During a measurement, the electrolyte flowed in at one of the sidetubes B and out through stopcocks OO into flask C.

Potentiometer.—The electromotive force measurements were made using a Leeds and Northrup potentiometer of type K which recently had been rebuilt and recalibrated. The standard Weston cell, against which all measurements were made, was checked at the Palmer Physical Laboratory of Princeton University through the kindness of Dr. Walter C. Michels and had an e. m. f. of 1.0175 volts at 25°.

Experimental Results

As preliminary work, the effect on the reproducibility of the potassium amalgam electrode of such factors as type and concentration of electrolyte, stationary or flowing electrolyte, form of dropping electrode, rate of flow and concentration of amalgam was investigated. In studying all but the last two factors, the same concentration cell consisting of a concentrated potassium amalgam (0.4395 g. K/100 g. Hg) and a dilute standard potassium amalgam (0.0500 g. K/100 g. Hg) was used since it had given repeatedly the reproducible value of 90.5 (±0.1) millivolts. With 0.1 and 1.0 *N* potassium chloride as an electrolyte, this same electromotive force of 90.5 (±0.1) millivolts was obtained irrespective of whether the electrolyte was stationary or flowing, or whether the U-shaped or jet form of dropping electrode was used. With 0.01 *N* potassium chloride and the U-droppers, a value of 88.0 was obtained but with a lesser degree of reproducibility (±1.0 for stationary and 2.0 for flowing electrolytes). With a jet electrode a higher value and greater reproducibility were obtained 90.2 (±0.2) millivolts. With 0.001 *N* potassium chloride still lower values were again obtained, namely, 65.0 (±5.0) for the U-dropper and 89.5 (±1.5) millivolts for the jet electrode. With 0.01 *N* potassium hydroxide the potential was 90.0 (±0.5), while 1.0 *N* sodium chloride or a mixture of 0.1 *N* potassium chloride and 0.9 *N* sodium chloride gave 98.0 (±7.0) and 100.0 (±5.0) millivolts, the electrolyte being stationary and a U-dropper electrode being used in each case. The low e. m. f.'s obtained with very dilute potassium chloride may be due either to a lowering of the ratio of the concentrations of the two amalgams or a change in the electrolyte. The first explanation would imply an increased rate of decomposition of the amalgams (especially the more concentrated one) in these dilute solutions, but this seems improbable as the activity of the hydrogen ion (or of the water molecule) cannot be much greater in 0.01 *N* than in 0.1 *N* potassium chloride. The formation of potassium hydroxide to a greater extent around the concentrated than around the dilute amalgam would, however, decrease the total electromotive force (due both to an increase in concentration of the potassium ion and to a liquid junction between potassium hydroxide and potassium chloride) and this effect would be the more noticeable the more dilute the solution of potassium chloride. If this is the correct explanation, the layer of potassium hydroxide must be formed very rapidly and be difficult to remove since with the U-shaped droppers the use of flowing electrolyte caused no improvement in 0.01 *N* solutions and even the jet droppers gave an electromotive force which was 0.3 millivolt low. The result obtained with 0.01 *N* potassium hydroxide is in agreement with this explanation as there would be less reaction in this case. The measurement using a mixed electrolyte 0.1 *N* in potassium chloride and 0.9 *N* in sodium chloride was made to see if the amalgam electrode is reversible to the ion in question when a large concentration of other ions is also present. That this obviously is not the case is indicated by the very high value 100.0 (±5.0) millivolts obtained. Judging from the electromotive forces, the amalgams do not appear to behave any more reversibly in the mixed electrolyte than in pure sodium chloride.

The effect of the rate of flow of the amalgams on the electromotive force was studied in each cell investigated. The only consistencies noted were: (a) most accurate readings were obtained if both electrodes were flowing uniformly at a rate of five or more drops per minute. (A uniform rate of ten drops per minute proved very satisfactory.) (b) The electromotive forces decreased when both amalgams were kept stationary. (In a very few cases the electromotive force reading was at first high, but finally fell off to a lower value.) (c) Highest values were obtained when the dilute amalgam was stationary and the concentrated amalgam was flowing. (d) Lowest values were obtained when the concentrated amalgam was stationary and the dilute amalgam was flowing.

It seems probable that the fall in electromotive force observed when both amalgams were stationary is due to a change in the concentrations of the amalgams rather than to any change in potential which might be caused by the formation of a very small amount of potassium hydroxide in a relatively concentrated solution of potassium chloride (usually 1 normal). If both amalgams were losing potassium at the same relative rate, the electromotive force would remain constant. If the loss of potassium from the two amalgams increased the ratio of the concentrations of the two amalgams, the electromotive force would increase, and *vice versa.* Here the decrease of the electromotive force indicates that decomposition of both amalgams results in a decreased ratio of their concentrations, indicating that the concentrated amalgam lost potassium relatively more rapidly. If one amalgam is kept stationary and the other allowed to flow (thus keeping its potential constant), it is possible to estimate the rate at which the stationary amalgam is losing potassium, provided the relation between electromotive force and concentration is known (see equations (1), (2) and (3)). Such calculations indicate that, in general, the concentration of potassium decreases relatively more rapidly in the more concentrated amalgams.

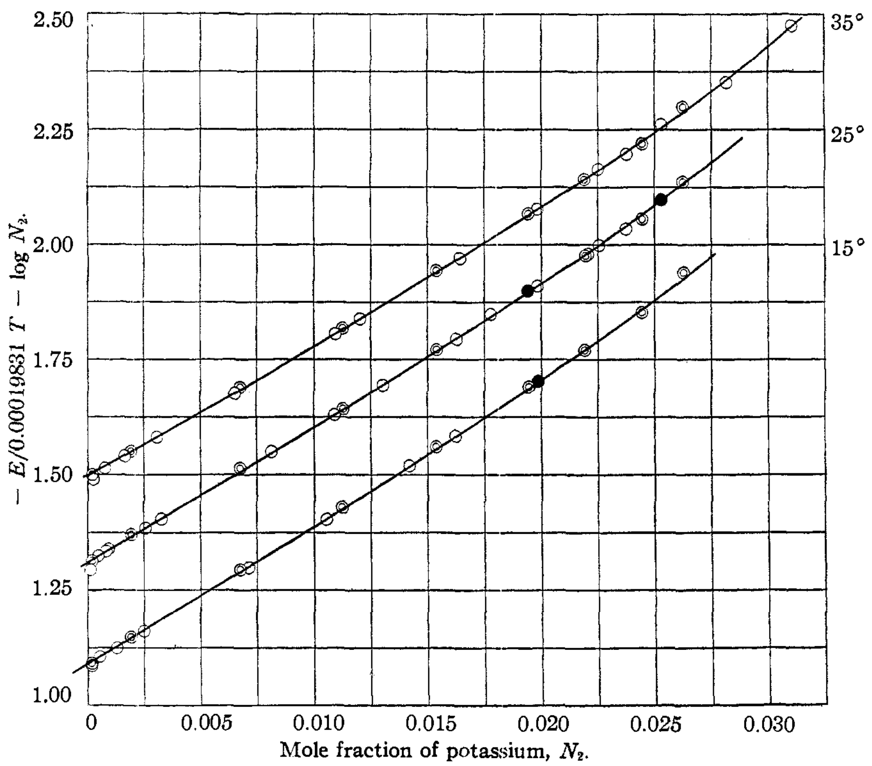

Fig. 3.—○, Armbruster and Crenshaw; ◎, Bent and Gilfillan; ●, both.

Following these preliminary experiments, an attempt was made to determine approximately the range of concentration of amalgam within which the potassium amalgam electrode gives reproducible values. Measurements of the potassium amalgam concentration cell

K (c_2) (amalgam)/KCl (1 N)/K (c_1) (amalgam)

were made at 25° over the range of concentrations of liquid potassium amalgams from 0.0005 g. K/100 g. Hg up to saturation. The electrolyte was kept stationary and the U-shaped form of dropping electrode was employed. One electrode vessel was filled with dilute standard amalgam (0.0500 g. K/100 g. Hg) and the other contained potassium amalgams of various concentrations made up by adding a definite weight of analyzed potassium amalgam to a weighed amount of mercury. It was found that when the amalgams were as concentrated as 0.01 g. K in 100 g. Hg, the electromotive forces were easily reproducible to better than 0.1 millivolt. For amalgams more dilute than this, the reproducibility decreased progressively with increasing dilution, the most dilute amalgam measured showing a variation of ±10 millivolts. These very dilute amalgams also seem to give too great an electromotive force against the standard, since a plot of the data (*cf.* Fig. 3) shows that the value of the quantity ($-E/0.00019831\ T - \log N_2$) for amalgams as dilute as this falls considerably below the best curve drawn. The most dilute amalgam (0.0005 g. K/100 g. Hg) gave an average electromotive force which is more than twenty millivolts off the curve. If this is due entirely to a change in concentration of the amalgam, it means that this amalgam loses more than half of its potassium almost instantaneously when it comes in contact with an aqueous solution. Whereas it seems that for a pair of amalgams of moderate concentrations the more concentrated loses its potassium relatively more rapidly, when one amalgam is very dilute this is no longer the case. As in the case of cadmium and zinc amalgams,[13,14] potassium amalgams when very dilute seem to lose their dissolved metal very rapidly when in contact with aqueous solutions. The reason for this behavior is not clear, but it is obvious that potassium amalgams more dilute than 0.01 g. K/100 g. Hg should not be used.

TABLE I

ACTIVITY OF POTASSIUM IN AMALGAMS AT 15°

N_2	$-E$ calcd., volts	$-E$ obs., volts	Δ mv.	a_2
0.01984 (satd.)	+0.00017	0	0	0.08186
.01622	− .01188	−0.01182	±0.02	.05036
.01418	− .01902	− .01890	± .02	.03778
.01055	− .03287	− .03279	± .01	.02163
.007121	− .04854	− .04851	± .03	.01150
.002503	− .08224	− .08226	± .04	.002959
.001300	− .10050	− .10064	± .05	.001418
.000526	− .12424	− .12418	± .08	.000545
.000194	− .14955	− .1501	± .3	

ACTIVITY OF POTASSIUM IN AMALGAMS AT 25°

N_2	$-E$ calcd., volts	$-E$ obs., volts	Δ mv.	a_2
0.02530 (satd.)	0.01705	0.01733	±0.02	0.1523
.02375	.01234	.01191	± .02	.1268
.02254	.00861	.00851	± .02	.1096
.02252	.00854	.00844	± .02	.1094
.02205	.00708	.00683	± .02	.1033
.01984	.00007	0		.07864
.01941	− .00132	− .00117	± .03	.07450
.01777	− .00671	− .00657	± .02	.06037
.01628	− .01177	− .01191	± .01	.04958
.01301	− .02359	− .02359	± .02	.03130
.01091	− .03191	− .03192	± .02	.02263
.008113	− .04449	− .04421	± .03	.01387
.003272	− .07614	− .07618	± .02	.004044
.002669	− .08239	− .08217	± .02	.003171
.002620	− .08295	− .08281	± .03	.003103
.002568	− .08355	− .08341	± .02	.003031
.002559	− .08365	− .08367	± .02	.003018
.000917	− .11274	− .11267	± .06	.000972
.000819	− .11581	− .11590	± .1	.000863
.000472	− .13053	− .13066	± .02	.000486
.000111	− .16829	− .16955	± .1	

ACTIVITY OF POTASSIUM IN AMALGAMS AT 35°

N_2	$-E$ calcd., volts	$-E$ obs., volts	Δ mv.	a_2
0.03106 (satd.)	0.03539	0.03613	±0.02	0.2866
.02819	.02656	.02605	± .02	.2055
.02530	.01757	.01762	± .03	.1464
.02375	.01268	.01206	± .04	.1218
.02252	.00875	.00860	± .02	.1051
.01984	.00002	0		.07561
.01642	− .01164	− .01159	± .03	.04873
.01203	− .02809	− .02790	± .05	.02622
.01094	− .03259	− .03238	± .04	.02213
.006510	− .05419	− .05408	± .04	.009809
.003069	− .07999	− .07991	± .05	.003711
.001644	− .09892	− .09887	± .04	.001819
.000762	− .12077	− .12095	± .1	.000798
.000254	− .15076	− .1516	± .3	

The data of the measurements made at 15, 25 and 35° are recorded in Table I. The first column gives the concentration in terms of mole fraction of potassium; the second column represents the electromotive force in volts calculated from empirical equations (1), (2) and (3), of any particular amalgam measured against a "least-square" standard amalgam; the third column gives the corresponding observed electromotive force in volts; the fourth column indicates the variation in millivolts of the observed electromotive force during the measurements; and the last column gives the activity of potassium in the amalgam.[15]

The experimental data have been treated analogously to Lewis and Randall's[16] treatment of the data for thallium amalgams obtained by Richards and Daniels.[17] By plotting the expression ($-E/0.00019831\ T - \log N_2$) against the mole fraction of potassium, N_2, the points in Fig. 3 are obtained. (The data of Bent and Gilfillan[6] have been included in these plots and will be discussed later.)

The curves drawn in Fig. 3 are plots of the empirical equations (1), (2) and (3), respectively, corresponding to series of measurements made at temperatures of 15, 25 and 35°. (In order to separate the curves, the plots of measurements at 25 and 35° have been displaced vertically by adding the arbitrary constants 0.2063 and 0.3750, respectively, to the ordinates.) The equations were obtained from the experimental data by the method of least squares, the most dilute amalgam being omitted in each case. In these equations, E is the electromotive force in volts of an amalgam of mole fraction N_2 measured against an idealized "least-square" amalgam of mole fraction 0.019844 at the temperature indicated.[18]

$$\frac{-E_{288}}{0.057153} - \log N_2 = 1.0900 + 28.9885\ N_2 - 3.90\ N_2^2 + 5367\ N_2^3 \quad (1)$$

$$\frac{-E_{298}}{0.059135} - \log N_2 = 1.1056 + 27.705\ N_2 + 123.02\ N_2^2 \quad (2)$$

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(13) Hulett and De Lury, THIS JOURNAL, **30**, 1805 (1908).

(14) Crenshaw, *J. Phys. Chem.*, **14**, 158 (1910).

(15) In the use of all data, the physical constants employed are those of Birge, *Phys. Rev. Supplement, Reviews of Modern Physics*, 1 (1929).

(16) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 352.

(17) Richards and Daniels, THIS JOURNAL, **41**, 1736 (1919).

(18) If the actual amalgam of mole fraction 0.019844 is taken as a standard for calculation, it is equivalent to forcing the curves in Fig. 3 to pass through the point for this amalgam. The least square solution avoids the giving of infinite weight to this one point on each curve.

$$\frac{-E_{308}}{0.061119} - \log N_2 = 1.1218 + 26.478\ N_2 + 130.37\ N_2^2 + 564.0\ N_2^3 \quad (3)$$

Since the equations were obtained by the method of least squares, the electromotive force calculated from them should be more accurate than the single observations although the electromotive force in a single experiment rarely varied by more than 0.03 millivolt. The probable error in calculating the electromotive forces at 15° from equation (1) is estimated as ±0.07 millivolt; in the case of electromotive forces at 25 and 35° calculated from equations (2) and (3), respectively, the corresponding probable error is ±0.12 and ±0.19 millivolt. It is interesting that the probable error increases with the temperature. This is perhaps due to an increase in the rate of reaction of the amalgams with the water solution. As will be seen, the calculated and observed values of the electromotive force agree most closely for mole fractions of potassium between about 0.0005 and 0.02. The relatively large probable error is caused largely by the deviations outside of this range. It is surprising that the more concentrated amalgams do not give more uniform results and no explanation of this fact can be given. Figure 3 also shows that the points for the more concentrated amalgams do not fall on any smooth curve that can be drawn. Apparently then, most reliable results are obtained if the amalgams are not more dilute than 0.01 g. K/100 g. Hg and not more concentrated than 0.40 g. K/100 g. Hg, corresponding roughly to the mole fractions given above.

Discussion of Results

Through these series of measurements, the reliability of the potassium amalgam electrode can be indicated conclusively only by agreement of the free energy values obtained for the transfer of potassium from one amalgam to another with those obtained by independent methods. First, an attempt was made to use the vapor pressure measurements of potassium amalgams by Millard.[19] These data were obtained for temperatures of 200 to 300° and extrapolation to the temperature of our measurements did not prove feasible. However, the recent work of Bent and Gilfillan[6] has afforded an independent method for comparison since electromotive force measurements of potassium amalgams in non-aqueous solution of potassium salts, in which the amalgams do not react with the electrolyte, were made.

The good agreement of the two investigations is shown graphically in Fig. 3. The two sets of data may be brought together in this type of plot by merely shifting the curves along the ordinate until they coincide. The two series of results at each temperature fall on curves of similar slopes, and within the lower range of concentration agree well. The only exception to this is the case of our most dilute amalgams which do fall off the curve as has already been stated. In the more concentrated range of liquid potassium amalgams, it is seen that the results of Bent and Gilfillan do not fall any more regularly on the line drawn than do ours. In their paper,[6] they use an equation analogous to equations (1), (2) and (3) but containing the fourth power of N_2 and omitting the square and cube. Their equation does not fit all the results any better than the ones given above. In general, their points which fall most off the curves in Fig. 3 are those for which their calculated and observed values are in poor agreement, the differences in some cases being as much as 0.6 millivolt. Their calculated values would fall much better on the curves. These discrepancies cannot be explained at present. However, it does seem to indicate that potassium amalgams more concentrated than about 0.02 mole fraction do not behave analogously to amalgams less concentrated than this, and their behavior cannot be expressed, with great accuracy, as simply.

Comparison of the two investigations may be made also by calculation of the three thermodynamic quantities, partial molal free energy, partial molal heat content, and partial molal entropy using round values of the concentration. Taking solid potassium as the reference state,[20] these partial molal quantities for potassium were calculated from equations (1), (2) and (3) and the measurements of Lewis and Keyes,[8] who found the electromotive force between solid potassium and an amalgam of mole fraction 0.011267 to be 1.0478 volts at 25° (corrected to the new international volt) and the temperature coefficient to be −0.000272 volt per degree. From the above equations and the Duhem equation, the following equations were obtained for the activity coefficients of mercury in these amalgams at 15, 25 and 35°, respectively.

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[19] Millard, THIS JOURNAL, 49, 3003 (1927).

[20] In calculating the activity of potassium (Table I), an infinitely dilute amalgam has been taken as the reference state.

$$\log (a_1/N_1) = -14.49\ N_2^2 - 7.1\ N_2^3 - 4030\ N_2^4 \qquad (4)$$

$$\log (a_1/N_1) = -13.85\ N_2^2 - 91.2\ N_2^3 - 68\ N_2^4 \qquad (5)$$

$$\log (a_1/N_1) = -13.24\ N_2^2 - 95.7\ N_2^3 - 495\ N_2^4 \qquad (6)$$

These equations were used in calculating the corresponding partial molal quantities for mercury. Since the values obtained were practically identical with those given by Bent and Gilfillan[6] only a few of them have been recorded in Table II. Some of their results, indicated by (B), have been included for comparison. In order to show the very satisfactory agreement between the two investigations, the free energy of transfer of potassium ($\Delta \overline{F}_2'$) from each of the amalgams to the one of mole fraction 0.001 is given, since these values are independent of the value of the potassium electrode.

TABLE II

THERMODYNAMIC QUANTITIES FOR POTASSIUM AMALGAMS

Quantity	Temp., °C.	$N_2 = 0.001$	$N_2 = 0.005$	$N_2 = 0.01$	$N_2 = 0.02$
$-\Delta \overline{F}_2$	15	26,020	24,940	24,350	23,520
	25	26,010	24,900	24,290	23,450
(B)[a]	25	26,019	24,906	24,295	23,465
	35	26,000	24,860	24,230	23,370
$-\Delta \overline{F}_2'$	15	0	−1,075	−1,669	−2,496
(B)	15	0	−1,079	−1,674	−2,488
	25	0	−1,108	−1,720	−2,559
(B)	25	0	−1,113	−1,724	−2,554
	35	0	−1,139	−1,765	−2,623
(B)	35	0	−1,145	−1,772	−2,619
$\mathrm{d}E/\mathrm{d}T$	15–25	−0.000032	−0.000177	−0.000257	−0.000309
	25–35	− .000071	− .000203	− .000261	− .000346
$-\Delta \overline{H}_2$	25	26,370	26,210	26,070	25,700
$-\Delta \overline{S}_2$	25	1.19	4.38	5.97	7.55
$-\Delta \overline{F}_1$	25	0.6056	3.462	7.961	20.53
$-\Delta \overline{H}_1$	25	0.02113	0.4502	1.460	7.260
$-\Delta \overline{S}_1$	25	−0.001960	−0.01010	−0.02180	−0.04450

[a] Bent and Gilfillan apparently did not correct the electromotive force of Lewis and Keyes to the new volt. If we use the uncorrected value, our results are in even better agreement with theirs.

The values for the formation of KHg_{12}[21] (from $\Delta \overline{F}_1$ and $\Delta \overline{F}_2$ for the saturated amalgams) determined by the two investigations also show excellent agreement. Our value for the free energy of formation of solid KHg_{12} at 25° is −23,424 calories (corrected to the new volt) and −23,431 calories (not corrected to the new volt), which is very close to their value −23,430 calories (apparently not corrected to the new volt).

The close agreement of the free energy values seems to indicate rather conclusively that the only significant reaction both in aqueous and nonaqueous cells of this type is a transfer of potassium from one amalgam to the other. Therefore, the potassium amalgam electrode when used under the proper conditions may be considered reversible to the potassium ion in water solutions.

The Standard Electrode Potential of Potassium

To recalculate the standard electrode potential of potassium without the uncertainty due to liquid junctions as in Lewis and Keyes[8] measurement, a potassium amalgam of mole fraction 0.002559 was measured at 25° against both the calomel electrode and the silver–silver chloride electrode in aqueous potassium chloride solution of known concentration.

Calomel Electrodes.—The calomel was prepared electrolytically using mercury and molar hydrochloric acid. The method of preparation and apparatus used was the same as that employed in the preparation of mercurous sulfate and mercurous chloride by Hulett.[22,23] A current density of 2 amperes per hundred square centimeters of electrode surface was used. The crystalline product was slightly gray in color due to the presence of finely divided mercury. The potassium chloride solution used in these measurements had been boiled out, saturated with hydrogen and analyzed.

Silver–Silver Chloride Electrodes.—Several types of silver–silver chloride electrodes were tried.

Type 1.—This was the same as Güntelberg[24] has found extremely reproducible. This kind of

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[21] Smith and Bennett, THIS JOURNAL, **32**, 624 (1910).

[22] Hulett, *Phys. Rev.*, **22**, 334 (1906); **32**, 261 (1911).

[23] Hulett, THIS JOURNAL, **38**, 22 (1916).

[24] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

electrode was finally discarded since it was very difficult to obtain good contact and since the other types were simpler to prepare and proved reproducible.

Type 2.—These were prepared according to the directions given by Noyes and Ellis.[25]

Type 3.—This type proved most satisfactory. It is the same as Type 2 except that no electrolytic silver is deposited on the platinum spiral. Thus, there is the advantage of not having to wash the electrode free of all traces of electroplating solution. The electrodes of Type 2 and also those of Type 3 gave closely agreeing electromotive forces. The results with Type 3 electrodes were, however, almost 0.1 millivolt higher than with Type 2 electrodes.

For a measurement, one side of the H-cell (Fig. 2) contained the U-dropper and the other either four calomel electrodes or three silver–silver chloride electrodes. Previous to measuring the electromotive force of the cell, these electrodes were left in contact with the potassium chloride solution for a period of twenty-four hours.

In Table III the mean values of the electromotive force at 25° of an amalgam of mole fraction 0.002559 measured against the calomel electrodes in 0.10245 M potassium chloride and of the same amalgam measured against the silver–silver chloride electrodes in 1.0168 M potassium chloride are given; the total variation in volts during a series of twenty or more measurements for each determination is indicated. Since an electromotive force greater than 1.5 volts could not be read on the potentiometer, a Weston cell, repeatedly checked during the measurements, was put in opposition in the circuit. The rate of flow of the amalgam during measurements with the calomel electrodes was 12 to 14 drops per minute, and during measurements with the silver–silver chloride electrodes was 13 to 16 drops per minute. As Table III indicates, these electrodes were all reproducible within ±0.03 millivolt. The mean value of the several silver–silver chloride electrodes of Type 3 was about 0.06 millivolt greater than that of silver–silver chloride electrodes of Type 2.

TABLE III

ELECTROMOTIVE FORCE MEASUREMENTS AT 25° OF THE CELLS

$$\begin{array}{l|l|c|l} \text{K amalgam} & \text{KCl} & \text{HgCl} & \text{Hg}\quad E_{298} = 1.2029 + 1.01875 \\ (N_2 = 0.002559) & (0.10245\ M) & & \qquad\qquad = 2.2217 \text{ volts} \end{array}$$

$$\begin{array}{l|l|c|l} \text{K amalgam} & \text{KCl} & \text{AgCl} & \text{Ag}\quad E_{298} = 1.0516 + 1.01876 \\ (N_2 = 0.002559) & (1.0168\ M) & & \qquad\qquad = 2.0704 \text{ volts} \end{array}$$

Electrode	No. 1	No. 2	No. 3	No. 4	Weston cell
Hg/HgCl	1.20293 ±0.00002	1.20295 ±0.00002	1.20292 ±0.00003	1.20295 ±0.00003	1.01875 ±0.00001
Ag/AgCl (Type 2)	1.05156 ±0.00002	1.05153 ±0.00001	1.05153 ±0.00002		1.01876 ±0.00002
Ag/AgCl (Type 3)	1.05160 ±0.00003	1.05159 ±0.00002	1.05163 ±0.00002		1.01876 ±0.00001

From equation (2) we find that our amalgam would have given an electromotive force of 0.0532 volt against the amalgam used by Lewis and Keyes[8] and therefore 1.1010 volts against solid potassium. By combination of this with our measurements given in Table III we obtain for

$$\begin{array}{l|l|l|l} \text{K (s)} & \text{KCl} & \text{HgCl} & \text{Hg, } E_{298} = 2.2217 + 1.1010 \\ & (0.10245\ M) & & \qquad\qquad = 3.3227 \end{array}$$

$$\begin{array}{l|l|l|l} \text{K (s)} & \text{KCl} & \text{AgCl} & \text{Ag, } E_{298} = 2.0704 + 1.1010 \\ & (1.0168\ M) & & \qquad\qquad = 3.1714 \end{array}$$

For further calculations, it is necessary to know the activity coefficients for these concentrations of potassium chloride. Using the empirical equation given by Harned[26]

$$\log \gamma = -\frac{0.356\sqrt{2c}}{1 + 0.76\sqrt{2c}} + 1.0171(2c) - \log (1 + 0.036\ m)$$

in which c is the normality[27] and m is the molality, we obtain: $\gamma = 0.7625$ when $m = 0.10245$; and $\gamma = 0.5975$ when $m = 1.0168$. By interpolation in the table given by Spencer,[3] we find for γ at the above concentrations 0.769 and 0.612, respectively.[28] From the equation

$$E = E^0 - \frac{RT}{NF}\log_e(\text{K}^+)(\text{Cl}^-) = E^0 - 0.1183 \log m\gamma$$

there is obtained for

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[25] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).

[26] Harned, *ibid.*, **51**, 424 (1929).

[27] Determined from the densities of the potassium chloride solutions given in "Int. Crit. Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 87.

[28] There is apparently an error in Spencer's table at $m = 0.2$. We have used the value 0.7215 for γ at this concentration, which agrees with the value of $-\log \gamma$ given.

$$\mathrm{K(s)/K^+(l)//Cl^-(l)/HgCl/Hg}\quad \begin{cases} E^0_{298} = 3.3227 - 0.1310 = 3.1917\ \text{v.}\ \ \text{(H)} \\ E^0_{298} = 3.3227 - 0.1305 = 3.1922\ \text{v.}\ \ \text{(S)} \end{cases}$$

and for

$$\mathrm{K(s)/K^+(l)//Cl^-(l)/AgCl/Ag}\quad \begin{cases} E^0_{298} = 3.1714 - 0.0256 = 3.1458\ \text{v.}\ \ \text{(H)} \\ E^0_{298} = 3.1714 - 0.0244 = 3.1470\ \text{v.}\ \ \text{(S)} \end{cases}$$

from the activity coefficients of Harned (H) and Spencer (S), respectively. Using the present generally accepted values of -0.2676 volt,[29,30,31] for the standard calomel electrode potential and -0.2221 volt[26,29,31,32] for that of the silver–silver chloride electrode, we obtain for

$\mathrm{K(s)/K^+{}_{(HgCl/Hg)}}$ $E^0_{298} = 2.9241$ v. (H); 2.9246 v. (S)
$\mathrm{K(s)/K^+{}_{(AgCl/Ag)}}$ $E^0_{298} = 2.9237$ v. (H); 2.9249 v. (S)

As can be seen, our measurements do not agree very well with the activity coefficients given by either Harned[26] or Spencer.[3] If we take the average of Harned's and Spencer's activity coefficients (namely, 0.766 for $m = 0.10245$ and 0.605 for $m = 1.0168$), the agreement is much better. For example

$\mathrm{K(s)/K^+{}_{(HgCl/Hg)}}$ $E^0_{298} = 2.9244$ v. (av. H and S)
$\mathrm{K(s)/K^+{}_{(AgCl/Ag)}}$ $E^0_{298} = 2.9243$ v. (av. H and S)[33]

We believe the value 2.9243 volts is not in error by more than half a millivolt. This value is not very different from that given by Lewis and Randall[16] (p. 417). Their value for the molal electrode potential of potassium is 2.9224 volts, and being dependent on the standard calomel electrode potential very probably becomes 2.9241 volts,[29,34] using the present value (-0.2676 v.) mentioned above for this electrode.

Solubility of Potassium in Mercury

The only actual experimental data for the solubility of potassium in mercury to be found in the literature are those roughly approximated by Kerp and co-workers.[35] For this reason, it was of interest to determine the solubility of potassium in mercury over the temperature range of 0 to 35°. Samples of potassium amalgams were drawn off at 5° intervals within this temperature range from liquid amalgams in equilibrium with large crystals of the solid phase at the particular temperature. The method of analyzing these samples was similar to that already described.

The method of least squares was applied to the results (omitting the result at 35°) and the following equation obtained

$$x = 0.2502 + 8.686 \times 10^{-3}t + 6.091 \times 10^{-5}t^2 \quad (7)$$

in which x is the grams of potassium per hundred grams of mercury and t is the temperature in degrees centigrade. The graph of this equation and the experimental data are shown in Fig. 4. Bent and Gilfillan[6] give data for the solubility of potassium in mercury, which were obtained by the simultaneous solution of two of their empirical equations. In this way they were able to calculate the mole fraction of an amalgam which would give zero electromotive force against a two-phase amalgam at any temperature. Using their equations, we have made independent calculations for the temperatures of Table IV but have not been able to check their results exactly. These data ("obs" B) have been recorded in Table IV together with the values calculated from equation (7) and our results obtained by analysis. For the most part, our determinations agree well with the "observed" values of Bent and Gilfillan. They do not agree so well, however, with the values calculated from their empirical equation representing the solubility of potassium in mercury as a function of the temperature. The calculated and

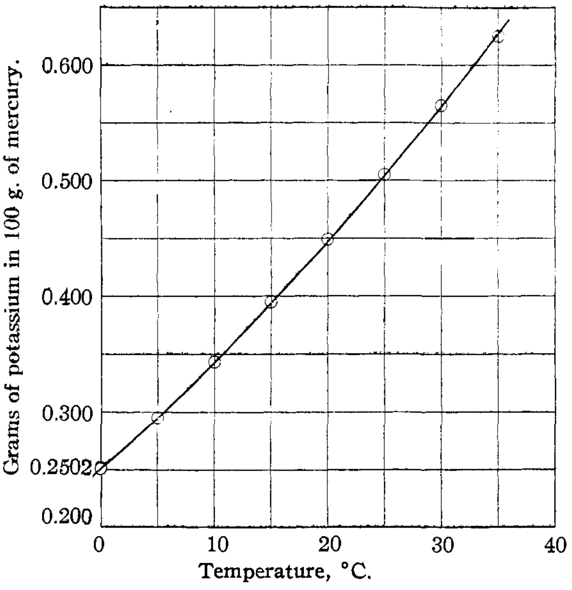

Fig. 4.

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(29) "Int. Crit. Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 332.

(30) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

(31) Spencer, *ibid.*, **54**, 3467 (1932), gives 0.2677 v.

(32) Carmody, *ibid.*, **54**, 192 (1932). (Carmody gives -0.2223 volt, Harned[26] -0.2224 volt and Spencer[31] -0.2222 volt.)

(33) Interpolating from the very recent values of γ given by Robinson and Sinclair [THIS JOURNAL, **56**, 1830 (1934)] we obtain 2.9243 v. through HgCl and 2.9240 v. through AgCl.

(34) Gerke, *Chem. Rev.*, **1**, 377 (1925).

(35) Kerp, *et al.*, *Z. anorg. allgem. Chem.*, **17**, 300 (1898); **25**, 1 (1900).

TABLE IV

SOLUBILITY OF K IN Hg IN GRAMS OF K IN 100 GRAMS OF Hg

	0°	5°	10°	15°	20°	25°	30°	35°
	0.25074	0.29446	0.34266	0.39458	0.44898	0.50553	0.56547	0.62479
	.25086	.29461	.34277	.39442	.44894	.50560	.56529	.62488
				.39460		.50515	.56515	.62467
							.56561	
Av.	.2508	.2945	.3427	.3945	.4490	.5054	.5654	.6248
Calcd.	.2502	.2952	.3432	.3942	.4483	.5054	.5656	.6288
"Obs." B	.2509	.2948	.3430	.3950	.4499	.5071	.5659	.6250

observed values agree very closely, except for the value at 35°, in both investigations. The observed value for 35° is, however, considerably lower than the calculated, which seems to indicate that between 30 and 35° a change takes place in the nature of the solid phase, causing a break in the solubility curve. Accurate determinations of the solubility at temperatures above 35° are necessary to settle this point since Kerp and Böttger[35] state that the solid phase, KHg_{12}, is stable from 0 to 72°.

Summary

1. The electromotive force of the concentration cell

K (c_2) (amalgam)/KCl (solution)/K (c_1) (amalgam)

has been measured at 15, 25 and 35° over a wide range of concentrations of liquid potassium amalgams using aqueous electrolyte and dropping electrodes.

2. It may be concluded from this investigation that: (a) amalgams of a concentration less than 0.01 g. of potassium per hundred grams of mercury do not give reliable electromotive force values. Under proper conditions, amalgams of concentrations between 0.01 and 0.40 g. of potassium per hundred grams of mercury give electromotive forces which are reproducible to a few hundredths of a millivolt. (b) With amalgams in the above range of concentration, if the concentration of the electrolyte is as great as 0.1 *N*, reproducible electromotive forces are obtained regardless of whether the electrolyte is stationary or flowing and regardless of whether the U-shaped or jet form of dropping electrode is used. (c) Whereas the form of dropping electrode is immaterial in working with electrolytes of a concentration as great as 0.1 *N*, the jet form is to be preferred if electrolytes of lower concentration than this are used. (d) Variation of a uniform rate of flow of both amalgams from one drop per minute to a continuous stream produced only slight fluctuations of the potentials measured. Uniform dropping from both electrodes at a moderate rate of ten to twenty drops per minute is most desirable. (e) The probable error of the measurements is greater the higher the temperature.

3. Graphical comparison of our results with those of Bent and Gilfillan[6] on the activity of potassium in mercury at 15, 25 and 35° has been made. Comparison of the two investigations as to the free energy values for the transfer of potassium from one amalgam to another shows agreement within a few calories. The latter indicates rather conclusively that the potassium amalgam electrode is reliable in aqueous solutions.

4. Measurements of a potassium amalgam ($N_2 = 0.002559$) were made against calomel and silver–silver chloride electrodes in potassium chloride solutions of 0.10245 and 1.0168 weight molality, respectively. Using these measurements, the standard electrode potential of potassium has been recalculated and the value 2.9243 volts at 25° obtained as an average for the two cells.

5. The solubility of potassium in mercury over the temperature range of 0 to 35° has been determined.

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