outcome upholds the analogy between the fifth valence of nitrogen and that of an alkali metal.

Data necessary to reduce all results to a comparable concentration basis are not available, but evidence is given that the corrections should be reckoned in millivolts rather than in centivolts.

The small differences in oxidation potentials, if conditioned by chemical composition, are not readily correlated with the latter.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE FREE ENERGY AND HEAT OF TRANSFER OF BARIUM IN ITS LIQUID AMALGAMS

BY PAUL A. ANDERSON

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The electromotive measurement of a series of liquid-amalgam concentration cells is capable of furnishing quite exact information regarding both the thermodynamic properties of the system and the specific state of the metal solute in its mercury solution. While this type of investigation has been extended to many of the commoner mercury-soluble metals, none of the amalgams of the alkaline earth group of metals has been subjected to satisfactorily exact study. Such a study of barium amalgam was the object of the work to be described.

The two general methods available for determination of the electromotive forces of concentration cells of the reactive alkali and alkaline earth amalgams involve, respectively, measurement in an aqueous electrolyte with the use of some form of renewable electrode, and measurement in some non-aqueous electrolyte that does not decompose the amalgam. Richards and Conant[1] applied the former method to sodium amalgam concentration cells and by the use of synchronously flowing drop electrodes obtained reproducible potentials down to a concentration of 0.17 atomic per cent. of sodium. Cady[2] applied the second method in his measurements of two cells of the type: Ba amalgam (C_1), BaI_2 in pyridine, Ba amalgam (C_2). Comparison of Cady's analyses with the solubility data of Kerp and Böttger[3] indicates that the amalgam of his concentrated electrode was highly supersaturated. His results, therefore, are of only qualitative significance.

Examination of Electrolytes

The problem involved in the measurement of the potentials of barium amalgam concentration cells was found to resolve itself largely into a

[1] Richards and Conant, THIS JOURNAL, **44**, 601 (1922).

[2] Cady, *J. Phys. Chem.*, **2**, 551 (1898).

[3] Kerp and Böttger, *Z. anorg. Chem.*, **25**, 1 (1900).

search for a satisfactory electrolyte. The criteria for such an electrolyte are (1) an electrical conductance sufficiently high to allow accurate potentiometric measurement of the cell, and (2) a rate of reaction with the amalgam sufficiently low to bring the measurements within the limits of constancy and reproducibility required for their adequate interpretation. The facts that liquid barium amalgam saturated at 25° contains only 0.27 atomic per cent. of barium and that most of the measurements must be made upon very dilute amalgams emphasize the importance of the second criterion for the case in point.

Six electrolytes have been examined in the course of this work: (1) aqueous barium hydroxide prepared from barium amalgam and conductivity water, (2) ethyl alcohol-barium iodide, (3) *n*-propyl alcohol-barium iodide, (4) pyridine-barium iodide, (5) ethylamine-barium iodide, and (6) hydrazine-barium chloride. The preparation of the materials employed in the cell finally adopted for study is described below in detail; all other materials were purified by conventional methods. Each of the non-aqueous solvents was intensively dehydrated after purification and allowed to stand over barium amalgam for a month to a year before it was introduced into a cell. Electrolytes 1, 2 and 3 were tested in a modified form of the Richards and Conant[1] apparatus with closed electrode compartment and found to react with the barium at a rate that precluded a more than approximate estimate of potentials. With the pyridine electrolyte in this cell the potentials were found to fall rapidly, a behavior unique among the electrolytes studied and similar to that observed by Richards and Garrod-Thomas[4] for a pyridine-lithium chloride solution. The ethylamine-barium iodide electrolyte was tested in a cell comprising three non-renewable electrodes each composed of about 40 cc. of amalgam. Shortly after introduction into the cell this solution precipitated its barium iodide with consequent lowering of its conductance to a value too low to permit a reliable estimate of potentials.[5]

In the further search for a satisfactory solvent, anhydrous hydrazine suggested itself on the basis of its high dielectric constant and probable inertness toward barium amalgam. An intensively dehydrated solution of barium chloride in this solvent has permitted the attainment of a constancy of ± 0.001 mv. (millivolt) in the measurement of barium amalgam concentration cells.

Experimental Methods

Materials.—Mercury was purified by repeated spraying through a 2-meter tower, two distillations in a current of air, and one in a vacuum. Barium chloride was precipitated twice by gaseous hydrogen chloride and once by redistilled ethyl alcohol with thorough centrifuging of each precipitate. The hydrogen employed in washing out and

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[4] Richards and Garrod-Thomas, *Carnegie Inst. Pub.*, No. **118** (1909).

[5] Lewis and Keyes, THIS JOURNAL, **34**, 119 (1912).

filling the cell and reservoirs was obtained from a Richards zinc amalgam generator and purified by passage through solid potassium hydroxide, neutral permanganate solution, hot platinized asbestos, and phosphorus pentoxide in an all-glass system.

Five hundred g. of a 33% aqueous solution of hydrazine monohydrate was partially dehydrated by the method of Raschig.[6] Dehydration was completed by refluxing over crude barium oxide for eight hours in an atmosphere of hydrogen by the method of Lobry de Bruyn[7] and of Hale and Shetterly.[8] The final distillate of anhydrous hydrazine was collected in a receiver over a quantity of barium amalgam and sufficient anhydrous barium chloride, estimated from the data of Welsh and Broderson,[9] to give a nearly saturated solution at 15°, the lowest temperature at which measurements were made. The receiver was ground to fit both the condenser and a delivery tube. The latter, which was fitted with a glass-wool filter and mercury-sealed, ungreased stopcock, was introduced against a stream of dry hydrogen after completion of the distillation. The receiver thus served as the electrolyte reservoir without necessity of further transfer. The solution was allowed to stand over the barium amalgam for a month before introduction into the cell.

Preparation and Analysis of Amalgams.—The amalgams were prepared by electrolysis of a saturated solution of barium chloride between a mercury cathode and platinum anode, carried out in a separatory funnel from which the amalgam could be conveniently withdrawn. The amalgam was shaken with three changes of conductivity water, partially dried by filter paper, drawn into an evacuated reservoir and stored under hydrogen. Traces of water and oxygen were removed by reaction with the amalgam itself and the small amount of barium oxide thus formed removed incidentally to the introduction of the amalgam into the cell.

Triplicate analyses were made after each set of potential measurements. Samples, varying in amount from 50 to 150 g. with the dilution of the amalgam, were run from the cell directly into a slight excess of standard hydrochloric acid and the excess was titrated back with standard barium hydroxide solution after decomposition was complete. The mercury was dried in a vacuum desiccator and weighed. Bromothymol blue was used as indicator and weight burets were employed exclusively in titration. Analyses were reproducible to within 0.1% in the case of the more concentrated and within 0.5% for the more dilute amalgams. The probable accuracy of the analyses is of the same order, with the single exception of the most dilute amalgam measured, observed mole fraction 0.000158, which is given special consideration below.

The Cell.—The cell employed (Fig. 1) consists essentially of three amalgam reservoirs, R, R′ and R″, communicating by 1-mm. capillary tubes with renewable electrodes E, E′ and E″, which were sealed into the closed electrolyte chamber V. One of the reservoirs was equipped with a magnetic stirrer S consisting of a soft iron armature completely enclosed

[6] Raschig, *Ber.*, **43**, 1927 (1910).

[7] Lobry de Bruyn, *Rec. trav. chim.*, **14**, 83, 88 (1895); **15**, 174 (1896).

[8] Hale and Shetterly, THIS JOURNAL, **33**, 1071 (1911).

[9] Welsh and Broderson, *ibid.*, **37**, 816 (1915).

by Pyrex glass blown in the form shown. The dimensions of this stirrer were such that it floated in the position depicted when at rest. F, F′ and F″ are capillary filter tubes of 0.2mm. bore through which the amalgams were introduced into the cell. The upper ends of these tubes were ground to fit the amalgam storage reservoir. The tube P fitted with platinum glower and containing a small quantity of phosphorus pentoxide served to remove any trace of oxygen present in the incoming hydrogen. The pressure of hydrogen within the cell was regulated by a mercury leveling bulb connected at T to the mercury chamber Q. The electrolyte chamber V was sealed to the electrodes at an inclination of about 20° to the horizontal; the amalgam overflowing from the electrodes thus collected in the small well at the lower end of the chamber and could easily be drawn off as it accumulated. The electrode orifices were blown in the form of small cups, a design found preferable to that of Richards and Conant when a continuous synchronous flow of amalgam is not required. The 3-way stopcocks placed between the reservoirs and electrodes served to regulate the supply of amalgams to the latter and to furnish a convenient means of drawing off analysis samples at D.

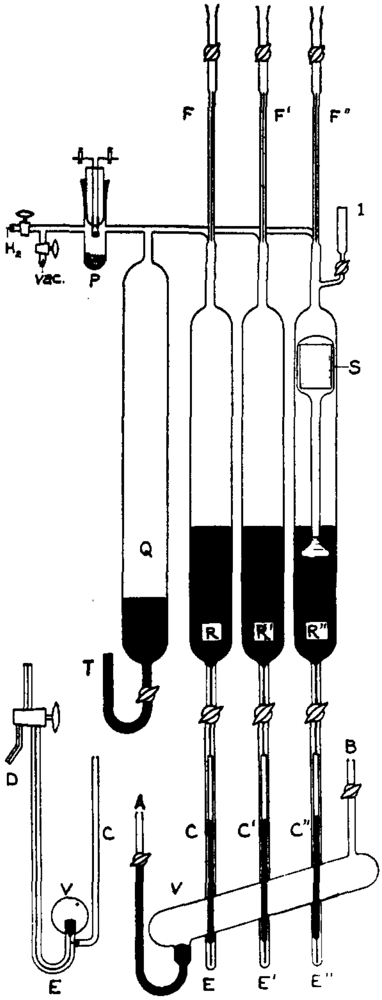

Fig. 1.

Procedure.—The cell was examined for pinhole leaks by the spark test, thoroughly cleaned and dried, and the stopcocks were lightly greased. After repeated alternate evacuation and filling with pure, dry hydrogen, Reservoirs R and R″ were filled with amalgam of concentration slightly less than that corresponding to saturation at 15°. R′ was filled with a relatively dilute amalgam. The complete exclusion of air and moisture during the filling operation was proved by the fact that the amalgam surfaces retained the appearance of pure mercury for some time after the measurements were completed. The amalgams in R and R′, to be designated hereafter as Amalgams A and B, respectively, remained at constant concentration throughout the run. The amalgam in R″, Amalgam C, was progressively diluted by small increments of mercury introduced at I. Mixing of the diluted amalgams was effected by the application of a portable bipolar electromagnet, by which the iron-cored stirrer was forced to move rapidly down and up. The efficacy of this mixing method was attested by the fact that the triplicate analyses of Amalgam C, made upon samples drawn successively from the reservoir, invariably checked within the limit of reproducibility for an unquestionably homogeneous amalgam of the same concentration. The magnetic-stirring method thus provided for the preparation, *in situ*, of an indefinitely extensive series of amalgams of progressively increasing dilution. Any advantage that this method may have is contingent upon the delivery at the electrode orifice of amalgam truly representative of the bulk of Amalgam C in the reservoir. This point was easily tested by following the potential between E″ and one of the electrodes of constant composition. It was found that the withdrawal of 10 cc. of amalgam from the orifice of Electrode E″ invariably brought the concentration at the orifice to that of the bulk of amalgam in the reservoir, further withdrawal of amalgam producing no detectable change of potential. The error introduced by the use of this method is perhaps less than that involved in the graphical combination of a series of measurements upon individual amalgam pairs while the manipulative advantage is decided. At each dilution of Amalgam C the potentials of two concentration cells were obtained. The use of two reference electrodes not only furnished a check upon the consistency of each set of readings but also, by preventing any possible variations in composition, and hence potential, of either of the reference amalgams from passing unnoticed, furnished a valuable check upon the reliability of the whole series of potential values recorded during a run.

Electromotive-Force Measurements

Measurements of the potentials of 23 concentration cells have been made at 25.00° ± 0.05° over the concentration range 0.2629, slightly below saturation, to 0.0108 weight per cent. of barium. Three cells of composition chosen to cover most of this concentration range have also been measured at 15° and 35°. By direct subtraction of observed potentials, made possible by the use of the reference electrodes, data for 55 more cells are made available without recourse to graphical interpolation.

The conductance of the hydrazine-barium chloride electrolyte was sufficiently high to permit potentiometric measurement to 0.001 mv. (millivolt) and its rate of reaction with the amalgam very low. In the case of the more concentrated amalgams, the initial potentials between freshly renewed electrodes remained constant within 0.001 mv. during the time required for a series of readings and within 0.01 mv. for several hours, while even in the most dilute amalgam measured, which contained one part of barium in ten thousand of amalgam, the variation did not exceed a few microvolts during the reading time. The readings were reproducible within 0.005 mv. after renewal of all the electrodes and the consistency as shown by cross checks between the three electrodes fell within this limit.

The electromotive-force measurements at 25.00° ± 0.05° are recorded in Table I to the nearest 0.005 mv. In the cell designation, the positive electrode is given first and the dilutions of Amalgam C are indicated by Roman numerals. As stated above, C I was of the same concentration as Amalgam A.

TABLE I

SUMMARY OF OBSERVED ELECTROMOTIVE FORCES AT 25°

Electrodes	Amalg. C, Wt. % of Ba	E.m.f., mv.	Electrodes	Amalg. C, Wt. % of Ba	E.m.f., mv.
C II A	0.2362	2.050	B CII	0.2362	10.855
C III A	.2085	4.270	B CIII	.2085	8.645
C IV A	.1783	7.005	B CIV	.1783	5.910
C V A	.1496	9.850	B CV	.1496	3.055
B A	....	12.910	C VI B	.1160	1.050
C VI A	.1160	13.965	C VII B	.08994	4.950
C VII A	.08994	17.865	C VIII B	.06804	9.080
C VIII A	.06804	22.000	C IX B	.05033	13.335
C IX A	.05033	26.240	C X B	.03106	19.980
C X A	.03106	32.890	C XI B	.01894	26.625
C XI A	.01894	39.530	C XII B	.01083	34.210
C XII A	.01083	47.125			

Reference Amalgam A: 0.2629% of Ba by wt.
Reference Amalgam B: 0.1228% of Ba by wt.

The electromotive force-concentration curve of the A-C series of cells with the potential of Reference Amalgam A taken as zero is given in Fig. 2. When the potential for the cell composed of Reference Amalgams A and B, indicated by the crossed circle, was plotted upon this graph it was found to fall upon the curve representing the change of potential of A toward C with the dilution of the latter, a fact which affords quite conclusive evidence for the reliability of the dilution method employed.

Free Energy of Transfer and Activity of Barium

The third and fourth columns of Table II present the comparison of the observed potentials for the A-C series of barium amalgam cells with the potentials calculated by the simple concentration law $E = [RT/nF \ln(N_2/N_2')]$. It is apparent that the law fails to account for the observed electromotive forces, which are markedly higher than the calculated values. As would be expected, the deviations increase with the dilution ratio and, for a given dilution ratio, decrease with the concentration. The positive sign of the deviations is in accord with Ramsay's observation[10] that

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[10] Ramsay, *J. Chem. Soc.*, **55**, 521 (1889).

barium lowers the vapor pressure of mercury to a much greater degree than Raoult's law requires. Further, for the range of atomic concentrations involved, barium amalgam exhibits a greater deviation from the concentration law than any of the numerous amalgams previously investigated.

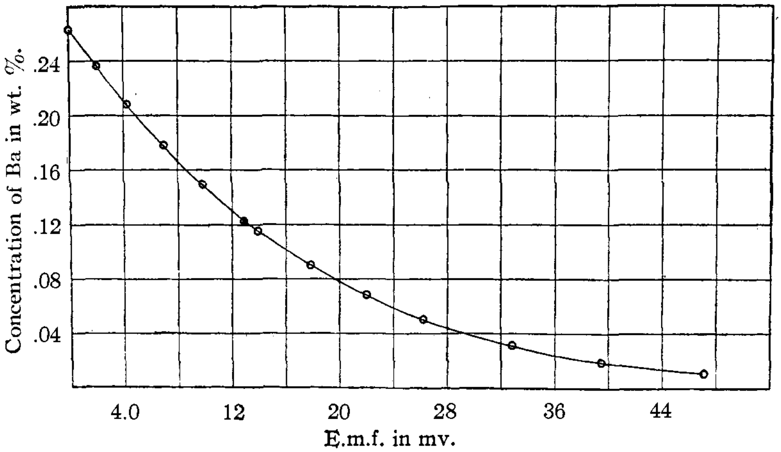

Fig. 2.

TABLE II

FREE ENERGY OF TRANSFER AND ACTIVITY OF BARIUM

Electrode	Mole fraction of Ba (N_2) × 10^3	E.m.f., Obs.	Mv., Calcd.	Activity of barium (a_2)	a_2/N_2	$-\Delta F$, Calcd.
A	3.835	0.00	0.00	0.006209	1.619	00
C II	3.448	2.05	1.37	.005293	1.535	95
C III	3.041	4.27	2.98	.004453	1.464	197
C IV	2.604	7.01	4.98	.003599	1.383	323
C V	2.183	9.85	7.24	.002884	1.321	455
C VI	1.693	13.97	10.50	.002093	1.236	644
C VII	1.312	17.87	13.78	.001547	1.179	824
C VIII	0.993	22.00	17.35	.001121	1.129	1015
C IX	.734	26.24	21.23	.000805	1.097	1211
C X	.453	32.89	27.43	.000480	1.060	1518
C XI	.276	39.53	33.78	.000286	1.035	1824
C XII	.155*	47.12	41.18	.000158	1.019	2174
			∞	.0	1.0	

The thermodynamic treatment of solutions that do not conform to Raoult's law at solute concentrations practicable for experimental investigation has been facilitated by the use of the so-called activity function. The electromotive force of an amalgam concentration cell is given, according to the definition of this function, by the equation $E = -(RT/nF) ln(a_2/a_2')$, where a_2 and a_2' for the case in point are the activities of barium in the concentrated and dilute electrodes, respectively. The extrapolation of the data of the second and third columns of Table II is carried out by the method of Lewis and Randall[11] in Fig. 3. It is interesting to note that the curve approximates closely to a straight line and that log (a_2/N_2), therefore, is apparently a straight-line function of N_2. Eleven of the twelve points fall close to the curve. The point for Amalgam C XII is probably low and, since no tendency to downward flexure is apparent in preceding points, has been disregarded in the extrapolation. The deviation of this point probably is to be attributed to an error in analysis corresponding to an error of 3×10^{-6} in the mole fraction of barium. The probable correct value of 0.000155 indicated by the curve has been substituted for the observed value of 0.000158 in Table II and indicated by an asterisk.

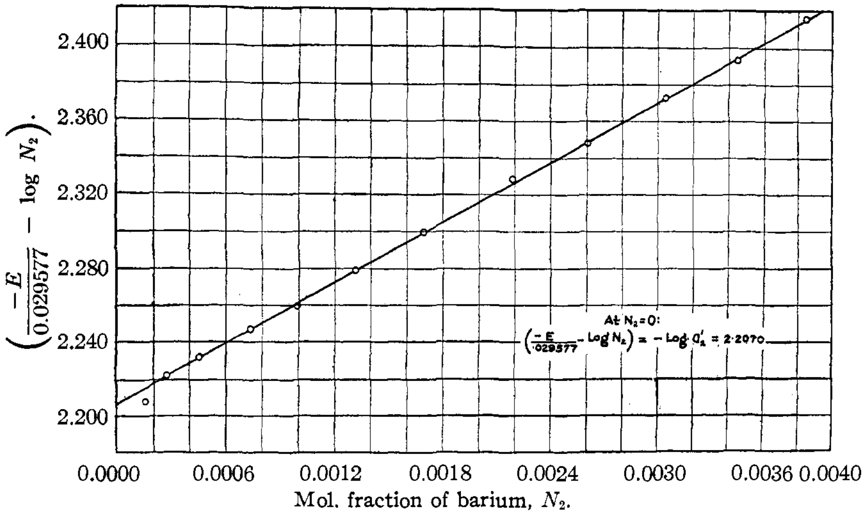

Fig. 3.—Extrapolation of data for activity of reference amalgam.

The activity values are tabulated in Col. 5 and the activity-mole fraction ratios in Col. 6 of Table II. In the last column are tabulated the computed values for the free-energy decrease attending the transfer of one mole of barium from an infinitely large quantity of Amalgam A to an infinitely large quantity of each of the more dilute amalgams.

The Heat of Transfer of Barium

The results of a careful measurement of three cells at 15°, 25° and 35° are recorded in Table III.

$\Delta E/\Delta T$ is in each case slightly higher between 25° and 35° than between 15° and 25°. In the case of the more dilute C X-B cell this difference is of the order of reproducibility of potentials, but in the other cells is quite unmistakable. The temperature coefficient of electromotive force for

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[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 265.

Table III

Temperature Coefficients of Electromotive Force

Electrodes	E.m.f., mv. 15°	 25°	 35°	$\Delta E/\Delta T$, mv. 15–25°	 25–35°	 15–35°
C X-B	19.355	19.980	20.610	0.0625	0.0630	0.06275
C X-A	31.935	32.890	33.890	.0955	.1000	.09775
B-A	12.590	12.910	13.290	.0320	.0380	.03500

barium amalgam concentration cells is, therefore, apparently a function of the temperature; $\mathrm{d}^2E/\mathrm{d}T^2$ is positive and, as would be expected, increases with the concentration. The heats of transfer computed by the Helmholtz equation $-\Delta H = nFE - nF(\mathrm{d}E/\mathrm{d}T)T$ are recorded in Table IV. Since the change of volume attending the transfer process probably is small, $-\Delta H$ represents quite accurately the total energy decrease undergone by the system. That the heat of transfer is not, in general, equal to the heat change involved in the dilution of Amalgam C_1 by pure mercury, a quantity determinable only by thermochemical measurement, has been pointed out by Richards and Daniels.[12]

Table IV

The Heat of Transfer of Barium

Ba, % by wt. C_1	 C_2	$E^{25°}$, mv.	$\frac{\mathrm{d}E}{\mathrm{d}T}$ 15–35°, mv./degree	nEF, joules	$nFT(\mathrm{d}E/\mathrm{d}T)$, joules	$-\Delta H$, joules
0.1228	0.03106	19.980	0.06275	3856	3610	246
.2629	.1228	12.910	.03500	2492	2014	478
.2629	.03106	32.890	.09775	6347	5623	724

The heat of transfer of barium is of the same sign as that of sodium[1] and of thallium and indium[13] and is of opposite sign to that of zinc, tin and lead.[4] For the range of atomic concentrations involved, its magnitude is greater than that of any of the amalgams previously investigated, a result consistent with the greater deviations of barium amalgams from the concentration law.

Recognizing the failure of the unmodified concentration formula to account for the electromotive forces of the amalgam concentration cells that he had under observation, Cady[2] proposed to equate the electrical energy not to the osmotic energy alone but to the sum of the osmotic energy and the heat of dilution of the solute metal, or $nFE = RT\ ln$-

Table V

Application of Data to Test Cady Equation

Ba, mole fraction N_2	 N_2'	E.m.f., mv. at 25° Obs.	 Concn. law	 Cady eq.	Deviations Concn. law	 Cady eq.
0.003835	0.001792	12.91	9.77	12.25	3.14	0.66
.001792	.000453	19.98	17.65	18.92	2.33	1.06
.003835	.000453	32.89	27.42	31.18	5.47	1.71

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[12] Richards and Daniels, This Journal, **41,** 1761 (1919).

[13] Richards and Wilson, *Carnegie Inst. Pub.*, No. **118** (1909), p. 34.

$(N_2/N') + U$. U is to be identified with the corresponding term, $-\Delta H$, of the Helmholtz equation and like the latter represents the heat of transfer rather than, as assumed by Cady, the heat of dilution of the solute. Table V records the results of the application of Cady's equation to the data of the present investigation.

While the Cady equation is evidently more successful than the simple concentration formula, the deviations from it are much greater than the probable experimental error and are more marked than in any amalgam system yet investigated at equivalent atomic concentration. Departures from the Cady equation are to be attributed to one or both of at least two factors; (1) a failure of the stoichiometric osmotic energy term to represent the actual osmotic effect; (2) a heat-capacity change attending the transfer of solute.[14] In the present case the first factor, presumably due to the formation of hydrargyrates of type formula Ba_mHg_n is responsible for nearly all of the deviation. A simple relation, apparently overlooked heretofore, that exists between the change of heat capacity and d^2E/dT^2 may be utilized to determine from electromotive data alone the sign and order of magnitude of the second factor. Combination of the differentiated Helmholtz equation, $d\Delta H/dT = nFT(d^2E/dT^2)$, with the Kirchhoff equation gives $\Delta C_p = nFT(d^2E/dT^2)$. A positive value of d^2E/dT^2 indicates an increase in heat capacity and *vice versa.* The lack of equality between the temperature coefficients of amalgam concentration cells for low and high ranges, which has frequently been observed and often assigned to experimental error only is, then, presumably to be expected on theoretical grounds. The present measurements indicate that d^2E/dT^2 is positive for barium amalgams, that the free-energy change associated with the chemical effect in the transfer of barium is slightly greater than the change in heat content, and that, in consequence, the part of the observed potential due to the chemical reaction is greater than the value given by the heat of transfer term of the Cady equation. Both of the factors that condition the deviation from the Cady equation, then, apparently operate to make the observed potential greater than the calculated value.

I wish to express my indebtedness to Professor Theodore W. Richards under whose direction the major part of this work was carried out.

Summary

1. The experimental conditions required for an exact electromotive study of liquid barium amalgam concentration cells have been worked out. By the use of a solution of barium chloride in anhydrous hydrazine as electrolyte a constancy and reproducibility of well within 0.01 mv. has been obtained in the measurement of potentials.

2. Twenty-three cells have been measured at 25° over the concentra-

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[14] Richards, *Proc. Am. Acad. Arts Sci.*, **38,** 308 (1902).

tion range 0.2629, slightly below saturation, to 0.0108 of barium by weight. Three cells have also been measured at 15° and 35°.

3. The observed potentials are markedly higher than the values calculated by the concentration law. The data are extrapolated to infinite dilution and the activities of barium calculated. The free energies of transfer are computed.
4. The heats of transfer of barium are calculated. The temperature coefficient of electromotive force is apparently a function of the temperature and d^2E/dT^2 positive.
5. The data are applied to test the Cady equation.

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[Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology No. 8]

THE COLOR OF THE TERVALENT TITANIUM ION

By Jean Piccard

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In inorganic chemistry as well as in organic chemistry there are methods which enable us in certain cases to deduce the color of a compound from its formula. Piccard and Thomas were able to predict that certain salts which are usually considered as colorless should be yellow when observed in sufficiently thick layers. This proved to be the case with cadmium iodide and with mercury dibromide.[1]

In the present paper we shall see the reverse case, that of an ion which is perfectly colorless although generally considered as being violet.

In the textbooks of inorganic chemistry we are told that—with the exception of certain complex salts which are yellow or green—tervalent titanium gives violet solutions. Incidentally, I have made the observation that the violet solution of titanium trichloride becomes much more strongly colored when one adds ammonium thiocyanate to it. Titanium thiocyanate is an intensely violet molecule or complex and the suspicion arose that perhaps titanium trichloride solutions may also owe their color not to the titanium ion but to the titanium trichloride molecule. We can easily confirm this hypothesis if we take two flat-bottom test-tubes with 2 cc. of a 0.025 N titanium trichloride solution in each. We place these tubes side by side while we look vertically down through them. Then if we add water to one of the test-tubes we immediately notice that the color in the dilute solution diminishes, and after an addition of 20 cc. of water the violet color has disappeared.[2] The law of Beer is not followed,[3] and it is proved

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[1] Piccard and Thomas, *Helvetica Chim. Acta*, **6**, 1040 (1923).

[2] This phenomenon is not due to hydrolysis, because it can also be observed when we dilute with weak hydrochloric acid solution, so that the hydrogen-ion concentration remains constant or even increases. Also, hydrolysis would increase the color,