quanta supplied by light, heat or solvent, etc. The chemical composition is not changed but only the reactivity.

Dr. Dehn lastly quarrels with my use of the phrase residual affinity. He apparently views residual affinity as being only the property of molecules which are unsaturated as regards the primary valencies of the atoms composing the molecules. I plead guilty at once to the use of the phrase in a far less restricted sense. Every chemist of the present day must surely recognize the possession by compounds, saturated as regards their primary valencies, of properties which may best be classified as residual affinity. Whether these properties are attributed to secondary valencies or to any other cause, the properties exist and it is these that I speak of as residual affinity and define as the residuum of affinity which is left after the force lines of the atomic fields have condensed together with the maximum possible escape of energy. It is to this escape of energy that the heat of reaction may be traced. No chemical theory can exist without affinity although there seems to be no satisfactory definition or explanation thereof. I have ventured to show that in the electromagnetic force-fields of the atom as devised by the physicist an explanation can be found. *Hinc illae lachrymae.*

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[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, PRINCETON UNIVERSITY.]

A CALOMEL STANDARD CELL.

BY G. F. LIPSCOMB AND G. A. HULETT.

Received September 28, 1915.

Experimental investigations on standard cells have been confined mainly to two combinations, the Clark cell and the Weston cell. These have been characterized by their reproducibility and their constancy, while other combinations which have been studied have proved lacking in these characteristics. For the construction of standard cells it has been found necessary to employ liquid electrodes, owing to the inconstancy of potential shown by a metal in the solid state against a given solution, so mercury and amalgams are used. Further, it is necessary that the base metal exist in only one state of oxidation and well removed from mercury in the electromotive series. The salts of the base metals should be well defined and be quite soluble. It has been assumed that the depolarizer must possess a certain solubility which must not be too small, since mercury has shown a constant potential only against the electrolytes which contained reproducible and constant amounts of mercury in solution. This idea has been regarded as militating against the employment of mercurous chloride as depolarizer. On the other hand, if the solubility be too great, as in the case of $CuSO_4$ of the Daniell cell, diffusion of the depolarizer may take place, and cause inconstancy of the cell. With mercury as cathode, the depolarizer must be a mercurous salt; and the sulfate seems best to have answered all these requirements. From the experience obtained with the Weston and Clark cells it has been found that uniformity in the size of particles of the mercurous sulfate is essential, or at least that very fine grains are to be avoided. This has been ascribed to surface tension effects influencing the solubility of the salt. The desired uniformity has been obtained by the electrolytic method of preparation, employing mercury and a solution of the acid alone.[1] This procedure obviates impurities in the product, which would occur by adsorption of the material used in the chemical preparation of the salt. Further, the presence of the relatively soluble mercuric salts in the depolarizer is reduced to a minimum by such a method of preparation.

From the experience in this laboratory, extending over some twelve years, it has been found that Weston cells containing as depolarizer gray mercurous sulfate—obtained by the electrolytic method and owing its color to finely divided mercury—have shown the greatest constancy and reproducibility. This fact may probably be explained by the reducing action which the finely divided mercury would exert on any mercuric salts which might be formed by oxygen from the solution or materials of the cell. It seemed possible, therefore, that the inconstancy of results which had hitherto been obtained in the case of "calomel electrodes" might be ascribed to the very great effect which the presence of a small quantity of mercuric salts would have on the concentration of the mercury in solution, for the concentration of the mercurous chloride in its saturated solution is exceedingly small. With finely divided mercury present, such variation should not be possible. Further, the smaller solubility of calomel, as compared with mercurous sulfate, should reduce any effect due to diffusion of the depolarizer.

Zinc chloride cannot be regarded as an easily handled, well defined, salt, owing to its hygroscopic nature, but it has been shown by Dietz[2] and Cohen[3] that cadmium chloride forms a remarkable well defined salt with $2^1/_2$ molecules of water of crystallization. The range of stable existence extends from —10° to +34.1° and, for all ordinary purposes to which standard cells may be put, this range of temperature is amply sufficient. Its solubility, as determined by Dietz, was found to be 110 g. in 100 g. H_2O at 15°, and 120 g. in 100 g. H_2O at 25°, which was sufficiently great to fulfil the conditions requisite in standard cell work. We have therefore investigated this combination

$$\text{Cd Amg.} \mid CdCl_2.2^1/_2H_2O\ Hg_2Cl_2 \mid Hg,$$

and the results obtained and set forth in the following show a reproduci-

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[1] *Phys. Rev.*, **22**, 334 (1906).

[2] *Z. anorg. Chem.*, **20**, 253 (1899).

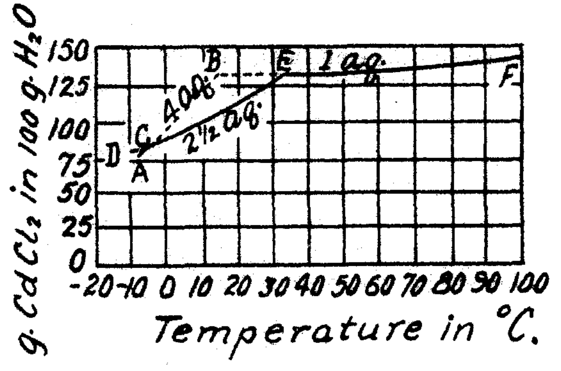
[3] *Z. physik. Chem.*, **14**, 73 (1894).

bility and constancy rather better than that of either of the Clark or Weston cells, both of which are liable to vary somewhat with time. We have observed these cells about nine months.

Preparation of Materials.

a. **Mercury.**—The mercury was shaken with a nitric acid solution of $HgNO_3$ in a separatory funnel and then distilled twice in a vacuum.

b. **Cadmium Chloride.**—A high grade cadmium chloride was brought into solution, and a small quantity of cadmium was precipitated as cadmium sulfide with hydrogen sulfide. The solution was allowed to stand for several days until the precipitate had settled. The resulting clear solution was syphoned off, and allowed to crystallize. The procedure was adopted in order to displace any metals from solution having a lower electrolytic potential than cadmium, and in addition any of the metals with sulfides more insoluble than that of cadmium. The solution was allowed to evaporate at room temperature, and thereby large and well formed crystals of the chloride were obtained. An analysis of a carefully dried specimen of this product yielded 19.5% of water.



The salt was therefore $CdCl_2.2^1/_2H_2O$ in agreement with the observations of Dietz.[1]

Calomel Electrode.

The Preparation of Calomel.—We have found that it is readily prepared electrolytically from Hg and HCl. The apparatus used for the preparation of the calomel was the same as that employed[2] for the preparation of mercurous sulfate, except that a tungsten wire of 2 mm. diameter, rounded to fit easily into the jar, served as cathode. The cathode remained perfectly bright throughout the operation, as tungsten does not amalgamate with mercury, while platinum does and has a slight solubility in the mercury.

Mercury to a depth of about 2 cm. was put into the jar and covered with a molar hydrochloric acid solution to a depth of 15 cm. A current density of 2 amps. per 100 sq. cm. of electrode surface was used. The product obtained was crystalline and gray in color, due to the presence of finely divided mercury. The preparation separated from the mass of

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[1] *Z. anorg. Chem.*, **20**, 257 (1899).

[2] *Phys. Rev.*, **22**, 334 (1906).

mercury by stirring, decantation and the use of separatory funnel, using molar hydrochloric acid. The preparation was kept in a dark place under the acid.

Cadmium Amalgam.—A 10% cadmium amalgam was used in the construction of the cells. This amalgam was prepared by means of electrolysis, using distilled mercury and pure crystals of cadmium sulfate.

Preparation of the Paste.—A little filter was cut from filter paper with a large cork borer and fitted to a Gooch crucible. The calomel was brought into the Gooch crucible and the acid removed as completely as possible by suction; it was then washed 5 or 6 times with absolute alcohol. The absolute alcohol was next removed by washing several times with a saturated solution of cadmium chloride. For thorough washing it is best not to have the chloride in the Gooch crucible over 2 cm. deep. The washed chloride was mixed with about one-half its volume of finely powdered cadmium chloride and then the saturated solution of cadmium chloride added with stirring until a homogeneous paste was formed. The paste should be of such a consistency that it will flow from a 5 mm. glass tube.

The H type of cell was used, as it is easily filled and allows the contents of each electrode rapidly to come to the temperature of the bath. Thin walled tubing about 12 mm. in diameter was employed in their construction. The amalgam and mercury were introduced by means of a 5 mm. thin-walled glass tube about 30 cm., long drawn out at the lower end to about 3 mm. diameter. This tube was provided with a flexible rubber mouth piece and was also used for the introduction of the paste. The mercury amalgam and paste were each from 10 to 15 mm. in depth. A layer of cadmium chloride crystals about 3 mm. in depth was placed over the calomel and the amalgam. The cell was then filled to the top of the cross tube with a saturated solution of cadmium chloride, and the glass parts sealed off by using two small blast flames. The cells were arranged in supports, with lead wires so that they could readily be compared when in the bath.

Two groups of cells were made at different times, using calomel and cadmium chloride from two different preparations. These cells were placed in a thermostat regulated to 0.01°. The measurements were made by the Poggendorf compensation method, using a Broca galvanometer as zero instrument in connection with a Wolff potentiometer. The voltage could be read directly to 0.00001 V and the 6th place estimated. Weston standard cells were employed as reference. A number of these cells were available, some of them being 12 years old. The compensation current was obtained from an accumulator, the constancy of which was checked after each measurement. The voltages of

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[1] *Phys. Rev.*, 22, 33.

these cells were determined at 25° over a period of several months. After this value had been established they were placed in other thermostats at 15° and 30° and their voltages measured in order to determine the temperature coefficient.

TABLE I.

			1915.					
No. of cell.	Date of constr.	Dec. 22, 1914. 25°.	Jan. 4 25°.	Jan. 25. 25°.	Feb. 12. 25°.	March 26. 25°.	April 26. 25°.	
1	Dec. 22..	0.67080	0.67080	0.67080	0.67081	0.67079	0.67080	...
2	Dec. 22..	0.67080	0.67080	0.67080	0.67080	0.67081	0.67081	...
3	Dec. 22..	0.67080	0.67080	0.67080	0.67080	0.67079	0.67080	...
		March 4.	March 9.	March 15.	May 1.	June 10.	July 12.	
4	Mar. 4...	0.67078	0.67079	0.67079	0.67079	0.67079	0.67080	...
5	Mar. 4...	0.67078	0.67080	0.67079	0.67078	0.67078	0.67079	...
6	Mar. 4...	0.67078	0.67080	0.67079	0.67078	0.67079	0.67098	...
		May 1. 25°.	June 10. 25°.	March 12. 15°.	March 15. 15°.	April 23. 30°.	April 24. 30°.	April 26. 30°.
1	Dec. 22..	0.67079	0.67080	0.67156	0.67157	0.67022	0.67044	0.67023
2	Dec. 22..	0.67080	0.67079	0.67157	0.67157	0.67022	0.67022	0.67022
3	Dec. 22..	0.67079	0.67080	0.67157	0.67157	0.67022	0.67023	0.67022

Examination of Table I will show that the combination is reproducible to the fifth decimal place and it rapidly attained a constant E. M. F. which is then steadily maintained, and no gradual decrease in E. M. F. has been noticed in any of these cells as is frequently the case with Weston cells.

Discussion of the Results.

Since the cell under consideration is capable of yielding an E. M. F. of such constancy and reproducibility, it is obvious that it may be employed to evaluate the various thermodynamic and thermochemical relations in connection with the reaction occurring in the cell. We may represent this reaction by the equation:

$$Hg_2 + CdCl_2 = Hg_2Cl_2 + Cd$$

As is well known, the heat change accompanying a given reaction may be derived from measurements of the E. M. F. generated in a cell in which such reaction occurs. The Gibbs-Helmholtz equation connecting these factors is:

$$Q = 0.2387\, nF\, [E + T\, dE/dT]$$

where

Q is the heat of reaction at temperature $T°$ abs.

0.2387 volt coulombs = 1 cal.

E is the observed E. M. F. at temp. $T°$.

n the electrochemical equivalent involved in the reaction.

To evaluate this equation for Q it is necessary first to obtain the temperature coefficient of the reaction. This may be obtained in the following manner: The electromotive force at any given temperature may be set forth as a function of the temperature of the E. M. F. at any given temperature. Thus we may set

$$E_T = E_{25} + a(T - 25) + b(T - 25)^2 + \ldots .$$

If the temperature range be such that higher powers of T than T^2 may be neglected, it is obvious that the values of the constants a and b in the general equation may be obtained from measurements of the E. M. F. at three temperatures. The measurements at 15°, 25° and 30° were employed to this end and the equation developed took the form:

$$E_T = 0.67080 - 0.000102(T - 25) - 0.0525(T - 25)^2$$

This equation reproduces the values at 15° and 30° C. exactly, and from it the E. M. F. at any temperature within this range may be obtained. Differentiation of this equation with respect to temperature gives the desired temperature coefficient.

Employing this equation, the E. M. F. at 18° C. was evaluated and gave $E_{18} = 0.67159$ v. while the temperature coefficient

$$dT/dE = -0.000067.$$

Substitution of these values in the Gibbs-Helmholz equation gives:

$$Q_{18} = 46092[0.67159 - 291(0.000067)] = 30060 \text{ cal.}$$

The thermochemical data provide an interesting check upon the calculation.

The heat of the reaction

$$Hg_2 + CdCl_2 = HgCl_2 + Cd$$

numerically is equal to the difference between the heat of formation of the two salts. For cadmium chloride the value given by Thomsen is 93240 cal. For mercurous chloride the most recent and reliable figure is, according to Thomsen, 63674. Hence the heat of reaction:

$$93240 - 63674 = 29566 \text{ cal.}$$

Since, however, the salt in equilibrium is the hydrated form of cadmium chloride the heat of hydration of the anhydrous salt must be taken into consideration, as well as the heat change accompanying the solution of the salt. As shown by Cohen[1] the total heat change which this involves may be represented by the general equation:

$$L_2 = m/m - w/H - w/m - w/l$$

where

m = gram mols per mol.
w = no. of mols of water of crystallization.
H = heat of hydration.
l = heat of solution of the anhydride.
L_2 = heat of formation of the hydrate.

The value of m at 18° may be obtained from the solubility data of

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[1] *Z. physik. Chem.*, **34**, 62 and 612 (1900).

Dietz as 9.15 g. mols water per molecule of anhydrous salt. The values for H and l were obtained from Thomsen's data as 5290 and 3010 cals., respectively. Using these data the value $L_2 = 6150$ was obtained.

Further, the heat change accompanying the solution of Cd in cadmium amalgam must also be considered. According to Cohen, this amounts to —5436 cal. per gram equivalent with 14.3% amalgam at 18°. This value was obtained from a study of the element Cd | $CdSO_4$ | Cd amalgam, which gave between 0 and 25° the voltage

$$E_t = 0.0499 - 0.000233\ (t - 25).$$

This applies to amalgams containing 5 to 14% Cd. According to Hulett,[1] who had made a careful investigation of such cells, the

$$\text{E. M. F.} = 0.05175 - (0.000244)\ (t - 20)$$

which would give a value = 5680 cals. The total heat change, therefore, accompanying the reaction which takes place in the cell is:

$$Q = 29566 + 6150 - 5680 = 30036$$

This value shows an extraordinary agreement with that obtained from the electromotive force data, *viz.*, 30060, an agreement, indeed, well within the errors of measurement in thermochemical data.

It is obvious, therefore, that the element under consideration would form a very interesting basis for calculations according to the Nernst Heat Theorem. To this end the specific heat of the various substances are required. At the present time, however, the values for cadmium chloride appear to be lacking and the calculations must therefore be postponed until such data are forthcoming. We are undertaking work with this end in view.

In order to make the investigation of this cell more complete, unsaturated cells of the combination were constructed with a view to obtaining a cell of much smaller or zero temperature coefficient. Three groups of cells were constructed using different concentrations of cadmium-chloride solutions but none of the solid $CdCl_2.2^1/_2H_2O$ was used for the paste or in the cell. The data obtained are collected in Table II.

TABLE II.

	Concentration of $CdCl_2$ sol. G. per 100 g. solution.	E. M. F. at 20°.	E. M. F. at 25°.	E. M. F. at 25°.
1	52 g. in 100 g. sol.	0.67978	0.68120	0.68257
2		81	20	57
3		81	20	57
4	50 g. in 100 g. sol.	0.68134	0.68276	0.68412
5		33	78	11
6		35	79	11
7	48 g. in 100 g. sol.	0.68221	0.68368	0.68498
8		36	67	502

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[1] *Trans. Am. Electrochem. Soc.*, 1905, 333.

The temperature coefficients of these groups at 18° were 0.000265, 0.000285, and 0.000290. From these results it is obvious that the temperature coefficient of the electromotive force of the combination changes very little with the concentration of the solution, although the voltages obtained are much higher than in the case of the saturated element.

Summary.

The possibility of employing calomel as depolarizer in the construction of precision standard cells has been established. Ordinary calomel, when suitably modified so as to contain finely divided mercury, giving the material a gray color, forms a depolarizer for cells, gives constant and reproducible electromotive forces, and this preparation should give better results in calomel electrodes.

Saturated and unsaturated cells of composition $Hg | HgCl_2 | CdCl_2 | Cd$ amalgam have been constructed, their E. M. F.'s measured and their temperature coefficients obtained.

The thermodynamics of the saturated combination has been investigated and satisfactory agreement between the heat of the reaction as calculated from the electromotive force data and that obtained from thermo-calomel measurements has been established.

PRINCETON, N. J.

SOME SOURCES OF ERROR IN VISCOSITY MEASUREMENT.

By EUGENE C. BINGHAM, H. I. SCHLESINGER AND ARTHUR B. COLEMAN.[1]

Received September 9, 1915.

While using the viscometer recently described by Bingham,[2] it was observed that the viscosities (η) when calculated by the now generally accepted formula

$$\eta = Ctp - C'\rho/t \qquad (1)$$

were not constant, but varied considerably when the applied pressure p was varied. In the above formula t is the time of flow, ρ the density, and C and C' are constants. As the instrument differed in what were at first considered minor details from the instrument originally successfully used by Bingham, it was thought that by its use some errors had been made apparent which might have been masked in the original viscometers and that these errors might be of such a nature as to require corrections for all viscosity measurements made in similar types of apparatus. The instrument differed from the original one in that the capillaries were rather wide so as to make possible the measurement of liquids of relatively low fluidities and, for the convenience of the manufacturer, was

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[1] Part of the work reported in this article constitutes the basis of a dissertation submitted by A. B. Coleman to the faculty of the University of Chicago in part fulfillment of the requirements for the degree of Master of Science.

[2] *J. Ind. Eng. Chem.*, 6, 233 (1914).