

entropy from the known absolute entropy, giving the value  $33.98 - R \ln 4 = 31.23$  E.U.

This is in agreement with the fact that the ordinary, and incorrect, application of the third law to hydrogen has, in general led to discrepancies which would be reduced by the use of this value.

We wish to emphasize that while some uncertainty may remain as to the effect of nuclear spin on other substances, no reasonable doubt exists as to the value of the entropy of hydrogen.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

## A STUDY OF THE CADMIUM-LEAD CHLORIDE VOLTAIC CELL<sup>1</sup>

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The difference between two values reported for the electromotive force of the cell

$\text{Cd(Hg)} \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O (sat.)} \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O (sat.)}, \text{PbCl}_2 \text{ (sat.)} \mid \text{Pb(Hg)}$  (1)  
namely 0.1408 v.<sup>2</sup> and 0.13859 v.<sup>3</sup> at 25°, respectively, is too great to be attributed to experimental error.

The value for Cell 1 can be calculated from the values of the cells

$\text{Cd(Hg)} \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O (sat.)} \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O (sat.)}, \text{Hg}_2\text{Cl}_2 \text{ (sat.)} \mid \text{Hg}$  (2)

$\text{Pb(Hg)} \mid \text{PbCl}_2 \text{ (sat.)} \mid \text{PbCl}_2 \text{ (sat.)}, \text{Hg}_2\text{Cl}_2 \text{ (sat.)} \mid \text{Hg}$  (3)

Lipscomb and Hulett<sup>4</sup> found for Cell 2 the value  $E_{25} = 0.67080$  v. For Cell 3 Gerke<sup>5</sup> found the value  $E_{25} = 0.5299$  v. Calculating the electromotive force of Cell 1 from these values gives a result which agrees well with the value found by Obata. Cell 3 and the similar cell with a solid lead electrode have been studied by numerous other investigators.<sup>6</sup> Values calculated for Cell 1 from the results for Cell 3 obtained by some of these investigators are in better agreement with Vosburgh's value. Cells 1 and 3 have therefore been studied further.

The electromotive force-temperature curve of Vosburgh's cell shows a transition point at 26° which does not correspond to the transition point of cadmium chloride. An explanation of this was sought also.

<sup>1</sup> Taken from a thesis presented by Rudolf J. Pripke in partial fulfilment of the requirements for the degree of Master of Arts at Duke University in June, 1930.

<sup>2</sup> Obata, *Proc. Phys. Math. Soc. Japan*, [3] 3, 64, 136 (1921).

<sup>3</sup> Vosburgh, *THIS JOURNAL*, 49, 2222 (1927).

<sup>4</sup> Lipscomb and Hulett, *ibid.*, 38, 20 (1916).

<sup>5</sup> Gerke, *ibid.*, 44, 1698 (1922).

<sup>6</sup> (a) Babinski, Dissertation, Leipzig (1906); (b) Timofejew, *Z. physik. Chem.*, 78, 310 (1912); (c) Brönsted, *Z. Electrochem.*, 19, 754 (1913); (d) Lewis and Brighton, *THIS JOURNAL*, 39, 1906 (1917); (e) Günther, *Z. Electrochem.*, 23, 197 (1917); (f) Krahmer, *ibid.*, 26, 97 (1920); (g) Getman, *THIS JOURNAL*, 40, 611 (1918).

### Preparation of Materials

Mercury was purified by washing with mercurous nitrate solution and distilling under reduced pressure in a current of air.

Water for the preparation of materials was redistilled from alkaline permanganate. Water for the electrolyte solutions was redistilled a second time in an all-silica still.

Three preparations of mercurous chloride were used. Preparation 1 was made by adding dilute hydrochloric acid slowly to mercurous nitrate solution. Preparation 2 was made by adding mercurous nitrate solution to dilute hydrochloric acid. Preparation 3 was made by a modification of the electrolytic method of Hulett.<sup>4</sup> All three preparations were digested under dilute hydrochloric acid at a temperature near the boiling point for at least eight hours.

Lead chloride was precipitated by adding a solution of recrystallized lead nitrate drop by drop to a solution of redistilled hydrochloric acid.

Baker's c. p. cadmium chloride and potassium chloride were recrystallized from redistilled water.

Lead amalgam was made electrolytically from purified mercury and lead chloride and contained approximately 6% of lead.

To make cadmium amalgam, cadmium was electrolyzed from c. p. metal sticks into commercial redistilled mercury through cadmium sulfate solution. From the amalgam thus formed the cadmium was again electrolyzed into purified mercury, forming a 12% amalgam. This was diluted with mercury to make a 10% amalgam.<sup>7</sup>

### Experimental

**Preparation of Cells.**—The cells were set up in glass H-vessels 16 cm. high and 5.5 cm. wide. The tubes had an inside diameter of 10 mm. In the preparation of Cells 2A and 2B, the mercurous chloride was filtered in a Gooch crucible and mixed in an agate mortar with crystals of cadmium chloride. This paste was transferred to a separatory funnel and washed several times in an atmosphere of nitrogen with the electrolyte solution. It was then put into the cell vessel on top of the mercury, the end of the separatory funnel being kept under the surface of some electrolyte solution above the mercury. Cadmium chloride crystals were then placed above the paste. The melted amalgam was put into the vessel by means of a heated glass tube, and the surface washed with some slightly acidified electrolyte solution to remove cadmium oxide. Then the surface was washed several times with electrolyte solution and finally crystals of cadmium chloride and electrolyte were put on top of it. The vessels were filled to the cross arm with electrolyte and closed with paraffin-coated corks. All the other cells (except Cells 3C and 3D, which were prepared without precautions to protect from air) were prepared in a similar manner. In the preparation of Cells 1C, 1D, 1E, 2C, 2D, 3E and 3F the paste was not washed in a separatory funnel. Instead, the cells were alternately evacuated and filled with nitrogen several times. Cells 2E, 2F, 3G and 3H were prepared using both these precautions.

In Cells 3A and 3B saturated lead chloride solution was used as the

<sup>7</sup> The cadmium amalgam was prepared by Kelly L. Elmore.

electrolyte. In Cells 3G and 3H, 1.0 *N* potassium chloride solution was used. All the other cells contained saturated cadmium chloride solution as the electrolyte. In cells with saturated cadmium chloride solution as the electrolyte, cadmium chloride crystals were mixed with the paste and were present in excess in both arms of the cell.

The cells were kept at 25°, except as otherwise indicated, in an electrically controlled oil thermostat, the temperature of which fluctuated not more than  $\pm 0.01^\circ$  and under favorable conditions not more than  $\pm 0.005^\circ$ . The temperatures are probably correct to within  $\pm 0.02^\circ$ .

**Electromotive Force Measurements.**—The electromotive forces were measured by means of a calibrated Leeds and Northrup Type K potentiometer. Standard Weston cells Nos. 353–356 and 496 previously described<sup>8</sup> were used as reference standards. They were found to agree within one or two parts in 100,000 with two portable saturated cells certified by the Bureau of Standards.

A number of the cells started with abnormally high electromotive forces. The electromotive forces of such cells decreased continuously over a period of several weeks until finally constant values were obtained. Changes in temperature appeared to hasten the attainment of a constant value. Other cells were practically constant from the beginning. Table I shows the initial and final constant values of cells of each of the three types. In most cases the constant values of duplicate cells agreed to within 0.1 mv., but in two cases duplicates differed by 0.6 mv. The latter were given less weight in selecting the final values.

Of the three types of cells, the calomel standard cell of Lipscomb and Hulett, Cell 2, was the easiest to reproduce. The quality of Cell 3 depended somewhat on the electrolyte used, potassium chloride giving the best results. When no electrolyte other than the lead chloride was used, the electromotive force was about 1 mv. too high, and the cells did not agree well.

TABLE I  
ELECTROMOTIVE FORCES AT 25°

Cells	E. m. f., v.		Cells	E. m. f., v.		Electrolyte
	Initial	Constant		Initial	Constant	
1A, 1B	0.1393	0.1405 <sup>a</sup>	3A, 3B	0.5315	0.5310	PbCl <sub>2</sub> , sat.
1C	.1365	.1400	3C, 3D	.5337	.5301	CdCl <sub>2</sub> , sat.
1D, 1E	.1345	.1406	3E, 3F	.5366	.5301	CdCl <sub>2</sub> , sat.
2A, 2B	.6706	.6707	3G, 3H	.5298	.5297	KCl, 1 <i>N</i>
2C, 2D	.6740	.6703				
2E, 2F	.6706	.6706				

<sup>a</sup> After a number of later temperature changes Cell 1A assumed the value 0.1407 v. Cell 1B was variable after a series of temperature changes.

Two temperature coefficient determinations were made, the first using a limited number of cells and the second all cells which had come to equi-

<sup>8</sup> Vosburgh, THIS JOURNAL, 47, 1257 (1925); 49, 85 (1927).

TABLE II

ELECTROMOTIVE FORCES AT VARIOUS TEMPERATURES					
Temp., °C.	Cells 1A, 1B, v.	Cell <sup>d</sup> 1A, v.	Cells 2A, 2B, v.	Cells 2E, 2F, v.	Cells 3G, 3H, v.
25	0.14052	0.14072	0.67063	0.67062	0.52974
20	.14166	.14185	.67108	.67108	.52907
17	....	.14248	.67130	.67128	.52862
20	....	.14185	.67108	.67106	.52888
25	.14055	.14069	.67060	.67058	.52973
30	.13933	.13945	.67007	.67007	.53040
35	.13854	.13854	.66995	.66989	.53110
40	.13927	.13925	.67135	.67136	.53178
35	.13857	....	....	....	....
30 <sup>a</sup>	.13787	.13786	.66857	.66851	.53038
25 <sup>a</sup>	.13716	.1365 <sup>e</sup>	.67131 <sup>e</sup>	.66706	.52963
25 <sup>b</sup>	.14075 <sup>e</sup>	.1407	.67067	.67059	....

<sup>a</sup> Cells 1 and 2 were metastable at these temperatures. <sup>b</sup> These values were obtained after stable equilibrium had been reattained. <sup>c</sup> This value was for Cell 1A. Cell 1B did not come back to a definite equilibrium. <sup>d</sup> This is a second determination of the temperature coefficient of Cell 1A. <sup>e</sup> One leg of each of these cells became stable while the other remained metastable.

librium. Beginning at 25° the temperature was changed as indicated in the first column of Table II. Usually three days or more were allowed for

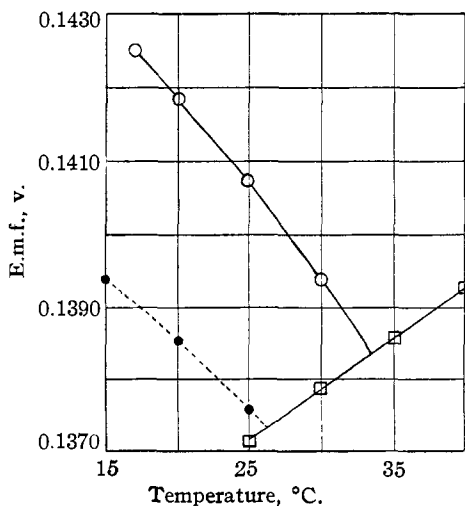


Fig. 1.—Variation of the electromotive force of Cell 1 with temperature. The circles are values of Cell 1 obtained in this investigation. The dotted curve gives the values previously found by Vosburgh. The squares are points at which Vosburgh's cell and Cell 1 were in close agreement and represent the values of the electromotive force when monohydrated cadmium chloride is the solid phase.

the cells to come to equilibrium at each temperature. In a few cases, when measurements at intervals showed no change taking place, less time was allowed. Electromotive force measurements were made every day. The results are given in Table II.

Since cadmium chloride changes from the hemipentahydrate to the monohydrate at about 34°, there was a sharp change of slope at that point in the electromotive force-temperature curve of the cells with cadmium amalgam electrodes, as illustrated by Fig. 1. On decreasing the temperature, the monohydrate did not change back to the hemipentahydrate immediately, sometimes not even at 25°. To hasten this change, after the first tempera-

ture coefficient determination, the cells were put into an ice-salt mixture for a day. After the second determination, instead of this treatment the cells were opened and seeded with crystals of the hemipentahydrate. The latter method is much more effective. The electromotive forces then returned to the values for the stable cells at 25°, except in the case of Cell 1B which, after being cooled, became variable.

### Discussion

The value found for Cell 2,  $E_{25} = 0.6706$  v., was about 0.2 mv. lower than the value given by Lipscomb and Hulett.<sup>4</sup> This, while not a serious disagreement, may perhaps have been caused by the digestion of the mercurous chloride. It has been shown<sup>9</sup> that digestion of mercurous sulfate gives a more stable preparation, leading to lower and more reproducible results when used in Weston cells. The same was found to be true in the case of lead dioxide.<sup>10</sup>

Cell 2 became metastable when the temperature was raised above 34° and then cooled again. The metastable cells readily assumed their normal value at 25° on being seeded with hemipentahydrate crystals or subjected to cooling treatment. The electromotive force of Cell 2 between 20 and 30° is given by the formula

$$E = 0.6706 - 0.000102 (t - 25) - 0.0000025 (t - 25)^2$$

the temperature coefficients being those found by Lipscomb and Hulett. From 34 to 40° and for the metastable cell between 25 and 34° the electromotive force is given within 0.1 mv. by the formula

$$E = 0.6699 + 0.000284 (t - 35)$$

Five cells of the type of Cell 1 were made which gave good results. Three of them did not come to equilibrium until the middle of the temperature coefficient determination, but their values in the metastable state as well as their values in the final stable state at 25° were in good agreement with the other two cells.

The values at different temperatures of Cell 1A, which was subjected to both temperature coefficient determinations, are given in Table III, together with those calculated from the formula given by Obata.<sup>2</sup>

TABLE III  
ELECTROMOTIVE FORCE OF CELL 1 AT DIFFERENT TEMPERATURES

Temp., °C.	17	20	25	30
Cell 1A, v.	0.14248	0.14185	0.14072	0.13945
Obata, v.	.14243	.14186	.14080	.13956

When Cell 1 has monohydrated cadmium chloride as the solid phase in equilibrium (or metastable equilibrium) with the electrolyte, the re-

<sup>9</sup> Vosburgh, *THIS JOURNAL*, **46**, 104 (1924).

<sup>10</sup> Vosburgh and Craig, *ibid.*, **51**, 2012 (1929).

lation between the electromotive force and the temperature is practically linear. Table IV gives the electromotive force at different temperatures of Cell 1 of this investigation with monohydrate crystals together with those calculated from the values given by Vosburgh<sup>3</sup> for his cell under the same conditions.

TABLE IV  
ELECTROMOTIVE FORCE OF CELL 1 WITH MONOHYDRATE CRYSTALS

Temp., °C.	25	30	35	40
E. m. f., Cell 1, v.	0.13716 <sup>a</sup>	0.13784 <sup>b</sup>	0.13850 <sup>b</sup>	0.13918 <sup>b</sup>
Vosburgh, v. <sup>c</sup>	.13716	.13788	.13857	.13927

<sup>a</sup> Cells 1A and 1B. <sup>b</sup> Cells 1A, 1B, 1D and 1E. <sup>c</sup> It is to be noted that Vosburgh used an amalgam containing lead. His values have been corrected as indicated in his paper (Ref. 3) and the values given here apply to a cell with pure cadmium amalgam, and so are comparable with the values of Cell 1.

The data in Tables III and IV are plotted in Fig. 1. The tables and figure show that the values of Cell 1 agree with Obata's value rather than with Vosburgh's from 17 to 30°. When the monohydrated cadmium chloride is the solid phase they agree well with the values given by Vosburgh for his cell when in a similar condition. The cadmium chloride in Vosburgh's cell must have been in some unknown metastable state before his temperature coefficient determination. This would account for the transition point being at 26° instead of at 34°. An attempt to duplicate Vosburgh's cells as they were before carrying above the transition point was not successful.

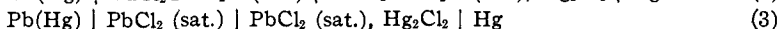
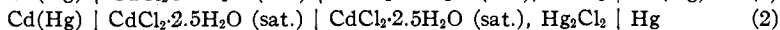
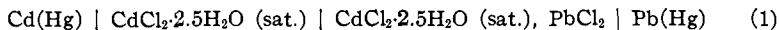
Of the cells of the type of Cell 3, Cells 3C, 3D, 3F, 3G and 3H gave the best results. Table V gives the electromotive forces of these cells at different temperatures, together with the values calculated from Gerke's value<sup>5</sup> with his temperature coefficient. The line marked "Calcd. I" gives the values calculated by subtracting the value of Cell 1 from the corresponding value of Cell 2. The line marked "Calcd. II" gives the values calculated in the same way from the same cells with monohydrated cadmium chloride as the solid phase.

TABLE V  
ELECTROMOTIVE FORCE OF CELL 3 AT DIFFERENT TEMPERATURES

Temp., °C.	20	25	30	35	40
Cells 3C, 3D, v.	0.53006	0.53030	0.53097	0.53144	0.53206
Cells 3F, 3G, 3H, v.	.52905	.52971	.53037	.53114	.53182
Gerke, v.	.5293	.5299	.5306	.5312	.5318
Calcd. I, v.	.52923	.52989	.53062	....	....
Calcd. II, v.	....	.52990	.53070	.53142	.53217

### Summary

The following cells have been set up and their electromotive forces and temperature coefficients measured.



When hemipentahydrated cadmium chloride was the solid salt in equilibrium with the electrolyte in Cell 1, the values were in good agreement with the values found by Obata. When monohydrated cadmium chloride was the solid salt in equilibrium (or metastable equilibrium) with the electrolyte, the values were in good agreement with those found by Vosburgh when his cells had the monohydrate as the solid phase.

A value only slightly lower than that of Lipscomb and Hulett was found for Cell 2.

From the values for Cells 1 and 2 a value for Cell 3 was calculated which agreed with the observed values for Cell 3 and with Gerke's values for this cell. Of the three this cell was the most difficult to reproduce.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## KINETICS OF THE ACETYLENE-OXYGEN REACTION

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Although of extraordinary technical and general interest, the problem of the mechanism of hydrocarbon combustion has yielded very little exact, reproducible information despite numerous investigations, principally owing to the complexity of the process and the consequent possibility of considerable variation in the course of reaction with changing conditions. However, the results of more recent experimental work on the slow oxidations of gaseous hydrocarbons have led several workers to postulate a chain mechanism.<sup>1</sup> Thus, it was found that in vessels packed with pieces of the same material as that of the containing walls, the reaction velocity is slower and the products are, in general, somewhat different. An even more direct evidence in favor of this hypothesis has been obtained by Spence and Taylor,<sup>2</sup> who showed that small amounts of ozone introduced into a stream of slowly reacting oxygen and ethylene accelerate the rate of reaction between the latter. In the few cases that have been studied, the reaction kinetics appear to be somewhat unusual and favor the assumption of a chain mechanism. Thompson and Hinshelwood<sup>1</sup> observed that the velocity of the ethylene-oxygen reaction is proportional to a high power of ethylene concentration and is almost independent of oxygen. Very similar

<sup>1</sup> Pease, *THIS JOURNAL*, 51, 1839 (1929); Pope, Dykstra and Edgar, *ibid.*, 51, 2203, 2213 (1929); Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, 125A, 277 (1929); Kistiakowsky and Lenher, *Nature*, 124, 761 (1929); *THIS JOURNAL*, 52, 3785 (1930).

<sup>2</sup> Spence and Taylor, *ibid.*, 52, 2399 (1930).