

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

**Saturated Standard Cells with Small Temperature Coefficients. IV. The Addition of Various Sulfates to the Electrolyte of the Weston Cell**

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Modification of the saturated Weston cell by the addition of bismuth to the amalgam and the double salt of sodium and cadmium sulfates to the electrolyte in excess gives a saturated cell of smaller temperature coefficient than that of the normal Weston cell.<sup>1</sup> Some cells made by the addition of other sulfates and double sulfates to the electrolyte of the Weston cell have now been studied.

The details of the preparation and measurement of the cells were essentially as described previously.<sup>1a</sup> The amalgam was a 10% cadmium amalgam, except as otherwise noted. The added salt was sometimes added merely in the form of the specially purified simple salt, with the expectation that any double salt formation necessary for stable equilibrium would take place within the cell. Care was taken to provide an excess of hydrated cadmium sulfate, except as mentioned below. In some of the cells the proper double salt was added, along with cadmium sulfate. Enough sulfuric or acetic acid was added to the electrolytes to make them either 0.01 molar with respect to sulfuric acid or about 0.07 molar with respect to acetic acid.

The cells in Table I all contained hydrated cadmium sulfate as one solid phase, and contained a second solid salt which was either the salt in the first column, or a hydrate of this, or a double salt formed from this salt and cadmium sulfate. The cells were kept at 25° until the electromotive forces were constant and then measured at other temperatures. The temperatures were probably correct within 0.05°. For comparison, data for sodium sulfate from a previous paper<sup>1a</sup> and for the Weston cell (no added salt), and for the amalgam cell,<sup>1</sup> Cd(Bi,Hg)/Cd<sup>++</sup>/Cd(Hg) have been added. The last was included because it was found that the cells of lowest temperature coefficient could be made by the use of a cadmium-bismuth amalgam instead of cadmium amalgam. The electromotive force of such a cell can be calculated by combination of the data for a Weston-type cell (made with cadmium amalgam) with that

for the amalgam cell as if the two were connected in series. The temperature coefficient of the combination cell is the algebraic sum of the coefficients of the amalgam cell and the Weston-type cell.

TABLE I  
MODIFIED WESTON CELLS CONTAINING AS SOLID PHASES HYDRATED CADMIUM SULFATE AND AN ADDITIONAL SULFATE OR DOUBLE SULFATE

| Sulfate added                                       | No. of cells | $E_{25}$ , v.        | $-\frac{E_2 - E_{25}}{T - 25}$ , v. $\times 10^4$ |     |     |      |
|---|--------------|----------------------|---|-----|-----|------|
|   |              |                      | 15°   | 20° | 30° | 35°  |
| (Amalgam cell) <sup>a</sup>                         | ...          | 0.00170              | -55   | -32 | 36  | 78   |
| (Weston cell)                                       | ...          | 1.01805              | 40  | 23  | -26 | -56  |
| (Na <sub>2</sub> SO <sub>4</sub> cell) <sup>b</sup> | ...          | 1.01668              | 45  | 24  | -28 | -64  |
| Li <sub>2</sub> SO <sub>4</sub>                     | 3            | 1.01411              | 52  | 28  | -31 | -66  |
| K <sub>2</sub> SO <sub>4</sub>                      | 5            | 1.01769              | 41  | 23  | -24 | -56  |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>     | 2            | 1.01598              | 118   | 64  | -71 | +343 |
| CaSO <sub>4</sub>                                   | 2            | 1.01801              | 46  | 25  | -27 | -57  |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>     | 1            | 1.01612              | 42  | 21  | -27 | -57  |
| Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>     | 2            | 1.01779 <sup>c</sup> | 45  | 25  | -27 | -59  |
| Zr(SO <sub>4</sub> ) <sub>2</sub>                   | 2            | 1.01737 <sup>d</sup> | 43  | 24  | -28 | -58  |

<sup>a</sup> Ref. 1. <sup>b</sup> Ref. 1a. <sup>c</sup> The two cells differed by 0.1 mv.

<sup>d</sup> The two cells differed by 0.2 to 0.25 mv.

From the data in Table I it can be seen that the cell containing lithium sulfate when combined with the amalgam cell should give a cell of lower temperature coefficient than the sodium sulfate cell.

A number of cells were made in which the electrolyte was saturated with cadmium and lithium sulfates<sup>2</sup> and the amalgam was cadmium-bismuth. These cells were made in four different groups and at different times. All were more or less disturbed by temperature changes, and sometimes they assumed new electromotive forces that seemed constant after changes in temperature. This could not be ascribed to impurities, because one pair of these cells which behaved abnormally was made at the same time and so far as possible with the same materials as three of the potassium sulfate cells of Table I, and the latter behaved normally.

The lithium sulfate cells shown in Table II have two objections as standards in comparison with the sodium sulfate cells,<sup>1a</sup> they are more variable and they have an electromotive force somewhat different from saturated and unsaturated Weston cells. The temperature coefficient has the low value predicted. The disagreement

(1) (a) Paper II, Vosburgh, Guagenty and Clayton, *THIS JOURNAL*, **59**, 1256 (1937); (b) Paper III, Vosburgh and Parks, *ibid.*, **61**, 652 (1939).

(2) Parks, Patterson and Vosburgh, *THIS JOURNAL*, **59**, 2141 (1937).

of Cells 817-822 in temperature coefficient may be the result of temperature hysteresis, which was somewhat pronounced in these cells.

TABLE II  
MODIFIED WESTON CELLS CONTAINING LITHIUM SULFATE  
AND CADMIUM-BISMUTH AMALGAM

| Cells                    | $E_{25}$ , v. | $\overline{E_t - E_{25}}$ , v. $\times 10^4$ |     |     |     |
|--------------------------|---------------|--|-----|-----|-----|
|                          |               | 15°  | 20° | 30° | 35° |
| (Calcd.)                 | 1.01581       | -3   | -4  | 5   | 12  |
| 817-22                   | 1.01593       | +4   | +5  | 0   | ..  |
| 831-34                   | 1.01591       | -6   | -5  | 4   | 13  |
| 837, 839-40 <sup>a</sup> | 1.01587       | ...  | -4  | 7   | 13  |
| 841-42                   | 1.01597       | ...  | +1  | 6   | 5   |

<sup>a</sup> These cells had an electromotive force of 1.01581 v. at 25° which was constant for several weeks when first prepared.

A few cells were made in which the electrolytes were saturated with a double salt of cadmium sulfate and potassium or ammonium sulfate together with an excess of potassium or ammonium sulfate. These cells had cadmium amalgams. In one group of these cells the electrolyte was saturated with both the double salt<sup>3</sup>  $K_2SO_4 \cdot CdSO_4 \cdot 1\frac{1}{2}H_2O$  and potassium sulfate, and in another the electrolyte was saturated with the double salt<sup>4</sup>  $(NH_4)_2SO_4 \cdot CdSO_4 \cdot 6H_2O$  and ammonium sulfate. Both cells had electromotive forces larger than that of the Weston cell, and much larger temperature coefficients. The results are shown in Table III.

TABLE III  
CELLS CONTAINING A DOUBLE SALT OF CADMIUM SULFATE  
BUT NO CADMIUM SULFATE SOLID PHASE

| No. of cells | Solid phases   | $E_{25}$ , v. | $\overline{E_t - E_{25}}$ , v. $\times 10^5$ |      |
|--------------|--|---------------|--|------|
|              |  |               | 20°  | 30°  |
| 2            | $K_2SO_4 \cdot CdSO_4 \cdot 1.5H_2O$ ; $K_2SO_4$         | 1.04780       | 79   | -75  |
| 3            | $(NH_4)_2SO_4 \cdot CdSO_4 \cdot 6H_2O$ ; $(NH_4)_2SO_4$ | 1.05975       | 378  | -401 |

In the previous paper on the sodium sulfate cells<sup>1a</sup> the most important data were for cells between one and two months old. The same cells, nos. 749-758, have now been observed for a much longer time, and some others of the same kind have been made. A new group, Cells 761-764, was made by Dr. Roger G. Bates. They were like Cells 754-758, the electrolyte having been made by the saturation of 0.1 M acetic acid solution with cadmium sulfate and the double salt. The amalgam for all these cells was cadmium-bismuth. Three of the newer group of cells when newly prepared agreed within 0.01 mv. with

(3) Benrath and Thönnessen, *Z. anorg. allgem. Chem.*, **208**, 408 (1932).

(4) Malhotra and Suri, *J. Phys. Chem.*, **34**, 2106 (1930).

Cells 749-758. The fourth was 0.02 to 0.04 mv. lower.

Cells 749-758 eight months after they were prepared agreed almost exactly with the values reported previously. At that time, Cells 750, 752 and 754 were withdrawn from the group for a test at room temperature. From Cells 761-764, Cell 764 was taken for test at room temperature and Cell 763 was accidentally broken. The remaining nine cells of the two groups were observed from time to time at constant temperature, and their record is given in Table IV. While these cells have shown no change in two years larger than the error of measurement, a group of unsaturated Weston cells could be expected to decrease in electromotive force by something of the order of magnitude of 0.1 mv.<sup>5</sup> during that time.

TABLE IV  
ELECTROMOTIVE FORCES OF MODIFIED WESTON CELLS  
CONTAINING SODIUM SULFATE AT VARIOUS AGES

| Cells         | $\overline{E_{25} - 101,800}$ , volts $\times 10^5$ |    |    |       |       |
|---------------|---|----|----|-------|-------|
|               | 3 mo.   | 8  | 13 | 17-23 | 24-29 |
| 749, 751, 753 | 41  | 41 | 41 | 41    | 40    |
| 755-758       | 39  | 38 | 38 | 38    | 38    |
| 761-762       | 37  | 37 | .. | 37    | 36    |

Four of the sodium sulfate modified cells were measured occasionally for a period of more than eight months at room temperature. The cells were mounted in wooden boxes to ensure uniformity of temperature.<sup>6</sup> The temperature as measured inside one of the boxes varied from 20 to 28.7°, while the average electromotive force of the four varied from 1.01835 to 1.01845 when no correction for temperature was applied. A correction for temperature would reduce the variation considerably.

It may be concluded that the sodium sulfate cell is more nearly constant in electromotive force at constant temperature than the unsaturated Weston cell, for periods of over two years at least. Its variation under ordinary room-temperature conditions is not large enough to cause serious error for many purposes if it should be used as a standard.

### Summary

Modified Weston cells were prepared in which the electrolytes were saturated with two sulfate salt phases, one phase being either hydrated cad-

(5) (a) Vosburgh, *J. Optical Soc. Am.*, **11**, 59 (1925); (b) Smith, *Rev. Sci. Instruments*, **5**, 425 (1934).

(6) For the mounting of these cells and for some of the electromotive force measurements the authors are indebted to Mr. Harry Pfann.

mium sulfate or a double salt of cadmium sulfate. These cells were measured at different temperatures.

The temperature coefficient of the cell containing lithium sulfate was such that if made with cadmium-bismuth amalgam it would have a temperature coefficient less than that of the sodium sulfate cell previously reported.

A number of the lithium sulfate cells with ternary amalgams were not as constant or reproducible as the sodium sulfate cell.

Further observations on the constancy and reproducibility of the sodium sulfate cell are reported.

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## The System $\text{Li}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ at $0^\circ$

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Systematic studies of the ternary system  $\text{Li}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$  have been carried out at  $30^\circ$ <sup>1</sup> and at  $0^\circ$ <sup>2</sup> and in both cases it was concluded that the only solid phases in equilibrium were  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ . In the study at  $0^\circ$ , the solubility of pure lithium sulfate was found to be 25.43%, while for aluminum sulfate the value found was 27.02%. The former value differs considerably from that found by Friend,<sup>3</sup> namely, 26.51%, which was determined using carefully prepared and purified lithium sulfate and employing an analytical method which was direct and not subject to appreciable error. The aluminum sulfate value given above is considerably higher than the values found by Poggiale<sup>4</sup> and by Kremann and Hüttinger<sup>5</sup> and definitely lower than a recently found value<sup>6</sup> of 27.97%. The large differences in the values for both salts undoubtedly are due to differences in the purity of materials used, methods of obtaining equilibrium and the analytical methods employed.

Rather recently the existence and properties of a lithium alum have been reported.<sup>7</sup> The alum is supposedly formed at temperatures in the neighborhood of  $0^\circ$  although no definite temperature is mentioned.

In view of these claims as well as the disagreements in solubilities mentioned above, it was thought advisable to reinvestigate the ternary system at  $0^\circ$ , taking special care as to the materials used, methods of obtaining equilibrium and methods of analysis.

(1) Schreinemakers and de Waal, *Chem. Weekblad*, **3**, 539 (1906).

(2) Sanders and Dobbins, *J. Phys. Chem.*, **35**, 3086 (1931).

(3) Friend, *J. Chem. Soc.*, **128**, 2330 (1929).

(4) Poggiale, *Ann. chim. phys.*, [3] **8**, 463 (1843).

(5) Kremann and Hüttinger, *Jahrb. K. K. geol. Reichsanst.*, **58**, 645 (1908).

(6) Dobbins and Addeleston, *J. Phys. Chem.*, **39**, 637 (1935).

(7) Spencer, *Nature*, **138**, 169 (1936).

### Purification of Materials

**Lithium Sulfate.**—Reagent grade (Merck) lithium carbonate was recrystallized from hot water according to the method of Kraus and Burgess.<sup>8</sup> After drying, this salt was used to neutralize 6 *N* sulfuric acid. This solution was heated to boiling and slowly evaporated. The lithium sulfate which crystallized out was separated from the solution, drained and washed with 95% alcohol and then dried at  $130^\circ$ . It was then heated in platinum to expel traces of sulfuric acid.

**Aluminum Sulfate.**—The problem of obtaining hydrated aluminum sulfate of known composition for use in making up complexes offered some difficulties. Hill and Kaplan<sup>9</sup> attempted to prepare the octadecahydrate by allowing the recrystallized salt to come to constant composition in desiccators over some partially dehydrated aluminum sulfate, which consisted of a mixture with the next lower hydrate, the supposed  $16\text{H}_2\text{O}$ . This procedure was not wholly successful in that the salt thus produced usually contained more than the required amount of water (as revealed by aluminum determinations on the material). This also has been the experience of Smith.<sup>10</sup> It is questionable whether occluded water is removed by this method of drying. It is believed that the slow crystallization of aluminum sulfate is favorable to the occlusion of considerable amounts of water.

The material used in this investigation was prepared in the following manner. Reagent grade (Merck) aluminum sulfate was dissolved in water at  $60^\circ$  to make a solution of sp. gr. 1.33. The filtered solution was cooled slowly to room temperature. The crystals were filtered off and sucked as dry as possible. After washing with 95% alcohol, the crystals were again sucked as dry as possible. In order to free the crystals of occluded water, they were effloresced in vacuum desiccators over sulfuric acid. The desiccators were evacuated repeatedly to remove the alcohol. The salt, in a finely divided condition, was placed in small amounts (5–10 g.) on petri dishes in desiccators over a saturated solution of sodium bromide dihydrate. Analysis of the salt for aluminum by the quinolate method<sup>11</sup>

(8) Kraus and Burgess, *THIS JOURNAL*, **49**, 1227 (1927).

(9) Hill and Kaplan, *ibid.*, **60**, 551 (1938).

(10) Private communication from Mr. Norman Smith at New York University.

(11) Kolthoff and Sandell, *THIS JOURNAL*, **50**, 1900 (1928).