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lime-light extends much further. But it might be possible to establish a sort of spectroscopic scale of temperatures if the lines which are successively developed as the temperature rises were carefully noted. Thus the appearance of the iron line T seems to synchronize with temperature of about 3000°. The lithium blue line is invisible in the flame of an ordinary Bunsen burner, but is just visible at the temperature of the inner green cone formed by reducing the proportion of gas to air in such a burner, while in the exploding gas the green line too is seen. It seems to need a temperature above 3000° to get the aluminium lines at H. Probably no line is ever abruptly brought out at a particular temperature—it will always be gradually developed as the temperature rises; yet the development may be rapid enough to give an indication which may be useful in default of means of more exact measurement. In former papers treating of spectroscopic problems (Proc. Roy. Soc. vol. xxxiv. p. 130, and xxix. p. 489) we have more than once adverted to the necessity of the study of the spectra both of flames and of the electric discharge under modified conditions of pressure. The projected experiments on the arc in lime-crucibles have not yet been carried out; but the present is a first instalment of a study of flame-spectra under such conditions.

XXIII. *On Normal Elements for Electrometric Measurements.*
By H. W. BEETZ*.

IN order to measure a difference of potential in absolute units a normal element is required, having a perfectly definite electromotive force, which can either be put together once for all, or can always be set up in exactly the same way and without too much trouble. According to Kittler's experiments†, a Daniell element, having a porous cell, does not at all fulfil these conditions, since its electromotive force is subject to continuous change. On the other hand, an element composed of chemically pure zinc and pure copper, in dilute sulphuric acid and copper-sulphate solution of definite strength, the solutions being placed in connexion by means of a siphon-tube terminating in small openings and filled with the same sulphuric acid, has always the same electromotive force, and since it can easily be put together, forms

* Translated from Wiedemann's *Annalen*, xxii. p. 462.

† *Sitzungsber. d. k. bayer. Akad. d. Wiss.* p. 467 (1882); *Wied. Ann.* xvii. p. 865 (1882).

a convenient standard cell. Using concentrated copper-sulphate solution and dilute sulphuric acid of specific gravity 1·075, Kittler found the electromotive force of such an element to be 1·195 volt, which decreased to 1·059 volt when the dilute sulphuric acid was replaced by concentrated zinc-sulphate solution.

Of the Daniell elements hitherto employed for measurement of difference of potential, that of Raoult* best fulfils the conditions here laid down; that of Lodge†, employing dilute zinc-sulphate solution, less satisfactorily; whilst combinations containing porous cells, such as that proposed by Buff‡, are still less suited to serve as normal elements.

But none of these are able to maintain a constant electromotive force, as is now desirable for electrometric measurements, since in all gradual diffusion of the liquids takes place. I myself§ have formerly made use of similarly arranged normal elements, for measurements made according to the compensation-method; but they do not answer for electrometric measurements, and I have therefore been obliged continually to renew the element. For the length of time during which unbroken observation with the electrometer is usual, we may rely upon the constancy of the element.

The frequent putting together and taking apart of an element is a labour always willingly avoided. Hence the permanently-connected zinc and mercury element of Latimer Clark|| was gladly welcomed. Its electromotive force (1·457 volt) was found nearly constant in different preparations of the element according to the method described. But it has two undesirable properties: the one is the great variation of electromotive force with change of temperature, which, however, is easily allowed for in calculation, but which does not exist¶ in the case of the Daniell elements; the other is the great decrease which the electromotive force suffers if the circuit is closed even for a very short time. This may easily occur. An unintentional contact in some of the auxiliary apparatus employed in the measurements, for example in the key which I have described**, is sufficient to render the element useless for one or several days. I obtained a diminution of electromotive force, amounting to 2 per cent., in a Latimer-Clark

* *Ann. de Chim. et de Phys.* [4] ii. p. 345 (1864).

† *Phil. Mag.* [5] v. p. 1 (1878).

‡ *Lieb. Ann.* lxxv. p. 4 (1853).

§ *Wied. Ann.* iv. p. 5 (1878).

|| *Proc. Roy. Soc.* xx. p. 444 (1878); *Beibl.* ii. p. 565 (1878).

¶ Kittler, *loc. cit.* p. 371.

** *Wied. Ann.* x. p. 371 (1880).

element in which the circuit had been closed for only half a minute. A Daniell element would have shown scarcely any change under similar conditions.

But this defect of the Latimer-Clark element may be almost entirely remedied by giving to the cell so great a resistance that only an insignificant current can be generated.

A U-tube of 1 centim. diameter and legs 75 centim. long was filled with the paste of mercury-sulphate and zinc-sulphate solution, prepared according to the instructions, but heated so much that after cooling it became hard. The paste was boiled in the tube by means of a water air-pump. The zinc pole was introduced into the upper end of the tube and the mercury pole into the lower, and the openings were closed with paraffin. The element is very convenient for use on the laboratory-table, since the two poles may pass through holes bored in the table, the whole body of the tube being protected underneath the table. The internal resistance of the element was 15,700 ohms*. Its electromotive force was somewhat smaller than given by Latimer Clark. If, in fact, the electromotive force of a normal Daniell cell (with dilute sulphuric acid) be taken as 1.195 volt, then that of my mercury element was 1.442 volt (instead of 1.457 volt). When the element was short-circuited, its electromotive force was as follows:—

After 5 minutes	. . .	1.440 volt.
„ 1 hour	. . .	1.439 „
„ 4 hours	. . .	1.439 „
„ 6 „	. . .	1.437 „
„ 12 „	. . .	1.434 „
„ 48 „	. . .	1.408 „

We see therefore that the element resists the influence of polarization for a long time. Polarization could indeed only be very slight, since the current which passed through the element has only the intensity of 0.000091 ampere. The electromotive force only diminished 2 per cent. after use for 48 hours, a decrease which is very small indeed compared with the falling off in the usual form of the Latimer-Clark element. It is easy to avoid short-circuiting the element for such a length of time; but if the element has once become enfeebled, it recovers itself only slowly. Thus, after 24 hours I found its strength to be 1.430 volt.

The idea of replacing the fluid of an element by a solid body may be carried out also with a Daniell element. Fine alabaster plaster-of-Paris was mixed with concentrated copper-

* The resistances were measured by my first assistant, Dr. Pfeiffer, by the use of alternate currents.

sulphate solution to about the consistency employed in making plaster casts, and some more with concentrated zinc-sulphate solution. A U-shaped glass tube, of 4 millim. diameter and with legs 22 centim. long, was partly filled with the one paste, and after it had set was filled up with the other, so that the two were in close contact. A copper wire was introduced into the copper paste before it had set, and a zinc wire into the zinc paste. The upper part of each leg was cleared from plaster and filled up with paraffin.

Several dry Daniell elements thus prepared were compared with an element put together with concentrated solutions of copper sulphate and zinc sulphate, and tested in respect of the effect of change of temperature and of short-circuiting. Taking the electromotive force of the liquid element as equal to unity, the three dry elements I., II., and III. gave, when measured on different days:—

I.	II.	III.
0.996	0.993	1.000
0.998	0.996	0.996
1.000	0.999	0.993
...	0.998	0.998
Mean . . 0.998	0.996	0.997

The temperature varied in all these observations by a few degrees only; the small apparent variations in the electromotive force of the dry elements are partly at least accounted for by small changes in the electromotive force of the fluid element, which was put together fresh each time. On the whole, however, the dry element is a little weaker than the fluid element; it contains no amalgamated zinc, because such amalgamated wires are very brittle.

A second series of experiments was concerned with the influence of temperature. The elements II. and III., sometimes at the temperature of the air, sometimes in baths of different temperatures, were compared with the fluid element, which had always a temperature of nearly 20 °C. On account of the small conducting-power of the dry elements for heat, they remained always three quarters of an hour in the bath before the measurements were made. If the electromotive force of the fluid element is again taken as unity, that of the dry element was as follows:—

II.			III.		
At 0°		0.996	At 1°		1.007
„ 20		0.993	„ 21		1.000
„ 39		0.983	„ 32		0.995
			„ 55		0.981

The decrease in electromotive force of each of the two elements for low temperatures between 0° and 20° amounted to only 0.015 per cent. for an increase in temperature of 1° . But the temperature-coefficient increases with increase of temperature. With element II. it amounted to 0.053 between 20° and 30° ; with element III. to 0.045 between 21° and 32° , and between 32° and 55° even to 0.061. For Latimer-Clark's element, Helmholtz and von Kitter* agree in finding it to be 0.08. Within the narrow limits within which electrometric measurements are commonly made, the influence of temperature upon the electromotive force of the dry Daniell element may be altogether neglected.

The effect of short-circuiting is seen from the following experiments made with elements I., II., III.

The element was short-circuited for a certain length of time, then contact was broken, and the difference of potential measured. We do not thus obtain actually the lowest value which the difference of potential may attain, since this increases even during the few seconds which the measurement requires; but we do obtain the value with which we are actually concerned in our measurements.

The elements I. and II. were scarcely influenced at all by having the circuit closed for half a minute; but element II. sank from 1.000 to 0.997, but quickly recovered itself completely. The following changes were caused by more prolonged closing of the circuit:—

I.		II.	
	0.998		1.000
After 10 minutes ...	0.991	After 1 hour	0.994
„ 35 „ ...	0.988	„ 15 hours	0.988
„ 14½ hours	0.975	„ 20 „	0.988
.....	0.996		0.993
„ 15 „	0.986	„ 15½ „	0.987
5 minutes open	0.994	„ 24 „	0.986
		„ 39 „	0.987
		5 minutes open	0.994
III.			
			1.000
After 15 minutes	0.996		
„ 50 „	0.994		
„ 17 hours	0.989		
5 minutes open	0.992		

After the lapse of a quarter of an hour the open element had in all cases recovered its former electromotive force.

* Kitter, *Sitzungsb.* loc. cit. p. 501.

The dry Daniell elements have therefore this in common with Latimer-Clark's element, that they can be prepared once for all; but they have further this advantage, that they are scarcely at all influenced by temperature; and that an accidental closing of the circuit produces only an insignificant decrease even in elements of small size (about 1 per cent.), which is very soon recovered. If the electromotive force of a Daniell element put together with copper, zinc, concentrated copper-sulphate solution, and concentrated zinc-sulphate solution be taken as 1.059 volt, then the mean electromotive force of a dry Daniell element = 1.056. It must, however, be remembered that the value 1.059 is based upon the assumption that the force of a Latimer-Clark element = 1.457 volt, which estimate is only to be considered as a preliminary one.

The resistance of element I. was 14,600 ohms, of element II. 13,500 ohms. The strength of current passing through a short-circuited element is therefore 0.000072 ampere for element II., and 0.000078 ampere for element III.; *i. e.* in the first 0.08 milligrm. copper would be deposited in the hour, and with the latter 0.09 milligrm. copper.

The dry Daniell elements are to be recommended for another purpose, *viz.* for charging a quadrant-galvanometer. Zamboni's pile has not proved successful for this purpose; it acts excellently for a time, but then the potential difference of its poles changes suddenly, especially with irregular changes of temperature. Apparently the deposition of moisture on the inside of the glass tube containing the pile produces a partial short-circuiting of the pile. With a water-battery these sudden changes do not occur, but the difference of potentials decreases gradually, if slowly. Errors in measurement cannot be caused thus; but the deflections of the electrometer become smaller and smaller, and, apart from the necessity of renewing the evaporated water from time to time, the whole battery every now and then has to be disconnected and cleaned from deposits of oxide and carbonate. I found the electromotive force of a newly prepared zinc and copper element filled with spring-water to be 0.992 volt. After twelve hours, during which the element remained open, it had sunk to 0.934 volt. Three of the elements forming my water-battery, which has stood now more than a year, were examined. They showed the following differences of potential:—

0.838 0.678 0.724 volt. Mean 0.743 volt.

The dry Daniell elements may conveniently be combined

into a battery which requires no filling, and upon which temperature and moisture are without influence.

Since the resistance of the elements is a matter of indifference, they may be made very small. I have filled glass tubes, 8 centim. long and 5 millim. diameter, half with the copper-sulphate plaster and half with the zinc-sulphate plaster, wires of copper and zinc being placed in the corresponding mixture, which wires were then soldered together, as shown in the accompanying figure. The ends of the tubes are closed with paraffin.

Twelve such elements form a row. Twelve such rows stand one behind the other, each connected with the preceding one by insulated binding-screws, so that each chain of twelve elements hangs between two binding-screws. Any desired number of such series of twelve elements may therefore be taken to produce the charge. The whole battery of 144 elements shows a polar difference of potential of 152 volts; whereas the same difference requires 156 elements of the freshly prepared water-battery and 200 of the enfeebled one. The whole dry battery covers a surface of 16 centim. square.

POSTSCRIPT.—In the elements last prepared the zinc wires are amalgamated at the ends and covered elsewhere with shellac, and the concentrated solutions have been diluted with one third of water.

XXIV. *The Molecular Volumes of Salt-Solutions.*—Part II.
Water of Crystallization. By W. W. J. NICOL, M.A., B.Sc.,
 F.R.S.E., F.C.S., Lecturer on Chemistry, Mason College,
 Birmingham*.

IN my previous paper† on this subject I showed that the molecular volumes in solution of the metals sodium and potassium, and those of certain acid-radicals—Cl, (SO₄), (NO₃), (ClO₃), and (OH)—are constant in whatever way these may be combined together to form salts, the essential point to be observed being that the solutions are sufficiently

* Communicated by the Author.

† Phil. Mag. August 1883; *Ber. der deut. Chem. Ges.* xvii. p. 492.