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Chemistry. — "The electromotive force of zinc amalgams". By Prof. ERNST COHEN and W. TOMBROCK. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of May 29, 1909).

1. After it had been found, in the development of the thermodynamics of the normal cells ¹), that the deviations which the E. M. F. of the WESTON-cell exhibits under definite circumstances must be attributed to the peculiar behaviour of the cadmium amalgam used therein, the researches of H. C. BIJL ²) have elucidated the matter so that we are now in a better position to judge. Yet, the latest researches of ERNST COHEN and H. R. KRUYT ³) have proved that the last word has not yet been spoken in this matter and that a continuation of the study of the cadmium amalgams in the direction indicated will be necessary before we arrive at the construction of an accurate temperature formula for that standard ⁴).

2. An investigation of the zinc amalgams whose electromotive force will have to be known accurately if the CLARK-cell is really to be used as a standard, was undertaken by one of us some years ago⁵). This field, however, is nearly quite barren. The most confused ideas still reign, as may be shown by the fact that the American Electrochemical Society at the Meeting, May 1907 made the following theme a subject of discussion "If an electrode of zinc and another of amalgamated zinc be placed in a solution of zinc and the electrodes connected externally, a current will flow in the external circuit from the zinc plate to the amalgamated one and zinc will be deposited in the former. What is the source of energy of this battery? It has been thought to be thermal, and that the liquid cools by virtue of this reaction, thereby absorbing heat from the air. If so, it would offer a direct means of changing the heat energy of the air into an electric current, and would seem to be contrary to the second law of thermodynamics."

We will again refer in detail to the theory of that phenomenon in our paper which will appear shortly in the Zeitschrift fur physikalische Chemie. Here it may be pointed out that, first described by

¹⁾ ERNST COHEN. Proc 1900 Vol. III, p. 91.

²) Zeitschr. für physik. Chemie 41, 641 (1902).

³) Zeitschr. fur physik. Chemie **65**, 359 (1909).

⁴⁾ Proc. 1900 Vol. III, p. 225.

⁵) Electrochemical and Metallurgical Industry, 5, 98 (1907).

HUMPHRY DAVY¹), it attracted the attention of FARADAY²), GAUGAIN³), POGGENDORFF¹), HENRICI⁵), ANTOINE BECQUEREL⁸), REGNAULT⁷), WILLARD GIBBS⁸), ROBB["]), GABRIEL LIPPMANN¹⁰) and SPENCER¹¹) and that theories to explain the *polar exchange* which was supposed to occur therein have not been wanting. We may state, however, that this phenomenon does not take place if only due precautions are taken and that there is no question of a "conflict" with the second law of thermodynamics.

3. In order to exclude secondary reactions our determinations for the measurement of the E.M.F. of different concentrated amalgams were carried out at 0° .5. The details of the experiments will be described fully later on. It should be mentioned that the materials used comply with high demands as to purity.

Chemically pure zinc possesses towards the solution of its salts a sharply defined potential, but only then when it has been deposited electrolytically in dendritic, or fungoid form¹²). We replaced it by a $10^{\circ}/_{\circ}$ amalgam such as is used in CLARK's normal cells and constructed H-shaped cells according to the scheme:

Zinc amalgam	dilute solution	Zinc amalgam
10º/, by weight	${\operatorname{of}}_{\operatorname{ZnSO}_4}$	$x^{o}/_{o}$ by weight

The $x^{0}/_{0}$ amalgams (x between 2,5 and $6^{0}/_{0}$) used therein were prepared by weighing and melting the materials with special precautions. The amalgams were then introduced into the H-shaped cells.

The amalgams of a lower concentration were investigated by means of the little apparatus shown in the Fig.

HOCKIN and TAYLOR, JOURN. Soc. Tel. Ing. 8, 282 (1879).

¹⁾ Phil. Trans. Roy. Soc. 116, 405 (1826).

²⁾ Phil. Trans. Roy. Soc. 1834, Part. I 459 § 1004 en 1005.

³) C. R. 42, 430 (1856).

¹) Poggendorffs Annalen 50, 262 (1840).

⁵) Poggendorrrs Annalen 58, 376 (1843).

⁶⁾ Traité d'Electricité et de Magnétisme, Paris 1854. Tome 1, p. 221.

⁷⁾ Ann. de chim. et de physique (3) 44, 453 (1855).

⁸⁾ Transactions of the Connecticut Acad. of Arts and Sciences 3, 343 (1878).

⁹⁾ WIEDEMANNS Annalen, N. F. 20, 798 (1883).

¹⁰) Journ. de Physique (2) 3, 388 (1884).

¹¹) Zeitschr. für Elektrochemie 11, 681 (1905).

CROVA, Ann. de chim. et de phys. (3) 69, 458 (1863).

ST. LINDECK, WIEDEMANNS Ann. N.-F. 35, 311 (1888).

¹²) TH. W. RICHARDS and LEWIS, Zeitschr. für physik. Chemie 28, 1 (1899),



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On the bottom of the right limb is placed a $10^{\circ}/_{\circ}$ zinc amalgam and in the left limb a weighed amount of pure mercury. The whole is filled up with a solution of zinc sulphate not saturated at 0°.5 (its reaction was perfectly neutral towards congo-red).-I and I are two rods of chemically pure zinc which are in communication with the polar terminals Zn_1 and Zn_2 , while P_1 and P_3 lead to the mercury and the $10^{\circ}/_{\circ}$ amalgam respectively. The apparatus is placed in a thermostat $(0^{\circ}.5)$ and Zn, and P, are now put in a circuit, in which is placed an accumulator with a resistance coil, in such a manner that on closing the same Zn, acts as anode and P_1 as cathode. A certain amount of metallic zinc is then precipitated from the zinc sulphate solution which dissolves in the mercury and so yields an

amalgam. In that circuit we also put a milliampèremeter; so if the time which the current has passed is known, the concentration of the amalgam formed will be accurately known. Our milliampèremeter was carefully checked by means of a silver coulometer, but by way of control we also put in during the experiment two silver coulometers besides the milliampèremeter.

If, now (by means of a swing) P_1P_2 or Zn_2P_2 , respectively, is introduced into the potentiometer of POGGENDORFF-DU BOIS-REYMOND, the E.M.F. between the $10^{\circ}/_{\circ}$ zinc amalgam and the *x*- $^{\circ}/_{\circ}$ amalgams formed may be measured at any moment, and also that between pure zinc (in rod shape) and the $10^{\circ}/_{\circ}$ amalgam.

Before each measurement the whole cell was shaken vigorously in order to stir up the zinc solution (whose concentration might change locally in consequence of the electrolysis) and also the amalgam.

5. Whereas for the sake of brevity we omit the description of these measurements and of the controlled apparatus employed we give in the following tables the results of our measurements. It should be stated that all the experiments were made in duplicate.

As required by theory the $10^{\circ}/_{\circ}$ amalgam forms at all concentrations where there is still an E. M. F. the negative (solution pole). The second and third column show how little defined is the potential of pure zinc; the rods Zn₁ and Zn₂ were two halves of the same rod.

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TABLE I.

Temperature 0°.5 C.

Е. М.	F. in	Volts of	a 10°/,	Zinc	amalga	m towa	rds:
۲	(This	amalgam	forms	the n	egative	pole).	

Amalgam	of <i>x</i> º/ ₀ Zn	Zinc pole Zn ₁	Zinc pole Zn ₂
x = 0.103	0.0285	0.0086	0.0146
0.309	0.0161	0.0079	0.0146
0.619	0.0078	0.0073	0,0113
1.031	0.0024	0.0065	0.0097
1.134	0.0016	0.0066	0.0090
1.237	0.0007	0.0069	0.0082
1.340	0.0000	0.0064	0.0076
1.443	0.0000	- 0.0067	0.0075
1.856	0.0000	0.0060	0,0066
2.268	0.0000	0.0060	0.0062

This again shows that zinc in this form is unfit for potential measurements.

In the tables now following the E. M. F. of the amalgam cells with amalgams of higher concentration are indicated at $0^{\circ}.5$ in volts. The times are hours after the construction of the cells. The + and - signs placed before the potential difference indicate that the *least* concentrated amalgam forms the positive, or the negative pole respectively of the cell investigated.

TA	BLI	ΞII.

1	0º/	ama	lgam-	-2.57°,	/. :	amalgam.

Time	E. M. F. in Volts.		
Time	Cell I	Cell II	
0	- 0.0003	- 0.0003	
0.5	0.0000	0.0000	
3.5	+ 0.0001	0.0000	
11.75	,+ 0.0001	+ 0.0001	
22 25	- 0.0001	- 0.0000	
	l		

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TABLE III.

10º/, amalgam-3.40º/, amalgam.

Time	E. M. F. in Volts.		
Thire	Cell III	Cell IV	
0	+ 0.0004	+ 0.0001	
0.5	+ 0.0002	0.0000	
1.25	+ 0.0001	+ 0.0001	
7.25	+ 0.0002	+ 0.0001	
17.50	+ 0.0003	+ 0.0000	

TABLE IV.

1

 $10^{\circ}/_{\circ}$ amalgam-4.34°/ $_{\circ}$ amalgam.

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Time	E. M. F. in Volts.		
	Cell V	Cell VI	
0	-+0.0007	0.0000	
05	+0.0001	0.0000	
21.3	0.0000 0.0000		
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TABLE V. 10°/_o amalgam—7.88°/_o amalgam.

Time	E. M. F.	in Volts.
Time	Cell VII	Cell VIII
0	0.0000	0.0000
24.3	0.0000	0.0000

TABLE VI.

$10^{\circ}/_{\circ}$	amalgam-	$-20.34^{\circ}/_{\circ}$	amalgam.
		, ,	

Time	E. M. F.	in Volts.
Ime	Cell IX	Cell X
0	-+-0.0001	0.0001
3.5	+0 0004	+0.0004
7	+0.0001	+0.0001
3,5	-+-0.0001	-+0.0001

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TABLE VII.

 $10^{\circ}/_{\circ}$ amalgam—'38.82°/_o amalgam.

Time	E. M. F.	in Volts.
1 Inte	Cell XI	Cell XII
0	+0.0001	0.0000
4	0.0000	0.0000
7	+0.0001	+0.0001
13.5	+0.0001	+0.0001

TABLE VIII.

 $10^{\circ}/_{\circ}$ amalgam- $60^{\circ}/_{\circ}$ amalgam.

Time	E. M. F. in Volts	
	Ceil XIII	Cell XIV
0	+ 0.0008	+ 0.0007
3.5	+ 0.0006	+ 0 0006
7	+ 0.0006	+0.0006
13.5	+ 0.0001	+ 0.0001
23.5	0.0000	+ 0.0008
29.0	+ 0.0001	+ 0.0010
30.5	- 0 0008	+ 0.0008
31.25		+ 0.0008
37.25	-	+ 0.0009
47.75	+ 0.0009	+ 0.0009
	1	1

The previous measurements of ERNST COHEN have taught us that at 0° the potential difference between pure (dendritic) zinc and the $10^{\circ}/_{\circ}$ amalgam amounts to 0.000488 volts, the zinc forming the negative pole. From the above measurements we may conclude that in the cases where a potential difference between zinc and zinc amalgams does exist, this is always of such a nature that the zinc forms the negative pole.

All the objections arising from the fact that previous observations have been made with materials insufficiently electrically defined are thus removed and the "explanations" given for the occurrence of *polar exchange* also no longer count.

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As soon as the investigation as to the relation between the progressive change of the melting point line of the zinc amalgains and their electromotive force which is being carried out by Mr. P. J. H. VAN GINNEKEN, is completely drawn to a close we will revert to the question in regard to the CLARK-cells.

Utrecht, May 1909.

VAN 'T HOFF Laboratory.

Chemistry. — "On the action of active copper on linalool." By Dr. C. J. ENKLAAR. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the Meeting of May 29, 1909).

In a previous investigation¹) I have shown, that the tertiary aliphatic terpene alcohol linanool may be converted by means of active nickel and hydrogen into a saturated tertiary alcohol and a decane; I have prepared this alcohol synthetically and thus demonstrated the position of the (OH)-group in the formula of linalool. As in consequence, the existing differences of opinion as to this structural formula have been removed, I now accept with TIEMANN and SEMMLER the following formula for linalool:

$$CH_{3} - C = CH - CH_{2} - CH_{2} - CH_{2} - CH = CH_{2}$$

The usual methods to eliminate the elements of water from tertiary alcohols, and so to prepare hydrocarbons, are often incomplete when the products of the reaction are variable. For instance by the action of acids on linalool the terpenes dipentene and terpinene") occur amongst the products formed, whose structures bear no relation to the structural formula of the starting product. We may, therefore safely assume that the formation of dipentene and terpinene is accompanied by a radical shifting of bonds either in the linalool molecule or in that of a primarily formed hydrocarbon. In my opinion, the real dehydration product of linalool has, therefore, escaped notice and final products of an "inversion" have been obtained, which nearly every other terpene would have yielded.

¹⁾ Rec. Trav. Chim. 27, 411 (1908).

²) BERTRAM and WAHLBAUM, J. pr. Ch. [2], 45, 601 (1892).