

*Citation:*

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valve require no further explanation) to the tube  $H_0$ , in which the pressure is indicated by the manometer, and further along  $H_1$  to  $I$ . When the safety-valve  $C_{30}$  rises the canals  $C_{40}$  and  $C_{41}$  make a communication between the exhaust chamber behind  $C_{21}$  (fig. 4) and the forcing chamber behind  $C_5$ . This safety-valve is pressed by a long spring  $C_{33}$  with adjusting block  $C_{34}$  and adjusting pin  $C_{35}$ . The adjusting pin passes through the packingbox  $C_{36}$ , ends in a square head  $C_{3s}$ , and is adjusted for a given pressure by means of a wrench. If this is done we can allow the auxiliary compressor to work whether the mercury pump takes up the compressed gas or not.

**Chemistry.** — “*The alleged identity of red and yellow mercuric oxide*”. Part II. By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read January 27, 1900.)

1. It has been stated in my first communication<sup>1)</sup> that there exists between red and yellow mercuric oxide a difference in free energy 0.685 millivolts at 25.°0.

I now wish to communicate some details as to the determination of the temperature coefficient of the previously described mercuric oxide cell and discuss the thermic determinations made by VARET in 1895<sup>2)</sup>.

2. The E. M. F. of the mercuric oxide cell may be represented by the equation :

$$\pi = \frac{E_c}{n\epsilon_0} + T \frac{d\pi}{dT}$$

in which  $\pi$  is the E. M. F. of the cell at the temperature  $T$ ,  $E_c$  the chemical energy of the process taking place on the passage of  $\epsilon_0$  Coulombs, whilst  $n$  represents the valency of the mercury.

If  $\pi$  and  $T$  and also the temperature coefficient  $\frac{d\pi}{dT}$  are known we can calculate  $E_c$  with the aid of the said equation.

1) Proc. Royal Acad. Nov. 25, 1899, pg 273.

2) loc. cit. pg. 273, note 1.

3. In order to determine experimentally  $\frac{d\pi}{dT}$ , the same element which had been used for the measurements at  $25^{\circ},0$ <sup>1)</sup> was immersed in a thermostat kept at  $35^{\circ},0$ . The arrangement was quite the same as the one previously described. The standard cells (WESTON and CLARK) remained in the thermostat which I had used previously at  $25^{\circ},0$ .

From time to time the E. M. F. of the mercuric oxide cell was measured in the manner previously described; after it had become constant, the measurements were continued for a number of hours.

In this way was found:

E. M. F. of the mercuric oxide cell I at $35^{\circ},0$ .	
Hours after placing in the thermostat.	E. M. F. (millivolts).
$50\frac{1}{2}$	0.774
69	0.774

By way of control, the whole investigation was repeated. A new element (II) was fitted up; the same chemicals were used whose preparation and purification have been fully described in the first communication.

This element was afterwards heated to  $35^{\circ},0$ .

E. M. F. of the mercuric oxide cell II at $35^{\circ},0$ .	
Hours after the composition.	E. M. F. (in millivolts).
220	0.772
244	0.772

4. Finally the used WESTON-cell was again compared with the two CLARK-cells *A* and *B* in the same manner as before,

$$\frac{E.M.F. \text{ CLARK } A_{25^{\circ}}}{E.M.F. \text{ WESTON }_{25^{\circ}}} = 1.3942 \quad \frac{E.M.F. \text{ CLARK } B_{25}}{E.M.F. \text{ WESTON }_{25^{\circ}}} = 1.3940,$$

whilst in former experiments the relations 1.3946 and 1.3945 were found.

We now find for the temperature-coefficient of the mercuric oxide cell

$$\frac{0.773 - 0.685}{10} = 0,0088 \text{ millivolts.}$$

<sup>1)</sup> Proc. Royal Acad. Nov. 25, 1899, pg. 280.

If, now, we introduce into the equation

$$\pi = \frac{E_c}{n\epsilon_0} + T \frac{d\pi}{dT}$$

or

$$E_c = n\epsilon_0 \left( \pi - T \frac{d\pi}{dT} \right)$$

the found values  $\left( T = 298; \pi = 0.685; \frac{d\pi}{dT} = 0,0088 \right)$  and express everything in caloric measure we find

$$E_c = -2 \times 23,09 \times 1,9374 = -89.4 \text{ calories } ^1)$$

6. VARET has determined in 1895 the heat of reaction of red mercuric oxide with hydrocyanic acid. He finds this to be 31550 calories, whilst BERTHELOT found 31600 for the yellow oxide. VARET then observed: "On voit que la transformation de l'oxyde "jaune de mercure en oxyde rouge ne donne lieu à aucun effet "thermique appréciable."

The difference of  $-50$  calories certainly does not signify much considering it is a difference between two large figures and the ordinary calorimetric determinations are subject to rather great errors. Still I cannot help pointing out that the calculated results of  $-89$  calories and the experimental result obtained by VARET are of the same order, whilst our electrical measurements decidedly prove that there must exist a difference in chemical energy between the two varieties of mercuric oxide.

It is moreover somewhat illogical on the part of VARET <sup>2)</sup> to state that no appreciable thermic effect takes place when the yellow oxide changes into the red modification, when in his paper on the different modifications of mercury sulphide, real importance is attached to the caloric value of  $-60$  calories obtained as a difference between 240 and 300 calories.

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<sup>1)</sup> Strictly taken we ought to pay attention to the difference of heat of solution of HgO in the solutions of KOH.

<sup>2)</sup> Ann. de chimie et physique [VII] T. 8 p. 102. (1896).