

*Citation:*

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**Chemistry.** — “On a new principle for the direct determination of osmotic pressure”. By Prof. ERNST COHEN and G. DE BRUIN.

Direct determination of osmotic pressure in very dilute solutions i. e. solutions which obey VAN 'T HOFF'S law, are of great interest both to physico-chemists and biologists. As such measurements however are attended with great difficulties, until now physical chemists have generally employed indirect methods, such as lowering of the freezing point, elevation of the boiling point etc. Considering that in a dilute solution in water a lowering of the freezing point of  $\frac{1}{1000}$  of a degree corresponds to an osmotic pressure of 124 mm. water, the superior accuracy of the direct determination becomes evident. We describe here a principle which avoids the above mentioned difficulties. The vessel *B* in the figure is to receive a dilute solution in water (for instance of cane-sugar). Its bottom is formed by a membrane which is semi-permeable with respect to this solution.

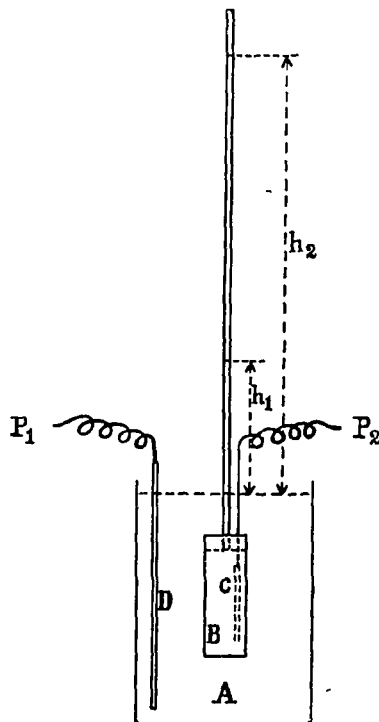
Copper ferrocyanide may be used for the purpose. The vessel *A* contains water. The top of *B* is tightly closed with a stopper through which is passed a fine capillary tube and a wire which carries the half of a reversible electrode. A copperplate will serve. The other part of the electrode is put into the water in *A*.

If *B* is new immersed in the water in *A* the liquid rises, as is well known, in the capillary. When it has reached a certain height, say  $h_1$ , which is noted on a millimetrescale, the rise of the liquid is stopped by introducing between the electrodes *C* and *D* (at  $P_2$  and  $P_1$ ) a certain potential-difference ( $E_1$ ). According to the researches of G. WIEDEMANN and those of VON HELMHOLTZ<sup>1)</sup>, we can write then:

$$P - h_1 = k E_1 \quad \dots \quad (1)$$

where  $P$  is the osmotic pressure to be measured and  $k$  is a constant.

<sup>1)</sup> Comp. G. WIEDEMANN, Die Lehre von der Elektrizität; 1, 993 seq. Braunschweig 1893 CHWOLSON, Lehrbuch der Physik. 4, (2) 583 Braunschweig 1903.



If we cut out now the potential-difference  $E_1$  the liquid will rise again in consequence of osmosis. When it has reached the height  $h_2$ , we stop it again by introducing a new potential difference ( $E_2$ ) between  $P_1$  and  $P_2$ .

Now the equation holds:

$$P - h_2 = k E_2. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2) it follows:

$$P = h_1 + (h_1 - h_2) \frac{E_1}{E_2 - E_1}$$

so that the osmotic pressure to be measured is known.

The great difficulties which arise when a semi-permeable membrane is used for direct determination of osmotic pressure may thus be avoided. These difficulties are.

1<sup>st</sup>. The long time needed to reach equilibrium. During this time diffusion takes place with consequent change in the concentration of the solution. In the above method the measurement is made at the beginning when the rise is greatest and is completed in a short time so that diffusion is avoided.

2<sup>nd</sup>. That the semi-permeable wall is pressed on one side until equilibrium is reached. Here, on the contrary, osmotic pressure is compensated by the electro-endosmotic pressure; consequently the wall is not pressed.

3<sup>rd</sup>. By the entrance of solvent the concentration within the cell changes. Here, on the contrary, this change of concentration may be avoided by making  $h_1$  and  $h_2$  and also the internal diameter of the capillary tube small.

One might inquire whether the laws of electro-endosmosis which play a rule in the principle described, are valid when electro-endosmosis takes place through a semi-permeable membrane. It will be shown later that it is possible to construct the apparatus in such a way that the principle holds even if this question must be answered in the negative.

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**Chemistry.** — “*The influence of pressure on the E. M. F. of the lead-accumulator*”. By Prof. ERNST COHEN and G. DE BRUIN.

According to chemical and thermodynamical investigations which have been carried out recently<sup>1)</sup> the reactions which take place in the lead-accumulator when it is discharged (charged) can be represented by the equation:

<sup>1)</sup> DOLEZALSK, die Theorie des Bleiakкумуляtors”, Halle 1901.