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**Chemistry.** — “*The solubility of calcium carbonate in sea-water*”.

By Dr. ERNST COHEN and Mr. H. RAKEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

Whilst engaged in forming a theory on the age of the earth, it was of importance to Professor EUGÈNE DUBOIS to possess further data as regards the solubility of calcium carbonate in sea-water under the usual conditions of temperature and pressure.

It is at his request that we undertook a research in order to obtain those data.

The *modus operandi* was, that sea-water in contact with the atmosphere (having the normal amount of carbon dioxide) was saturated with calcium carbonate and that after this point was reached, the amount of  $\text{CaCO}_3$  dissolved in an aliquot part of the liquid was estimated by analytical means.

*Arrangement of the Experiments.*

We prepared some litres of sea-water accepting as its composition that found by DITTMAR <sup>1)</sup>.

He finds the total percentage of salts to be 3.5 consisting of:

NaCl	77.758
MgCl <sub>2</sub>	10.878
MgSO <sub>4</sub>	4.737
CaSO <sub>4</sub>	3.600
K <sub>2</sub> SO <sub>4</sub>	2.465
MgBr <sub>2</sub>	0.217
Ca CO <sub>3</sub>	0.345 <sup>2)</sup>
	<hr/> 100.000

The calcium carbonate was precipitated  $\text{CaCO}_3$  previously rested for the absence of other carbonates. As the solubility is dependent on the temperature this had to be carefully regulated. The experiments were made at 15°, which temperature was kept constant within 0.03—0.05° for some months. For this purpose we employed a thermostat with a toluene regulator also a spiral of composition tube through which streamed the water from the mains. This tube was placed in the water of the thermostat. The cooling thus caused

<sup>1)</sup> Report on the scientific results of the voyage of H. M. S. Challenger 1873—'76 1884, pag. 204.

<sup>2)</sup> The  $\text{CaCO}_3$  was only added afterwards when determining the solubility.

was automatically compensated for by means of a gas flame connected with the regulator.

In the thermostat in which a few puddle-boards were kept in motion by a HENRICI hot-air motor, were placed two bottles containing the sea-water with a large excess of  $\text{CaCO}_3$ . The bottles were closed by trebly-perforated corks. Through the first hole passed a glass tube down to the bottom of the flasks, through the second one a glass tube ending immediately below the cork. Through the third hole passed a thermometer. A current of air was passed through the tubes reaching to the bottom of the flasks; this current was always strong enough to thoroughly stir up the calcium carbonate. The air entered the room through a glass tube which was pushed through an opening of the window then passed through a meter in which its volume was measured and was then conducted through a spiral of composition tube 10 meter in length which was placed in the thermostat. In this manner it was heated to  $15^\circ$  before entering the sea-water.

The tubes which ended underneath the corks of the flasks were connected with a water-suction airpump which drew the current of air through the water.

A slight evaporation of the sea-water takes place which is but trifling as the air takes up water from the meter, but we have still taken notice of this and carefully marked the level of the liquids so as to be able to keep this regularly constant.

The time of saturation was varied in order to be sure that equilibrium had indeed set in. Therefore, an analysis was made after passing the air for 8 days and nights and another after the lapse of 17 days and nights; these gave the same results so that it may be taken for granted that 8 days and nights are already sufficient to reach a state of equilibrium.

From time to time the  $\text{CO}_2$  of the air which had passed through was estimated. To do this, we interposed in the arrangement a large flask holding about 5 litres through which the air passed before reaching the meter. After 1— $1\frac{1}{2}$  hour the  $\text{CO}_2$  was estimated by shaking with standard barium hydroxide and titrating the excess with succinic acid. In calculating, due regard was paid to the temperature and pressure.

When the experiment was finished, the current of air was stopped and the  $\text{CaCO}_3$  was allowed to deposit. Then the liquid was filtered at  $15^\circ$ .

*Analyse.*

Under the circumstances described, there existed in the water <sup>1)</sup> after the experiment:

1. Carbon dioxide in the free state.
2. Neutral calcium carbonate.
3. Acid calcium carbonate.

Through the clear solution was now conducted a current of air which was completely freed from  $\text{CO}_2$  by passing it through a 2 meter long tube filled with soda-lime and some washbottles containing aqueous caustic potash. On passing a neutral gas such as air, both the free carbonic acid and that of the acid calcium carbonate are expelled whilst neutral calcium carbonate is precipitated.

Specially conducted experiments, one of which lasted  $4\frac{1}{2}$  and the other 100 hours, proved that after  $4\frac{1}{2}$  hours the decomposition of the acid calcium carbonate and the expulsion of the carbon dioxide is complete.

The solution thus treated was now examined as to its amount of combined carbon dioxide ( $\text{Ca CO}_3$ ) by decomposing this with hydrochloric acid and weighing the expelled  $\text{CO}_2$  in soda-lime tubes, according to the method of KOLBE-FRESENIUS <sup>2)</sup> which was carefully followed in every particular.

*Results.*

300 cc. of sea-water were used for each analysis.

a. Solution of  $\text{Ca CO}_3$  through which was first passed a current of atmospheric air for 8 days and nights and then a current of air free from  $\text{CO}_2$  and saturated with water vapour, for  $4\frac{1}{2}$  hours.

According to the indication of the meter, 41100 litres of air had passed through the solution in 8 days and nights which is about 108 litres per hour.

Three estimations of carbon dioxide made during this time on different days gave as result 0,0371, 0,0323 and 0,0290 per cent of  $\text{CO}_2$  by volume.

Found 16,2 milligrs of  $\text{CO}_2$  in 300 cc. of solution saturated at  $15^\circ$ , or 53.94 milligrs per litre.

b. Solution of  $\text{Ca CO}_3$  through which was first passed a current of atmospheric air for 17 days and nights and then a current of air free from  $\text{CO}_2$  and saturated with watervapour for 100 hours.

Found 17.2 milligrs in 300 cc. or 57.27 milligrs per litre. We, therefore, find that sea-water saturated at  $15^\circ$  with calcium carbonate

<sup>1)</sup> Compare GMELIN-KRAUT, Handbuch Anorg. Chemie, Part 1, 358.

<sup>2)</sup> FRESENIUS, Anleitung zur quant. Chem. Analyse, Bd. I (1875) § 449.

contains an amount of 55.6 milligrs of neutral-combined  $\text{CO}_2$  per litre.

It now appears from the researches of JACOBSEN<sup>1)</sup>, TORNØE<sup>2)</sup> and DITTMAR<sup>3)</sup> (CHALLENGER Expedition) that the amount of neutral combined  $\text{CO}_2$  in sea-water varies from 52.8—55 milligrs. per litre.

Our research, therefore, leads to the result that sea-water is saturated with calcium carbonate.

*Amsterdam*, Chemical University Laboratory, March 1900.

**Physics.** — “*On the phenomena of condensation in mixtures in the neighbourhood of the critical state*”. By Dr. CH. M. A. HARTMAN (Communication N<sup>o</sup>. 56 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES).

In a communication of DUHEM<sup>4)</sup> the hypothesis is laid down that in a mixture of two entirely miscible substances the experimental and the theoretical isothermals for one and the same temperature, situated between the temperature of the plaitpoint and that of the critical point of contact, intersect twice in the area of the unstable conditions.

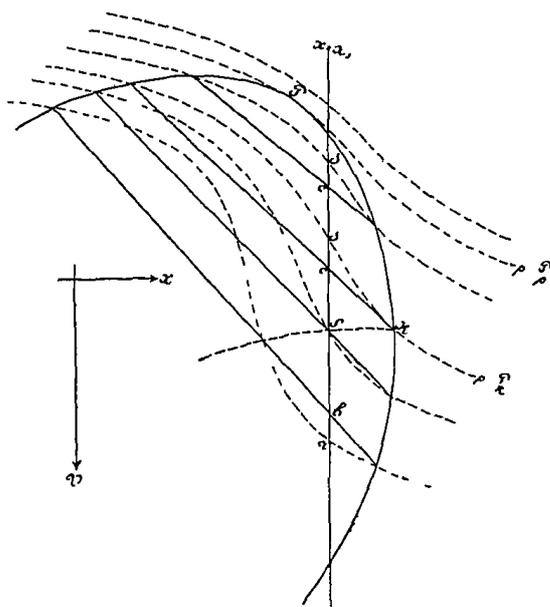


Fig 1.

On p. 31 and in thesis I of my dissertation for the doctorate<sup>5)</sup> I have drawn attention to the fact that this hypothesis is at variance with VAN DER WAALS' theory of mixtures<sup>6)</sup>.

The following may serve as a nearer explanation.

The actual condition may be seen from the annexed figure, derived from my dissertation in which the lines of equal pressure on the  $\psi$ -surface in the neighbour-

<sup>1)</sup> LIEBIG's Ann. 167. S. 1 (1873); Jahresbericht der Commission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel. 1872, S. 43.

<sup>2)</sup> Den Norske Nordhavs-Expedition 1876-78.

<sup>3)</sup> l. c.

<sup>4)</sup> Procès-Verbaux des séances de la Soc. des Sc. phys. et nat. de Bordeaux, 1899.

<sup>5)</sup> Metingen omtrent de dwarsplooi op het  $\psi$ -vlak van VAN DER WAALS by mengsels van Chloormethyl en Koolzuur. Leiden, Juni 1899.

<sup>6)</sup> VAN DER WAALS, Arch. Néerl. XXIV, p. 1-56, 1889.