A Gran Titration of Sea Water on Board Sagitta
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In the conventional method of titrating the alkalinity of sea water a 1 excess of acid is added to a sample of the water, boiled to expel CO₂, cooled and back-titrated with carbonate-free NaOH. The author as well as other members of the Stockholm school of solution chemistry have for many years used the Gran I and II methods for indicating equivalent points in potentiometric titrations. However, this technique has to my knowledge not been used in oceanography.

The titration was performed on May 11, 1965 on board Sagitta, the research ship of the Swedish National Science Research Council, in the following way by two assistants, Ing-Britt Jonasson and Helge Martander, under the supervision of Dr. Herbert Hellwege. Into a 250 ml beaker covered with “Parafilm” a 150 ml sample of sea water was introduced from a “Knudsen” bottle. This sample was taken at Vingassand (57°39’N, 11°41’E) at 25 m; the temperature of the sea water at that depth was 4.8°C and the salinity 34.80 %. Holes were made in the “parafilm” for a 5 ml buret, a glass electrode (Radiometer G200B) and a saturated calomel electrode (Radiometer K100). The sea water was then titrated with V ml of 0.1000 M HCl containing 0.44483 M NaCl to keep the chloride concentration in the solution constant. The emf was measured with a battery operated valve potentiometer (Radiometer pH Meter 4). The temperature in the cabin was ca. 14°C. The following readings were made of the volume in ml of 0.1000 M HCl added versus the potential in mV:
0 (–106.6), 0.2 (–93.7), 0.4 (–56.9), 0.6 (–40.0), 0.8 (–30.9), 1 (–21.8), 1.2 (–14.7), 1.4 (–7.2), 1.6 (–1.0), 1.8 (+ 5.0), 2 (+ 9.9), 2.2 (+ 15.3), 2.4 (+ 22.6), 2.6 (+ 29.1), 2.8 (+ 35.3), 3 (+ 43.8), 3.2 (+ 55.4), 3.4 (+ 70.3), 3.6 (+ 103.8), 3.8 (+ 129.4), 4 (+ 144.1), 4.2 (+ 155.7), 4.4 (+ 161.4), 4.6 (+ 167.8), 4.8 (+ 171.6), 5 (+ 176.8).

As the medium is practically constant during the titration the emf is given by

$$E = E_0 + 57 \log [H^+]$$

Using Gran II the equivalence point was found by plotting $V \times 10 \exp (100 - E)/57$ and 10 exp $(E - 100)/57$ against $V$, the volume of HCl. From the intersection of these straight lines at 3.64 ± 0.03 ml the alkalinity was calculated as 0.00243 ± 0.000002 M. Using a plot of $(3.64 - V)$ 10 exp $(E - 100)/57$ against $V$ we could also find an equivalence point at $V = 0.14$ ml corresponding to CO₃²⁻. Furthermore the hydrogen ion concentration [H⁺] and $E_0$ could be calculated from the excess of HCl between 4 and 5 ml using the formulas

$$[H^+] = \frac{(V - 3.64) \cdot 0.1}{150 + V}$$

and

$$E_0 = E - 57 \log [H^+]$$

We obtained $E_0 = 350.3 ± 0.6$ mV and thus $-\log [H^+]$ of the sea water could be calculated as

$$-\log [H^+] = (350.3 + 106.6)/57 = 8.02 ± 0.01$$

It should be emphasized that [H⁺] is a well-defined quantity, i.e. concentration of H⁺ per mass or volume of sea-water, while pH refers to some kind of standard buffer at some temperature. It is quite reasonable that the value of $-\log [H^+]$ should be lower than the pH of sea-water as the activity factor of H⁺ is less than one in sea-water ($-\log [H^+]$ ca. 0.1). From the readings of $V$ between 1.2 and 2.4 ml pKₐ for the dissociation constant [H⁺][CO₃²⁻]/[CO₂aq] for sea-water could be calculated as 0.02 ± 0.01 at 14°C. This means that the concentration of CO₂aq in the sea-water was [CO₂aq] = 0.00224 × 10⁻⁶ aq × 10⁻⁶ aq = 2.24 × 10⁻⁶ M. Using 0.14/3.36 for the ratio [CO₂aq]/[HCO₃⁻] the following value of Kₐ for [H⁺][CO₂aq]/[HCO₃⁻]²⁺ = 10⁻⁶ aq was obtained. In general HCO₃⁻ is the main alkaline species in sea-water. To a slight extent (<5 %) H₂BO₄⁻, HPO₄²⁻ and P⁻ also consume H⁺ in a titration with HCl.


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