A Gran Titration of Sea Water on Board Sagitta

DAVID DYRSSEN

Department of Analytical Chemistry,
University of Gothenburg, Gothenburg,
Sweden

In the conventional method of titrating the alkalinity of sea water[1] an excess of acid is added to a sample of the water, boiled to expel CO_2, 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[2,3] 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 Vingasand (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 0.4483 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

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

Using Gran II[3] 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 calcuiated as 0.00243 ± 0.00002 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 CO_3^{2-}. Furthermore the hydrogen ion concentration $[\mathrm{H}^+]$ and E_0 could be calculated from the excess of HCl between 4 and 5 ml using the formulas

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

and $$E_0 = E - 57 \log [\mathrm{H}^+]$$

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

$-\log [\mathrm{H}^+] = (350.3 + 106.6)/57 = 8.02 \pm 0.01$

It should be emphasized that $[\mathrm{H}^+]$ 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 $-\log [\mathrm{H}^+]$ should be lower than the pH of sea-water as the activity factor of H^+ is less than one in sea-water ($-\log f_{\mathrm{H}^+}$ is *ca.* 0.1). From the readings of V between 1.2 and 2.4 ml $\mathrm{p}K_\mathrm{a}$ for the dissociation constant $[\mathrm{H}^+][\mathrm{HCO}_3^-][\mathrm{CO}_2\mathrm{aq}]^{-1}$ in sea-water could be calculated as 6.02 ± 0.01 at 14°C. This means that the concentration of CO_2aq in the sea-water was $[\mathrm{CO}_2\mathrm{aq}] = 0.00224 \times 10^{-8.02} \times 10^{6.02} = 2.24 \times 10^{-5}$ M. Using 0.14/3.36 for the ratio $[\mathrm{CO}_3^{2-}]/[\mathrm{HCO}_3^-]$ the following value of K_a for $[\mathrm{H}^+][\mathrm{CO}_3^{2-}][\mathrm{HCO}_3^-]^{-1} = 10^{-9.40}$ was obtained. In general HCO_3^- is the main alkaline species in sea-water. To a slight extent (< 5 % of HCO_3^-) CO_3^{2-}, $H_2BO_3^-$, HPO_4^{2-} and F^- also consume H^+ in a titration with HCl.

1. Barnes, H. *Apparatus and methods of oceanography, Part I. Chemical,* George Allan & Unwin, London 1959.
2. Gran, G. *Acta Chem. Scand.* **4** (1950) 559.
3. Gran, G. *Analyst* **77** (1952) 661.

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