Short Communication

THE DETERMINATION OF HYDROXIDE AND CARBONATE IN CONCENTRATED SODIUM CHLORIDE SOLUTIONS

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Summary. A computer method for the determination of carbonate and hydroxide in concentrated (2.89 M) sodium chloride solutions is described. The method is based on multi-parametric curve-fitting and can also be applied to salts of dibasic acids with unknown equilibrium constants. The systematic error is not more than 1%. The titration and calculation takes less than 20 min.

In the potentiometric titration with hydrochloric acid of hydroxide and carbonate of concentrations less than 0.01 M it is often impossible to determine the equivalence point of hydroxide from the inflexion point or first derivative [1]. The calculation of the hydroxide concentration from the equivalence points of carbonate is not very accurate. Straightforward Gran plots are sometimes curved, while more sophisticated linearization techniques require accurate values of the equilibrium constants [2, 3]. Another method with at least comparable versatility is multiparametric curve-fitting [4—8].

This paper describes the adaptation of the Wentworth method [9], as used earlier by Bos [8] for the titration of mixtures of a weak and a strong acid with sodium hydroxide, for the determination of hydroxide and carbonate in 2.89 M (3.00 m) sodium chloride solutions. Four parameters from the charge-balance equation are adjusted to obtain a least-squares fit, the concentrations of hydroxide and carbonate, and both the equilibrium constants of carbonate.

Theory

The symbols are defined in Table 1.

Charge-balance equations. The charge-balance equation valid for each point of the titration curve of a salt of a dibasic acid and a strong base with hydrochloric acid is given by

$$M_{H^+} + M_{M^+} - M_{Cl^-} - 2M_{Y^{2-}} - M_{HY^-} - M_{OH^-} = 0 \qquad (1)$$

TABLE 1

Glossary of symbols

a	activity	K_2	second dissociation constant of the
f	activity coefficient		acid
M	concentration	K_1^0	initial estimate of K_1
C_{OH^-}	concentration of sodium hydroxide	K_2^0	initial estimate of K_2
	at start of titration	K_w	dissociation constant of water
$C_{Y^{2-}}$	concentration of weak acid at start	a_w	activity of water
	of titration	T	titer of hydrochloric acid
$C_{OH^-}^0$	initial estimate of C_{OH^-}	V	volume of hydrochloric acid added
$C_{Y^{2-}}^0$	initial estimate of $C_{Y^{2-}}$	V_0	volume at start of titration
K_1	first dissociation constant of the	F_i	function relating V and a_{H^+}
	dibasic acid	H_2Y	weak acid
		MOH	strong base

Combination of this equation with the following relationships:

$$M_{M^+} = C_{OH^-} + 2C_{Y^{2-}}; \quad K_1 = a_{HY^-}a_{H^+}/a_{H_2Y}; \quad M_{HY^-} = K_1 a_{H_2Y}/f_{HY^-} a_{H^+};$$

$$K_2 = a_{Y^{2-}} a_{H^+}/a_{HY^-}; \quad M_{Y^{2-}} = K_2 a_{HY^-}/f_{Y^{2-}} a_{H^+} = K_2 K_1 a_{H_2Y}/f_{Y^{2-}} a_{H^+}^2;$$

$$K_w = a_{H^+} a_{OH^-}/a_w$$

and (if the activity coefficient of the uncharged a_{H_2Y} is taken as unity)

$$C_{Y^{2-}} = M_{H_2Y} + M_{HY^-} + M_{Y^{2-}} = M_{H_2Y} [1 + (K_1/f_{HY^-} a_{H^+}) + (K_1 K_2/f_{Y^{2-}} a_{H^+}^2)]$$

gives

$$F_i = 0 = \frac{a_{H^+}}{f_{H^+}} + \frac{C_{OH^-} V_0}{V_0 + V} - \frac{TV}{V_0 + V} + \frac{V_0 C_{Y^{2-}} (2a_{H^+} + K_1/f_{HY^-})}{(V_0 + V)[a_{H^+} + (K_1 K_2/f_{Y^{2-}} a_{H^+}) + (K_1/f_{HY^-})]}$$

$$- \frac{K_w a_w}{f_{OH^-} a_{H^+}} \tag{2}$$

Multiparametric curve-fitting. Equation (2) relates the experimental data V and a_{H^+} and contains the parameters f_{H^+}, f_{OH^-}, V_0, K_w, T, a_w, $C_{Y^{2-}}$, C_{OH^-}, K_1, and K_2. K_w, T, and V_0 are known previously. The activity coefficients and the water activity are constant during a titration in 2.89 M sodium chloride: $K_w = 0.894 \times 10^{-14}$; $a_w = 0.893$; $f_{H^+} f_{OH^-}/a_w = 0.962$; and $f_{OH^-} f_{H^+} = 0.859$ [10]. In order to calibrate the glass electrode for hydrogen ion concentrations, f_{H^+} is assumed to be 1.000 [4]; this gives f_{OH^-} as 0.859. $f_{Y^{2-}}$ and f_{HY^-} are also assumed to be 1.000.

The parameters to be evaluated by least-squares analyses are therefore $C_{Y^{2-}}$, C_{OH^-}, $K_1 = a_{H^+} M_{HY^-}/a_{H_2Y}$, and $K_2 = a_{H^+} M_{Y^{2-}}/a_{H_2Y}$. The Wentworth method requires the partial derivatives of F_i with respect to V, to a_{H^+}, and to the four parameters. These are listed in the following equations:

$$\delta F_i/\delta V = -\{(C_{OH^-} V_0)/(V_0 + V)^2\} - \{TV_0/(V_0 + V)^2\} - \{V_0 C_{Y^{2-}} (2a_{H^+} + K_1)/$$

$$(V_0 + V)^2 [a_{H^+} + (K_1 K_2/a_{H^+}) + K_1]\}$$

$$\delta F_i/\delta a_{\mathrm{H}^+} = 1 + \{a_w K_w/(f_{\mathrm{OH}^-} a_{\mathrm{H}^+}^2)\} + \{K_1 V_0 C_{\mathrm{Y}^2-} (1 + K_2/a_{\mathrm{H}^+}) (4 + K_1/a_{\mathrm{H}^+})/$$

$$(V_0 + V) [a_{\mathrm{H}^+} + (K_1 K_2/a_{\mathrm{H}^+}) + K_1]\}$$

$$\delta F_i/\delta C_{\mathrm{OH}^-} = V_0/(V_0 + V)$$

$$\delta F_i/\delta C_{\mathrm{Y}^2-} = V_0(2a_{\mathrm{H}^+} + K_1)/(V_0 + V) [a_{\mathrm{H}^+} + (K_1 K_2/a_{\mathrm{H}^+}) + K_1]$$

$$\delta F_i/\delta K_1 = -V_0 C_{\mathrm{Y}^2-} (2K_2 + a_{\mathrm{H}^+})/(V_0 + V) [a_{\mathrm{H}^+} + (K_1 K_2/a_{\mathrm{H}^+}) + K_1]^2$$

$$\delta F_i/\delta K_2 = -V_0 C_{\mathrm{Y}^2-} K_1(2 + K_1/a_{\mathrm{H}^+})/(V_0 + V) [a_{\mathrm{H}^+} + (K_1 K_2/a_{\mathrm{H}^+}) + K_1]^2$$

Experimental

Chemicals. The chemicals were of analytical grade; sodium chloride (Merck) was used as received, whereas sodium carbonate (Merck) was dried for 2 h at 120°C. Sodium hydroxide and hydrochloric acid solutions were prepared by adding the content of a Merck titrisol ampoule to a calculated quantity of sodium chloride, and diluting with carbon-dioxide-free water to the specified volume.

Equipment. The titrations were controlled and evaluated by a PDP 11-10 computer with 16K core memory RK 05 disk, and a laboratory peripheral system (LPS) comprising a 12-bit ADC and a Teleprint telewriter. The pH was measured with a Schott combined glass—calomel electrode (type N) with a platinum wire diaphragm and a Knick industrial pH meter (type Din). The titrant was added with a Mettler DV 11 automatic burette into a Metrohm thermostatted titration vessel. A Lauda ultra-thermostat (type 43/58/12) was used to maintain 25.0 ± 0.1°C in the titration vessel.

Calibration of the combined electrode. To prevent any effect of a change in the liquid junction potential on the calibration constants, the combined electrode was calibrated in 2.89 M sodium chloride solutions. The pH values of 0.01 M HCl, 0.01 M NaOH, and 0.01 acetate buffer were calculated to be 2.00, 12.03, and 4.79, respectively. These standards were used to calculate the calibration constants in the pH regions 2.00—5.00 and 5.00—12.00.

Titrations. Samples were prepared by mixing sodium carbonate and sodium hydroxide solutions and diluting with 2.89 M NaCl to 50 ml. The electrodes were allowed to equilibrate for 5 min whereafter the titration with 0.1000 M HCl in 2.89 M NaCl was started. The titrations were done under nitrogen at 25.0 ± 0.1°C by addition of constant increments (0.30 ml) of titrant. After each addition, there was a constant time-delay of 30 s to attain equilibrium before pH measurement.

Computer programs. The monitoring program with three real-time tasks divides the memory into four parts, for three real-time programs and the background. The background program runs in the time that is not used for a real-time task. The calibration program calculates the slope and standard potential of the electrode from e.m.f. data for two buffers, taken by the ADC of the LPS from the pH meter and their pH values read from the teletype. Output of the calibration constants is to the teletype. Before each

TABLE 2

Results of titrations of sodium hydroxide and sodium carbonate with hydrochloric acid at different titration speeds

NaOH ($\times 10^{-3}$ M)		Error (%)	Na_2CO_3 ($\times 10^{-3}$ M)		Error (%)	K_w (int) ($\times 10^{-14}$)	Titration time (s)
added	found		added	found			
4.00	4.024	0.6	4.00	4.024	0.6	0.702	990
2.00	1.991	—0.5	8.00	7.964	—0.5	0.680	920
2.00	1.998	—0.2	7.96	7.952	—0.2	0.712	960
4.00	4.016	0.4	6.00	6.024	0.4	0.711	990
2.00	1.978	—1.1	8.00	7.912	—1.1	0.701	690
2.00	1.991	—0.5	8.00	7.964	—0.5	0.758	1380
2.00	2.009	0.5	7.96	7.963	0.5	0.732	1280
2.00	2.001	<0.1	7.96	7.966	<0.1	0.780	1600
10.00	10.040	0.4	5.00	5.020	0.4	0.780	2790
2.00	2.010	0.5	8.00	8.040	0.5	0.818	2970

TABLE 3

Results of titrations of sodium hydroxide and sodium carbonate with hydrochloric acid calculated with an average K_w (int) for series of titrations completed within about the same time

NaOH ($\times 10^{-3}$ M)		Error (%)	Na_2CO_3 ($\times 10^{-3}$ M)		Error (%)	K_w (int) average ($\times 10^{-14}$)	Titration time (s)
added	found		added	found			
4.00	4.022	0.55	4.00	4.026	0.65	0.701	990
2.00	2.004	0.20	8.00	7.956	—0.55	0.701	920
2.00	1.986	—0.70	7.96	7.996	0.45	0.701	960
4.00	4.020	0.50	6.00	6.000	0.00	0.701	990
2.00	1.986	—0.70	8.00	8.012	0.15	0.745	1380
2.00	2.015	0.75	7.96	7.964	<0.10	0.745	1280
10.00	10.060	0.60	5.00	5.013	0.26	0.799	2790
2.00	1.988	—0.60	8.00	8.048	0.60	0.799	2970

titration, the volume of a titrant addition, its number, the time-delay between additions and pH measurements, and the sample identification are entered via the teletype and stored in the disk file. The e.m.f. readings which are measured after each addition are stored in the same disk file as the sample data.

The initial estimates for the curve-fitting program, $C^0_{OH^-}$, $C^0_{Y^{2-}}$, K^0_1, and K^0_2 are obtained from the titration curve. The titration curve, a_{H^+} vs. ml, is calculated from the e.m.f. readings, the calibration constants, the number of additions, and the volume of each addition. $C^0_{OH^-}$ is taken as $K_w a_w/(a_{H^+} f_{OH^-})$ with the a_{H^+} value of the first point of the curve. $C^0_{Y^{2-}}$ is calculated from the volume of titrant when pH 4.0 has been reached. K^0_2, and K^0_1 are assumed

to be equal to the a_{H^+} values at the volumes where half the estimated amounts of Y^{2-} and HY^- have been neutralized.

Results and discussion

To test this method of end-point calculation for the determination of sodium hydroxide and sodium carbonate several synthetic samples were titrated and evaluated. It proved necessary to alter one of the remaining parameters, f_{H^+}, f_{OH^-}, and K_w, to remove a systematic deviation, involving an excessive hydroxide and deficient carbonate concentration. This deviation depended on the total titration time. Variation in K_w or f_{OH^-} had a larger effect on the calculated concentrations than f_{H^+}. Decrease in K_w increased the carbonate result and decreased the hydroxide result. A plot of the relative deviations for these two analytes versus K_w showed two straight lines; the intersection corresponded to a relative deviation of less than 0.5% of both concentrations. When about the same total time was used for titrations of different ratios of hydroxide and carbonate concentrations, the K_w corresponding to the point of intersection, K_w (int), did not vary very much (Table 2). These titrations were also evaluated with an average K_w (int). The systematic deviations were less than 1% (Table 3). An increase in the titration time did not improve the accuracy; a decrease to less than about 15 min seemed to worsen it.

The pH measurements must be accurate to ±0.01 pH unit. The pH of the standards was calculated from literature values for the dissociation constant of acetic acid, K_w, and the calculated f_{H^+} and f_{OH^-}. Separate sets of calibration constants were determined for the pH region 2—5 and for pH > 5. The differences in the constants of these sets can be attributed to the pH influence on liquid junction potentials. The calculations involving a 30-point titration take about 2.5 min.

The initial estimates of the parameters do not have to be very accurate. The calculations of the titrations listed in Table 2 can be started with the same set of initial estimates.

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