R. A. ROBINSON MEMORIAL LECTURE

Potentiometric Titrations of Aqueous Carbonate Solutions

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1 Introduction

When carbon dioxide dissolves in water, as is well known,[1] it forms a weak acid, carbonic acid H_2CO_3, which dissociates to give hydrogencarbonate (bicarbonate) and carbonate ions. Only a small fraction of dissolved CO_2 forms carbonic acid and, depending in extent on pH, four forms can be present, namely, CO_2, H_2CO_3, HCO_3^-, and CO_3^{3-} thus complicating the usual dissociation process of a weak diprotic acid. The basic equations are summarized in Table 1. In view of the importance of the carbonate system to environmental, biological, and industrial processes, it has been much studied and is the subject of a book[2] and several reviews.[3–5]

Originally, our interest in the aqueous carbonate system arose from the possible role of carbonate impurity in the results for the ionization constants for H_2O and D_2O obtained from the cells:

$$\mathrm{Pt|H_2|MOH}\ (m_1),\ \mathrm{MCl}\ (m_2)\mathrm{|AgCl|Ag} \qquad \text{(I)}$$

$$\mathrm{Pt|D_2|MOH}\ (m_1),\ \mathrm{MCl}\ (m_2)\mathrm{|AgCl|Ag} \qquad \text{(II)}$$

where M = an alkali metal and $m_1 = 0.01$, $m_2 > 0.01$ mol kg^{-1}. From the temperature variation of the e.m.f. of cells I or II over the range, usually, of 0—55 °C, values for the enthalpy of ionization of H_2O and D_2O can be derived. For H_2O, $\Delta H^\circ = 56.61$ kJ mol^{-1} from cell I,[6] whereas by calorimetric methods systematically lower values of 55.81 kJ mol^{-1} have been found.[7] For D_2O the situation is reversed and the calorimetric value is higher.

In searching for an explanation, suspicion fell upon the role of a systematic error in the hydroxide ion concentration (m_1) resulting from absorption of atmospheric

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* This review is based on the third R. A. Robinson Memorial Lecture, 'The Carbonate-Bicarbonate System Revisited', given at the University of Singapore, Kent Ridge; the Universiti Sains Penang; and the University of Malaya, Kuala Lumpur, in January 1984.

[1] W. Stumm and J. J. Morgan, 'Aquatic Chemistry', Wiley, New York, 1970, chapter 4.

[2] R. E. Loewenthal and G. R. Marais, 'Carbonate Chemistry of Aquatic Systems', Ann Arbor Science Publ., Ann Arbor, Michigan 1976, pp. 102—8.

[3] J. T. Edsell, *NASA Spec. Report No. 188*, 1969, 15.

[4] D. M. Kern, *J. Chem. Educ.*, 1960, **37**, 14.

[5] Gmelin Handbuch der Anorganischen Chemie, Carbon, 8th Edition, Vol. C3, ed. R. J. Meyer, Verlag Chemie, Weinheim, 1973.

[6] A. K. Covington, M. I. A. Ferra, and R. A. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1721.

[7] G. Olafsson and L. G. Hepler, *J. Solution Chem.*, 1975, **4**, 127.

Table 1 *The equilibrium distribution of solutes in aqueous carbonate solution (system closed to the atmosphere)*[1]

Species

$$CO_2(aq),\ H_2CO_3,\ HCO_3^-,\ CO_2^{3-},\ H^+,\ OH^-$$

$$[H_2CO_3^*] = [CO_2{\cdot}aq] + [H_2CO_3]$$

Equilibrium constants

$$[CO_2(aq)]/[H_2CO_3] = K \qquad (1)$$

$$[H^+][HCO_3^-]/[H_2CO_3^*] = K_1 \qquad (2)$$

$$[H^+][HCO_3^-]/[H_2CO_3] = K_{H_2CO_3} \qquad (2a)$$

$$[H^+][CO_3^{2-}]/[HCO_3^-] = K_2 \qquad (3)$$

$$[H^+][OH^-] = K_w \qquad (4)$$

Concentration condition

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (5)$$

Ionization fractions

$$[H_2CO_3^*] = C_T\alpha_0; \quad [HCO_3^-] = C_T\alpha_1; \quad [CO_3^{2-}] = C_T\alpha_2$$

$$\alpha_0 = \left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)^{-1} \qquad (6)$$

$$\alpha_1 = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)^{-1} \qquad (7)$$

$$\alpha_2 = \left(\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1\right)^{-1} \qquad (8)$$

carbon dioxide in spite of stringent precautions to exclude it. The acquisition of a new automatic titrator provided the opportunity to investigate the potentiometric titration of hydroxide solutions contaminated with known additions of carbonate in an attempt to determine the lower limit of detection by this method. The titrator was unique in type in providing a true first derivative output, d*E*/d*V*, from measured potential difference (*E*) between sensor and reference electrodes with volume (*V*) delivered, rather than mathematically derived slopes. Our first derivative titration with this apparatus revealed an artefact, in that an additional maximum in the first derivative curve appeared between those expected for the protonation of carbonate to hydrogencarbonate and hydrogencarbonate to carbonic acid (Figure 1). Whilst attempting to locate an experimental origin of this unexpected feature, Robinson and I began looking into the calculation of first derivative titration curves and how the heights of the maxima varied with the concentration conditions of the titration.[8] Figure 2 shows the three expected maxima for the three protonation steps in a titration with acid. Alkali titrations are simply the reverse. Clearly, experiment and theory were discrepant and a systematic study was commenced to establish the reproducibility of the experimental titration curves and the effect of varying conditions on the manifestation of the additional maximum.

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[8] A. K. Covington, R. A. Robinson, and M. Sarbar, *Anal. Chim. Acta*, 1978, **100**, 367.

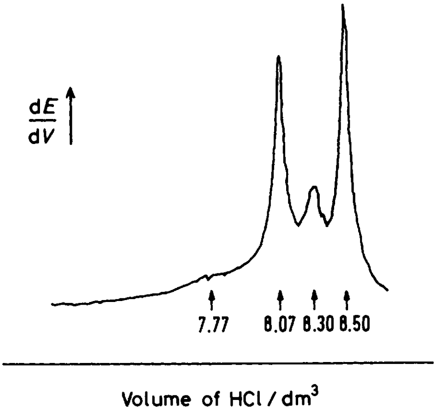

Figure 1 *Titration of* 10 cm^3 *of* 0.2 mol dm^{-3} NaOH + 6 mg Na_2CO_3 *with* 0.25 mol dm^{-3} HCl

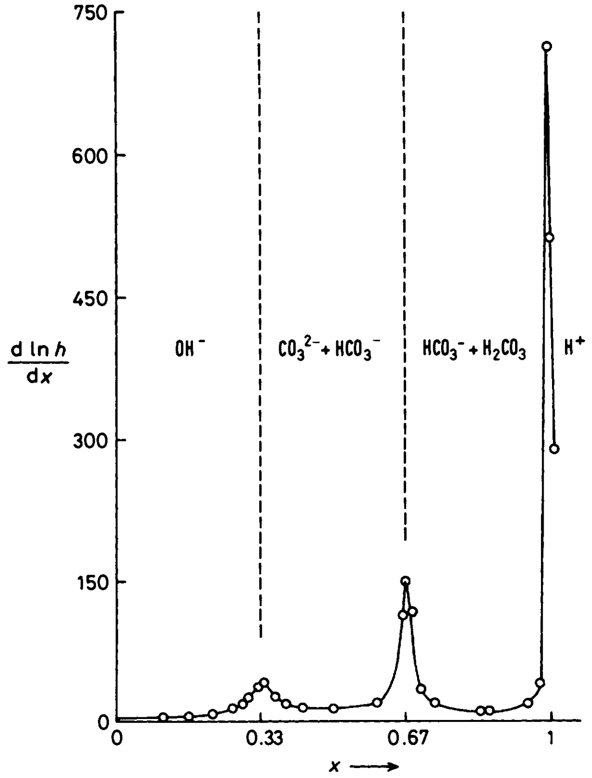

Figure 2 *Theoretical differential titration curve for titration with* HCl *of* 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} Na_2CO_3, *x is the degree of advancement of the titration*

2 Experimental

Titrations were carried out in a 25 cm^3 cylindrical vessel thermostatted at 25 °C by circulating water in an outer jacket. The top of the vessel was sealed tightly with a lid containing ports for glass and reference electrodes, thermometer, nitrogen gas-entry, and titrant-entry. The titration solution was stirred by means of a Teflon-coated magnetic follower. The Mettler titrimeter (Zurich, Switzerland) comprised the modular units of a 10 cm^3 burette, conversion, control, and electrometer units and display of the derivative titration curve (dE/dV) of dE/dpH on chart recorders. A variety of glass electrodes was used. Some of these were combination electrodes, but others were used with saturated calomel reference electrodes. Titrations were also carried out using a carbon dioxide gas electrode (Radiometer Type PS1–904–123). Sodium hydroxide was carbonate-free solution (BDH, Poole). Hydrochloric acid solutions were prepared from BDH AVS ampoules. Sodium and potassium carbonates were AnalaR grade. Further experimental details are available.[9]

3 Results

Figure 3 shows the results[9] of derivative titrations with 0.05 mol dm^{-3} HCl. Figure 4 shows the effect of varying the temperature. The additional maximum moves closer to that for hydrogencarbonate to carbonic acid at 5 °C from its position at

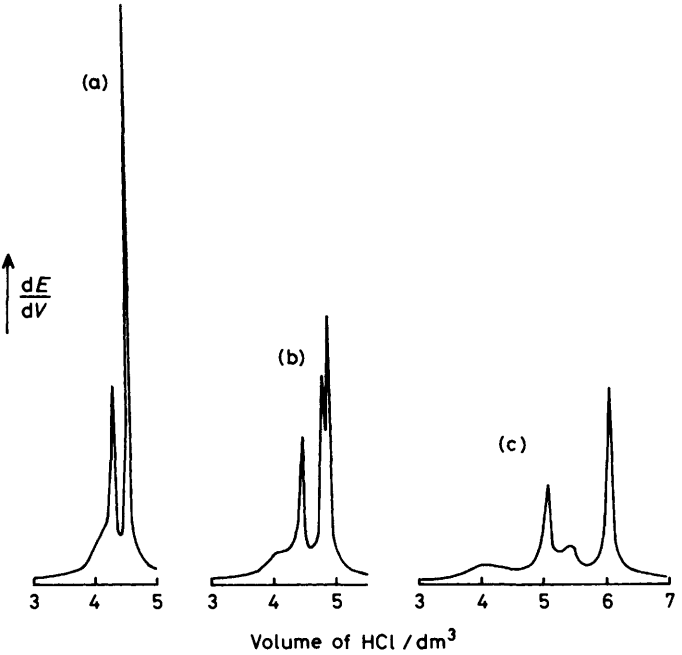

Figure 3 *Titration of* 0.1 mol dm^{-3} NaOH + Na_2CO_3 *solutions with* 0.25 mol dm^{-3} HCl *at various* CO_3^{2-}/OH^- mol %: (*a*) 5%, (*b*) 10%, (*c*) 25%

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[9] A. K. Covington, R. A. Robinson, and M. Sarbar, *Anal. Chim. Acta*, 1981, **130**, 93.

25 °C, and disappears into the maximum for carbonate to hydrogencarbonate as the temperature approaches 55 °C. Figure 5 shows that the effect is present in a series of experiments at constant carbonate concentration instead of constant hydroxide with variations in carbonate/hydroxide ratio; with no hydroxide the effect is absent. Identical titrations were obtained if potassium was substituted for sodium, but with tetramethylammonium instead of an alkali metal the additional maximum was less apparent and the other two maxima were greater in height. If nitrogen was bubbled through the solution instead of passed over it, then no additional maximum is seen, presumably because of loss of carbon dioxide. This also occurs if hydrogen gas is bubbled through the solution, so a platinum hydrogen gas electrode does not show the extra maximum but other hydrogen-ion responsive electrodes do. Figure 6 shows the results with a rhodium–rhodium oxide pH-responsive electrode, which is slower in response than a glass electrode, so the new feature appears as a shoulder rather than a separate maximum. Successive titrations with a glass electrode newly brought into service show the same effect; as the electrode becomes conditioned its speed of response increases and the maximum becomes better defined. Otherwise, the results are independent of the type of glass electrode (and reference electrode) used.

Figure 7 shows the titration curves obtained when a carbon dioxide gas electrode was used. The maximum in these curves coincides with the minimum between the second and extra maximum in the glass electrode titration curves. A point of

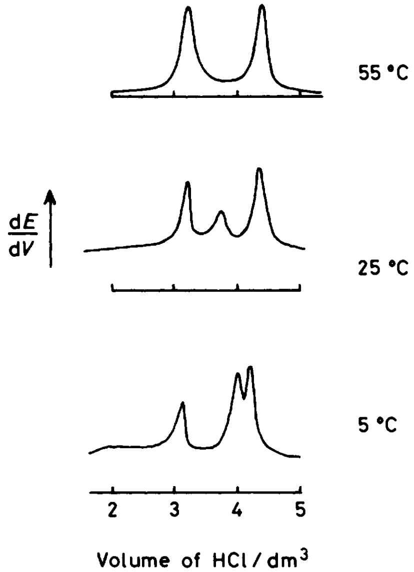

Figure 4 *Titration of* 0.1 mol dm^{-3} NaOH + Na_2CO_3 (5 mol % CO_3^{2-}/OH^-) *with* 0.05 mol dm^{-3} HCl *at* 5, 25, *and* 55 °C

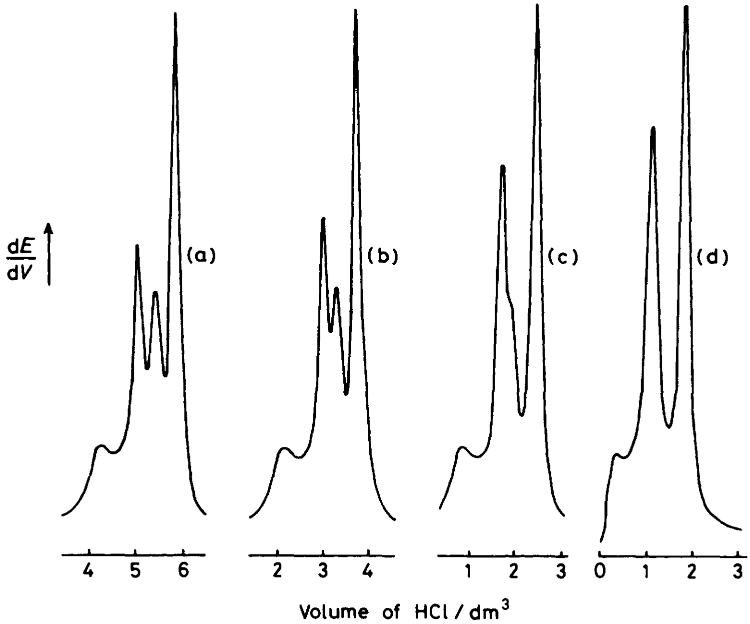

Figure 5 *Titration of* 0.01 mol dm^{-3} Na_2CO_3 (25 dm^3) *containing various amounts of* NaOH *at different* mol % *with* 0.25 mol dm^{-3} HCl: (*a*) 20%, (*b*) 40%, (*c*) 125%, (*d*) *no* NaOH *added*

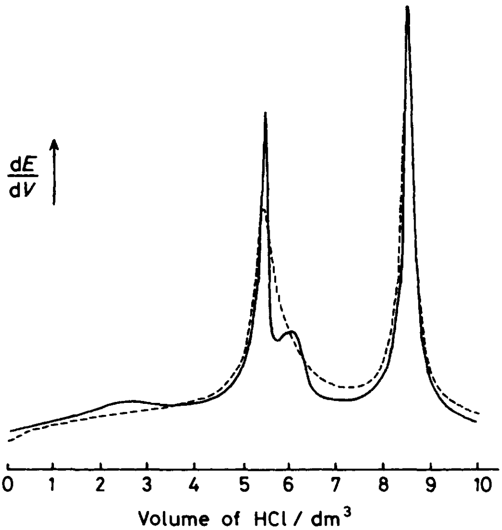

Figure 6 *Titration of* 25 cm^3 0.04 mol dm^{-3} NaOH + 0.006 mol dm^{-3} Na_2CO_3 *with* 0.05 mol dm^{-3} NaOH (1 cm^3/4 min) *using glass electrode* (*solid curve*) *and rhodium–rhodium oxide electrode* (*hatched curve*)

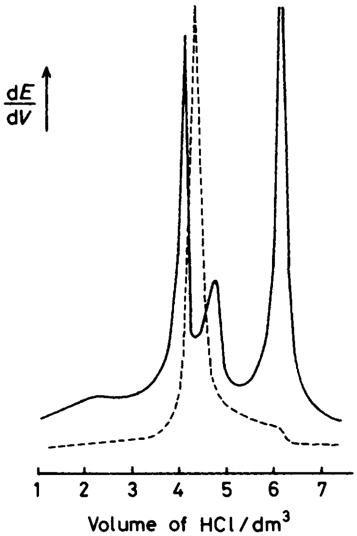

Figure 7 *Titration of* 0.1 mol dm^{-3} NaOH + Na_2CO_3 (10% CO_3^{2-}/OH^- mol%) *with* 0.05 mol dm^{-3} HCl *using glass electrode* (*solid curve*) *and carbon dioxide gas electrode* (*hatched curve*)

inflection is found corresponding to the hydrogencarbonate–carbonic acid conversion. At higher temperatures, the carbon dioxide electrode maximum moves closer to the carbonate–hydrogencarbonate maximum in the pH titration.

The extra maximum was also found when the entire titration of NaOH–Na_2CO_3 was carried out with DCl in D_2O at 5 and 25 °C. As in light water, it was not present above 55 °C. Addition of amounts of ethanol in the mol fraction range 0.02—0.20 produced changes in the titration curves. In the mol fraction range 0.13—0.20 the extra feature was absent. It was also eliminated by the addition of t-butyl alcohol at mol fraction 0.1. The position of the extra maximum is changed if the acid titrant concentration is changed (Figure 8). If the rate of change of hydrogen ion concentration is kept constant for a diluter titrant by a compensating increase in the speed of delivery, then the extra maximum is in the same position in the two titrations.

We then turned to alkalimetric titations[10] of solutions containing dissolved carbon dioxide. These can be prepared very simply with a commercial soda-syphon bottle. In Figure 9 titration curves are shown for both glass and carbon dioxide electrodes. There are three maxima and a shoulder on the right-hand side of the central maximum in the pH titration. A shoulder in the carbon dioxide electrode derivative titration is located near the first maximum in the glass electrode titration. It is clear for the glass electrode titration in Figure 9 that the shoulder on the middle maximum lies exactly between the first and third maxima. In comparison with acid titrations, it is the middle maximum which is the additional feature and not the

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[10] A. K. Covington and M. Sarbar, in preparation.

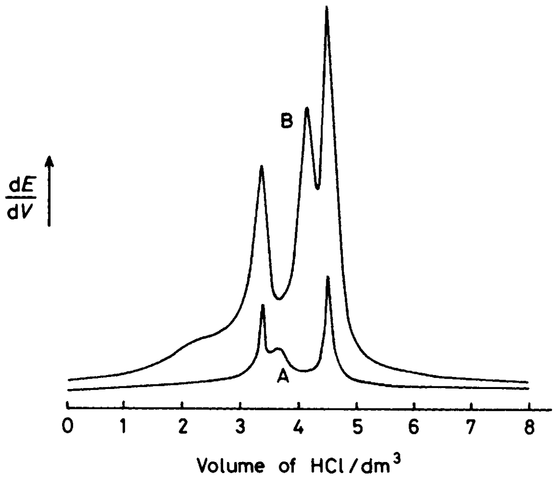

Figure 8 *Effect of rate of titration on titration curves of* 0.04 mol dm^{-3} NaOH + Na_2CO_3 (5 mol % CO_3^{2-}/OH^-) *with* 0.05 mol dm^{-3} HCl. *A*, 1 cm^3 HCl *in* 4 min; *B*, 1 cm^3 HCl *in* 48 s

shoulder, for it is the maximum in the CO_2 electrode titration which corresponds with the shoulder in the pH titration. Figure 10 shows the effect of varying the temperature of titration of CO_2–water. At 5 °C, the new feature has moved towards the first maximum in the titration. Above 55 °C, the titration is that expected with the centre maximum of increased height. Figure 11 illustrates the effect of back titration with acid, and then a further back titration with alkali on the results at 5 °C, and indicates that the effects are entirely reproducible.

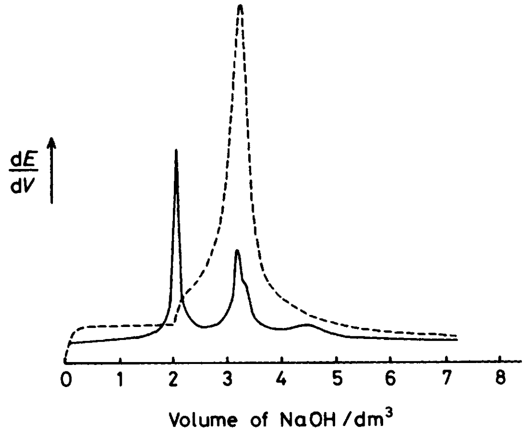

Figure 9 *Titration of* 25 cm^3 *of* 0.02 mol dm^{-3} HCl + 0.0125 mol dm^{-3} *of dissolved* CO_2 *solution with* 0.1 mol dm^{-3} NaOH (*rate of addition* 1 cm^3 NaOH/4 min) *using glass electrode* (*solid curve*) *and carbon dioxide gas electrode* (*hatched curve*)

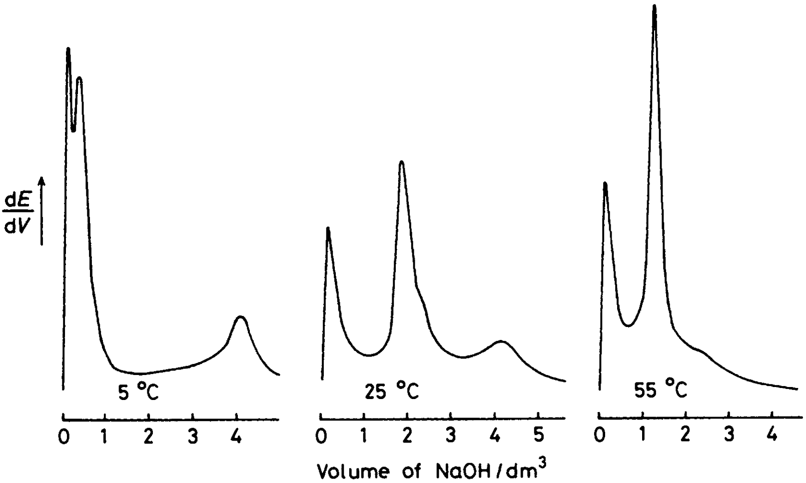

Figure 10 *Titration of* 25 cm^3 *of* 0.022 mol dm^{-3} *dissolved* CO_2 with 0.25 mol dm^{-3} NaOH (*rate of addition* 1 cm^3/48 s) *at* 5, 25, *and* 55 °C. *At* 55 °C *some* CO_2 *is lost from the solution due to lower solubility*

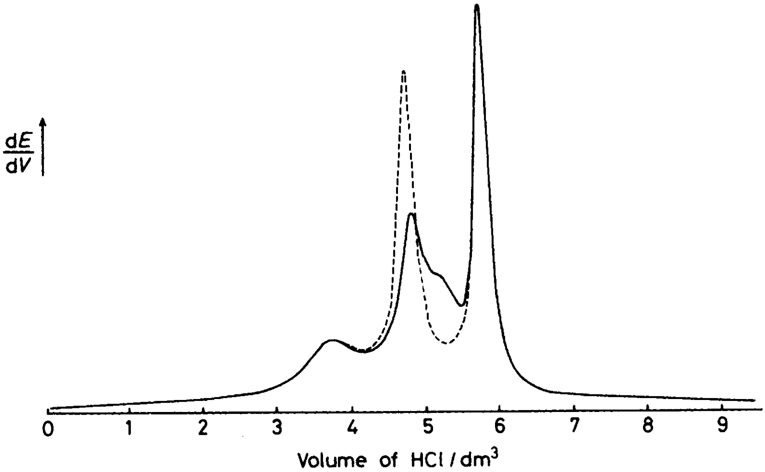

Figure 11 *Effect of bovine carbonic anhydrase on glass electrode titration of* 25 cm^3 0.04 mol dm^{-3} NaOH + 0.008 mol dm^{-3} Na_2CO_3. *Solid curve, without carbonic anhydrase; hatched curve, with carbonic anhydrase* (1 mg) *added*

The slow kinetics of the hydration of carbon dioxide and dehydration of carbonic acid are well documented[3,4] (equation 9)

$$CO_2 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2CO_3 \qquad (9)$$

with $k_f = 0.03\ s^{-1}$, $k_r = 20\ s^{-1}$, and we considered whether this could give rise to a spurious maximum in the titration curves. The enzyme, carbonic anhydrase, speeds up these hydration–dehydration reactions, so the effect of addition of a small amount to the titration solution was investigated, taking care not to add the enzyme to solutions of extreme pH to avoid destroying enzyme activity. The results are shown for acid glass-electrode titration in Figure 11. For all titrations addition of carbonic anhydrase completely removes the extra feature. Neither Robinson or I liked the obvious conclusion that the new feature arose from the slow kinetics, so, assisted by R.N. Goldberg, who had had experience of computer simulation of liquid junction potentials,[11] computer modelling of titration curves was developed taking into account the slow kinetics in the system.[12] The algorithm used is indicated in Figure 12. First the 'equilibrium' case with no slow steps was derived, then the carbonic acid concentration as a function of time was introduced in accordance with equation 9 and solved for $[H^+]$ numerically. Figure 13 shows that the only effect of the slow kinetics was to change the height of the maximum at pH about 8.5. To make sure that the same was true if the kinetics were even slower, the values were changed from their accepted values by the amounts shown in the Figure caption. Again only a change in the height of the maximum was observed, unless the rate of addition of alkali was speeded up, when some displacement of the maximum was observed, as expected, but no new features in the titration curve were found.

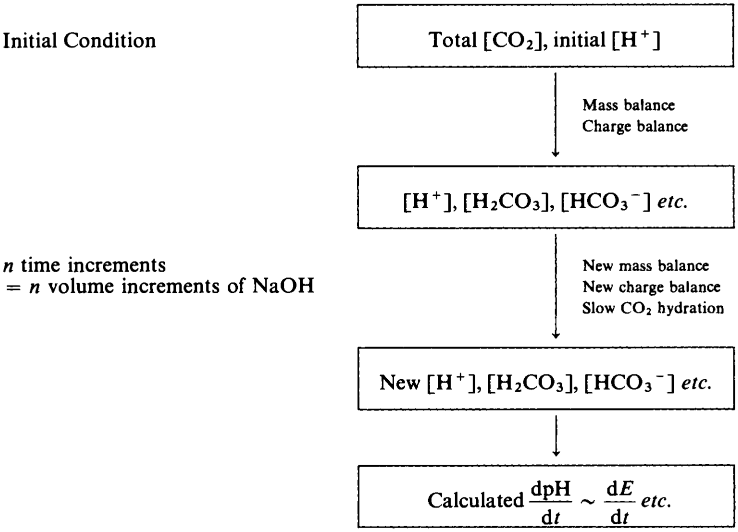

Figure 12 *Flow chart of computer simulation of titration curves with slow kinetics*

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[11] H. S. Frank and R. N. Goldberg, *J. Phys. Chem.*, 1972, **76**, 1758.

[12] A. K. Covington, R. N. Goldberg, and M. Sarbar, *Anal. Chim. Acta*, 1981, **130**, 103.

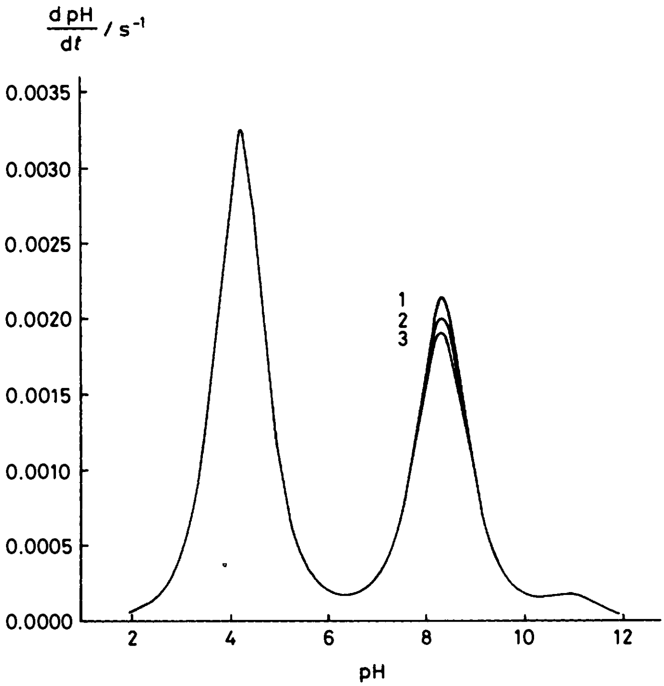

Figure 13 *Calculated values of* dpH/d*t as a function of* pH *for titration of* 0.01 mol *of* CO_2 *and* 0.01 mol *of* HCl *with* NaOH (*rate of addition* 10^{-6} mol/s). *The thermodynamic, and kinetic rate, constants given in the text were used to calculate curve* 2. *Curve* 1 *was calculated by removing all time delays in* $CO_2 \longrightarrow H_2CO_3$ *conversion. Curve* 3 *was obtained by setting* $k_f = 0.015\ s^{-1}$ *and* $k_f = 10.0\ s^{-1}$

4 Discussion

The evidence presented above suggests that the new feature in the first derivative titration curves is a property of the titrated solution, which is detected by glass electrodes and certain other hydrogen-ion responsive electrodes, but not by the platinum–hydrogen gas electrode because the hydrogen gas sweeps carbon dioxide out of the solution. The position of the extra maximum between the carbonate and hydrogencarbonate equivalence points suggests that the new feature is the result of protonation of a novel species with p*K* intermediate between those for carbonate and hydrogencarbonate. The most likely structure for this complex ion is a singly charged ion, formed by

$$HCO_3^- + CO_2 + H_2O \longrightarrow H_3C_2O_6^- \qquad (10)$$

or

$$HCO_3^- + H_2CO_3 \longrightarrow H_3C_2O_6^- \qquad (11)$$

The difference between these two processes is, of course, the hydration of carbon dioxide (equation 9). If the equilibrium constant associated with equation (11) is denoted by K_3 then

$$[H_3C_2O_6^-] = K_3[HCO_3^-][H_2CO_3] \tag{12}$$

$$= (K_3/K_1K_2^2)[H^+]^3[CO_3^{2-}]^2 \tag{13}$$

and computer-simulated titration curves can be obtained (Figure 14).

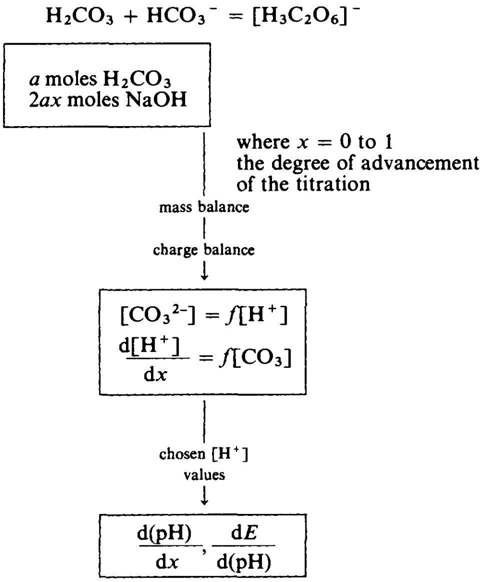

Figure 14 *Flow chart for computer simulation of titration curve with presence of additional species*

Figure 15 shows the species distribution diagram for the carbonate system based on $K_3 = 1.2 \times 10^3$ dm^3 mol^{-1}, since comparison of the computer simulation titration curves (Figure 16) with experimental dE/dpH curves[13] suggests K_3 is about 10^3 from the height of the extra maximum. Theoretical carbon dioxide gas-electrode first-derivative titration curves are shown in Figure 17. The maximum in these curves at pH 11 is not seen experimentally (Figures 7 and 9) because the carbon dioxide concentration at this pH is well below the detection limit of the electrode.

The most probable structure for the new anion species is two planar carbonate moieties linked by bridging hydrogen bonds to oxygen atoms. There is evidence for the existence of such strong hydrogen bonds.[14] A computer program generation

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[13] A. K. Covington and M. Sarbar, in preparation.

[14] J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.

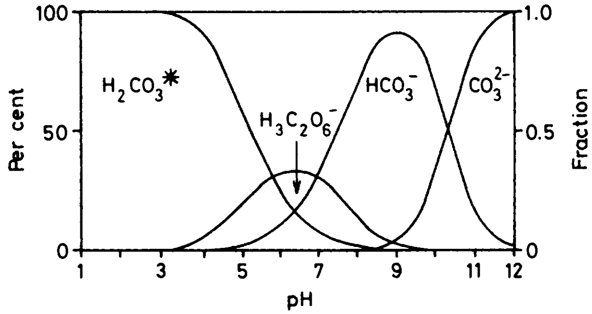

Figure 15 *Species distribution diagram for the carbonate system based on* $K_3 = 1.2 \times 10^{-3}$ $dm^3\ mol^{-1}$ in *equation* 9

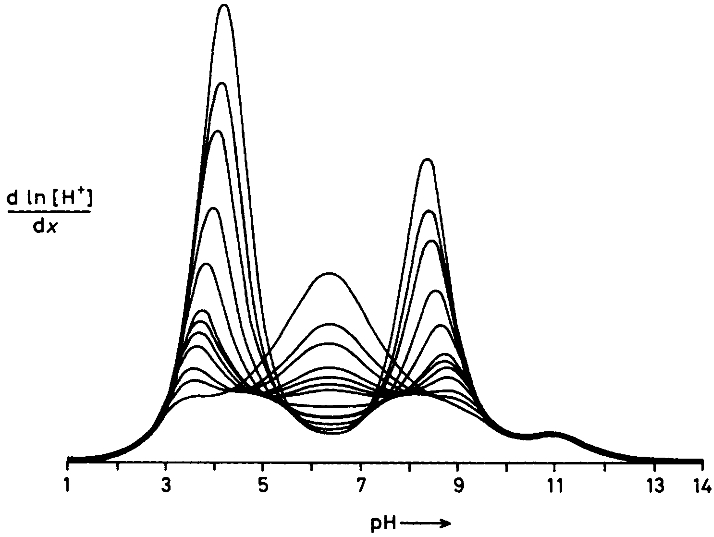

Figure 16 *Superimposed theoretical* pH *titration curves for different values of* K_3. *Reading upwards at* pH 4 *the curves refer to* $K_3 = 10^4$, 5×10^3, 3.5×10^3, 2×10^3, 1.5×10^3, 1.2×10^3, 5×10^2, 2.5×10^2, 50, 0 $dm^3\ mol^{-1}$

of this structure is shown in Figure 18. The bond lengths of C–O and H–O were taken from Edsell[3] and Brown *et al.*[15] The suggestion is related to sodium sesquicarbonate (Na_2CO_3,$NaHCO_3$,$2HC_2O$), which exists as the mineral, trona. In the crystal structure of sodium sesquicarbonate,[15] two carbonate ions are linked through hydrogen bonds (O–H–O) with a bond length of 0.253 nm forming a complex ion species $(HC_2O_6)^{3-}$. Protonation of this species yields dimeric hydrogencarbonate ions and then the proposed new species (equation 14).

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[15] C. J. Brown, H. S. Peiser, and A. Turner-Jones, *Acta Cryst.*, 1949, **2**, 167.

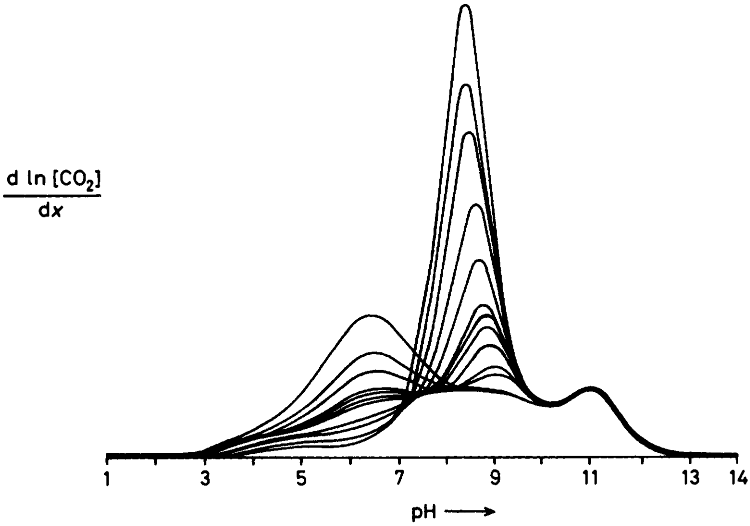


Figure 17 *Superimposed theoretical* CO_2 *gas electrode titration curves for different values of* K_3. *Reading upwards at* pH 9 *the curves refer to the values of* K_3 *given in figure* 16

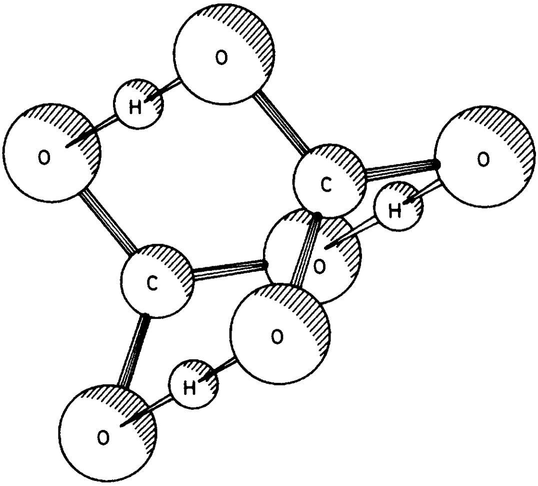
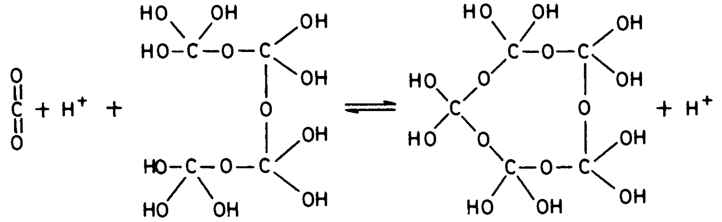


Figure 18 *Structure of the new anion species consisting of two planar carbonate moieties linked by three hydrogen bonds to the oxygen atoms*

$$(HC_2O_6)^{3-} + H^+ \rightleftharpoons (H_2C_2O_6)^- + H^+ \rightleftharpoons (H_3C_2O_6)^- \qquad (14)$$

Thus the suggested species is the form sesquicarbonate exists in near neutral pH aqueous solution. The existence of dimeric hydrogencarbonate ion and sesquicarbonate ion in aqueous solution may be difficult to prove.

It is pertinent to enquire whether any other anomalous behaviour of the carbonate system has been reported. Kern[4] and Edsell[3] have drawn attention to inconsistencies in kinetic data for the hydration–dehydration reactions. Koefoed and Engel[16] explained their results for the acid catalysis of the hydration reaction by invoking catalysis by a new species, trimeric carbonic acid formed as shown in equation 15.


(15)

Edsell[3] pointed out that there were differences between the rate constants for the dehydration of carbonic acid depending upon whether the measurements were derived from studies at acid pH or at pH 6—8 as shown in Figure 19.

Laser Raman spectra of carbonic acid solutions have been reported,[17–21] but no anomalous spectral lines were found. Abbott *et al.*[20] determined ^{13}C n.m.r. spectra

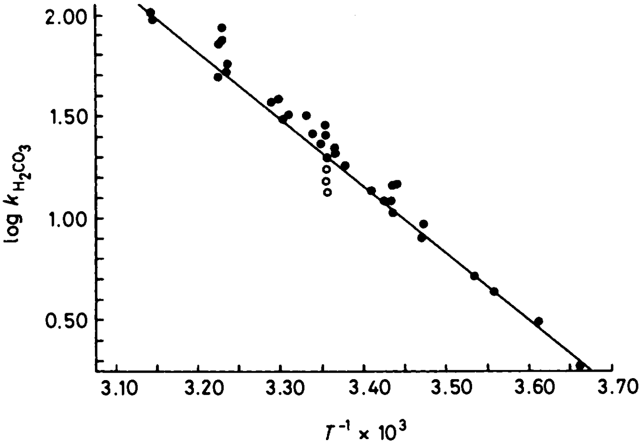


Figure 19 *Variation of the rate constant for the dehydration of* H_2CO_3 *with* $1/T$ (*ref.*3). ● *measurements made in buffer* (pH 6—8); ○ *measurements made at low* pH (HCO_3^- + HCl)

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[16] J. Koefoed and K. Engel, *Acta Chem. Scand.*, 1961, **15**, 1319.
[17] A. R. Davis and B. G. Oliver, *J. Solution Chem.*, 1972, **1**, 329.
[18] A. R. Davis and B. G. Oliver, *Can. J. Chem.*, 1973, **51**, 698.
[19] Y. K. Sze, W. A. Adams, and A. R. Davis, in 'Chemistry and Physics of Aqueous Gas Solutions', The Electrochemical Society, New York, 1975, p. 42.
[20] T. M. Abbott, G. W. Buchanan, P. Kruus, and K. C. Lee, *Can. J. Chem.*, 1982, **60**, 1000.
[21] C. W. Davies and L. J. Hudleston, *J. Chem. Soc.*, 1924, **125**, 260.

and detected signals ascribed to $CO_2(aq)$, hydrogencarbonate, and carbonate ions. No direct evidence for carbonic acid was obtained but an unstable species was found with a shift, relative to TMS, or 151.3 p.p.m. compared to 161.3 p.p.m. for hydrogencarbonate and 163.5 for carbonate was found.

The new species could be considered as

$$HCO_3^{-}\cdot H^{+}\cdot HCO_3^{-}$$

and such triple ions have been reported to exist for a variety of acids in aqueous solution. The best known[21,22] is probably HF_2^-, but triple ion formation constants have also been determined for phosphoric[23,24] and iodic[25] acids. From solubility measurements, Kolthoff and Bosch[26] postulated the existence of a benzoic acid–benzoate 'inner complex', and Martin and Rossotti[27] have reported formation constants for monocarboxylic acid triple ions from pH titrations in perchlorate media. These data are collected in Table 2, from which it may be noted that the formation constant for the carbonate species is appreciably higher than those found previously.

Table 2 *Triple-ion formation constants*

Acid	*Triple-ion*	K_3/dm^3 mol^{-1}	*Ref.*
HF	HF_2^-	4.7, 3.86	21, 22
H_3PO_4	$H_2PO_4^-\cdot H_3PO_4$	3, 1.26	23, 24
HIO_3	$H(IO_3)_2^-$	4	25
RCOOH[a]	$R\cdot COOH\cdot RCOO^-$	0.32, 0.46, 0.45, 0.58	27

[a] R = H, Me, Et, Pr^n

Finally, a comment on the removal of the new feature in the titration by carbonic anhydrase is necessary. Although addition of carbonic anhydrase affects the kinetics of the hydration–dehydration reaction, it is also likely to affect the kinetics of formation of the new species. The existence of the new species shows up in the first-derivative titration curves when the pH of the solution is changed at an appropriate rate. The species concentration diagram (Figure 15) shows that 30% of the carbon dioxide is in the form of the new species at pH 6—8 based on comparison of experimental and theoretical titration curves of the same heights of the maximum. This could be misleading without recognizing the kinetic aspects of its existence. Although it should be possible to introduce into the computer modelling rate constants for the formation and decomposition of the new species, this has not yet been done.

Owing to the physiological[28] and technical importance of the new species,

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further spectroscopic investigations would be valuable, and using modern instrumentation, a new study of the kinetics of the hydration and dehydration reactions.

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Tribute. I first met R. A. Robinson when he was in R. G. Bates' Electrochemical Analysis Section at the National Bureau of Standards in 1966 during my sabbatical leave. He was still a keen experimentalist with his isopiestic technique, which I learnt from him, but also he avidly devoured experimental e.m.f. results from M. Paabo, H. B. Hetzer, and myself as they were recorded. His consuming passion was the working over of experimental results and devising new theoretical treatments particularly for multielectrolyte problems. His sound knowledge of chemical principles and thermodynamics and a shrewd intuition made scientific discussions with him catalytic and exhilarating. Perhaps the attribute I most admired was his tenacity of purpose in attacking seemingly intractable problems.