POTENTIOMETRIC TITRATIONS WITH ION-SELECTIVE ELECTRODES OF AQUEOUS CARBONATE SYSTEMS AND STUDY OF A NOVEL CARBONATE SPECIES

THESIS SUBMITTED TO THE UNIVERSITY OF
NEWCASTLE UPON TYNE FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

BY

M. SARBAR, B.Sc., M.Sc.

DECEMBER, 1980

NEWCASTLE UPON TYNE
TY LIBRARY
ACCESSION No. 80 07714
LOCATION Thesis L2363

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Dr. A.K. Covington for the invaluable guidance, assistance and encouragement which he has given me throughout the course of this work.

I am also grateful to Dr. R.N. Goldberg of the National Bureau of Standards, USA, Dr. M.N.S. Hill, Mr. Ian McKeag, Dr. Ian Edwards and the technical staff of the Department of Physical Chemistry and Miss R. Parkinson, the secretary of the Department, for their assistance.

Appreciation is expressed to my family for their patience and understanding and their encouragement throughout the tenure of this work.

I would like to thank the University of Tabriz in Iran, the Ministry of Culture and Higher Education of Iran and my brother Ali for financial support.

Finally, I would like to thank my friends Dr. S.M. Golabi, Mr. M.H. Montakhab, Dr. S. Lotfi, Mr. N. Daneshvar, Mr. M. Arami, Miss H.J. Gallagher, Mr. A.P. Childs, Miss J.M. Mayne and Mr. M. A. Megrazi for their help and encouragement at home and in the UK.

TO MY PEOPLE AND
MY HOMELAND, IRAN

CONTENTS

Page

Chapter 1: INTRODUCTION

Chapter 2: THEORY OF FIRST DERIVATIVE POTENTIOMETRIC CURVES

Chapter 3: DETERMINATION OF CARBONATE IN THE PRESENCE OF HYDROXIDE IONS AND DESCRIPTION OF THE FIRST DERIVATIVE POTENTIOMETRIC TITRATION CURVES

Chapter 6: COMPUTER SOLUTION OF TITRATION CURVES AND COMPARISON WITH EXPERIMENTAL CURVES

Chapter 7: DETERMINATION OF CARBONATE IONS BY DIRECT POTENTIOMETRIC METHOD, USING ION-SELECTIVE ELECTRODES.

Chapter 8: ISOPIESTIC MEASUREMENTS OF K_2CO_3 AND $NaHCO_3$:

Chapter 9: DISCUSSION

ABSTRACT

Mathematical consideration of the course of neutralization of a solution containing a strong base (e.g. NaOH) and a salt of a weak dibasic acid (e.g. Na_2CO_3) with a strong acid (e.g. HCl) shows that first derivative of the potentiometric titration curve should contain three maxima. The first corresponds to neutralization of most of the hydroxide, the second and the third peak correspond to conversion of CO_3^{2-} to HCO_3^- and HCO_3^- to H_2CO_3 (CO_2 + H_2O) respectively.

Plots of (dE/dV) against Vol. of HCl (V) for sodium hydroxide containing different concentrations of Na_2CO_3 using glass electrodes show an additional, unexpected maximum in the titration curves. This is not detected when ethanol (mole fraction $>$ 0.2) or t-butanol (mole fraction $>$ 0.1) are added, when the temperature is raised above 55°C, when hydrogen gas is bubbled through the solution or when the hydrogen gas electrode is used instead of the glass electrode. Change of solvent from H_2O to D_2O and change of cation from Na^+ to K^+ had no effect on the additional maximum, and also when back titrations of a solution of hydrochloric acid containing different concentrations of dissolved CO_2 with NaOH were carried out.

The rate of addition of hydrochloric acid or, in other words, the rate of introducing CO_2 into the solution during the course of titration has an effect on the position of this unexpected maximum. This suggests that a kinetic stage is involved in the formation of the maximum. The extra feature was not recorded when a trace of carbonic anhydrase was introduced into the titration solution. Computer simulation was carried out considering the effect of slow kinetics of hydration of CO_2 on the form of the titration curve, but the only effect was on the height of the maximum for the conversion of H_2CO_3 to HCO_3^- .

There is strong evidence that the extra maximum is a result of formation of a complex of CO_2 and HCO_3^- in the presence of H_2O ($H_3C_2O_6^-$). Assuming values for the equilibrium constant for this process, the appropriate equations were solved on the computer to obtain titration curves identical to the experimental curves. Also the molecular structure of this new species was plotted by using an IBM/360/370 computer.

Along with analysis of titration curves attempts were made to use liquid membrane electrodes, PVC membrane electrodes, Ag/Ag_2CO_3 electrodes, in direct potentiometric measurements of carbonate ions. Also isopiestic technique was applied to measure osmotic coefficients of K_2CO_3 and $NaHCO_3$ solutions.

1. INTRODUCTION

1.1.1. INTRODUCTION

In view of the importance of the carbonate system to industrial, environmental and biological studies, much relevant work has been performed and much information is available, so that the system is thought to be well understood. The carbonate system consists of different species of CO_2, H_2CO_3 , HCO_3^- ,and CO_3^{2-} . These species are in equilibrium and their amounts are dependent on the pH of the aqueous solution.

The titration method, by obtaining the first derivative of potentiometric curve,has been used to investigate this system and determine the concentration of different species. Titration of carbonate ions in the presence of hydroxide ions and dissolved carbon dioxide in the presence of H^+ ions were studied. An extra feature, which was present in both titration curves, was investigated and removed. Since CO_2 plays a central role in this investigation so it is important to describe aspects of its chemistry first.

1.2.1. CARBON DIOXIDE IN NATURE:

Carbon dioxide is the major end product of metabolism and is continuously produced by all cells in all tissues. It is the fourth most abundant gas in the earth's atmosphere amounting to some 0.0003 atm. (0.03% by mass). In spite of such a small fraction, it is as important as oxygen to life on earth. Carbon dioxide and oxygen pass through global cycles under the influence of energy input from the sun. They participate intimately in the production and destruction of life.

One important property for the development of life on the earth is the maintenance of the pH at around 7. Here carbon dioxide and its chemical compounds occupy a central position of importance.

Fluctuations of carbon dioxide in the atmosphere are principally due to photosynthesis in daylight hours, this fixes approximately 6 x 10^{10} tonnes (1) of carbon dioxide per year, and biological respiration and decay which release about the same amount. Without the oceans it is very likely that fluctuations of carbon dioxide in the atmosphere would be far more pronounced. However, the oceans serve as a giant source and sink to attenuate the fluctuations. As Henderson pointed out, carbon dioxide is unique among the gases in distributing itself, in almost equal amounts per unit volume (2) , between air and water at ambient temperature. Thus it is constantly undergoing exchange between the atmosphere and the ocean. In the ocean, it forms a component of the world's largest buffer solution as shown in the following reaction:

$$CO_2\ (g) \rightleftharpoons CO_2(aq.) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (1)$$

As a result of these reactions only a small percentage of total carbon dioxide in sea water is presented as aqueous carbon dioxide. Since the Industrial Revolution, massive quantities of carbon dioxide have been injected into the atmosphere from the burning of fossil fuels, about 6 x 10^9 tonnes per year (1). But the massive buffering capacity of the oceans makes it impossible to state categorically, that a significant change in the atmosphere has taken place. However, any rise of concentration of carbon dioxide in the atmosphere will bring problems to mankind on the earth. Thus measurement of the carbon dioxide in the solutions by direct titration with sodium hydroxide and analysis of the first derivative of potentiometric curves using a glass electrode and carbon dioxide electrode has great importance for environmental and industrial studies.

Understanding the first derivative curves requires knowledge about the structure of carbon dioxide and carbonate ions, the solubility of carbon dioxide in water, velocity of hydration of carbon dioxide and kinetics of the reactions involved in the process, as described very briefly in the following.

a) The structure (2) of carbon dioxide and the carbonate ion:

The carbon dioxide structure is based on spectroscopic data on the molecule in the gas phase, whereas the structure for the carbonate ion has been determined by x-ray diffraction measurements on calcite crystals. When the molecules and ions are in aqueous solutions, the dimensions may be slightly different from those given below, but it is assumed such differences, from values in figure (1) are small (2)

Figure 1: Physical dimensions of carbon dioxide and carbonate ions.

Carbon dioxide is a symmetrical linear molecule with zero dipole moment. The C-O distances, $1{\cdot}159^{o}$A , are shorter than those found in a typical C=O double bond (1.22^{o}A) and indicate the contribution of resonance. The carbonate ion is planar and symmetrical, with three equivalent C-O bonds, intermediate in character between single and double bonds. When it binds a proton to form the carbonate ion, the three-fold symmetry is destroyed and the C - (OH) bond becomes longer, while the other two C - O bonds acquire a more double-bond character and shorten. The addition of a second proton to form H_2CO_3 carries the process further. Even after both protons are bound, all the C - O bonds still retain enough double-bond character to maintain the planar triangular arrangement of carbon and three oxygens. Thus when carbon dioxide is hydrated to form H_2CO_3 or HCO_3^- , the two C - O bonds must lengthen and must bend towards one another, the angle between them decreasing from 180^{o} to about 120^{o}, as shown in figure 1. The slowness of hydration and dehydration reactions must be associated with the necessity of making these electronic rearrangements.

b) Solubility of carbon dioxide

When carbon dioxide dissolves in water, it is present almost entirely as unhydrated carbon dioxide. Little information is available about interactions between carbon dioxide molecules and the surrounding water molecules. Perhaps carbon dioxide molecules induce an orientation of the water molecules around them, either by electrostatic interactions or by hydrophobic bonding or something analogous to it. Although the molecule as a whole is non-polar, each of the two C - O bonds may act as a small dipole, with the oxygen at the negative end, and these dipoles could attract and orient surrounding water molecules.

The higher relative solubility of carbon dioxide for certain organic compounds such as ethanol in comparison to water shows that the affinity of carbon dioxide for hydrophobic polar solvent is greater than for water (2). This helps us to understand the effect of alcohol and tetra methyl ammonium-chloride (TMACl) addition in titrations. However, the carbon dioxide molecule dissolves much more readily in water than most gases do; it dissolves even better in hydrophobic solvents and it dissolves most readily of all in solvents that contain polar groups, with $\overset{+}{C}-\overset{-}{O}$ dipoles adjoining non-polar residues.

c) Kinetics (3)

The neutralization of carbon dioxide is a slow process compared with that of other weak acids. This is because only a small fraction of dissolved carbon dioxide exists in the hydrated form of H_2CO_3. Two mechanisms for neutralization of dissolved carbon dioxide are summarised below. Which mechanism predominates is determined by the pH of the solution. At pH lower than 8 the predominate mechanism is via direct hydration:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{2}$$

$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O\text{(instantaneous)} \qquad (3)$$

The rate law is pseudo-first order (3)

$$-d(CO_2)/dt = k_{CO_2}(CO_2) \;,\; k_{CO_2} = 0.03\cdot s^{-1}\ (mol/l)^{-1} \qquad (4)$$

At pH higher than 10, direct reaction with OH^- predominates:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (5)$$

$$HCO_3^- + OH^- \rightleftharpoons CO_2 + H_2O\text{(instantaneous)} \qquad (6)$$

with the rate law:

$$-d(CO_2)/dt = k_{OH}\cdot(OH^-)(CO_2) \;,\; k_{OH} = 8500\ s^{-1}(mol/l)^{-1} \qquad (7)$$

In the pH range 8-10, both mechanisms are important.

There are corresponding dehydration processes for the two slow reactions above:

$$H_2CO_3 \rightleftharpoons H_2O + CO_2 \;,\; k_{H_2CO_3} = k_{CO_2}\cdot K = 20\ s^{-1}(mol/l)^{-1} \qquad (8)$$

$$HCO_3^- \rightleftharpoons OH^- + CO_2 \qquad (9)$$

$$k_{HCO_3^-} = k_{OH}\cdot K\cdot K_w/K_a = 0.0002\ s^{-1}(mol/l) \qquad (10)$$

For the equilibrium: $H_2CO_3 \rightleftharpoons CO_2 + H_2O$,

$$K = ((CO_2)/(H_2CO_3)) = ((k_{H_2CO_3})/(k_{CO_2}) = \text{ca. } 600(3) \qquad (11)$$

A consequence of this equilibrium is that the true ionization constant of H_2CO_3 , ($K_a = (H^+)(HCO_3^-)/(H_2CO_3)$) must be much greater than the apparent constant listed as K_1 for carbonic acid dissociation constant:

$$K_1 = (H^+)(HCO_3^-)/(CO_2 + H_2CO_3) = 4.45\times10^{-7}\ mol/l \qquad (12)$$

As the observed ionization originates from only a small fraction of the total carbon dioxide constant, it can easily be shown that:

$$K_a = K_1(1 + K) = \text{ca. } 2.5\times10^{-4}\ (3) \qquad (13)$$

1.1.3. A BRIEF REWIEW OF PREVIOUS WORK ON TITRATION OF THE CARBONATE SYSTEM:

As was mentioned before, because of importance of the carbonate system, there have been many attempts made to understand the system and attempts have been made particularly to analyse the titration curves. In 1963 R.H. Stokes(4) introduced a general equation for the relation between pH and stoichiometric degree of neutralization in the titration of monoprotic and diprotic weak acids (or bases) with strong base (or acid). From these equations, the number and positions of inflexion points in the curves are derived and their relation to equivalent points was shown. Also application of the Gran plot method of determination of end-point of titration curves of pH vs. volume of strong acid have been described by Stumm and Morgan(5). The relationship between titration inflexion point in titration curves, buffer capacity and equivalence point was discussed by Loewenthal and Marais(6). Also the log(species) - pH diagram titration curve and buffer capacity diagrams were given in reference (6). Very recently the use of a logarithmic diagram for the estimation of the pH value at the equivalence point and the titration error when one or two acids are titrated with standard alkali has been described by Wänninen(7).

1.2.1. TITRIMETRIC ANALYSIS, CLASSIFICATION AND ITS AUTOMATION

Titrimetric analysis is basically a technique for measuring the concentration of a solution. In the most straightforward applications, there are solutions of each of two reagents which react together stoichiometrically. A measured volume of one solution (titrand) is placed in the titration cell, and the other solution (titrant) is added from a burette. At some particular stage the reaction will have occurred exactly according to the stoichiometry, and neither reagent will be in excess. This is called the stoichiometric point. If the concentration of one of the solutions is known, the concentration of the other can be calculated from the values of the reacting solutions at the stoichiometric point and from the stoichiometric equation.

Titrimetric methods may conveniently be classified into four groups (8), which include most of the major applications in use at the present time as follows:

a) Acid-base titrations;
b) Complexometric titrations;
c) Precipitation titrations;
d) Redox titrations.

Of these, the first are the most commonly used. However, the principles underlining each of the above four classes are similar.

The colour change which occurs in the solution is detected visually in classical methods of titrimetric analysis to detect the end-point of the titration. Such a process has certain limitations. Favourable working conditions are required as well as experimental adroitness. In some cases a suitable indicator cannot be found, for instance where the solution is dark or coloured or the reactions involved in the titration process are slow the visual determination of the end-point is difficult.

Instrumental methods of end-point detection not only enable one to overcome these and other similar difficulties, but are also preferable because they lead to greater precision. Many extensive physical quantities can be measured,.hence the large number of electrochemical, optical and radiochemical methods which can be applied for end-point detection in titrimetric analysis. The titrant is added in small increments and after each addition the extensive physical quantity is measured. The titration is generally carried out past the equivalence point, when the build-up of excess titrant can be measured. The titration curve is constructed from the results and the end-point determined graphically.

Automatic titrimeters can be constructed based on many instrumental methods of end-point detection. Thus, potentiometric, conductometric, amperometric, radio-frequency, spectrophotometric and coulombetric titrations can be automated very easily. Potentiometry is the most important of these. Much work has been done in the past 30 years to develop automatic potentiometric titrimeters, based on potentiometric end-point detection.

1.2.2. HISTORY OF ACHIEVEMENTS IN AUTOMATIC TITRATIONS:

From an historical point of view some achievements in automatic titrations are as follows:

1914: First automatic end-point titrator (9)
1922: First recording titrator (10)
1928: First photometric, automatic end-point titrator (11)
1933: First automatic end-point titrator with automatic sampling (12)
1945: First coulometric, continuous titrator (13)
1947-8: End-point anticipation methods for potentiometric titrators (14, 15)
1951: Development of the pH stat (16)
1954: Second derivative automatic end-point titrators (17, 18)

1.2.3. PRINCIPLES OF AUTOMATIC POTENTIOMETRIC TITRATION:

The end-point in automatic potentiometric titrations is detected from the change of the electromotive of a similar galvanic cell formed from the sample solution and sensing and a reference electrode. The titrant is added from an auttomatic burette with vigorous stirring of the solution. Titration curves can be obtained by plotting the volume of titrant dispersed against the electromotive force of the cell. By the obtained titration curves the end-point can be evaluated precisely. Alternatively, the abrupt change in the electromotive force which occurs at the end-point can be used to operate an electric circuit, which stops the titration by closing the burette at this point. The value of titrant dispensed can be read then from the burette, and the titrand concentration can be calculated in the usual way. Hence automatic potentiometric titrations are based on the measurement of an electrode potential against a reference electrode, therefore the Nernst equation has a central role in the interpretation of the processes taking place in automatic potentiometric titrations.

1.3.1. DESCRIPTION OF THE METTLER APPARATUS:

The Mettler apparatus (Mettler A.G., Zurich, Switzerland) was used, which is one of the most advanced for automatic titrations. The parts were as follows:

1) DV11: (digital burette) for adding of titrant solution with 10ml burette, synchronised with DK10 and GA10.

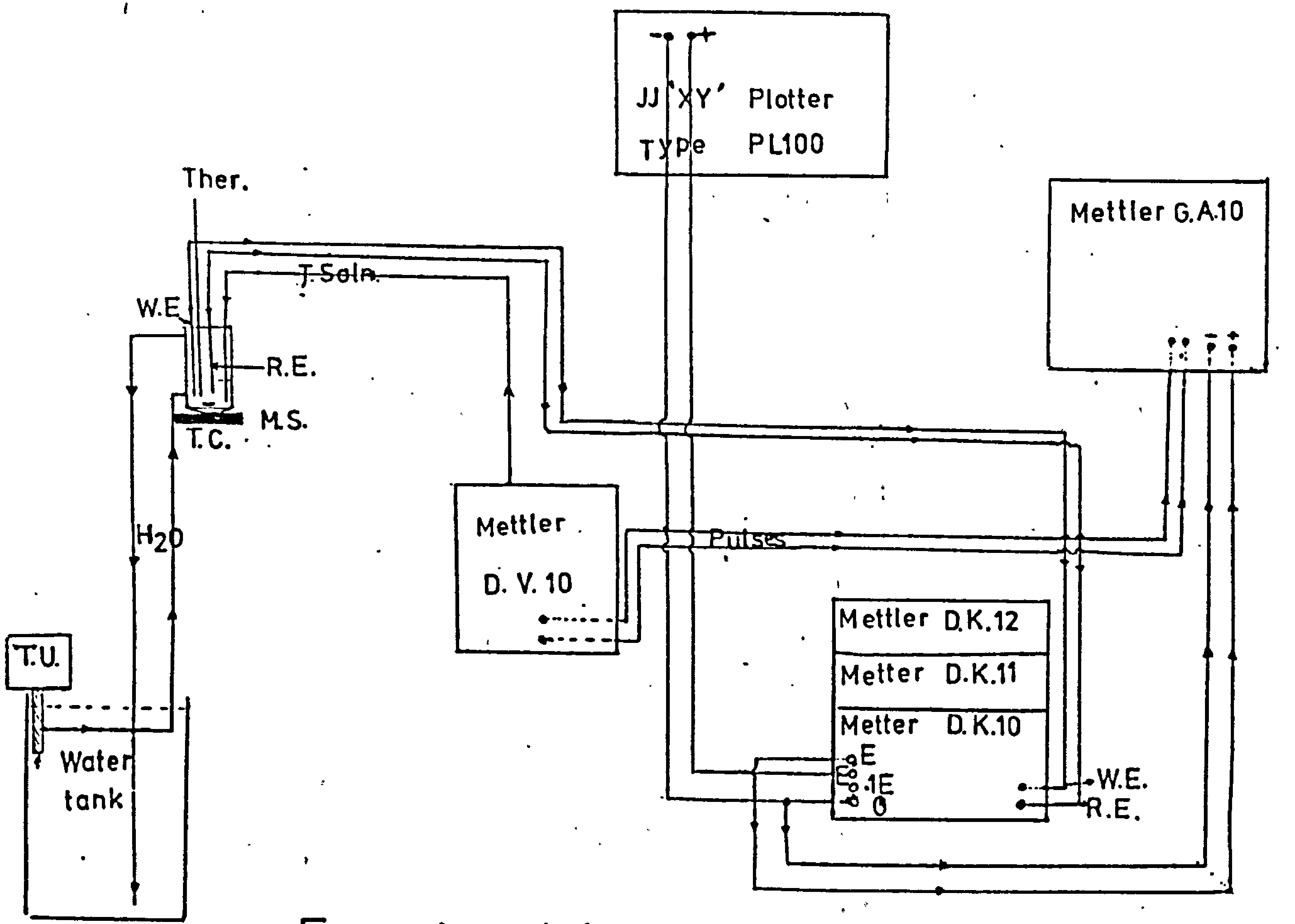
2) DK10: the basic instrument of DK Series is a high-resistance electrometer for input impedances up to 10^{10} ohms (potentiometric measurements). The amplifier output is grounded and galvanically separated from the input. An output with a differentiated signal is also available (dE/dV); it was also this unit which was used in all the experiments described below.

3) DK11: this part of the Mettler apparatus makes end-point pre-selection possible for automatic titration to a pre-selected end-point. It also performs reaction kinetics measurements and records the voltage curve with automatic slope fitting, DK11 combined with DK10, DV10 and a stepping motor recorder GA10.

4) DK12: this is an E-pX converter which is an analogue computer for converting electrode potentials into the corresponding pX values; by using the output from DK12 it is possible also to display pX values by employing a digital voltmeter.

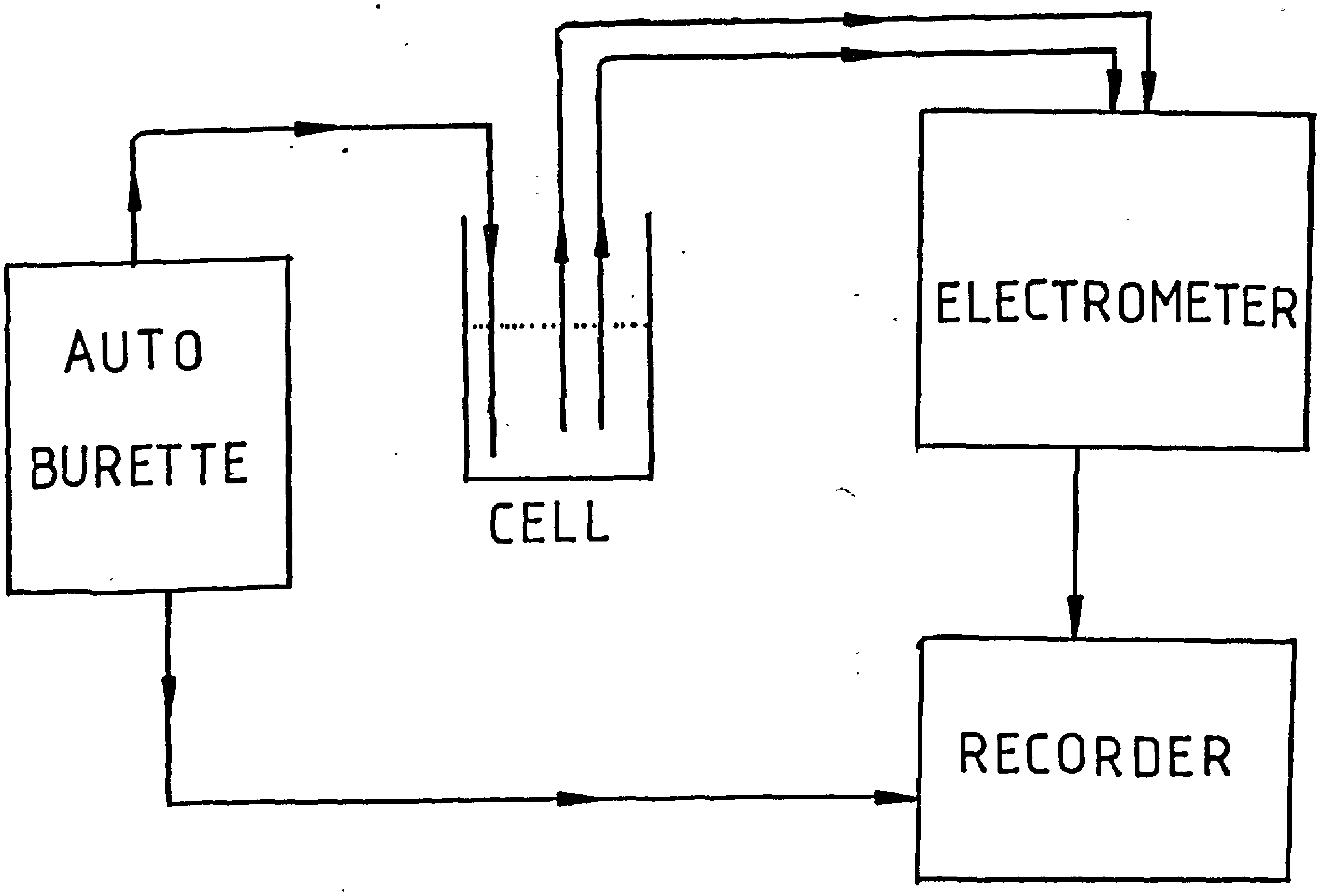
5) GA10 is a stepping motor recorder, which can be driven by internal and external pulses. This is synchronised with DV10, so that chart drive becomes proportional to the volume output.

The experimental equipment is shown in detail in figure 1-2; also a simplified version is given in figure 1-3. The reference electrode was connected to the front of the DK10, and the working electrode (glass or other type) was connected to the rear input of DK10.



Experimental Equipment

FIG 1-2



Experimental Equipment

FIG 1-3

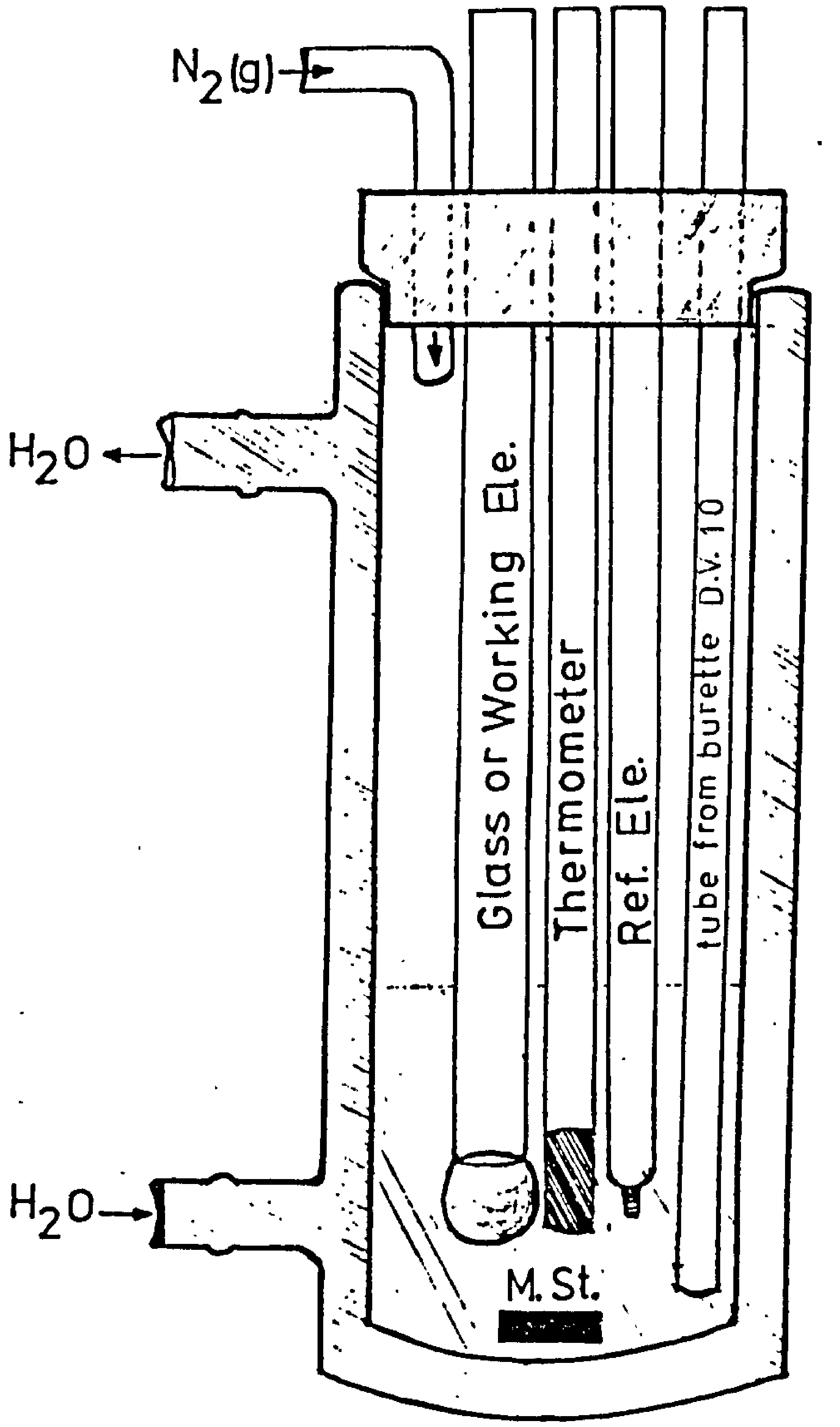
1.3.2. DESCRIPTION OF THE EXPERIMENTAL CELL:

The cell used for these experiments was a glass cylinder with an internal diameter of 40mm; external diameter of 50mm, and height of 120mm (see figure 1-4). Constant temperature was maintained by pumping water from a thermostatically-controlled tank through the jacket of the cell (see figure 1-2). A thermoregulator type TU-14-Tempunit made by Techne Limited (Duxford, Cambridge, U.K.) was used to maintain a constant temperature in the tank and to keep the circulation of water through the jacket of the cell at approximately two litres per minute.

A high-speed magnetic stirrer (Type S/Mag/Minor, Voss Instruments Ltd., Essex, U.K.) was used for mixing the solution in the cell thoroughly. The top of the cell was covered with a plastic lid with holes in for 1) A reference electrode; 2) A working electrode; 3) A thermometer; 4) A tube for introducing nitrogen gas on to the surface or for bubbling through the solution depending on the experiment being carried out; 5) A tube for inserting titrant solution, which was connected to a 10ml burette of DV10.

1.4.1. DETERMINATION OF CO_3^{2-} BY DIRECT POTENTIOMETRIC MEASUREMENTS:

The original intention of this project was analysis of the carbonate system by titrimetry. Some other investigations were carried out on this system along with the analysis of titration curves. A direct potentiometric method



Titration Cell

FIG 1-4

was used. Attempts were made to use a liquid membrane electrode, a PVC membrane electrode and Ag/Ag_2CO_3 electrode. This investigation is described in detail in chapter 7.

1.5.1. ISOPIESTIC MEASUREMENTS OF K_2CO_3 AND $NaHCO_3$:

Because of the lack of data, the osmotic coefficients of K_2CO_3 solutions were determined by using the isopiestic technique. The solubility of K_2CO_3 was determined both by titration and isopiestic methods. Also measurements of osmotic coefficients were carried out for $NaHCO_3$ solutions. It has to be mentioned that the available data were very poor (19) when we started this work. Pitzer's values (20) evaluated from Harned's work were published recently, but still there remain some uncertainties about these results. These investigations are described in detail in chapter 8.

1.6.1. REFERENCES:

1) R.E. Loewenthal and G.V. Marais "Carbonate Chemistry of Aquatic Systems" ANN ARBOR Science Press, Ann Arbor, Michigan, U.S.A. 1976, Chapter 1.

2) J.T. Edsall, NASA, Spec. Publ. 15, <u>188</u>, 1969.

3) D.M. Kern, J. Chem. Educ., 14, <u>37</u>, 1960.

4) R.H. Stokes, Aust. J. Chem., 759, <u>16</u>, 1963.

5) W. Stumm and J.J. Morgan, "Aquatic Chemistry", Wiley, New York, chap. 4 , 1970.

6) R.E. Loewenthal and G.V. Marais "Carbonate Chemistry of Aquatic Systems" ANN ARBOR Science Press, Ann Arbor, Michigan, pp102-108, 1976.

7) E.Wanninen, Talanta, 29,27,1980.

8) E.E.Aynsley and A.B.Littlewood, " Principle of Titrimetric Analysis " Royal Institute of Chemistry, No.6, 1962.

9) H.Ziegel, Z.Anal. Chem. 755,53, 1914.

10) E.A.Keeler, Ind. Eng. Chem. 395, 14, 1922.

11) R.H.Muller and H.M.Partridge, Ind. Eng. Chem. 423, 20, 1928.

12) K.Hickman and C.R.Sanford, Ind. Eng. Chem. Anal. Ed. 65, 5, 1933.

13) P.A.Shaffer, Jr., A.Briglio, Jr., and J.A.Brockman Jr., Anal Chem. 1008, 20, 1948.

14)R.A.Robinson, Trans. Electrochem. Soc. 445, 92, 1947.

15) J.J.Lingane, Anal. Chem. 285, 20, 1948.

16) C.F.Jacobsen and J.Leonis, Compt, rend. Trav. Lab. Carlsberg Ser. Chim. 333, 27, 1951.

17) H.V.Malmstadt and E.R.Fell, Anal. Chem. 1348, 26, 1954.

18) S.Takagi and Y.Maekawa, Buneki Kagaku, 478, 3, 1954.

19) W.J.Hamer and Y.C.Wu. J.Phys. Chem, 385, 6,1977.

20) K.S.Pitzer and E.Peiper, J. Phys. Chem. 2396, 84, 1980.

2. THEORY OF FIRST DERIVATIVE POTENTIOMETRIC TITRATION CURVES:

2.1.1. INTRODUCTION:

In an acid-base titration, advances in instrumentation enable not only the pH to be recorded automatically during an acid-base titration, but also the rate of change of pH with the titre, (dpH/dV) or the rate of change of cell e.m.f. (E) with titre, (dE/dV). In view of the importance to industrial and environmental studies of the titration of solutions containing both strong base (eg. sodium hydroxide) and salt of a weak dibasic acid (eg. sodium carbonate) with a strong acid (such as HCl), it is desirable to be able to predict at what values of b (acid) there will be marked changes in dpH/db and what will be values of any maxima in dpH/db with the titration solution containing a moles of NaOH and a moles of Na_2CO_3. The solution of this problem is not easy and is best approached in stages as follows.

2.2.1. TITRATION OF NaOH WITH HCl:

This is the simplest case. Consider a solution containing a moles of NaOH to which HCl is added in a linearly increasing amounts, $b = xa$, where x can be regarded as the degree of advancement of the neutralization; x less than 1 if there is alkali left to be neutralized, $x = 1$ at the end point and x greater than 1 when an excess of acid has been added. The condition for electroneutrality is:

$$(Na^+) + (H^+) = (Cl^-) + (OH^-)$$

or $$a + h = ax + K_w/h \qquad (1)$$

where $(H^+) = h$

then $$dh/dx = a - (K_w/h^2)\ (dh/dx)$$

or $(d\ln h/dx)\ (1+(K_w/h^2)) = a/h$ (2)

and it may be noted that $dpH/dx = -0.4343(d\ln h/dx)$.

Except in the immediate vicinity of the end point, two approximations are valid. If $b < a$, $x < 1$, $h^2 < K_w$

and since, $(OH^-) = a - b = a(1 - x)$ (3)

in eq. 2 $K_w/h^2 \gg 1$

so: $(d\ln h/dx) = (ah/K_w) = (a/(OH^-)) = (1/(1-x))$ (4)

and if $b > a$, $x > 1$, $h^2 > K_w$

then: $h = b - a = a(x-1)$ (5)

and, $(d\ln h/dx) = a/h = 1/(x-1)$ (6)

At the end-point, $x = 1$, $h^2 = K_w$, so

$(d\ln h/dx) = a/2h = a/2K_w^{\frac{1}{2}}$ (7)

This is a maximum value because, from equation (2),

$(d\ln h/dx) = (ah/(h^2 + K_w))$, and

$$(d^2\ln h/dx^2) = (a/(h^2 + K_w) - 2ah^2/(a^2 + K_w)^2)(dh/dx) =$$
$$(a(K_w - h^2)/(h^2 + K_w)^2)(dh/dx)$$

When $h^2 = K_w$, the above second derivative is equal to zero. So eq.(7) which relates to the end point is the maximum value.

It may not be generally realised that the approximations expressed by equations (3), (4), (5) and (6) are good even close to the end-point. For example, with a 0.1 mol/l and $x = 0.99999$, $(1-x) = 10^{-5}$, equation (3) gives $(OH^-) = 10^{-6}$ mol/l so that $h \doteq 10^{-8}$ mol/l and equation (4) gives $d\ln h/dx = 10^5$, where as equation (1) gives $h = 0.99 \times 10^{-8}$ mol/l and equation (2) gives $d\ln h/dx = 0.98 \times 10^5$. Figure 2-1 shows $d\ln h/dx$ in the immediate vicinity of the end-point. The open circles are values calculated by means of approximate equations (3)-(6), leading to "infinity catastrophe" at $x = 1$ which is avoided by using the exact equation (2) as shown by filled circles.

2.3.1. TITRATION OF THE SALT OF A WEAK ACID (NaA) WITH HCl:

If A is the anion of a weak acid, HA, then $K = h(A^-)/(HA)$ and if a is the initial concentration of salt: $a = (HA) + (A^-) = (A^-)(1 + h/K)$ and the condition for electroneutrality gives:

$$a + h = ax + aK/(h + K) + K_w/h) \qquad (8)$$

and $$(dh/dx)(1 + aK/(h + K)^2 + K_w/h^2) = a \qquad (9)$$

If the acid, HA, is not very weak, two useful approximations are available:

$$h/a \ll 1 \text{ and } h \geqslant 10^{-7},\ K_w/h^2 \ll 1$$

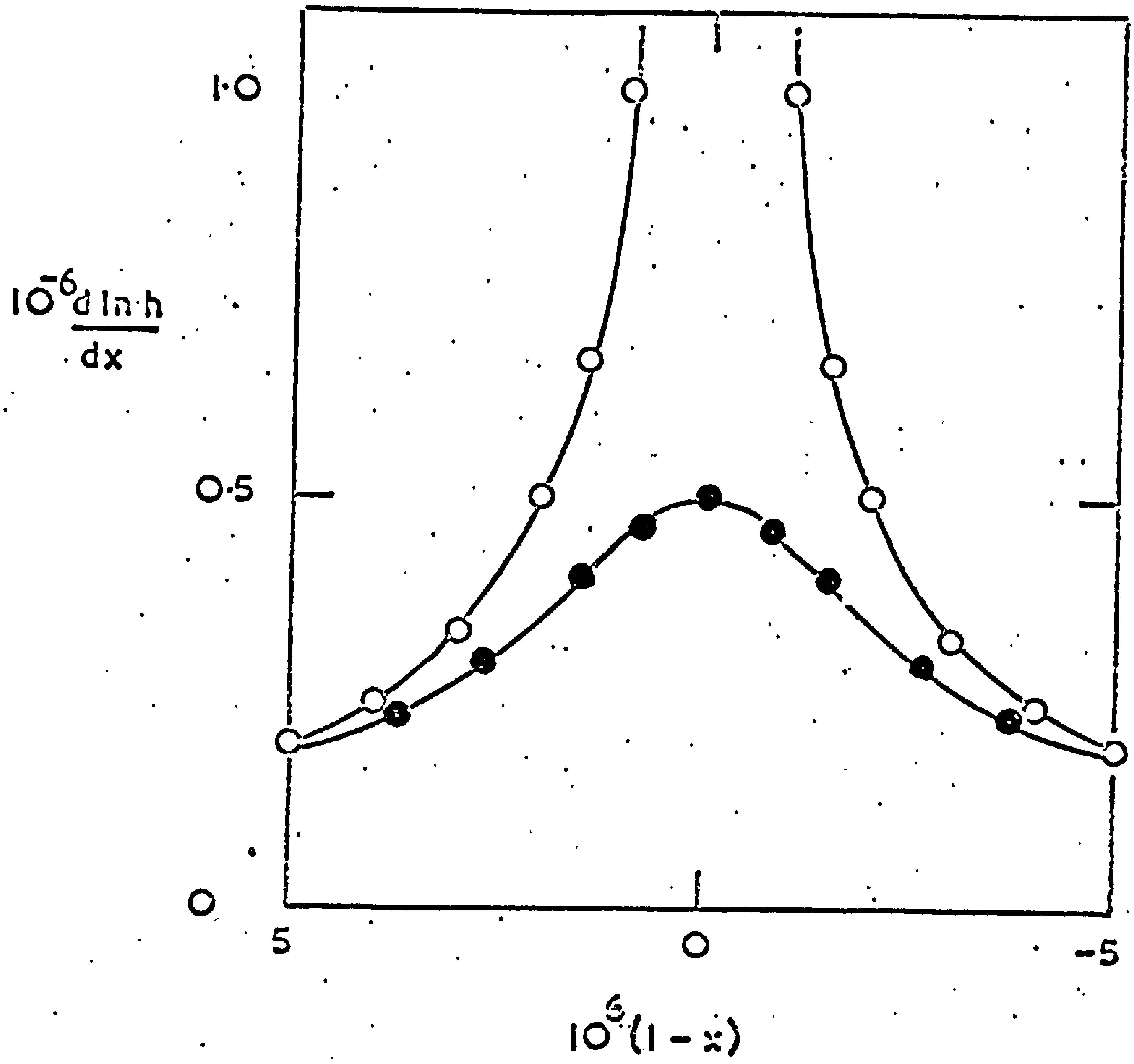
then: $(1-x) \simeq K/(h + K)$ and (8a)

$$(dh/dx)(1 + aK/(h + K)^2) \simeq a \qquad (9a)$$

In particular:

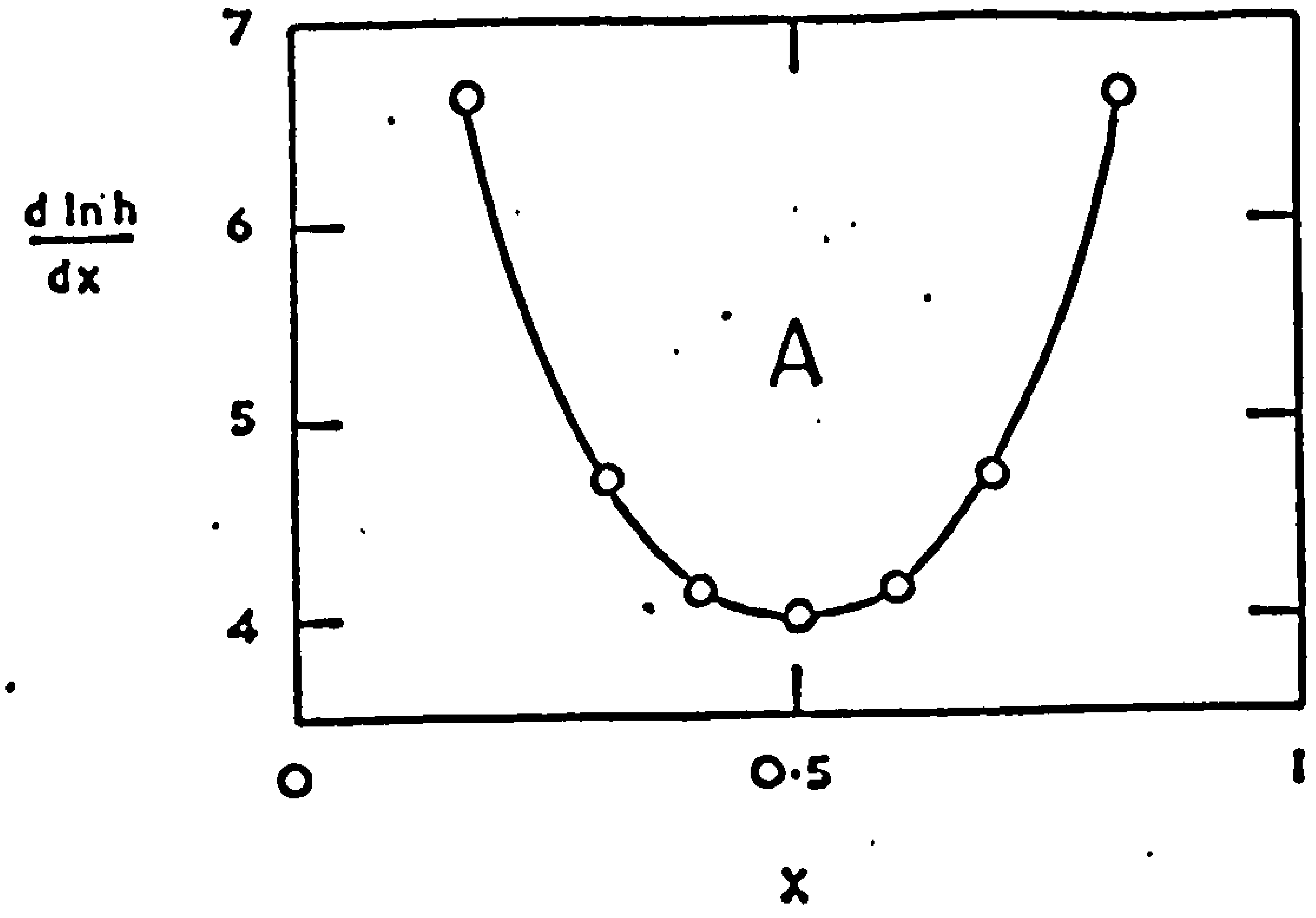
1) When $h \approx K$, $x \simeq 0.5$, $d\ln h/dx \approx 4$ (independent of the value of K or a) figure 2-2-A shows the change of $d\ln h/dx$ during the titration. It is clear that $d\ln h/dx$ has a minimum value at $x \approx 0.5$. The pH value of minimum corresponds to the point where $pH = pK$.

2) When $x \simeq 1$, $h \simeq \sqrt{Ka}$, $d\ln h/dx \approx \frac{1}{2}\sqrt{a/K}$, ($x \approx 1.50$, $HA \approx a$ and $h = A^-$), for example if $K = 4.5 \times 10^{-7}$ mol/l (The first dissociation constant of carbonic acid if kinetic complications are ignored) and $a = 0.1$ mol/l, $d\ln h/dx = 235.6$. Figure 2-2-B shows how $d\ln h/dx$ varies in the vicinity of $x = 1$ at $a = 0.1$mol/l;

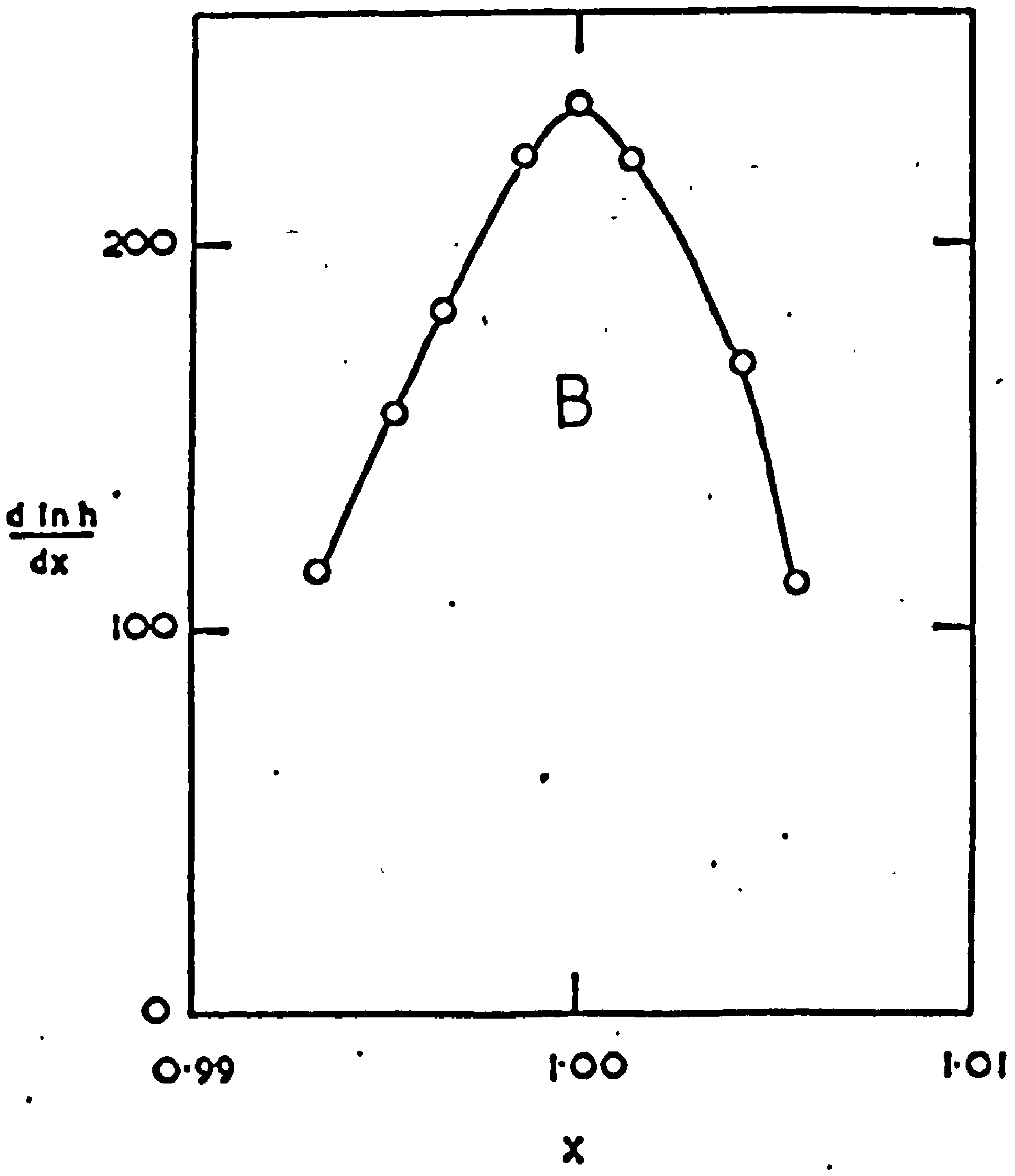


Theoretical differential curve for titration of NaOH with HCl in vicinity of $x = 1$. 0 calculated from approximate equations 3 -.6. ● calculated from exact equation 2.

FIG 2-1



Theoretical differential curve for titration of weak acid salt NaA with HCl in vicinity of x = 0.5.



Theoretical differential curve for titration of weak acid salt NaA with HCl in the vicinity of x = 1.

FIG 2-2

dlnh/dx has a maximum value when $x = 1$.

2.4.1. TITRATION OF NaOH + NaA WITH HCl:

We now consider the titration of a solution containing a moles of sodium hydroxide and a moles of the sodium salt of a weak acid (HA) with a dissociation constant of K, b moles ($\simeq 2ax$) of HCl is added.

Then $2a + h = 2ax + Ka/(h + K) + K_w/h$ (10)

$(dh/dx)(1 + Ka/(h + K)^2 + K_w/h^2) = 2a$ (11)

and if $K = 4.7\times10^{-11}$ mol/l (the second dissociation constant of carbonic acid), the approximation is valid that:

$$(dh/dx)(Ka/(h + K)^2 + K_w/h^2) = 2a \qquad (11a)$$

and, when $x = 0.5$, and $a = 0.1$ mol/l, $h^2 \simeq KK_w/a$, then $h = 2.168\times10^{-12}$ mol/l, dlnh/dx = 22.66. A more exact solution of equation (10) gives $h = 2.22\times10^{-12}$ mol/l at $x = 0.5$ and dlnh/dx = 22.70. This is not the maximum value, however, as is shown in figure 2-3, the maximum value 22.76, occurs at $x = 0.50035$. We now take up our main problem of titration of salt of a weak dibasic acid in the presence of a strong base with a strong acid.

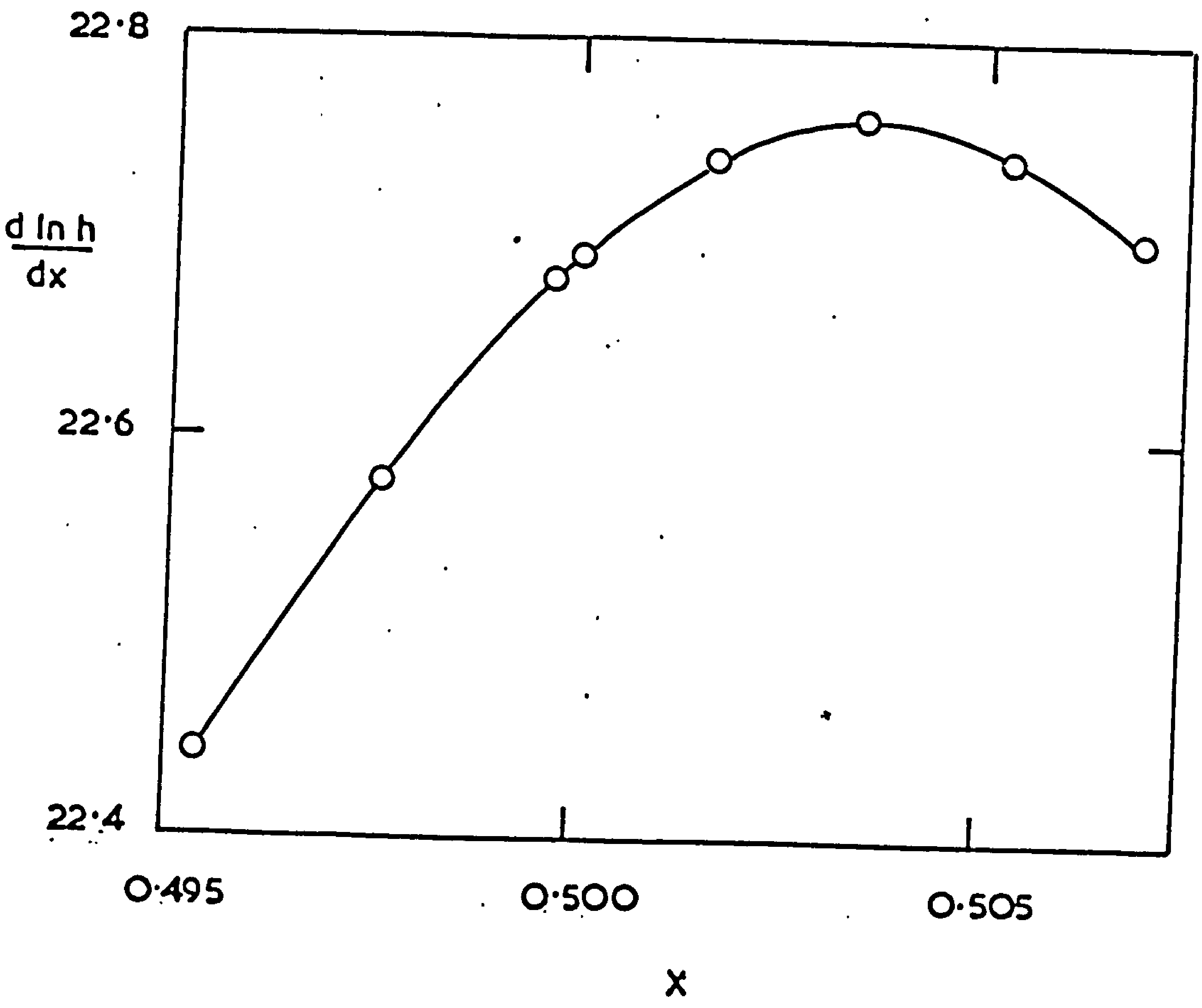
2.5.1. TITRATION OF NaOH + Na_2CO_3 WITH HCl:

For simplicity, it is assumed that K_a for the following process is the same as K_1.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

and the kinetic stage of hydration and dehydration of carbon-dioxide in aqueous solutions was ignored. We will discuss this problem later on.

Consider a solution containing a moles of NaOH and a moles of Na_2CO_3



Theoretical diffential curve for titration of a mixture of NaOH + NaA with HCl in vicinity of $x = 0.5$

FIG 2-3

to which b $(=3ax)$ moles of HCl are added.

The condition for the electroneutrality is:

$$(Na^+) + (H^+) = (Cl^-) + (HA^-) + 2(A^{2-}) + (OH^-)$$

where $HA^- = HCO_3^-$ and $A^{2-} = CO_3^{2-}$.

then $K_1 = h(HA^-)/(H_2A)$, $K_2 = h(A^{2-})/(HA^-)$ and

and $(H_2A) + (HA^-) + (A^{2-}) = a$

therefore $(A^{2-})(1 + h/K_1 + h^2/K_1K_2) = a$

and $$(A^{2-}) = K_1K_2a/\Sigma \ , \ (HA^-) = hK_1a/\Sigma \tag{12a}$$

where $\Sigma = h^2 + hK_1 + K_1K_2$

so $$3a + h = 3ax + aK_1(h + 2K_2)/\Sigma + K_w/h \tag{12}$$

and $$(dh/dx)(1 + aK_1 . (h^2 + K_1K_2 + 4hK_2)/\Sigma^2 + K_w/h^2) = 3a \tag{13}$$

Equation (12) is a quartic in h and cannot be solved for h as a function of (a,K_1,K_2,K_w). The inverse calculation of x at a series of values of h, using equation (12) and then the calculation of dlnh/dx at these values of h and x, using equation (13) is possible but very laborious; Many attempts along these lines have been made in the past (1-3), usually after introducing some approximations into these equations. However, this problem can be solved by using programmable calculators. As $K_1 = 4.5\times10^{-7}$ mol/l and $K_2 = 4.7\times10^{-11}$ mol/l, that is K_1 and K_2 are well separated and there is little overlapping, so the first stage of dissociation of H_2CO_3 to H^+ and HCO_3^- is almost complete before the second dissociation of HCO_3^- to H^+ and CO_3^{2-} commences. Thus, when $x = 0.67$, $a = 0.1$ mol/l $h^2 = K_1K_2$, most of the carbonate is in the form of HCO_3^-. Thus the considerations of the previous sections lead us to anticipate that there will be four stages in the titration as follows:

1) In which most of the hydroxide is converted to chloride.

2) In which most of the CO_3^{2-} is converted to HCO_3^- with a maximum value of $d\ln h/dx$ about $x = 0.33$ and a minimum value at $x = 0.5$ ($pH = pK_2$)

3) In which most of the HCO_3^- is converted into H_2CO_3 with a maximum value of $d\ln h/dx$ at $x = 0.67$, $h^2 = K_1K_2$ or $pH = \frac{1}{2}(pK_1 + pK_2)$ and a minimum value at $x = 0.83$ ($pH \approx pK_1$).

4) A stage in which HCl is present in excess with a maximum value of $d\ln h/dx$ at $x = 1$.

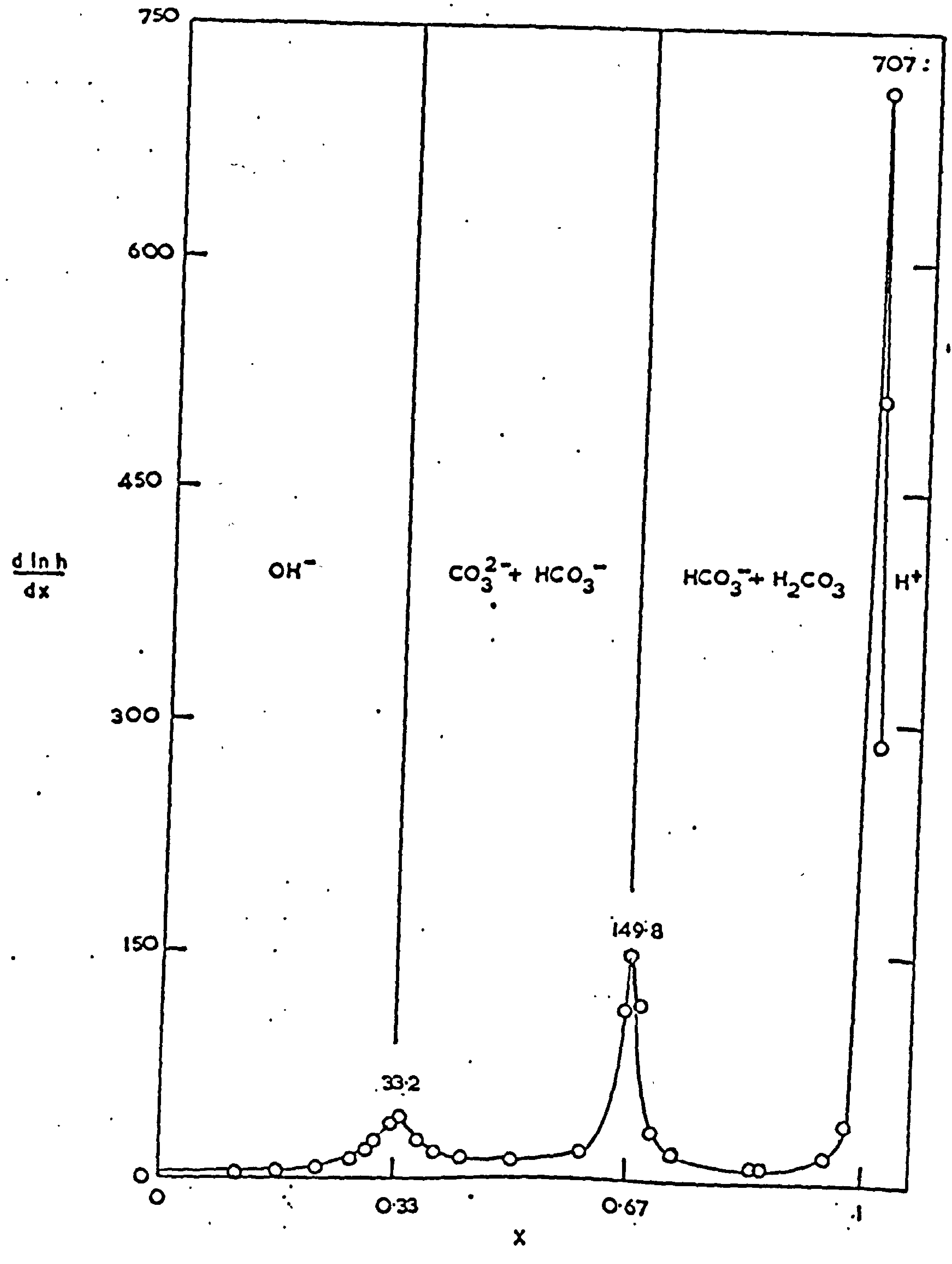
We will now discuss these three maxima and two minima in detail (see fig 2-4) When $x = 1$, all carbonate is converted to carbonic acid.
so: $h \approx \sqrt{K_1 . a}$, and $d\ln h/dx \simeq 1.5 \sqrt{a/K_1}$ from equation 12 and 13. At $x = 0.83$, $pH \approx pK_1$; at $x = 0.5$, $pH \approx pK_2$ so there will be two minima, with $d\ln h/dx = 12$, both independent of the values of a and K_1 or K_2. At $x = 0.67$, $h^2 \simeq K_1K_2$ and with $K_1 = 4.5\times10^{-7}$ mol/l, and $K_2 = 4.7\times10^{-11}$ mol/l, equation (13) reduces to:

$$d\ln h/dx(435.4a + 0.0473) = 0.6522\times10^5 . a$$

The second term on the left is the contribution of the K_w/h^2 term; neglecting this, $d\ln h/dx = 149.8$ independent of a. This is a good approximation, for even at $a = 0.01$ mol/l, $d\ln h/dx = 148.2$ and at $a \simeq 0.001$ mol/l $d\ln h/dx = 135$. At $x = 0.33$, $h = (K_2K_w/a)^{\frac{1}{2}}$ and $(dh/dx)(aK_2/(K_2 + h)^2 + K_w/h^2) = 3a$ For this, $d\ln h/dx$ is approximately equal to $105a^{\frac{1}{2}}$. This has one important consequence; at $a = 0.01$ mol/l, $d\ln h/dx = 12$, i.e. the maximum value of $d\ln h/dx$ at $x = 0.33$ is equal to the minimum value at $x = 0.5$. The result is that the maximum and minimum disappear as shown in figure 2-5 for $a = 0.01$ mol/l.

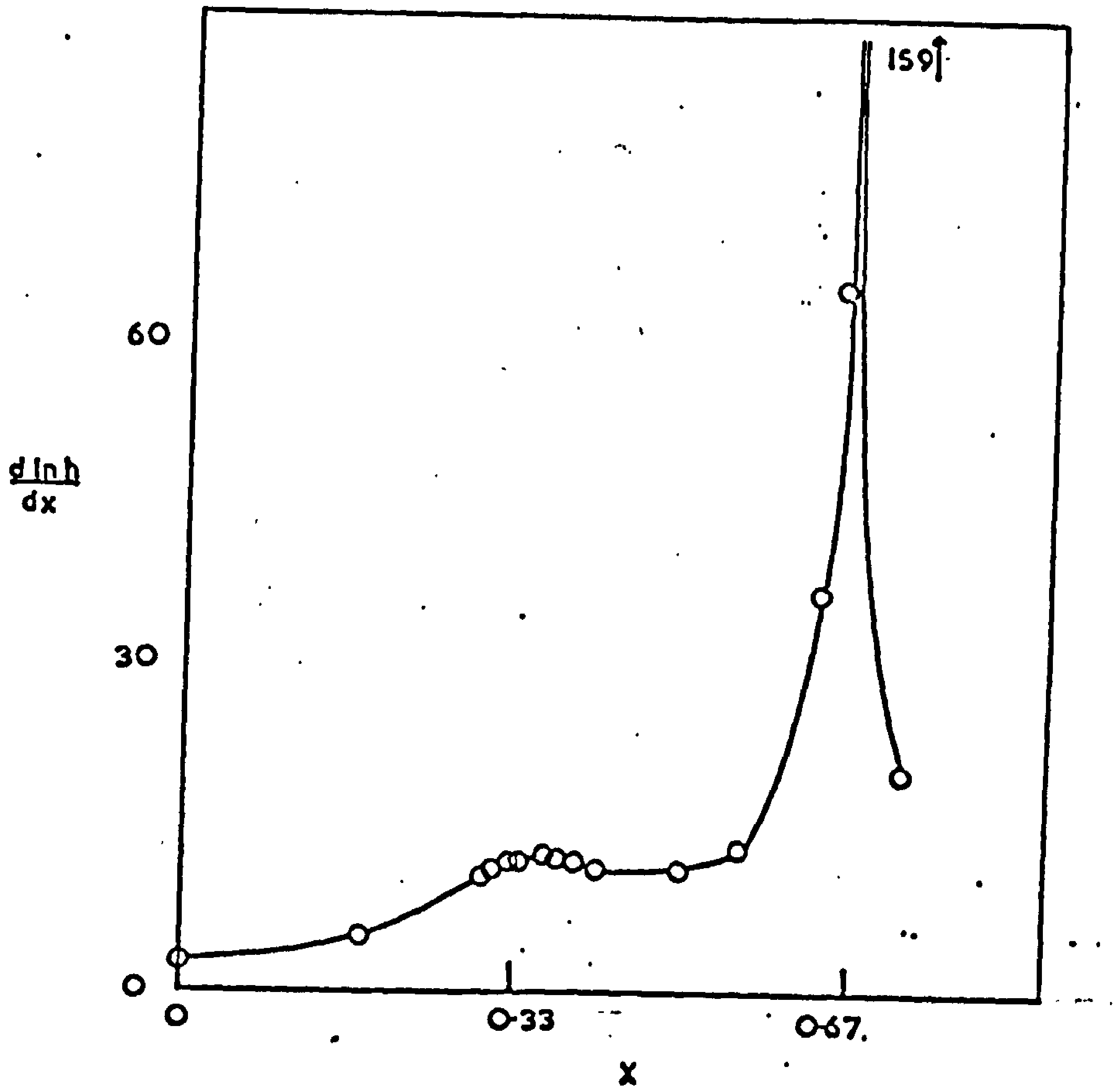
2-6-1: TITRATION OF NaOH, CONTAMINATED BY Na_2CO_3, WITH HCl:

If we now consider a solution contains a_1 moles of NaOH and a smaller quantity a_2 moles of Na_2CO_3 so $a_2 = Ka_1$, and we add $b \approx (a_1 + K)x$ moles of



Theoretical diffential curve for titration of NaOH (a) + Na_2CO_3 (a) where a = 0.1 mol l^{-1}, with HCl

FIG 2-4



Theoretical diffential curve for titration of NaOH (a) + Na_2CO_3 (a) where a = 0.01mol l^{-1}, with HCl

FIG 2-5

HCl, then equation (12) becomes:

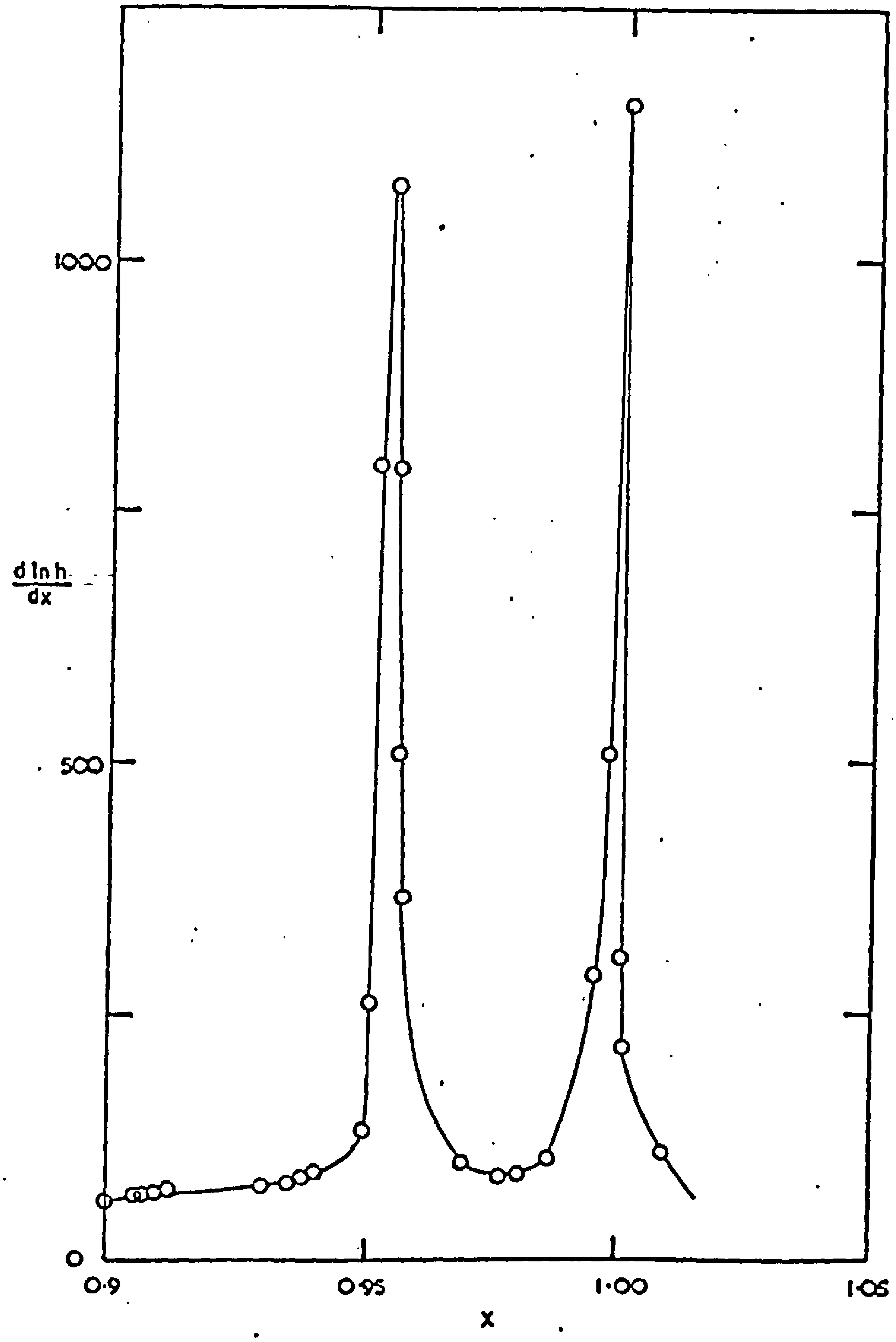
$$(dh)/(dx)\,(1 + (a_2K_1(h^2 + K_1K_2 + 4hK_2)/\Sigma^2) + K_w/h^2) = a_1(1 + 2k) \qquad (15)$$

The effect on figure 5 is to expand the first section and to contract the second and the third equally. Maxima will occur at $b = a_1$, $b = a_1 + a_2$ and $b = a_1 + 2a_2$ given by values of $x = 1/(1 + 2k)$, $x = (1 + k)/(1 + 2k)$ and $x = 1$ respectively, with approximate heights of $35(1 + 2k)a_1^{\frac{1}{2}} / k^{\frac{1}{2}}$, $49.9(1 + 2k) / k$ and $0.5(1+ 2k)a_1^{\frac{1}{2}} /(K_1k)^{\frac{1}{2}}$. It can be readily seen that these reduce to the previously given values if $k = 1$. The net effect of reducing a_2 is that the third and first peaks should be little affected but the second should be increased independently of magnitudes of a_1 and a_2.

Figures 2-6, 2-7, and 2-8 show the results of applying equation (15) to the calculation of dlnh/dx, after finding b for a chosen value of h, for the presence of 5%, 1% and 0.1% carbonate in hydroxide. The growth with decrease of carbonate of the second peak at the expense of the third may be noted. For 5% carbonate, the second peak maximum occurs not at $x = 0.95$ but at $x = 0.9545$.

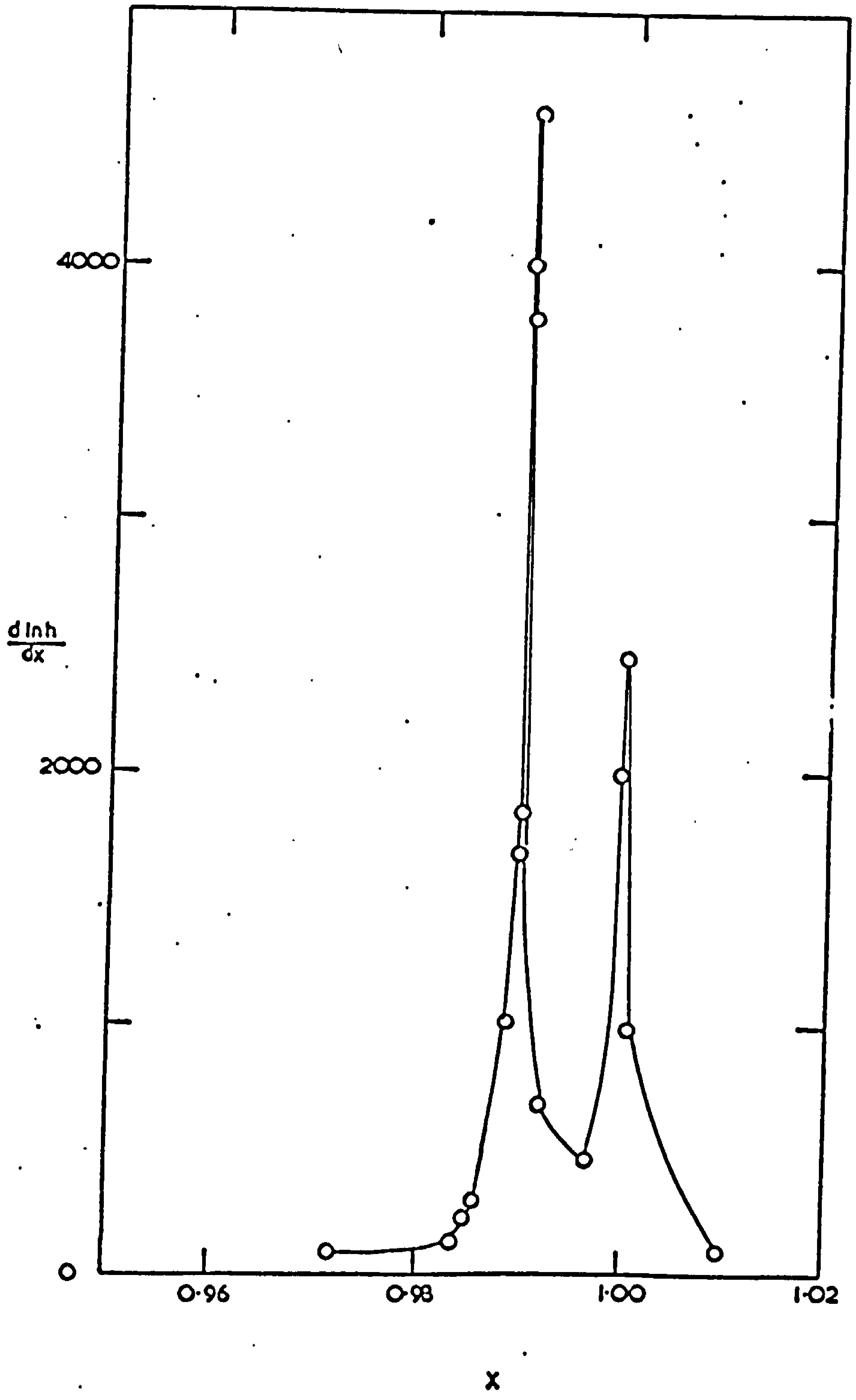
2.7.1. EFFECT OF SLOW KINETICS OF CARBON DIOXIDE HYDRATION ON THE FIRST DERIVATIVE POTENTIOMETRIC TITRATION CURVE OF CARBONATE SYSTEM:

It has to be noted that for simplicity, K_1, in the previous equations was regarded as an equilibrium constant of the following process:



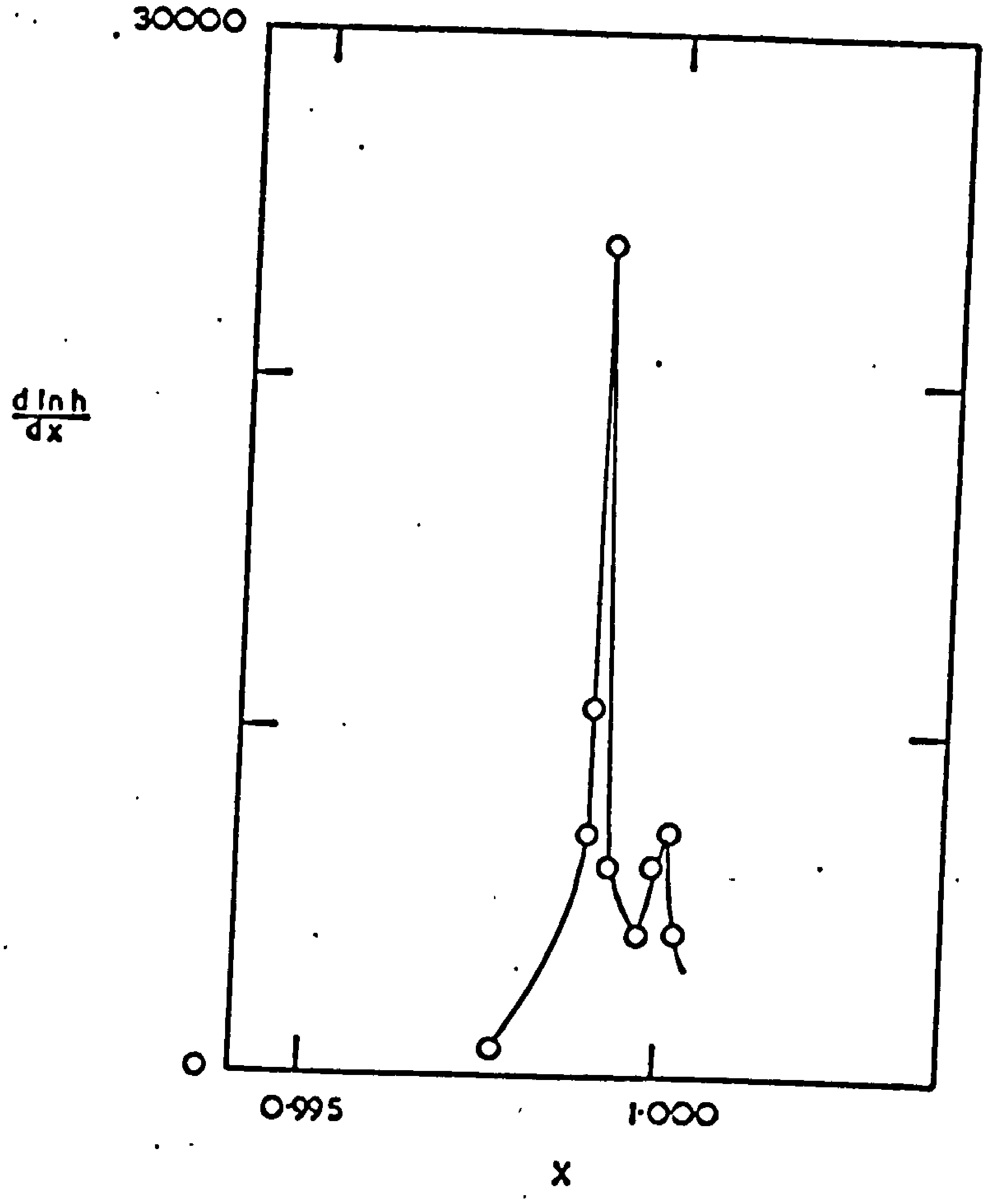
Theoretical differential curve for titration of NaOH (a_1) + Na_2CO_3 (a_2) with HCl where a_1= 0.1 mol l^{-1}, a_2= 0.005.

FIG 2-6



Theoretical differential curve for titration of NaOH (a_1) + Na_2CO_3 (a_2) with HCl where a_1= 0.1 mol l^{-1}, a_2= 0.001.

FIG 2-7



Theoretical differential curve for titration of NaOH (a_1) + Na_2CO_3 (a_2) with HCl where a_1= 0.1 mol l^{-1}, a_2= 0.0001.

FIG 2-8

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_a = 3\times10^{-4} \text{mol/l}$$

Magnitude of K_1 assumed was 4.5×10^{-7} mol/l. But, in fact, K_1 is an apparent equilibrium constant for the following process:

$$H_2CO_3 + CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \quad K_1 = (H^+)(HCO_3^-)/(H_2CO_3 + CO_2).$$

The true equilibrium constant of carbonic acid is $K_a = (H^+)(HCO_3^-)/(H_2CO_3)$. According to Koefoed (4), and Kern (5), carbonic acid is itself a much stronger acid than previously thought. Most of the carbonic acid remains as dissolved carbon dioxide (5) in aqueous solutions according to the following equation:

$$K_1 = K_a/(1 + K) = K_a/(1 + (1/K_h)) \qquad (16)$$

Therefore in the real case it is important to introduce the hydration and dehydration processes of carbon dioxide in aqueous solutions, as follows:

$$CO_2 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2CO_3 \qquad (17)$$

where $k_f = 0.03s^{-1}$ (5), and $k_r = 20s^{-1}$ (5) for which:

$$K = (CO_2)/(H_2CO_3) = k_r / k_f = 20/0.03 \approx 600 \qquad (18)$$

It follows also that the concentration of H_2CO_3 produced in the titration process is a function of time, as follows:

$$(d\,(H_2CO_3))/(dt) = k_f(CO_2) - k_r(H_2CO_3) \qquad (19)$$

Therefore computer simulation calculations, applying numerical methods, to solve the concentration of various species present as a function of time are necessary. This topic is discussed in chapter 6.

2.8.1. REFERENCES:

1) R.H. Stokes, Aust. J. Chem., 759, 16 , 1963.

2) R.E.Loewenthal and G.R. Marais, "Carbonate Chemistry of Aquatic Systems", Ann/Arbor, Michigan, pp 102-108, 1976.

3) W. Stumm and J.J. Morgan, "Aquatic Chemistry", Wiley, New York, chapter 4, 1970.

4) J. Koefoed and K. Engel, Acta Chem. Scand , 1319, 5 , 1961.

5) D.M. Kern, J. Chem. Educ.,14, 37 , 1960.

3.1.1. INTRODUCTION

As discussed in chapter two, in view of the importance of the titration of solution containing both hydroxide and carbonate, with a strong acid e.g. hydrochloric acid, to industrial and environmental studies, it is important to analyse the first derivative of the potentiometric curves.

The mathematical solution of these curves as shown in chapter two (1) gives three maxima. The first corresponds to the neutralization of most of the hydroxide ions; the second and third correspond to the conversion of carbonate ions to bicarbonate ions and bicarbonate ions to carbonic acid or carbon dioxide respectively. (CO_3^{2-} to HCO_3^- and HCO_3^- to $H_2CO_3(CO_2 + H_2O)$)

Assuming the concentration of sodium hydroxide and sodium carbonate are both a moles per litre, the height of the first maximum is proportional to $a^{\frac{1}{2}}$; the height of the second maximum, to a good approximation, should be independent of a; and the height of the third peak is proportional to $a^{\frac{1}{2}}$.

However, the experimental curves show an extra, unexpected peak between the first and second neutralization peaks of carbonate ions, which has not previously been found.

The experiments described below were carried out to study and remove this extra peak in the titration curve. The Mettler apparatus, consisting of DV10, DV12 and GA10 as described in chapter one, was used and the cylindrical glass cell with constant temperature jacket was used. This was also described in chapter one.

3.2.1. PLOTS OF dE/dV AGAINST $V_{HCl(0.25\ mol/l)}$ FOR SODIUM HYDROXIDE SOLUTION CONTAINING DIFFERENT CONCENTRATIONS OF SODIUM CARBONATE.

Different titrations with 0.25 mol/l hydrochloric acid were carried out for 25 ml of 0.04 mol/l sodium hydroxide solution containing different mole concentrations of sodium carbonate . To prepare the titration solutions of the required concentrations, volumetric sodium hydroxide solution (0.1 mol/l) free from carbonate was used (BDH Chemicals Ltd., Poole, England product no. 19150),manufactured from AnalaR reagents. This was diluted with distilled water free from carbon dioxide. 0.1 mol/l sodium carbonate stock solution was also prepared from anhydrous sodium carbonate (BDH,product no. 30121) and degassed distilled water. This was used for making the titration solutions. The same make of concentrated volumetric hydrochloric acid (product no. 18005) was used and diluted with distilled water.

It has to be noted that the distilled water used in titrations in all cases, and also for making the solutions, was boiled and degassed previously. This was to ensure that it would be free from dissolved carbon dioxide gas.

A Radiometer (Copenhagen, Denmark) Glass Electrode type(G202B) was used as a working electrode and a Radiometer saturated calomel electrode (type K401-QL-1) was used as a reference electrode.

As shown in figures(3-1, 3-2, 3-3) experiments were carried out for different mole percentages of sodium carbonate relative to the concentration of sodium hydroxide at 25°C.

When the mole concentration of sodium carbonate becomes equal to, or greater than 1% of the mole concentration of sodium hydroxide, it is possible to see a separate peak for carbonate ions in the titration curve. By decreasing the concentration of hydrochloric acid from 0.25 to 0.05 mol/l

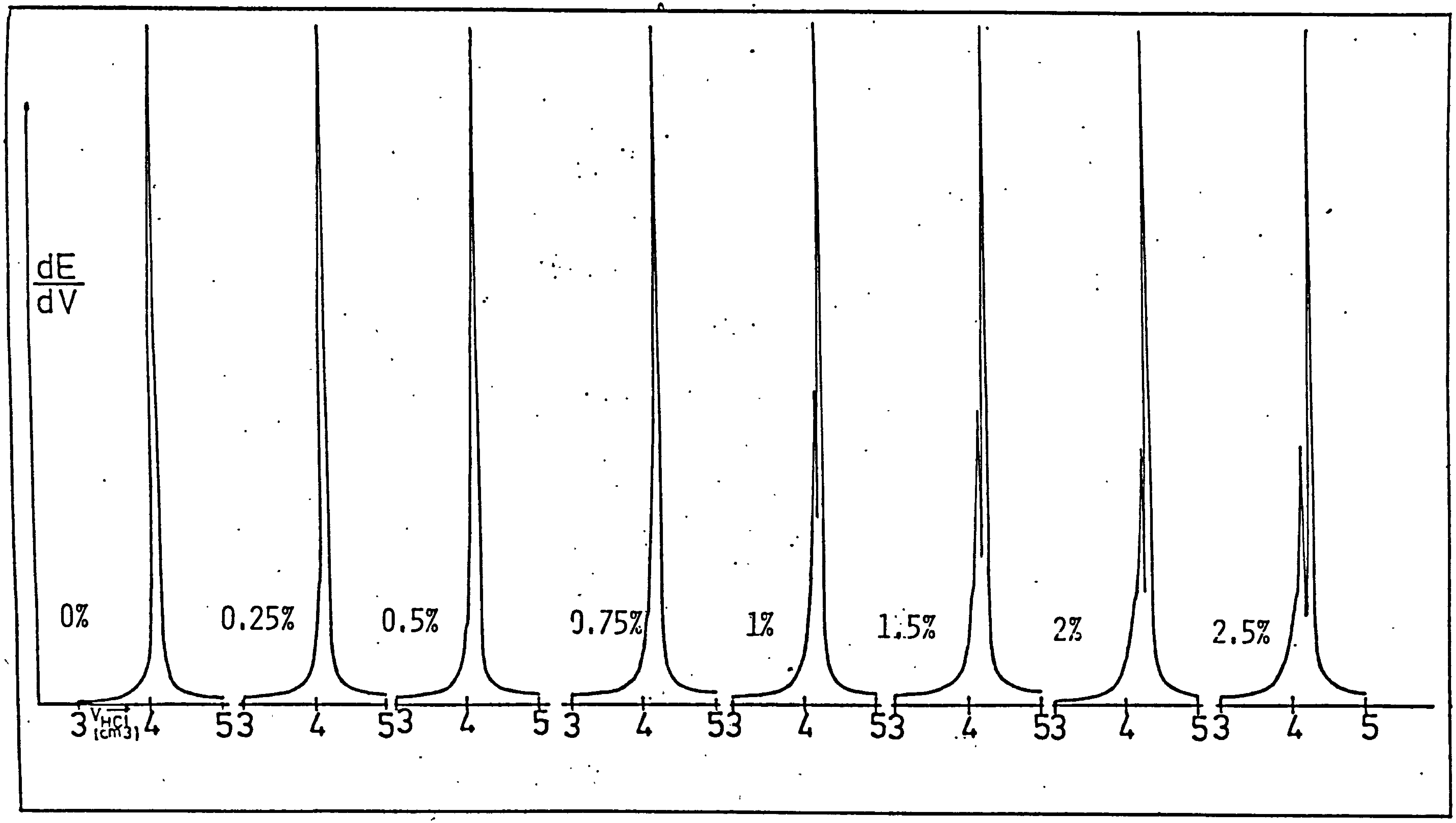
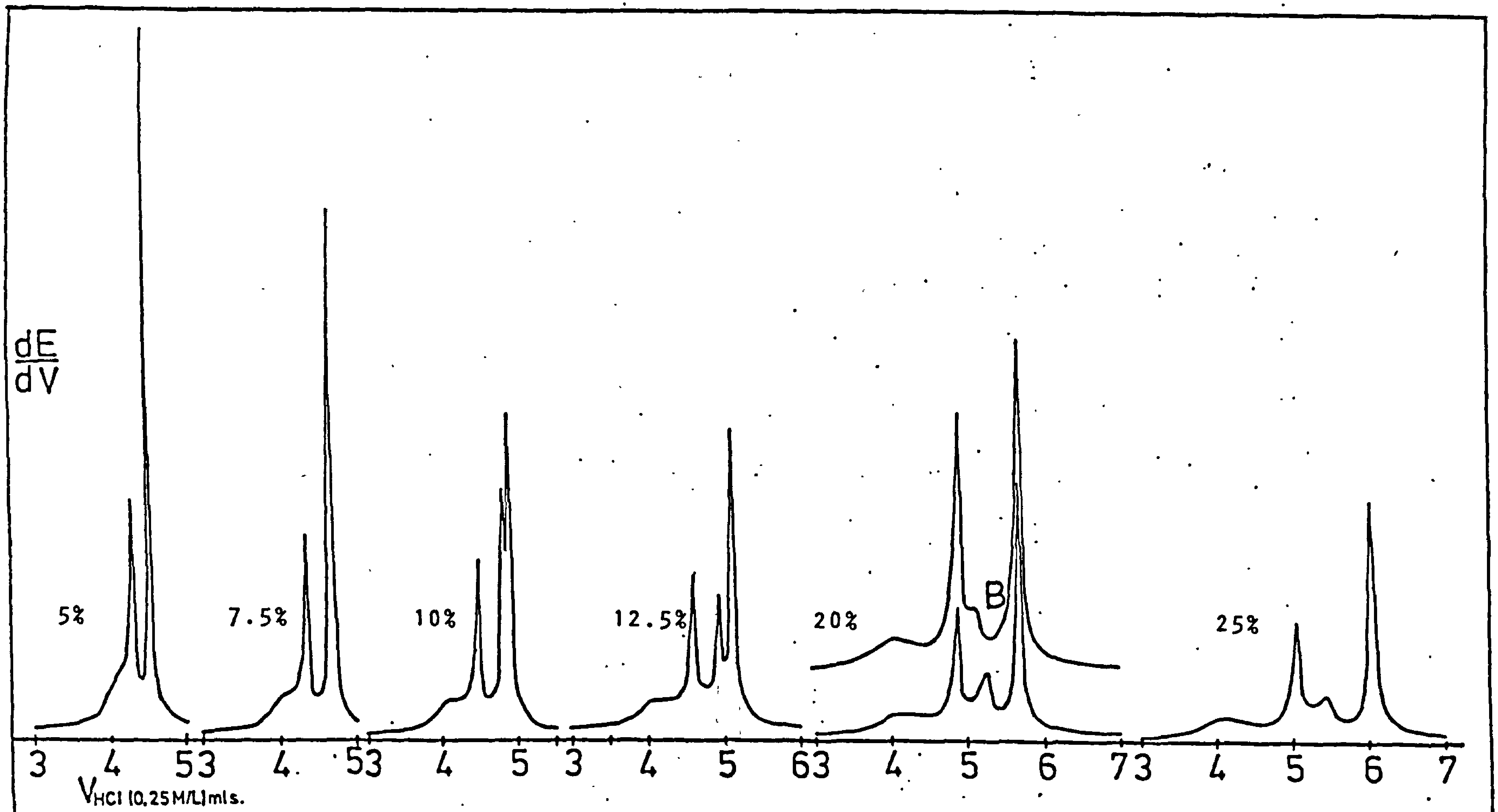

dE/dV
0%
0.25%
0.5%
0.75%
1%
1.5%
2%
2.5%
V_HCl (cm3)
3 4 5 3 4 5 3 4 5 3 4 5 3 4 5 3 4 5 3 4 5 3 4 5

FIG. 3-1



mole con. of Na_2CO_3 in NaOH solutions

In B(20% MOL CON.) Na ions were replaced by T.M.A=$(NH_3)_4N$ ions.

FIG. 3-2

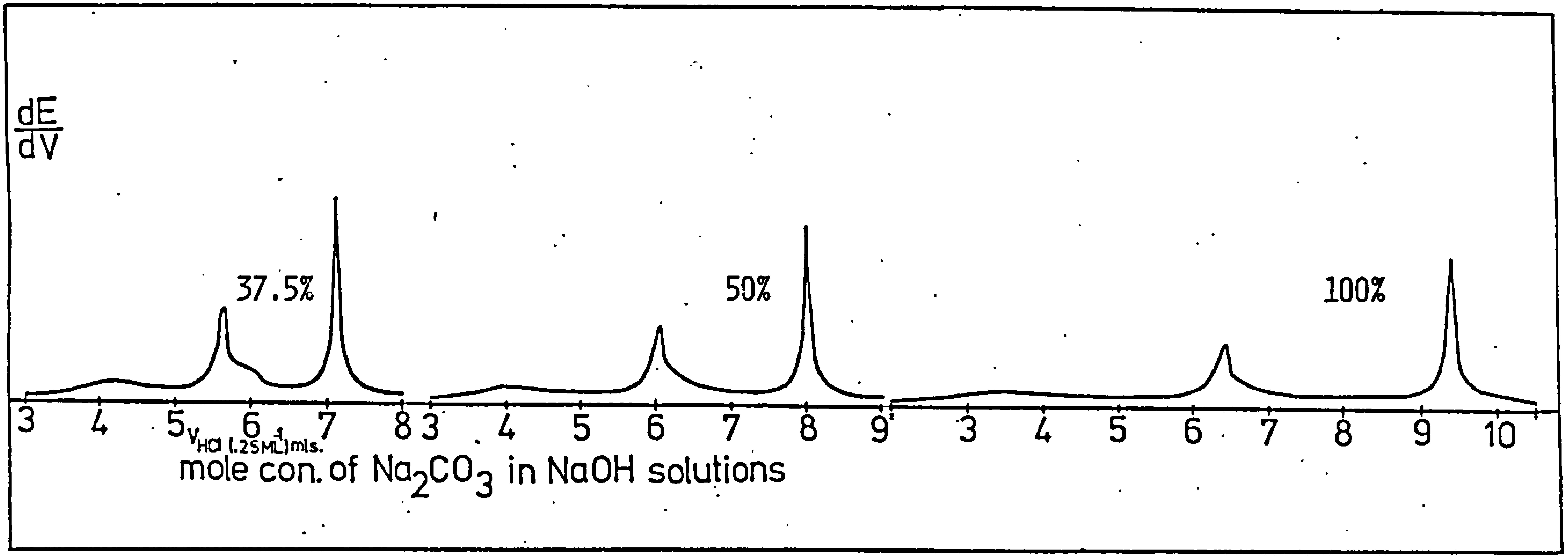

$\frac{dE}{dV}$
37.5%
50%
100%
3
4
5
6
7
8
3
4
5
6
7
8
9
3
4
5
6
7
8
9
10
$V_{HCl\ (.25ML^{-1})\ mls.}$
mole con. of Na_2CO_3 in NaOH solutions

FIG. 3-3

and increasing the chart speed it was possible to increase the limits of discrimination of carbonate from sodium hydroxide.

Computer or Gran plot analysis of the titration curves might enable this to be pushed lower.

3.3.1 TITRATION CURVES FOR HYDROCHLORIC ACID (0.05 MOL/L) AND THE FIRST DERIVATIVE CURVES FOR THE CARBON DIOXIDE ELECTRODE

As is shown in figures 3-4, and 3-5, different titrations with 0.05 mol/l hydrochloric acid were carried out for 25 ml of 0.04 mol/l of sodium hydroxide solution containing 0, 1.5, 2.5, 3.75, 5, 7.5, 10, 12.5, 15 and 20 mole percent of sodium carbonate. Both the Radiometer glass electrode type (G202B) and Radiometer carbon dioxide electrode type (PS-1-902-123) were used for obtaining the first derivative potentiometric curves. Before titration with 0.05 mol/l of hydrochloric acid, about 3.5 ml of 0.25 mol/l of hydrochloric acid were added to the titration solution. This was to bring the titration curves within the range of 10ml of titrant (the Mettler burette is 10ml capacity). This also speeds up the initial titration process which has no effect on titration curves. This is shown in (3-5-2). The rate of addition of 0.05 mol/l hydrochloric acid was 1ml in four minutes (the same as 3-2-1).

The comparison of titration curves for 3-2-1 and 3-3-1 shows clearly that the unexpected peak is more defined at about 12.5 percent. (See figure 3-2), but in the case of titration with 0.05 mol/l hydrochloric acid, it was possible to see the peak at 3.75 per cent. (See figure 3-4 below). Knowing that the rate of addition of moles of hydrochloric acid

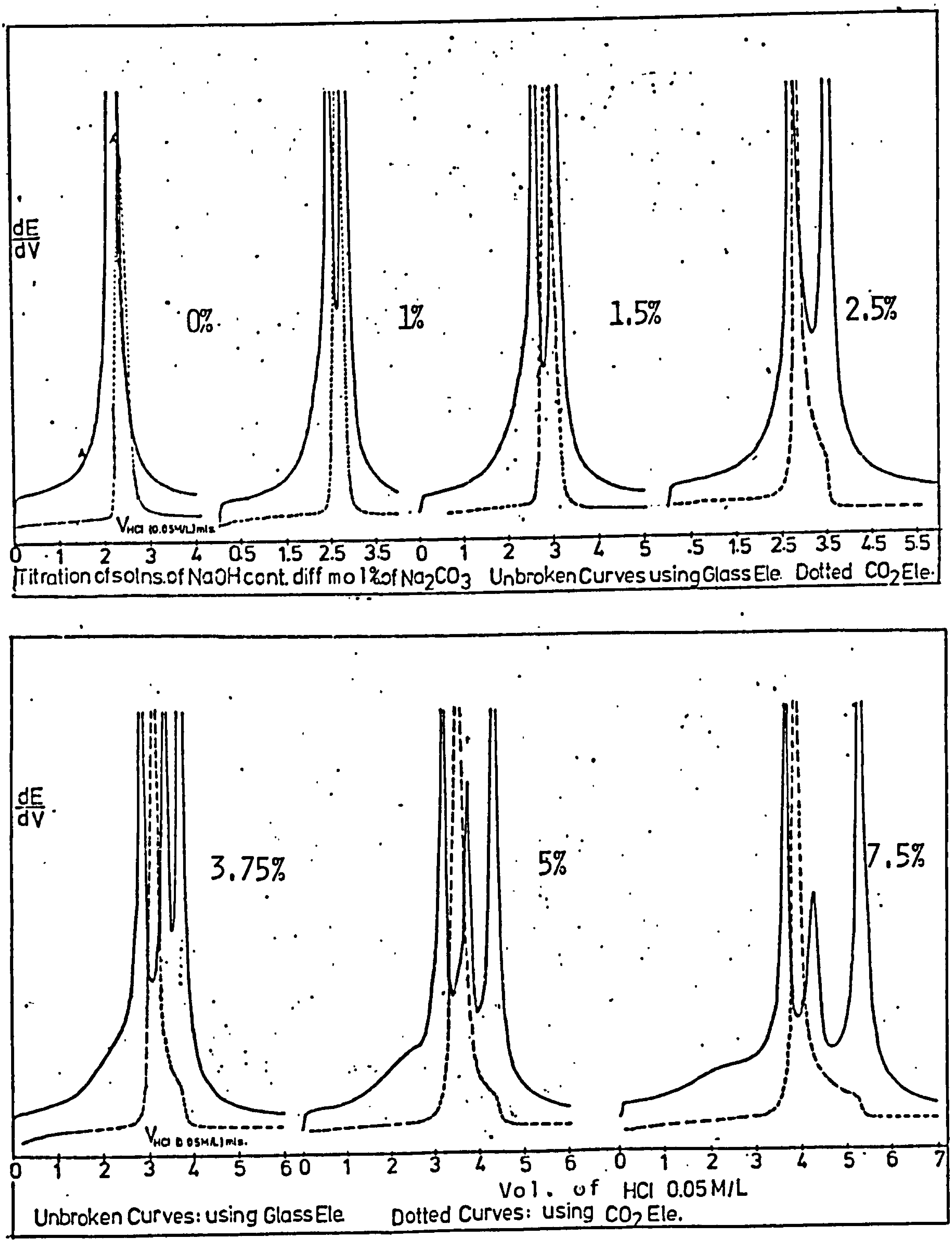

dE/dV
0%
1%
1.5%
2.5%
V_HCl (0.05M/L) mls.
0 1 2 3 4
0.5 1.5 2.5 3.5
0 1 2 3 4 5
.5 1.5 2.5 3.5 4.5 5.5
Titration of solns. of NaOH cont. diff mo l % of Na2CO3 Unbroken Curves using Glass Ele. Dotted CO2 Ele.
dE/dV
3.75%
5%
7.5%
V_HCl 0.05M/L) mls.
0 1 2 3 4 5 6
0 1 2 3 4 5 6
0 1 2 3 4 5 6 7
Vol. of HCl 0.05 M/L
Unbroken Curves: using Glass Ele
Dotted Curves: using CO2 Ele.

FIG. 3-4

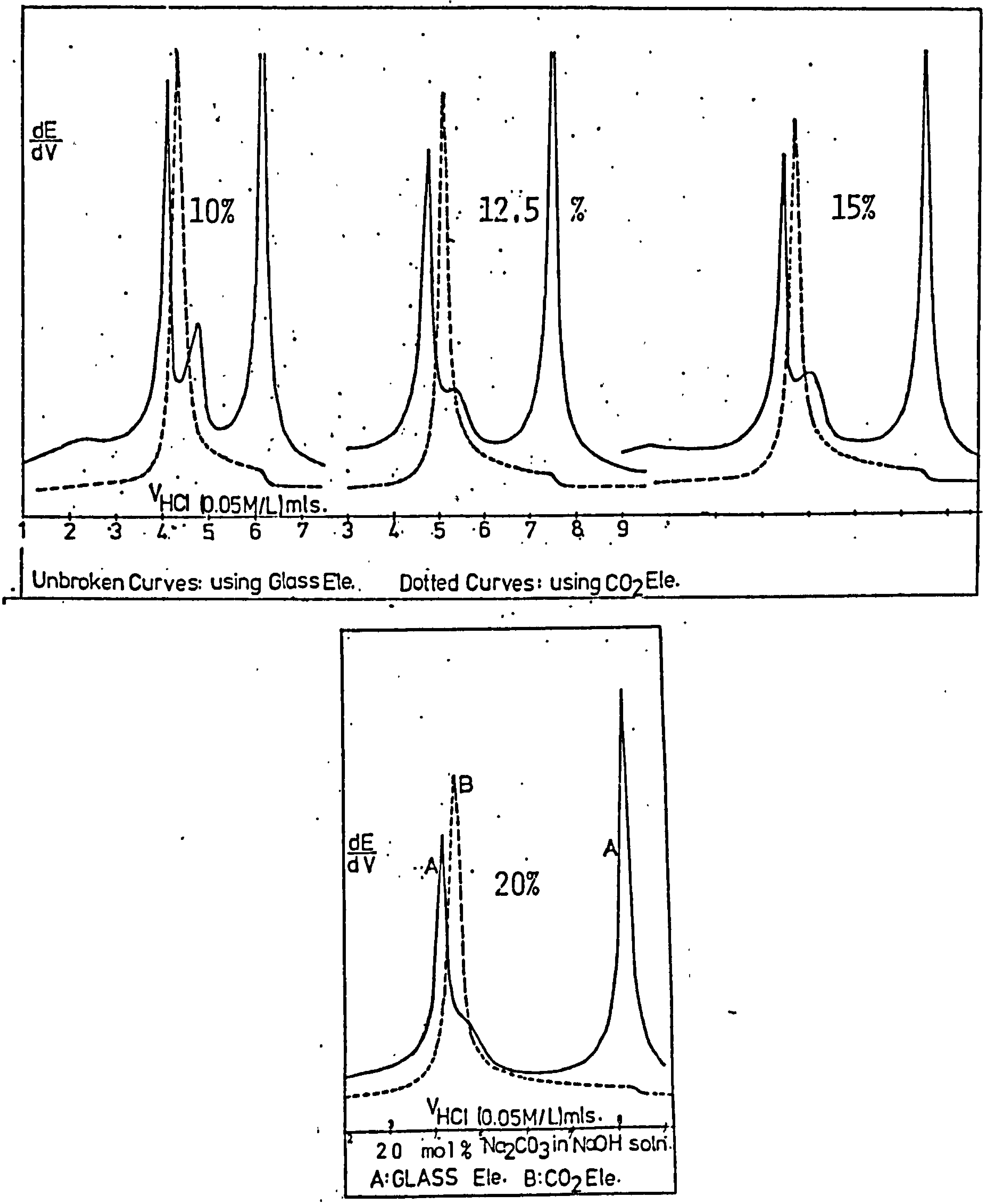

dE/dV
10%
12.5 %
15%
VHCl (0.05M/L)mls.
1 2 3 4 5 6 7 3 4 5 6 7 8 9
Unbroken Curves: using Glass Ele.
Dotted Curves: using CO2 Ele.
dE/dV
B
A
A
20%
VHCl (0.05M/L)mls.
20 mol % Na2CO3 in NaOH soln.
A: GLASS Ele. B: CO2 Ele.

FIG. 3–5

in 3-2-1 was five times faster than in 3-3-1; it can be concluded that in some way the kinetics of hydration of carbon dioxide is involved in the appearance of the extra peak.

Considering the first derivative curve of dE/dV against volume of hydrochloric acid (0.05 mol/l) for the carbon dioxide electrode, there is a peak and a shoulder. These correspond to the appearance of carbon dioxide in the solution and to the end of production of carbon dioxide in the titration process respectively. Hence, the peak should correspond to the first titration peak of the glass electrode for carbonate ions and the shoulder should correspond to the end of conversion of bicarbonate ions to carbon dioxide, but there is some delay in the appearance of the peak for the carbon dioxide electrode. This may either be due to the slow diffusion of carbon dioxide through the membrane, or to some other unknown factors. More experiments were carried out to study this problem.

3.4.1. TITRATION CURVES FOR SODIUM CARBONATE CONTAINING DIFFERENT CONCENTRATIONS OF SODIUM HYDROXIDE.

In this series of experiments, the concentration of sodium carbonate was kept constant and the concentration of sodium hydroxide was varied.

Different titrations with hydrochloric acid were carried out for 25ml of 0.008 mol/l of sodium carbonate containing different mole concentrations of sodium hydroxide. The concentration of sodium hydroxide was varied in such a way that it made it possible to obtain different percentage mole concentrations of sodium carbonate to sodium hydroxide as shown in figure 3-6. The rate of addition of

Titration Curves for Solns. of Const.[Na_2CO_3], (25ml 0.01M) Containing Varied [NaOH] at 25°C
Radiometer Glass Elec.

FIG. 3–6

hydrochloric acid was 1ml in 48s, and all titrations were carried out at 25°C.

As is clear from figure (3-6), by increasing the concentration of carbonate ions to hydroxide ions the height of the first peak of carbonate ions is increased; at the same time the height of the extra peak decreased. At about 125% the extra peak reduced to a shoulder on the first peak of carbonate. This suggests that the presence of hydroxide ions increases the speed of response of the glass electrode in the titrations. As is described by F.G.K. Baucke (3-4) and A. Wikby (5), the structure and thickness of the "gel layer" or "swollen layer" of glass electrode membranes depends on the pH values of the solution. The thickness of this layer is greater for smaller pH values of solution. As described by Baucke (1971), at pH=1, the thickness of the gel layer is 300Å (±20 per cent) and at pH=9 it is 150Å (±20 per cent). So, sweeping the pH from very high values to very acidic values, removes some of the hydration layer on the glass electrode and exposes a fresh surface. This could be the reason for a better definition of the extra peak, when sodium hydroxide is added to the titration solutions.

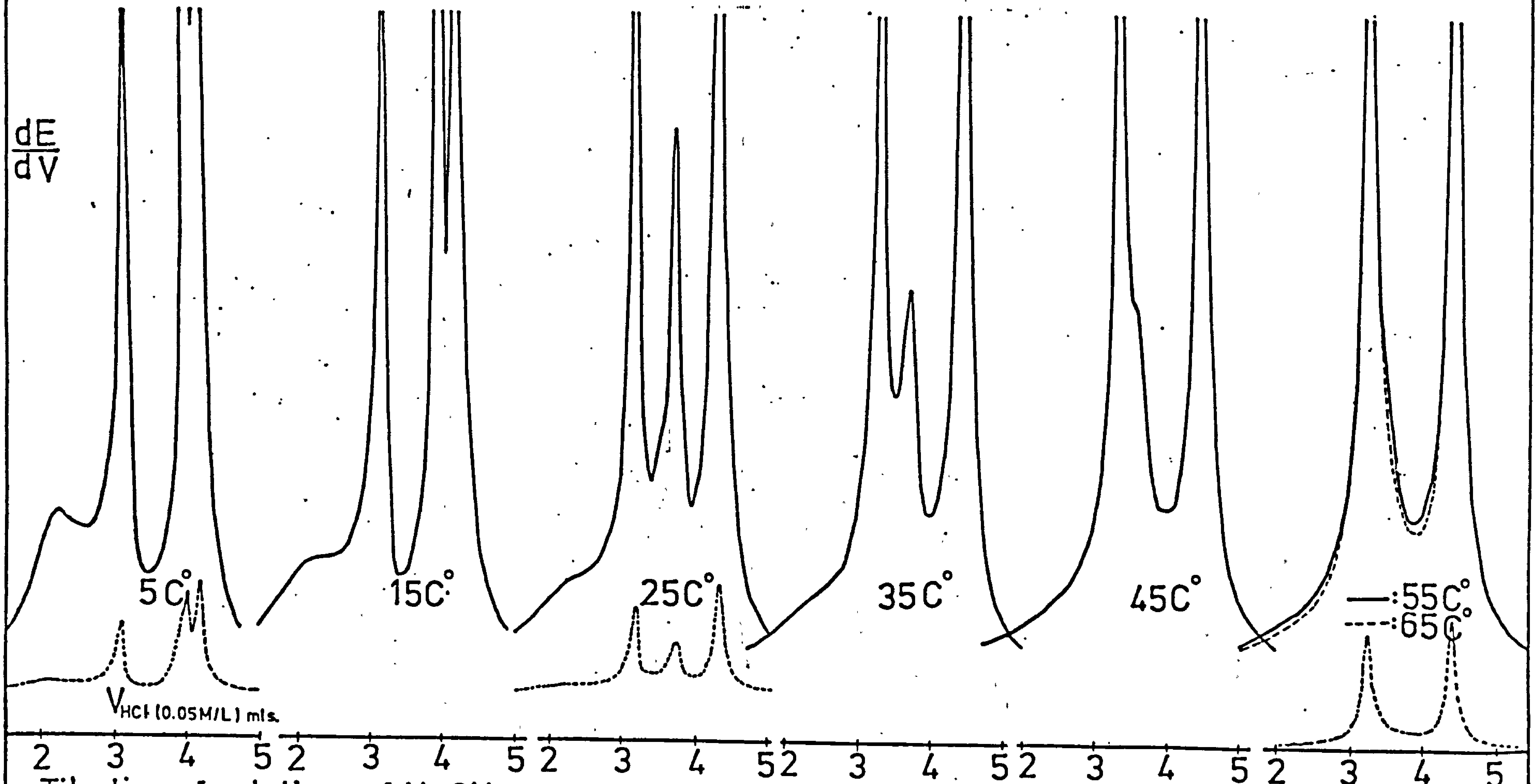
3.5. EXPERIMENTS FOR FURTHER INVESTIGATION OF THE UNEXPECTED EXTRA PEAK

To study the characteristics and to identify the origin of the extra peak, several experiments were carried out as described in the following.

3.5.1. EFFECT OF TEMPERATURE

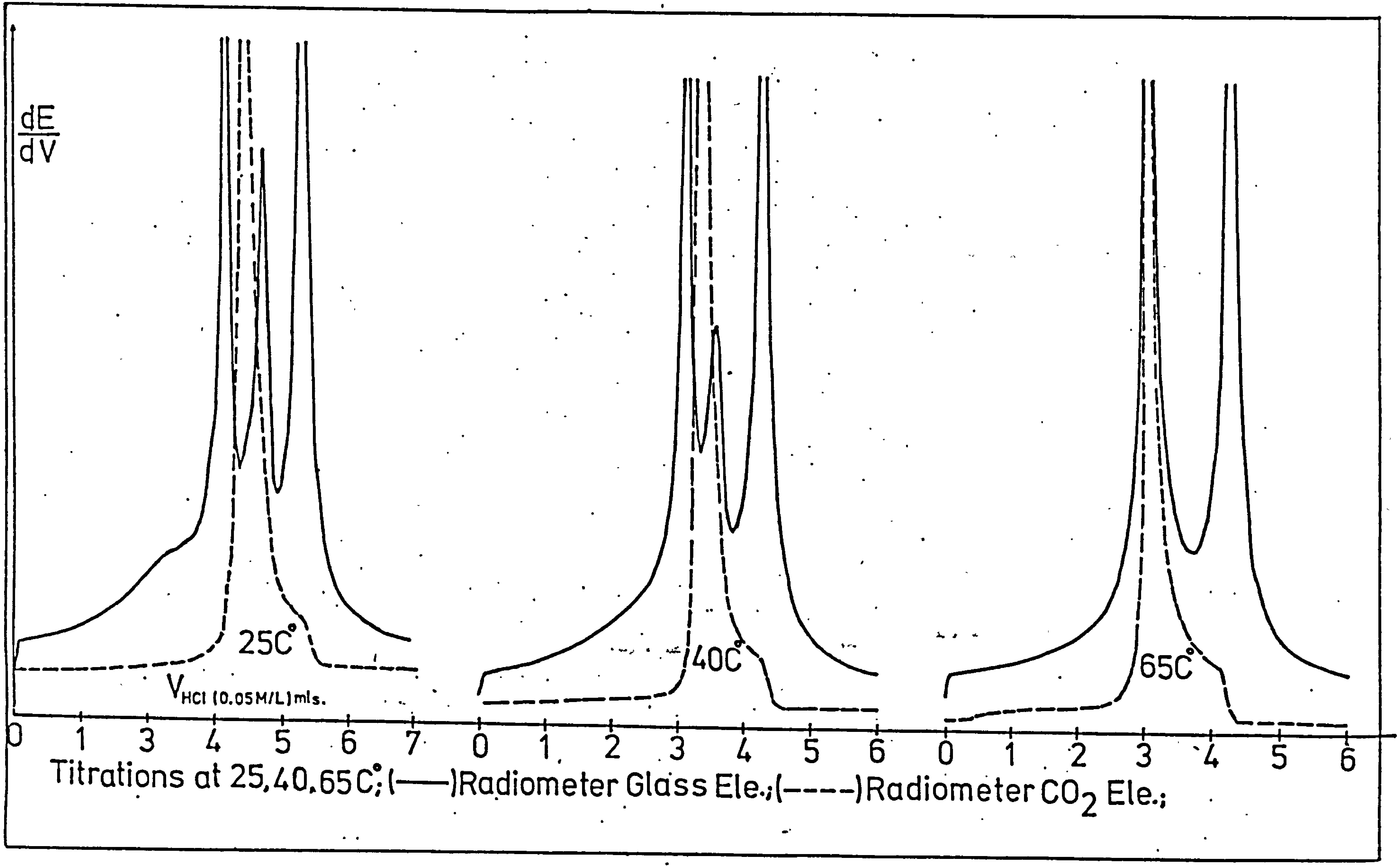
A series of experiments was carried out at different temperatures as shown in figure 3-7, When the temperature was raised above the normal titration temperature (25°C), the extra peak moved nearer to the first sodium carbonate neutralization peak. It was hardly visible between 40°C and 50°C and nearly absent above 50°C. This can be explained by the lack of solubility of carbon dioxide at high temperatures, and also the effect of high temperatures on slow kinetics which is involved in the neutralization process of bicarbonate. When the temperature was decreased below 25°C the unexpected peak moved towards the second sodium carbonate neutralization peak. This reflects the high solubility of carbon dioxide at lower temperatures and the slower kinetic reactions involved at lower temperatures which possibly results in complex formation in the solution and the appearance of a clear extra peak.

Corresponding titrations were carried out using a Radiometer carbon dioxide electrode Type (PS-1-904-123) at 25°C. This showed that the carbon dioxide electrode peak lies between the unexpected extra peak and the first peak of sodium carbonate (for glass electrode); shown in figure 3-8. However, as the temperature is increased the carbon dioxide peak moves towards the first neutralization peak of carbonate ions. Above 50°C the extra peak disappears and the peak for the carbon dioxide electrode occupies the same position as the first carbonate ions' neutralization peak for the glass electrode. This is partly because of an increase of rate of diffusion of carbon dioxide through the membrane of the carbon dioxide electrode at high temperature. This peak(carbon dioxide electrode peak) becomes less sharp with decreasing temperature.



Titration of solutions of NaOH containing 5 MOLE % of Na_2CO_3 with HCL(0.05M/L) at different temperatures: 5, 15, 25, 45, 55, 65C.

FIG 3–7



Titrations at 25,40,65C°; (——) Radiometer Glass Ele.; (-----) Radiometer CO_2 Ele.;

FIG 3-8

3.5.2. EFFECT OF RATE OF ADDITION OF HYDROCHLORIC ACID

Because of the kinetics involved in the titration processes, the rate of addition of titrant occupies a very important role in the investigation of the extra peak. A number of experiments were carried out, as described below to investigate this.

i) Titration of 25ml of 0.04 mol/l sodium hydroxide solution containing sodium carbonate with 5% mole concentration, using a Radiometer glass electrode Type (G202B) at 25°C. In the first titration, the rate of addition of 0.05 mol/l hydrochloric acid was 1ml in four minutes and in the second one the rate of addition was 1ml in 48s.

It is clear in figure (3-9) that the extra peak is shifted towards the second neutralization peak of carbonate ions as the rate of addition of hydrochloric acid is increased.

ii) The same type of experiment was carried out for 25ml of 0.04 mol/l sodium hydroxide solution containing 15% more concentration of sodium carbonate under the same conditions as above. Except that the rates of addition of hydrochloric acid were altered to 1ml in 37.5s and 1ml in 141s, and the concentration of hydrochloric acid was changed from 0.05 mol/l to 0.25 mol/l. The effect of increasing the rate of addition of hydrochloric acid was the same as in the previous experiments (see figure 3-10).

iii) To clarify the effect of the addition rate of hydrochloric acid on the titration curve, and the position of the peaks, and to find out what was the most sensitive region of the titration curves to the rate of addition of hydrochloric acid, another set of experiments consisting of four titrations was carried out. The results are shown

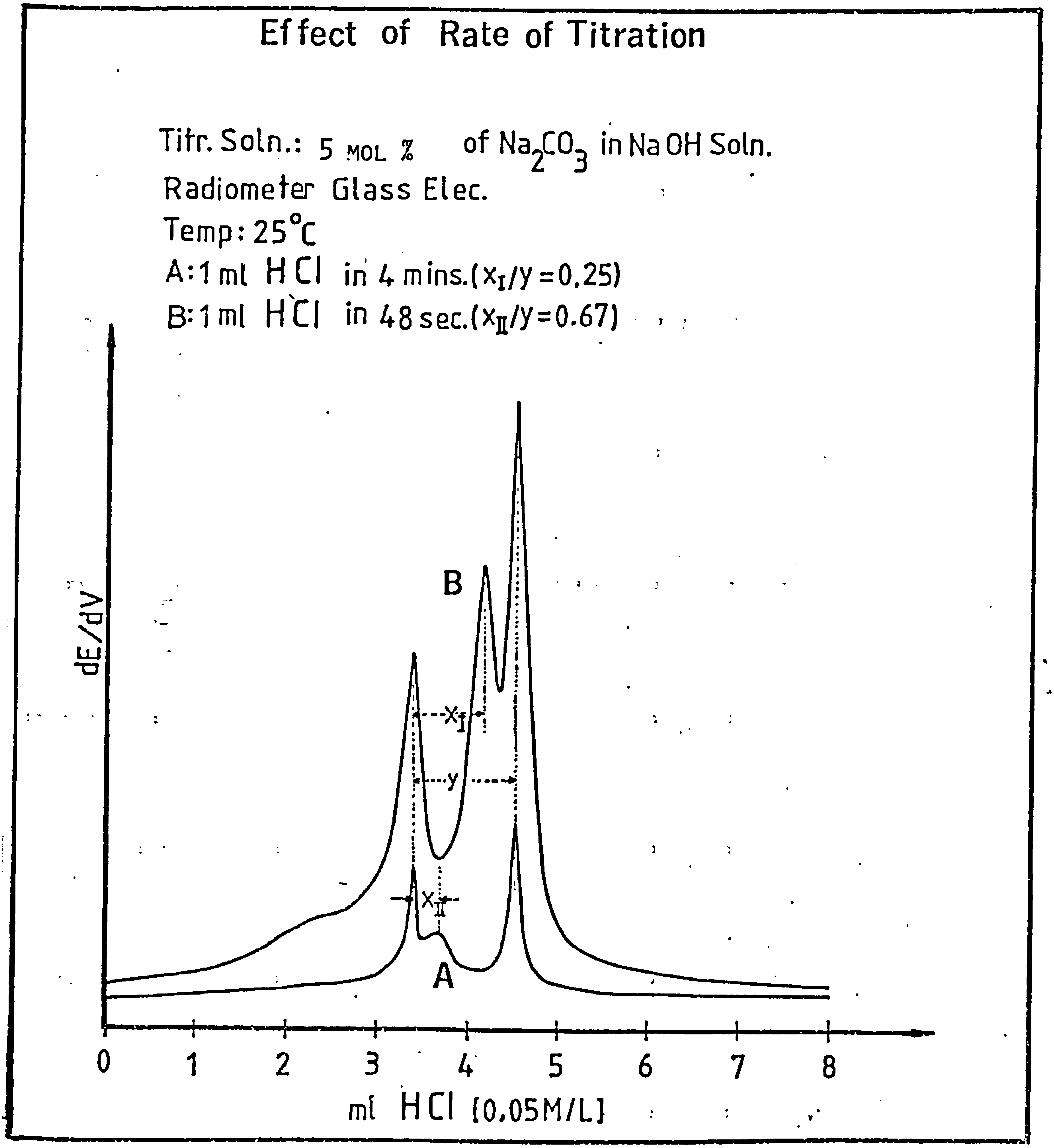

Effect of Rate of Titration
Titr. Soln.: 5 MOL % of Na_2CO_3 in NaOH Soln.
Radiometer Glass Elec.
Temp: 25°C
A: 1 ml HCl in 4 mins. ($x_I/y = 0.25$)
B: 1 ml HCl in 48 sec. ($x_{II}/y = 0.67$)
dE/dV
B
A
x_I
y
x_{II}
0
1
2
3
4
5
6
7
8
ml HCl [0.05M/L]

FIG 3-9

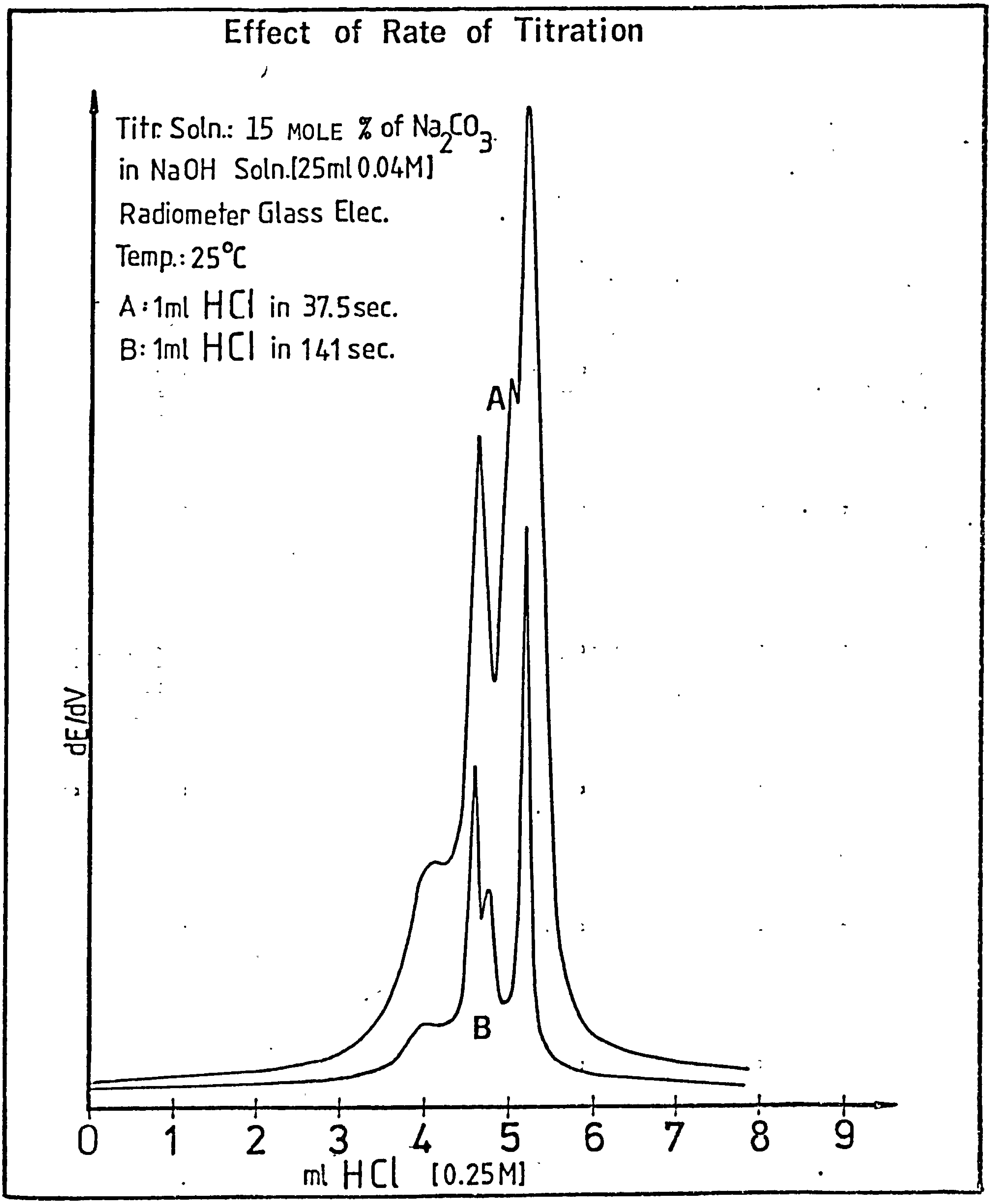

Effect of Rate of Titration
Titr. Soln.: 15 MOLE % of Na_2CO_3
in NaOH Soln.[25ml 0.04M]
Radiometer Glass Elec.
Temp.: 25°C
A: 1ml HCl in 37.5sec.
B: 1ml HCl in 141 sec.
A
B
dE/dV
0
1
2
3
4
5
6
7
8
9
ml HCl [0.25M]

FIG. 3–10

in figure 3-11 and described below. It must be noted that the only region which is involved in a slow reaction in the titration curves is between the first and the second neutralization peak of sodium carbonate.

In all cases the titration solutions were again 25ml of 0.04 mol/l of sodium hydroxide containing 5% mole concentration of sodium carbonate, and titrations were carried out at 25°C using a Radiometer glass electrode Type (G202B) and the same make of saturated calomel electrode as a reference electrode.

a) The rate of addition of hydrochloric acid was 1ml in four minutes, over the whole range of the titration process.

b) The first 3.5ml of hydrochloric acid was added at a faster rate of 1ml in forty eight seconds; (five times faster than a) and then continued at the slower rate of 1ml in four minutes. Knowing that most of the sodium hydroxide was titrated at the faster rate, by comparing the titration curves for (a) and (b), it is clear that the rate of addition of hydrochloric acid has no effect on the position of both the hydroxide peak and also the other peaks.

c) In this case the first 4.1ml of hydrochloric acid was added at the faster rate of 1ml in forty eight seconds and then continued at the slower rate of 1ml in four minutes. According to the figure 3-11 in this case the neutralization of most of the carbonate ions to bicarbonate ions was carried out at the faster rate, but there was no effect on the position of the peaks. This gives a strong indication that the rate of addition of acid has no effect of the position of the first peak of carbonate ions in the neutralization course.

d) In the fourth experiment of this set, the whole range of titration was carried out at the faster rate of addition (1ml in

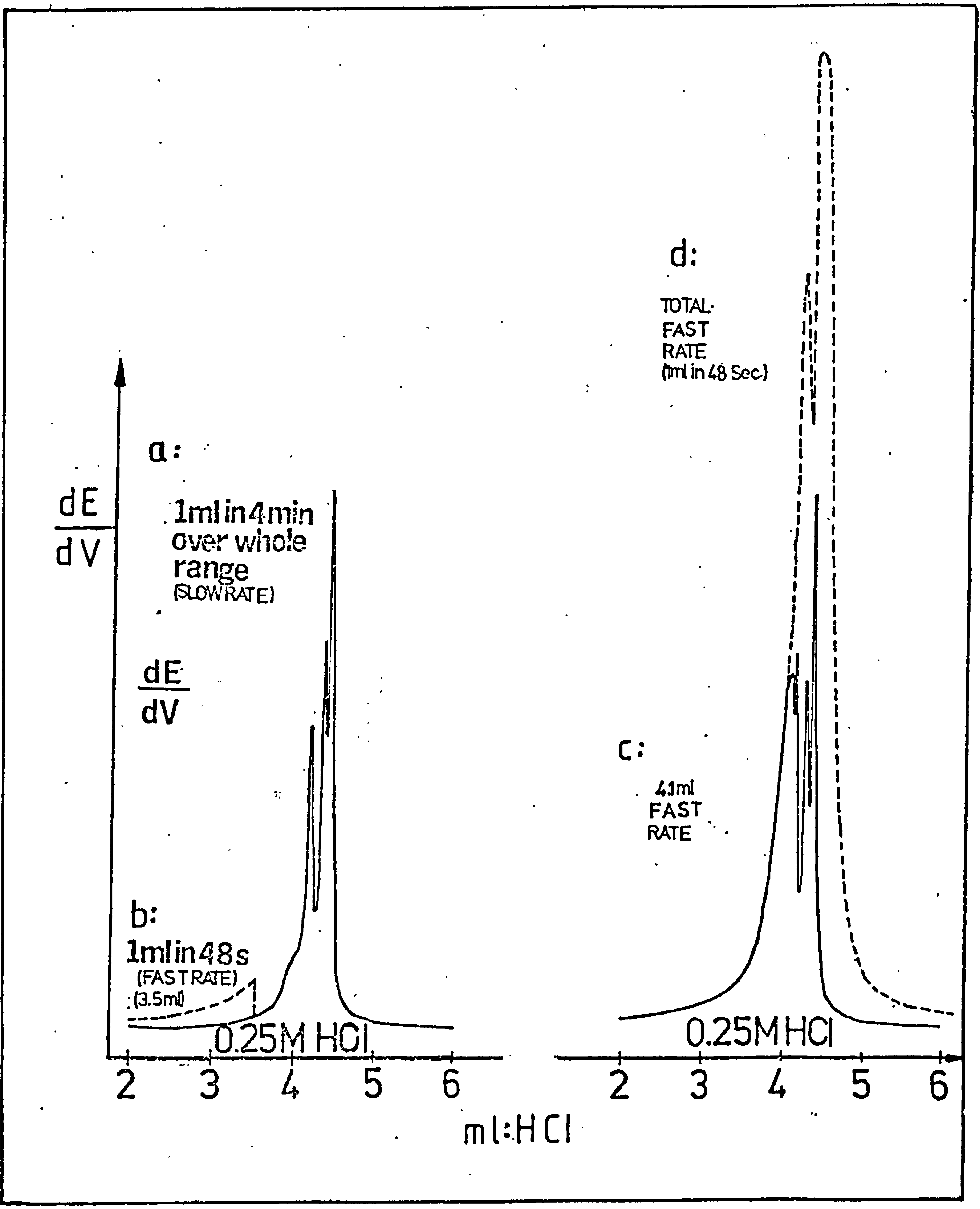

dE
dV
a:
1ml in 4min over whole range (SLOW RATE)
dE
dV
b:
1ml in 48s (FAST RATE)
(3.5ml)
0.25M HCl
2
3
4
5
6
d:
TOTAL FAST RATE (1ml in 48 Sec.)
c:
4.1ml FAST RATE
0.25M HCl
2
3
4
5
6
ml:HCl

FIG 3—11

forty eight seconds). As is clear from comparing these four titration curves for (d), the extra peak was not resolved and it moved towards the second peak of carbonate ion neutralization. This was the only peak whose position was affected by the rate of addition of moles of acid. The rate of addition has an important effect only between the first and second neutralization peaks of carbonate ions, where slow kinetics are involved.

The extra peak is not affected by changes of rates at other stages of the titration process. The position of the other peaks, remain constant in all cases. From these experiments it can be concluded that a slow reaction is involved in producing the extra peak and that hydroxide ions do not take part in that process. As was mentioned in 3.4, hydroxide ions, however, increase the speed of response of the glass electrodes only.

3.5.3 THE EFFECT OF STIRRING ON THE EXTRA PEAK

For further study of the extra peak the effect of stirring the solution during the course of the titration was investigated. Once again titrations were carried out for solutions of 25ml of 0.04 mol/l of sodium hydroxide solution containing 5%.mole concentration of sodium carbonate. One experiment was carried out with fast stirring of the solution, and in the second one stirring was slower.

With fast stirring, the extra peak moved towards the first peak of carbonate ions, and the other peak remained unaffected (see figure 3-12). Fast stirring of the solution reduces the concentration of dissolved CO_2

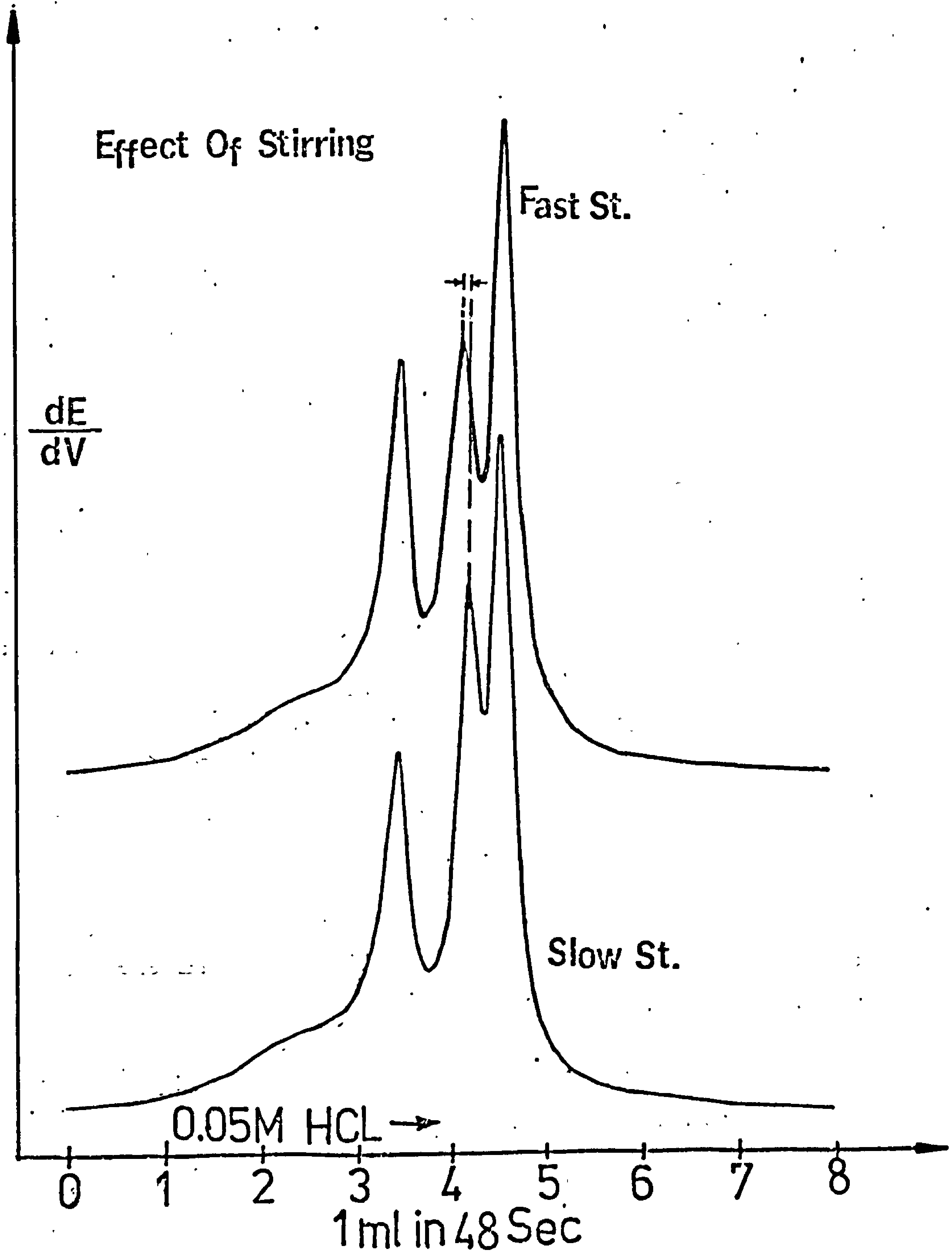

Effect Of Stirring
Fast St.
Slow St.
dE/dV
0.05M HCL →
0
1
2
3
4
5
6
7
8
1 ml in 48 Sec

FIG 3–12

gas in the titration solution and at the same time it changes the position of the extra peak. Hence there must be a relation between these two which will be discussed later.

In this experiment the rate of addition of hydrochloric acid was 1ml in forty eight seconds with a concentration of 0.05 mol/l.

3.5.4. THE EFFECT OF DIFFERENT GLASS ELECTRODES AND SURFACE STUDY

A comparison of different glass electrodes with particular emphasis on properties of the glass electrode surface plays an important part in demonstrating that the extra peak is a property of the solution and not of the glass electrode. The following glass electrodes were used:

i) Radiometer glass electrode (G202) consisting of two glass types (B) and (C). (Radiometer A/S, Copenhagen, Denmark).

ii) Beckman electrode single glass electrode.

iii) EIL combination glass electrode with silver/silver chloride external reference elecrode with ceramic contact (type 33).

iv) Ingold glass electrode type 10-402-3022, Swiss made.

v) Jena combination glass electrode type No. 65 (Jena Glasswerk, Schott & Gen., Mainz, West Germany).

All the experiments and treatments were carried out as described below:

A) Radiometer, Copenhagen glass electrode. These are standard types of Radiometer glass electrodes which were used with a K401 saturated calomel electrode for titrations. The type B electrode is useful in the pH range 0-14 without correction, whereas type C requires a correction for Na^+ error above pH 12, when accurate measurements are required. Type C electrodes may be used in the temperature range from 0° to 60°C, while type B gives a "low" response below 20°C (according to the manufacturers).

i) Type G202B-KS-2

Several titrations were carried out using this electrode, and different studies were made on its surface, but in all cases at 25°C the extra peak was present. The following solutions were used throughout:

Cell solution; 10ml 0.1mol/l of sodium hydroxide
5ml 0.01mol/l of sodium carbonate
3.5ml 0.25mol/l of hydrochloric acid
0.5ml of distilled water

Titrant; 0.025 mol/l of hydrochloric acid.

(a) The effect of 0.1mol/l of HCl on the surface of the electrode; the electrode was soaked for eighteen hours in 0.1mol/l hydrochloric acid before use. For all titrations the extra peak was again present.

(b) The effect of distilled water at high temperature (60°C); the electrode was left in distilled water at 60°C for fifteen minutes before use, but the extra peak was present. The experiment was repeated after soaking the electrode firstly in distilled water at 60°C for three hours and secondly in hydrochloric acid (0.1mol/l, 110hours, 25°C) but the extra peak was again present for all titrations. As shown by F.G.K.Baucke(4) on increasing the temperature, the development of a new steady state corresponds to layer formation on the surface of the glass electrode. On lowering the temperature the thick layer present at high temperature, dissolves to reach a new steady state. Hence this process of soaking the glass electrode in distilled water at high temperature results in the loss of some of the surface of the glass electrode and reveals a new surface. However, the extra peak was still present for all titrations.

(c) The effect of soaking the glass electrode in nitrogen gas saturated with distilled water;
after 12 hours the titration revealed the presence of the extra peak.

(d) The effect of soaking the electrode in 0.1mol/l of sodium bicarbonate;

after both 14 hours and 20 hours soaking of the bulb of the glass electrode, the titration results were as follows; the height of the extra peak had diminished slightly, and it had also moved towards the first peak of carbonate.

ii) Type G202B-TN-1 Radiometer glass electrode.

This was a new electrode being used for the first time. It was previously conditioned as specified by the manufacturers. The electrode was left for 10 hours in hydrochloric acid (0.1mol/l at 25°C) and then soaked for several hours in buffer solution at pH4.

(a) For the first titration the extra peak was a little closer to the first sodium carbonate neutralization peak, but in a second titration, the position of the extra peak was the same as in the case of G202B-KS-2 (see figure 3-13). This can be explained by the development of a gel layer on the glass electrode helped by the presence of carbon dioxide. This was shown by H Bach and F G K Baucke 1976 (6) for moistened glass electrodes in the gas phase in the following reaction, which is likely to occur in solution as well.

$$2 \equiv \mathrm{SiOLi}(\text{glass}) + \mathrm{H_2O}\ (\text{surface}) + \mathrm{CO_2}(\text{surface}) \rightleftharpoons 2 \equiv \mathrm{SiOH}(\text{glass}) + \mathrm{Li_2CO_3}(\text{surface})$$

So the growth rate of the layer is faster in the presence of carbon dioxide. This gives a better response from the glass electrode.

(b) The electrode was soaked at pH4 at 25°C for 14 days before the titration. The only effect was that the extra peak moved a little towards the second sodium carbonate neutralization peak and became slightly sharper.

(c) Etching of the glass electrode was carried out for 2 minutes at 25°C with 5% hydrofluoric acid as described by Wikby (5) and followed by 2 days soaking of the glass electrode in distilled water at 25°C prior to the titration. Again the result was the same as before. On etching the hydrated glass electrode with hydrofluoric acid, the gel layer takes part in the following reaction (7):

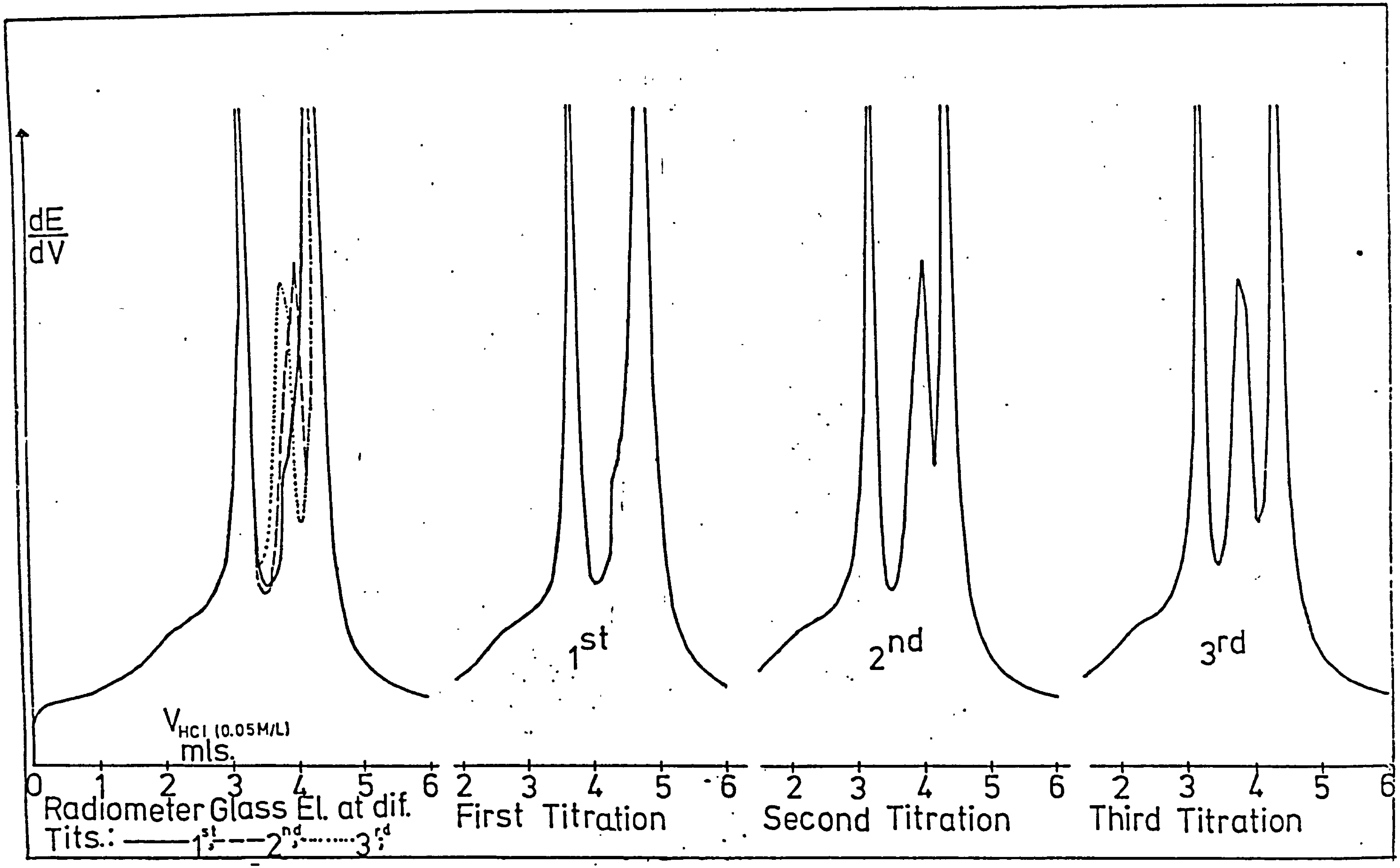
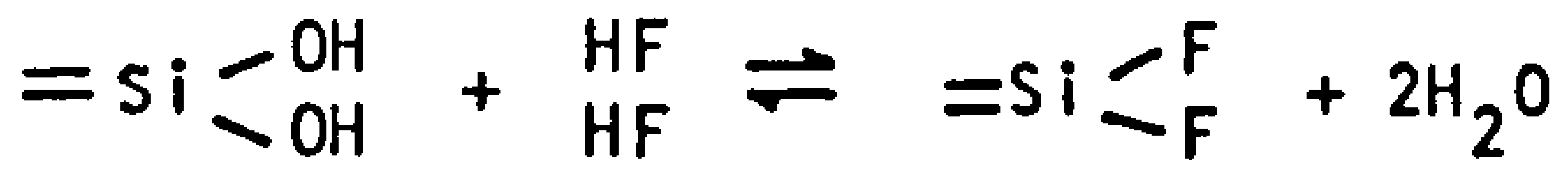

dE/dV
$V_{HCl\ (0.05M/L)}$ mls.
0
1
2
3
4
5
6
Radiometer Glass El. at dif. Tits.: —— 1st; – – – 2nd; ········ 3rd;
1st
First Titration
2nd
Second Titration
3rd
Third Titration

FIG 3–13



$$=Si\begin{smallmatrix}OH\\OH\end{smallmatrix} + \begin{smallmatrix}HF\\HF\end{smallmatrix} \rightleftharpoons =Si\begin{smallmatrix}F\\F\end{smallmatrix} + 2H_2O$$

The release of silicon from the surface of the structure occurs through the reaction between SiF_2 and bifluoride giving SiF_4. SiF_4 reacts further with hydrofluoric acid and the final etching product is hexafluorosilicate:

$$SiF_4 + 2HF \rightleftharpoons H_2(SiF_6)$$

So, by the etching process, the gel layer was eliminated. By soaking the electrode in distilled water or a buffer solution at about pH 4 and considering the interaction between aqueous solution and the glass electrode again, two reactions occur.

The hydration process involves ion exchange between univalent alkali ions in the glass and hydrogen ions in the solution. The exchange rate decreases by the square root of time (7,8). After several days, the reaction proceeds linearly with time. Parallel with the ion exchange, a rupture of silicon - oxygen bonds occurs by the reaction with water according to:

$$\equiv Si-O-Si\equiv + H_2O \rightleftharpoons 2\equiv Si-OH$$

but this is a slow process at room temperature. Thus, the surface structure is broken, leaving a loose hydrolysed network. This structured transformation, together with the ion exchange, results in an outer layer of glass surface which is, in fact, a new gel layer. Because of the existence of the extra peak after the etching process of the glass electrode, it can be concluded that the extra peak is not a property of the glass electrode.

iii) G202C KS-1

The same titrations were carried out with this electrode. The extra peak was present for all titrations. For the first titration the extra peak was nearer to the second peak of neutralization of carbonate ions, but for the second titration the position of the extra peak was the same as in the case of the G202B type. This electrode was also soaked in 0.1 mol/l hydrochloric acid for 18 hours before using it in a titration, but there was no effect on any of the peaks. Soaking the electrode in the buffer solution at pH 4 also had no effect on any of the peaks.

iv) G202C UY-1

This was again a new unused glass electrode, conditioned as specified by the manufacturers. The results for the first and second titrations were the same as type B. A third titration was carried out, after soaking the electrode for 14 days in buffer solution at pH 4. Again the result was as previously found.

Since soaking the glass electrode in buffer solutions (pH 4 or 7) gives a very stable structure to the surface and for many electrodes this stage is reached after 70 hours, as shown by Wikby in 1971 (7), this is further proof that the extra peak is not due to the glass electrode or its surface.

B) Beckman Glass Electrode:

The same experiments were carried out, but the Radiometer glass electrode was replaced by a Beckman single glass electrode. All the results were the same as previously found.

C) E.I.L. (Electronic Instruments Limited, Chertsey, Surrey) Combination (Ag/AgCl as a reference) Glass Electrode:

The same type of experiments were carried out but the results were the same as previously found and the extra peak was recorded.

D) Ingold Glass Electrode:

The results of the same experiments which were carried out using this type of electrode, as described below, were the same as for the previous glass electrodes. In the first titration the height of the extra peak was low, but in the second titration, the position of the extra peak in relation to the others and its height were the same as for the other glass electrodes.

The bulb of the electrode was soaked in 0.1 mol/l hydrochloric acid for 14 hours, but this had no noticeable effect on the extra peak. Again the electrode was left in buffer solution of pH 4 for 13 days before the titration, the only effects was that the extra peak moved slightly towards the second neutralization peak of sodium carbonate; it also became a little sharper than before.

The following three etching treatments of the Ingold electrode were also carried out:

1) the bulb of the electrode was soaked in 5% HF for two minutes and then stored for 60 hours in distilled water before use in the titration.

2) 5 minutes in 5% HF and 2 hours in distilled water.

3) 13 minutes in 10% HF and 5 minutes in the solution, which was to be titrated before starting the titration.

In all three cases the results (height and position of the extra peak) were almost the same as previously found.

E) Jena Glass Electrode: (Combination electrode with saturated calomel electrode as a reference electrode) No. 65:

The same titrations were carried out using three different unused Jena glass electrodes of the same type. In the case of these electrodes, the results were the same as before except that the position of the extra peak stabilised after three experiments see figure 3-14. In the first experiment, the extra peak was not very clear as in the case of the other glass electrodes.

The following experiments were carried out using one of the Jena electrodes, which had not been used before.

1) Soaking in 0.1 mol/l sodium bicarbonate solution for 17 hours before titration.

2) Soaking in 0.1 mol/l sodium bicarbonate solution for 13 days before

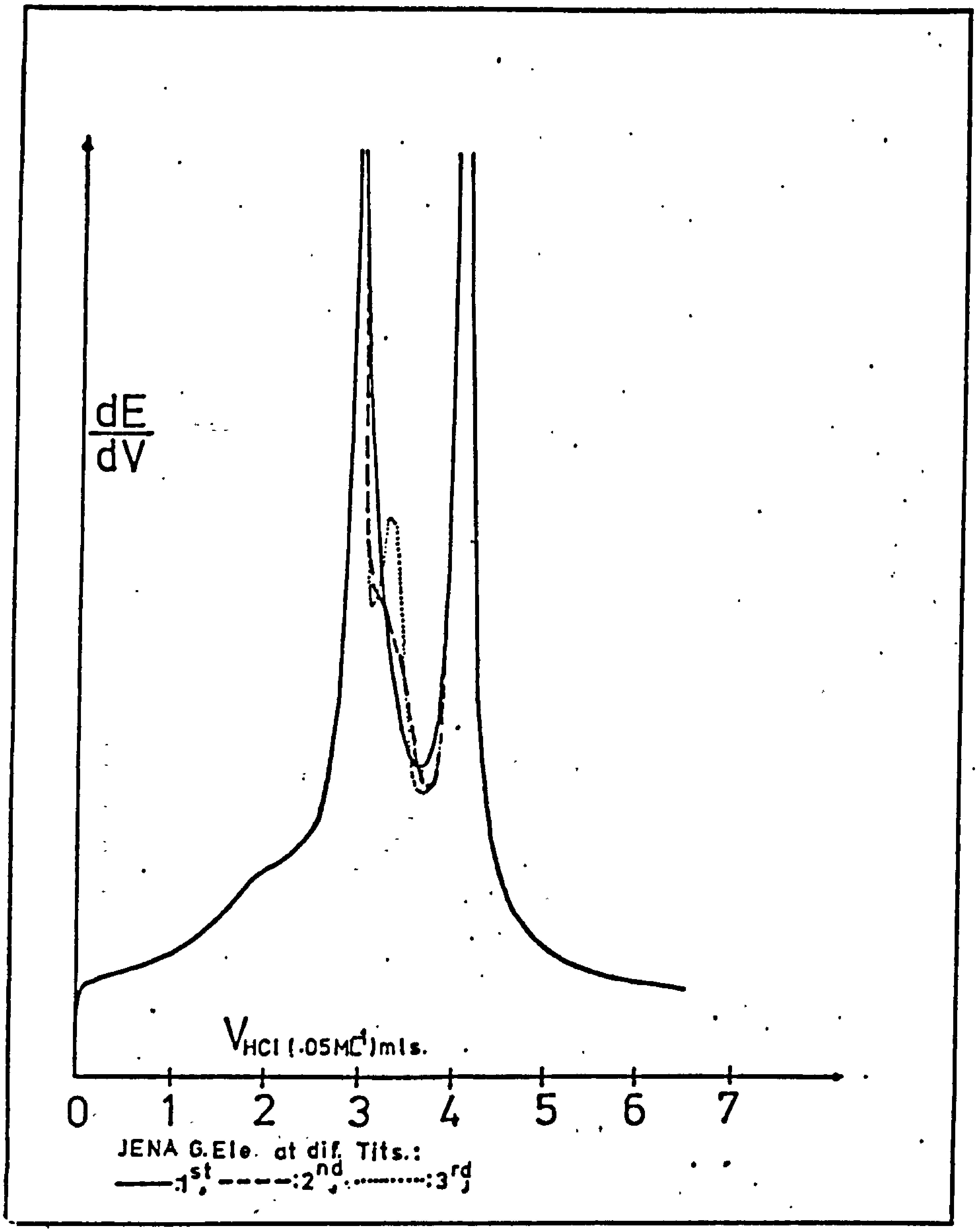

dE/dV
V_{HCl} (.05ML^{-1})mls.
0
1
2
3
4
5
6
7
JENA G.Ele. at dif. Tits.:
——:1st, – – – –:2nd, ··········:3rd

FIG 3 –14

titration.

3) Soaking in 5% HF for 2 minutes and then storing in distilled water for 2 days (at 25°C) before titration.

4) Soaking in 5% HF for 2 minutes, and then washing with distilled water and soaking in the titration solution for 15 minutes before starting the titration with hydrochloric acid.

5) Soaking in 5% HF for 15 minutes, and after washing with distilled water stirring for 15 minutes in the titration solution, before titration.

In all cases the extra peak was present. The following experiments were carried out, using the second new Jena glass electrode. For surface studies, the electrode was soaked in the following solution before use in the titrations.

1) In distilled water saturated with carbon dioxide gas for 5 days.

2) In 0.1mol/l sodium bicarbonate for 4 hours.

3) In 1 mol/l sulphuric acid solution for 16 hours.

4) 15 minutes in 1 mol/l sulphuric acid at 65°C.

5) In 0.1 mol/l sodium bicarbonate($NaHCO_3$) solution saturated with carbon dioxide gas for 13 days.

No effects were noticeable in all cases, and in all cases the extra peak was present.

Again the same type of treatments were carried out for another new Jena glass electrode with different lenghts of time, but in all cases there was no change from previous results.

It has to be noted that soaking the glass electrode in sodium bicarbonate solution probably increases the response of the glass electrode by increasing the growth rate of the gel layer. The effect has to be the same as the effect of carbon dioxide gas on the surface of the glass electrode (6) as described previously. Soaking the electrode in sulphuric acid has a rather different effect on the gel layer. Although Cl^- ions penetrate into the outer surface of the gel layer, this does not happen for SO_4^{2-} because of the large size of this ion.

All the different glass electrodes gave the same results and soaking the glass electrodes in different solutions for different lengths of time as in the following list:

a) 0.1 mol/l hydrochloric acid
b) 1mol/l hydrochloric acid
c) 0.1 mol/l sulphuric acid
d) 1mol/l sulphuric acid
e) 10 mol/l sulphuric acid
f) 0.1 mol/l sodium bicarbonate
g) 0.1 mol/l sodium carbonate solution saturated with carbon dioxide gas.
i) buffer solution having pH4
j) distilled water at different temperatures of 25 and 65°C
k) nitrogen gas-saturated distilled water
l) etching of the electrodes for different lengths of time.

had no noticeable effect on the position and the height of the extra peak.

Thus there is strong evidence to suggest that the extra peak is a property of titration solution which is detected by the electrodes as mentioned before.

3.5.5. EFFECT OF SOAKING THE GLASS ELECTRODE IN FERRIC IONS BEFORE USE IN THE TITRATION.

By soaking the electrode in ferric ions (Ferric chloride) with a concentration of 10^{-4} mol/l at about pH2 at 25°C and doing the titration after a period of time (four hours) the extra peak became more distinct. (Compare curve B with curve A in figure 3-15). Increasing the length of soaking time, from four hours to twenty hours (C) and repeating the titration the additional peak moved nearer to,a central position between the first and second peak of sodium carbonate and became well defined.

INCREASE OF THE RESPONSE OF THE GLASS ELECTRODE BY SOAKING IT IN Fe^{3+} SOLUTION (0.0001M) IN PH=2 AT 25°C

TITATION SOLUTIONS ARE 25 MILLILITRES OF NAOH (0.04M) + NA_2CO_3 (0.008M)

A) NORMAL TITRATION CURVE OF GLASS ELECTRODE

B) TITRATION CURVE OF GLASS ELECTRODE SOAKED IN Fe^{3+} SOLUTION FOR 4 HOURS

C) TITRATION CURVE OF GLASS ELECTRODE SOAKED IN Fe^{3+} SOLUTION FOR 20 HOURS

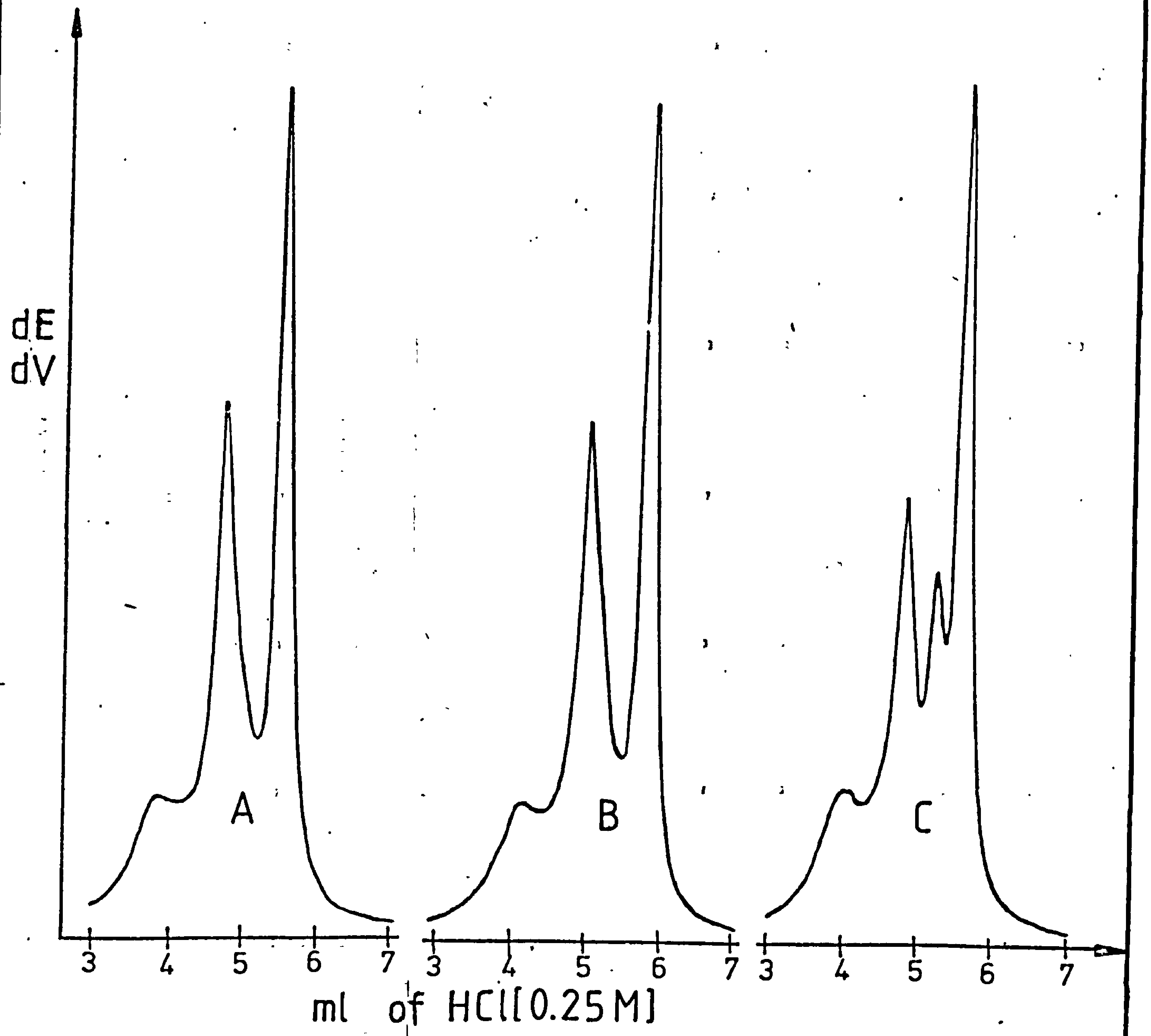


FIG 3-15

The titration solution was 25 ml of 0.04 mol/l of sodium hydrochloride and 0.008 mol/l of sodium carbonate and the rate of addition of hydrochloric acid.was 1ml in four minutes and its concentration was 0.25 mol/l. The experiments again were carried out at 25°C. Also by repeating the same titration the additional peak moved towards its original position after a few repetitions.

This effect of the ferric ions is mainly due to the increase is the local concentration of ferric ions on the outer surface of the glass electrode, which penetrate on soaking the glass electrode in solution containing ferric ions (in acidic solution) into the outer part of the gel layer. This process results in an increase in the speed of response of the glass electrodes, but as described in 3.4.1. repeating the titration has the effect of sweeping the pH from a very high to a very low value. This process removes some of the hydrated layers from the surface of the glass electrode(6) and exposes a fresh surface. It also decreases the concentration of the penetrated ferric ions, which is greatly reduced after a few titrations. This is mainly why the position of the extra peak returned to its original place as mentioned above.

Soaking the glass electrode in a solution of divalent ions (Mg^{2+}) has the same effect of improving the definition of the extra peak, but it is less effective than trivalent ions (Fe^{3+}).

3.5.6. EFFECT OF GAS BUBBLING:

The height of the extra peak is influenced by bubbling nitrogen gas through the titration solution. The additional peak was not resolved when nitrogen gas was bubbled through the solution before the titration (for an hour). Experiments were carried out for 10, 20,and 30 %

mole concentrations of sodium carbonate in 25ml of 0.04 mol/l sodium hydroxide solution, The rate of addition of 0.25 mol/l hydrochloric acid was 1ml in four minutes. When nitrogen gas was bubbled through, the second peak of carbonate became very sharp. At the same time the extra peak disappeared, because of the nitrogen saturation of the solution. This leads to the suggestion that the presence of dissolved carbon dioxide is essential for the appearance of the extra peak.

Considering the equation $HCO_3^- \rightleftharpoons CO_2 + H_2O(H_2CO_3)$, this effect is due to the removal of the produced carbon dioxide gas from the solution by bubbling the nitrogen gas into it before and during the titration period. The equilibrium of the above equation is displaced to the right hand side.

The same type of experiment was carried out where nitrogen gas was replaced by hydrogen gas. The results were the same,as is shown in figure 3-16 where in the middle the titration curves for 40% of sodium carbonate in 0.04 mol/l sodium hydroxide solution using a Radiometer glass electrode. In the right hand side of figure 3-16 hydrogen gas was bubbled through the solution for 90 minutes before the start of titration and continued until the end of titration with vigourous stirring . The extra peak was not resolved. It is therefore not surprising that the use of a hydrogen gas electrode does not show the additional peak either (more explanation is given about this in 3.6.1.).

3.5.7. EFFECT OF CHANGE OF THE SOLVENT FROM H_2O TO D_2O:

Different experiments were carried out using 0.25 mol/l deuterohydrochloric acid-d (concentrated DCl : BDH product no. 14084 was diluted with D_2O to the required concentration), was added at a rate of 1ml in four minutes for 25 ml of 0.04 mol/l of sodium hydroxide containing

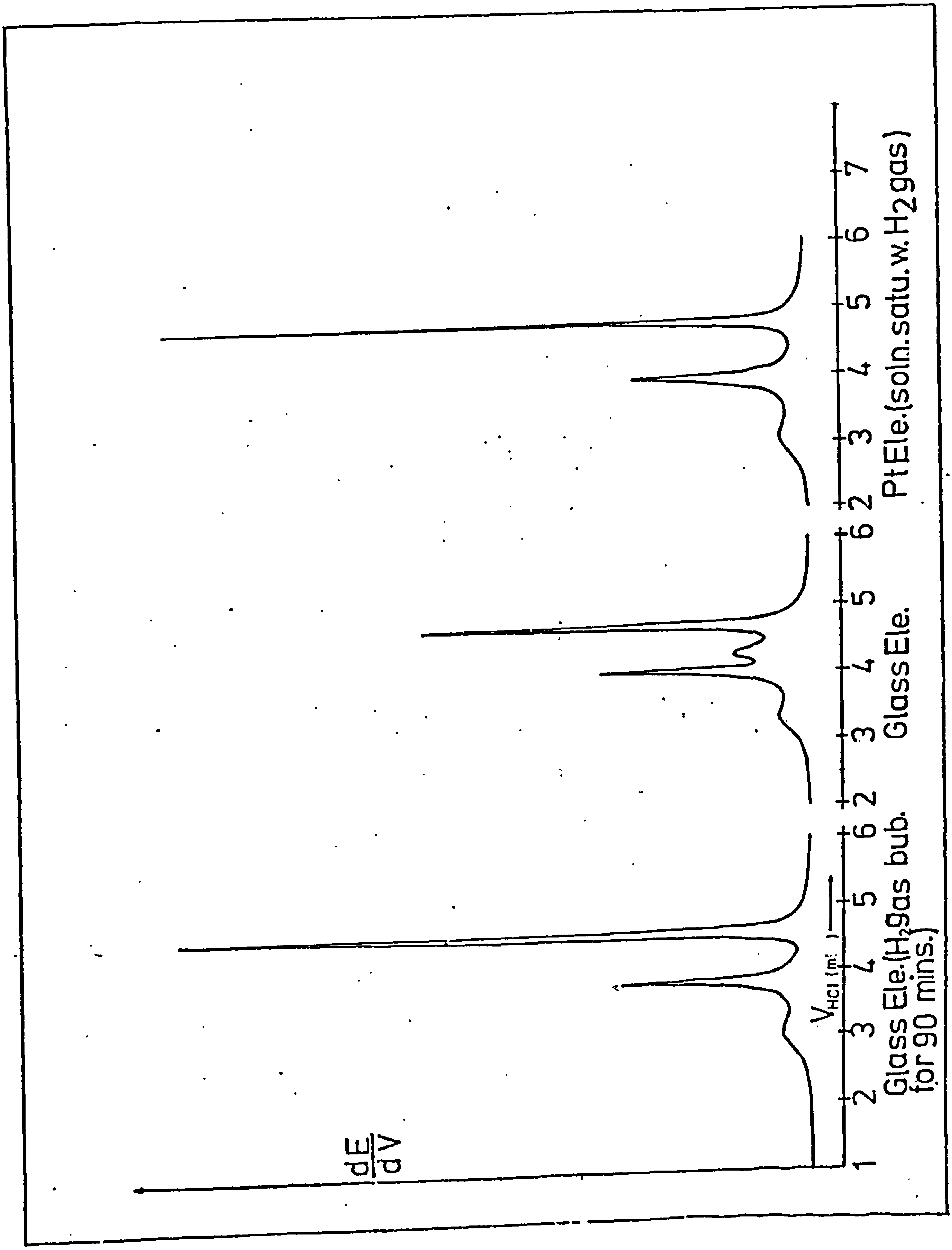

$\frac{dE}{dV}$
1
2
3
4
5
6
V_{HCl} (ml)
Glass Ele.(H_2gas bub. for 90 mins.)
2
3
4
5
6
Glass Ele.
2
3
4
5
6
7
Pt Ele.(soln.satu.w.H_2gas)

FIG 3—16

different mole percentages (10, 20, 30, and 50) of sodium carbonate.

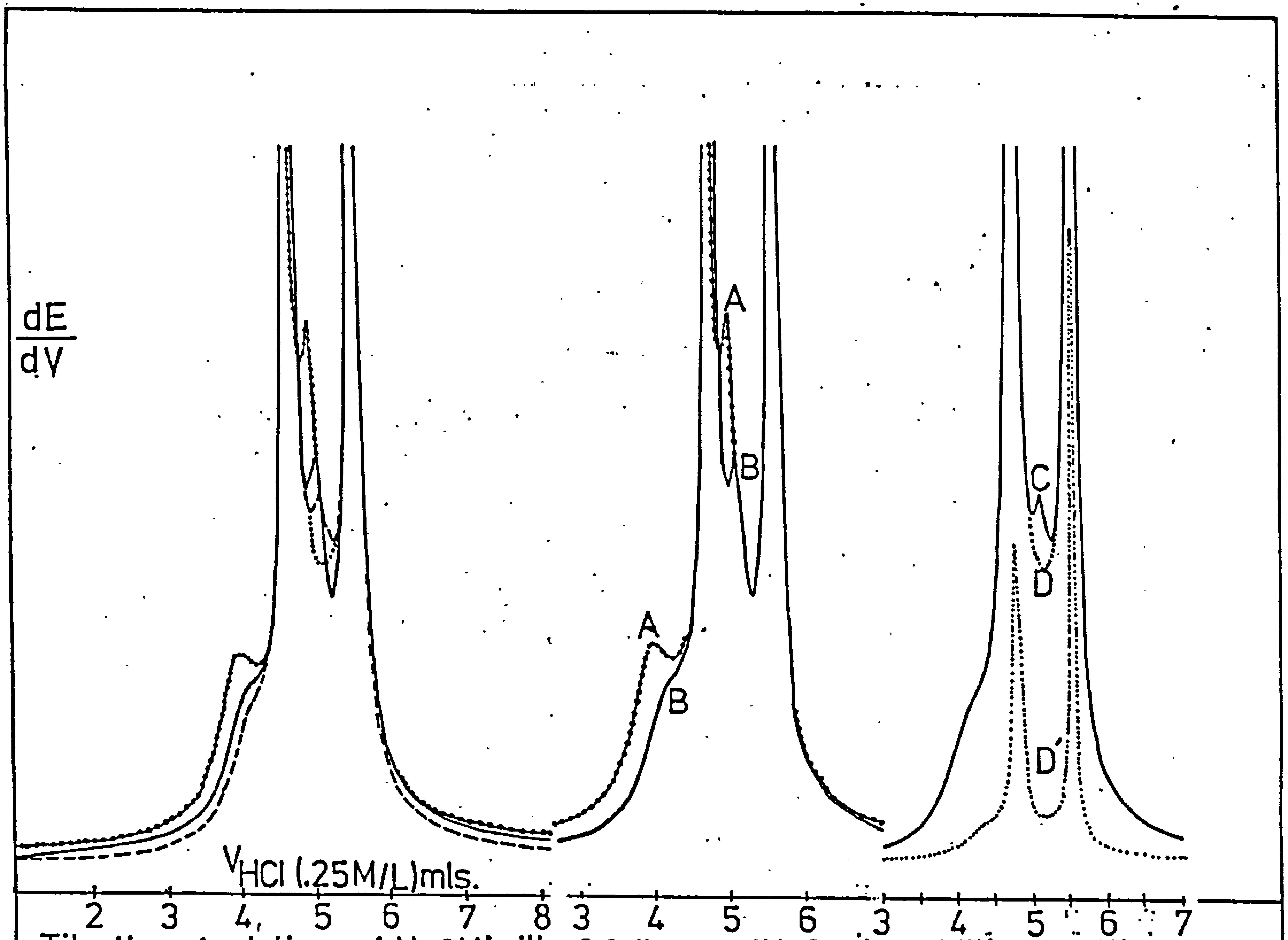
In all cases distilled water was replaced by deuterium oxide as a solvent (D_2O 99.7% was from Norsk-Hydro-Electric). This had no effect on the formation of the additional peak in the titration curves.

3.5.8. EFFECT OF ADDITION OF DIFFERENT ALCOHOLS AT VARIOUS MOLE FRACTIONS TO THE TITRATION SOLUTION.

Several experiments were carried out using methanol, ethanol and t-butanol, as described below:

i) Methanol: titration of 25ml of 0.04mol/l of sodium hydroxide containing 0.008mol/l sodium carbonate was carried out (the rate of addition of 0.25mol/l hydrochloric acid was 1ml in 4 minutes) with the addition of different mole fractions of methanol. When the mole fraction of methanol was equal or greater than 0.25, the extra peak was removed from the titration curve. For $X_2 = 0.2$ the peak was present, but only just visible. The sodium hydroxide peak was diminished in height, but the other peaks were extremely sharp.

ii) When other alcohols were tried with larger side groups, smaller amounts of alcohol were required to make the peak disappear; for example for ethanol $X_2 = 0.19$ was sufficient, but the peak was still visible for $X_2 = 0.1$ and 0.13 (see figure 3-17). For $X_2 = 0.19$ several experiments were carried out for 25ml of 0.04mol/l sodium hydroxide containing 10, 20 and 30 mole percent of sodium carbonate and in all cases the peak was absent. Again the sodium hydroxide neutralization peak was hardly visible and the two other peaks for sodium carbonate were very sharp.



Titration of solutions of NaOH 'with 20 % of Na_2CO_3 by addition of different amounts of EtOH to the solutions' by HCl soln.

A(·······):x(mole fraction of EtOH in soln.)=02; B(——)x=0.1; C(----)x=0.13; D,D′(——)x=19

FIG 3 – 17

iii) t-butanol

An even smaller amount of t-butanol was required to make the extra peak disappear. Experiments were carried out using the following mole fractions of it (X_2 = 0.02, 0.04, 0.08, 0.09, 0.112, 0.126, 0.136 and 0.18) in 25ml of 0.04mol/l of sodium hydroxide containing 0.008 mol/l of sodium carbonate. For X_2 greater than 0.08 the extra peak was hardly visible and for X_2 equal or greater than 0.126 it had completely disappeared (see figure 3-18). The experiment was carried out for a fixed mole fraction of alcohol (0.126) but with variations in the sodium carbonate mole percentages of 10,20 and 30. The extra peak, was absent in all cases. - Again the sodium hydroxide peak was diminished in height for high mole fractions of alcohol, but the sodium carbonate neutralization peaks, especially the second one, were much sharper. Hence, it seems that in all cases the addition of alcohol makes the end-point determination of carbonate ions much clearer.

3.5.9. EFFECT OF ADDITION OF DIFFERENT CONCENTRATIONS OF TMACl

The same type of titration was carried out using a Radiometer glass electrode type B and the same make of calomel electrode (type K401 QL-1) as a reference electrode, with the addition of different concentrations of tetra methyl ammonium chloride. The concentrations used were 0.01, 0.5, 1, 2, 10, 20, 50 and 80 times the sodium ions concentration (see figure 3-19).

When the concentration of TMACl was larger than half of the concentration of sodium ions, the extra peak was very close to the first sodium carbonate neutralization peak, and it was hardly visible, but in all cases the extra

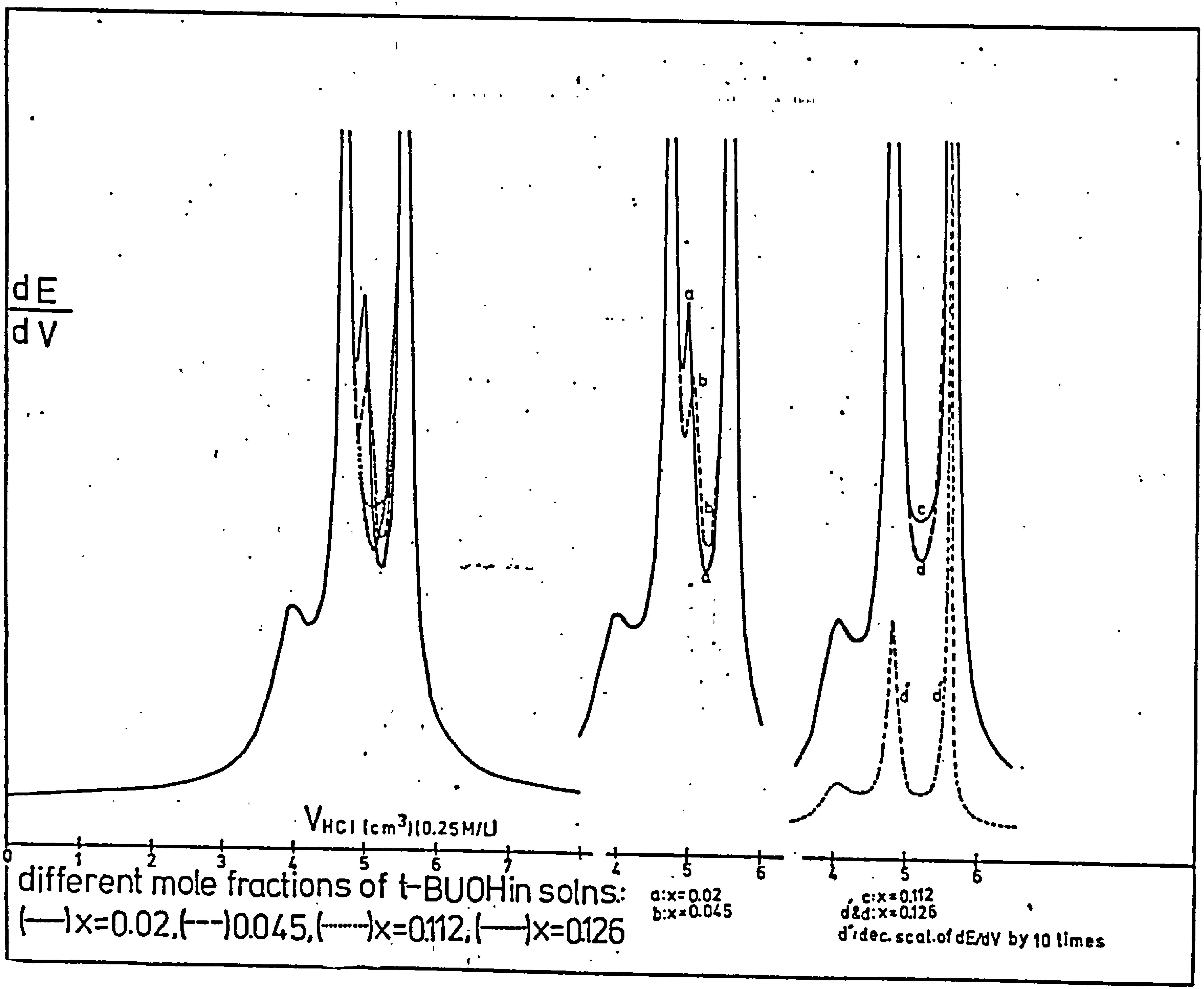
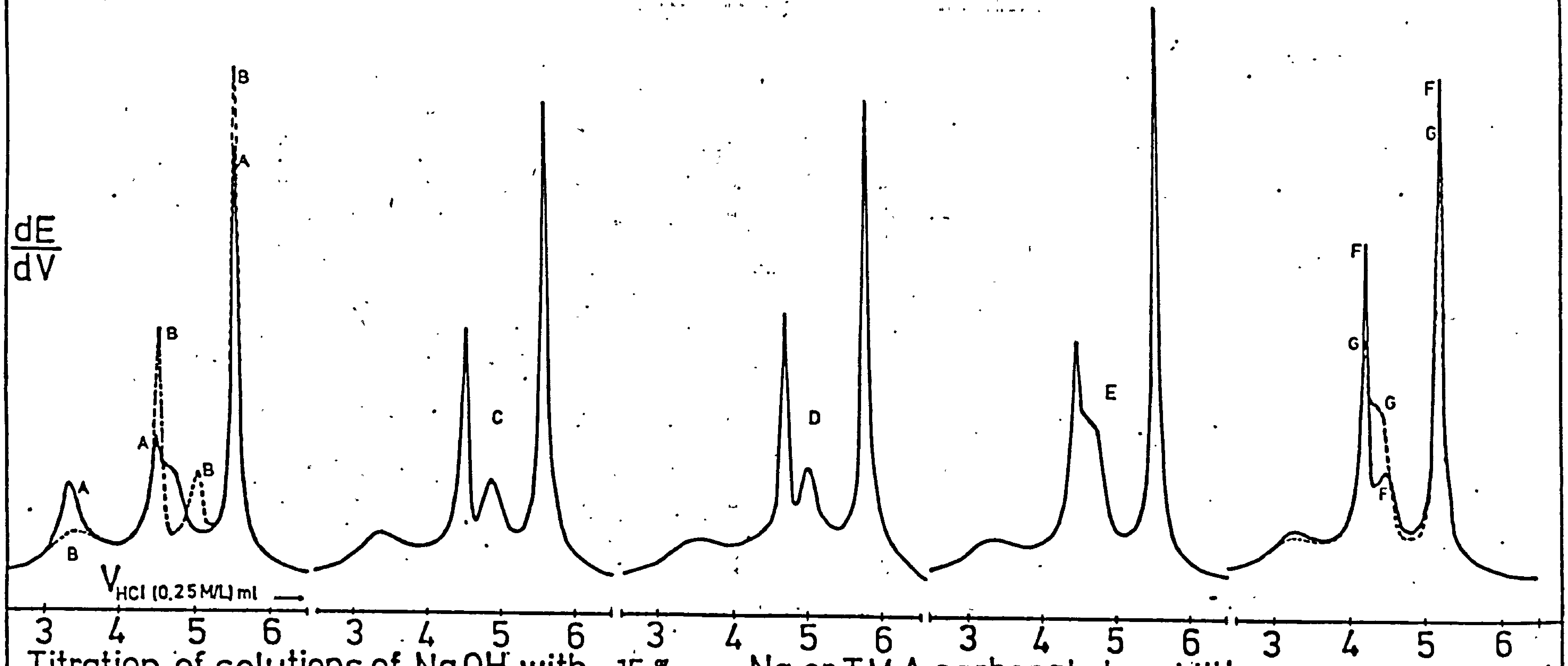

dE/dV
V_HCl (cm³)(0.25M/l)
0
1
2
3
4
5
6
7
4
5
6
4
5
6
a
b
b
a
c
d
d'
d'
different mole fractions of t-BUOHin solns.:
(—)x=0.02,(---)0.045,(······)x=0.112,(—)x=0.126
a:x=0.02
b:x=0.045
c:x=0.112
d&d':x=0.126
d':dec. scal. of dE/dV by 10 times

FIG 3-18



Titration of solutions of NaOH with 15% Na or T.M.A carbonate by addition of NaCl or T.M.A.Cl to the solutions by HCL soln.:

A: NaCarb. + 6.54grms.(con.of NaCl=4.5M/L) · B: Na Carb. · C: Na Carb. +0.77grms T.M.A.Cl.($C_{Na^+} = 1/5\,C_{T.M.A.^+}$). D: NaCarb. +3.1grms. T.M.A.Cl.($C_{Na^+} = .05\,C_{T.M.A^+}$). E: Na Carb. +12.27grms T.M.A.Cl.($C_{Na^+} = 1/80\,C_{T.M.A.^+}$). F: T.M.A..Carb. · G: T.M.A. Carb. +12.27grms T.M.A.Cl(con. of T.M.A.Cl.=4.5M/L).

FIG 3–19

peak was present. With the addition of TMACl the neutralization peak of sodium hydroxide was sharper than in the previous experiments. This is because TMAOH is a stronger base than NaOH.

3.5.10 CHANGE OF CATION FROM Na^+ TO TMA^+ AND K^+

i) K^+ ions:

The same type of experiment was carried out using a Radiometer glass electrode type B and the same make calomel reference electrode type K401-QL-1) for 25ml of 0.04 mol/l potassium hydroxide containing 0.008 mol/l of potassium carbonate at 25°C (all sodium ions were replaced by potassium ions in the titration solutions). The results were the same as before.

ii) TMA^+:

Again the same type of experiment was carried out using KS-2 G202B, UY-1 G202C, TN-1 G202B and KS-1 G202C Radiometer glass electrodes as for the titration of different mole concentrations of sodium carbonate in 25ml of 0.04mol/l of sodium hydroxide (10, 20, and 30%) at 25°C. In all these cases sodium ions were replaced by $((CH_3)_4N)^+ = TMA^+$ ions. It was found that the extra peak moved towards the first neutralization peak of carbonate ions, but it was still present (compare curve C with curve F in figure 3-19). It seems that in these cases the character of the solution was changed by presence of side groups in tetra methyl ammonium ions, and interaction between carbon dioxide and the hydrophobic groups of TMA^+ ions had an effect on the formation of the extra peak. The neutralization peak of TMAOH was again sharper than in the case of NaOH as mentioned in3.5.9.

3.5.11. EFFECT OF AMMONIUM CHLORIDE (NH_4Cl) ON TITRATION CURVES

Two titrations were carried out to show the effect of addition of ammonium chloride. In both cases hydrochloric acid (0.25 mol/l) was used as the titrant with a rate of addition of 1ml in 48 seconds.

A) This was a normal titration of 25ml of aqueous solution of sodium hydroxide 0.04 mol/l containing about 0.008 mol/l of sodium carbonate. As is clear in figure 3-20 three peaks were recorded and the extra peak was situated so close to the first peak of sodium carbonate that it became a shoulder on the first peak. Therefore, the first peak of neutralization is asymmetric.

B) In this case, the titration solution was the same as A) except that about 0.5 mol/l ammonium chloride added into the titration solution. As is shown in figure 3-20-B, the sodium hydroxide peak was not recorded and the first peak of carbonate was greatly diminished in height. This is because hydroxide ions are neutralized by ammonium ions, and because the pK_a value for ammonium hydroxide and pK_2 for sodium carbonate were not very different from each other. Hence, there was no clear peak for conversion of carbonate to bicarbonate. Instead, the conversion of ammonium hydroxide to ammonium chloride was recorded with less height in comparison with the first peak of carbonate ions neutralization.

3.6.1. TITRATION CURVES FOR Pt/HYDROGEN GAS ELECTRODE

The titration was carried out for Pt/hydrogen gas electrode in a solution of sodium hydroxide with sodium carbonate saturated by hydrogen gas .

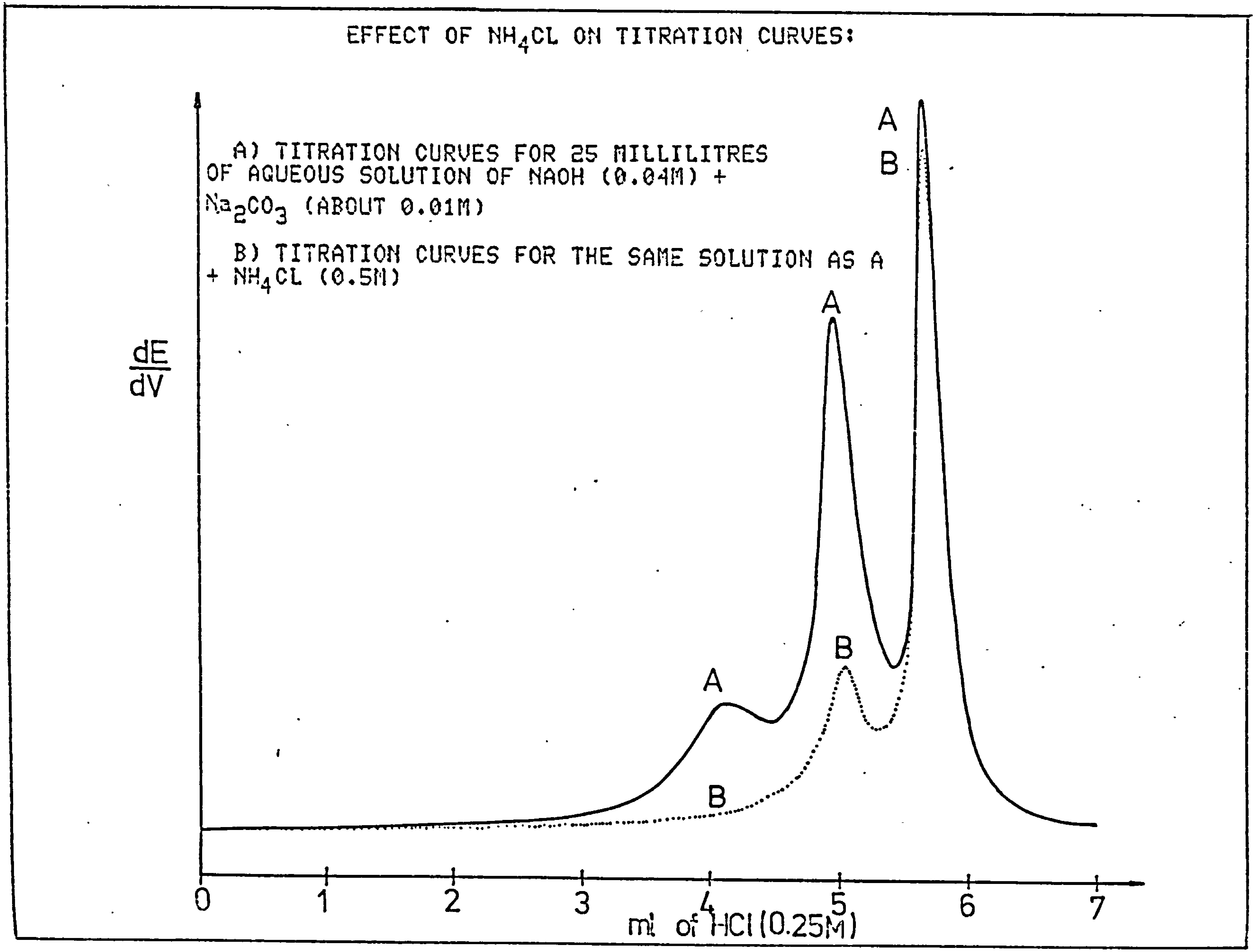

EFFECT OF NH_4CL ON TITRATION CURVES:
A) TITRATION CURVES FOR 25 MILLILITRES OF AQUEOUS SOLUTION OF NAOH (0.04M) + Na_2CO_3 (ABOUT 0.01M)
B) TITRATION CURVES FOR THE SAME SOLUTION AS A + NH_4CL (0.5M)
$\frac{dE}{dV}$
A
B
A
B
A
B
0
1
2
3
4
5
6
7
ml of HCl (0.25M)

FIG 3-20

The Pt electrode was made by Ferra (9) as described below was used for these experiments. One end of a piece of platinum wire(No.26) (about 2cm in length) was sealed in a soda glass tube and the other end spot-welded to a piece of platinum foil (1cm square and 0.1 mm thick). A small amount of mercury inside the tube made contact between the Pt wire and copper wire lead.

The platinization was done as described by Ferra. The platinum foil was coated with platinum in chloro platinic acid in 2mol/l hydrochloric acid containing 0.02% lead acetate. A current of 300mA was passed for 3 minutes between the elctrode to be coated (cathode) and a similar electrode which was used as the anode. After the platinization the electrode was washed and stored in distilled water.

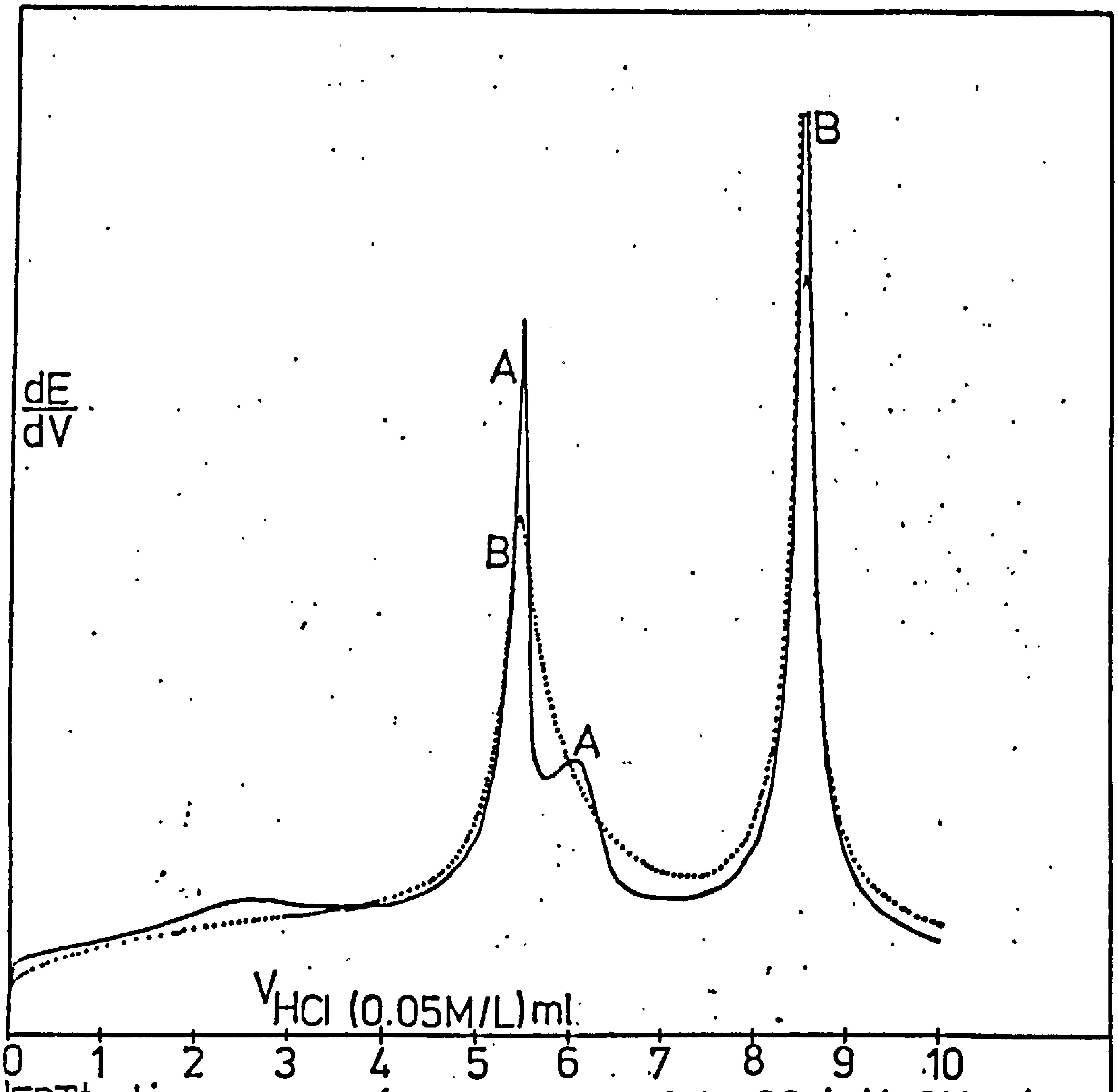
Plots of dE/dV against $V_{(HCl 0.25mol/l)}$ were made using the platinum electrode and a Radiometer saturated calomel electrode(type K401 QL-1) as a reference electrode , for solutions of 0.04 mol/l of sodium hydroxide containing 10, 20, and 30% of mole concentration of sodium carbonate. The titration solutions were saturated with hydrogen gas at 25°C before the titration started for one hour. Hydrogen gas was bubbled both through the titration solution and the hydrochloric acid that was to be used in the titration . The titration solution was vigourously stirred throughout. In all cases the extra peak was absent and the height of the other peaks in comparison with peaks for Radiometer glass electrode in which the solution was saturated with hydrogen gas for one hour before starting the titration, were the same (see figure 3-16 the curves on the left and right hand side). In other words there was no difference between the curves for Radiometer glass electrode and Pt electrode when solutions were saturated with hydrogen gas.

3.7.1. TITRATION CURVES FOR Rh/Rhoxide ELECTRODES

In this series of experiments, studies of Rh/Rhoxide electrode including the effect of temperature were carried out. The electrode was made (10) by plating Rh on Rh wire at potential of -400 millivolts with respect to the saturated calomel electrode for ninety minutes. The length and diameter of the wire were 0.9mm and 0.51mm respectively. This electrode was used for plots of dE/dV against volume of hydrochloric acid, with a concentration of 0.25mol/l, as previously, with an addition rate of 1ml in four minutes. In another series 0.05mol/l hydrochloric acid was used for the titration. Titrations were carried out, initially at 25°C and comparison was made with corresponding glass electrode results.

As is clear in figure 3-21 (titration of 25ml of 0.04mol/l sodium hydroxide containing 0.006 mol/l sodium carbonate with hydrochloric acid 0.05 mol/l with a rate of addition of 1ml in four minutes) the sodium hydroxide peak was clearer in the case of the glass electrode than for Rh/Rhoxide electrode where it was hardly visible. The first sodium carbonate neutralization peak was sharper for the glass electrode, but the second peak was sharper for the Rh/Rhoxide electrode. In addition the trough between the two peaks was higher for the Rh/Rhoxide electrode. The extra peak was not clear in the case of Rh/Rhoxide electrode and it became a shoulder on the first peak of carbonate in titration curve. (See figure 3-21).

A number of titrations were carried out at the following temperatures: 55, 50, 45, 41, 35, 30 and 25°C. About 40°C the sodium hydroxide neutralization peak was not clear, the first peak of sodium carbonate became sharper, and the shoulder (the extra peak) disappeared from this peak,



FDTitration curves for 15 % of Na_2CO_3 in NaOH solns.
A(——): GLASS Ele.
B(------) Rh Oxide Ele.

FIG 3-21

whereas the height of the second peak fell slightly. Variations of the sodium carbonate concentrations had no noticeable effect on titration curves.

3.8.1. TITRATION CURVES FOR QUINHYDRONE ELECTRODE

This electrode system is now little used as a means of pH determination, but the first derivative curves can be obtained by using this electrode. As is shown in figure 3-22, the titration curves with 0.05 mol/l hydrochloric acid at an addition rate of 1ml in four minutes for 25ml of 0.04 mol/l of sodium hydroxide containing 7.5 mol% of sodium carbonate.

Results for quinhydrone elctrode (Pt electrode in 10^{-3} mol/l H_2Q AnalaR reagent of BDH in titration solution) and the glass electrode were compared. It is clear that the first peak of sodium carbonate was sharper with a shoulder in place of the well-defined extra peak found using the glass electrode in similar titrations. In addition, the second peak of carbonate diminished in height for the quinhydrone electrode compared to the glass electrode titration peak.

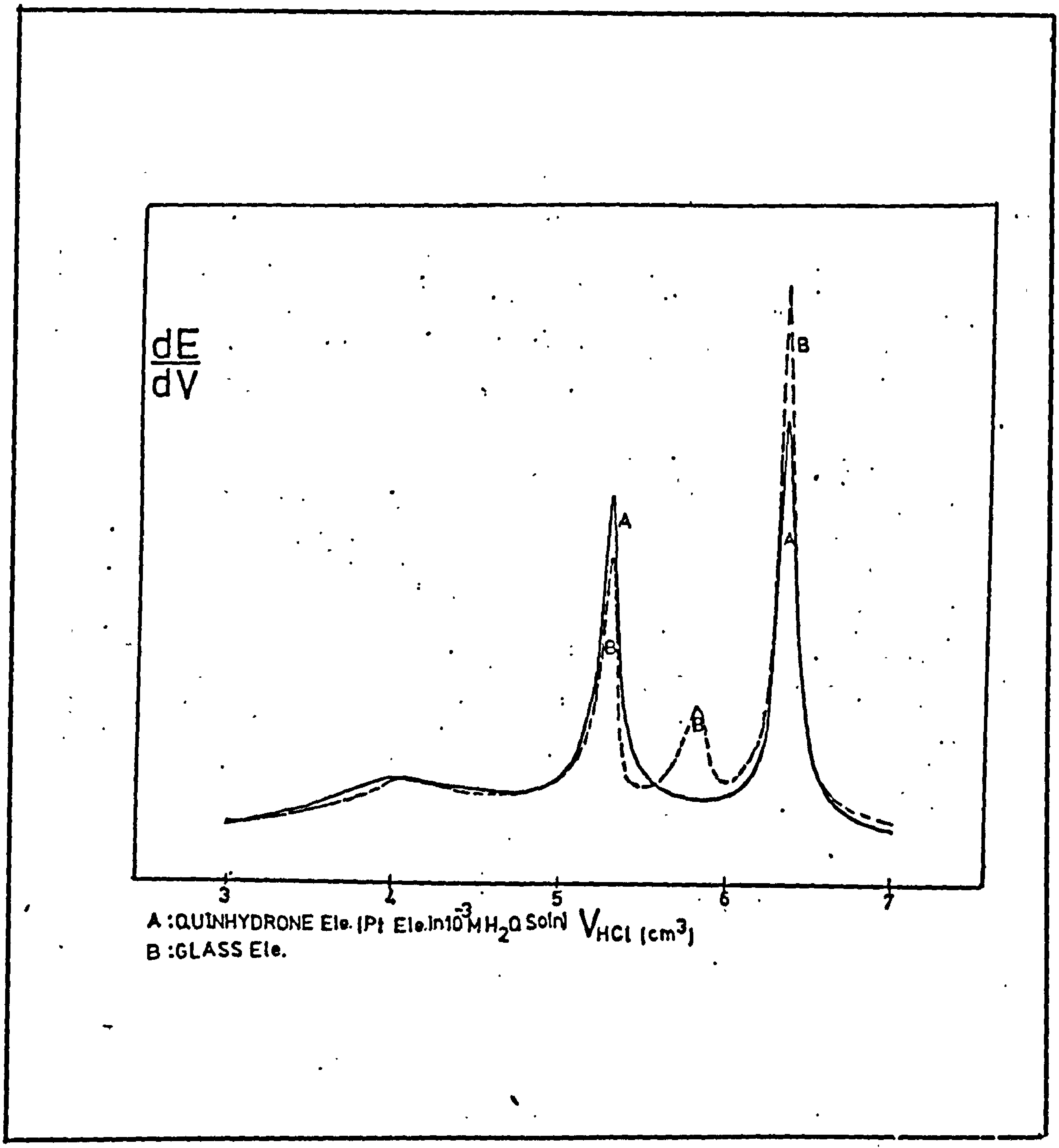

dE/dV
A
B
A
B
A
B
B
A
3
4
5
6
7
A :QUINHYDRONE Ele. (Pt Ele.In 10^{-3} M H_2Q Soln)
V_{HCl} (cm^3)
B :GLASS Ele.

FIG 3–22

3.9.1. REFERENCES

1) A.K. Covington, R.A. Robinson and M. Sarbar, Anal. Chim. Acta, 1978, 100, 367

2) Orion Research Incorporated Cambridge, Mass. Newsletter 3 , Numbers 1 and 2

3) H. Bach and F.G.K. Baucke, Electrochimica Acta, 1971, 16, 1311

4) F.G.K. Baucke J. Non-Crystalline Solids 1975, 19, 75

5) A. Wikby, Physics and Chemistry of Glasses, 1974, 15, 37

6) H. Bach and F.G.K. Baucke, Physics and Chemistry of Glasses, 1974, 15, 123

7) A. Wikby J. Electroanalytical Chemistry and Interfacial Electrochemistry, 1971, 33, 145

8) P.K.A. Flynn, MSc thesis , University of Newcastle upon Tyne, 1980, chapter 1

9) M.I.A. Ferra,PhD thesis, University of Newcastle upon Tyne, 1977 chapter 3

10) D.G. Jones, PhD thesis, University of Newcastle upon Tyne, 1977 chapter 2

4.1.1. INTRODUCTION

The titration process which was described in the previous chapters can be reversed to neutralize the dissolved carbon dioxide in acidic solution with a strong base such as NaOH. Again titration curves should contain three maxima. The first corresponds to neutralization of most of the strong acid; the second corresponds to conversion of carbonic acid to bicarbonate (carbonic acid produced through the hydration process of dissolved carbon dioxide) and the third peak corresponds to the conversion of bicarbonate ions to carbonate ions.

However, the experimental curves again show an extra unexpected peak between the first and second peak of titration. The experiments described below were carried out for further investigation of this peak using the Mettler apparatus.

4.2.1 PREPARATION OF CARBON DIOXIDE SOLUTION

To obtain a constant concentration of carbon dioxide in water a "Sparklet" syphon was used (a product of British Oxygen Company). It was filled with distilled water. The syphon tube was then fitted and screwed on tightly. A bulb was inserted into the bulb holder and screwed firmly on to the syphon head in accordance with the manufacturers' instructions. The bulb was automatically pierced and the carbon dioxide discharged. When the gas was no longer heard bubbling into the distilled water, the syphon was charged (this took about thirty seconds) and the syphon was shaken vigorously for ten seconds. The bulb holder was then removed. It was now ready for use. For each experiment about

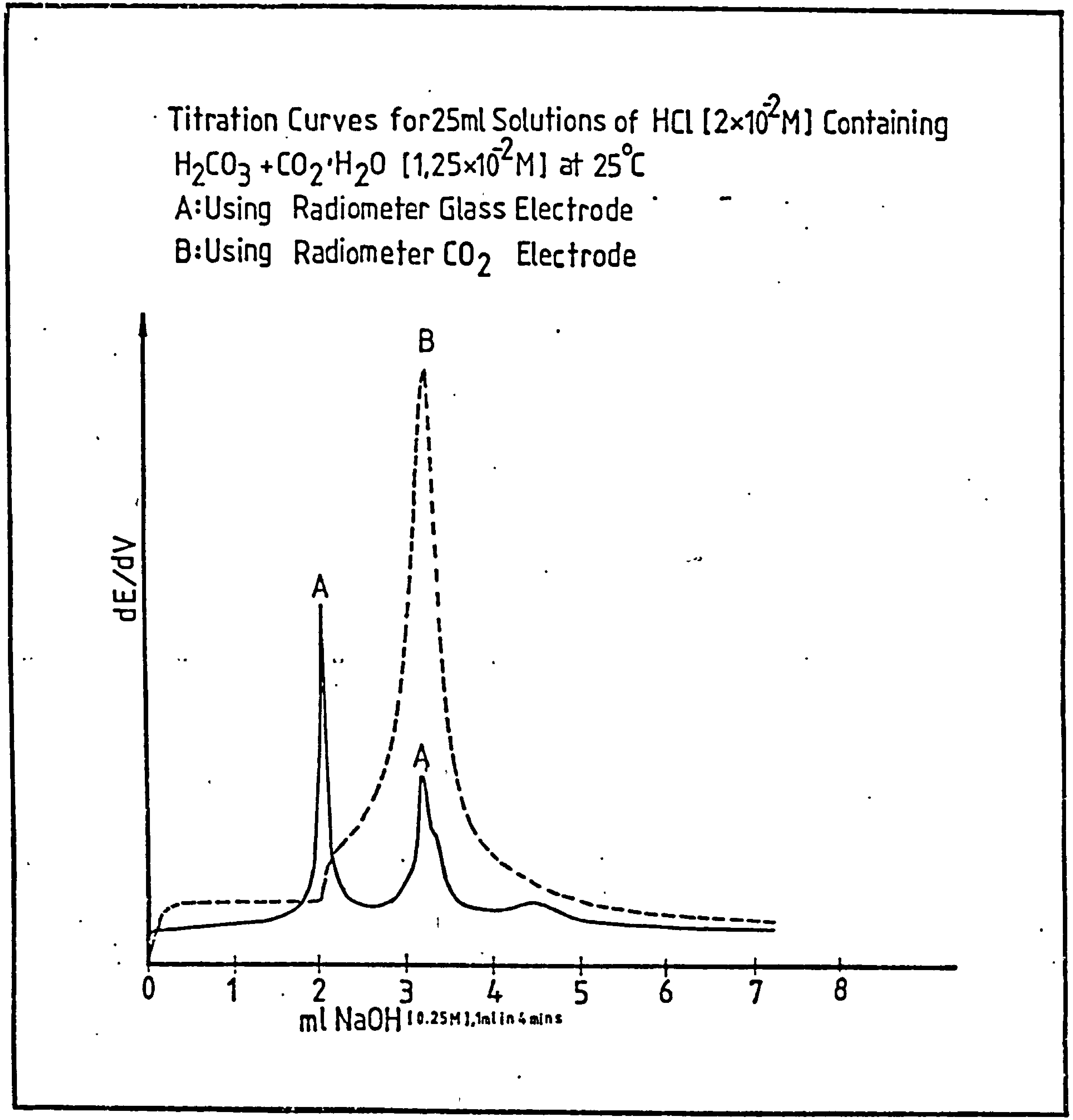
20ml of solution was discharged from the syphon into a beaker. This was then pipetted from the beaker into the titration cell to obtain the required concentration of dissolved carbon dioxide.

4.2.2. PLOTS OF dE/dV vs V_{NaOH} (0.1M) FOR GLASS ELECTRODE AND CARBON DIOXIDE ELECTRODE, AND APPEARANCE OF AN EXTRA PEAK IN THE TITRATION CURVES

Different titrations were carried out for 25ml of 0.02 mol/l of hydrochloric acid containing different concentrations of dissolved carbon dioxide. The titrant was 0.1 mol/l sodium hydroxide free from carbon dioxide, with a rate of addition of 1ml in four minutes. Again all the chemicals used in these titrations were made by BDH.

A Radiometer glass electrode type G202B with the same make of calomel reference electrode type K401-QL-1 was used for producing the first derivative curves of potential against volume of titrant added. The same type of curve was produced using the Radiometer carbon dioxide electrode type PS-1-902-123.

In figure 4-2, the first derivative curves are shown both for glass and carbon dioxide electrodes. The hydrochloric acid contained about 0.0125 mol/l dissolved carbon dioxide, and, as mentioned before, most of the dissolved carbon dioxide is available in molecular carbon



Titration Curves for 25ml Solutions of HCl [2×10^{-2}M] Containing $H_2CO_3 + CO_2 \cdot H_2O$ [1.25×10^{-2}M] at 25°C

A: Using Radiometer Glass Electrode

B: Using Radiometer CO_2 Electrode

FIG-4-2

dioxide form and a small fraction of it is in the form of carbonic acid. As the titration proceeds, first most of the hydrogen ions, which are produced from hydrochloric acid together with a very small fraction of hydrogen ions produced by ionisation of carbonic acid, are neutralized and the first peak in the titration curve appears as indicated by the glass electrode. At the same time a shoulder, shown by the carbon dioxide electrode, indicates the start of the change in the dissolved carbon dioxide concentration. The increase in volume of titrant neutralizes the carbonic acid which was produced by the hydration of carbon dioxide in the following reactions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 + NaOH \rightleftharpoons NaHCO_3 + H_2O$$

This produced a peak followed by a shoulder in the titration curves, when a glass electrode was in use. (See figure 4-2).

Further addition of sodium hydroxide neutralizes the formed bicarbonate to carbonate in the following fast reaction:

$$NaHCO_3 + NaOH \rightleftharpoons Na_2CO_3 + H_2O$$

The end of titration of this reaction produces another peak in the titration curve. Further addition of sodium hydroxide remained unreacted in the titration solution. This was indicated by no change in the first derivative of the potentiometric titration curve.

It seems the end of the conversion of dissolved carbon dioxide to bicarbonate is indicated by the shoulder on the right hand side of the middle peak in the titration curve. So the attached peak is the extra peak. This is because the position of the shoulder is halfway between the peak for titration of most of hydrochloric acid (first peak) and the peak for the conversion of produced bicarbonate ions to carbonate ions (the third peak of the titration curve). The carbon dioxide electrode reacts to dissolved carbon dioxide which has to diffuse through the membrane of the electrode. Since the peak for the carbon dioxide electrodes and the extra peak (the middle peak for the glass electrode) has occupied the same position in the titration curves, it can be concluded that the middle peak for the glass electrode (the extra peak) appeared in the titration process when the free dissolved carbon dioxide had been exhausted.

4.3.1. EFFECT OF TEMPERATURE ON THE TITRATION CURVES AND REVERSE TITRATION AT DIFFERENT TEMPERATURES

A series of experiments was carried out at different temperatures as shown in figures 4-3 and 4-4. The titration solution was 0.022 mol/l dissolved carbon dioxide. The rate of addition of 0.25 mol/l sodium hydroxide as 1ml in 48 seconds.

Effect of Different Temperaturs on Titration Curves (5,10,15,20,25,35,55,65°C)

Titration Solutions: 25 ml $H_2CO_3+CO_2+H_2O$ [≈2.2×10^{-2} M]

FIG-4-3


dE/dV
25°C
35°C
55°C
65°C
0
1
2
3
4
5
0
1
2
3
4
0
1
2
3
4
0
1
2
3
4
ml Na OH [0.25 M], 1ml in 48 sec.

FIG.

A comparison of the curves for temperatures lower than 25°C with the one for 25°C shows that the extra peak, which is the highest of the four peaks moves towards the peak of neutralization of protons, as the temperature decreases. By increasing the temperature of the titration solution the extra peak shifts towards the middle peak of the titration curve and at temperatures higher than 35°C the extra peak disappears and makes the original peak of carbonate much sharper, as is shown in figure 4-4 below. Also back (reverse) titrations of the titrated solutions were carried out at different temperatures as is shown in figure 4-5, in case (A) the titration of 25ml of 0.0185 mol/l of dissolved carbon dioxide was carried out. The titrant was 0.25 mol/l sodium hydroxide. Back titration of titrated solution of titration (A) was carried out using 0.25 mol/l of hydrochloric acid (case B in figure 4-5) and in case C back titration of titrated solution of B again was carried out producing curve C. Comparison of the curves A and C shows that these two curves (A and C) are almost identical to each other and demonstrates the reproducibility of the titration curves at the same conditions. (All three titrations were carried out at 5°C with the rate of addition of titrant 1ml in 48 seconds). In both curves A and C, the extra peak is present in addition to the three main peaks of the titration process. The height of the middle peak is very small. The extra peak is very sharp. In addition, the extra peak is present in case (B) as a shoulder on the right hand side of the middle peak.

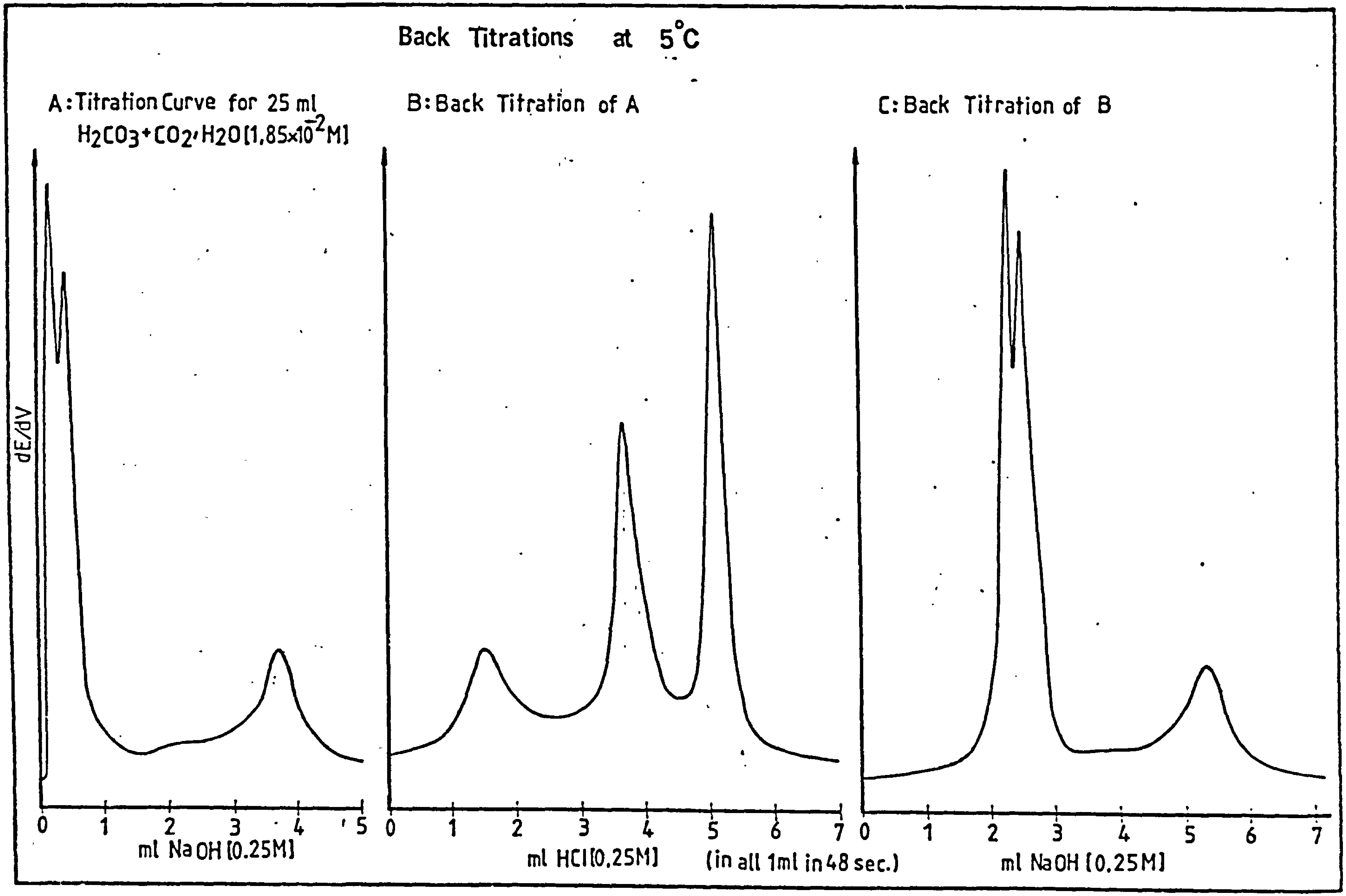

Back Titrations at 5°C
A: Titration Curve for 25 ml $H_2CO_3 + CO_2 \cdot H_2O$ [$1,85 \times 10^{-2}$ M]
B: Back Titration of A
C: Back Titration of B
dE/dV
0
1
2
3
4
5
ml NaOH [0.25M]
0
1
2
3
4
5
6
7
ml HCl [0,25M]
(in all 1ml in 48 sec.)
0
1
2
3
4
5
6
7
ml NaOH [0,25M]

FIG-4-5

In figure 4-6 the titration curves for the same type of experiments as the previous ones are shown. The only difference is that, in this case, the titrations were carried out at 65°C. Again curve A is almost the same as curve C. A comparison of curves A and B in figure 4-5 with the same curves in figure 4-6 makes it quite clear that the extra peak is not present at 65°C but it is well defined at 5°C. Furthermore at high temperatures, the middle peak is symetrical, due to the absence of the extra peak.

In figure 4-7, 4-8 and 4-9 the titrations and corresponding back titrations are shown at 25, 35, and 55°C respectively. In all cases the increase in temperature removes the presence of the extra peak in both titrations and back titrations.

4.3.2. EFFECT OF ADDITION OF TMACl AND NaCl ON TITRATION CURVES:

Three titrations were carried out to show the effect of addition of tetra methyl ammonium chloride and sodium chloride to the titration solutions. In all cases the titrant was 0.25 mol/l sodium hydroxide with a rate of addition of 1ml in 48 seconds. All titrations were carried out at 25°C as follows:

a) This was a normal titration of 25ml of 0.02 mol/l dissolved carbon dioxide. As is clear from the curve on the lefthand side in figure 4-10 the extra peak was present and the main middle peak appears as a shoulder on the right hand side of the extra peak.

b) In this case the titration solution and also the titration conditions were the same as a) except that 4.5 mol/l of tetra methyl ammonium chloride was added to the titration solution. As is shown in figure 4-10 the extra peak (middle peak) was not present and the main middle peak was much sharper than the one on the left hand side.

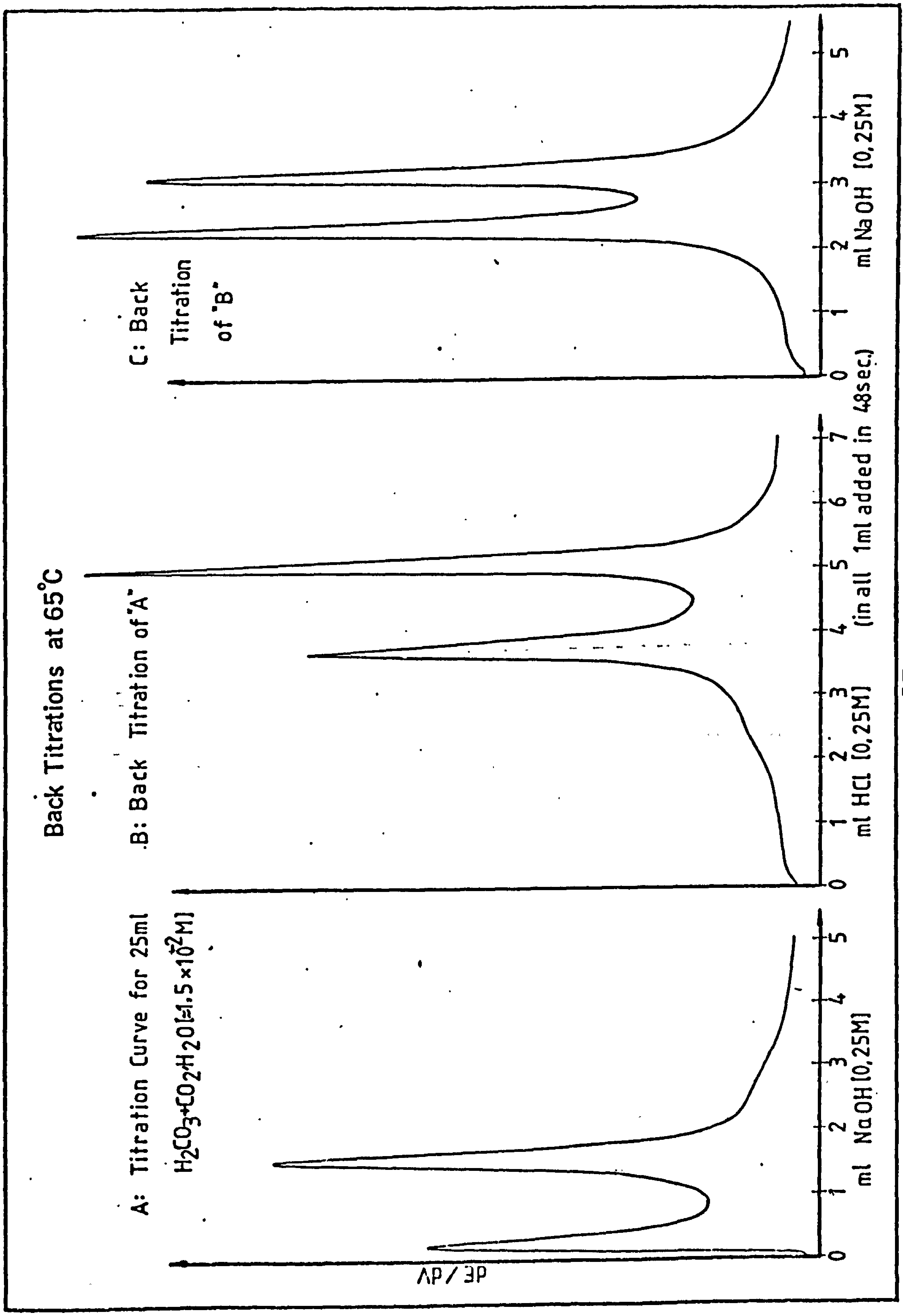

Back Titrations at 65°C
A: Titration Curve for 25ml
$H_2CO_3+CO_2+H_2O$ [=1,5×10^{-2}M]
B: Back Titration of "A"
C: Back Titration of "B"
dE/dV
ml NaOH [0,25M]
0
1
2
3
4
5
ml HCl [0,25M] (in all 1ml added in 48sec.)
0
1
2
3
4
5
6
7
ml NaOH [0,25M]
0
1
2
3
4
5

FIG-4-6

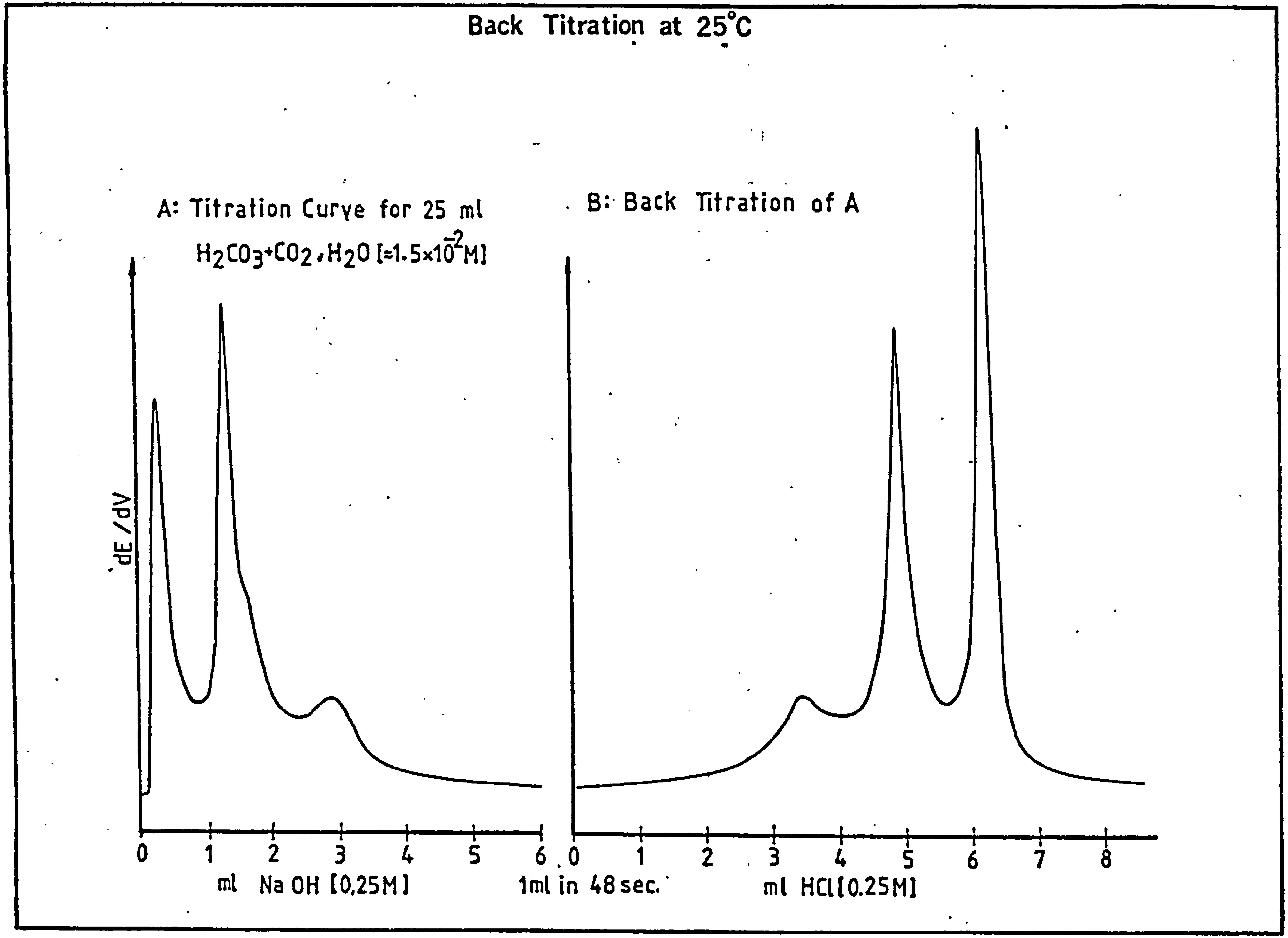

Back Titration at 25°C
A: Titration Curve for 25 ml
$H_2CO_3+CO_2,H_2O$ [=1.5×10^{-2}M]
B: Back Titration of A
dE / dV
0
1
2
3
4
5
6
ml Na OH [0,25M]
1ml in 48 sec.
0
1
2
3
4
5
6
7
8
ml HCl [0.25M]

FIG-4-7

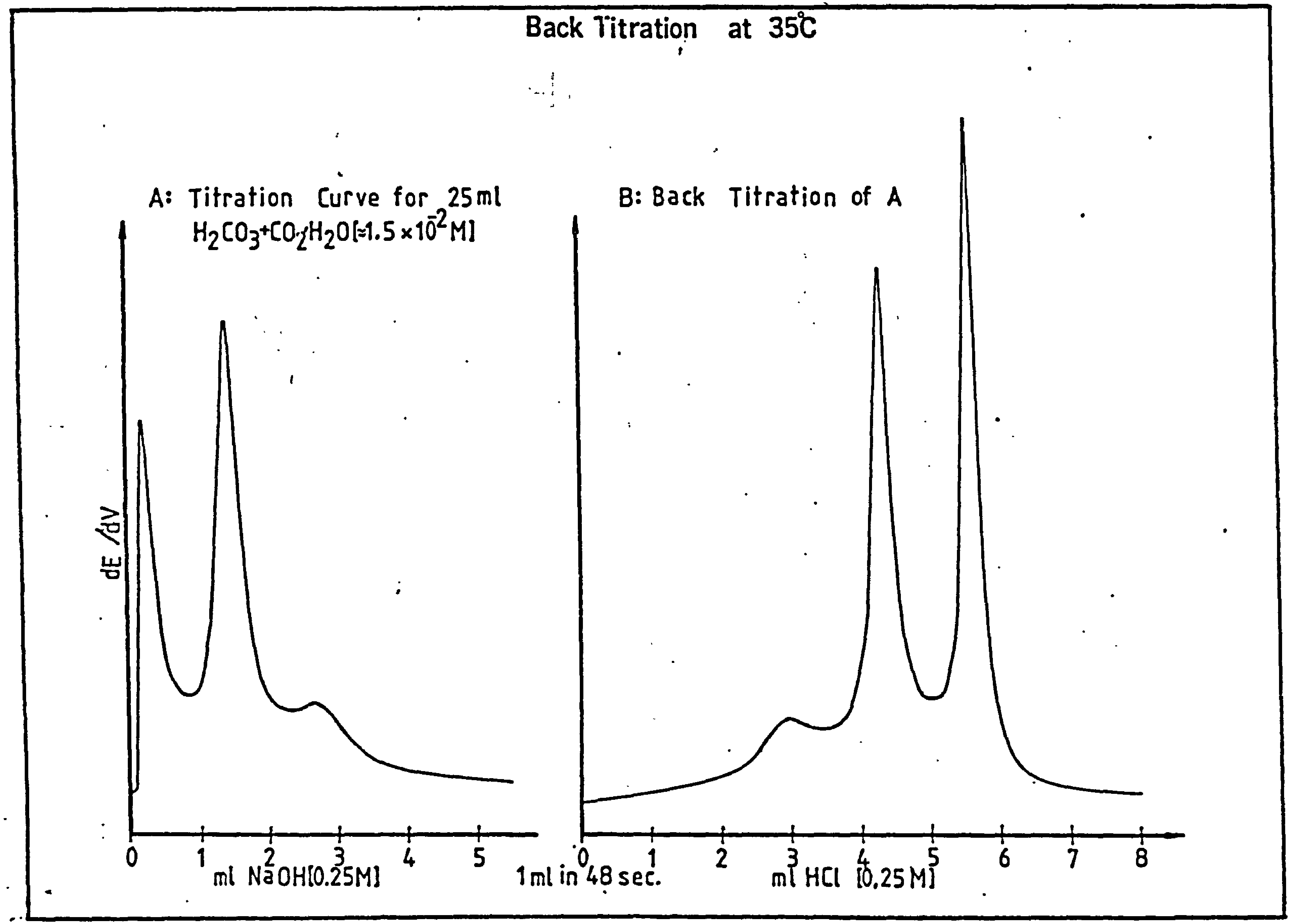

Back Titration at 35°C
A: Titration Curve for 25ml $H_2CO_3+CO_2/H_2O$ [≈1.5×10⁻² M]
B: Back Titration of A
dE /dV
0
1
2
3
4
5
ml NaOH [0.25M]
1ml in 48 sec.
0
1
2
3
4
5
6
7
8
ml HCl [0.25 M]

FIG-4-8

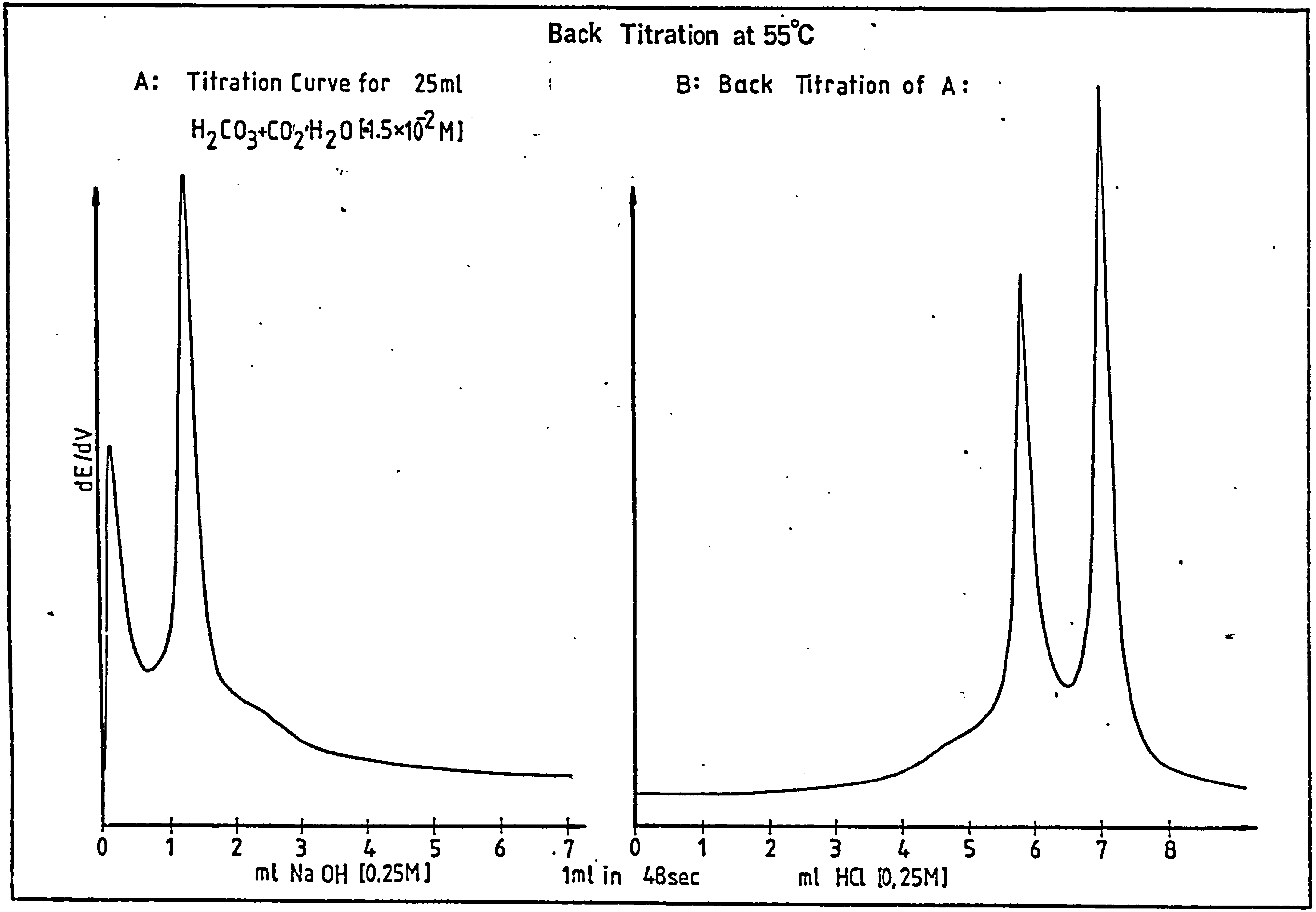

Back Titration at 55°C
A: Titration Curve for 25ml
$H_2CO_3+CO_2 \cdot H_2O$ [1.5×10^{-2} M]
B: Back Titration of A:
dE/dV
0
1
2
3
4
5
6
7
ml Na OH [0.25M]
1ml in 48sec
0
1
2
3
4
5
6
7
8
ml HCl [0,25M]

FIG-4-9

c) In this case the titration solution and the conditions were the same as b) except that TMACl was replaced with NaCl at the same concentration. A comparison of the curve on the right hand side of figure 4-10 with the one on the left hand side shows clearly that the presence of NaCl had little effect on the extra peak in comparison with the effect when TMACl was present in the titration solution.

4.4.1. TITRATION WITH 0.01 mol/l $Ca(OH)_2$

Two types of experiments were carried out for the titration of 25ml of 0.00215 mol/l of dissolved carbon dioxide at 25°C using a Radiometer glass electrode (Type G202B) and the same make of saturated calomel electrode (Type K401 QL-1) as a reference electrode.

In the first experiment titration was carried out with sodium hydroxide at a concentration of 0.02 mol/l. The rate of addition of titrant was 1ml in 48 seconds. The corresponding titration curve is shown on the left hand side of figure 4-11.

The second experiment was exactly the same as the first except that 0.02 mol/l sodium hydroxide was replaced with 0.01 mol/l calcium hydroxide (BDH), but as is shown in figure 4-11 there was no significant effect on the extra peak. It has to be noted that, because of the low solubility of calcium hydroxide in water, these experiments were carried out at lower concentrations of dissolved carbon dioxide and titrants.

4.5.1. TITRATION CURVES IN THE PRESENCE OF NH_4Cl

Again two titrations were carried out with 0.1 mol/l sodium hydroxide with a rate of addition of 1ml in 48 seconds at 25°C. Radiometer glass electrode was used in these titrations(see figure 4-12). In case

Effect of Addition of T.M.A.Cl = $(CH_3)_4NCl$ [4.5M/L] and NaCl [4.5M/L] on Titration Curves at 25°C

Titration Solutions: 25ml $H_2CO_3 + CO_2 \cdot H_2O$ [≈0.02M]

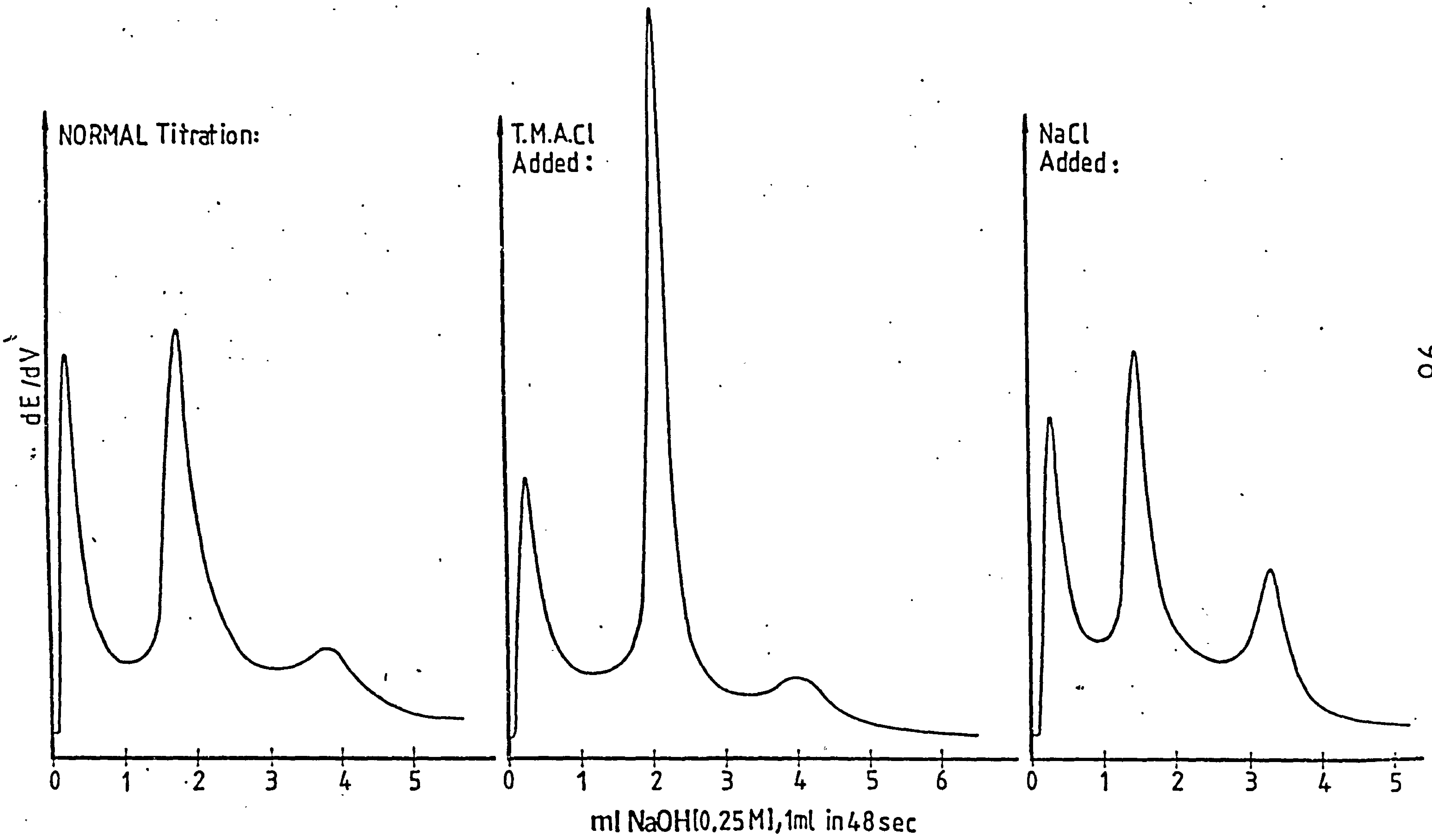


FIG-4-10

Effect of Replacement of Titrant from NaOH to $Ca(OH)_2$ at 25°C

Titration Solutions: 25 ml $H_2CO_3+CO_2{\cdot}H_2O$ [$2{,}15\times10^{-3}$ M]

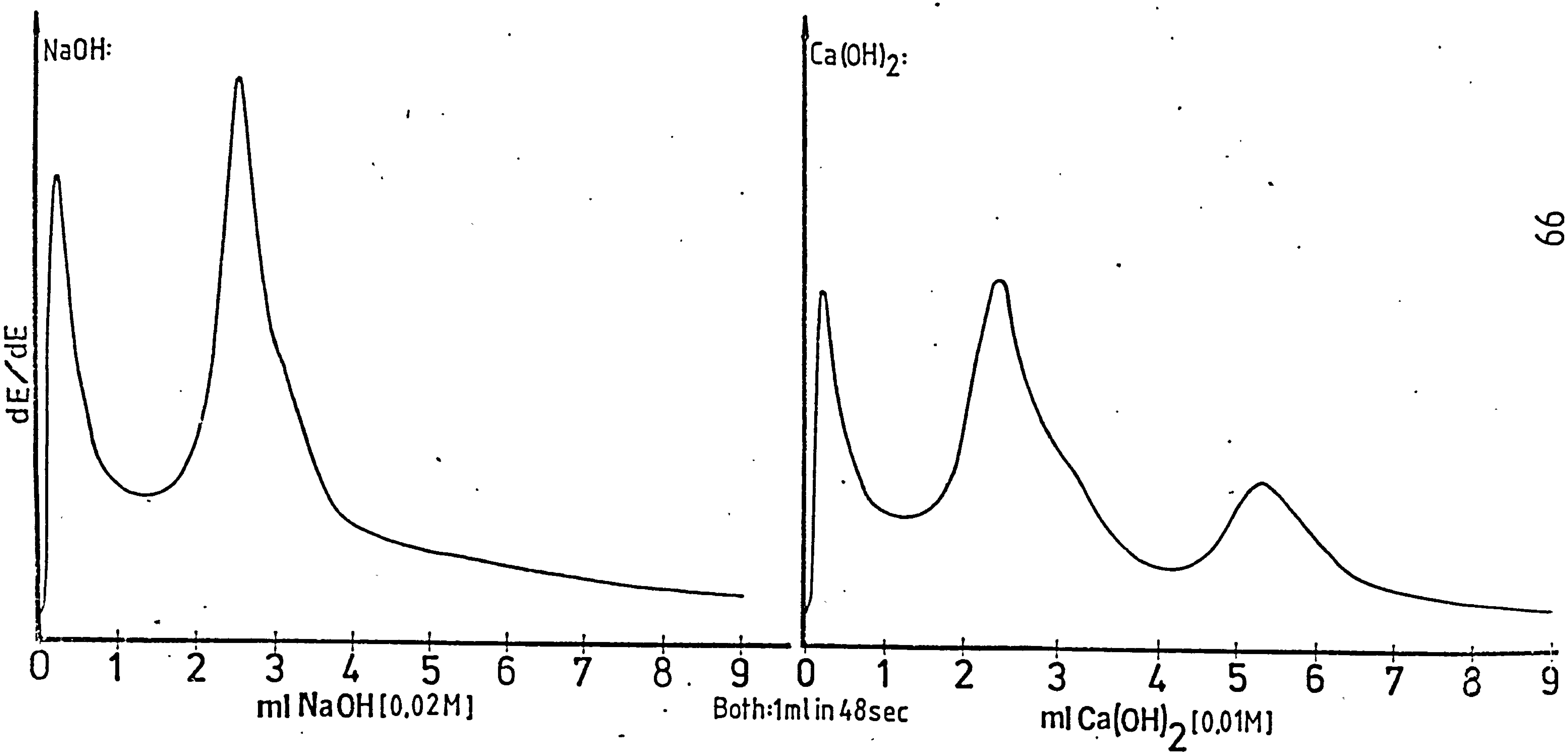
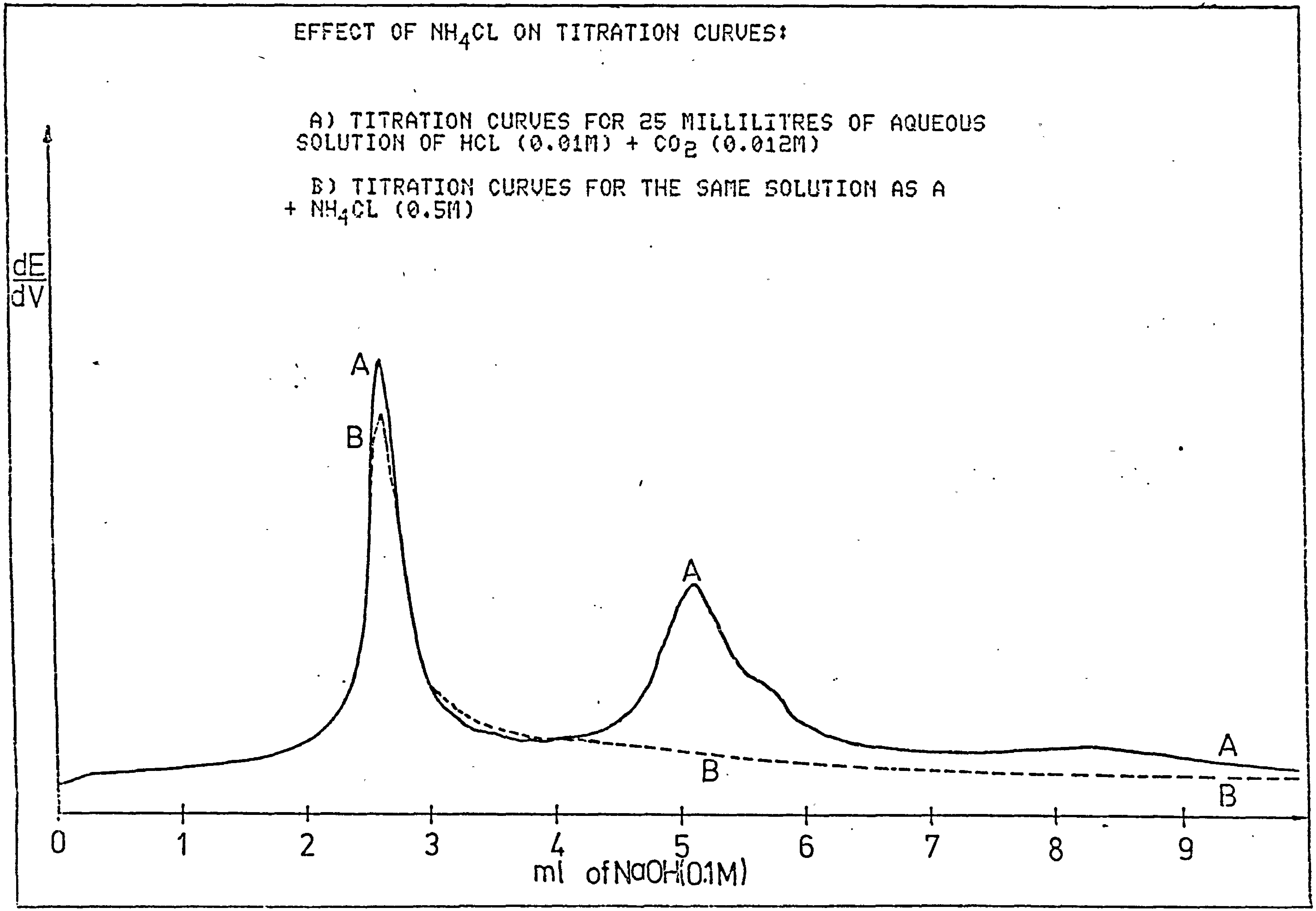


FIG-4-11



EFFECT OF NH_4CL ON TITRATION CURVES:

A) TITRATION CURVES FOR 25 MILLILITRES OF AQUEOUS SOLUTION OF HCL (0.01M) + CO_2 (0.012M)

B) TITRATION CURVES FOR THE SAME SOLUTION AS A + NH_4CL (0.5M)

FIG-4-12

(A) the titration solution was 25 ml of aqeous solution of 0.01 mol/l hydrochloric acid containing about 0.012 mol/l dissolved carbon dioxide again three peaks and a shoulder were recorded in the titration curve. In case (B) the titration solution was the same as (A) except that 0.5 mol/l ammonium chloride (BDH: AnalaR reagent: product no. 395280) was added to the titration solution. Comparing curve (A) with (B) shows clearly that in the presence of ammonium chloride only one clear peak was recorded and that this corresponds to the neutralization of hydrochloric acid. The other peaks are not clear.

Further experiments were carried out to measure the concentration of dissolved carbondioxide in the presence of aqueous solutions of ammonium chloride. This will be described later, where carbonic anydrase was introduced to the titration solution.

4.6.1. REFERANCES:

1) D. M. Kern, The hydration of carbon dioxide, J. Chem. Education, 1960, 37, 14.

2) J. T. Edsall,"Carbon dioxide, carbonic acid and bicarbonate ion, Physical properties and kinetics of Interconversion", NASA, Spec. Publ., 1969, 188, 15.

3) R. E. Loewenthal and G. V. R. Marais, "Carbonate chemistry of aquatic systems.Theory and application", ANN ARBOR Science Press USA, 1976, Chap. 1.

EFFECT OF CARBONIC ANHYDRASE ON TITRATION CURVES

5.1.1.. INTRODUCTION

The carbonic anydrases are extremely efficient catalysts for the reversible hydration of carbon dioxide with maximum turnover number among the highest known for any enzyme (1). The catalytic efficiency of enzymes towards carbon dioxide is, however, several orders of magnitude greater than towards all other substrates so far investigated, and the physiological functions of enzymes are ascribed to the carbon dioxide reaction. The carbonic anhydrases play an important role in respiration as well as in other physiological processes, where the rapid interconversion of carbon dioxide and the bicarbonate ion is essential to the organism. In other words, it has the effect of facilitating the transport of metabolic carbon dioxide in respiration and it is also involved in the transfer and accumulation of H^+ or HCO_3^- in a wide variety of organisms.

Carbonic anhydrase is very widespread in the natural world and occurs in animals (2), plants (3) and certain bacteria.

Mammalian carbonic anhydrase was first reported in 1932 by Meldrum and Roughton who gave it the name carbonic anhydrase (2). But in the plant kingdom (3) carbonic anhydrase was first detected in 1939 in green plants in a study of the composition of certain metabolites and their relative distribution in chloroplasts and cytoplasm.

In 1939, Keilin and Mann (4-5) demonstrated that carbonic anhydrase is a zinc-containing enzyme. Molecular weights for mammalian carbonic anhydrase are about 30,000 (6), whereas the enzymes isolated from plants (e.g. parsley) appear to be considerably larger molecules in size (about 180,000 i.e. six times that of the mammalian enzymes (1 and 7).

From the point of view of composition, all of the mammalian carbonic anhydrases studied, as well as the Neisseria enzyme, are composed of one zinc ion and a single polypeptide chain containing approximately 260 amino acid residues. However, plant enzymes have a hexameric quaternary structure (7, 8). Each polypeptide chain is weakly bonded to a zinc ion, hence there are six zinc ions in the holo enzyme. Each monomer unit, consisting of one polypeptide chain (containing approximately 260 amino acid residues) and one zinc ion, has a molecular weight of about 30,000 (7) which is similar to the value of the mammalian carbonic anhydrase.

The zinc ion, which is located just off centre in the molecule, has been shown to be essential (9) for the activity of carbonic anhydrase. The zinc ion has the highest electron density of the whole map. It has three ligands from the protein molecule and a fourth ligand which seems to be a water or a hydroxyl ion in the active site cavity. The zinc coordination is close to the tetrahedral although rather distorted. The greatest deviation from the tetrahedral angles seems to be around 20°. The active site cavity has a depth of about 15 Å. The zinc ion is located about 12 Å from the ellipsoidal surface of the molecule. In the inner part of the cavity only one aromatic residue, probably a phenylalanine, is a observed. It is almost completely buried in the structure. Many other aromatic residues are found in the neighbourhood of the active site close to the centre. Both the aromatic residue of the structure and the other aromatic clusters are within 10 Å of the zinc ion (1).

Most of the carbonic anhydrases are stable between pH4 and 11.5. Laurent et al (10) showed that human carbonic anhydrase C is irreversibly denatured after exposure to pH12.7 for two minutes, whereas the bovine enzyme can be exposed to pH13 for thirty minutes at 0°C without any irreversible activity loss (11). In addition Rosenberg and Chakravarti (12) showed that there is a loss of structure at lower pH values for carbonic anhydrase enzymes.

CATALYTIC PROPERTIES

a) the catalyzed reactions:

Carbonic anhydrase is a widely distributed zinc metalloenzyme whose physiological role is to catalyse the reversible hydration of carbon dioxide formulated as following:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad (1)$$

This reaction has been studied before, over a wide range of pH, as described previously. Carbonic acid is neglected in equation 1 because it is a rather strong acid, $pK_{H_2CO_3} = 3.8$ at 25°C. The interconversion between H_2CO_3 and HCO_3^- is very fast (13, 14). Hence, in almost the whole pH range of interest for enzyme studies, the concentration of free H_2CO_3 is small compared to that of HCO_3^-. The value of the equilibrium constant K , for the reaction of equation 1 is almost identical with that of the apparent first dissociation constant of carbonic acid (14), K_1 at 25°C and zero ionic strength, $pK_1 \simeq 6.352$ (14). Thus the molecular ratio of concentrations of dissolved carbon dioxide and carbonic acid is approximately 600 at equilibrium. The value of pK_2 for carbonic acid is 10.3; hence CO_3^{2-} can be neglected at pH values below 8.

b) kinetic studies:

McIntosh (15) has improved a useful method suitable for kinetic studies. The hydration reaction is carried out at a constant pH with the aid of an automatic titrimeter.

The rate of carbon dioxide hydration can be determined directly from the rate of base consumption. In the neutral pH range and at low temperatures, using this method, it is possible to measure rates up to 15 times (15) faster than the rate of nonenzymic reactions. The carbonic anhydrases follow a simple Michaelis-Menten behaviour with respect to both carbon dioxide and bicarbonate ions (1). The rate of the enzyme catalyzed reaction, (ν) is:

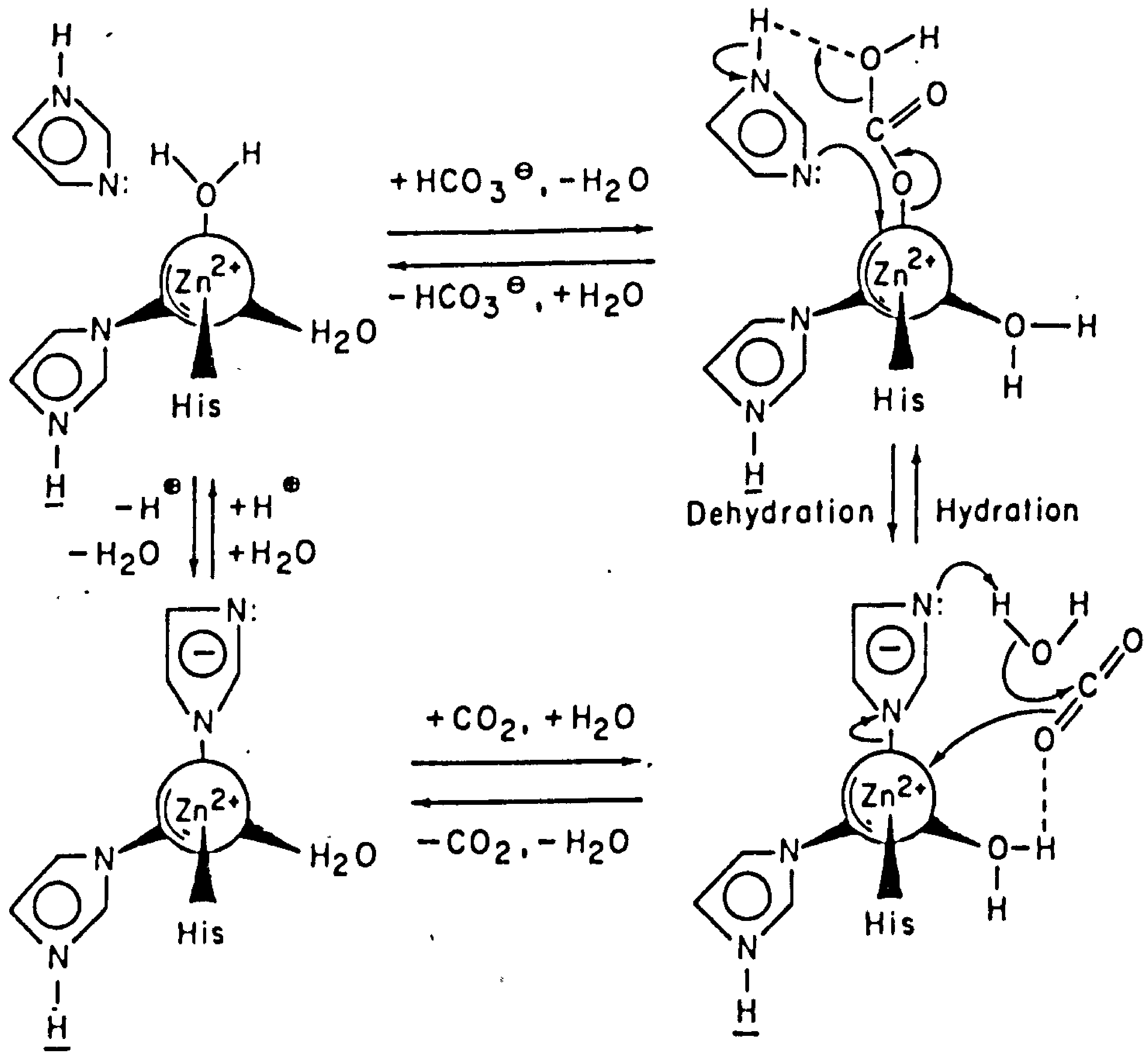
$$\nu = \frac{k_{cat}(S)(E_o)}{K_m + (S)} \qquad \text{Equation(2)}$$

In the following table selected kinetic parameters of bovine and human carbonic anhydrases are shown (1)

	Hydration reaction		Dehydration reaction	
Enzyme	k_{cat} $10^{-6}s^{-1}$	K_m m mol/l	k_{cat} $10^{-4}s^{-1}$	K_m m mol/l
Bovine	1	12	40	26
Human C	1.4	9	8.1	22
Human B	0.2	4	0.3	16

c) The catalytic mechanism:

The schematic model for the catalytic mechanism (16) is shown in figure (5-1). pH dependence of carbonic anhydrase catalyzed reactions has been interpreted as meaning that the activity depends on a group in the enzyme with a pK_a of approximately 7.0. As is shown in this figure the thing which is essential for the function of carbonic anhydrase is the existence of a zinc coordinated water molecule and an aromatic group in the active site and the ionization-governed activity is closely coupled to the metallic ion.



Schematic model for the pH dependence of active site groups and the proposed model for the catalytic mechanism.

FIG 5-1

5.2.1 . EFFECT OF CARBONIC ANHYDRASE ON THE TITRATION CURVES OF dE/dV AGAINST VOLUME WITH 0.25 mol/l HYDROCHLORIC ACID USING THE GLASS ELECTRODE.

To investigate the effect of a trace of carbonic anhydrase enzyme on the titration curves, the following two experiments were carried out using a Radiometer glass electrodes type G202B at 25°C.

The first experiment was the titration of 25 ml of 0.04 mol/l aqueous solution of sodium hydroxide containing 0.004 mol/l sodium carbonate. The rate of addition of 0.25 mol/l hydrochloric acid was 1ml in 48s. The corresponding titration curve is shown on the left hand side of figure 5.2. The second titration was the same as the above except that approximately 5×10^{-7} mol/l (1 milligram) of carbonic anhydrase was added to the titration solution. As is shown on the right hand side of figure 5-2. the extra peak was removed and because of this the minimum between the two peaks of carbonate was decreased considerably.

In another series of experiments the titration solutions contained 0.008 mol/l sodium carbonate and the rate of addition of 0.25 mol/l hydrochloric acid was the same as before. As is shown in figure 5-3, the effect of carbonic anhydrase is the same as before, and is responsible for the removal of the extra paek. Because of this, the first peak for carbonate becomes sharper (compare curves B and A in figure 5-3).

5.2.2. EFFECT OF CARBONIC ANHYDRASE ON THE TITRATION CURVES IN THE PRESENCE OF AMMONIUM CHLORIDE USING A GLASS ELECTRODE.

To clarify the effect of carbonic anhydrase on the titration of sodium hydroxide solution containing both sodium carbonate and ammonium hydroxide at 25°C, the following two titrations were carried out, using a Radiometer glass electrode. The first titration was carried out with 0.25 mol/l

Effect of Addition of CARBONIC ANHYDRASE ENZYME [C.A.] into The Titration Solution at 25 C°:

FIG-5-2

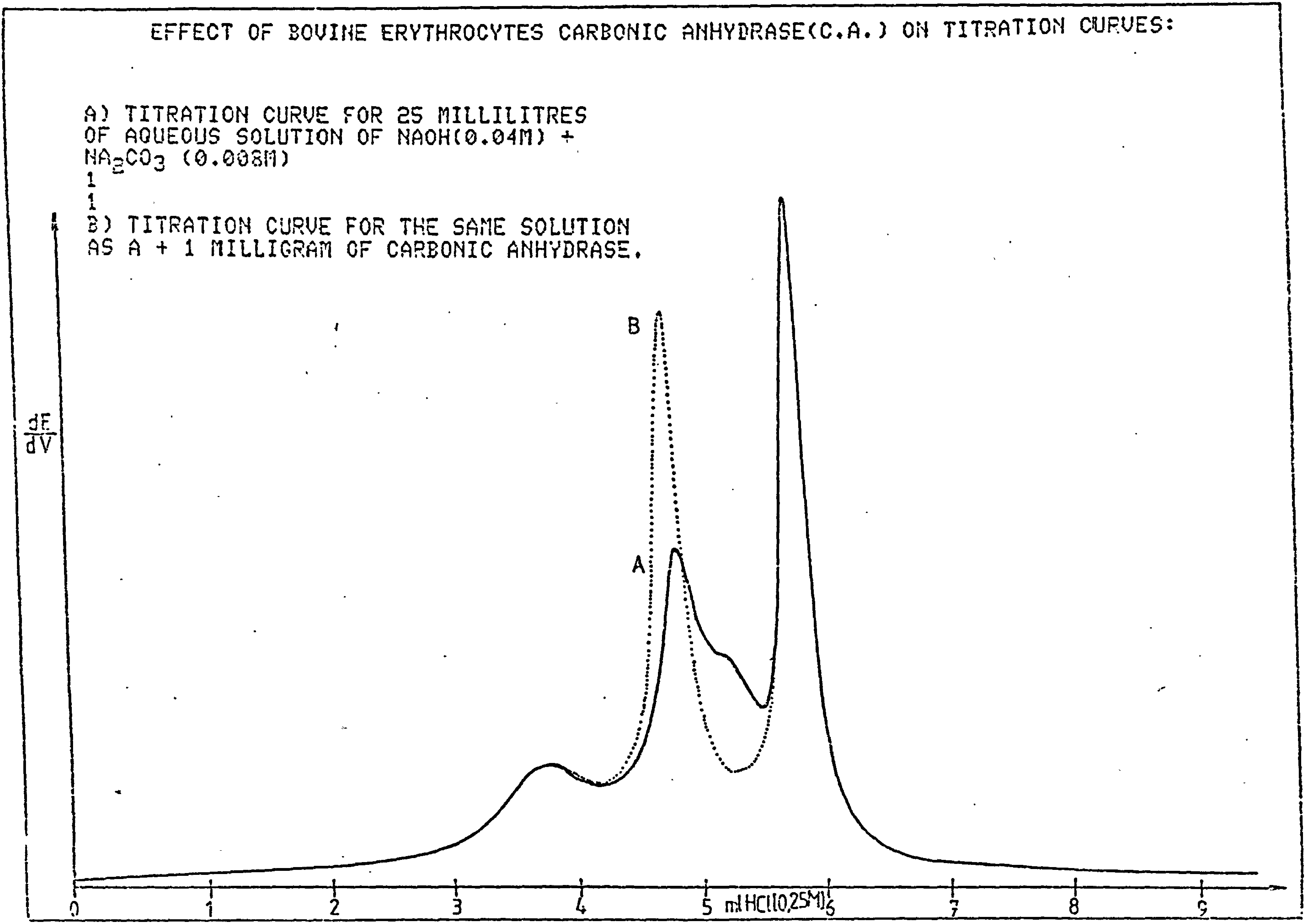
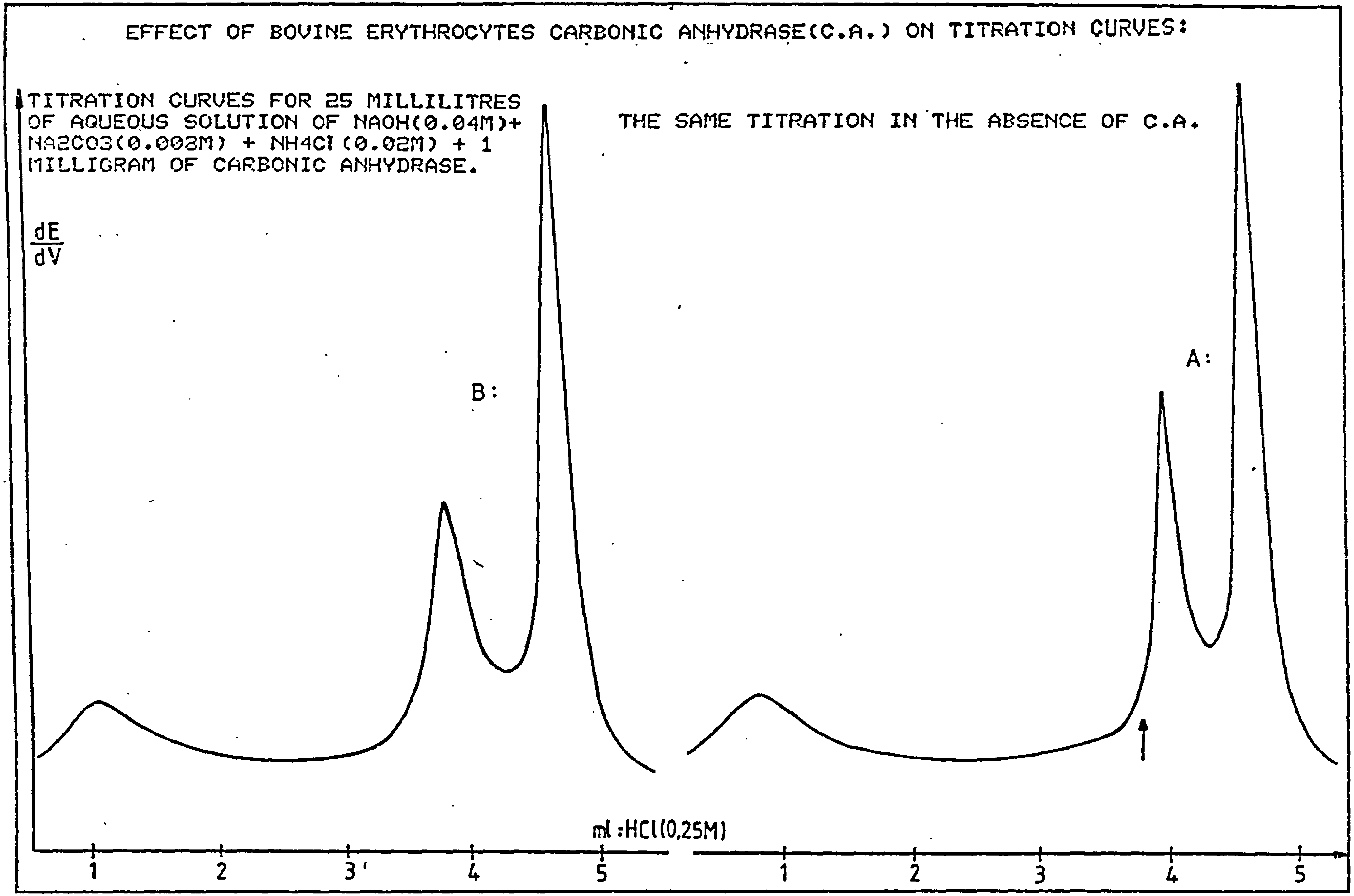

EFFECT OF BOVINE ERYTHROCYTES CARBONIC ANHYDRASE(C.A.) ON TITRATION CURVES:
A) TITRATION CURVE FOR 25 MILLILITRES OF AQUEOUS SOLUTION OF NAOH(0.04M) + NA$_2$CO$_3$ (0.008M)
1
1
B) TITRATION CURVE FOR THE SAME SOLUTION AS A + 1 MILLIGRAM OF CARBONIC ANHYDRASE.
B
A
dE/dV
0
1
2
3
4
5
ml HCl(0,25M)
6
7
8
9

FIG-5-3

hydrochloric acid witha rate of addition of 1 ml in 48s, for 25ml aqueous solution of 0.04 mol/l of sodium hydroxide containing 0.008mol/l sodium carbonate and 0.03mol/l ammonium chloride.(0.03mol/l ammonium chloride will react with sodium hydroxide to form 0.03mol/l ammonium hydroxide, so the remaining composition of the solution is 0.01mol/l sodium hydroxide, 0.008 mol/l sodium carbonate and 0.03mol/l ammonium hydroxide).

In the titration curve, the first peak is due to the neutralization of both ammonium hydroxide and sodium carbonate. This is because there is not enough difference between the pK values of these two compounds, and hence there is no separate peak for each of them. A shoulder on the middle peak in the titration curve indicates the end point for the conversion of carbonate ions to bicarbonate ions and ammonium hydroxide to ammonium chloride. (as indicated by an arrow on the titration curve on the right hand side of figure 5-4). By continuing the titration, first the middle peak appeared and then the third peak, which indicates the end point of the conversion of bicarbonate to carbon dioxide gas.

The second titration was the same as the previous one, except that 1 milligram of carbonic anhydrase was introduced to the titration solution. As shown in figure 5-4-B in the titration of this solution, the middle peak moved towards the first peak of titration to the same position as the shoulder for the middle peak in the first titration and combined with it, but the other two peaks were unaffected. This indicates that in the first titration the middle peak is the extra peak and the main peak of the titration is the shoulder. Since the distance between the middle peak and the third peak of neutralization, in the second titration corresponds to the concentration of carbonate ions. Hence, by using this value and also the value of titrant which was used between the first and second peak of neutralization in the second run, it is possible to calculate both the concentration of carbonate and ammonium hydroxide, which would not be possible in the absence of C.A.



EFFECT OF BOVINE ERYTHROCYTES CARBONIC ANHYDRASE(C.A.) ON TITRATION CURVES:

TITRATION CURVES FOR 25 MILLILITRES OF AQUEOUS SOLUTION OF NAOH(0.04M)+ NA2CO3(0.008M) + NH4CI (0.02M) + 1 MILLIGRAM OF CARBONIC ANHYDRASE.

THE SAME TITRATION IN THE ABSENCE OF C.A.

FIG-5-4

5.3.1. EFFECT OF CARBONIC ANHYDRASE ON dE/dV AGAINST VOLUME OF 0.1mol/l SODIUM HYDROXIDE .

Titration were carried out to clarify the effect of the presence of carbonic anhydrase on the titration curve of acidic solution containing dissolved carbon dioxide at 25°C using a Radiometer glass electrode type G202B.

As is shown in figure 5-5, two titrations were carried out for 25ml solution of 0.02 mol/l of hydrochloric acid containing about 0.0105 mol/l dissolved carbon dioxide with 0.25mol/l sodium hydroxide solution. In the first titration no carbonic anhydrase was added into the titration solution, in the second titration a trace of carbonic anhydrase (1milligram) was introduced into the titration solution.

As is clear from figure 5-5, in the absence of carbonic anhydrase the extra peak was well-defined and recorded, but in the presence of carbonic anhydrase the extra peak was not recorded in the titration curve, and a shoulder on the middle peak, representing the main peak of the carbonate system, became more pronounced.

5.3.2. EFFECT OF CARBONIC ANHYDRASE ON THE TITRATION CURVES IN THE PRESENCE OF AMMONIUM CHLORIDE.

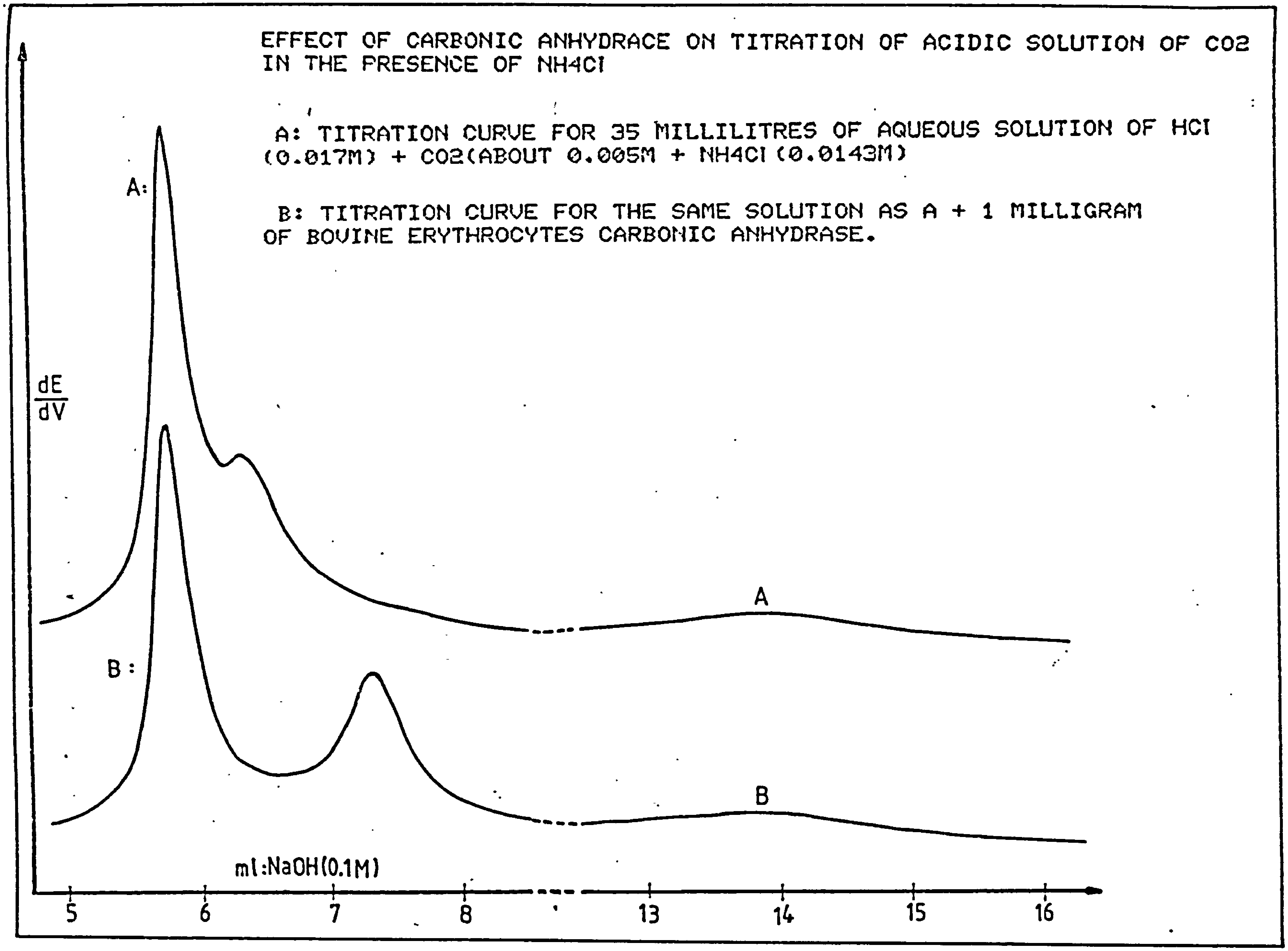
The same type of titrations as before were carried out but in the presence of ammonium chloride. A Radiometer glass electrode type G202B was again used at 25°C . The titration solutions were 35ml aqueous solution of 0.017 mol/l hydrochloric acid containing 0.005mol/l dissolved carbon-dioxide and 0.0143 mol/l ammonium chloride.

As shown in figure 5-6 in case of A, where no carbonic anhydrase was introduced into the titration solution; first a sharp peak indicating the end of protonation of hydrochloric acid appeared and then the next peak

Effect of CARBONIC ANHYDRASE on Titration Curves Using Radiometer Glass Electrode at 25°C

Titration Solution: 25ml HCl [2×10^{-2}M] Containing $H_2CO_3 + CO_2 \cdot H_2O$ [$1{,}05\times10^{-2}$M]

FIG-5-5



EFFECT OF CARBONIC ANHYDRACE ON TITRATION OF ACIDIC SOLUTION OF CO_2 IN THE PRESENCE OF NH_4Cl

A: TITRATION CURVE FOR 35 MILLILITRES OF AQUEOUS SOLUTION OF HCl (0.017M) + CO_2(ABOUT 0.005M + NH_4Cl (0.0143M)

B: TITRATION CURVE FOR THE SAME SOLUTION AS A + 1 MILLIGRAM OF BOVINE ERYTHROCYTES CARBONIC ANHYDRASE.

FIG-5-6

was the additional peak, and a very diminished peak at about 7.2 ml of titrant also appeared, indicating the end of protonation of dissolved carbon dioxide to bicarbonate. The recorded peak at about 14ml of titrant is an indication of the end point of the protonation of bicarbonate and ammonium chloride.This is due to the pK values for these two compounds being nearly the same. This makes it impossible to see a separate peak for ammonium chloride protonation. However, since the middle peak is very ill-defined (see figure 5-6), it is hardly possible to indicate the concentration of dissolved carbon dioxide in acidic solutions containing ammonium chloride.

Introducing a trace of carbonic anhydrase into the titration solution solved this problem. The extra peak disappeared from the titration curve and the middle peak became sharper, thus providing a good indication of the end point of neutralization of dissolved carbon dioxide. At the same time, the other peaks were not affected.

Using the volume of titrants between the middle peak and the third peak, which is an indication of the conversion of both ammonium chloride to ammonium-hydroxide and bicarbonate ions to carbonate ions, it is possible to calculate the concentration of both dissolved carbon dioxide and ammonium chloride by titrimeteric analysis. In other words it becomes possible, to measure the dissolved carbon dioxide concentration in ammonium chloride solution. This effect of carbonic anhydrase on these titration curves could be used in enviromental and industrial studies.

5.4.1. EFFECT OF EXCESS AMOUNT OF CARBONIC ANHYDRASE ON THE TITRATION CURVES AND THE CORRESPONDING BACK TITRATIONS:

To clarify the effect of the addition of excess amount of carbonic anhydrase on the titration curves, three more titrations with 0.25mol/l hydrochloric acid and corresponding back titrations with 0.25mol/l sodium hydroxide were carried out at 25°C.

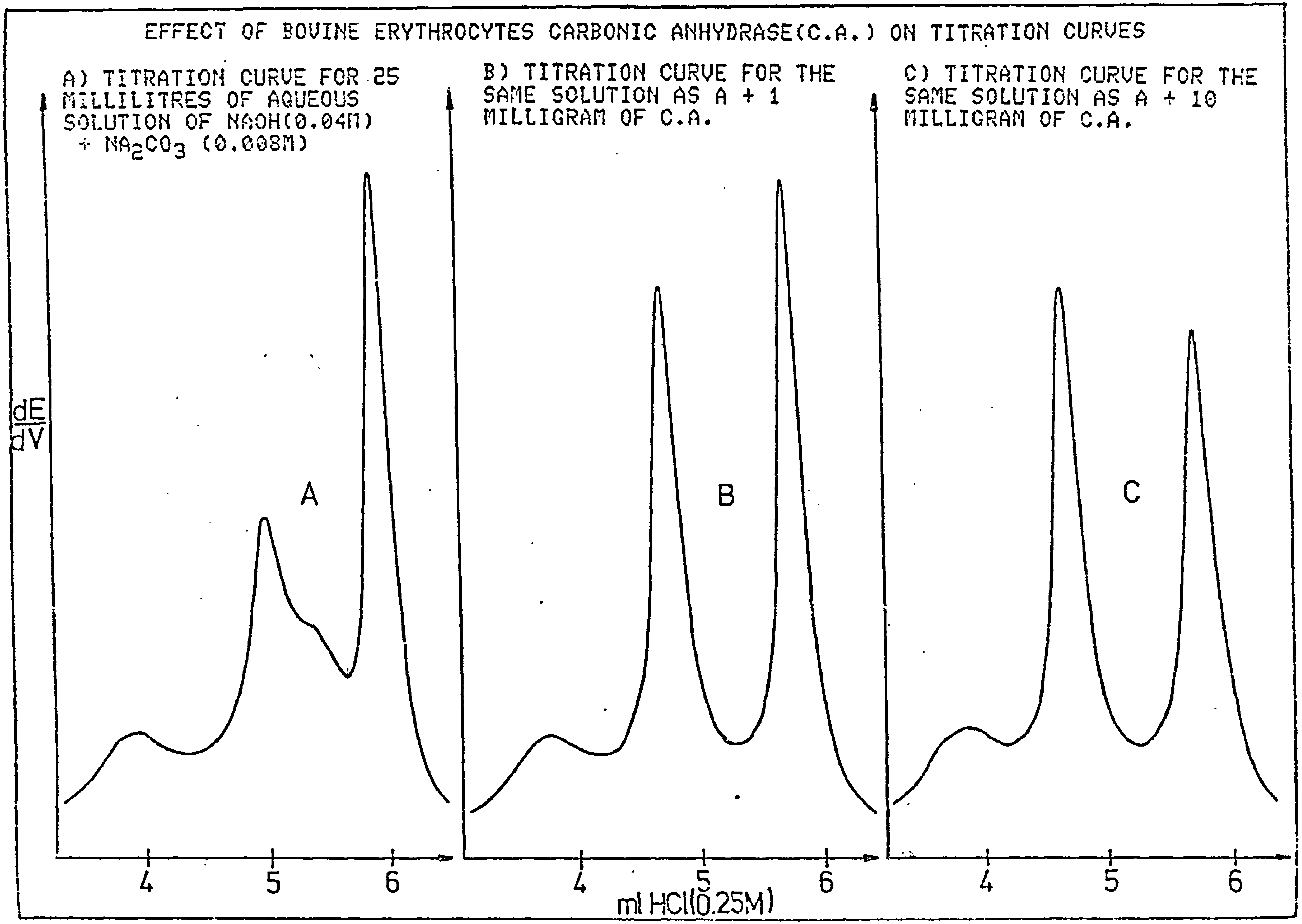
The titrations solutions were 25ml of aqueous solution of 0.04 mol/l sodium hydroxide containing 0.008mol/l sodium carbonate. As is shown in figure 5-7 in the case of B and C, 1 milligram and 10 milligrams of carbonic anhydrase respectively were added into the titration solution. In the case of B the extra peak was not recorded and the middle peak was sharper. But in the case C, the 3rd peak diminished in height and the other two peaks remained unchanged. In addition a white precipitation appeared in the titration process. However, as can be concluded from these results, to obtain the best results using carbonic anhydrase as a catalytical reagent in these titrations, about 1 milligram of carbonate anhydrase should be added to 25ml of titration solution .

Corresponding back titrations of titrated solutions of A,B and C were carried out with 0.1mol/l sodium hydroxide, as shown in figure 5-8. (A1, B1 and C1). In addition better results were obtained with the addition of 1 milligram of carbonic anhydrase to the titration solutions as shown in figure B1. The rate of addition of titrant was 1ml in 48s and all of the experiments were carried out at 25°C.

5.5.1. EFFECT OF CARBONIC ANHYDRASE ON THE TITRATION CURVES OF dE/dV AGAINST VOLUME OF 0.1mol/l SODIUM HYDROXIDE FOR THE CARBON-DIOXIDE ELECTRODE.

To investigate the effect of carbonic anhydrase on the titration curves of the carbon dioxide electrode, two titrations were carried out using a Radiometer carbon dioxide electrode at 25°C.

The titration solution in both cases was 25ml 0.02mol/l hydrochloric acid containing 0.01mol/l dissolved carbon dioxide. The rate of addition of 0.1 mol/l sodium hydroxide in both titrations was 1ml in 4 minutes. The first titration was a normal titration as shown on the left hand side of figure 5-9. In the second titration 1 milligram of carbonic anhydrase was introduced into the titration solution(as shown on the right hand side of figure 5-9).



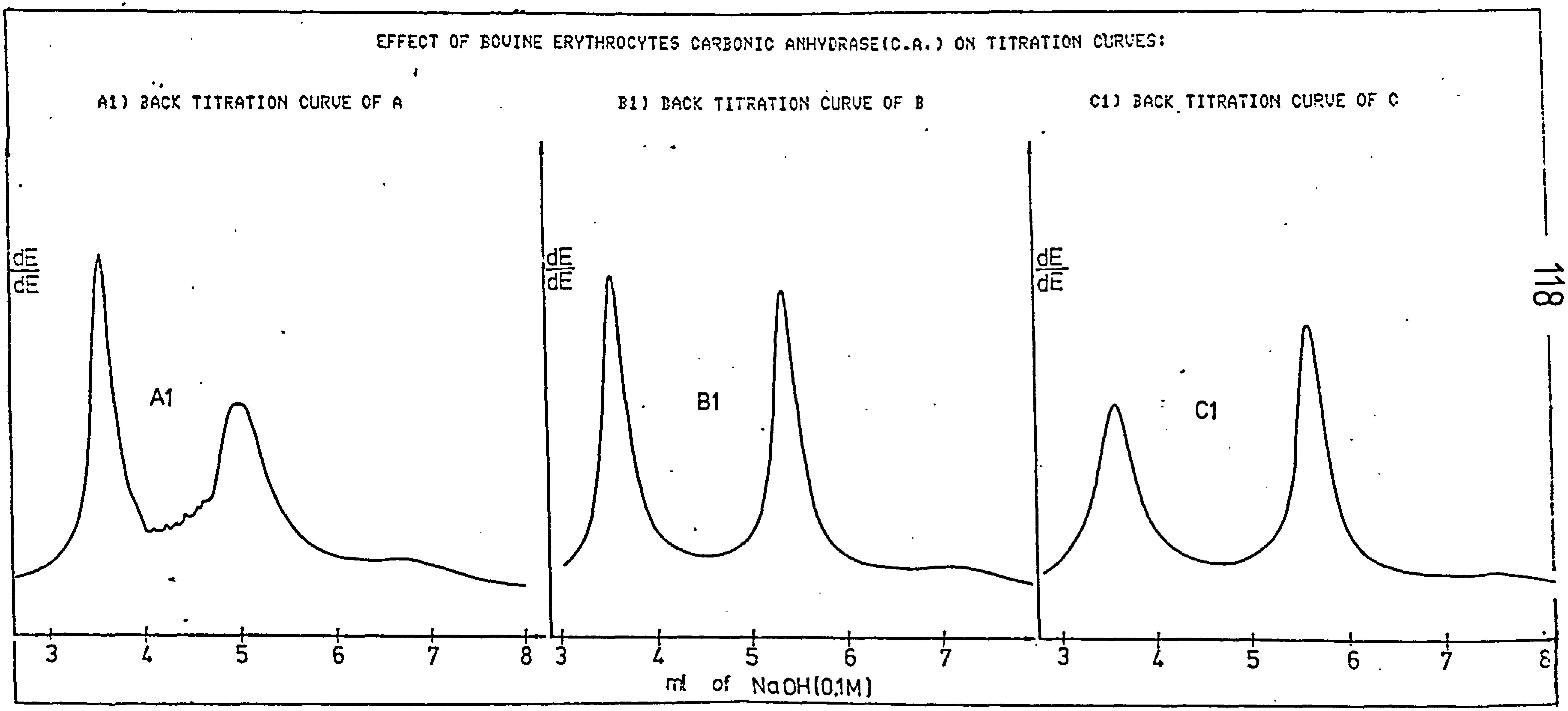
EFFECT OF BOVINE ERYTHROCYTES CARBONIC ANHYDRASE(C.A.) ON TITRATION CURVES

A) TITRATION CURVE FOR 25 MILLILITRES OF AQUEOUS SOLUTION OF NAOH(0.04M) + NA_2CO_3 (0.008M)

B) TITRATION CURVE FOR THE SAME SOLUTION AS A + 1 MILLIGRAM OF C.A.

C) TITRATION CURVE FOR THE SAME SOLUTION AS A + 10 MILLIGRAM OF C.A.

FIG-5-7



EFFECT OF BOVINE ERYTHROCYTES CARBONIC ANHYDRASE(C.A.) ON TITRATION CURVES:

A1) BACK TITRATION CURVE OF A

B1) BACK TITRATION CURVE OF B

C1) BACK TITRATION CURVE OF C

FIG-5-8

Effect of CARBONIC ANHYDRASE on Titration Curve Using Radiometer CO_2 Electrode at 25°C

Titration Solution: 25 ml HCl [2×10^{-2} M] Containing $H_2CO_3 + CO_2 \cdot H_2O$ [10^{-2} M]

FIG-5-9

As a result of this the peak for the carbon dioxide neutralization became sharper. This is due to the fast kinetics of the carbon dioxide hydration in the presence of carbonate anhydrase in aqueous solutions as mentioned previously.

5.6.1. TITRATION CURVES FOR BALANCED SALT SOLUTION OF WARM-BLOODED ANIMALS AND THE EFFECT OF C.A. ON THE TITRATION CURVES.

A simple version of Earle's solution (1943) was made up as follows;

6.8g	NaCl	BDH	AnalaR
0.4g	KCl	BDH	AnalaR
2.2g	$NaHCO_3$	BDH	AnalaR

500 ml of this solution was saturated with 5% carbon dioxide in air at 37°C, by bubbling gas through the solution for four hours.

10 ml of this solution was taken and 15ml distilled water added before titration which was carried out at 25°C. Using 0.1 mol/l sodium hydroxide , with a rate of addition of titrant of 1 ml in 48s, titration curves were obtained as shown on the left hand side of figure 5-10.

Back titration of titrated solution was carried out with 0.25mol/l hydrochloric acid at 25°C to obtain the curve on the right hand side of figure 5-10.

Again back titration of titrated solution was carried out, titrating firstly with 0.1mol/l sodium hydroxide ant then with 0.25 mol/l hydrochloric acid. Corresponding titration curves are shown in figure 5-11.

As is clear from these titration curves, the extra peak is present, and comparing the two curves on the right hand side in figures 5-10 and 5-11 shows that the extra peak is repeatable for balanced salt solution. The same type of titrations were again carried out using the same balanced salt solution as above at the same conditions except that $5x10^{-7}$ mol/l carbonic anhydrase was added to the titration solution before starting the

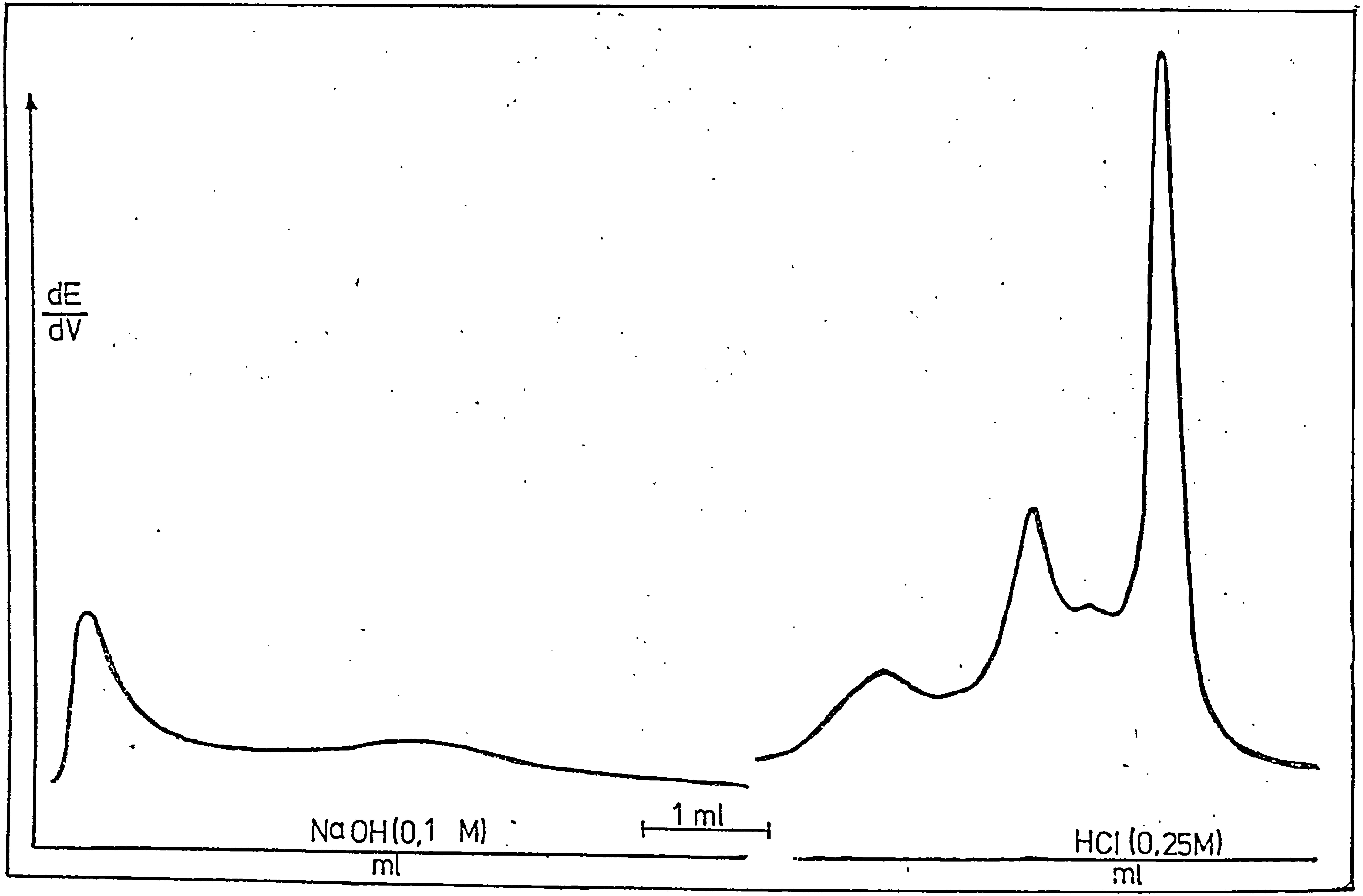
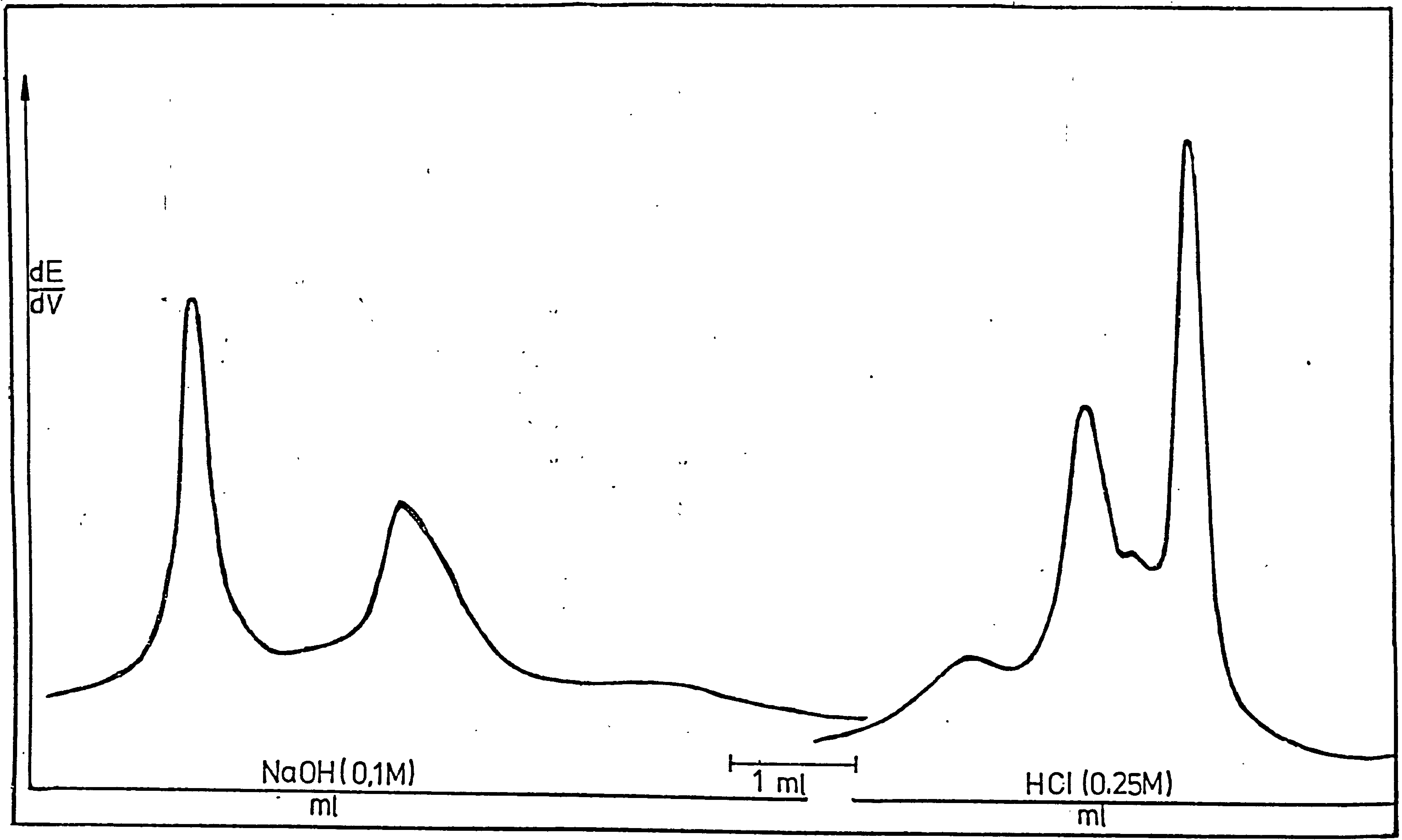


FIG – 5-10



FIG—5-11

titration. Corresponding titration curves are shown in figure 5-12 and figure 5-13. A comparison of figures5-10 and 5-11 with figures 5-12 and 5-13 respectively, shows that in the presence of carbonic anhydrase the height of the middle peak increased but the extra peak was not recorded .

Another titration was carried out with 0.25mol/l hydrochloric acid for the same balanced salt solution and the above conditions . The curve on the left hand side of figure 5-14 was obtained. The same type of titration was again carried out with 5×10^{-7} mol/l carbonic anhydrase added to titration solution before the titration begon; the titration curve is shown on the right hand side of figure 5-14. Comparison of these two curves in figure 5-14 also shows clearly that the extra peak was not recorded in the presence of carbonic anhydrase.

6.7.1. EFFECT OF CARBONIC ANHYDRASE ON TITRATION CURVES OF dE/dV Vs. pH;

The same type of titration was carried out, but dE/dV was recorded against pH rather than the volume of titrant . The result is shown in figure 5-15 on the left hand side. The extra peak is also recorded as expected in this type of titration curve, but it was again removed when a trace of carbonic anhydrase was introduced into the titration solution, as shown on the right hand side of this figure.

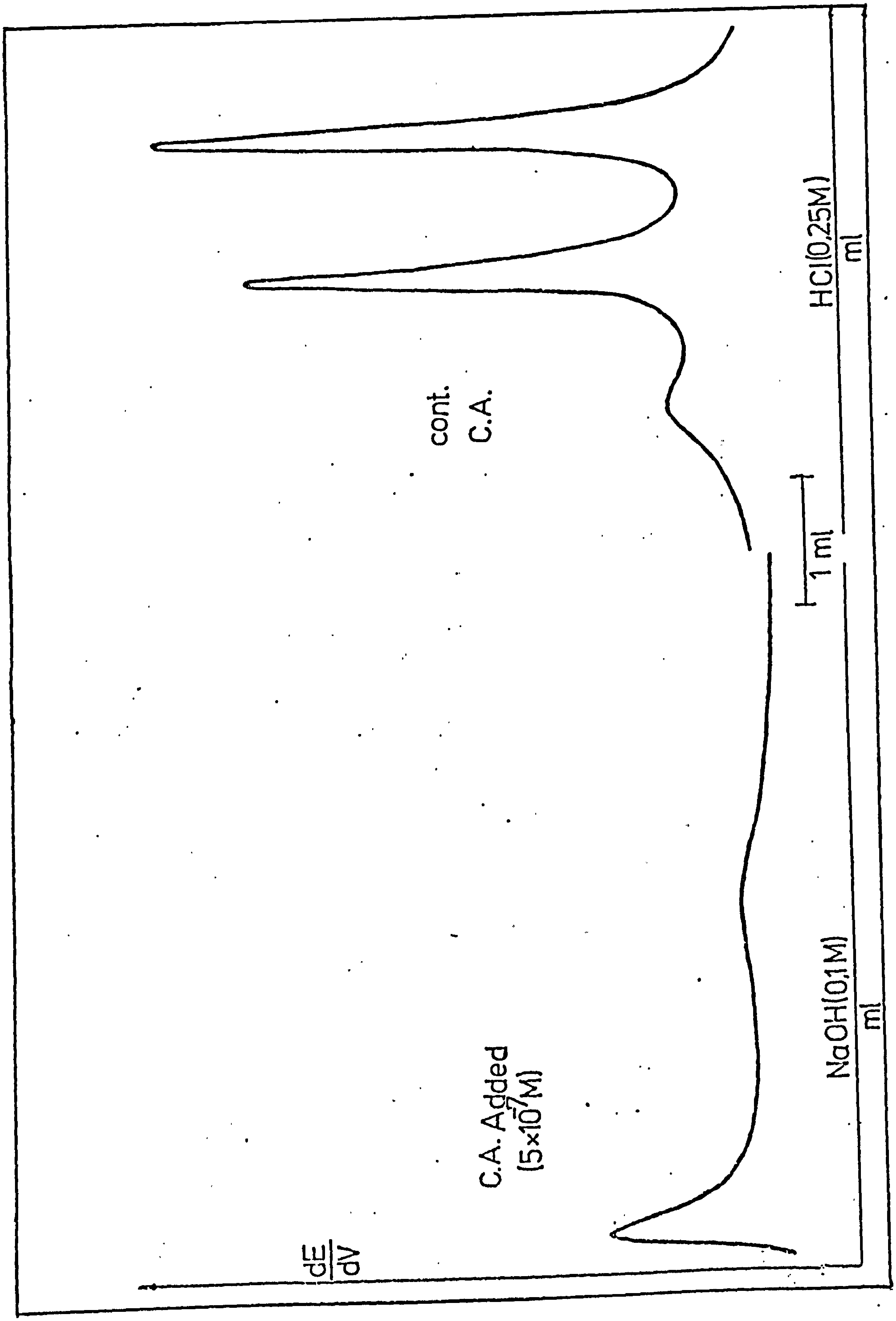


FIG-5-12

FIG – 5–13

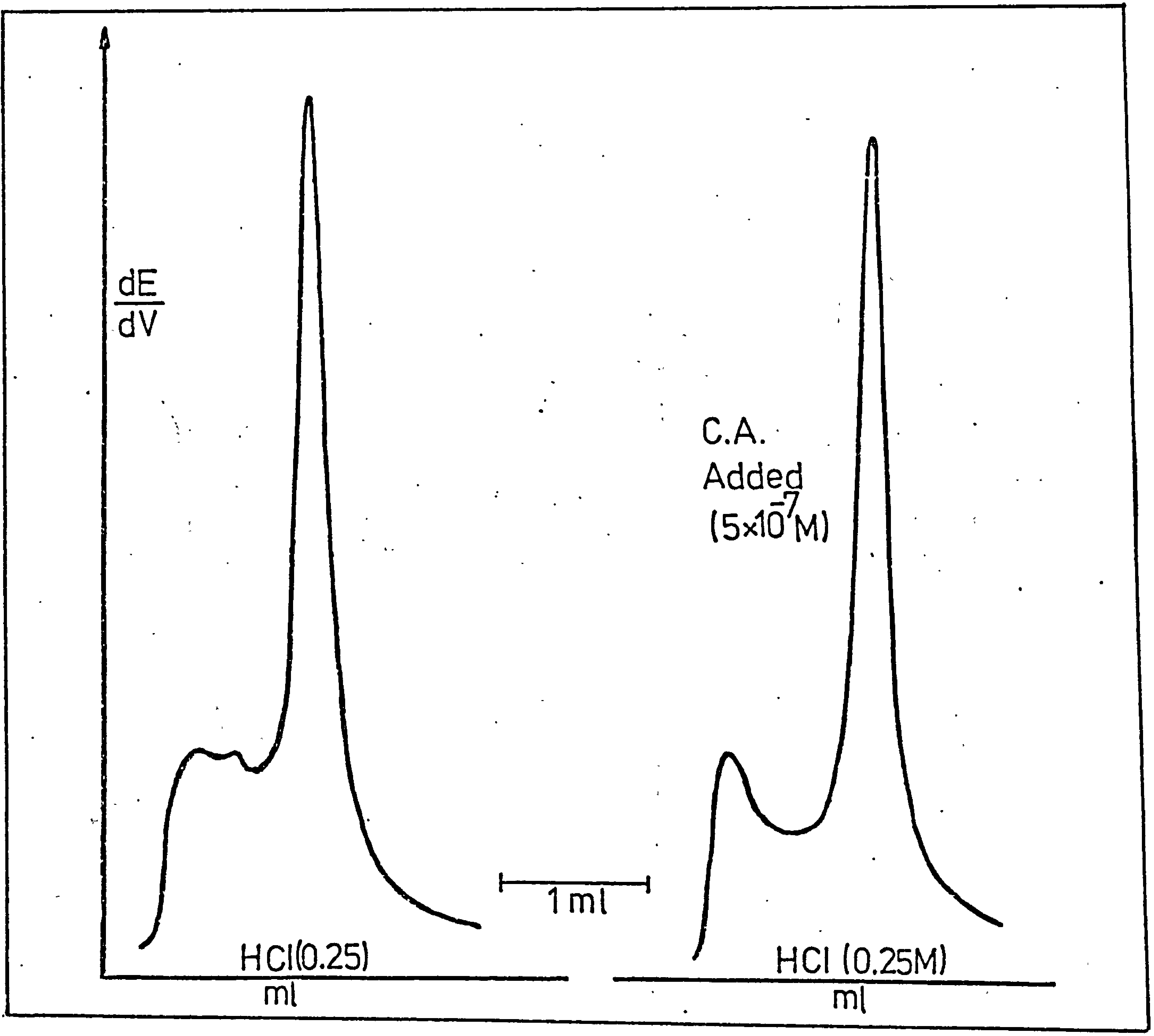


FIG-5-14

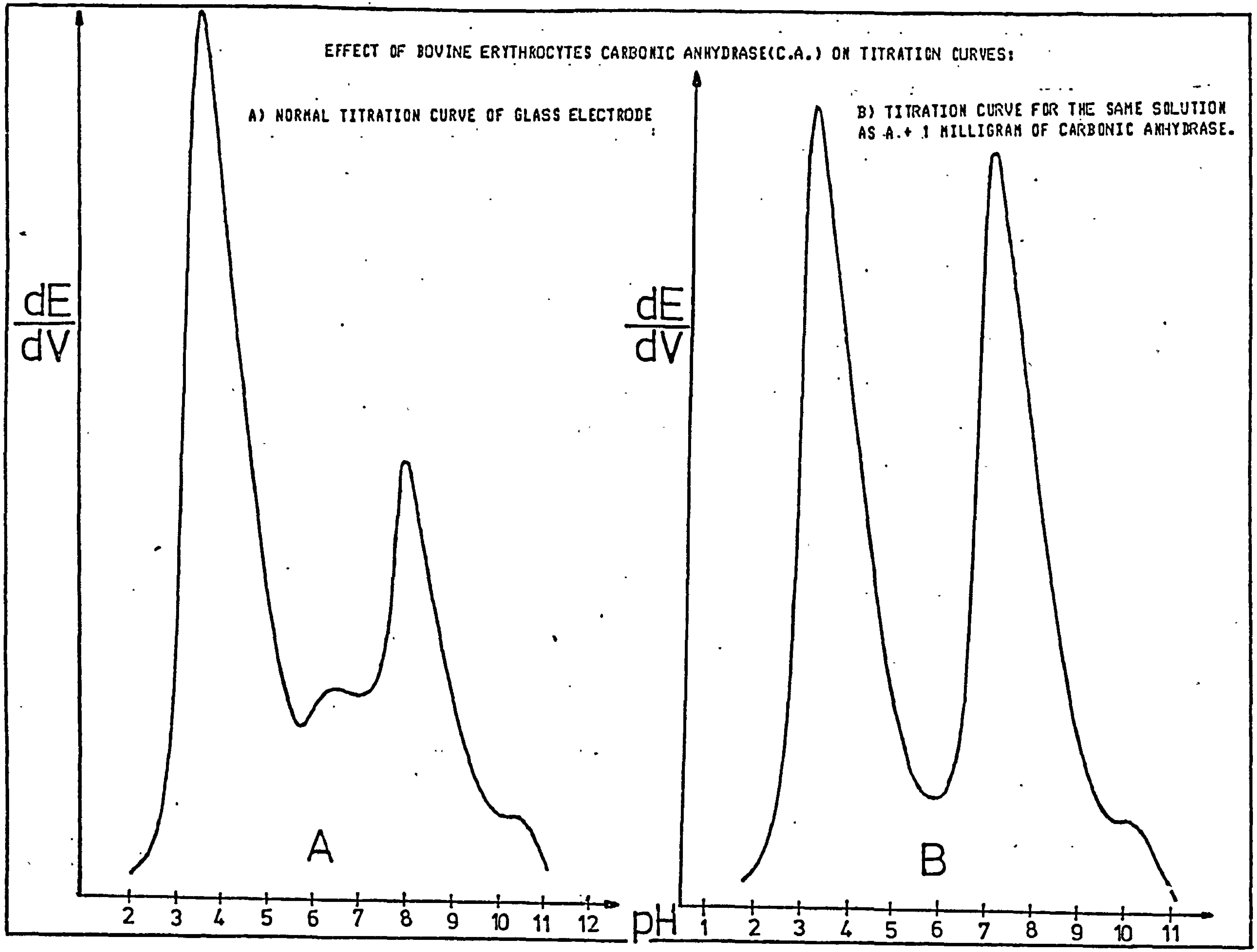

EFFECT OF BOVINE ERYTHROCYTES CARBONIC ANHYDRASE(C.A.) ON TITRATION CURVES:
A) NORMAL TITRATION CURVE OF GLASS ELECTRODE
B) TITRATION CURVE FOR THE SAME SOLUTION AS A.+ 1 MILLIGRAM OF CARBONIC ANHYDRASE.
dE/dV
A
2
3
4
5
6
7
8
9
10
11
12
pH
dE/dV
B
1
2
3
4
5
6
7
8
9
10
11

FIG-5-15

6.8.1 REFERENCES.

1- Boyer, "The Enzymes" 3rd ed. Academic Press , 1971, 5,587.

2- N.U. Meldrom and F.J.W. Roughton, J.Physiol. (London) 1932,75,4; Proc. Roy. Soc. BIII,296,1932.

3- A.D. Neish, Biochem. J., 1939,33, 300.

4- D.Keilin and T.Mann, Nature, 1939, 144 , 442.

5- D.Keilin and T.Mann,J.Biochem. ,1940,34,1163.

6- Nostran.I.Vaara and K.K.Kannan, in Isozymes,I.Molecular Structure (C.L. Markert, Ed.) Academic Press, New York 1975,575.

7- Y.Pocker, and J.S.Y. Ng, Biochemistry,1973,12,5127.

8- A.J.Tobin, J.Biochem. 1970,245,2656.

9- S.Lindskog, and B.G. Malmstrom, J.Biochem. 1962,237,1129.

10- G.Laurent, D.Garcon, M.Charrel and Y.Derrien, Compt. Rend. Soc. Biol. 1963,157,2028.

11- A.Nilsson and S.Lindskog, European J.Biochem. 1969,2,309.

12- A.Rosenberg and K.Chakravarti. J.Biochem. 1968,243,5193.

13- M.Eigen and G.Hammes,Advances in Enzymology,1963,25,1

14- J.T. Edsall NASA Spec. Publ. 1969,188,15.

15- J.E.A. McIntosh, Biochem. 1968,109,208.

16- R.K. Gupta and J.M. Pesando, J.Biological Chem. 1975,250(No.7),2630.

6.1.1. COMPUTER SIMULATION OF TITRATION CURVES

6.1.1 INTRODUCTION

Computer simulation of the titration curves was carried out to obtain theoretical titration curves and clarify the origin of the extra peak in the titration curves. As mentioned previously, the rate of addition of hydrochloric acid, and therefore the rate of introducing carbon dioxide into the titration solution during the course of the titration, has an effect on the position of this unexpected maximum. This suggests that a kinetic stage is involved in the formation of this maximum. Assuming that slow carbon dioxide hydration kinetics could be responsible for the appearance of the extra peak in the titration curves, computer simulation was carried out considering the effect of this slow kinetics stage. The rate constants from the literature were used. It will be shown that the only effect of this slow kinetic stage on theoretical titration curves was on the height of maximum for the conversion of H_2CO_3 to HCO_3^- in these titration curves. This suggests that the additional peak is due to a new species. Mathematical equations were derived assuming that the adddItional peak represents a new discrete species. Assuming values for the equilibrium constant for the formation of this species, and substitution of assumed equilibrium constant values into a computer program for modelling titration curves, produces titration curves identical to the experimental curves and the estimate of the equilibrium constant. In the following pages these simulations are described in detail.

6.2.1. COMPUTER SIMULATION OF TITRATION CURVES FOR CARBON DIOXIDE SLOW HYDRATION KINETICS

Computer simulation of titration curves was made using the fundamental equilibrium and kinetic rate constant data. To clarify the effect of kinetics and in order to make the appropriate comparisons the simulations were carried out in two stages. Firstly assuming there is no time delay because of kinetic complications, and secondly, introducing into the simulation, the kinetics of the hydration of carbon dioxide in aqueous solutions.

6.2.2. THE EQUILIBRIUM CASE

Considering the titration of an aqueous solution containing a moles of dissolved carbon dioxide and a moles of hydrochloric acid, with sodium hydroxide with a rate of addition of d(NaOH)/dt(mole s^{-1}), the relevant equilibrium and their equilibrium constants are as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad K_o \qquad (1)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_a \qquad (2)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2 \qquad (3)$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w \qquad (4)$$

For simplicity in the calculation it is assumed that, the change of volume of titration solution during the titration is so small as to be negligible. Application of the condition of electroneutrality requires that:

$$h + (Na^+) = (Cl^-) + (OH^-) + 2(CO_3^{2-}) \qquad (5)$$

where $h = (H^+)$

$$a = (CO_2) + (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) \qquad (6)$$

where a is defined to be the total amount of different carbonate species present in a given solution, which is equal to initial concentration of carbon dioxide.

Substitution of expressions for the equilibrium constants K_o, K_1 and K_2 into equation (6) and rearrangement yields:

$$a = (CO_3^{2-}).(\frac{h^2}{K_oK_aK_2} + \frac{h^2}{K_aK_2} + \frac{h}{K_2} + 1)$$

$$a = (CO_3^{2-}).B \qquad (7)$$

where the value of B is defined as the quantity in the second bracket in the above equation which only includes the h and the other thermodynamic constants for carbonate system. In the following equations, the concentration of the different species are represented in terms of B.

$$(CO_3^{2-}) = aB^{-1} \qquad (8)$$

$$(HCO_3^-) = \frac{h}{K_2} B^{-1} \qquad (9)$$

$$(H_2CO_3) = \frac{h^2}{K_aK_2} B^{-1} \qquad (10)$$

$$(CO_2) = \frac{h^2}{K_oK_aK_2} B^{-1} \qquad (11)$$

$$(OH^-) = \frac{K_w}{h} \qquad (12)$$

By substituting equations (8) to (12) into equation (5) the following equation was obtained:

$$B(h^2 + (NaOH)h - (HCl)h - K_w) - \frac{h^2}{K_2} a - 2ah^2 = 0 \qquad (13)$$

Knowing (CO_2), (HCl) and the equilibrium constats, K_o, K_a, K_2 and K_w, it is possible to solve the equation for h. This may be accomplished numerically using a successive approximation method.

The equilibrium case corresponds to that where the rates of interconversion of all of the species, in particular CO_2 to H_2CO_3, , is much faster than the performance of the titration.

6.2.3. NON-EQUILIBRIUM CASE

In order to deal with the case when there is a time delay in the process

(1), a_1 is defined to be the total accessible carbonate. (Note that in order for the titration to be carried out in a normal way CO_2 has to be hydrated to H_2CO_3 and then H_2CO_3 will take part in the neutralization reaction).

$$a_1 = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) \qquad (14)$$

It is known (3) that the rate of transformation between the above three species is effectively instantaneous.

A similar procedure to the above was used to obtain the following equation, where B_1^{-1} is defined as the quantity in the second bracket: by using this equation the concentration of different species can be calculated in terms of B_1.

$$a_1 = (CO_3^{2-})\left(\frac{h^2}{K_aK_2} + \frac{h}{K_2} + 1\right) = (CO_3^{2-})B_1^{-1} \qquad (15)$$

Using the electroneutrality condition for the system, the following equation can be written:

$$B_1(h^2 + (NaOH)h - (HCl)h - K_w) - \frac{ha_1}{K_2} - 2ha_1 = 0 \qquad (16)$$

A numerical solution was applied to solve this equation, in which interconversion of CO_2 to H_2CO_3 is considered to be given by:

$$d(H_2CO_3)/dt = k_f(CO_2) - k_r\,(H_2CO_3) \qquad (17)$$

where k_f and k_r are forward and reverse rate constants for the process (1) respectively. Computer simulation was carried out to calculate the concentrations of various species as a function of time.

6.2.4. CALCULATION PROCEDURE OF THEORETICAL TITRATION CURVES:

A listing of the computer program, as written in IBM Fortran IV (1) is given in the following pages. The equations (13) and (16) are solved

```
 1      C      THIS PROGRAM SIMULATES A TITRATION CURVE IN WHICH NAOH IS
 2      C      ADDED TO HCL CONTAINING CO2.. JUNE 2, 1980.
 3      C
 4      C
 5      C      DEFINITION OF TERMS
 6      C      CO2T  IS SUM OF NO. OF MOLES OF ALL CO2 DERIVED SPECIES.
 7      C      HCL   IS NO. OF MOLES OF HCL
 8      C      NAOH  IS NO. OF MOLES OF NAOH.
 9      C      CO2   IS NO. OF MOLES OF CO2.
10      C      H2CO3 IS NO. OF MOLES OF H2CO3.
11      C      H     IS NO. OF MOLES OF H ION.
12      C      KW    IS EQUIL. CONST. FOR: H2O = H+1 + OH-1
13      C      KO    IS EQUIL. CONST.. FOR: CO2 + H2O = H2CO3
14      C      KA    IS EQUIL. CONST. FOR: H2CO3 = H+1 + HCO3-1
15      C      KB    IS EQUIL. CONST. FOR: HCO3-1 = H+1 +CO3-2
16      C      RF    IS RATE CONST. FOR: CO2 + H2O = H2CO3 IN SEC-1.
17      C      RR    IS REVERSE RATE CONSTANT FOR THE ABOVE PROCESS.
18      C      T     IS TIME IN SECONDS.
19      C      PH    IS -LOG10(H)
20      C      TAC   IS TOTAL ACCESSIBLE CARBONATE = CO3 + HCO3 + H2CO3
21      C      TINT  IS THE ASSUMED TIME INTERVAL THROUGH WHICH THE SIMULATION PROGRESSES
22      C      TTOT  IS THE TOTAL TIME OF THE EXPERIMENT.
23      C      RNAOH IS THE RATE OF ADDITION OF NAOH IN MOLE SEC-1.
24      C      DERIV IS D(PH)/DT.
25      C      A,B   DEFINE THE RANGE OF THE SEARCH PROCEDURE FOR SOLVING FOR H, A IS LESS THAN B.
26      C      EPS   IS THE TOLERANCE IN SOLVING FOR H.
27      C      IFAIL IS INDICATOR OF SUCCESS OR FAILURE OF SEARCH PROCEDURE.
28      C      TPP   IS TIME INTERVAL ALLOWED FOR PRINTING OF RESULTS.
29      C      TP    IS TIME AT WHICH LAST SET OF RESULTS WAS PRINTED.
30      C      PHO   IS PH AT T=T-TINT.
31      C      FN    IS A FUNCTION CALCULATED IN FUNCTION FN(H)...
32      C      U     IS DEFINED IN FUNCTION FN(H).
33      C      TERM  IS DEFINED ON LINE 79.
34      C      FEPS  IS USED IN SETTING THE VALUE OF EPS(SEE LINE 114).
35      C      FH    IS USED IN SETTING THE VALUE OF A(SEE LINE 113).
36      C      FAST  IS 1 IF WANT TO IGNORE KINETICS.
37      C      DELTA IS CHANGE IN CONCENTRATION OF CO2 AND H2CO3 DURING A GIVEN TIME INTERVAL.
38      C      THE VOLUME IS ASSUMED TO BE ONE DM-3 AND DOES NOT CHANGE DURING THE
39      C      TITRATION. THEREFORE ALL CONCENTRATIONS ARE IN MOLES PER DM-3.
40      C
```

```
C
C      DECLARATIONS FOLLOW.
       DOUBLE PRECISION H,T,TTOT,RF,RR,KO,KA,KB,RNAOH,CO2,H2CO3,
      +TINT,CO2T,HCL,NAOH,KW,DELTA,U,TAC,A,B,EPS,
      +PH,TP,TPP,DERIV,PHO,FEPS,TERM,TINT1,TINT2,FH
       INTEGER IFAIL,FAST
       EXTERNAL FN
       COMMON T,U,KO,KA,KB,KW,TAC,NAOH,HCL,CO2T,FAST
C
C
C      DATA STATEMENTS
       READ(5,*) NAOH,CO2T,HCL,RF,RR,KA,KB,TTOT,RNAOH,TPP,TINT,FAST
C      WRITE(6,NAM1)
       KO=RF/RR
       KW=1.0D-14
       IFAIL=1
       TP=0.0D0
       FEPS=1.D-10
       FH=.01D0
C
C
C      SIMULATION SCHEME FOLLOWS
C      WRITE(6,9999)
       GO TO 120
 20    CONTINUE
       T=T+TINT
       IF(T.GT.TTOT) GO TO 999
       GO TO 110
 9999  FORMAT(5X,4HTIME,6X,2HPH,9X,3HCO2,3X,10HD(PH)/(DT))
 9998  FORMAT(1X,F8.2,1X,F7.4,1X,E12.5)
 9997  FORMAT(1X,F8.2,1X,F7.4,2(1X,E12.5))
 9996  FORMAT(5(1X,E11.4))
 9995  FORMAT(1X,2E11.4)
C
C
C      THIS SECTION MOVES THE CO2 CONCENTRATION.
 110   CONTINUE
       IF(FAST.EQ.1) GO TO 111
       TERM=-RF*CO2+RR*H2CO3
       DELTA=TINT*TERM
```

```
      CO2=CO2+DELTA
      H2CO3=H2CO3-DELTA
      TAC=CO2T-CO2
      GO TO 240
  111 CONTINUE
      TAC=CO2T
      CO2=H2CO3/KO
      GO TO 240
C
C
C     THIS SECTION ADDS SOME NAOH TO THE SOLUTION.
  240 NAOH=NAOH+RNAOH*TINT
      GO TO 130
C
C
C     THIS SECTION CALCULATES THE H ION CONCENTRATION.
C     FOR T=0.0
  120 CONTINUE
      A=0.0D0
      B=1.0D0
      EPS=1.D-12
      CALL C05ABF(A,B,EPS,FN,H,IFAIL)
      H2CO3=(H*H*CO2T)/(U*KA*KB)
      CO2=H2CO3/KO
      PH=-DLOG10(H)
      PHO=PH
C     WRITE(6,9996) T,PH,CO2
      GO TO 160
C
C     FOR ALL OTHER TIMES
  130 CONTINUE
      B=H
      A=FH*H
      EPS=FEPS*H
      CALL C05ABF(A,B,EPS,FN,H,IFAIL)
      PH=-DLOG10(H)
      H2CO3=(H*H*TAC)/(U*KA*KB)
      DERIV=(PH-PHO)/TINT
      PHO=PH
      IF((T-TP).GT.TPP) GO TO 300
```

```
        GO TO 160
  300   CONTINUE
        WRITE(6,9996) T,DERIV,PH,CO2,TAC
        TP=T
        GO TO 160
C
C
C       THIS SECTION DECIDES ON THE VALUE OF TINT TO BE USED IN THE SIMULATION.
  160   CONTINUE
        GO TO 20
C
C
  999   STOP
        END
C
        DOUBLE PRECISION FUNCTION FN(H)
        DOUBLE PRECISION T,H,U,KO,KA,KB,KW,TAC,NAOH,HCL,CO2T
        INTEGER FAST
        COMMON T,U,KO,KA,KB,KW,TAC,NAOH,HCL,CO2T,FAST
        IF(FAST.EQ.1) GO TO 205
        IF(T.GT.1.0D-5) GO TO 200
  205   U=(H*H+H*H*KO+H*KO*KA+KO*KA*KB)/(KO*KA*KB)
        FN=(U*(H*H+H*(NAOH-HCL)-KW))-(H*H*CO2T/KB)-(2.0D0*CO2T*H)
        GO TO 210
  200   U=(H*H+H*KA+KA*KB)/(KA*KB)
        FN=(U*(H*H+H*(NAOH-HCL)-KW))-(H*H*TAC/KB)-(2.0D0*TAC*H)
  210   RETURN
        END
```

by an iterative procedure (CO5ABF) called from Numerical Analysis Programs library (2). The schematic simulation process for obtaining titration curves with slow kinetics is shown in figure 6-1. The equilibrium and kinetic values used for this calculation are shown below:

$K_o = k_f/k_r = 0.0015$ $k_f = 0.03s^{-1}$(3) $k_r = 20s^{-1}$ (3)

$K_a = 3.10^{-4}$ $K_a = K_1(1 + 1/K_o)$

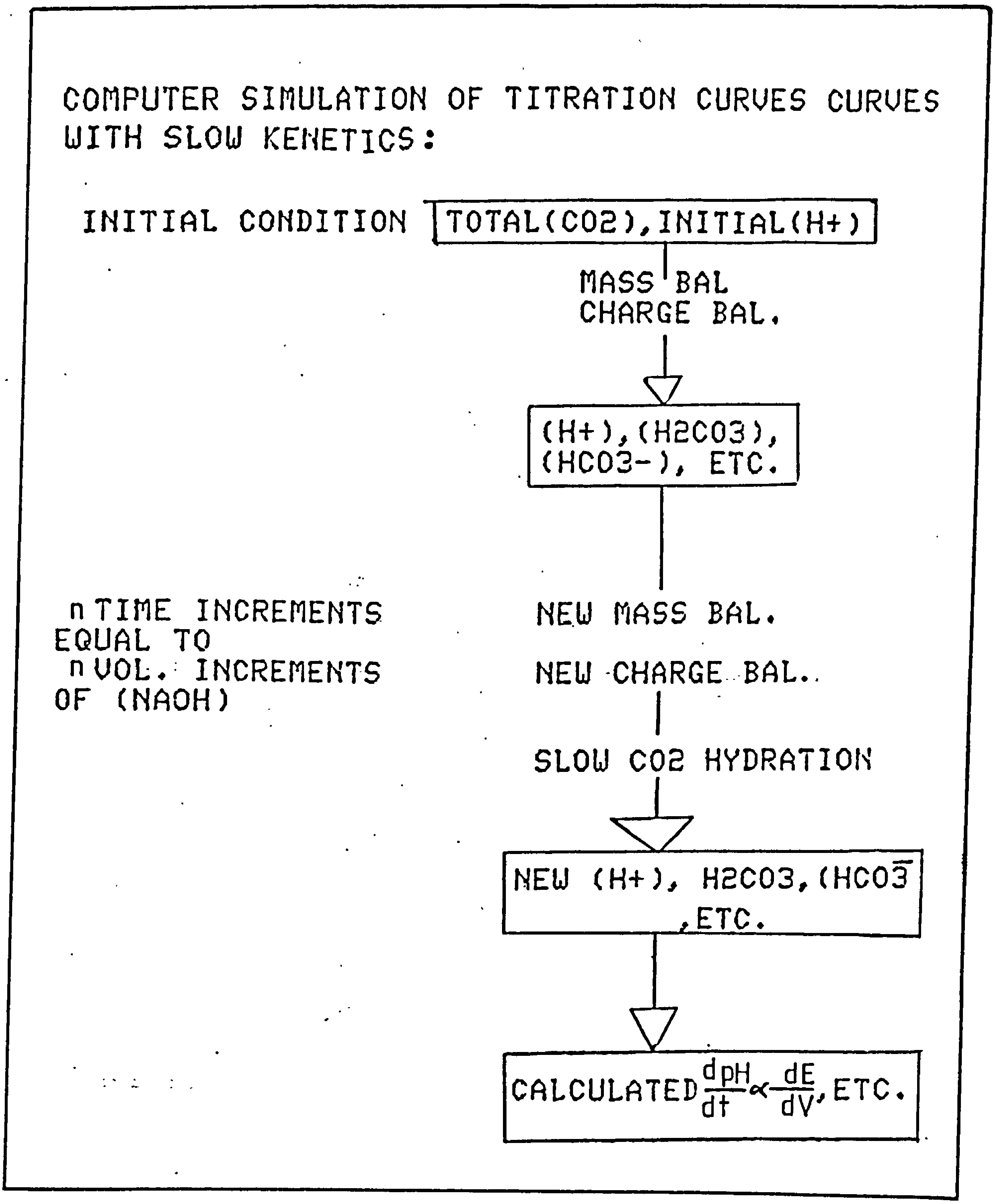
$K_2 = 4.7\times10^{-11}$ (4)

$K_w = 1.0\times10^{-14}$ (5)

the curves B in figures 6-2 and 6-3 were obtained using these values.

To clarify the effect of kinetics, two more simulations were carried out; in case C it is assumed that the hydration process for the carbon dioxide is 100% slower than that indicated by literature values. Curves C in figures 6-1 and 6-2 were obtained where the values for k_f and k_r were $0.015s^{-1}$ and $10s^{-1}$ respectively. In the third simulation calculation, it was assumed that the process (1) is fast, and all carbon dioxide is available in the form of H_2CO_3 , the calculations produced curves A in figures 6-2 and 6-3.

As is clear from 6-2 and 6-3, the only effect of slow kinetics of hydration of carbon dioxide is on the height of the middle peak (the maximum for the conversion of carbonic acid to bicarbonate ions) and the other peaks remained unaffected. These calculations were carried out in 40,000s with $\Delta t = dt = 0.1s$. The rate of addition of sodium hydroxide was 10^{-6}mol/s. (This is the same as the experimental case where 0.25mol/l sodium hydroxide was added to the titration solution at a rate of 1ml in 4 minutes.) Initial concentrations of both HCl and CO_2 were 0.01 mol/l.



FLOW DIAGRAMS FOR " TITRATION CURVES WITH SLOW KINETICS "

FIG 6-1

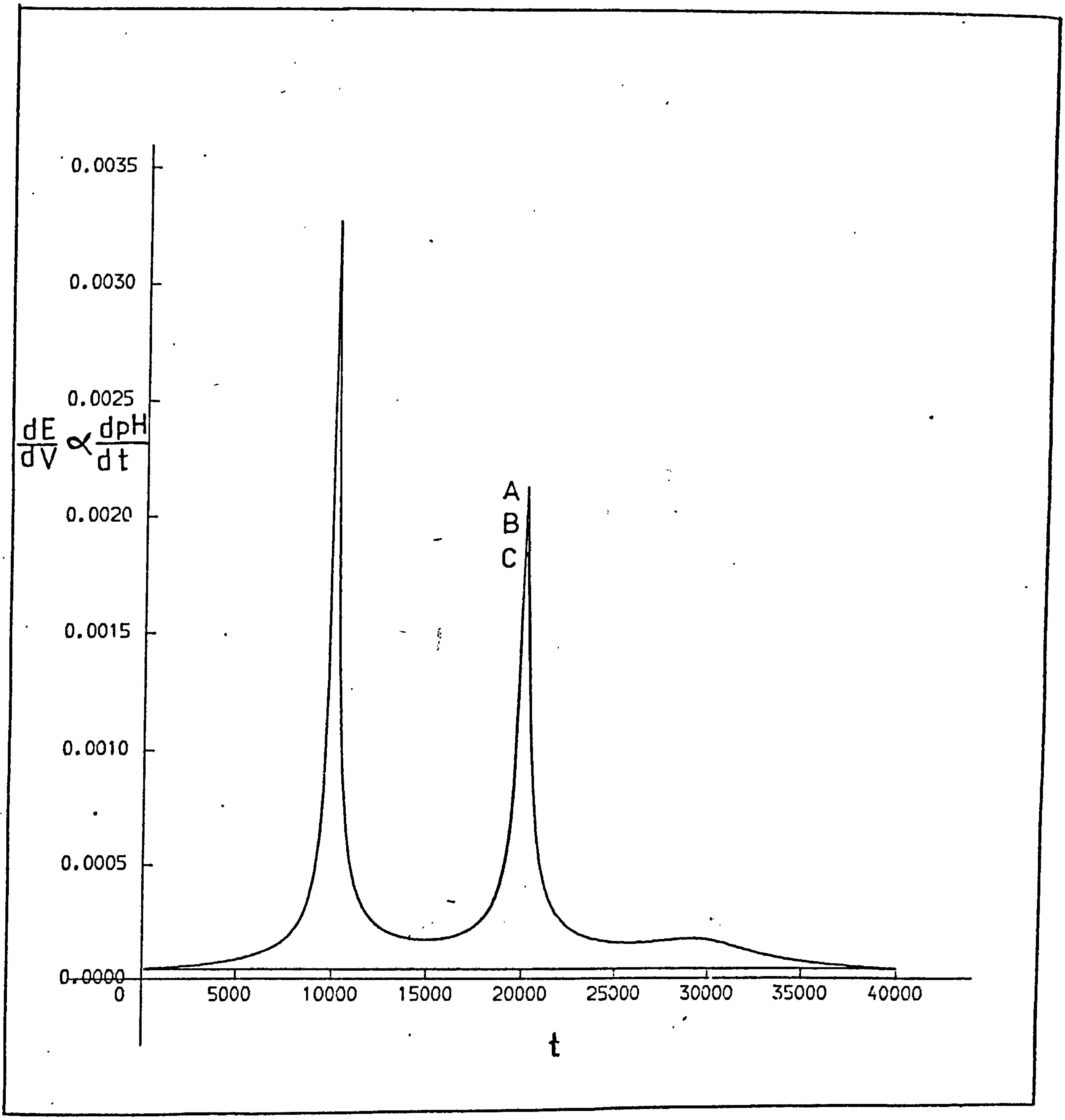

0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
$\frac{dE}{dV} \propto \frac{dpH}{dt}$
A
B
C
0
5000
10000
15000
20000
25000
30000
35000
40000
t

FIG 6-2

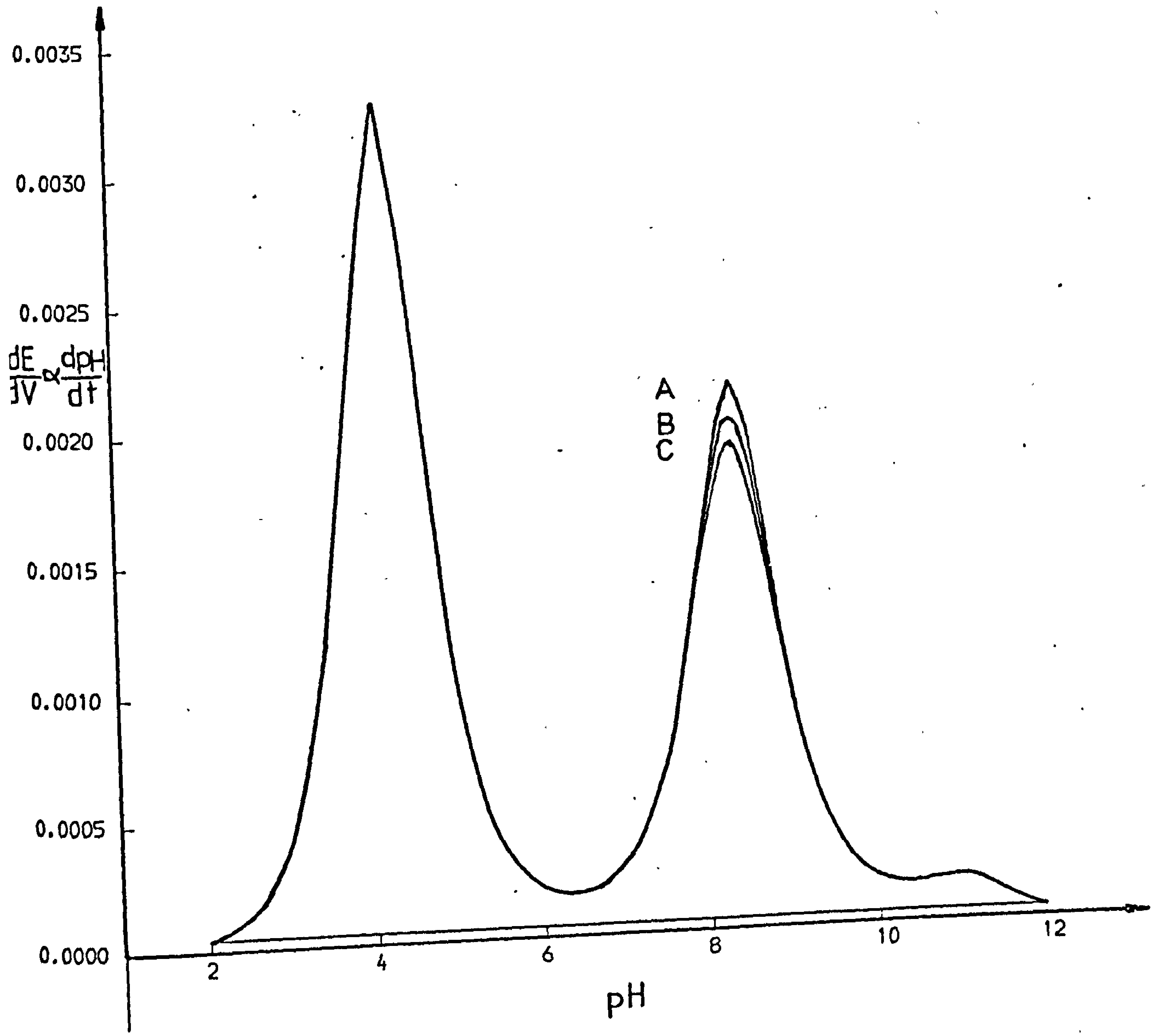

0.0035
0.0030
0.0025
dE/dV ∝ dpH/dt
0.0020
0.0015
0.0010
0.0005
0.0000
A
B
C
2
4
6
8
10
12
pH

FIG 6-3

6.2.5. EFFECT OF RATE OF ADDITION OF TITRANT ON THEORETICAL TITRATION CURVES

To clarify the effect of addition of HCl, more calculations were carried out. As shown in figure 6-4-1 and 6-4-2 when the rate of addition of HCl was 2×10^{-7} mol/s, the effect of kinetics of hydration of carbon dioxide on the height of the middle peak is also negligible as can be seen by comparing curves A (fast) with curves B (kinetics involved in calculations).

Figures 6-4-3 and 6-4-4 correspond to the case where the rate of addition of HCl was 2.5×10^{-5} mol/s. It is clear that taking into account the kinetics of hydration has not only reduced the height of the middle peak but also has had an effect on the position of the middle peak, since the middle peak has appeared sooner than it should do. But as figure 6-4-4 shows it has had very little effect on the pH of the appearance of this peak (again curves A, B and C are the same as figure 6-2 and 6-3). By calculation it is found that when the rate of addition of HCl is greater than 10^{-5} mol/s, kinetics has an effect on the position of the middle peak.

6.3. COMPUTER SIMULATION OF TITRATION CURVES INCLUDING THE EFFECT OF THE PRESENCE OF AN ADDITIONAL SPECIES

Two different hypotheses can be postulated to describe the existence of an additional species as follows:

1) The extra peak results from a triple ion triply charged complex formed from CO_2 and CO_3^{2-}.

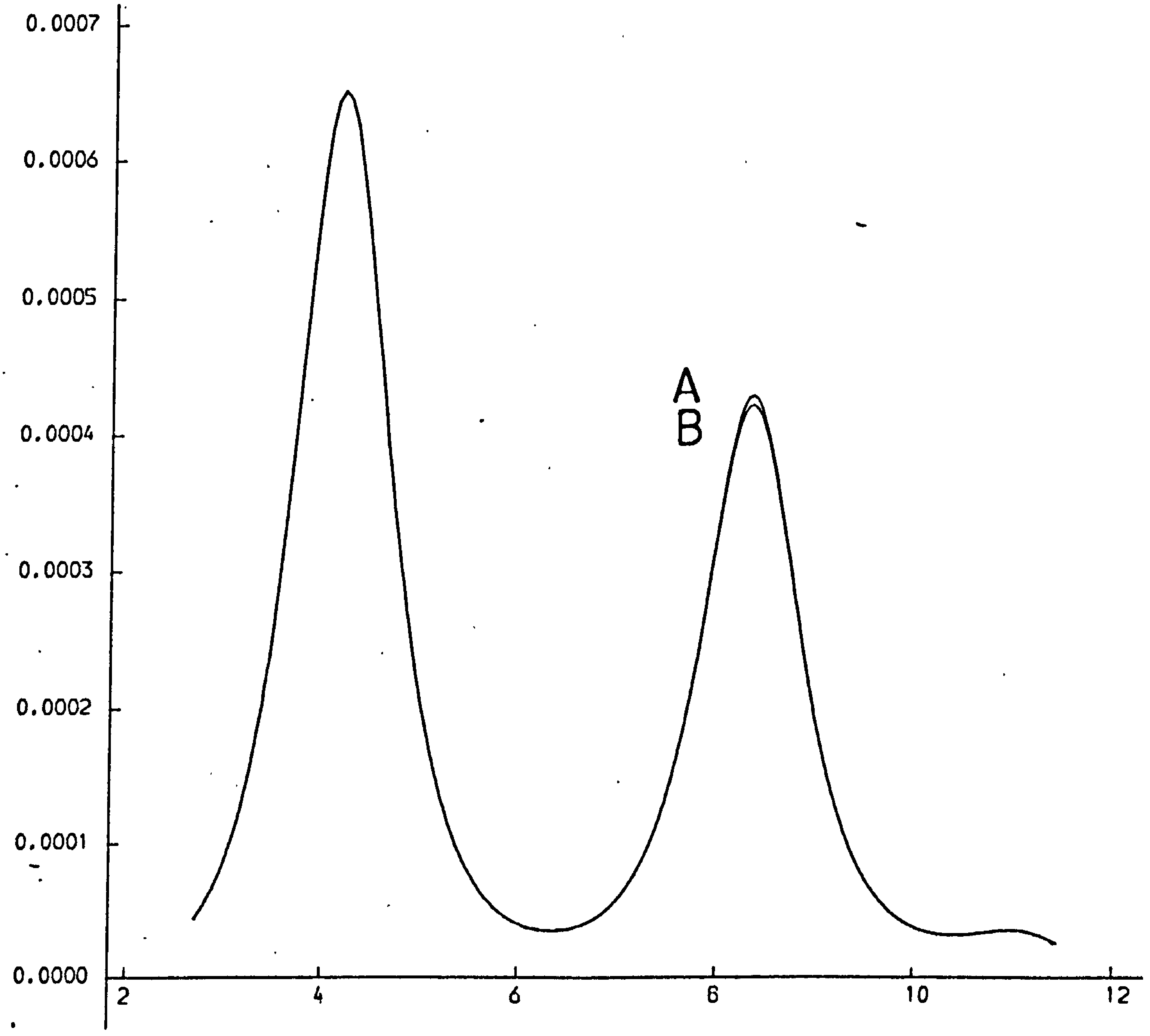

0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
2
4
6
8
10
12
A
B

FIG 6-4-1

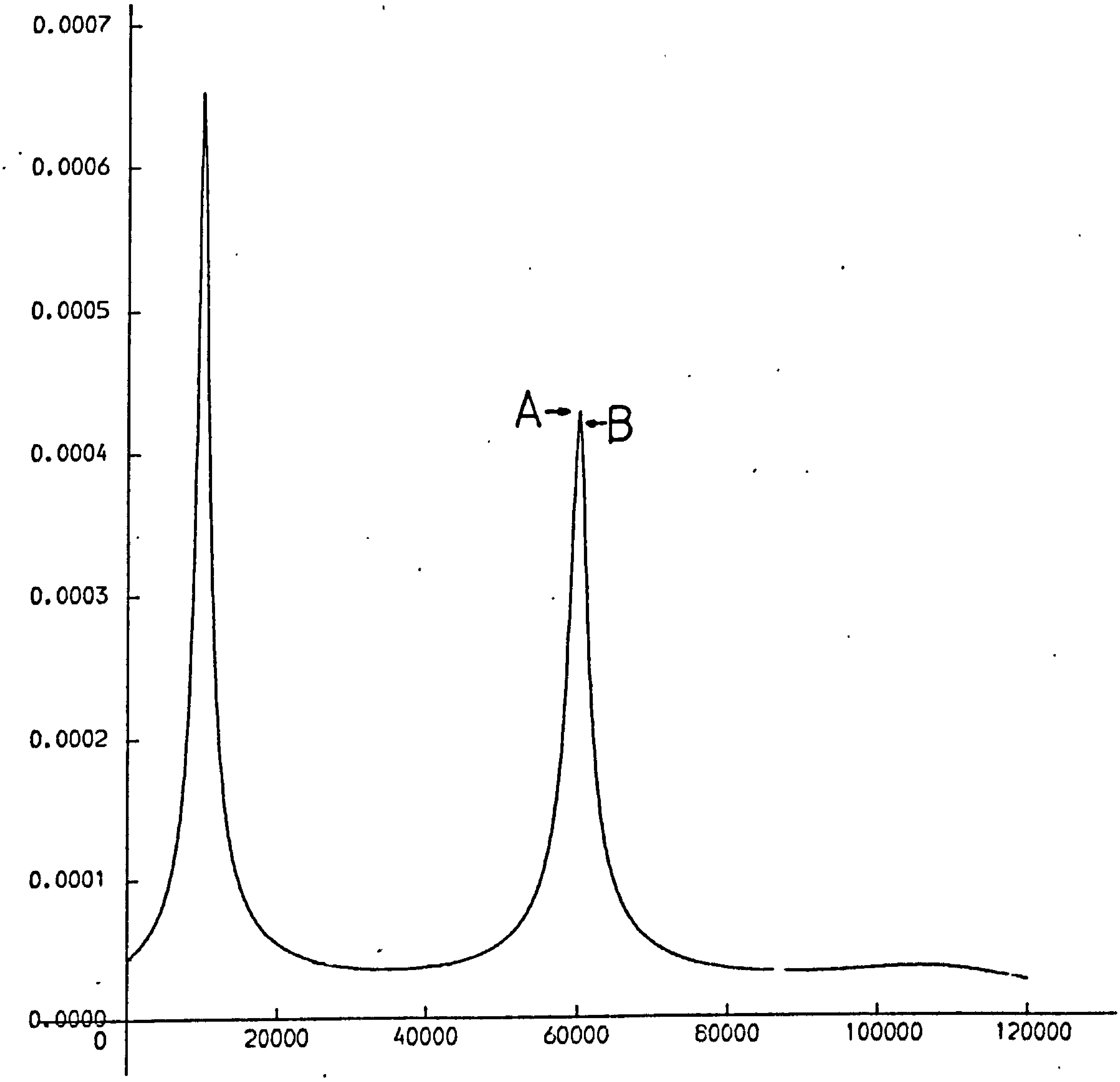

0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
0
20000
40000
60000
80000
100000
120000
A
B

FIG 6-4-2

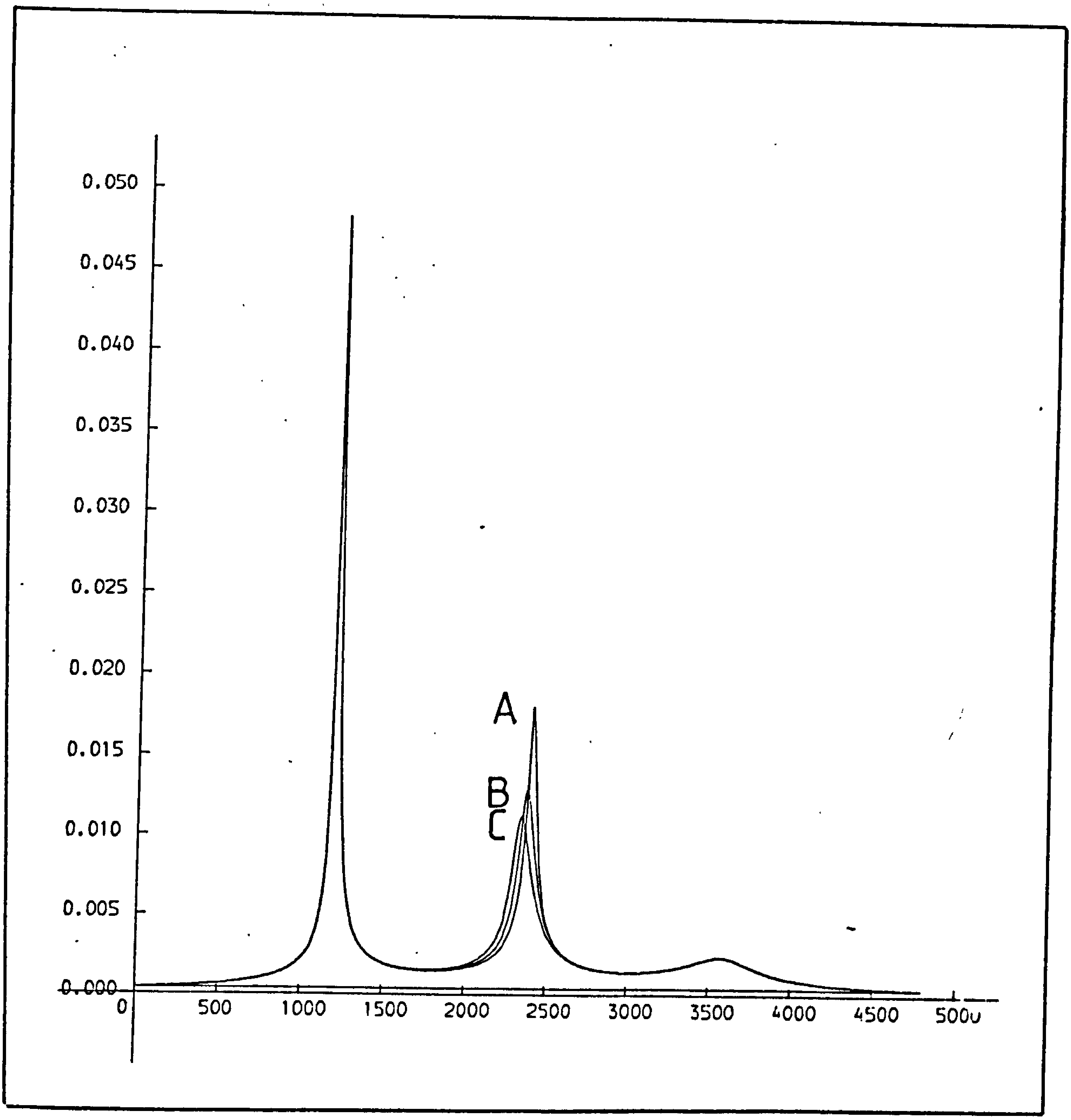

0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
A
B
C

FIG 6-4-3

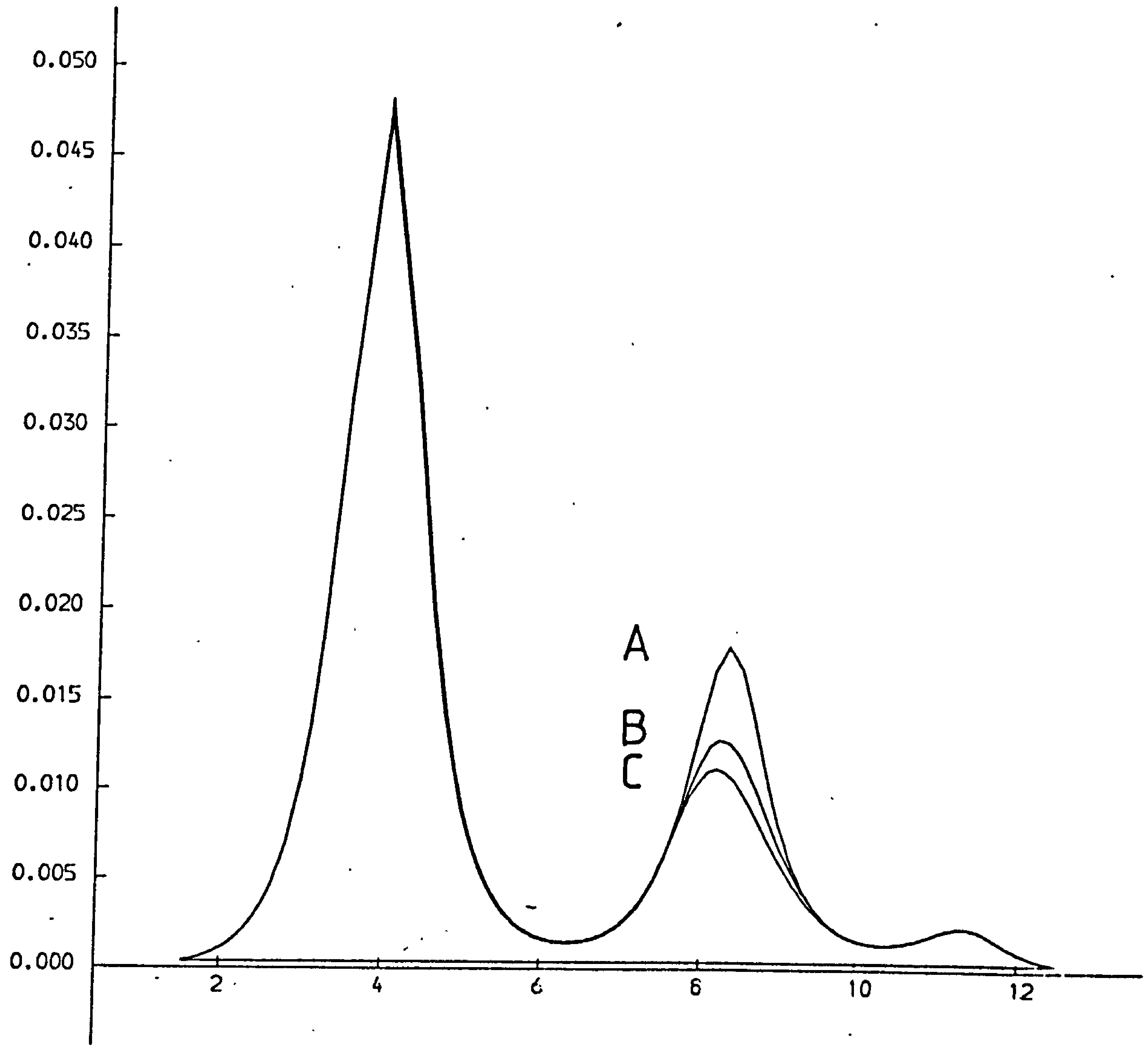

0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
2
4
6
8
10
12
A
B
C

FIG 6-4-4

2) The extra peak is a result of a triple ion singly charged complex formed from CO_2 and HCO_3^-:

For simplicity, in this section the kinetic stage was ignored, therefore it is assumed that all the CO_2 is available in the form of H_2CO_3 in aqueous solutions. So in equation number 2, K_a is replaced by K_1 (apparent constant value.

6.3.1. HYPOTHESIS 1 (H1)

This assumes that the novel feature relates to the formation of a complex triple ion of two carbonate ions and a hydrogen ion with a structure of $H(CO_3)_2^{3-}$, and formed by the reaction as follows:

$$CO_2 + OH^- + CO_3^{2-} \rightleftharpoons H(CO_3)_2^{3-} \qquad (18)$$

Consider a solution containing a moles of H_2CO_3 to which NaOH is added in increasing amounts b(= 2ax) moles, where x can be regarded as the degree of advancement of neutralization.

From equilibrium considerations:

$$(HCO_3^-) = \frac{h}{K_2}(CO_3^{2-}) \qquad (19)$$

$$(H_2CO_3) = \frac{h}{K_1}(HCO_3^-) = \frac{h^2}{K_1K_2}(CO_3^{2-}) \qquad (20)$$

Suppose

$$(HCO_3^-) + (CO_3^{2-}) = (H(CO_3)_2)^{3-} \qquad (21)$$

$$(H(CO_3)_2^{3-}) = K_3(HCO_3^-)(CO_3^{2-}) = \frac{K_3h}{K_2}(CO_3^{2-})^2 \qquad (22)$$

Mass balance for carbonate system is as follows:

$$a = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) + 2(H(CO_3)_2^{3-}) \qquad (23)$$

$$a = (h^2/K_1K_2 + h/K_2 + 1)(CO_3^{2-}) + 2K_3h(CO_3^{2-})^2/K_2 =$$

$$(h^2 + hK_1 + K_1K_2)(CO_3^{2-})/(K_1K_2) + 2K_3h(CO_3^{2-})^2/K_2 \qquad (24)$$

Equation (24) is quadratic in (CO_3^{2-}) and differentiation of this equation yields:

$$0 = d(((h^2 + hK_1 + K_1K_2)(CO_3^{2-}))/K_1K_2)/dx + (2K_3/K_2)(d(h(CO_3^{2-})^2)/dx) =$$

$$(2h + K_1)(CO_3^{2-})(dh/dx)/K_1K_2 + (h^2 + hK_1 + K_1K_2)(d(CO_3^{2-})/dx)/K_1K_2$$
$$+ 2K_3(CO_3^{2-})^2(dh/dx)/K_2 + 2K_3h{\cdot}2(CO_3^{2-})(d(CO_3^{2-})/dx)/K_2$$

$$(d(CO_3^{2-})/dx)((h^2 + hK_1 + K_1K_2)/K_1K_2 + 4K_3h(CO_3^{2-})/K_2) =$$
$$-(dh/dx)((2h + K_1)(CO_3^{2-})/K_1K_2 + 2K_3(CO_3^{2-})^2/K_2) \qquad (25)$$

or $$d(CO_3^{2-})/dx = -M(dh/dx) \qquad (25)$$

where $M = ((2h + K_1)(CO_3^{2-})/K_1K_2 + 2K_3(CO_3^{2-})^2/K_2)/((h^2 + hK_1 + K_1K_2)/K_1K_2 + 4K_3h(CO_3^{2-})/K_2)$

Charge balance requires that:

$$h + (Na^+) = (HCO_3^-) + 2(CO_3^{2-}) + 3(HC_2O_6^{3-}) + (OH^-) \qquad (26)$$

$$(dh/dx) + 2a = (CO_3^{2-})(dh/dx)/K_2 + (h/K_2 + 2)(d(CO_3^{2-})/dx) -$$
$$(K_w/h^2)(dh/dx) + (3K_3(CO_3^{-2})^2/K_2)(dh/dx) +$$
$$(3K_3h.2(CO_3^{2-})/K_2)(d(CO_3^{2-})/dx) = (dh/dx)(((CO_3^{2-})/K_2) -$$
$$M((h/K_2) + 2) + (3K_3(CO_3^{2-})^2/K_2) - 3K_3h.2(CO_3^{2-})M - K_w/h^2))$$

$$(dh/dx) + 2a = N(dh/dx) \qquad \text{so:} \qquad (dh/dx) = 2a/(N - 1)$$

Then: $$(d\ln h/dx) = (2a/(N - 1)h) \qquad (27)$$

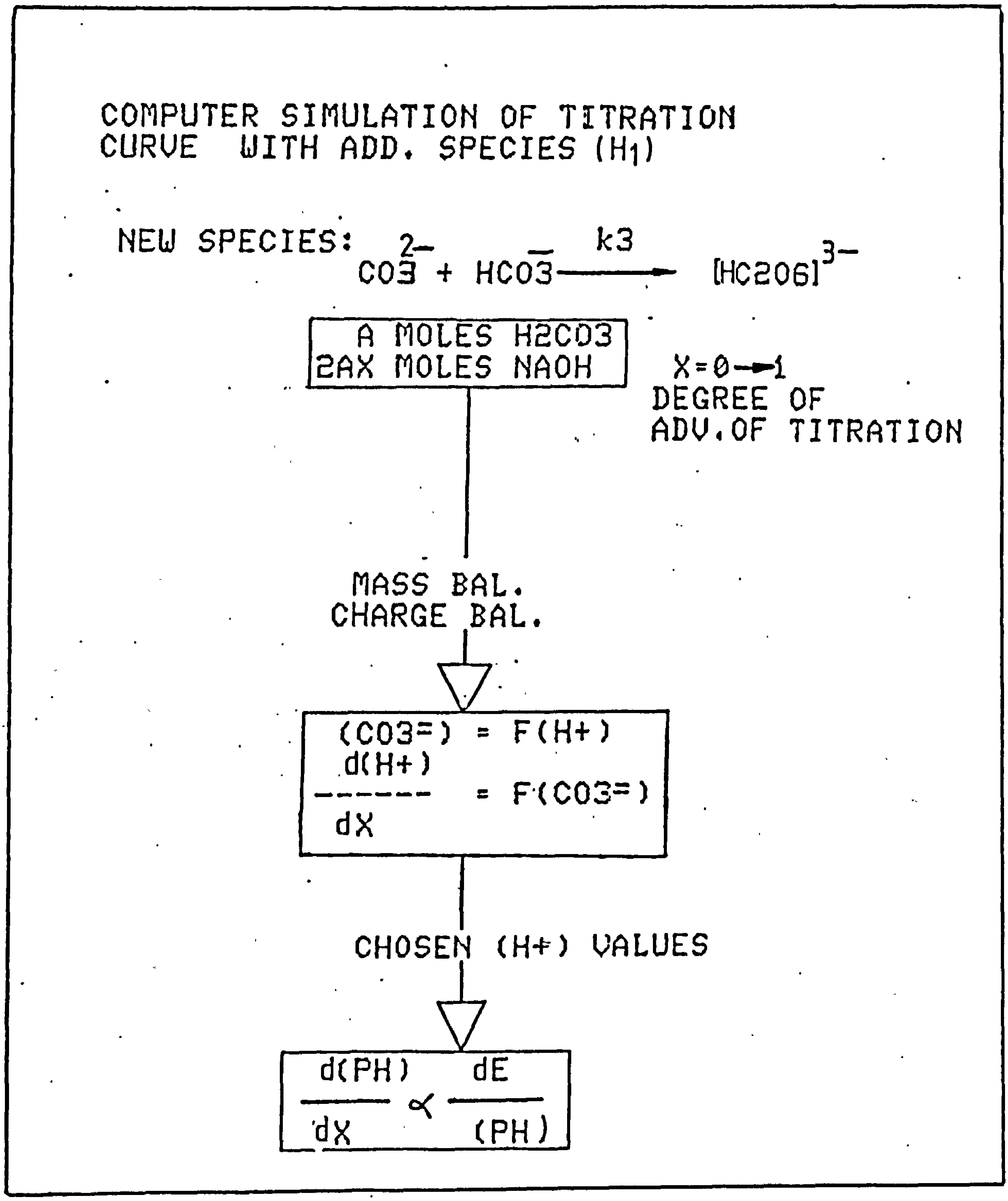
where: $N = (((CO_3^{2-})/K_2) - M((h/K_2) + 2) + (3K_3(CO_3^{2-})^2/K_2) - (3K_3h.2(CO_3^{2-})M/K_2) - (K_w/h^2))$

Using the PDP8 computer, equation (27) was solved. A listing of the computer program, written in Fortran, and also the procedure for calculations are given in the following pages. Figure 6-4 shows the schematic simulation process for obtaining titration curves. Substitution of assumed equilibrium constant values (K_3) into this program for modelling the titration curves produced figures 6-5 to 6-10. The values chosen for K_3 were 1, 10, 10^2, 2×10^3, 10^4, and 10^5 respectively. The corresponding results are shown in Tables 1-6 of appendix. As shown in all the figures, the curve for dlnh/dx vs. pH and dlnh vs. pH and also the fraction of different species of carbonate system at different pH values are calculated and drawn by the computer.

As is clear by comparison of these theoretical curves, the height of the additional peak is comparable with the experimental one when the value for K_3 is around 10^3, but, as was expected, the additional peak appeared between the end-points of OH^- and CO_3^{2-} ions, which is not the right position when it is compared with the experimental curves. So the most probable hypothesis is hypothesis 2 (H_2) which is described as follows.

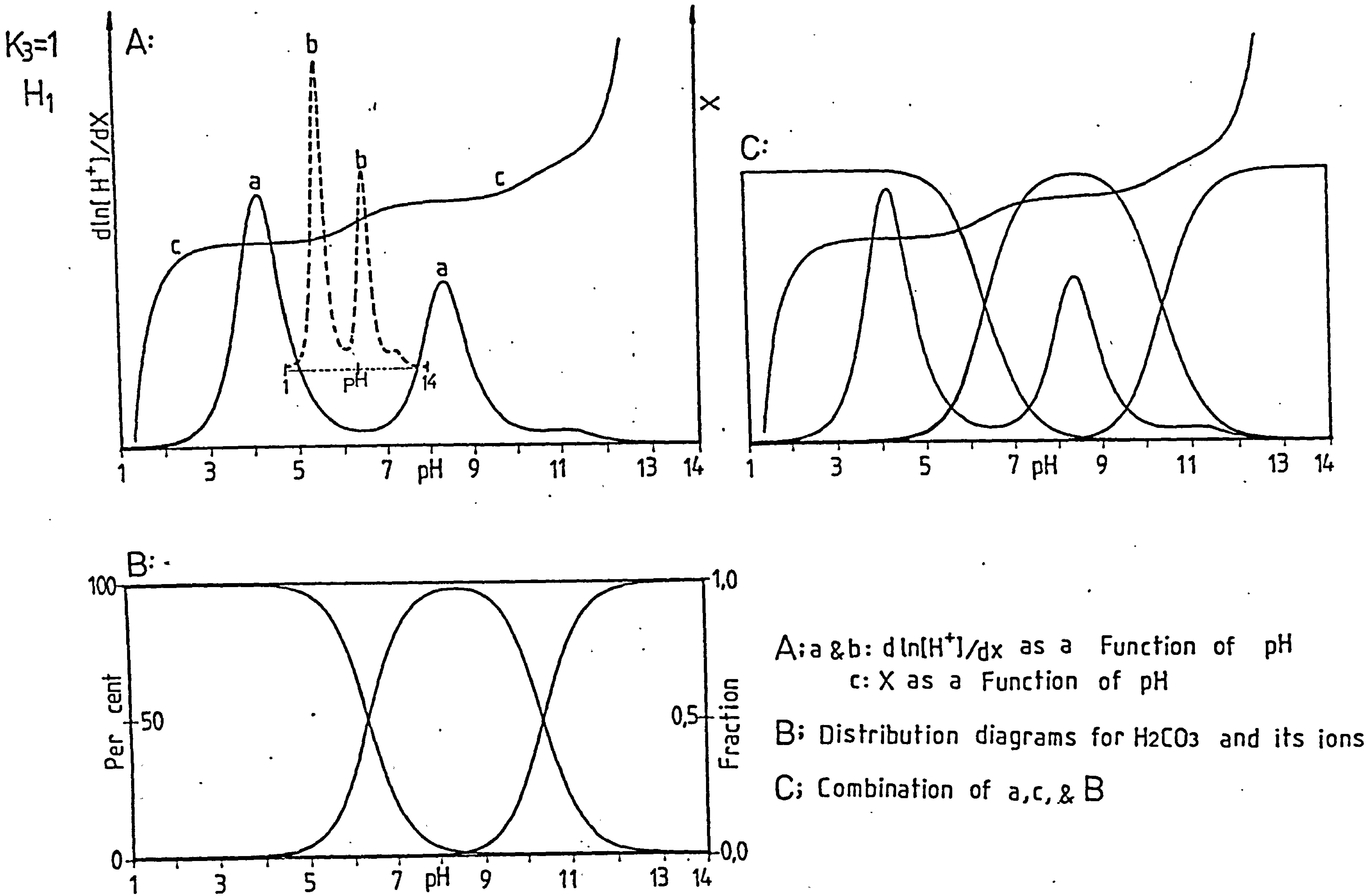
```
C       CATEQ8 - VERSION H1/NULL      19-JUL-79
C
        DIMENSION Y(8)
        WRITE (1,10)
 10     FORMAT (20X'CATEQ8     VERSION H1/NULL     19-JUL-79'//)
 20     READ (1,30)A
 30     FORMAT ('[A] = 'E10.2)
        READ (1,40)AK1
 40     FORMAT ('K1  = 'E10.2)
        READ (1,50)AK2
 50     FORMAT ('K2  = 'E10.2)
 55     READ (1,60)AK3
 60     FORMAT ('K3  = 'E10.2)
        READ (1,70)AKW
 70     FORMAT ('KW  = 'E10.2)
 100    WRITE (1,85)
 85     FORMAT (//)
        READ (1,110)IMODE
 110    FORMAT ('SELECT MODE - (1 = PRINT; 2 = GRAPHIC; 3 = RESTART:)  '
       1I1)
        IF (IMODE)100,100,120
 120    IF (IMODE-3)130,20,100
 130    IF (IMODE-2)140,140,20
 140    READ (1,150)N
 150    FORMAT ('NO. OF POINTS       = 'I4)
        IF (1024-N)140,155,155
 155    READ (1,160)AHF
 160    FORMAT ('INITIAL VALUE OF H = 'E8.4)
        READ (1,170)AHL
 170    FORMAT ('FINAL VALUE OF H   = 'E8.4)
 75     READ (1,80)IS
 80     FORMAT ('SELECT H INCREMENT - (1 = LIN; 2 = LOG:)  'I1)
        IF (IS)75,75,90
 90     IF (IS-2)175,175,75
 175    IF (IMODE-2)200,180,20
 180    READ (1,185)N1,N2,N3,N4
 185    FORMAT ('SELECT TERMS TO BE PLOTTED - '3(I1,2H; )I1,1H:)
        READ (1,190)S
 190    FORMAT ('DYNAMIC RANGE       = + OR - 'E12.4)
        S=2047./S
        F=(100.0*S)/A
        IR=-1
        GO TO 215
 200    WRITE (1,210)
 210    FORMAT (/7X'(1)'10X'(2)'11X'(3)'10X'(4)'8X'(5)'11X'
       1(6)'13X'(7)'10X'(8)'/6X'[H+]'11X'X'9X'DLN[H+]/DX'6X'PH'
       110X'T'10X'[CO3""]'9X'[HCO3"]'6X'[H2CO3]'/)
 215    IF (IS-1)220,220,230
 220    DH=(AHL-AHF)/FLOAT(N)
        GO TO 240
 230    DLH=(ALOG(AHL/AHF))/FLOAT(N)
 240    AH=AHF
        AK12=AK1*AK2
        AK23=AK3/AK2
        DO 330 I=1,N
        AH2=AH*AH
        AH3=AH*AH2
        AHK23=AH*AK23
        D1=AK12+AH*AK1+AH2
        IF (AK3)55,245,248
 245    D2=4.*AH*AK2+AK12+AH2
        D4=A*AH*AK1*D2/(D1*D1)
```

```
      D3=2.*A/(AH+D4+AKW/AH)
      A2=AK12*A/D1
      BC=AH*AK1*A/D1
      B=-AH+A*AK1*(AH+2.*AK2)/D1+AKW/AH
      HC=AH2*A/D1
      T=0
      GO TO 265
248   AI=D1/(2.*AK1*AK3*AH)
      ARG=AI*AI+2.*A/AHK23
      A2=(-AI+SQRT(ARG))/2.
      A22=A*AK12/D1
      IF (A2-0.000001*A)250,250,260
250   A2=A22
260   A2X=A2*A2
      AM=(2.*AH+AK1)*A2/AK12+2.*AK23*A2X
      AM=AM/(D1/AK12+4.*AK23*AH*A2)
      AN=AN1+A2/AK2-AM*(2.+AH/AK2)
      AN1=3.*AK23*A2X-6.*AK23*AH*A2*AM-AKW/AH2
      T=AK23*AH*A2X
      BC=A2*AH/AK2
      D3=2.*A/(AH*(1.-AN))
      HC=A2*AH2/AK12
      B=-AH+(2.+AH/AK2)*A2+3.*AH*A2X*AK23+AKW/AH
265   X=B/(2.*A)
      G=-0.43429*ALOG(AH)
      IF (IMODE-2)270,290,20
270   WRITE (1,280)AH,X,D3,G,T,A2,BC,HC
280   FORMAT (1X,3(E12.4,2X),F8.2,4(2X,E12.4))
      GO TO 300
290   Y(1)=AH
      Y(2)=X*200.0
      Y(3)=D3*S
      Y(4)=G
      Y(5)=T*F
      Y(6)=A2*F
      Y(7)=BC*F
      Y(8)=HC*F
      NP1=IFIX(Y(N1))
      NP2=IFIX(Y(N2))
      NP3=IFIX(Y(N3))
      NP4=IFIX(Y(N4))
      IA=(I-1)-2047
      CALL CAT (IA,NP1,IR)
      IA=IA+1024
      CALL CAT (IA,NP2,IR)
      IA=IA+1024
      CALL CAT (IA,NP3,IR)
      IA=IA+1024
      CALL CAT (IA,NP4,IR)
300   IF (IS-1)310,310,320
310   AH=AH+DH
      GO TO 330
320   AIH=ALOG(AH)+DLH
      AH=EXP (AIH)
330,  CONTINUE
      IF (IMODE-2)350,340,350
340   CALL CAT (0,0,-4)
350   GO TO 100
      END
```



FLOW DIAGRAMS FOR " H_1 "

FIG 6-4

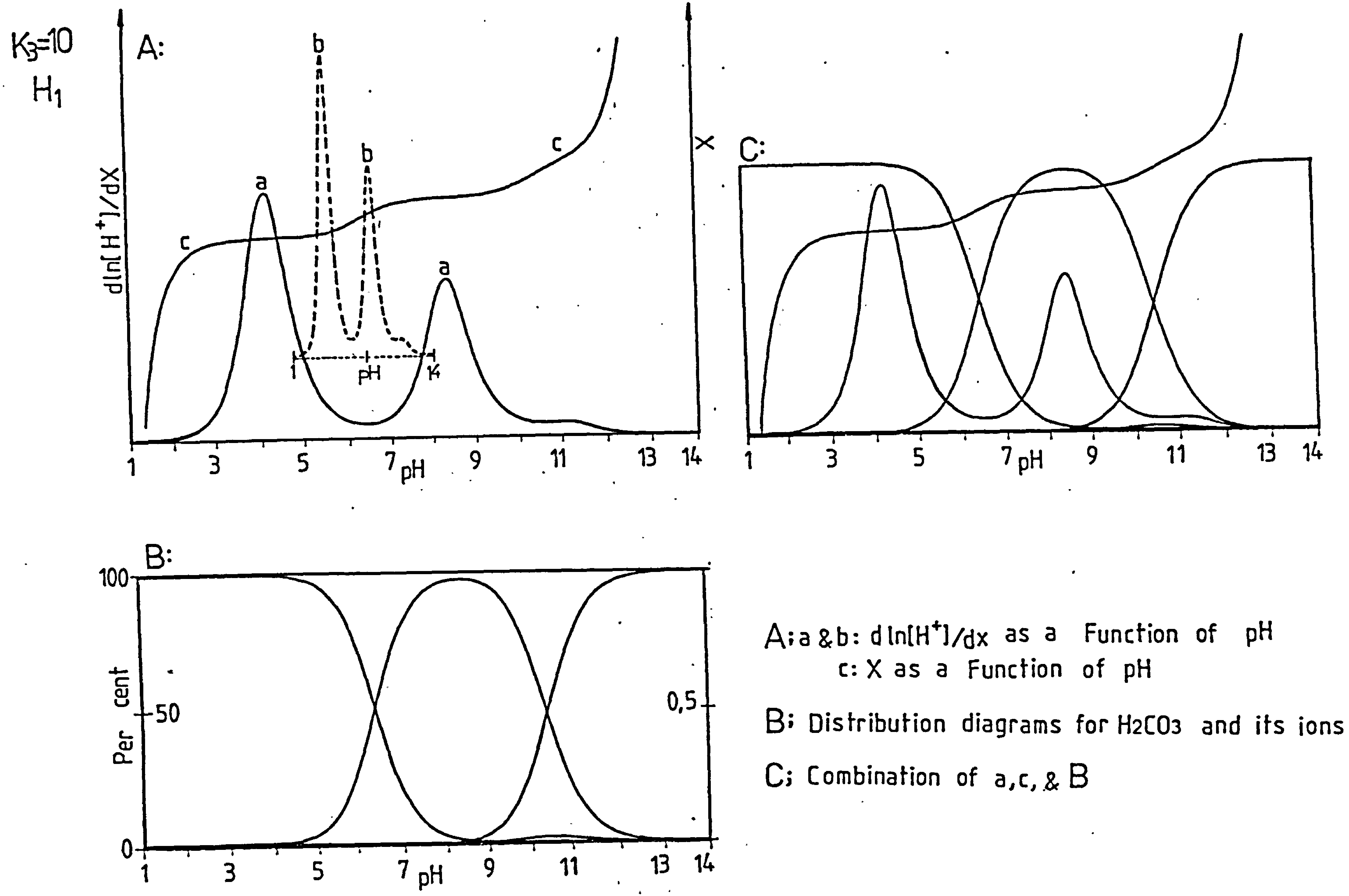


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-5

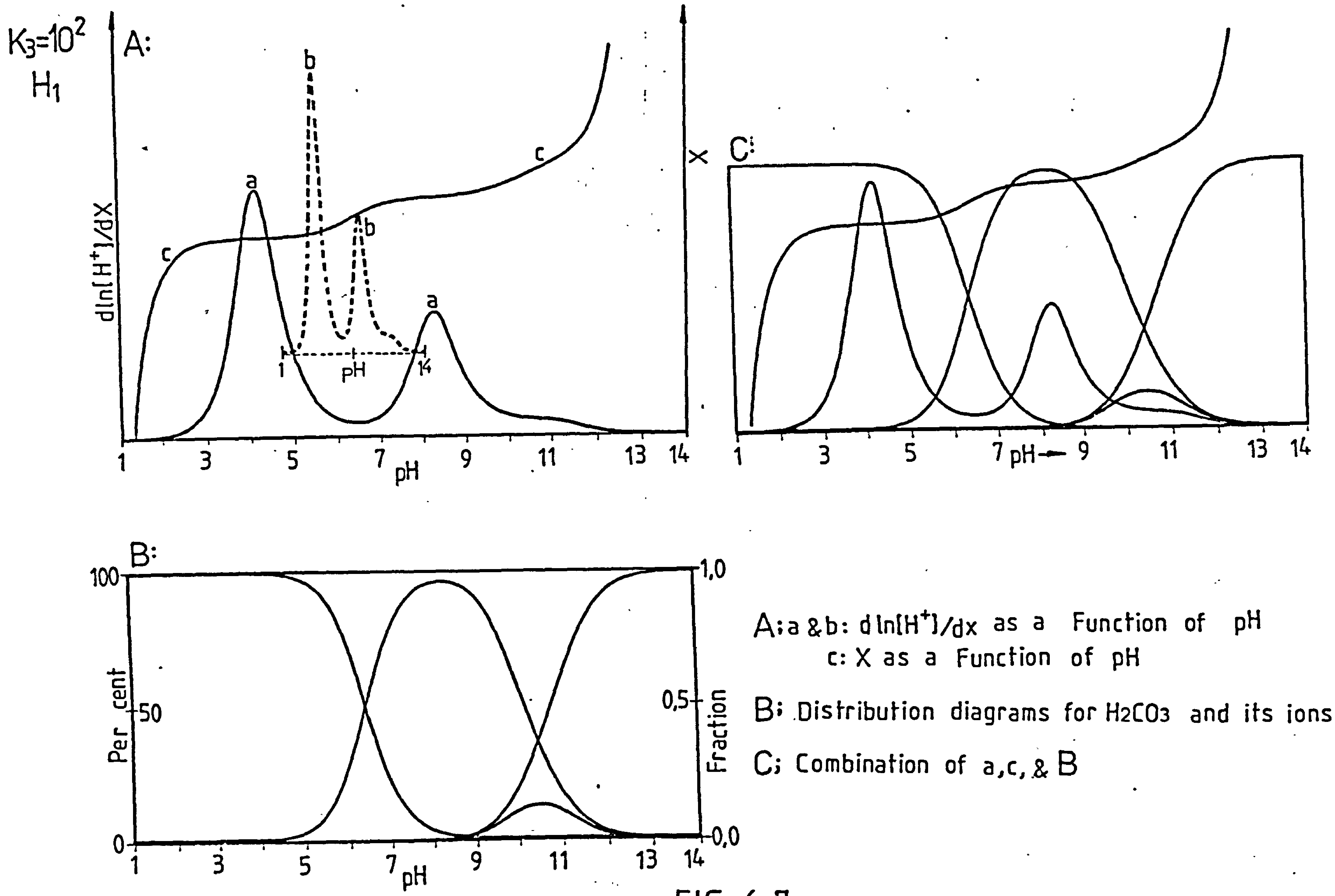


A: a & b: $d \ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C: Combination of a, c, & B

FIG 6-6

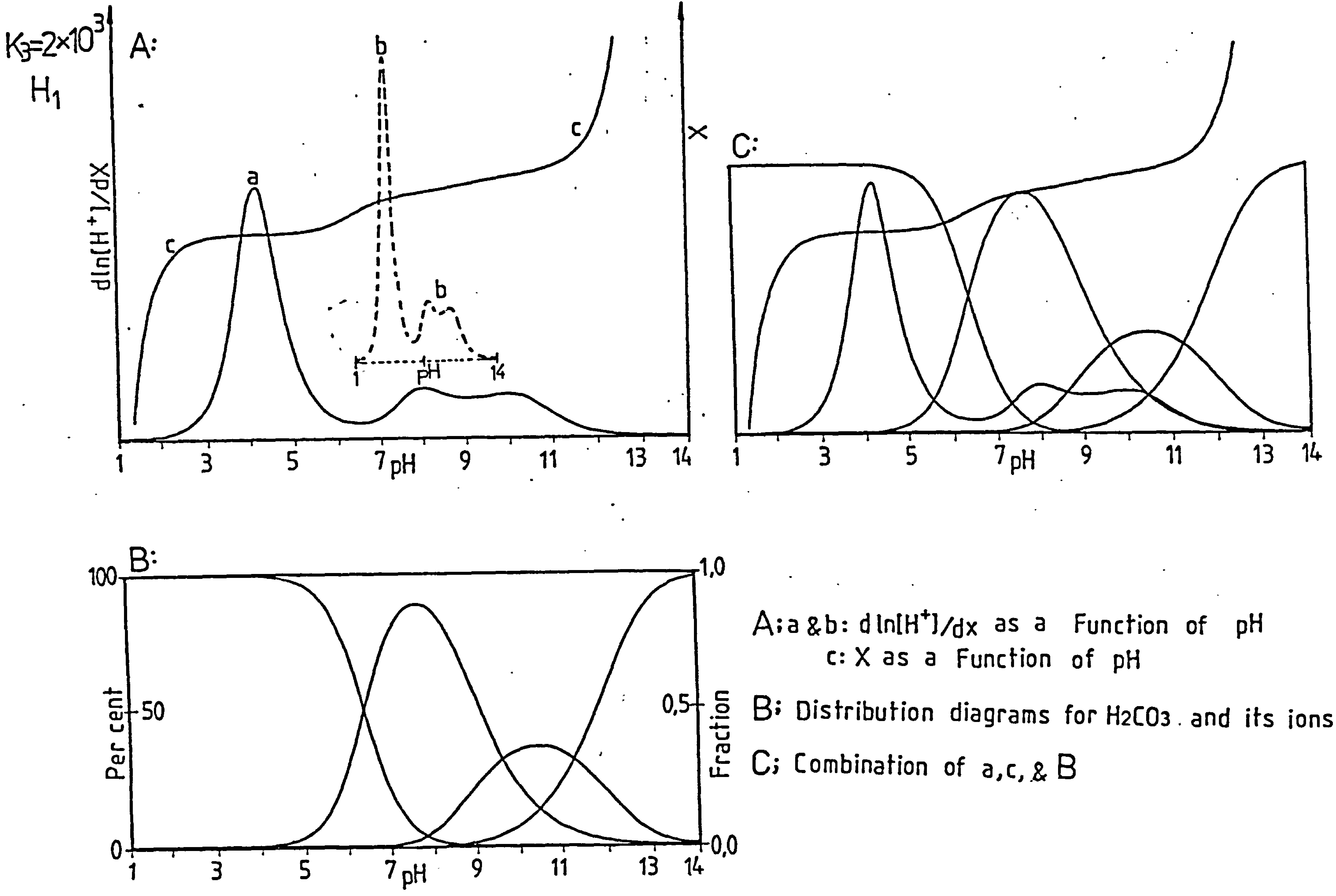


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C: Combination of a, c, & B

FIG 6-7

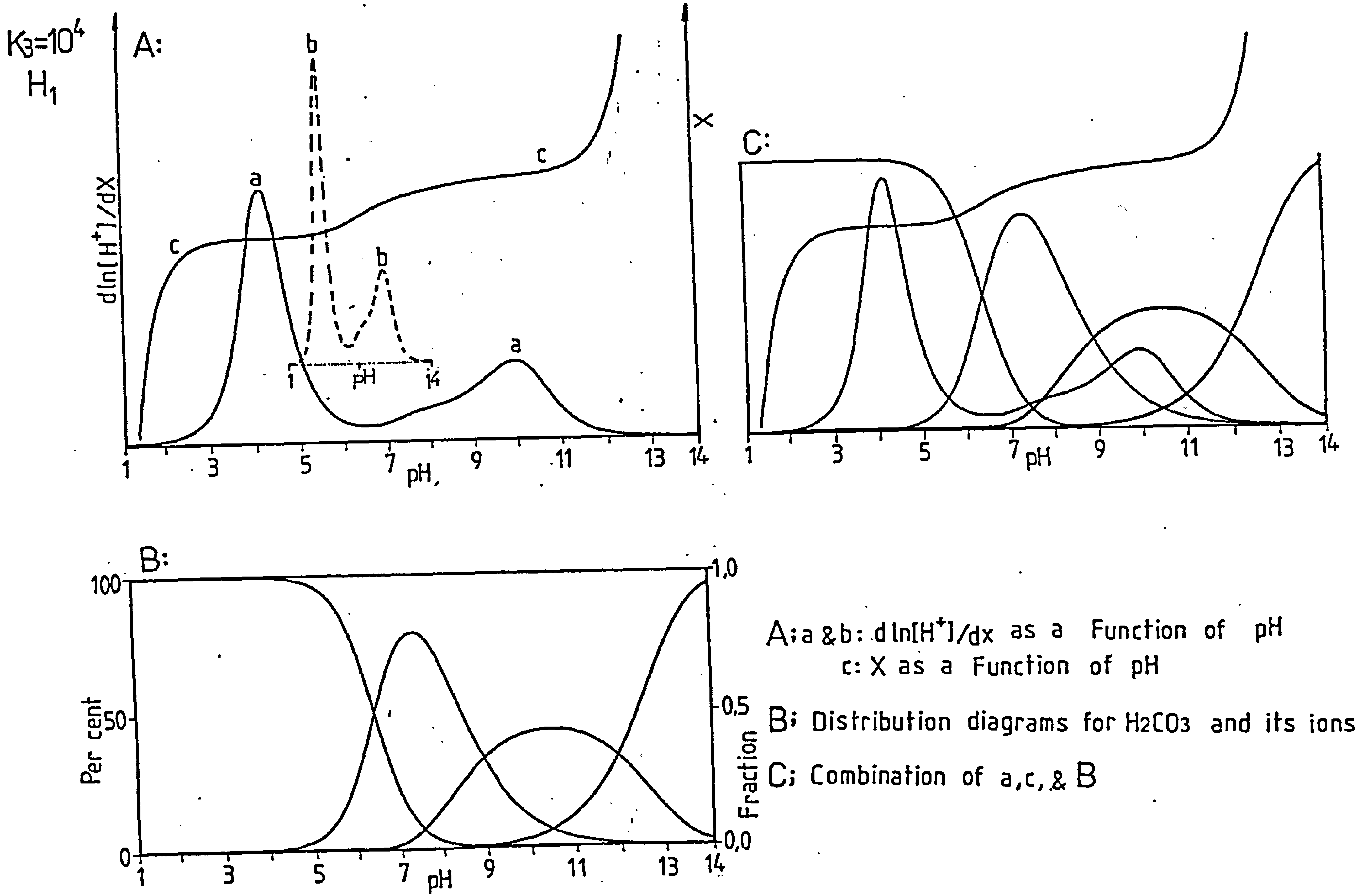


A; a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-8

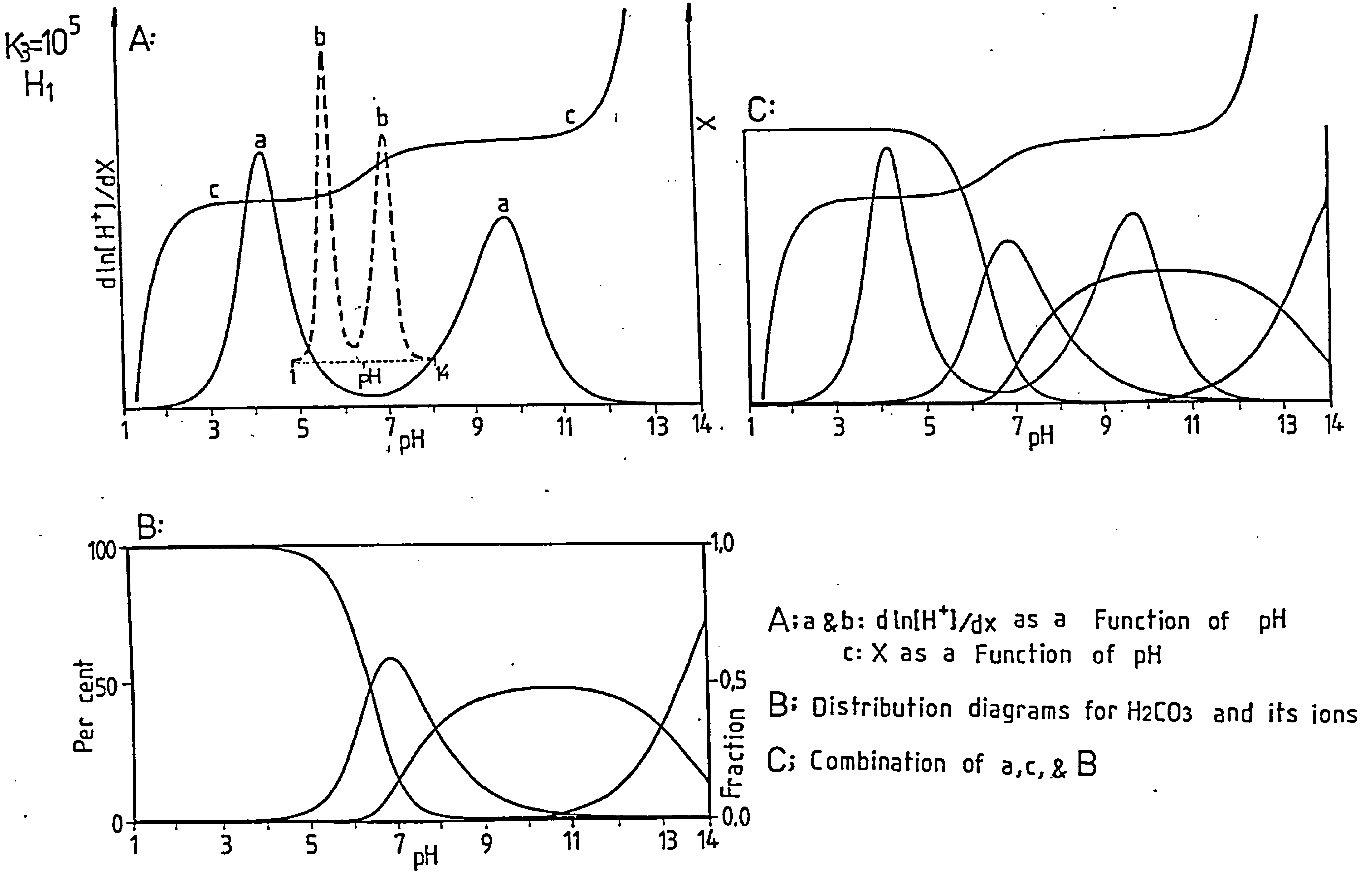


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-9



A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-10

6.3.2. HYPOTHESIS 2 (H2)

As described previously the additional peak may be due to CO_2 and HCO_3^- ion complexation forming a new species in the presence of water.

$$HCO_3^- + CO_2 + H_2O = H_3C_2O_6^-$$

For simplicity it is assumed that:

$$HCO_3^- + H_2CO_3 = H_3C_2O_6^- \qquad (28)$$

Again an equilibrium constant is associated with process (28), denoted by K_3:

$$(H_3C_2O_6^-) = K_3(HCO_3^-)(H_2CO_3) \qquad (29)$$

Using equations (19) and (20) and considering the above equilibrium process

$$(H_3C_2O_6^-) = (K_3/K_1K_2^2)h^3(CO_3^{2-})^2 \qquad (30)$$

Mass balance for carbonate system including the new species is as follows:

$$\begin{aligned} a &= (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) + 2(H_3C_2O_6^-) & (31)\\ &= ((h^2/K_1K_2) + (h/K_2) + 1)(CO_3^{2-}) + (2K_3/K_1K_2^2)h^3(CO_3^{2-})^2 \\ &= ((h^2 + hK_1 + K_1K_2)/K_1K_2)(CO_3^{2-}) + (2K_3/K_1K_2^2)h^3(CO_3^{2-})^2 & (32)\end{aligned}$$

This equation is again quadratic in (CO_3^{2-}) which is similar to hypothesis 1 (H1).

Differentiation of this equation gives:

$$\begin{aligned}0 &= d(((h^2 + hK_1 + K_1K_2)(CO_3^{2-}))/K_1K_2)/dx + (2K_3/K_1K_2^2)d(h^3(CO_3^{2-})^2)/dx \\ &= ((2h + K_1)/K_1K_2)(CO_3^{2-})(dh/dx) + ((h^2 + hK_1 + K_1K_2)/K_1K_2)(d(CO_3^{2-})/dx) \\ &\quad + (2K_3/K_1K_2^2)(CO_3^{2-})^2.3h^2(dh/dx) + (2K_3/K_1K_2^2)h^3.2(CO_3^{2-}). \\ &\quad (d(CO_3^{2-})/dx)\end{aligned}$$

$$\begin{aligned}&(d(CO_3^{2-})/dx)(((h^2 + hK_1 + K_1K_2)/K_1K_2) + (4K_3h^3(CO_3^{2-})/K_1K_2^2)) = \\ &\quad (-dh/dx)(((2h + K_1)/K_1K_2(CO_3^{2-})) + (6K_3h^2(CO_3^{2-})^2/K_1K_2^2))\end{aligned}$$

or $$(d(CO_3^{2-})/dx) = -M(dh/dx) \tag{33}$$

where: $$\begin{aligned}M = {}&(((2h + K_1)/K_1K_2)(CO_3^{2-})) + (6K_3h^2/K_1K_2^2)(CO_3^{2-}))/ \\ &(((h^2 + hK_1 + K_1K_2)/K_1K_2) + (4K_3h^3/K_1K_2^2)(CO_3^{2-}))\end{aligned}$$

Charge balance requires that:

$$h + (Na^+) = (HCO_3^-) + 2(CO_3^{2-}) + (H_3C_2O_6^-) + (OH^-) \tag{34}$$

$$h + 2ax = ((h/K_2) + 2)(CO_3^{2-}) + (K_3h^3/K_1K_2^2)(CO_3^{2-})^2 + K_w/h \tag{35}$$

$$\begin{aligned}(dh/dx) + 2a = {}&((CO_3^{2-})/K_2)(dh/dx) + ((h/K_2) + 2)(d(CO_3^{2-})/dx) - \\ &(K_w/h^2)(dh/dx) + (3h^2K_3/K_1K_2^2)(CO_3^{2-})^2(dh/dx) + \\ &(K_3h^2/K_1K_2^2).2\ (CO_3^{2-})(d(CO_3^{2-})/dx)\end{aligned} \tag{36}$$

substitution of values from equation (33) in equation (36) yields:

$$\begin{aligned}(dh/dx) + 2a = {}&(dh/dx)(((CO_3^{2-})/K_2) - M(h/K_2 + 2) + (3h^2K_3/K_1K_2^2)(CO_3^{2-})^2 - \\ &(2K_3h^2/K_1K_2^2)(CO_3^{2-})M - (K_w/h^2))\end{aligned}$$

so: $$(dh/dx) + 2a = (dh/dx)N$$

or: $$(dh/dx) = (2a/(N - 1)) \tag{37}$$

or: $$(d\ln h/dx) = (2a/(N - 1)h) \tag{38}$$

where: $$\begin{aligned}N = {}&(((CO_3^{2-})/K_2) - M(h/K_2 + 2) + (3h^2K_3/K_1K_2^2)(CO_3^{2-})^2 - (2K_3h^2/K_1K_2^2)(CO_3^{2-})M - \\ &- (K_w/h^2))\end{aligned}$$

Again the PDP8 computer was used to solve this equation. A listing of the computer program, as written in Fortran, is shown in the next pages. Also in figure 6-11, the procedure for calculation is shown.

Substitution of assumed equilibrium constant values (K_3) into this program for modelling titration curves produced figures 6-12 to 6-25. The values for K_3 are shown on each figure respectively. The corresponding results are shown in tables 7-20 of appendix, As shown in all figures, the curves for dlnh/dx vs. pH and lnh vs. pH and also the distribution diagrams of different species of carbonate at different pH values are calculated and drawn by computer.

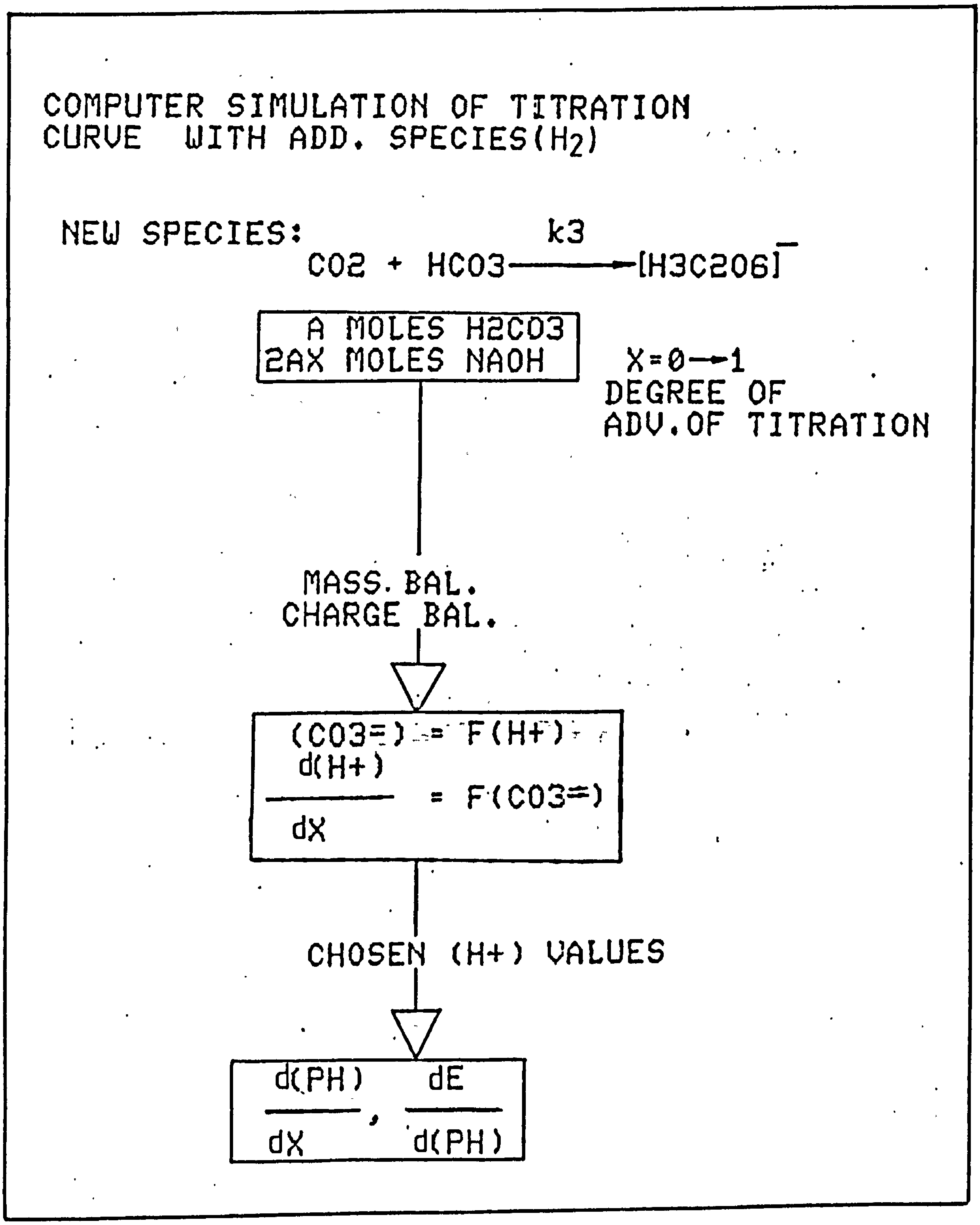
As is clear from these theoretical curves, the additional peak appeared between the first and the second neutralization peaks of carbonate ions which is comparable with the experimental peak. Also to clarify the effect of K_3 on the titration curves, a superimposed curve with different values for K_3 is shown in figure 6-26. For comparison of the theoretical and experimental curves and the determination of K_3, a series of curves (for different K_3 values) is shown in figure 6-27.

Comparing these curves with figures 6-28 to 6-30, where the experimental curves of dE/dV vs. pH is shown, indicates clearly that the value for K_3 is about 10^3.

```
 TY RXA1:CATEQ7.FT/T
C     CATEQ7 - VERSION H2/NULL     13-SEP-79
C
      DIMENSION Y(9)
      WRITE (1,10)
10    FORMAT (20X'CATEQ7     VERSION H2/NULL     13-SEP-79'//)
20    READ (1,30)A
30    FORMAT ('[A] = 'E10.2)
      READ (1,40)AK1
40    FORMAT ('K1  = 'E10.2)
      READ (1,50)AK2
50    FORMAT ('K2  = 'E10.2)
55    READ (1,60)AK3
60    FORMAT ('K3  = 'E10.2)
      READ (1,70)AKW
70    FORMAT ('KW  = 'E10.2)
100   READ (1,110)IMODE
110   FORMAT ('SELECT MODE - (1 = PRINT; 2 = GRAPHIC; 3 = RESTART:)  '
     1I1)
      IF (IMODE)100,100,120
120   IF (IMODE-3)130,20,100
130   IF (IMODE-2)140,140,20
140   READ (1,150)N
150   FORMAT ('NO. OF POINTS        = 'I4)
      IF (1024-N)140,155,155
155   READ (1,160)AHF
160   FORMAT ('INITIAL VALUE OF H = 'E10.2)
      READ (1,170)AHL
170   FORMAT ('FINAL VALUE OF H   = 'E10.2)
75    READ (1,80)IS
80    FORMAT ('SELECT H INCREMENT - (1 = LIN; 2 = LOG:)  'I1)
      IF (IS)75,75,90
90    IF (IS-2)175,175,75
175   IF (IMODE-2)200,180,20
180   READ (1,185)N1,N2,N3,N4
185   FORMAT ('SELECT TERMS TO BE PLOTTED - '3(I1,2H; )I1,1H:)
      READ (1,190)S
190   FORMAT ('DYNAMIC RANGE        = + OR - 'E12.4)
      S=2047./S
      F=(100.0*S)/A
      IR=-1
      GO TO 215
200   WRITE (1,201)
201   FORMAT (/////)
      WRITE (1,10)
      WRITE (1,410)A
      WRITE (1,400)AK1,AK2,AK3,AKW
      WRITE (1,210)
```

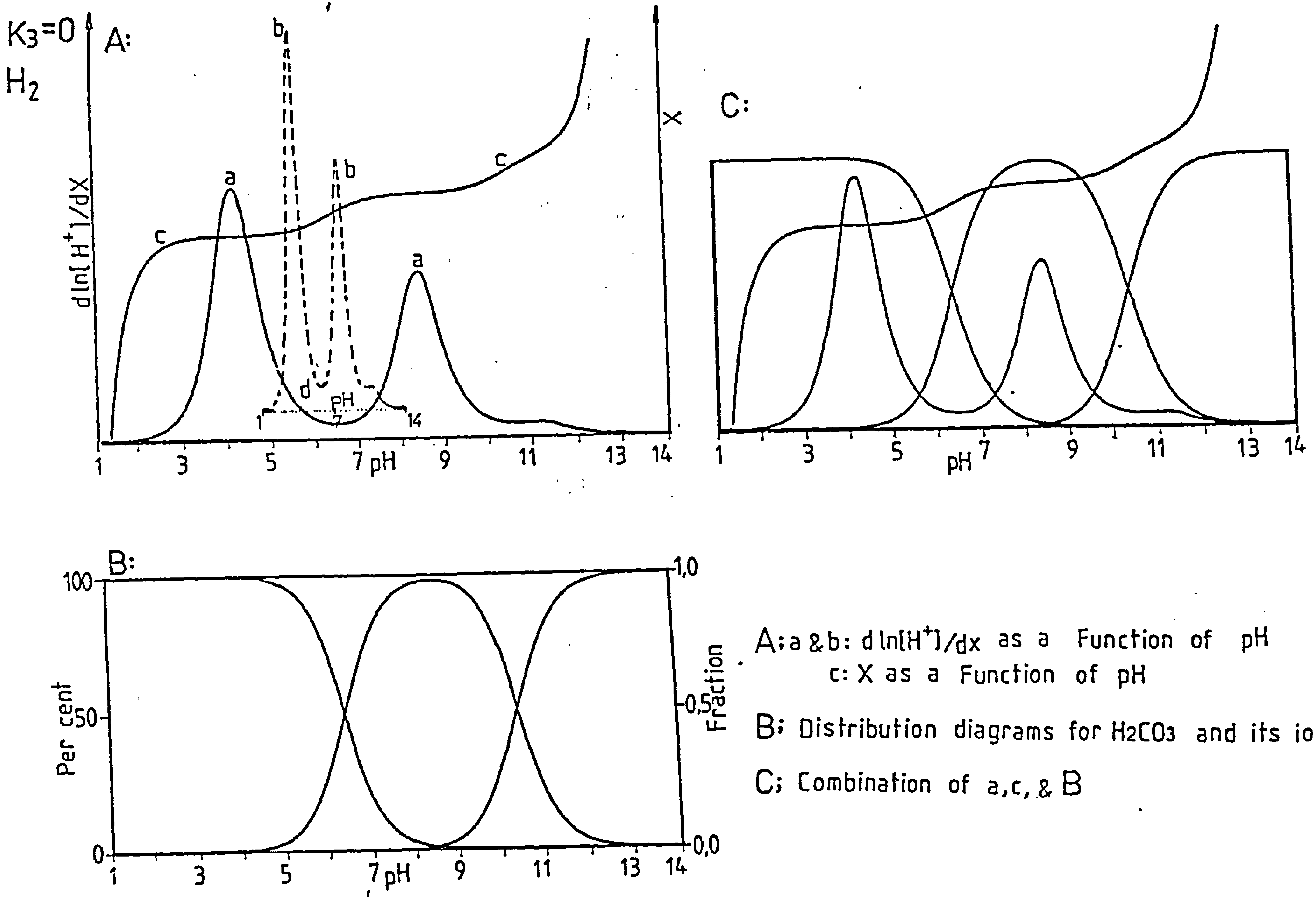
```
 210   FORMAT (/7X'(1)'10X'(2)'11X'(3)'10X'(4)'8X'(5)'11X'
      1(6)'13X'(7)'10X'(8)'10X'(9)'/6X'[H+]'11X'X'9X'DLN[H+]/DX'
      16X'PH'10X'T'10X'[CO3""]'9X'[HCO3"]'6X'[H2CO3]'5X
      1'DLN[CO2]/DX'/)
 215   IF (IS-1)220,220,230
 220   DH=(AHL-AHF)/FLOAT(N)
       GO TO 240
 230   DLH=(ALOG(AHL/AHF))/FLOAT(N)
 240   AH=AHF
       AK12=AK1*AK2
       AK23=AK3/AK2
       DO 330 I=1,N
       AH2=AH*AH
       AH3=AH*AH2
       AHK23=AH3*AK23
       D1=AK12+AH*AK1+AH2
       IF (AK3)55,245,248
 245   D2=4.*AH*AK2+AK12+AH2
       D4=A*AH*AK1*D2/(D1*D1)
       D3=2.*A/(AH+D4+AKW/AH)
       A2=AK12*A/D1
       BC=AH*AK1*A/D1
       B=-AH+A*AK1*(AH+2.*AK2)/D1+AKW/AH
       DC=AK1*(AH+2.*AK2)*D3/D1
       HC=AH2*A/D1
       T=0
       GO TO 265
 248   AI=D1/(2.*AHK23)
       AI=D1/(2.*AHK23)
       ARG=AI*AI+2.*A*AK12/AHK23
       A2=(-AI+SQRT(ARG))/2.
       A22=A*AK12/D1
       IF (A*0.9-A2)250,250,260
 250   A2=A22
 260   A2X=A2*A2
       AM=(2.*AH+AK1)*A2/AK12+6.*AK23*AH2*A2X/AK12
       AM=AM/(D1/AK12+4.*AHK23*A2/AK12)
       AN1=3.*AK23*AH2*A2X/AK12-2.*AHK23*A2*AM/AK12
       AN=AN1+A2/AK2-AM*(2.+AH/AK2)-AKW/AH2
       T=AK23*AH3*A2X/AK12
       BC=A2*AH/AK2
       D3=2.*A/(AH*(1.-AN))
       DC=(2.*A2-AH*AM)*D3/A2
       HC=A2*AH2/AK12
       B=-AH+(2.+AH/AK2)*A2+AHK23*A2X/AK12+AKW/AH
 265   X=B/(2.*A)
       G=-0.43429*ALOG(AH)
       IF (IMODE-2)270,290,20
```

```
270   WRITE (1,280)AH,X,D3,G,T,A2,BC,HC,DC
280   FORMAT (1X,3(E12.4,2X),F8.2,5(2X,E12.4))
      GO TO 300
290   Y(1)=AH
      Y(2)=X*800.0
      Y(3)=D3*S
      Y(4)=G
      Y(5)=T*F
      Y(6)=A2*F
      Y(7)=BC*F
      Y(8)=HC*F
      Y(9)=DC*S
      NP1=IFIX(Y(N1))
      NP2=IFIX(Y(N2))
      NP3=IFIX(Y(N3))
      NP4=IFIX(Y(N4))
      IA=(I-1)-2047
      CALL CAT (IA,NP1,IR)
      IA=IA+1024
      CALL CAT (IA,NP2,IR)
      IA=IA+1024
      CALL CAT (IA,NP3,IR)
      IA=IA+1024
      CALL CAT (IA,NP4,IR)
300   IF (IS-1)310,310,320
310   AH=AH+DH
      GO TO 330
320   AIH=ALOG(AH)+DLH
      AH=EXP (AIH)
330   CONTINUE
      IF (IMODE-2)335,340,100
335   WRITE (1,201)
      GO TO 100
340   CALL CAT (0,0,-4)
350   GO TO 100
400   FORMAT (8X'K1 = 'E10.2,10X'K2 = 'E10.2,10X'K3 = 'E10.2,
     110X'KW = 'E10.2,//)
410   FORMAT (7X'[A] = 'E10.2)
      END
```



FLOW DIAGRAM FOR " H_2 "

FIG 6-11

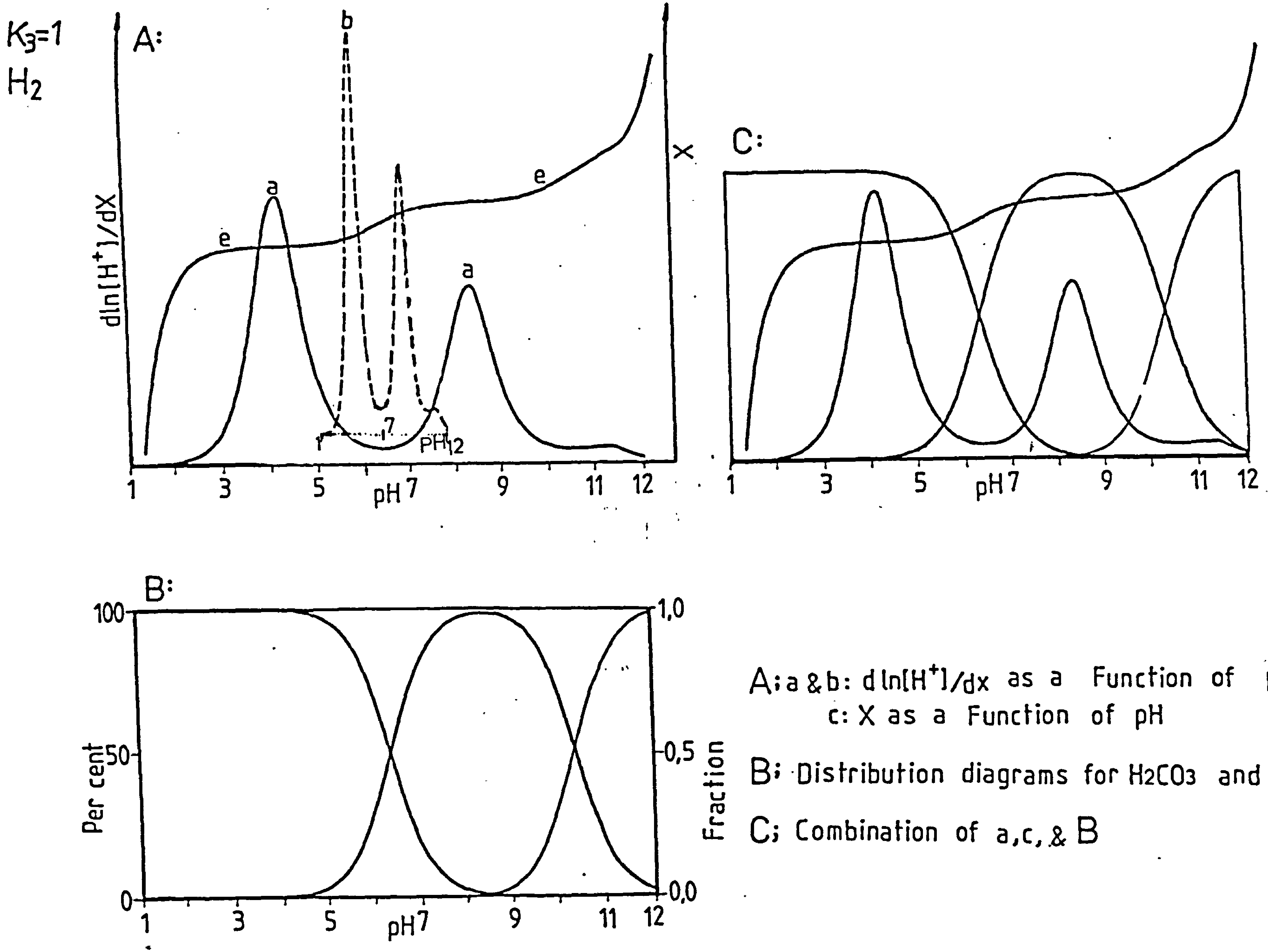


A; a & b: d ln[H$^+$]/dx as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a,c, & B

FIG 6-12

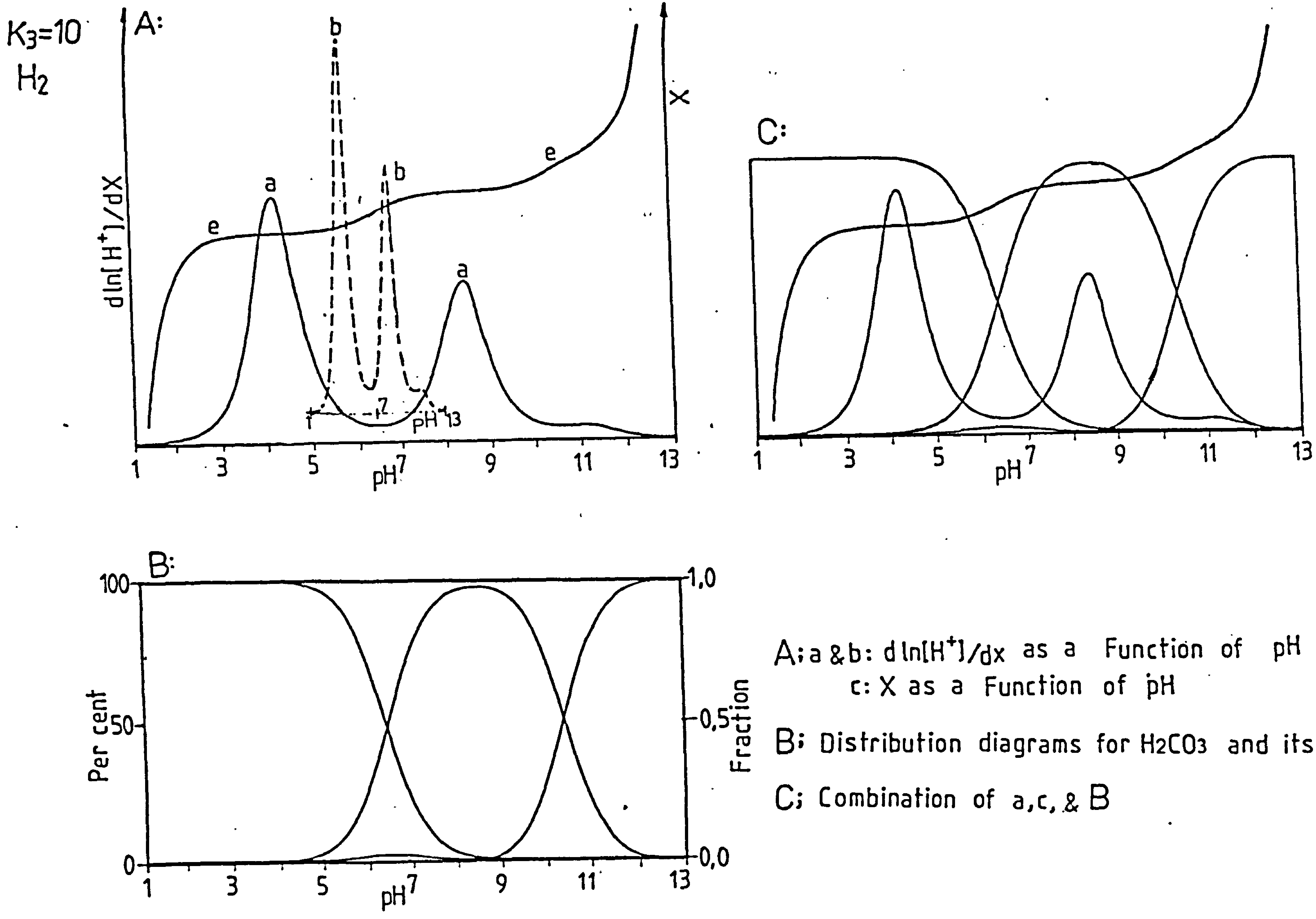


A; a & b: d ln[H^+]/dx as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-13

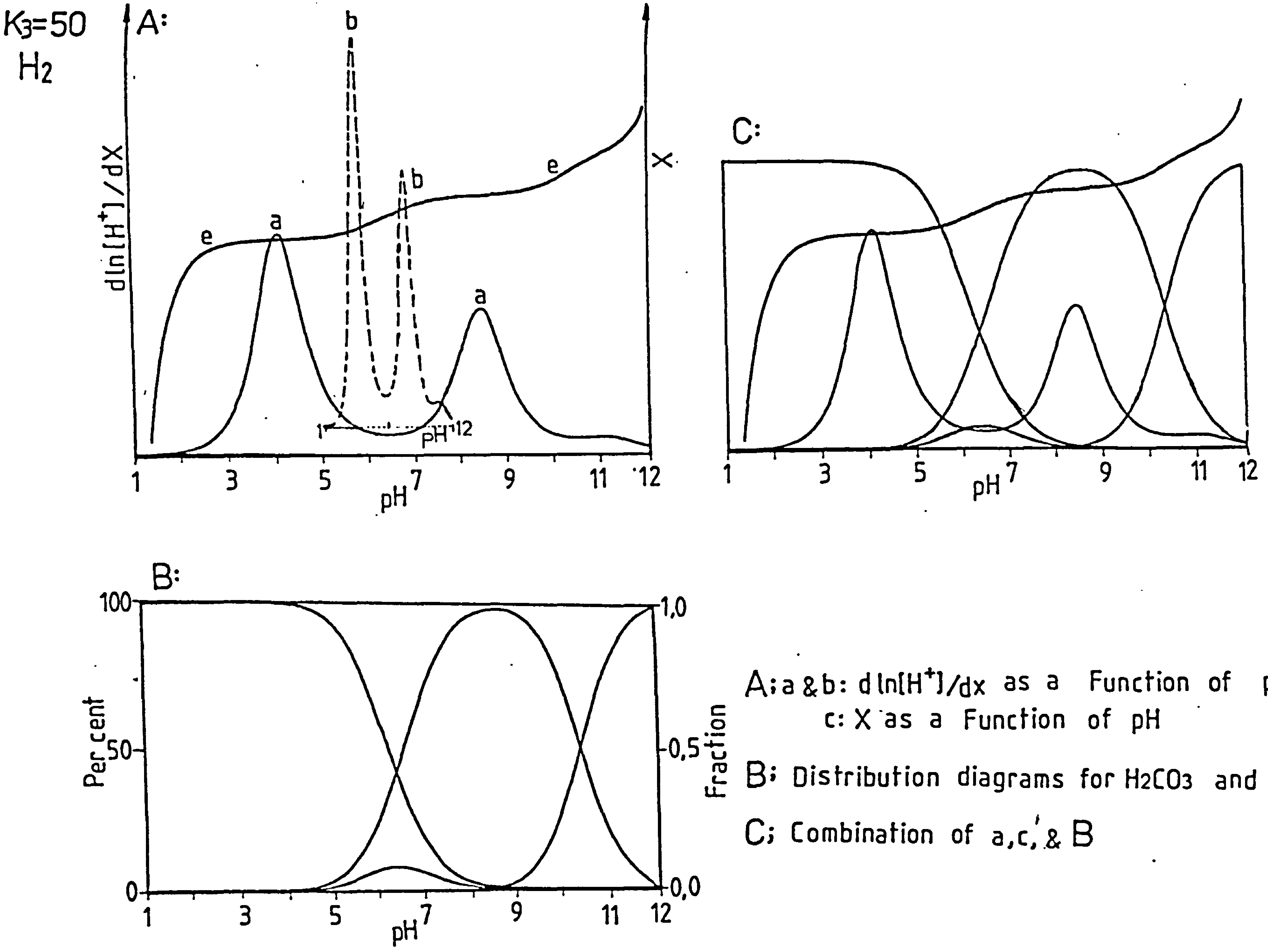


A; a & b: $d \ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6–14

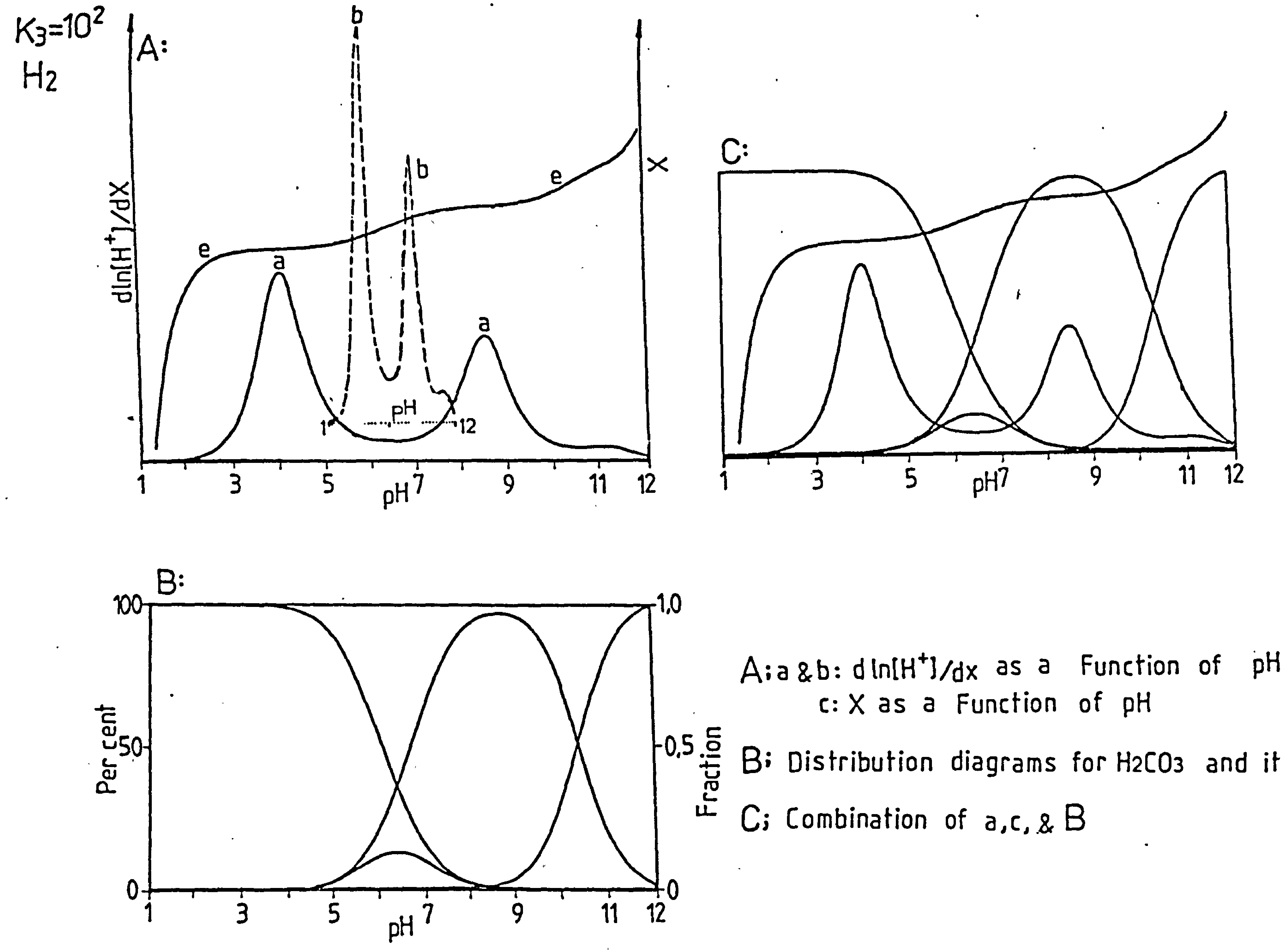


A; a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c', & B

FIG 6–15

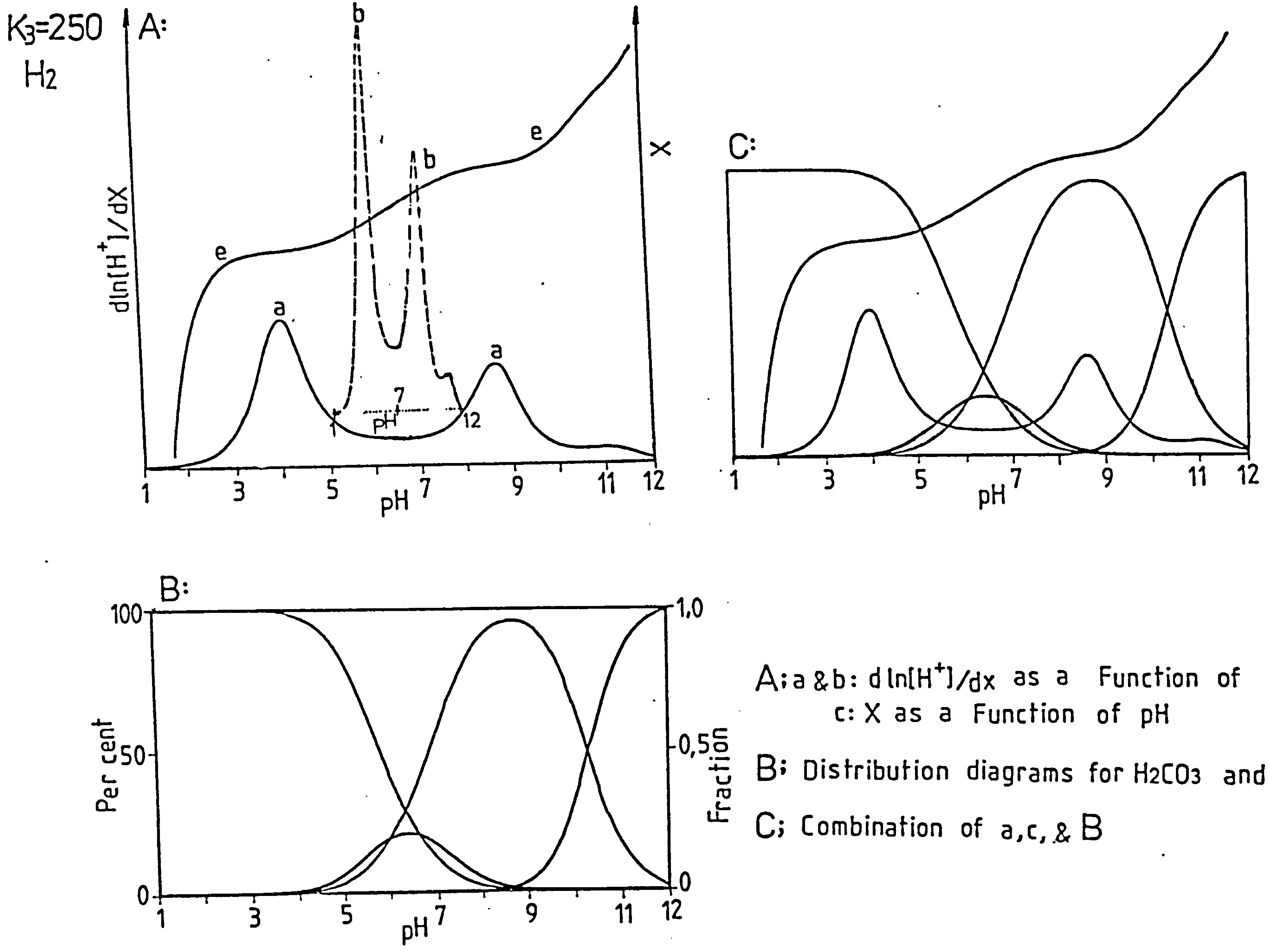


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C; Combination of a,c, & B

FIG 6-16

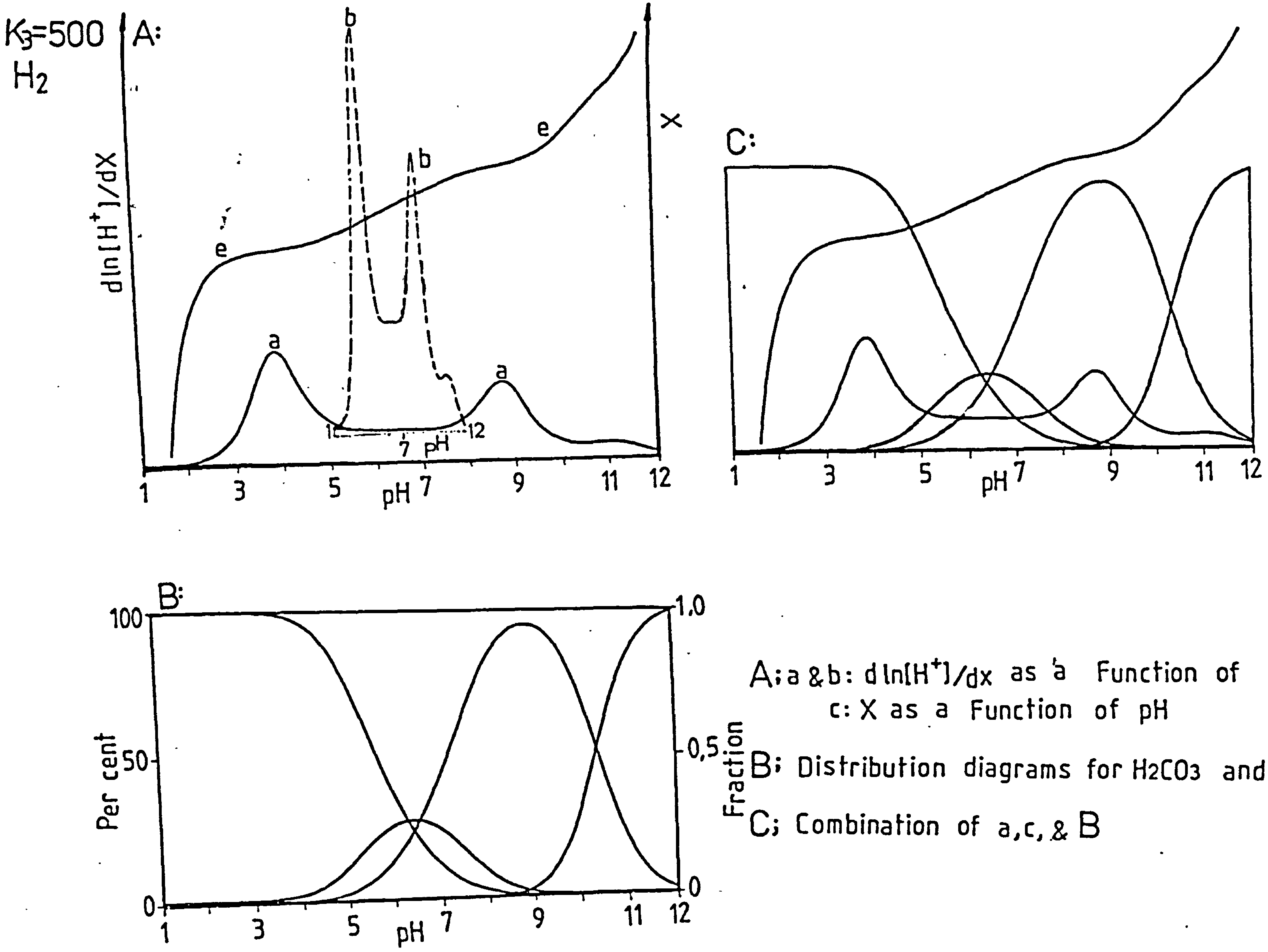


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C: Combination of a, c, & B

FIG 6–17



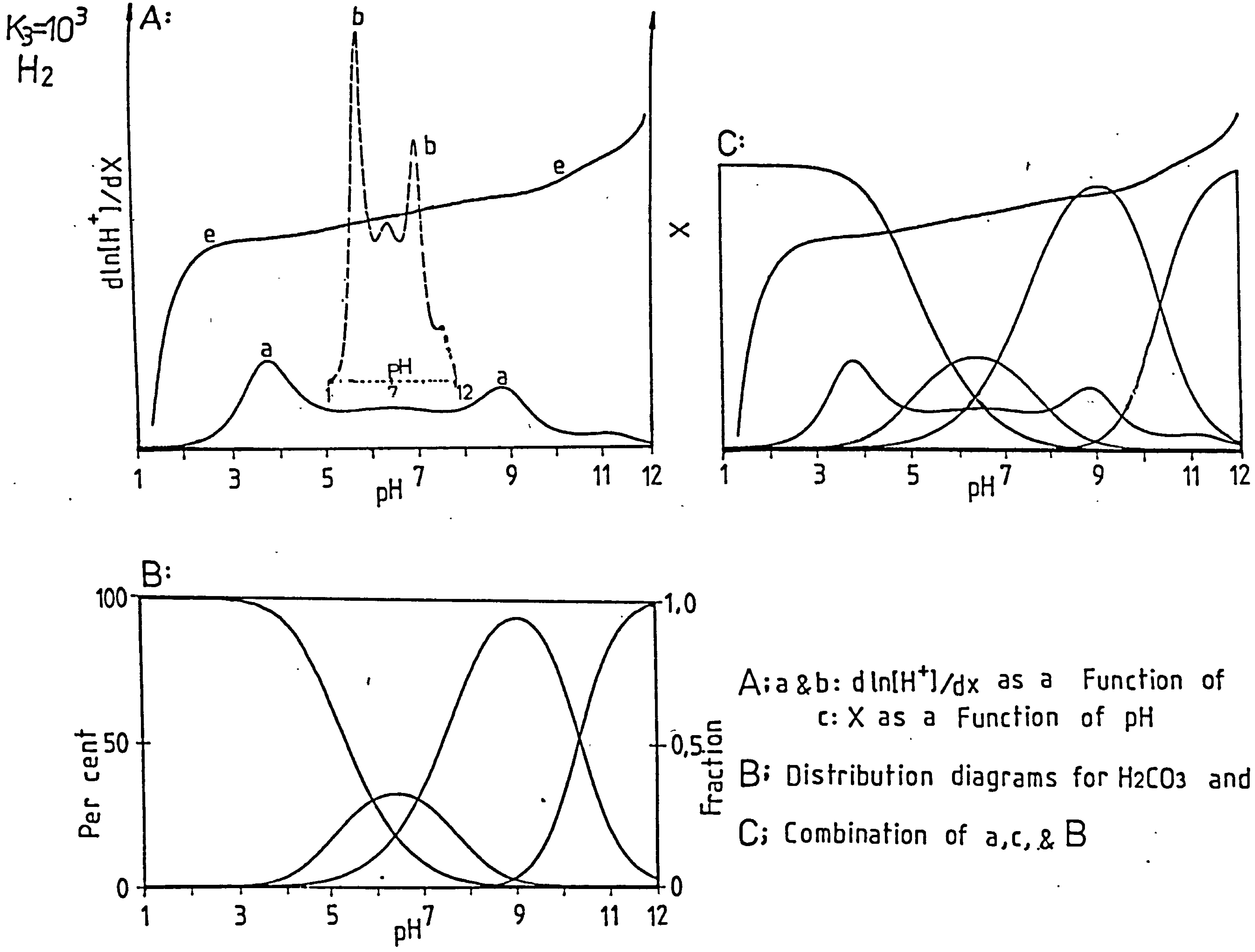
A; a & b: d ln[H^+]/dx as a Function of pH

c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6–18

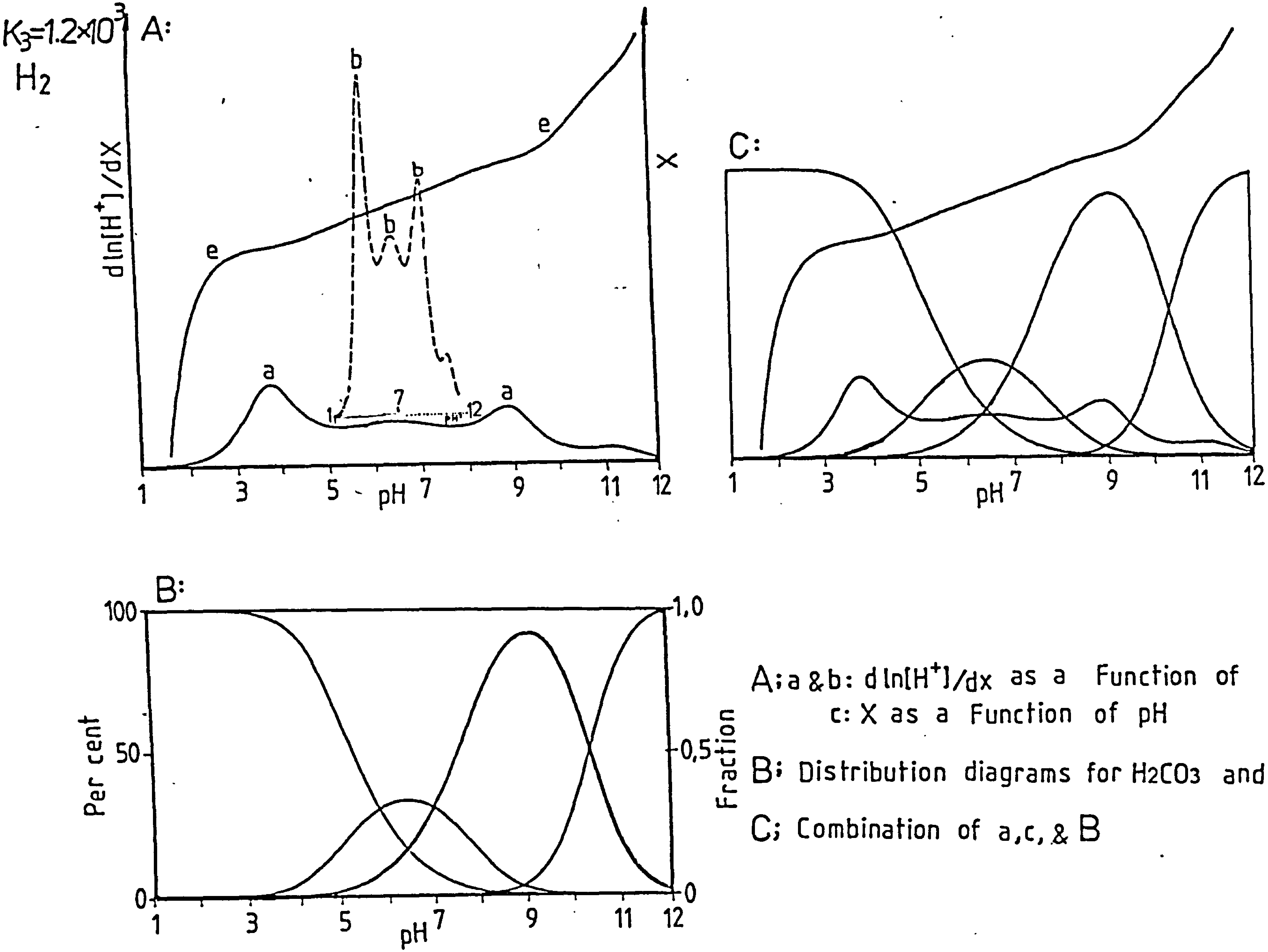


A; a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6 – 19

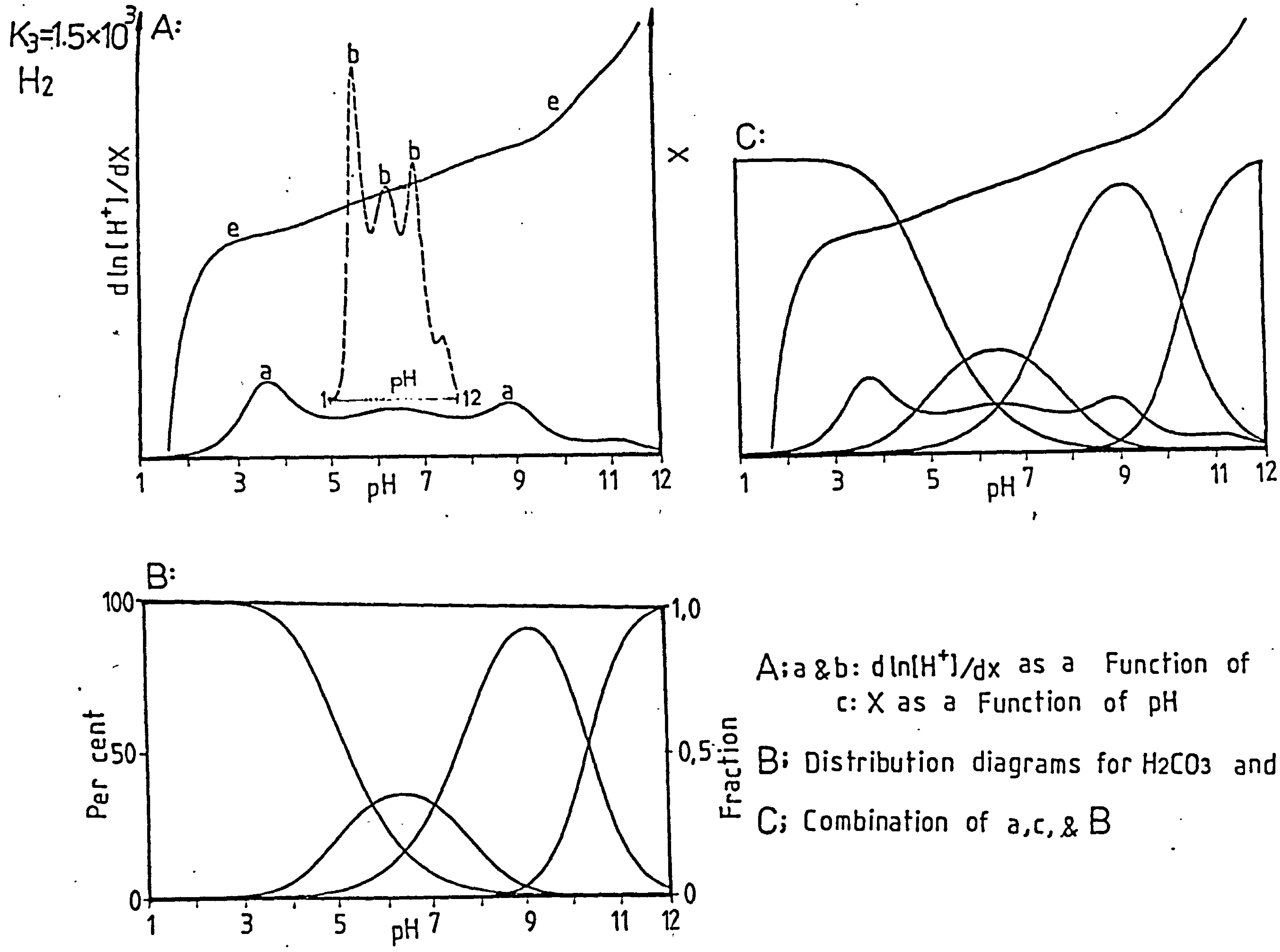


A; a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-20

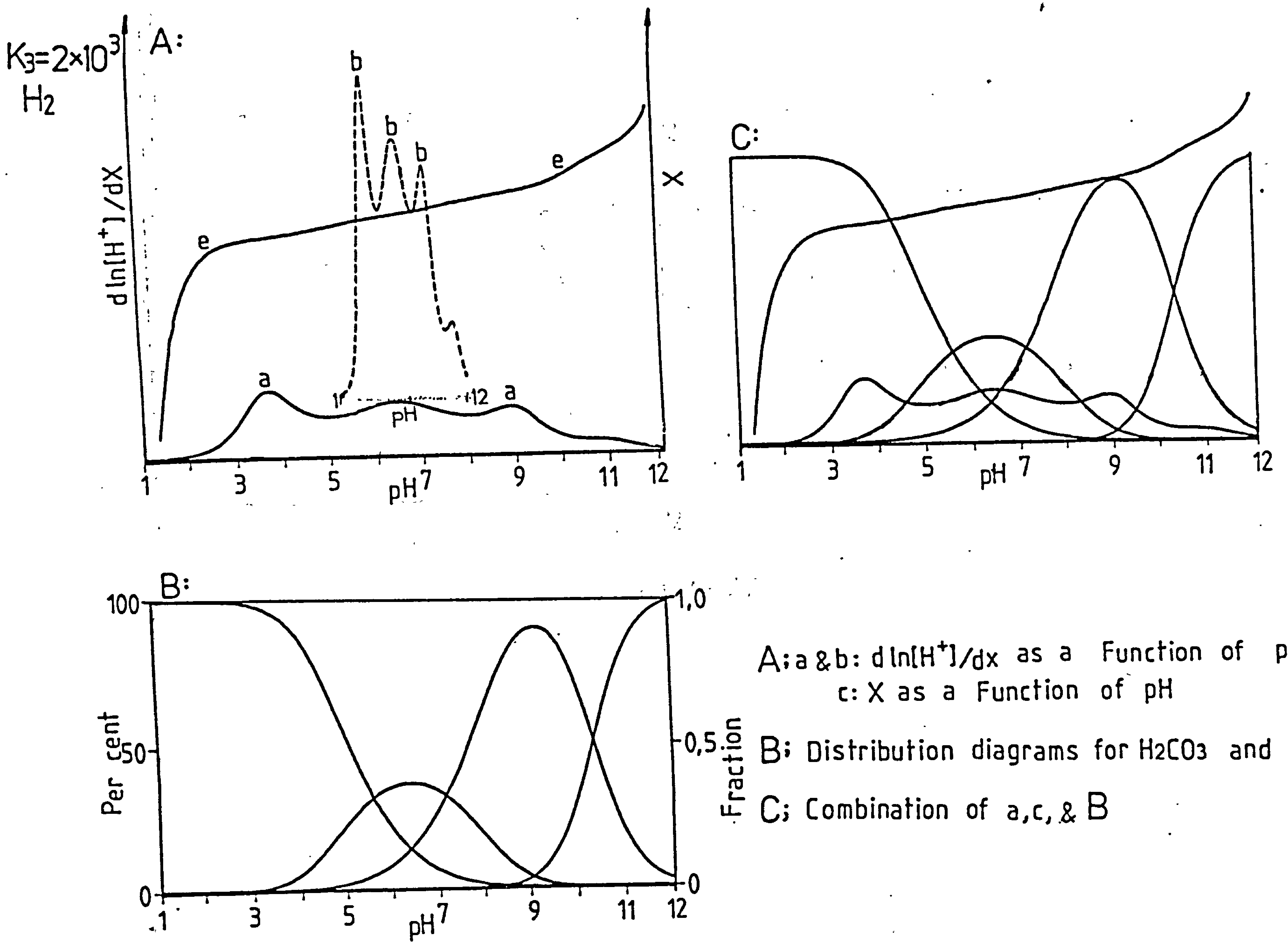


A; a & b: d ln[H$^+$]/dx as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6–21

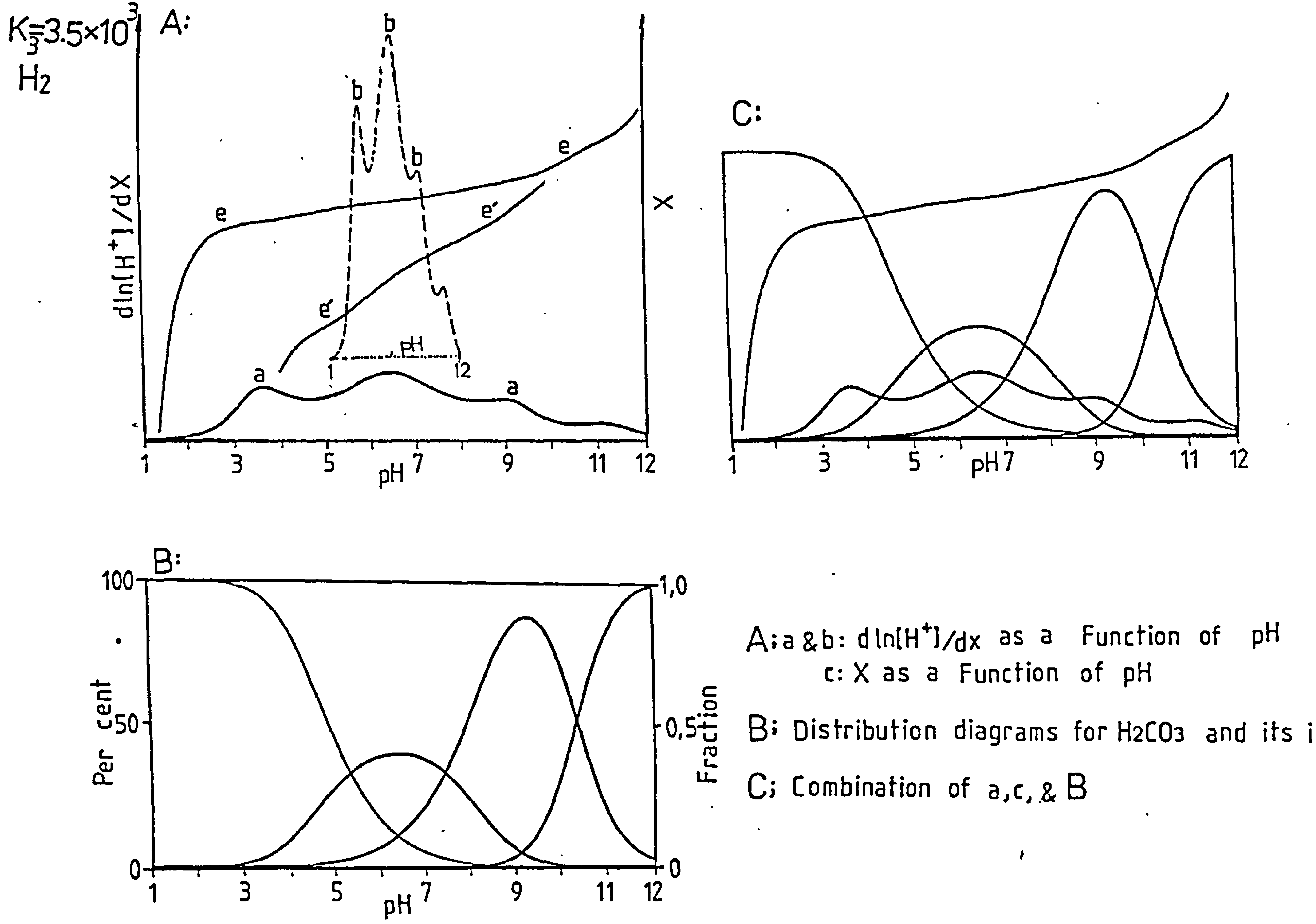


A; a & b: $d \ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B; Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-22

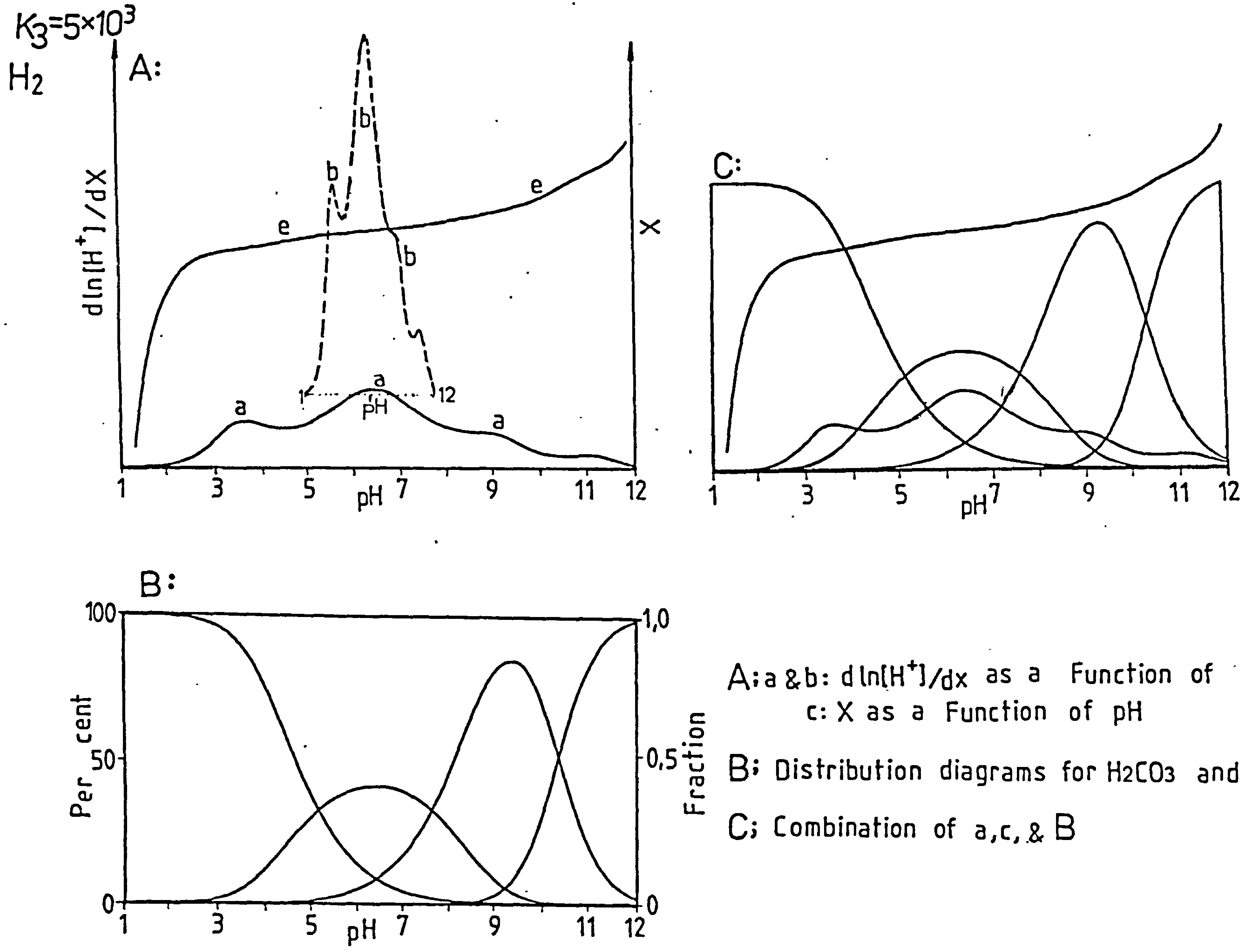


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C; Combination of a, c, & B

FIG 6-23

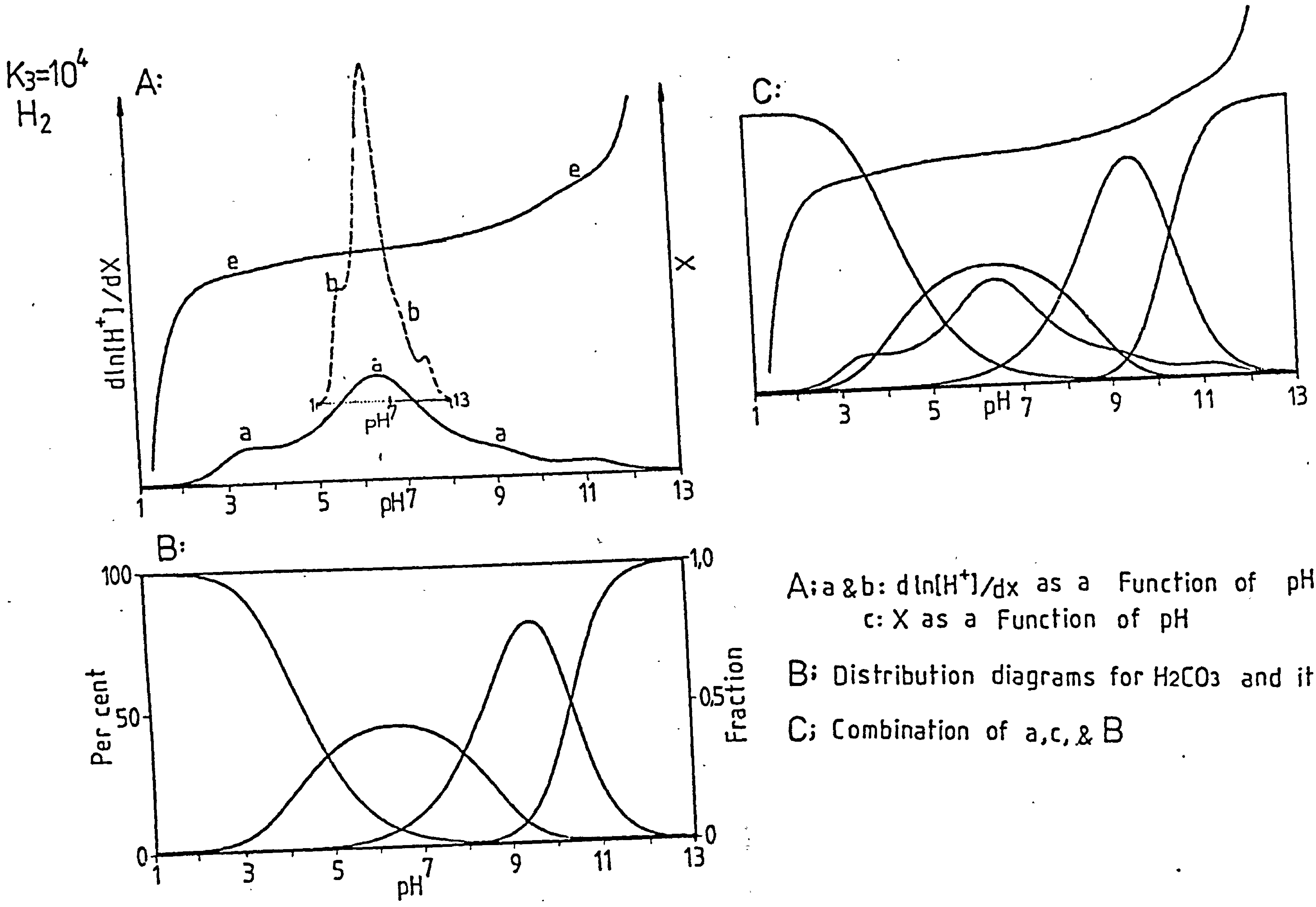


A: a & b: $d\ln[H^+]/dx$ as a Function of pH
c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C: Combination of a, c, & B

FIG 6-24



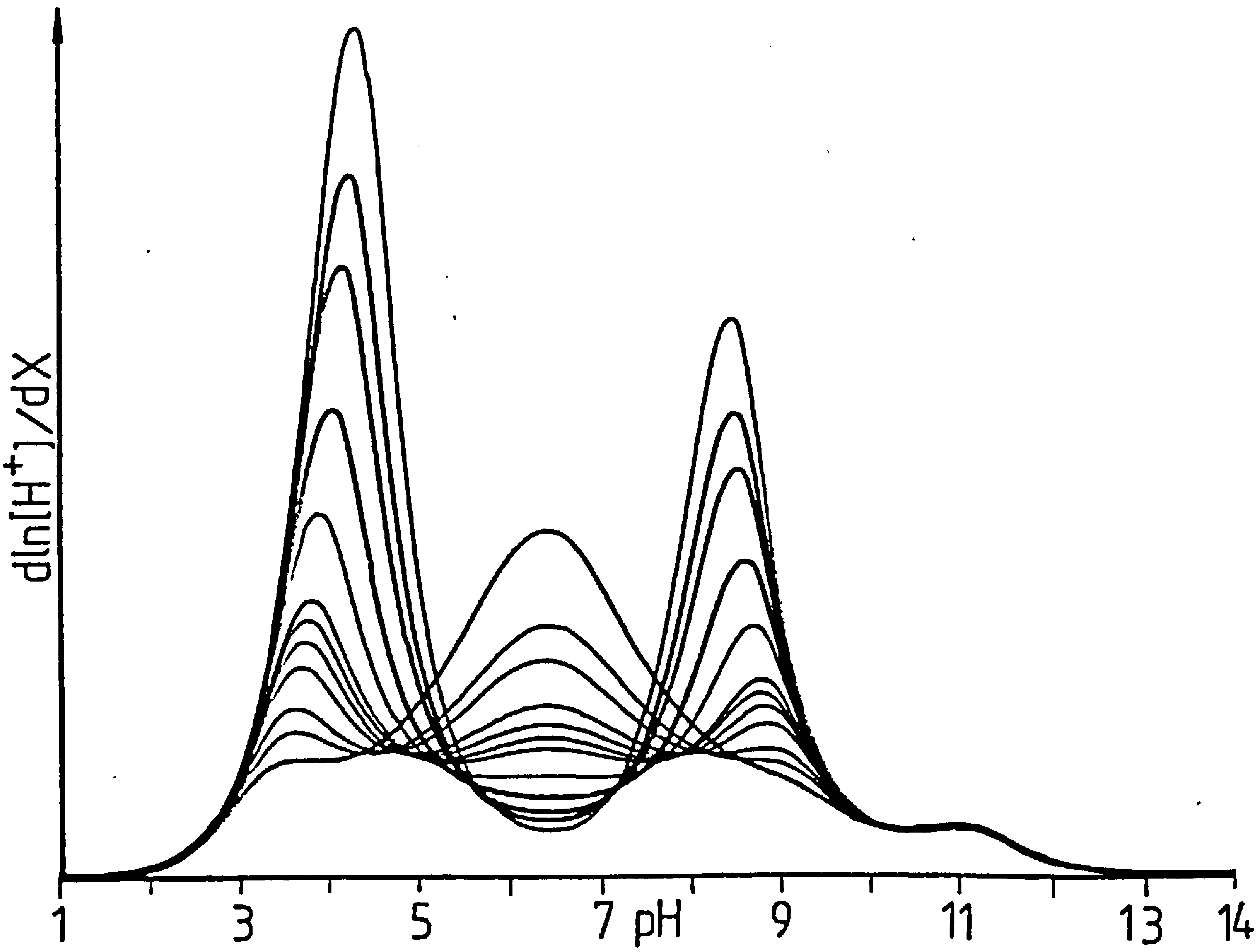
A: a & b: $d\ln[H^+]/dx$ as a Function of pH

c: X as a Function of pH

B: Distribution diagrams for H_2CO_3 and its ions

C; Combination of a,c, & B

FIG 6-25



Effect of changing of values of K_3 on "d ln[H^+]/dx as a Function of pH" curves.

Reading upwords at pH = 4 the curves refer to: $K_3 = 10^4, 5\times10^3, 3.5\times10^3, 2\times10^3, 1.5\times10^3, 2\times10^3, 10^3, 5\times10^2, 2.5\times10^2, 10^2, 50, 0$;

FIG 6–26

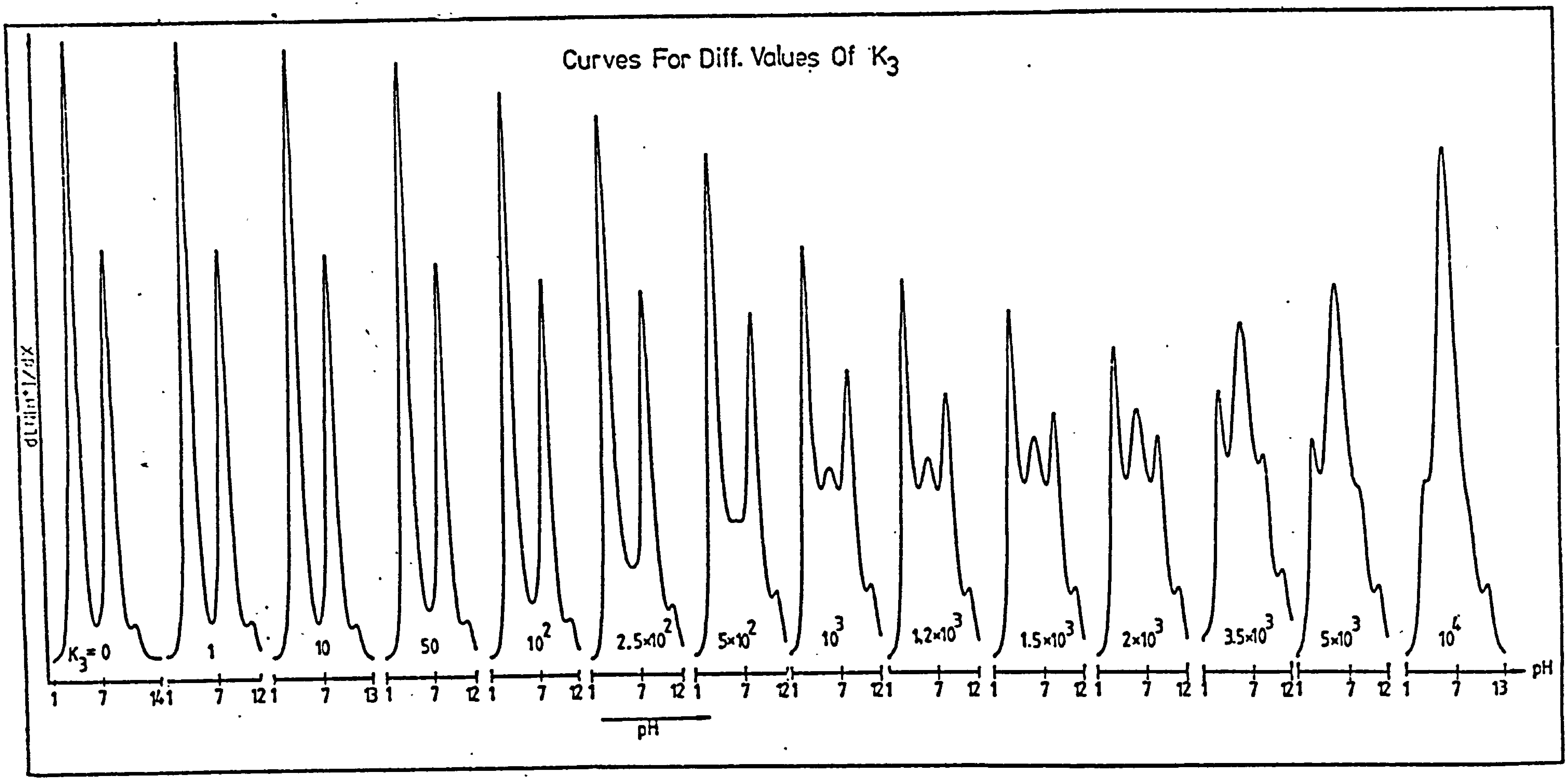
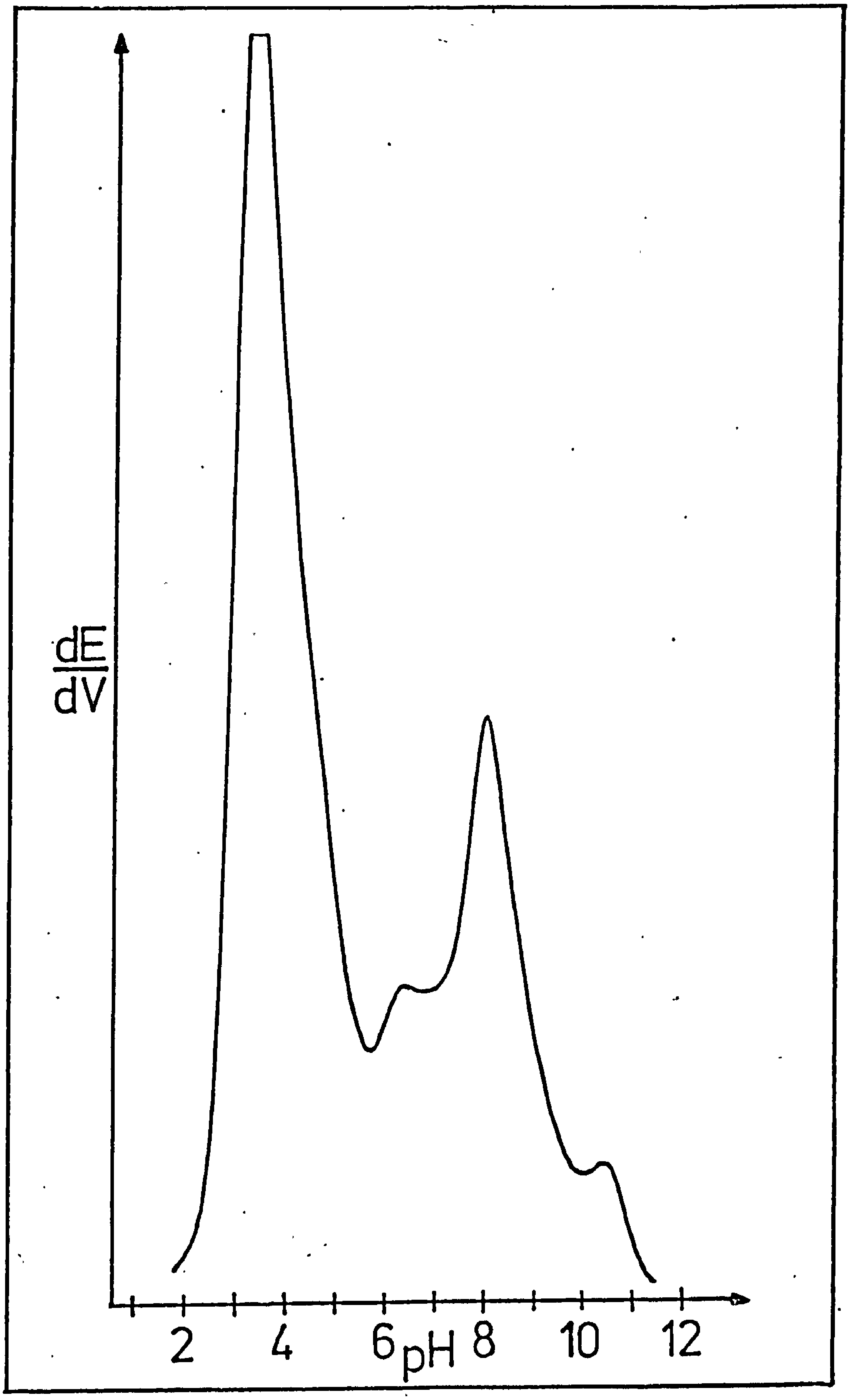
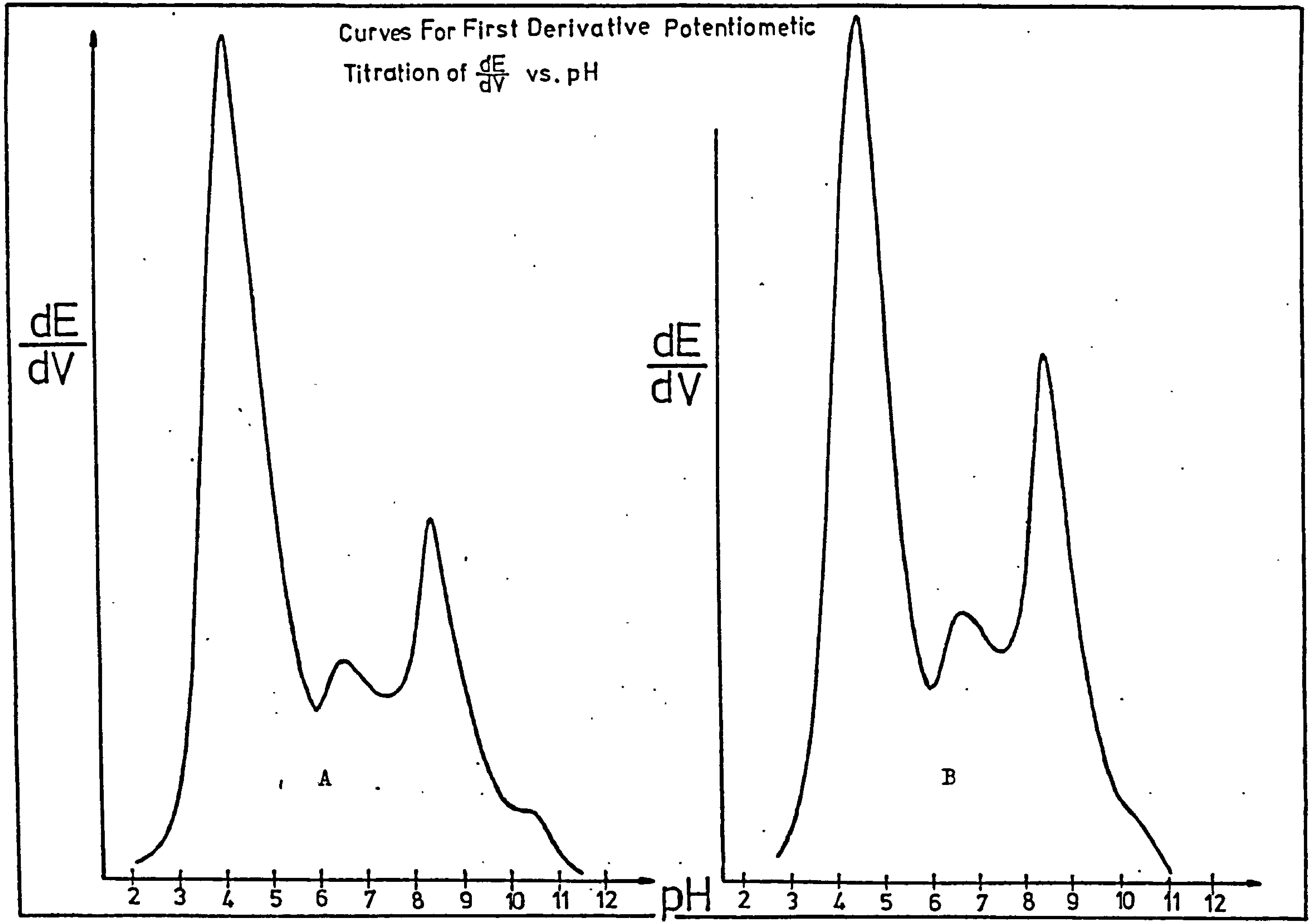

Curves For Diff. Values Of K3
K3 = 0
1
10
50
10^2
2.5×10^2
5×10^2
10^3
1.2×10^3
1.5×10^3
2×10^3
3.5×10^3
5×10^3
10^4
1 7 14
1 7 12
1 7 13
pH

FIG 6–27



Titration curve of d(pH)/dV for 25ml soln. of 0.04mol/l NaOH Containing 22 mole percent Na_2CO_3 with HCl 0.25mol/l(1ml in 1.5min.)

FIG 6-28

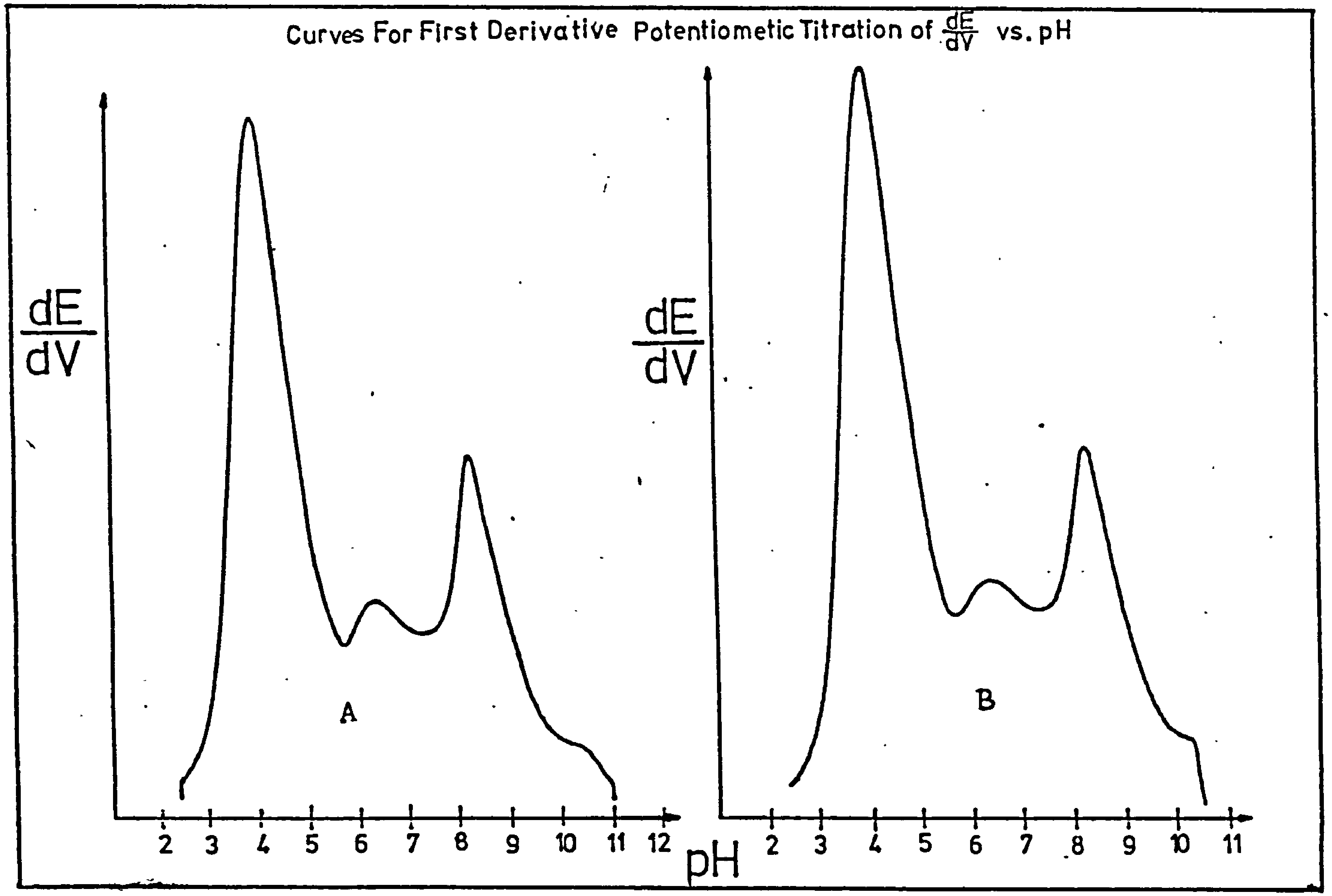


Titration Curves of d(pH)/dV for 25ml solution of 0.04mol/l NaOH

A: Containing 2,5 mole percent Na_2CO_3 with HCl 0.05mol/l (r.a. 1ml in 4 min)

B: Containing 10mole percent Na_2CO_3 with HCl 0.25mole/l(r.a. 1ml in 4 min)

FIG 6-29



Curves For First Derivative Potentiometic Titration of $\frac{dE}{dV}$ vs. pH

Titration Curves of d(pH)/dV for 25ml soln. of 0.04mole/l NaOHContaining
A:6.5 B:5 mole percent Na_2CO_3 with HCl 0.05mol/l(rate of addition:1ml in 1.3min)

FIG 6-30

6.4.1. MATHEMATICAL EQUATIONS AND THEORETICAL CURVE OF dln(CO_2)/dx VS. pH FOR CO_2 ELECTRODE:

According to equation (20) where the kinetics stage was ignored:

$$(H_2CO_3) = (CO_2) = (h^2/K_1K_2)(CO_3^{2-})$$

differentiation of this equation yields:

$$\begin{aligned}(d(CO_2)/dx) &= (2h/K_1K_2)(dh/dx)(CO_3^{2-}) + (h^2/K_1K_2)(d(CO_3^{2-})/dx)\\ &= (2h/K_1K_2)(dh/dx)(CO_3^{2-}) - (h^2/K_1K_2)M(dh/dx)\end{aligned}$$

since: $(d(CO_3^{2-})/dx) = -M(dh/dx)$

so: $(d(CO_2)/dx) = ((2h/K_1K_2)(CO_3^{2-}) - (h^2/K_1K_2)M)(dh/dx)$

and therefore:

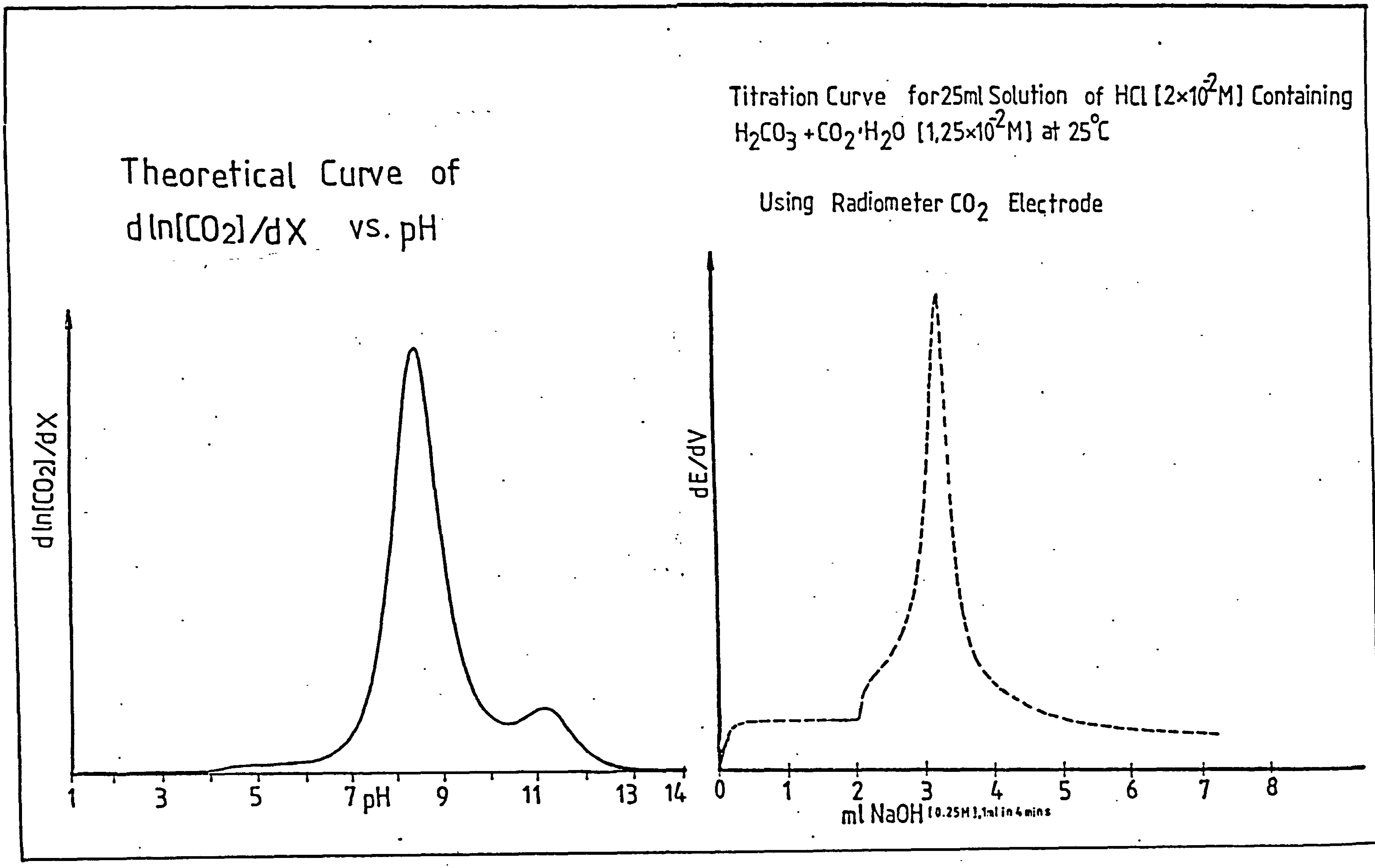
$$(i/(CO_2))(d(CO_2)/dx) = (d\ln(CO_2)/dx) = ((2h(CO_3^{2-}) - h^2M)/K_1K_2).\ (dh/dx)/(h^2/K_1K_2)(CO_3^{2-})$$

and

$$\begin{aligned}(d\ln(CO_2)/dx) &= ((2h(CO_3^{2-}) - h^2M)/h^2(CO_3^{2-}))(dh/dx)\\ &= ((2h(CO_3^{2-}) - h^2M)/h(CO_3^{2-}))(dnlh/dx)\\ &= ((2(CO_3^{2-}) - hM)/(CO_3^{2-}))(d\ln h/dx) \qquad (39)\end{aligned}$$

Using the PDP8 computer, equation (39) was solved. Figure 6-31 shows the theoretical titration curve along with the first derivative curve which was obtained using a Radiometer carbon dioxide electrode in the titration as described previously.

As is clear by comparison of these two curves, first of all, the theoretical curve is dln(CO_2)/dx vs. pH but the experimental curve is dE/dV vs. V_{NaOH} (it was not possible to obtain the experimental curve



Theoretical Curve of
$d\ln[CO_2]/dX$ vs. pH

Titration Curve for 25ml Solution of HCl [2×10^{-2}M] Containing
$H_2CO_3 + CO_2 \cdot H_2O$ [$1{,}25\times10^{-2}$M] at 25°C

Using Radiometer CO_2 Electrode

FIG 6-31

the same as the theoretical one for the carbon dioxide electrode, using the Mettler equipment). In spite of this, these two curves are the same except at high pH values (pH = 11). There is a clear peak in the theoretical curve but this is not very clear in the experimental curve. This could be due to sluggish response of the carbon dioxide electrode at high pH values.

6.5.1. REFERENCES:

1) IBM System/360 and 370, FORTRAN 4 Language, International Business Machines Corporation, New York, N.Y., May 1974.

2) NAG Fortran Library Manual, Mark 7 Edition, NAG Central Office, Oxford, U.K., 1978.

3) D.M. Kern, J.Chem. Educ. 14, 37 , 1960.

4) J.T. Edsall, National Aeronautics Space Administration, Spec. Pub., 15, 188, 1969

5) H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions". Third edition, Reinhold Pub. Co., New York, 1958.

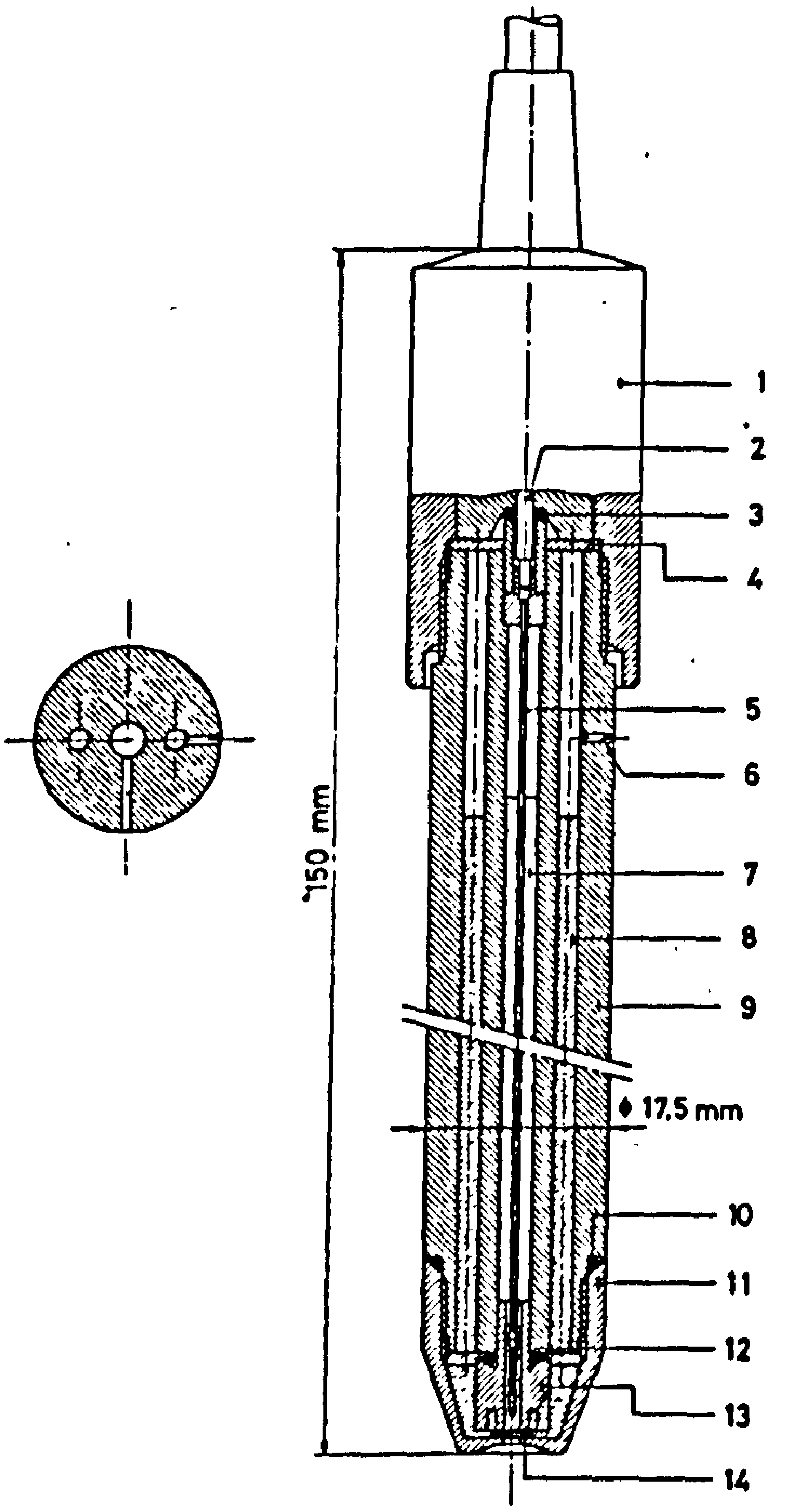
7. DETERMINATION OF CO_3^{2-} BY DIRECT POTENTIOMETRIC MEASUREMENTS USING AN ION SELECTIVE ELECTRODE:

7.1.1. INTRODUCTION:

The term ion-selective is applied to a range of membrane electrodes which respond selectively towards one or several ion species in the presence of others(1). I.S.E. is the abbreviation for the ion selective electrode. The main appeal of I.S.E's lies in the simplicity of the measurement technique and instrumentation and their suitability for continuous monitoring, which makes them particularly useful in routine analysis, pollution control and in biological and medical studies. Direct measurement of carbonate and bicarbonate concentrations is particularly important and this can be done by using such electrodes. Several papers have been published concerning a liquid carbonate-selective membrane electrode by Herman and Rechnitz (2,3). According to their work, a liquid membrane electrode, which is highly selective to carbonate, exhibits Nernstian response over a wide range of carbonate concentrations. Our experimental results were generally in agreement with their work. We also carried out some work using PVC and Ag/Ag_2CO_3 electrodes, which will be discussed in the following pages.

7.2.1. PREPARATION OF LIQUID MEMBRANE ELECTRODE:

The mechanically simplest arrangement of a liquid membrane electrode is obtained by placing the ion-selective material, which is dissolved in a water-immiscible solvent, between the sample solution and an aqueous reference solution. The Orion liquid-membrane electrode(Model 92) is based on such an arrangement, which is shown schematically in figure 7-1. A Millipore VC cellulose acetate support membrane with an average pore size of 0.1m μ and 4mm diameter, impregnated with the ion-selective solution acts as the membrane. Any ion-selective component lost is replaced from



Orion liquid-membrane electrode (model 92). (1) Plastic cap; (2) electric connection; (3) O ring; (4) rubber gasket; (5) inner reference electrode; (6) opening; (7) internal filling solution; (8) ion-selective liquid (ion exchanger); (9) electrode body (plastic); (10) O ring; (11) membrane support (plastic); (12) O ring; (13) hollow cylinder (plastic) pressing on membrane; (14) liquid membrane (filter paper impregnated with ion-selective liquid).

FIG 7–1

the reservoir 8 (as is shown in figure 7-1); this ensures a long life of the membrane electrode system. It should be mentioned that the support membrane is silylanized and is therefore hydrophobic. However, to form a stable interface, it is necessary that the membrane be soaked with the liquid ion exchanger before the aqueous inner solution is added. The electrode was stored in air when not in use. The active liquid phase consisted of Adogen 464 (methyl trialkyl (C_6-C_{10}) ammonium chloride: Aldrich Chemical Company Inc. U.S.A) dissolved in the special organic solvent. The salt was made up to 1% (v/v). A mixture of sodium chloride and sodium hydrogen carbonate, both 0.1mol/l was used as an inner reference solution. All measurements were carried out at 25°C using the Mettler apparatus and stirred slowly with a magnetic stirrer.

The organic solvent used to form the liquid membrane, trifluoroacetyl-p-butyl benzene, (CF_3-CO-C_6H_4-CH_2-CH_2-CH_2-CH_3) was synthesized by a Friedel-Crafts acetylation of butylbenzene with trifluoroacetic anhydride and anhydrous aluminium chloride catalyst(4). This solvent was synthesized by M.Hetmanski and N.Hughes in the Organic Dept of Newcastle University. Gas chromatographic analysis indicated that impurities are very low. The NMR spectrum confirmed the structure of the solvent.

7.2.2. EXPERIMENTAL RESULTS FOR E VS. $pa_{CO_3^{2-}}$

Plots of e.m.f. vs. $pa_{CO_3^{2-}}$ were obtained (e.m.f. measured against a saturated calomel reference electrode). Three different electrodes of the same type were prepared and calibration curves were obtained for each. The results were the same for all electrodes. Each exhibited Nernstian response to carbonate concentration in the range 5×10^{-2}mol/l to about 10^{-7} mol/l of 28-29 mV/dec. (see figure 7-2). All electrodes had response times, depending on the concentration employed, of 30s to 2mins. Due to the tendency for carbon-dioxide from the atmosphere to penetrate the carbonate solution, it is essential to cover the solutions and experimental cell.

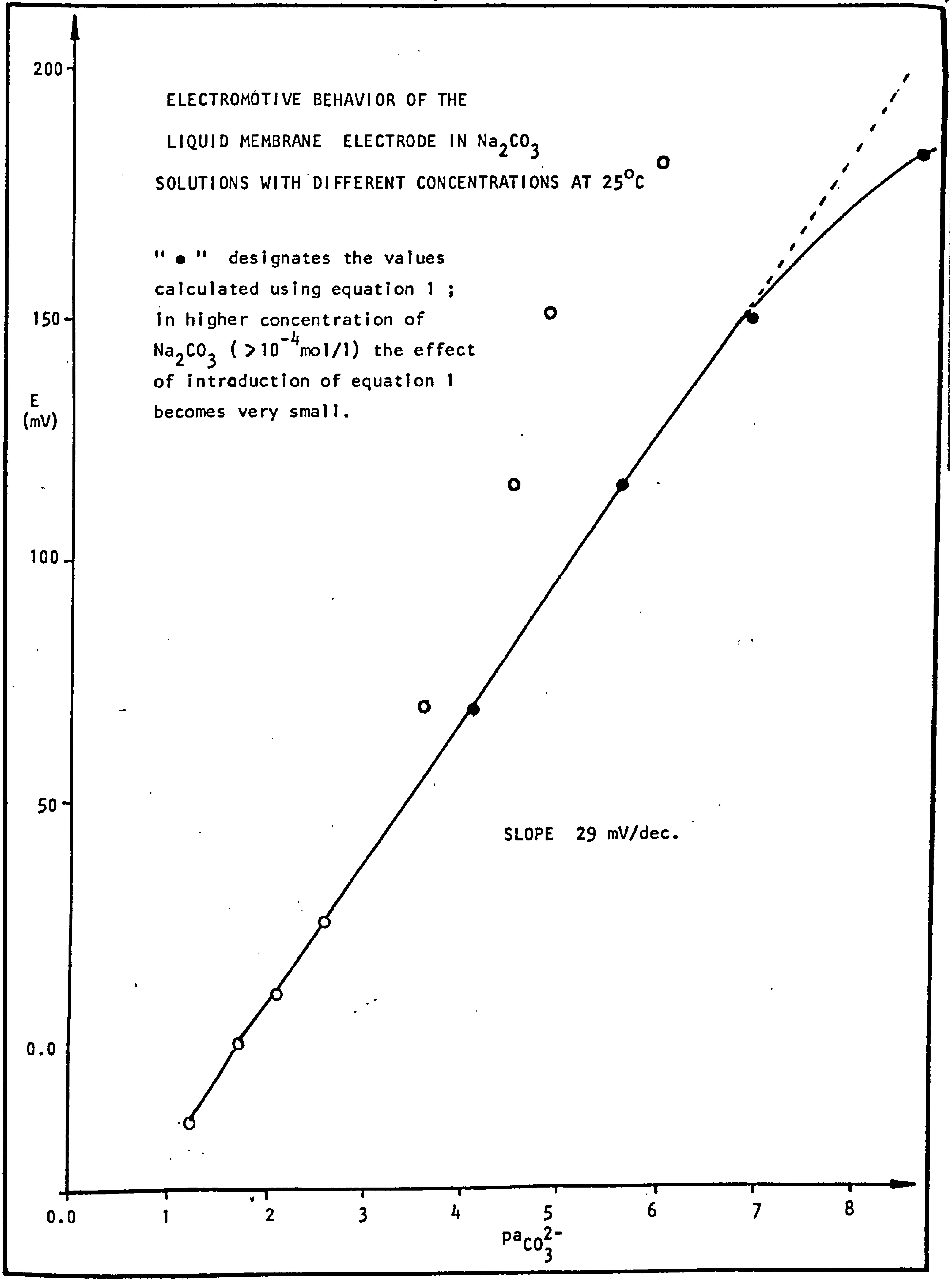

ELECTROMOTIVE BEHAVIOR OF THE
LIQUID MEMBRANE ELECTRODE IN Na_2CO_3
SOLUTIONS WITH DIFFERENT CONCENTRATIONS AT 25°C
" ● " designates the values calculated using equation 1 ; in higher concentration of Na_2CO_3 ($>10^{-4}$mol/l) the effect of introduction of equation 1 becomes very small.
SLOPE 29 mV/dec.
E (mV)
200
150
100
50
0.0
0.0
1
2
3
4
5
6
7
8
$pa_{CO_3^{2-}}$

FIG 7-2

In the calculations for obtaining the calibration curve, it has to be considered that, carbonate ions co-exist with bicarbonate ions in pH-dependent equilibrium. So it is important the pH of the solutions be recorded, then by using the pH values and equilibrium constant K_2, the ratio of carbonate to bicarbonate ions can be estimated with the following equation:

$$(CO_3^{2-})/(HCO_3^-) = K_2/(H^+) \tag{1}$$

The modified version of equation (12a) in chapter 2 was used to obtain the activity of carbonate ions in different solutions as follows:

$$a_{CO_3^{2-}} = K_1K_2\gamma_{CO_3^{2-}}C_T/(a_{H^+}^2.\gamma_{CO_3^{2-}} + K_1a_{H^+}.(\gamma_{CO_3^{2-}}/\gamma_{HCO_3^-}) + K_1K_2) \tag{2}$$

Where $a_{CO_3^{2-}}$ is the activity of carbonate ions and $\gamma_{CO_3^{2-}}$ and $\gamma_{HCO_3^-}$ are the activity coefficents of carbonate and hydrogen carbonate. C_T is the total concentration of carbonate species and a_{H^+} is the activity of hydrogen ions.

In the other series of experiments the composition of active liquid phase was varied by replacing Adogen 464 with other materials as the following list.

a) Tricaprylyl monomethyl ammonium chloride 75%(ICN Pharmaceuticals Inc.; Life Science Group. Plainview, New York. U.S.A.).

b) Adogen 464 A0944(Cambrian Chemicals).

c) Aliquat 336(General Mills Chemicals).

The results were the same as previously obtained.

In the other series of experiments, effect of support membrane was investigated. The following membranes were used:

1) VS WP 10mμ:(Millipore Corp. Mass. U.S.A., Bedford, Massachusetts).
2) OX01X 0.45μ : (Oxoid)
3) VP 0.1μ : (Millipore Corp. Mass. U.S.A., Bedford, Massachusetts).
4) PS ED02510 Millipore Pellicon : (Millipore Corp. Mass. U.S.A., Bedford,Mass).

A better calibration curve was obtained by using the last membrane.

7.3.1. P.V.C. MEMBRANE:

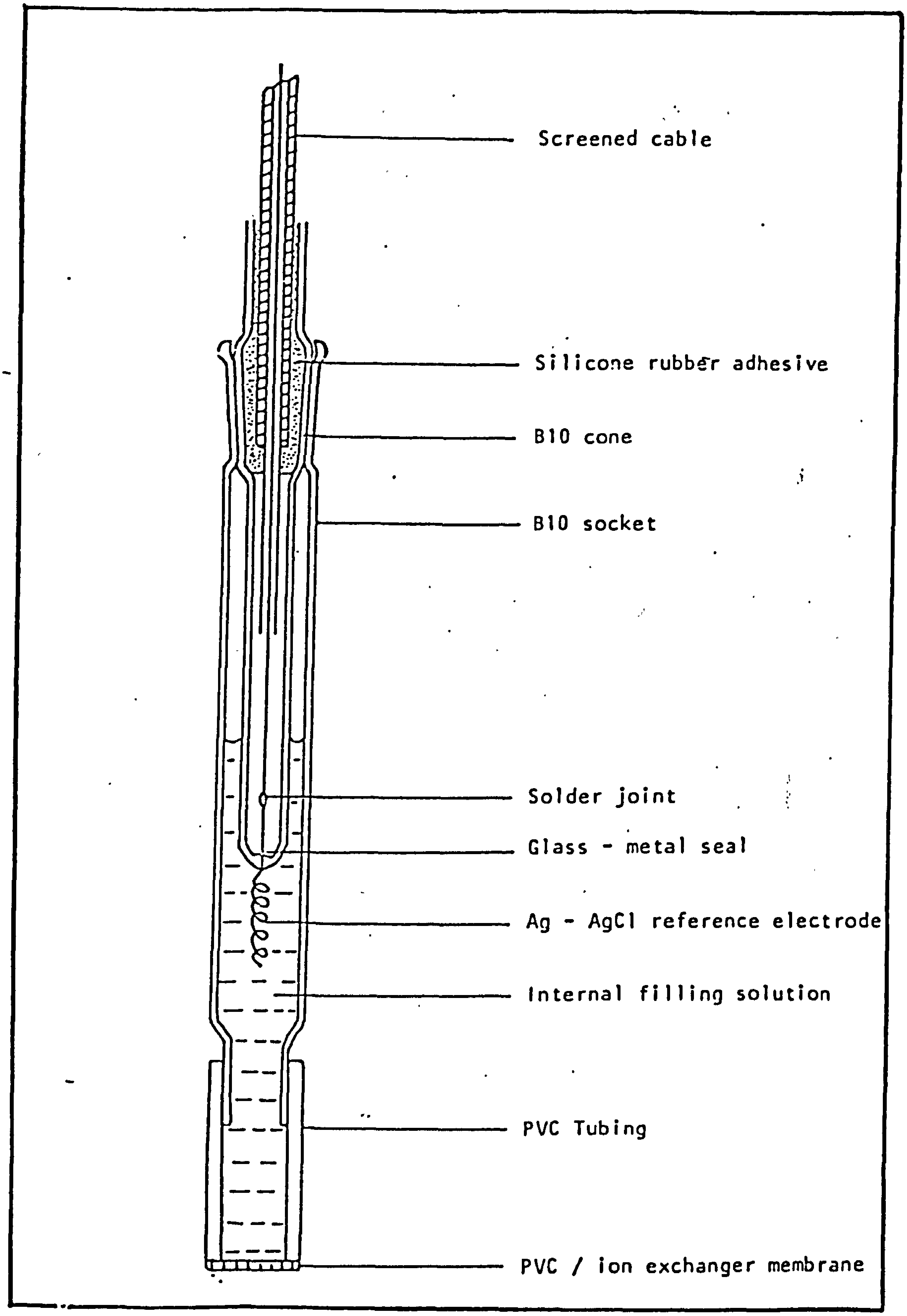
The P.V.C. membrane which was used in the experiments to obtain the calibration curves, was made by adding the active material to dissolved P.V.C. (BDH mwt 200,000) in tetrahydrofuran THF (AR grade, BDH). This mixture was transferred into a casting pot (5) made of PTFE (Fluon, ICI). Excess solvent was allowed to evaporate in a controlled manner over a 48hrs. period. The membrane, which had a diameter of 20mm and a thickness of 0.5mm, was removed at the end of this period. 8mm diameter membranes were cut from the master membrane and glued on the 10mm (O.D.) P.V.C. cube with P.V.C. /THF paste and used in electrode form as shown in Fig 7-3. The internal reference solution was the same as Orion electrode and Ag/AgCl was used as an internal reference electrode.

Calibration curves were obtained using this electrode. At the first attempt the electrode did not respond well, but after 5 days of soaking of the electrode in 0.01 mol/l Na_2CO_3 solution it showed better response. But the slope was 25mV/dec.(see figure 7-4). Also it should be mentioned that since there is no reservoir for the active material for the electrode, it is not expected to have a very long life time.

7.4.1. Ag/Ag_2CO_3 ELECTRODE:

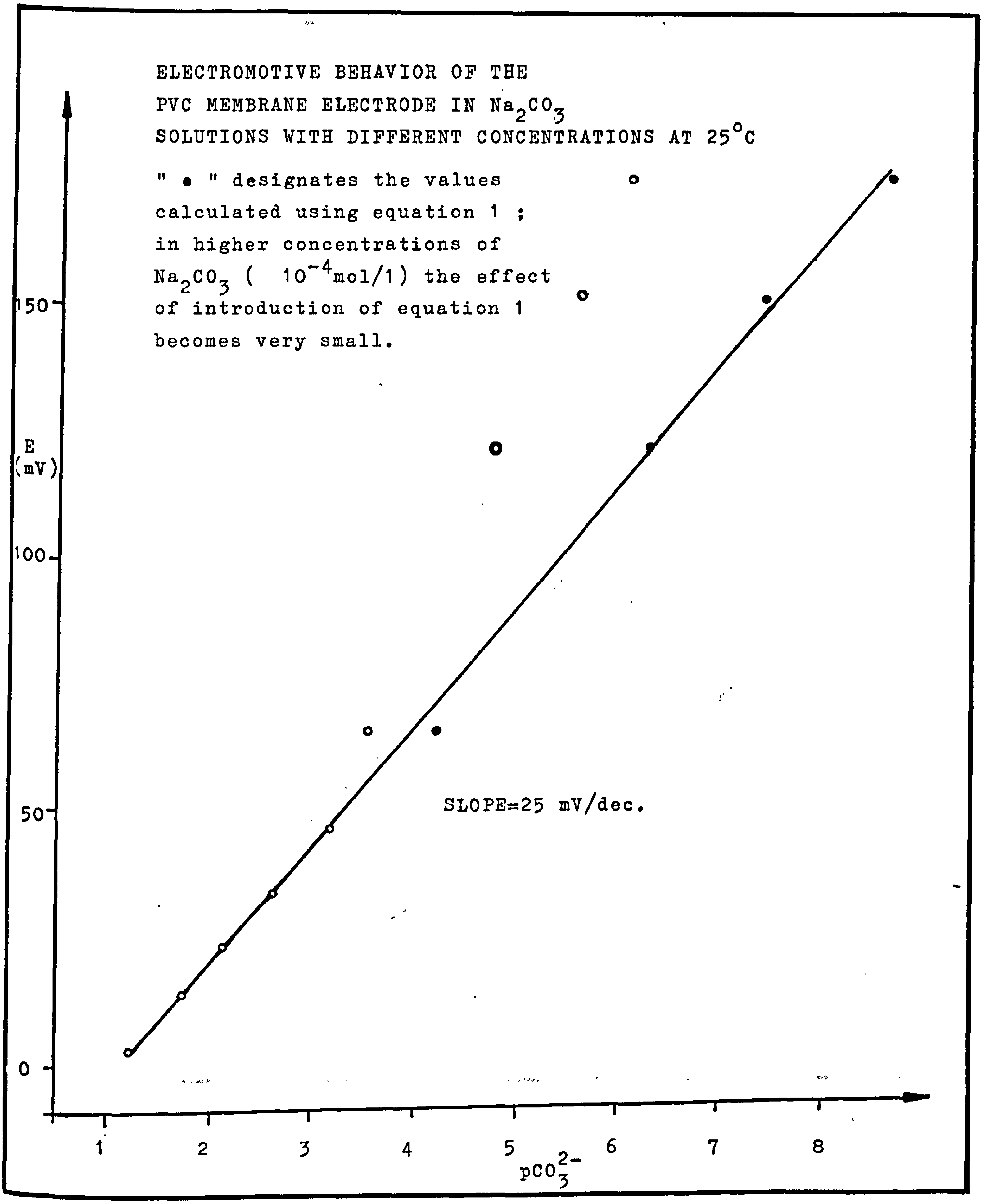
The procedure for making such an electrode is the same as for the Ag/AgCl electrode except that the electrode was electrolyzed for 2 hours with 200 mA/cm^2 in 0.5 mol/l Na_2CO_3 solution(6).

Thirteen electrodes of this type were made. Again e.m.f. measurements were carried out with respect to a saturated calomel electrode at 25°C. Plots of E against $-\log(CO_3^{2-})$ were obtained for the different electrodes in solutions of Na_2CO_3 with a concentration range of 10^{-1} to 10^{-5} mol/l. The Nernstian slope for different electrodes varied between 28 to 30 mV/dec. In figure 7-5 a calibration curve is shown for an Ag/Ag_2CO_3



PVC MEMBRANE ELECTRODE

FIG 7-3



ELECTROMOTIVE BEHAVIOR OF THE PVC MEMBRANE ELECTRODE IN Na_2CO_3 SOLUTIONS WITH DIFFERENT CONCENTRATIONS AT 25°C

" ● " designates the values calculated using equation 1 ; in higher concentrations of Na_2CO_3 (10^{-4}mol/1) the effect of introduction of equation 1 becomes very small.

SLOPE=25 mV/dec.

FIG 7-4

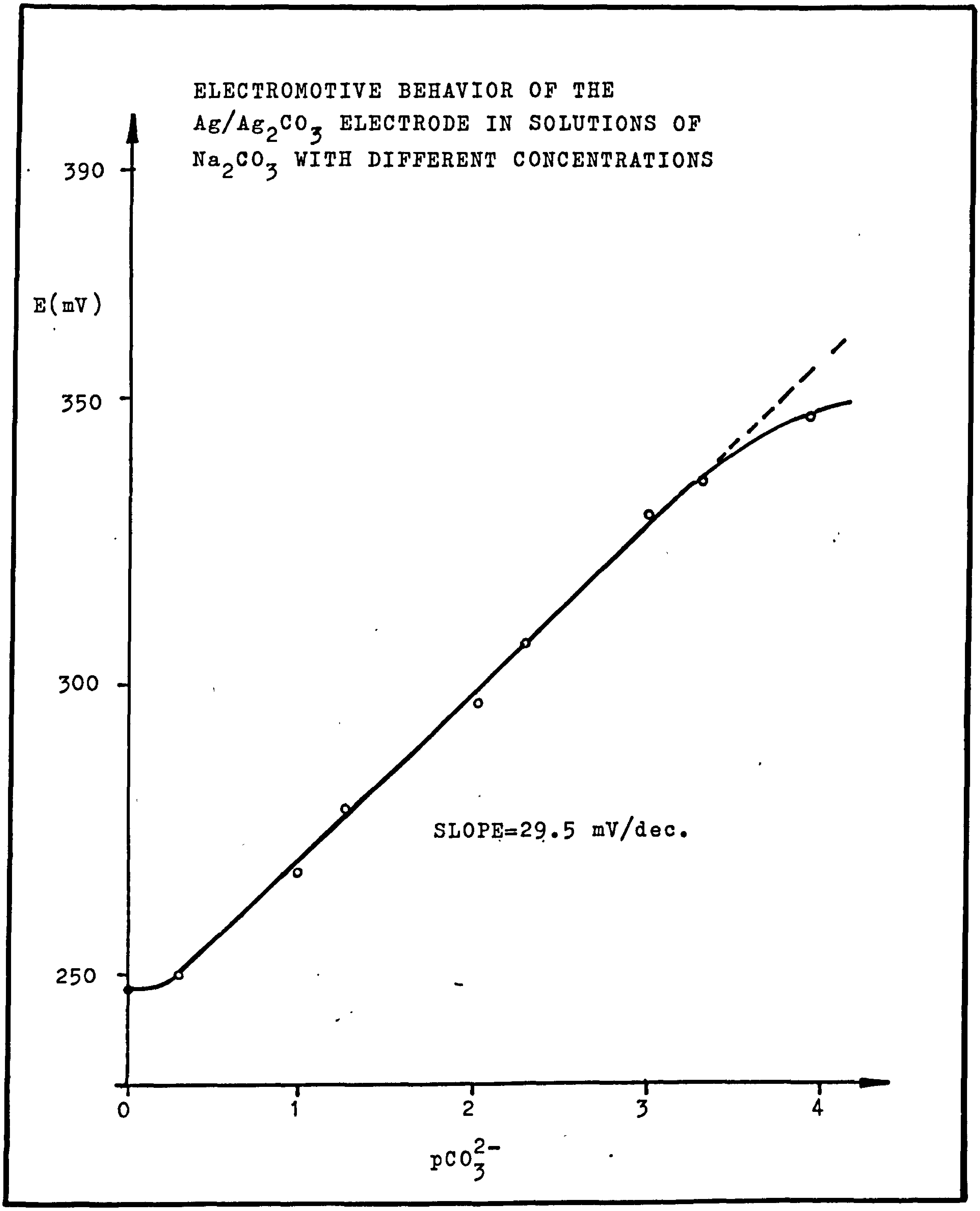

ELECTROMOTIVE BEHAVIOR OF THE
Ag/Ag_2CO_3 ELECTRODE IN SOLUTIONS OF
Na_2CO_3 WITH DIFFERENT CONCENTRATIONS
390
E(mV)
350
300
250
SLOPE=29.5 mV/dec.
0
1
2
3
4
pCO_3^{2-}

FIG 7-5

electrode. Also it has to be mentioned that these electrodes worked better than the previous ones and they should have a very long-life expectancy, but it can not be used below pCO_3^{2-} 4.

7.5.1. DISCUSSION:

This is the first time three carbonate electrodes of different kinds have been used and compared at the same time. The result for liquid membrane carbonate electrode were the same as previously obtained by Herman and Rechnitz(1,2). A similar electrode with a quarternary ammonium salt was reported to be a bicarbonate-selective electrode by Khuri et al (7). The liquid-ion exchanger consisting of a 3:1:6 mixture of tri-n-octylpropylammonium chloride to octanol to trifluoroacetyl-p-butylbenzene, differs in composition and the organic solvent (octanol). According to Khuri et al., the electrode gave a response of 55mV/dec., in a range of 10^{-1} to 10^{-4} mol/ℓ $NaHCO_3$ solutions. But this electrode is not useful for "real" systems since its selectivity for hydrogen carbonate over chloride ion is very low (3).

According to Herman and Rechnitz's work, when trifluoroacetyl-p-butylbenzene was substituted for 1-decanol the observed "bicarbonate" response became sigmoidal (3), and selectivity for carbonate over $NaHCO_3$ became too high to be measured. No apparent deviation from Nernstian behaviour was observed even when the concentration of hydrogen carbonate was about 1000 times that of carbonate (3). Since in the present work trifluoroacetyl-p-butyl benzene was used as a solvent, therefore it was not expected that hydrogen carbonate would be an interferent ion. Our experimental results proved this as shown in figure 7-2.

Also attempts were made to use P.V.C. membrane electrodes. The obtained Nernstian slope was 25 mV/dec. on a range of 10^{-1} to 10^{-5} mol/l of Na_2CO_3 solutions. Because of the absence of the reservoir for the active materials for this kind of electrode, so it is not expected to have a very long-life time. This is a disadvantage for P.V.C. membrane electrodes. Attempts made to use also Ag/Ag_2CO_3 electrodes. As mentioned previously these electrodes were the most reliable ones among the three different types of electrodes described in this chapter, But it has to be mentioned that Ag/Ag_2CO_3 electrode has its own limitation, because of the solubility of Ag_2CO_3 .

7.6.1. REFERENCES:

1) A.K,Covington, CRC Crit. Rev. Anal. Chem., 355, 8, 1974.
2) H.B.Herman and G.A.Rechnitz, Science, 1074, 184, 1974.
3) H.B.Herman and G.A.Rechnitz, Anal. Chim. Acta, 155, 76, 1975.
4) J.H.Simons, W.T.Black and R.F. Clark, J. Amer. Chem. Soc. 5621, 75,1953.
5) J.Kratchovil, D.M.Band and T.Treasure, Lab. Practice, 102, 26, 1977.
6) C.E.Taylor:, J. Phys. Chem. 653, 59, 1955.
7) R.N.Khuri, K.K.Bogharian and S.K.Agulian, Pflugers Arch., 285,349,1974.

8.1.1. INTRODUCTION:

The isopiestic technique was applied to obtain osmotic coefficients of K_2CO_3 and $NaHCO_3$. It is a simple and powerful method applicable to non-volatile solutes dissolved in a volatile solvent. By using molalities of the isopiestic solutions(1) (solutions in isopiestic equilibrium),where one of the salts is a reference with a known osmotic coefficient, the osmotic coefficient of the unkown salt can be calculated by using the following equation, where ν, m and ϕ indicate moles of ion per mole of salt, molality and osmotic coefficient of ions, respectively.

$$\nu_1 m_1 \phi_1 = \nu_2 m_2 \phi_2 \qquad (1)$$

This method demands good thermal control between solutions (2).

8.2.1. EXPERIMENTAL APPARATUS AND PROCEDURE.

The isopiestic apparatus consists of the following parts.

a: Bath: To maintain a constant temperature for the experiments a water bath was used, the temperature of which was regulated by a Haake type E3 proportional thermoregulator to within ± 0.01 °C at 25°C. The outer walls of the bath were covered with an insulating material(polystyrene).The top of the bath was also covered with the same material to minimize the evaporation of water and the heat exchange between water and the atmosphere.

b: Glass Desiccators: Four identical desiccator vessels were used. These must maintain vacuum , and keep out bath liquid.Ateflon tap (Corning Ltd. Stone, Staffordshire, UK) was used for closure. In order to speed up equilibration between the solutions in a desiccator, it is necessary to remove most of the air (a pressure of about 17 mm Hg was employed).

This was carried out by means of a water aspirator followed by a mechanical pump. Grease Apiezon type 'L' was used to seal the desiccator lids . Also to avoid concentration gradients and speed up equilibrations, desiccators were rocked,at a rate of 20 cycles per minute, using an electric motor. Rapid heat distribution was required inside the desiccators. Brass plates (2.5 cm thick and 20 cm in diameter) were used. The experimental cups were placed on these metal blocks within the desiccators. c: Isopiestic Cups (or dishes): These ideally should have very high thermal conductivity and be unreactive with the chemicals inside the cups. So gold-plated silver flap lid dishes were used. The cups were tightly capped when desiccators were opened for weighing after equilibrium, this was vital to avoid evaporation or condensation of water vapour.

Solutions of Na_2CO_3 or $NaHCO_3$ and the reference electrolyte(s) were freshly prepared on the day equibrations were begun. The empty cups were weighed; 2ml of solutions were placed into each cup which was then rapidly closed and weighed again. The reference cups and the other cups (four of each) were placed alternately on the brass plates in order to minimize effects of temperature gradients.

All weighings were carried out using a Mettler type A30 automatic electronic balance, having an imprecision of 0.1 mg. This allowed the weighings to be performed very rapidly, thus minimizing any evaporation losses from the cups.

The evaporation loss rate was measured and found to vary from 0.03 to 0.06 mg per minute which was considered to be negligible. All weighings were done within 5 minutes of the opening of the desiccators, relative to an N.P.L. standard weight. Test of accuracy of the apparatus and the procedures were performed by doing an inter-comparison of KCl and NaCl solution. The results were in agreement with the best literature values(3).

Few measurments were also carried out with Na_2CO_3 and NaCl solutions to test the accuracy of the apparatus . This was done by comparison of the obtained values with the literature values (9). In figure 8-1 the ratios of isopiestic molalities ($m_{Na_2CO_3}$ / m_{NaCl}) of present work is shown along with Robinson and Macaskill result(9). As is clear, the results are in a

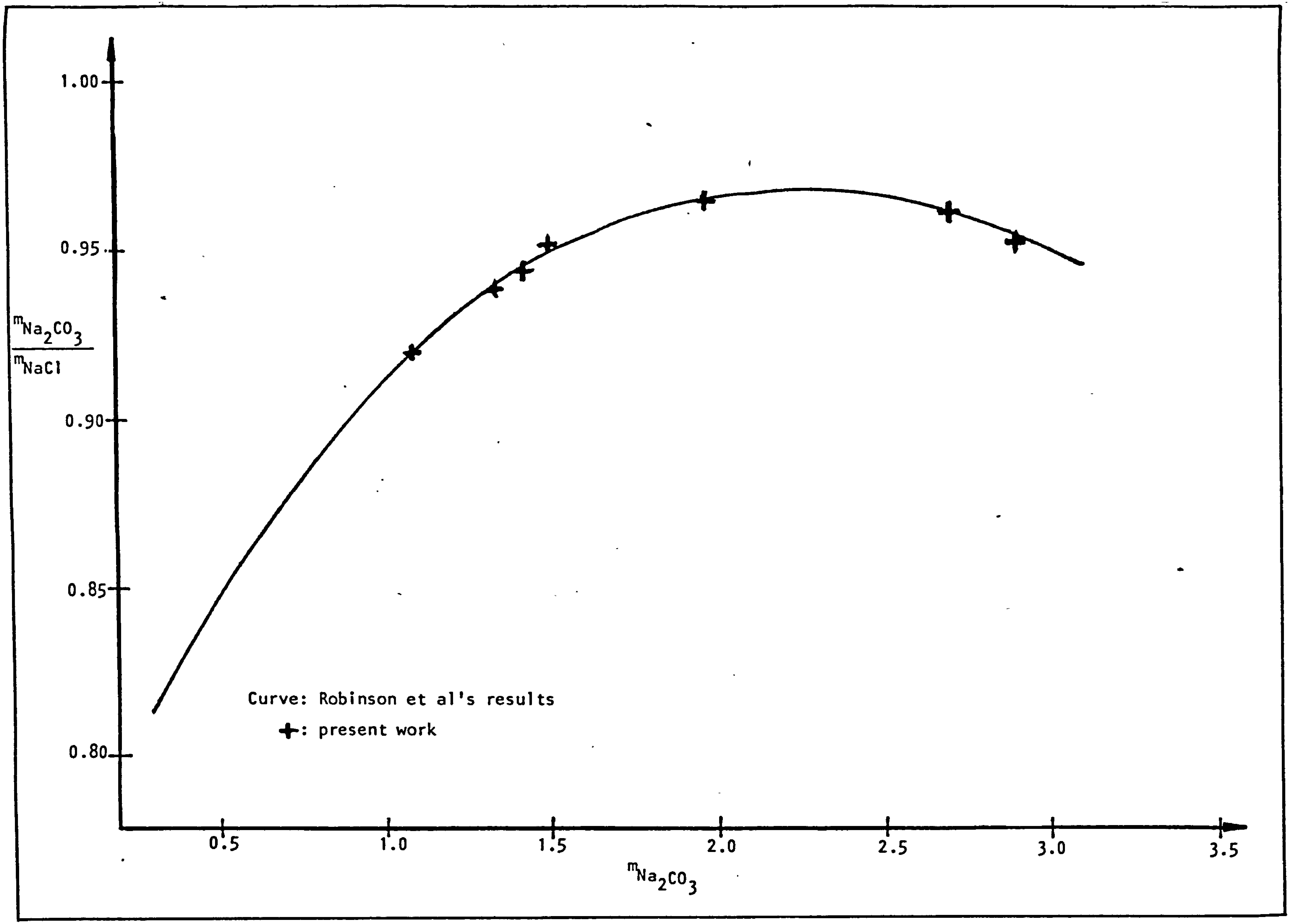

1.00
0.95
0.90
0.85
0.80
$\frac{m_{Na_2CO_3}}{m_{NaCl}}$
0.5
1.0
1.5
2.0
2.5
3.0
3.5
$m_{Na_2CO_3}$
Curve: Robinson et al's results
+: present work

FIG 8 - 1

good agreement. This is strong evidence for the accuracy of our apparatus, procedure and the available literature data values.

8.3.1. ISOPIESTIC MEASURMENTS FOR K_2CO_3:

Ground Analar K_2CO_3 (BDH: Poole, UK) was dried at 300°C for 4 days and stored in a desiccator containing sieves + drierite as a drying reagent. Since it is very difficult to remove the moisture content of K_2CO_3 , and mass spectroscopy gave clear evidence of the water content of dried K_2CO_3, a titration analysis, was carried out using the Mettler apparatus producing the first derivative curves . Solutions with different molalities were prepared from this solid(after determination of the assay by titration) and boiled-out degassed double distilled water.

The reference electrolyte (NaCl) was prepared under the same conditions after drying AnalaR NaCl (BDH) at 140°C for 48 hours. For higher molalities $CaCl_2$ was used as a reference electrolyte. A stock solution of $CaCl_2$ (near the saturation point) was prepared in degassed double distilled water and the molality of the solution determined gravimetrically. This solution was used and diluted for lower molalities as the experimental measurements required.

8.3.2. RESULTS AND CALCULATIONS:

The results of the isopiestic measurments are given in table 8-1. In each case the given molatily is the mean value obtained from three cups contained in a given desiccator.

In performing the calculations, we have adopted the following equation for the osmotic coefficient(ϕ):

$$\phi = 1 +((A_1)/(B^3 I))(-(1 + BI^{\frac{1}{2}})) + 2\ln(1 + BI^{\frac{1}{2}}) + 1/(1 + BI^{\frac{1}{2}}) + \tfrac{1}{2}Cm + 2/3\ Dm^2 + \tfrac{3}{4}Em^3 + \ldots, \qquad (2)$$

The corresponding equation for the mean activity coefficient ($\gamma^{\pm}$) is as follows;

$$\ln(\gamma\pm) = (-A_1 I^{\frac{1}{2}}/(1 + BI^{\frac{1}{2}})) + Cm + Dm^2 + Em^3 + \ldots, \qquad (3)$$

In these equations, A_1 and A_2 are constants(4,5). For 2-1 electrolytes in water at 25°C A_1 and A_2 are 2.3525 $mol^{-\frac{1}{2}}.kg^{-\frac{1}{2}}$ and 0.92238 mol^{-1}/kg respectively, m is the molality and I is the ionic strength on the molality basis assuming complete dissociation. B,C,D,E, etc. are adjustable parameters.

Using the isopiestic molalities from table 8-1 , osmotic coefficients for K_2CO_3 have been calculated. The evaluated values (4,5) of ϕ for NaCl and $CaCl_2$ solutions were used. The values of the parameters in the above equations were calculated. A previously documented least-squares procedure was used(4,5,6,). These values are given in table 8-2 together with their standard deviations. Table 8-3 contains activity and osmotic coefficients calculated at a selected molalities using the above equations and the coefficients given in table 8-2. Also standard deviations of calculated values of ϕ , $\ln\gamma\pm$ and $\gamma\pm$ at selected molalities are given at the bottom of table 8-3.

8.3.3. DETERMINATION OF SOLUBILITY OF K_2CO_3:

The solubility of K_2CO_3 in water at 25°C is quoted(7) as 8.110 mol /kg. We have measured the solubility by both equilibation and titration analysis. In the first case solubility was determined by equilibrating a solution containing an excess of K_2CO_3 with a slightly undersaturated solution of K_2CO_3(8). The vapour pressure of the saturated solution remains constant during the approach to equilibrium, while that of the other solution decreases and its concentration increases; at equilibrium, so that it has the concentration of the saturated solution. By this method, the solubility was found to be 8.1018 mol/kg. By titration of a solution which was in equilibration with solid K_2CO_3 (for a month at 25°C) the solubility was found to be 8.097mol/kg. All of these three values are in a good agreement.

(TABLE 8--1 ; ISOPIESTIC MOLALITIES)

****

m_{NaCl} (mol/kg)	$m_{K_2CO_3}$ (mol/kg)	m_{CaCl_2} (mol/kg)	$m_{K_2CO_3}$ (mol/kg)
0.07453	0.04922	2.1984	3.0733
0.1784	0.1352	2.7384	3.9139
0.4100	0.3163	3.0764	4.4304
0.6739	0.5290	3.2619	4.7110
1.1409	0.8965	3.6717	5.3411
1.3550	1.0650	4.0595	5.9498
1.6551	1.2900	4.0824	5.9704
2.1712	1.6763	4.2367	6.1783
3.2612	2.4438	4.5272	6.6098
4.2648	3.1107	4.6536	6.8100
5.3383	3.7830	4.8701	7.1359
5.3452	3.7761	4.9336	7.2367
		5.1755	7.6120
		5.2547	7.7301
		5.3424	7.9818
		5.4659	8.1018
		5.4935	8.2189

****

TABLE 8--2 COEFFICIENTS OF CORRELATING EQUTION (NO. 2)

Parameter:	STD. Dev.
1.363441936	0.348×10^{-1}
$-0.5974782091\times10^{-1}$	0.129×10^{-1}
$0.5711151804\times10^{-1}$	0.270×10^{-2}
-0.3166823891	0.187×10^{-3}

****

TABLE 8 - 3 :

MEAN IONIC ACTIVITY AND OSMOTIC COEFFICIENTS
OF AQUEOUS K_2CO_3 SOLUTIONS AT 25°C .

****

MOLALITY	GAMMA	PHI
0.001	0.8870	0.9614
0.002	0.8479	0.9477
0.003	0.8205	0.9380
0.004	0.7990	0.9303
0.005	0.7810	0.9238
0.006	0.7655	0.9182
0.007	0.7520	0.9133
0.008	0.7398	0.9089
0.009	0.7288	0.9049
0.010	0.7188	0.9012
0.020	0.6485	0.8755
0.030	0.6049	0.8597
0.040	0.5736	0.8485
0.050	0.5493	0.8400
0.060	0.5296	0.8332
0.070	0.5130	0.8276
0.080	0.4989	0.8230
0.090	0.4866	0.8190
0.100	0.4757	0.8156
0.200	0.4082	0.7973
0.300	0.3731	0.7909
0.400	0.3505	0.7889
0.500	0.3345	0.7893
0.600	0.3225	0.7912
0.700	0.3133	0.7942
0.800	0.3061	0.7981
0.900	0.3004	0.8027
1.000	0.2958	0.8080
1.250	0.2885	0.8241
1.500	0.2854	0.8436
1.750	0.2855	0.8663
2.000	0.2882	0.8920
2.250	0.2932	0.9204
2.500	0.3003	0.9513
2.750	0.3095	0.9845
3.000	0.3207	1.0199
3.250	0.3339	1.0571
3.500	0.3492	1.0961
3.750	0.3665	1.1366
4.000	0.3860	1.1784
4.250	0.4079	1.2213
4.500	0.4320	1.2650
4.750	0.4587	1.3094
5.000	0.4880	1.3542
5.250	0.5199	1.3993
5.500	0.5547	1.4443
5.750	0.5923	1.4892
6.000	0.6328	1.5336
6.250	0.6763	1.5774
6.500	0.7227	1.6203
6.750	0.7720	1.6622
7.000	0.8242	1.7027
7.250	0.8790	1.7417
7.500	0.9362	1.7790
7.750	0.9955	1.8143
8.000	1.0565	1.8474
8.219	1.1110	1.8745

MOLALITY	S(PHI)	S(LNGAM)	S(GAM)
0.001	0.0001	0.0002	0.0002
0.010	0.0007	0.0015	0.0011
0.100	0.0026	0.0069	0.0033
1.000	0.0025	0.0130	0.0038
2.000	0.0025	0.0123	0.0035
5.000	0.0021	0.0120	0.0058
8.219	0.0049	0.0120	0.0134

****

8.4.1. DETERMINATION OF THE OSMOTIC COEFFICIENTS OF $NaHCO_3$ SOLUTIONS:

The experimental apparatus was the same as for K_2CO_3. In this case, $NaHCO_3$ solutions were placed in experimental cups immediately after preparation, NaCl solutions were used as a reference electrolyte. Since there is appreciable vapour pressure of CO_2 above such solutions, the desiccators were evacuated to a pressure of about 25 mmHg and flushed 3times with CO_2 gas to replace the air in the desiccators, and then refilled with CO_2 to a pressure of about 70mmHg. The pressure of CO_2 in the desiccators retards the following process:

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2(g) \tag{4}$$

Subsequent to the equilibration, which lasted 14-30 days, the desiccators were removed from the bath, opened and the cups closed rapidly, and weighed within five minutes. The compositions of the solutions were determined by titration with HCl of known concentration, using the Mettler apparatus. The first derivative potentiometric curves were obtained with a Radiometer glass electrode and saturated calomel reference electrode. The titrations were carried out serially immediately after weighing the dishes. The results of these analyses enable the determination of the molalities of $NaHCO_3$ and Na_2CO_3 in the cups. The results of titrations obtained from different dishes were extrapolated to time equals 0 corresponding to the time when the desiccators were initially opened. Isopiestic molalities are shown in table 8-4.

Using the following equation:

$$\phi_{mix} = (\nu m\phi)_{ref} / \Sigma_{ions}(m_i) \tag{5}$$

where: $\Sigma_{ions} m_i = m_{NaHCO_3} + 3m_{Na_2CO_3}$ (6)

Values of ϕ_{mix} were calculated and are shown in table 8-4. The ionic strength fractions, also given in table 8-4, of sodium bicarbonate and

m_{NaHCO_3}	$m_{Na_2CO_3}$	m_{NaCl}	y_{NaHCO_3}	$y_{Na_2CO_3}$	I_{total}	ϕ_{mix}	ϕ_{NaHCO_3}
0.450000	0.111800	0.6780	0.5734	0.4266	0.7848	1.0158	1.2088
0.575200	0.067900	0.6264	0.7385	0.2615	0.7789	0.8546	0.8892
0.748800	0.091970	0.7952	0.7307	0.2693	1.0247	0.8325	0.8655
0.901900	0.126200	0.9673	0.7043	0.2957	1.2805	0.8282	0.8639
0.191100	0.015370	0.1967	0.8056	0.1944	0.2372	0.8486	0.8575
0.312600	0.026500	0.3407	0.7972	0.2028	0.3921	0.8899	0.9156
0.385800	0.028380	0.4190	0.3192	0.1808	0.4709	0.9002	0.9267
0.471800	0.043800	0.5100	0.7829	0.2171	0.6026	0.8747	0.9040
0.105400	0.002265	0.0828	0.9394	0.0606	0.1122	0.7125	0.7039
0.673100	0.054240	0.6921	0.8053	0.1947	0.8358	0.8489	0.8720
0.848600	0.083360	0.8891	0.7724	0.2276	1.0987	0.8309	0.8578
1.011300	0.096890	0.9981	0.7767	0.2233	1.3020	0.8073	0.8293

TABLE 8 – 4

sodium carbonate were calculated from:

$$y_{NaHCO_3} = I_{NaHCO_3}/I_{total} \qquad (7)$$

$$y_{Na_2CO_3} = I_{Na_2CO_3}/I_{total} \qquad (8)$$

In order to estimate the osmotic coefficients of pure $NaHCO_3$, it has been assumed that:

$$\phi_{mix} = y_{NaHCO_3} \cdot \phi^o_{NaHCO_3} + y_{Na_2CO_3} \cdot \phi^o_{Na_2CO_3} \qquad (9)$$

Where "o" designates the osmotic coefficient of the pure electrolyte evaluated at the total ionic strength of the mixture. Thus from measured ϕ_{mix}, y_{NaHCO_3} and y_{NaHCO_3} and $y_{Na_2CO_3}$, and knowing the values of $\phi^o_{Na_2CO_3}$ from the work of Robinson and Macaskill (9) calculated values of $\phi^o_{NaHCO_3}$ are obtained and given in table 8-4. The present results and Pitzer's values, calculated from Harned's (10) measurements, are also shown in figure 8-2.

8.5.1. DISCUSSION:

First of all it should be mentioned that the Pitzer's evaluated values for osmotic coefficients are the best values previously obtained. The difference between our results and these values may be due to the following factors:

1) Change in initial concentration of m_1(for $NaHCO_3$), since Harned et al. were dealing with the following electrochemical cell:

$$Pt,H_2,CO_2 \,/ NaHCO_3(m_1), NaCl(m_2), CO_2(m_3) \,/\, AgCl,Ag \text{ and}$$

and in Pitzer's calculation for osmotic coefficients it was assumed that m_1 was not varied. However the presence of excess CO_2 in $NaHCO_3$ solutions (in above cell) would form the new species described previously according to:

$$CO_2 + H_2O + NaHCO_3 \rightleftharpoons NaH_3C_2O_6$$

In addition, the possibility of loss of carbon-dioxide would also


1.0
φ
0.9
0.8
A
B
0.005(φ)
A: our results.
B: Pitzer et al's evaluated results.
0
0.1
0.3
0.5
0.7
molality
0.9
1.1
1.3

FIG 8 - 2

bring about a change in the concentration of initial $NaHCO_3$ (m_1) according to the process 8-4. Minor changes in the pH of solution, and the pressure of carbon-dioxide gas, would also cause changes in m_1.

In the following table, the concentration of total CO_2 is shown as a function of pCO_2 (mmHg) and pH for a system containing 0.02mol/l $NaHCO_3$ at 38°C (12):

pH	pCO_2(mmHg)	Total CO_2(mmol/l)
6.1	639	39.8
6.6	200	26.3
7.1	63	22.0
7.4	31.6	20.9
7.6	20.0	20.6
8.1	6.1	19.8
8.6	1.77	18.9
9.1	0.45	17.1
9.6	8.8×10^{-2}	14.3
10.6	1.40×10^{-3}	10.2
11.6	7.9×10^{-6}	5.1
11.9	0.00	0.0

2) Difference in experimental methods and data treatment could be another factor for these differences. However the differences are within the experimental error, at $m \geqslant 0.7$mol/kg.

It is necessary to mention that, the accuracy of equation 8-9 was tested for a mixture of NaCl, Na_2CO_3, using the values obtained by White et al (13). Again values of $\phi^o_{Na_2CO_3}$ was taken from Robinson and Macaskill's publication(9) and values for ϕ^o_{NaCl} was taken from Hamer's reference data(3). For example for a mixture of NaCl, Na_2CO_3 with ion strength fraction of Na_2CO_3 ($y_{Na_2CO_3}$) of 0.1713 and tolal ionicstrength of 1.047 (one of the nearest data to our experimental values), White's calculated value for ϕ_{mix} is 0.9056 and our calculated value for this mixture by using the equation 8-9 is 0.9053($\Delta\phi \simeq 0.0003$). Further checks were carried out, the values of $\Delta\phi$ were not significant.

8.6.1. REFERENCES:

1) W.R.Bousfield, Trans. Faraday Soc., 401, 13, 1918.

2) D.A.Sinclair, J. Phys.Chem. ,495, 37, 1933.

3) W.J.Hamer and Y.C.Wu, J. Phys. Chem. Ref. Data, 1047 ,1,1972.

4) B.R.Staples and R.L.Nuttall, J. Phys. Chem. Ref. Data, 385, 6,1977.

5) R.N.Goldberg and R.L.Nuttall, J. Phys. Chem. Ref. Data, 263, 7, 1978.

6) B.R.Staples and R.L.Nuttall, "Computer Program for the Evaluation of Activity and Osmotic Coefficients" N.B.S.(U.S.) Tech. Note, 928,(U.S. Gov't. Printing Office, Washington D.C. 1976).

7) A.Seidell, "Solubilities of Inorganic Compounds", D. Van. Nostrand Corp. New York 1941.

8) G.Scatchard, W.J.Hamer, and S.E.Wood, J. Amer.Chem. Soc., 306, 60,1938.

9) R.A.Robinson and J.B.Macaskill, J. Solution. Chem., 35, 8, 1979.

10) K.S.Pitzer and C.Peiper, J. Phys. Chem. 2396, 84, 1980.

11) W.Stumm and J.J.Morgan, "Aquatic Chemistry", Wiley, New York, 1970,Chap.4.

12) J.T.Edsall and J.Wyman, "Biophysical Chemistry", Academic Press, New York pp.550, Vol.1, 1958.

13) D.R.White,Jr, and R.G.Bates, Aut, J. Chem. 1903, 33, 1980.

9.1.1. DISCUSSION, CONCLUSIONS AND FUTURE WORK:

The aim of this work was a systematic study of the carbonate system, in particular the study of the derivative of the potentiometric titration curves. Mathematical consideration of the course of neutralization of a solution containing a_1 moles of a strong base (e.g. sodium hydroxide) and ($a_2 = ka_1$) moles of a salt of a weak dibasic acid (e.g. sodium carbonate) with a strong acid (e.g. hydrochloric acid) shows that the first derivative of the potentiometric titration curve should contain three maxima. The first corresponds to the neutralization of most of the hydroxide, the second and third peak correspond to conversion of carbonate ions to bicarbonate ions and bicarbonate ions to carbonic acid respectively with approximate heights of $35(1 + 2k)a_1^{\frac{1}{2}} / k^{\frac{1}{2}}$, $49.9 (1 + 2k) / k$ and $0.5 (1 + 2k)a_1^{\frac{1}{2}} / (K_1k)^{\frac{1}{2}}$.

Figures 3-1, 3-2 and 3-3 show the results of titrations of 25ml 0.04 mol/l sodium hydroxide containing different mole % of sodium carbonate with 0.25 mol/l hydrochloric acid using a glass electrode. It is clear that the second peak does not increase relative to the third as predicted by the ratios $1: 45.08/k^{\frac{1}{2}}: 21.3$ for $a_1 = 0.001$moles. The reason lies in the appearance of an additional, unexpected maximum which appears between the second and the third peak in the titration curves (see figures 3-1, 3-2 and 3-3).

The glass electrode could have been responsible for the appearance of the extra peak in the titration curves. Therefore, different glass electrodes were used and different treatments were carried out, with particular emphasis on properties of the glass electrode surface before using the electrodes in the titration process. Gel layers of different glass electrodes were removed by etching the electrode with HF solutions and new gel layers were developed on the surface of these electrodes. The electrodes were soaked in NaOH, Na_2CO_3, $NaHCO_3$, H_2SO_4 and HCl solutions of different concentrations and time lengths, in different buffer solutions, and other treatments were tried which have been described in detail in chapter 3. Then the electrodes were used in the titration after each treatment. In all cases, the extra peak was recorded; different glass electrodes gave the same results and these treatments had no noticeable effect on the position and height of the extra peak. Also the additional peak was present when a Rh/Rhoxide electrode was used as a working electrode. Similar results were obtained with quinhydrone electrode. However, it must be mentioned that soaking of glass electrodes in ferric ions solution (in pH $\simeq$ 2) results in an increase in speed of response of the glass electrodes.

Evidence suggests that the extra peak is a property of the titration solution which is detected by the electrodes. Experiments were carried out to investigate the origin of the unexpected additional peak. The extra peak was recorded after the appearance of the second peak of the titration where all carbonate ions had been converted to bicarbonate ions. Between the second and the third expected peak of the titration process, bicarbonate ions are converted to carbonic acid, and then part of the carbonic acid produced dehydrates to carbon dioxide. Therefore it can be concluded that the additional peak is due to the existence in the solution of remaining sodium bicarbonate , carbonic acid and carbon dioxide produced. The rate of addition of hydrochloric acid, that is the rate of production of carbonic acid, which is partly converted to carbon dioxide, has an effect on the position of this unexpected maximum. Since there is a kinetic stage involved in the hydration and dehydration process of carbon dioxide in aqueous solutions, then this kinetic stage could be responsible for the existence of the extra peak. Computer modelling of the titration curves with rate constants from the literature (1,2) was carried out but it did not exhibit the additional peak and the only effect of introducing the kinetic stage was a slight decrease in the height of the middle peak in the theoretical titration curves. Therefore, this definitely proves that the extra peak is not solely due to kinetic effects, but the extra peak represents a discrete species which was formed in the titration process.

According to Edsall (2) the measurements of dehydration rate constant for carbonic acid made at acid pH values tend to give higher than those made at neutral pH, or in buffered solutions in the pH 6 to 8 region. Also, in 1961 Koefoed and Engel (3) carried out investigations on the kinetics of carbon dioxide hydration on solutions of sodium bicarbonate which were kept saturated with carbon dioxide. They detected an acid catalysis and catalysis by hydrogen carbonate and carbonic acid for the hydration process of carbon dioxide. Also they concluded that a polymeric carbonic acid intermediate as shown in the following figure was present in sodium bicarbonate solutions saturated with carbon dioxide.

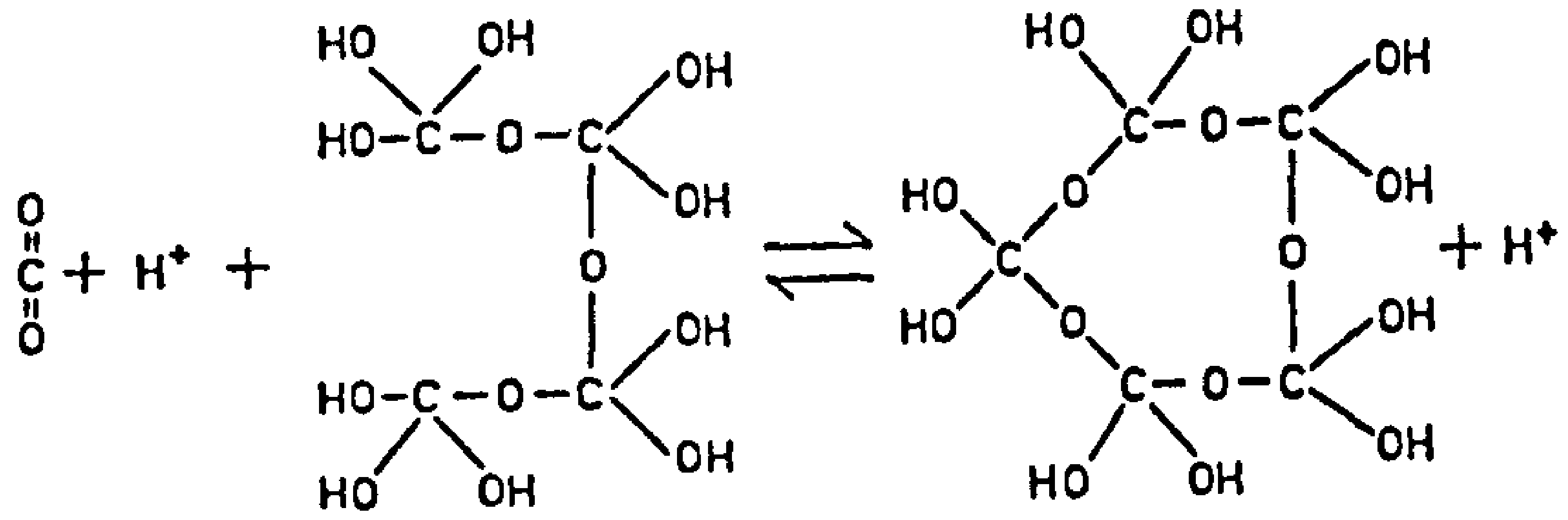


Figure 9-1: Effect of polymeric carbonic acid on hydration process of carbon dioxide.

Formation of such an intermediate could be the cause of the extra peak in our titration curves. However, further analysis of our experimental results will give a better identification of such a species as described below.

As shown in chapter 3 by increasing the temperature of the titration solution from the normal titration temperature (25°C), the extra peak moved nearer to the second expected peak of the titration and finally disappeared at above 50°C and the second peak of the titration curve became sharper, but by decreasing the temperature the extra peak moved towards the third expected peak of titration. This reflects the fact that since the dehydration process of carbonic acid is slow at low temperatures (2), and the solubility of carbon dioxide gas high at low temperature, the concentration of carbonic acid is also high at low temperature and its concentration is very low at high temperatures. Since the extra peak is not recorded at high temperatures (above 50°C) , this is a very clear indication that carbonic acid is one of the species which takes part in the formation of the new complex species in the titration process. However, since the extra peak indicates a protonation process in the course of titration, therefore the complex species should be an anion, so bicarbonate ions could be the other species which takes part in the formation of the complex.

Increasing the rate of addition of titrant (HCl) has exactly the same effect as decreasing the temperature. Again this could be due to higher concentration of carbonic acid, due to an increase in the rate of production of carbonic acid in the titration process. Fast stirring of the solution reduces the concentration of dissolved carbon dioxide and therefore helps the dehydration process and decreases the concentration of carbonic acid. This will cause a decrease in the concentration of the complex species which is indicated by a shift in the position of the extra peak towards the middle main peak of the titration as is shown in figure 3-12.

Bubbling of inert gases through the titration solution during the titration process again removes the carbon dioxide gas from the titration solution, and therefore inhibits the formation of the new complex. This is the reason for the extra peak not being recorded when nitrogen gas was bubbled through the titration solution. Again, in the absence of the extra peak, the middle peak became sharper. Also, the titration curves obtained with the hydrogen gas electrode as a working electrode were identical to the latter case; this is again due to the bubbling of hydrogen gas through the solution (see figure 3-16).

Addition of alcohols removes the extra peak from the titration curves as is shown in figure 3-17. This is because of the greater affinity of carbon dioxide for certain organic compounds which contain both more hydrophobic and strongly polar groups than water molecules (2). Therefore the existence of such compounds in the titration solution would have an effect on the dehydration process of carbonic acid and remove the extra peak from the titration curves. In the addition of alcohols with larger side groups into the titration solutions, it is expected that the smaller amount of alcohol would be required to make the peak disappear. Our experimental results proved this. The required mole fractions for the disappearance of the peak for methanol, ethanol and t-butanol were 0.25, 0.19 and 0.12 respectively. For the same reason addition of tetramethylammonium chloride had the same effect on the titration curves.

The extra feature was not recorded when a trace of bovine carbonic anhydrase enzyme was introduced into the titration solution. This could be due to an inhibiting effect of carbonic anhydrase on the formation of the new species.

It is not surprising that the change of cation from Na^+ to K^+ , or back titration with calcium hydroxide, or change of solvent from H_2O to D_2O had no significant effect on the appearance of the extra peak, simply because these changes have no noticeable effect on the dehydration process of carbonic acid.

These conclusions are also proved by the results of titration where a carbon dioxide electrode was used as shown in figure 4-2 where, titration curves for a glass electrode together with the corresponding first derivative titration curves for a Radiometer carbon dioxide electrode are shown. As is clear, the peak for the carbon dioxide electrode corresponds to a position where the extra peak appeared in the normal titration curves which were obtained by using a glass electrode. Since the main peak of titration only reflects the finishing stage of conversion of dissolved carbon dioxide to sodium bicarbonate in these titrations, therefore this is a clear indication of the fact that between the extra peak and the main second peak of neutralization, another species existed which was not detected by the carbon dioxide electrode.

This evidence suggests that the additional peak is due to carbonic acid and hydrogen carbonate ion complexation forming a new species in aqueous solutions according to the following process:

$$H_2CO_3 + HCO_3^- \rightleftharpoons H_3C_2O_6^-$$

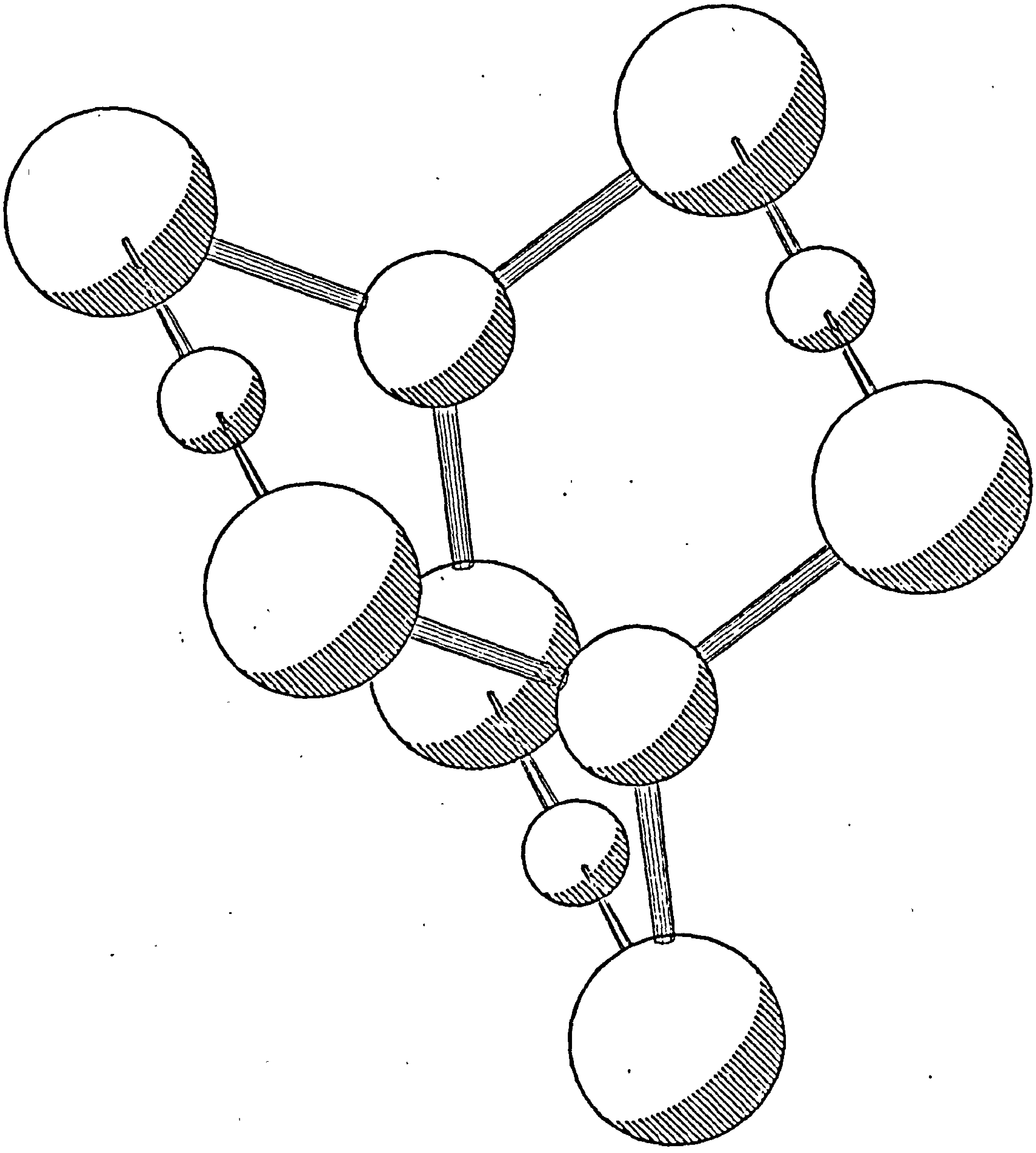
However, since there is a kinetic stage involved in the hydration and dehydration process of the conversion of carbon dioxide to carbonic acid in aqueous solutions, therefore naturally a kinetic stage is involved in the formation of such a complex species. The most probable structure for this anion species could consist of two planar carbonate moieties linked by bridge hydrogen bonds to the oxygen atoms. Existence of such strong (O-H-O) hydrogen bonds was also confirmed recently by Emsley (4).

A previously documented program was used to generate a computer plot of the structure of this new species. The bond length values of C-O and H-O were taken from Edsall (2) and Brown (6) respectively. The computer plotted structure of this molecule is shown in figure 9-2.

Comparing figure 9-1 with figure 9-2 makes clear that Koefoed and Engel assume that five carbonate molecules are polymerized through C-O double bonds, but in this work it is assumed that polymerization occurred through hydrogen bonds (O-H-O), and only two molecules of carbonate took part in such polymerization.

It has to be mentioned that sodium sesquicarbonate is one of the carbonate species which exists in crystal form naturally as the mineral, trona, and can be prepared synthetically (9). The structure of sesquicarbonate is very similar to the proposed new species, since it consists of one molecule of carbonate and one molecule of bicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) and the new species in solution consists of a molecule of carbonic acid and a bicarbonate ion ($H_2CO_3.HCO_3^-$). The only difference is two protonation stages.

According to investigations of the structure of sodium sesquicarbonate



* * *

THE NEW ANION SPECIES PROBABLY CONSISTS OF TWO PLANAR CARBONATE MOIETIES LINKED BY BRIDGE HYDROGEN BONDS TO THE OXYGEN ATOMS.

FIG 9–2

crystals by Brown and co-workers (6), two molecules of carbonate ions are bonded together through the hydrogen bonds (O-H-O) with a bond length of 2.53 Å, forming a complex anion species $(HC_2O_6)^{3-}$.

As is mentioned protonation of this species yields dimeric-bicarbonate ions and then the new species as follows:

$$(HC_2O_6)^{3-} + H^+ \rightleftharpoons (H_2C_2O_6)^{2-} + H^+ \rightleftharpoons (H_3C_2O_6)^-$$

It can be concluded that the new species which is the subject of the present work is a form of existence of the sesquicarbonate in aqueous solutions at neutral pH. Therefore this is a strong circumstantial evidence for the existence of the new species and that its structure consists of only two molecules of carbonate bonded together through three hydrogen bonds as mentioned before and shown in figure 9-2.

The existence of the sesquicarbonate ions at pH 8.5 to 10.5 is also probable, but because of the possible low concentration of this species and also the low signal in the region of the first peak of the titration curve, it is not very easy to detect.

According to the proposed theory which was described in detail in chapter 2, the minimum between the first and second peaks of titration curve is also independent of a; but as is clear from figures 3-1, 3-2 and 3-3 the height of this minimum varied in different curves. This could be taken as evidence for the existence of sesquicarbonate ions in aqueous solutions at pH 8.5 to 10.5. Logically therefore a dimeric bicarbonate ion in aqueous solutions may exist as an intermediate between these two complex species. This would be very difficult to prove. Such an intermediate species is shown in the above protonation process.

Attempts were made to detect this new species by using a laser Raman spectrophotometer, but because of the low concentrations of the titration solution and therefore the very low concentration of the new species and also the existence of high noise produced by the formation of carbon dioxide gas bubbles in the sample tube, the detection of a signal from the noise was impossible.

Also as described in detail in chapter 6 an equilibrium constant is associated with the above process and the appropriate equations were solved on the computer to obtain titration curves identical to the experimental curves. The corresponding equilibrium constant value was about 10^3.

It should be mentioned that formation of such a species is not expected in isopiestic measurements of K_2CO_3 and $NaHCO_3$. For K_2CO_3 solutions this is completely out of the question because such solutions contain very low concentrations of $NaHCO_3$ and H_2CO_3 . Also titrations of isopiestic solutions of $NaHCO_3$ with HCl indicated that the composition of all the solutions was a mixture of $NaHCO_3$ and Na_2CO_3 ; therefore, because of lack of CO_2 or H_2CO_3 species in these solutions the new species could not be formed.

Attempts were made to use carbonate liquid membrane electrodes in an investigation of the new complex species. Electrodes were used in titrations to obtain the first derivative curves, but this was not possible because the response was too sluggish. This could be due to poor response of the electrode to $NaHCO_3$ ions (3) and also the presence of chloride ions. It has been mentioned that the selectivity of this electrode for hydrogen carbonate over chloride ions is very low (3).

FUTURE WORK:

Because of the physiological and technical importance of the new species and its existence in bicarbonate solutions containing dissolved carbon dioxide (e.g. body fluids) further investigations could be very useful to understand more about the kinetics of formation of the new species. A pH stat technique will be a very useful method to investigate this.

Further investigation of the existence of sesquicarbonate ions and dimeric bicarbonate ions in aqueous solutions could be the subject of further research work. This could be approached by computer analysis curve fitting of titration data.

Thermodynamic values for mixed electrolyte of sodium chloride and sodium hydrogen carbonate also has a great importance to physiological systems. This could be the subject of another investigation, which could be approached by employing the isopiestic technique.

9.2.1.: REFERENCES:

1) D.M. Kern, J. Chem. Educ., 14, 37 , 1960.

2) J.T. Edsall, NASA, Spec. Publ., 15, 188 , 1969.

3) J. Koefoed and K. Engel, Acta Chem. Scand. , 1319, 15 , 1961.

4) J. Emsley, Chem. Soc. Rev., 91, 9 , 1980.

5) W. Clegg, Program for plotting molecular and crystal strucures, 1977. (Computer Centre of University of Newcastle upon Tyne, MTS System, UNSP:PLUTO).

6) C.J. Brown, H.S. Peiser and Miss A. Turner-Jones, Acta Cryst. , 167, 2 , 1949.

APPENDIX

TABLES FOR HYPOTHESIS 1 & 2(IN CHAPTER 6)

[A]= 1.E-2
K1 = 4.4E-7
K2 = 4.7E-11
K3 = 1.
KW = 1.E-14

(1) [H+]	(2) X	(3) DLN[H+]/DX	(4) PH	(5) T	(6) [CO3'']	(7) [HCO3']	(8) [H2CO3]
0.1000E+00	-0.5000E+01	0.2118E-14	1.00	0.9099E-24	0.2068E-16	0.4400E-07	0.1000E-01
0.3149E-01	-0.1575E+01	0.6351E+00	1.50	0.2913E-22	0.2085E-15	0.1397E-06	0.1000E-01
0.9918E-02	-0.4959E+00	0.2016E+01	2.00	0.9326E-21	0.2102E-14	0.4436E-06	0.1000E-01
0.3124E-02	-0.1561E+00	0.6400E+01	2.50	0.2985E-19	0.2119E-13	0.1408E-05	0.9999E-02
0.9837E-03	-0.4896E-01	0.2024E+02	3.00	0.9551E-18	0.2136E-12	0.4471E-05	0.9996E-02
0.3098E-03	-0.1478E-01	0.6174E+02	3.50	0.3052E-16	0.2152E-11	0.1418E-04	0.9986E-02
0.9756E-04	-0.2633E-02	0.1406E+03	4.00	0.9710E-15	0.2163E-10	0.4490E-04	0.9955E-02
0.3073E-04	0.5523E-02	0.1177E+03	4.50	0.3049E-13	0.2160E-09	0.1412E-03	0.9859E-02
0.9676E-05	0.6131E+00	0.1702E+01	5.00	0.7314E-09	0.5960E-07	0.1227E-01	0.9859E-02
0.3047E-05	0.4816E-01	0.2360E+02	5.50	0.1440E-10	0.1490E-07	0.9662E-03	0.6692E-02
0.9597E-06	0.1521E+00	0.9580E+01	6.00	0.4534E-09	0.1490E-06	0.3043E-02	0.6637E-02
0.3022E-06	0.2971E+00	0.8260E+01	6.50	0.5489E-08	0.9239E-06	0.5941E-02	0.4081E-02
0.9519E-07	0.4112E+00	0.1363E+02	7.00	0.3333E-07	0.4057E-05	0.8216E-02	0.1777E-02
0.2998E-07	0.4689E+00	0.3265E+02	7.50	0.1370E-06	0.1466E-04	0.9347E-02	0.6368E-03
0.9441E-08	0.4921E+00	0.7867E+02	8.00	0.4725E-06	0.4850E-04	0.9742E-02	0.2090E-03
0.2973E-08	0.5047E+00	0.9190E+02	8.50	0.1511E-05	0.1545E-03	0.9776E-02	0.6606E-04
0.9363E-09	0.5236E+00	0.4257E+02	9.00	0.4525E-05	0.4766E-03	0.9494E-02	0.2020E-04
0.2949E-09	0.5705E+00	0.1698E+02	9.50	0.1179E-04	0.1371E-02	0.8600E-02	0.5763E-05
0.9287E-10	0.6737E+00	0.8997E+01	10.00	0.2211E-04	0.3345E-02	0.6609E-02	0.1395E-05
0.2925E-10	0.8250E+00	0.8291E+01	10.50	0.2342E-04	0.6135E-02	0.3818E-02	0.2538E-06
0.9210E-11	0.9719E+00	0.1331E+02	11.00	0.1363E-04	0.8339E-02	0.1634E-02	0.3421E-07
0.2901E-11	0.1143E+01	0.2225E+02	11.50	0.5463E-05	0.9408E-02	0.5807E-03	0.3828E-08
0.9135E-12	0.1538E+01	0.1568E+02	12.00	0.1869E-05	0.9806E-02	0.1906E-03	0.3957E-09
0.2877E-12	0.2735E+01	0.5700E+01	12.50	0.6046E-06	0.9938E-02	0.6083E-04	0.3977E-10
0.9060E-13	0.6518E+01	0.1824E+01	13.00	0.1920E-06	0.9981E-02	0.1924E-04	0.3962E-11
0.2853E-13	0.1852E+02	0.5753E+00	13.50	0.6064E-07	0.9995E-02	0.6068E-05	0.3935E-12
0.8986E-14	0.5664E+02	0.1812E+00	14.00	0.1910E-07	0.9995E-02	0.1911E-05	0.3903E-13

TABLE 1

[A] = 1.0E-2
K1 = 4.5E-7
K2 = 4.7E-11
K3 = 1.0E 1
KW = 1.0E-14

(1) [H+]	(2) X	(3) DLN[H+]/DX	(4) PH	(5) T	(6) [CO3'']	(7) [HCO3']	(8) [H2CO3]
0.1000E+00	-0.5000E+01	0.1615E-14	1.00	0.9517E-23	0.2115E-16	0.4500E-07	0.1000E-01
0.3149E-01	-0.1575E+01	0.6351E+00	1.50	0.3047E-21	0.2132E-15	0.1429E-06	0.1000E-01
0.9918E-02	-0.4959E+00	0.2016E+01	2.00	0.9754E-20	0.2150E-14	0.4537E-06	0.1000E-01
0.3124E-02	-0.1561E+00	0.6400E+01	2.50	0.3122E-18	0.2168E-13	0.1440E-05	0.9999E-02
0.9837E-03	-0.1561E+00	0.2005E-02	3.00	0.4759E-04	0.4768E-06	0.1440E-05	0.9999E-02
0.3098E-03	-0.1476E-01	0.4356E+02	3.50	0.3192E-15	0.2201E-11	0.1450E-04	0.9985E-02
0.9756E-04	-0.2583E-02	0.1396E+03	4.00	0.1015E-13	0.2212E-10	0.4591E-04	0.9954E-02
0.3073E-04	0.5681E-02	0.1156E+03	4.50	0.3187E-12	0.2208E-09	0.1443E-03	0.9856E-02
0.9676E-05	0.2174E-01	0.4605E+02	5.00	0.9592E-11	0.2158E-08	0.4444E-03	0.9556E-02
0.3047E-05	0.6627E-01	0.1723E+02	5.50	0.2722E-09	0.2049E-07	0.1328E-02	0.8996E-02
0.9597E-06	0.1597E+00	0.9189E+01	6.00	0.4999E-08	0.1565E-06	0.3195E-02	0.6814E-02
0.3022E-06	0.2992E+00	0.8313E+01	6.50	0.5567E-07	0.9304E-06	0.5983E-02	0.4019E-02
0.9519E-07	0.4130E+00	0.1384E+02	7.00	0.3361E-06	0.4074E-05	0.8250E-02	0.1745E-02
0.2998E-07	0.4696E+00	0.3341E+02	7.50	0.1373E-05	0.1467E-04	0.9359E-02	0.6235E-03
0.9441E-08	0.4925E+00	0.8253E+02	8.00	0.4721E-05	0.4848E-04	0.9738E-02	0.2043E-03
0.2973E-08	0.5054E+00	0.1036E+03	8.50	0.1503E-04	0.1542E-03	0.9751E-02	0.6443E-04
0.9363E-09	0.5254E+00	0.4957E+02	9.00	0.4453E-04	0.4728E-03	0.9419E-02	0.1960E-04
0.2949E-09	0.5742E+00	0.1946E+02	9.50	0.1131E-03	0.1343E-02	0.8425E-02	0.5521E-05
0.9287E-10	0.6767E+00	0.9705E+01	10.00	0.2051E-03	0.3222E-02	0.6366E-02	0.1314E-05
0.2925E-10	0.8220E+00	0.7986E+01	10.50	0.2164E-03	0.5897E-02	0.3670E-02	0.2385E-06
0.9210E-11	0.9680E+00	0.1174E+02	11.00	0.1300E-03	0.8144E-02	0.1596E-02	0.3267E-07
0.2901E-11	0.1141E+01	0.2030E+02	11.50	0.5358E-04	0.9318E-02	0.5751E-03	0.3707E-08
0.9135E-12	0.1537E+01	0.1540E+02	12.00	0.1856E-04	0.9773E-02	0.1899E-03	0.3856E-09
0.2877E-12	0.2735E+01	0.5690E+01	12.50	0.6032E-05	0.9927E-02	0.6076E-04	0.3885E-10
0.9060E-13	0.6518E+01	0.1823E+01	13.00	0.1919E-05	0.9977E-02	0.1923E-04	0.3872E-11
0.2853E-13	0.1852E+02	0.5753E+00	13.50	0.6062E-06	0.9993E-02	0.6066E-05	0.3847E-12
0.8986E-14	0.5664E+02	0.1812E+00	14.00	0.1911E-06	0.9998E-02	0.1912E-05	0.3817E-13

TABLE 2

[A] = 1.E-2
K1 = 4.5E-7
K2 = 4.7E-11
K3 = 1.E2
KW = 1.E-14

(1) [H+]	(2) X	(3) DLN[H+]/DX	(4) PH	(5) T	(6) [CO3'']	(7) [HCO3']	(8) [H2CO3]
0.1000E+00	-0.5000E+01	0.1997E-14	1.00	0.9517E-22	0.2115E-16	0.4500E-07	0.1000E-01
0.3149E-01	-0.1575E+01	0.6351E+00	1.50	0.3047E-20	0.2132E-15	0.1429E-06	0.1000E-01
0.9918E-02	-0.4959E+00	0.2016E+01	2.00	0.9754E-19	0.2150E-14	0.4537E-06	0.1000E-01
0.3124E-02	-0.1561E+00	0.6400E+01	2.50	0.3122E-17	0.2168E-13	0.1440E-05	0.9999E-02
0.9837E-03	-0.4896E-01	0.2024E+02	3.00	0.9990E-16	0.2185E-12	0.4573E-05	0.9995E-02
0.3098E-03	-0.1476E-01	0.6168E+02	3.50	0.3192E-14	0.2201E-11	0.1450E-04	0.9985E-02
0.9756E-04	-0.2583E-02	0.1396E+03	4.00	0.1015E-12	0.2212E-10	0.4591E-04	0.9954E-02
0.3073E-04	0.5681E-02	0.1156E+03	4.50	0.3187E-11	0.2208E-09	0.1443E-03	0.9856E-02
0.9676E-05	0.2174E-01	0.4605E+02	5.00	0.9592E-10	0.2158E-08	0.4444E-03	0.9556E-02
0.3047E-05	0.6401E-01	0.1784E+02	5.50	0.2539E-08	0.1979E-07	0.1283E-02	0.8690E-02
0.9597E-06	0.1596E+00	0.9196E+01	6.00	0.4991E-07	0.1563E-06	0.3192E-02	0.6809E-02
0.3022E-06	0.2992E+00	0.8319E+01	6.50	0.5562E-06	0.9300E-06	0.5981E-02	0.4017E-02
0.9519E-07	0.4132E+00	0.1390E+02	7.00	0.3357E-05	0.4071E-05	0.8245E-02	0.1744E-02
0.2998E-07	0.4703E+00	0.3477E+02	7.50	0.1367E-04	0.1464E-04	0.9336E-02	0.6219E-03
0.9441E-08	0.4946E+00	0.1175E+03	8.00	0.4642E-04	0.4807E-04	0.9656E-02	0.2026E-03
0.2973E-08	0.5117E+00	-0.1962E+04	8.50	0.1427E-03	0.1502E-03	0.9502E-02	0.6278E-04
0.9363E-09	0.5409E+00	-0.3169E+03	9.00	0.3860E-03	0.4402E-03	0.8769E-02	0.1825E-04
0.2949E-09	0.6001E+00	0.6541E+02	9.50	0.8256E-03	0.1147E-02	0.7197E-02	0.4716E-05
0.9287E-10	0.6939E+00	0.1397E+02	10.00	0.1253E-02	0.2518E-02	0.4975E-02	0.1027E-05
0.2925E-10	0.8102E+00	0.7715E+01	10.50	0.1297E-02	0.4565E-02	0.2841E-02	0.1846E-06
0.9210E-11	0.9416E+00	0.7636E+01	11.00	0.9147E-03	0.6832E-02	0.1339E-02	0.2740E-07
0.2901E-11	0.1123E+01	0.1153E+02	11.50	0.4528E-03	0.8566E-02	0.5286E-03	0.3408E-08
0.9135E-12	0.1529E+01	0.1274E+02	12.00	0.1742E-03	0.9468E-02	0.1840E-03	0.3735E-09
0.2877E-12	0.2732E+01	0.5576E+01	12.50	0.5905E-04	0.9822E-02	0.6012E-04	0.3844E-10
0.9060E-13	0.6517E+01	0.1820E+01	13.00	0.1906E-04	0.9943E-02	0.1917E-04	0.3859E-11
0.2853E-13	0.1852E+02	0.5752E+00	13.50	0.6049E-05	0.9982E-02	0.6060E-05	0.3842E-12
0.8986E-14	0.5664E+02	0.1812E+00	14.00	0.1910E-05	0.9994E-02	0.1911E-05	0.3816E-13

TABLE 3

[A]=1.E-2
K1 = 4.5E-7
K2 = 4.7E-11
K3 = 2.E3
KW = 1.E-14

(1) [H+]	(2) X	(3) DLN[H+]/DX	(4) PH	(5) T	(6) [CO3""]	(7) [HCO3"]	(8) [H2CO3]
0.1000E+00	-0.5000E+01	0.2119E-14	1.00	0.1903E-20	0.2115E-16	0.4500E-07	0.1000E-01
0.3149E-01	-0.1575E+01	0.6351E+00	1.50	0.6094E-19	0.2132E-15	0.1429E-06	0.1000E-01
0.9918E-02	-0.4959E+00	0.2016E+01	2.00	0.1951E-17	0.2150E-14	0.4537E-06	0.1000E-01
0.3124E-02	-0.1561E+00	0.6400E+01	2.50	0.6245E-16	0.2168E-13	0.1440E-05	0.9999E-02
0.9837E-03	-0.4896E-01	0.2024E+02	3.00	0.1998E-14	0.2185E-12	0.4573E-05	0.9995E-02
0.3098E-03	-0.1476E-01	0.6168E+02	3.50	0.6384E-13	0.2201E-11	0.1450E-04	0.9985E-02
0.9756E-04	-0.2583E-02	0.1396E+03	4.00	0.2031E-11	0.2212E-10	0.4591E-04	0.9954E-02
0.3073E-04	0.5681E-02	0.1156E+03	4.50	0.6374E-10	0.2208E-09	0.1443E-03	0.9856E-02
0.9676E-05	0.2174E-01	0.4605E+02	5.00	0.1918E-08	0.2158E-08	0.4444E-03	0.9556E-02
0.3047E-05	0.6418E-01	0.1779E+02	5.50	0.5105E-07	0.1984E-07	0.1286E-02	0.8712E-02
0.9597E-06	0.1597E+00	0.9205E+01	6.00	0.9976E-06	0.1563E-06	0.3191E-02	0.6806E-02
0.3022E-06	0.3002E+00	0.8408E+01	6.50	0.1108E-04	0.9281E-06	0.5968E-02	0.4009E-02
0.9519E-07	0.4174E+00	0.1534E+02	7.00	0.6548E-04	0.4021E-05	0.8143E-02	0.1722E-02
0.2998E-07	0.4835E+00	0.1116E+03	7.50	0.2482E-03	0.1395E-04	0.8897E-02	0.5927E-03
0.9441E-08	0.5283E+00	-0.3236E+02	8.00	0.6997E-03	0.4173E-04	0.8383E-02	0.1759E-03
0.2973E-08	0.5778E+00	-0.2153E+02	8.50	0.1490E-02	0.1085E-03	0.6866E-02	0.4536E-04
0.9363E-09	0.6332E+00	-0.3307E+02	9.00	0.2418E-02	0.2463E-03	0.4908E-02	0.1021E-04
0.2949E-09	0.6853E+00	-0.1955E+04	9.50	0.3171E-02	0.5027E-03	0.3154E-02	0.2067E-05
0.9287E-10	0.7321E+00	0.3269E+02	10.00	0.3583E-02	0.9522E-03	0.1881E-02	0.3883E-06
0.2925E-10	0.7832E+00	0.1529E+02	10.50	0.3617E-02	0.1705E-02	0.1061E-02	0.6895E-07
0.9210E-11	0.8624E+00	0.9342E+01	11.00	0.3272E-02	0.2889E-02	0.5662E-03	0.1159E-07
0.2901E-11	0.1030E+01	0.6661E+01	11.50	0.2575E-02	0.4568E-02	0.2819E-03	0.1817E-08
0.9135E-12	0.1458E+01	0.5410E+01	12.00	0.1665E-02	0.6544E-02	0.1272E-03	0.2582E-09
0.2877E-12	0.2694E+01	0.3926E+01	12.50	0.8380E-03	0.8273E-02	0.5064E-04	0.3238E-10
0.9060E-13	0.6501E+01	0.1728E+01	13.00	0.3344E-03	0.9313E-02	0.1795E-04	0.3615E-11
0.2853E-13	0.1852E+02	0.5725E+00	13.50	0.1157E-03	0.9763E-02	0.5927E-05	0.3758E-12
0.8986E-14	0.5664E+02	0.1811E+00	14.00	0.3765E-04	0.9923E-02	0.1897E-05	0.3788E-13

TABLE 4

[A] = 1.E-2
K1 = 4.5E-7
K2 = 4.7E-11
K3 = 1.E4
KW = 1.E-14

(1) [H+]	(2) X	(3) DLN[H+]/DX	(4) PH	(5) T	(6) [CO3'']	(7) [HCO3']	(8) [H2CO3]
0.1000E+00	-0.5000E+01	0.1997E-14	1.00	0.9517E-20	0.2115E-16	0.4500E-07	0.1000E-01
0.3149E-01	-0.1575E+01	0.6351E+00	1.50	0.3047E-18	0.2132E-15	0.1429E-06	0.1000E-01
0.9918E-02	-0.4959E+00	0.2016E+01	2.00	0.9754E-17	0.2150E-14	0.4537E-06	0.1000E-01
0.3124E-02	-0.1561E+00	0.6400E+01	2.50	0.3122E-15	0.2168E-13	0.1440E-05	0.9999E-02
0.9837E-03	-0.4896E-01	0.2024E+02	3.00	0.9990E-14	0.2185E-12	0.4573E-05	0.9995E-02
0.3098E-03	-0.1476E-01	0.6168E+02	3.50	0.3192E-12	0.2201E-11	0.1450E-04	0.9985E-02
0.9756E-04	-0.2583E-02	0.1396E+03	4.00	0.1015E-10	0.2212E-10	0.4591E-04	0.9954E-02
0.3073E-04	0.5681E-02	0.1156E+03	4.50	0.3187E-09	0.2208E-09	0.1443E-03	0.9856E-02
0.9676E-05	0.2174E-01	0.4605E+02	5.00	0.9592E-08	0.2158E-08	0.4444E-03	0.9556E-02
0.3047E-05	0.6422E-01	0.1779E+02	5.50	0.2553E-06	0.1984E-07	0.1287E-02	0.8713E-02
0.9597E-06	0.1602E+00	0.9236E+01	6.00	0.4980E-05	0.1562E-06	0.3189E-02	0.6801E-02
0.3022E-06	0.3041E+00	0.8790E+01	6.50	0.5443E-04	0.9200E-06	0.5916E-02	0.3974E-02
0.9519E-07	0.4330E+00	0.2317E+02	7.00	0.2973E-03	0.3832E-05	0.7760E-02	0.1641E-02
0.2998E-07	0.5210E+00	-0.3957E+02	7.50	0.9165E-03	0.1199E-04	0.7646E-02	0.5093E-03
0.9441E-08	0.5883E+00	-0.2220E+02	8.00	0.1862E-02	0.3045E-04	0.6116E-02	0.1283E-03
0.2973E-08	0.6439E+00	-0.3185E+02	8.50	0.2835E-02	0.6695E-04	0.4235E-02	0.2798E-04
0.9363E-09	0.6866E+00	-0.7800E+02	9.00	0.3592E-02	0.1343E-03	0.2675E-02	0.5566E-05
0.2949E-09	0.7180E+00	0.4731E+03	9.50	0.4073E-02	0.2548E-03	0.1599E-02	0.1047E-05
0.9287E-10	0.7440E+00	0.6160E+02	10.00	0.4305E-02	0.4668E-03	0.9223E-03	0.1903E-06
0.2925E-10	0.7750E+00	0.2901E+02	10.50	0.4324E-02	0.8336E-03	0.5187E-03	0.3371E-07
0.9210E-11	0.8335E+00	0.1604E+02	11.00	0.4132E-02	0.1452E-02	0.2845E-03	0.5824E-08
0.2901E-11	0.9798E+00	0.9380E+01	11.50	0.3700E-02	0.2449E-02	0.1511E-03	0.9741E-09
0.9135E-12	0.1394E+01	0.5620E+01	12.00	0.2998E-02	0.3927E-02	0.7634E-04	0.1550E-09
0.2877E-12	0.2633E+01	0.3236E+01	12.50	0.2073E-02	0.5819E-02	0.3562E-04	0.2277E-10
0.9060E-13	0.6461E+01	0.1536E+01	13.00	0.1143E-02	0.7700E-02	0.1484E-04	0.2988E-11
0.2853E-13	0.1850E+02	0.5602E+00	13.50	0.4927E-03	0.9009E-02	0.5469E-05	0.3468E-12
0.8986E-14	0.5663E+02	0.1807E+00	14.00	0.1778E-03	0.9643E-02	0.1844E-05	0.3681E-13

TABLE 5

```
[A] = 1.E-2
K1  = 4.5E-7
K2  = 4.7E-11
K3  = 1.E5
KW  = 1.E-14

    (1)          (2)           (3)         (4)       (5)          (6)          (7)          (8)
   [H+]           X       DLN[H+]/DX       PH        T         [CO3""]      [HCO3"]      [H2CO3]

0.1000E+00  -0.5000E+01   0.2118E-14     1.00   0.9517E-19   0.2115E-16   0.4500E-07   0.1000E-01
0.3149E-01  -0.1575E+01   0.6351E+00     1.50   0.3047E-17   0.2132E-15   0.1429E-06   0.1000E-01
0.9918E-02  -0.4959E+00   0.2016E+01     2.00   0.9754E-16   0.2150E-14   0.4537E-06   0.1000E-01
0.3124E-02  -0.1561E+00   0.6400E+01     2.50   0.3122E-14   0.2168E-13   0.1440E-05   0.9999E-02
0.9837E-03  -0.4896E-01   0.2024E+02     3.00   0.9990E-13   0.2185E-12   0.4573E-05   0.9995E-02
0.3098E-03  -0.1476E-01   0.6168E+02     3.50   0.3192E-11   0.2201E-11   0.1450E-04   0.9985E-02
0.9756E-04  -0.2583E-02   0.1396E+03     4.00   0.1015E-09   0.2212E-10   0.4591E-04   0.9954E-02
0.3073E-04   0.5681E-02   0.1156E+03     4.50   0.3187E-08   0.2208E-09   0.1443E-03   0.9856E-02
0.9676E-05   0.2175E-01   0.4605E+02     5.00   0.9592E-07   0.2158E-08   0.4444E-03   0.9556E-02
0.3047E-05   0.6453E-01   0.1782E+02     5.50   0.2551E-05   0.1983E-07   0.1286E-02   0.8709E-02
0.9597E-06   0.1653E+00   0.9581E+01     6.00   0.4893E-04   0.1548E-06   0.3161E-02   0.6741E-02
0.3022E-06   0.3405E+00   0.1362E+02     6.50   0.4589E-03   0.8448E-06   0.5433E-02   0.3649E-02
0.9519E-07   0.5192E+00  -0.1071E+03     7.00   0.1576E-02   0.2790E-05   0.5650E-02   0.1195E-02
0.2998E-07   0.6243E+00  -0.5494E+02     7.50   0.2759E-02   0.6578E-05   0.4195E-02   0.2795E-03
0.9441E-08   0.6788E+00  -0.7562E+02     8.00   0.3617E-02   0.1342E-04   0.2696E-02   0.5655E-04
0.2973E-08   0.7094E+00  -0.1369E+03     8.50   0.4170E-02   0.2567E-04   0.1624E-02   0.1073E-04
0.9363E-09   0.7279E+00  -0.4015E+03     9.00   0.4502E-02   0.4754E-04   0.9470E-03   0.1970E-05
0.2949E-09   0.7403E+00   0.6721E+03     9.50   0.4686E-02   0.8642E-04   0.5422E-03   0.3553E-06
0.9287E-10   0.7516E+00   0.1676E+03    10.00   0.4769E-02   0.1554E-03   0.3070E-03   0.6335E-07
0.2925E-10   0.7697E+00   0.7758E+02    10.50   0.4775E-02   0.2770E-03   0.1724E-03   0.1120E-07
0.9210E-11   0.8141E+00   0.3886E+02    11.00   0.4707E-02   0.4901E-03   0.9604E-04   0.1966E-08
0.2901E-11   0.9425E+00   0.1912E+02    11.50   0.4544E-02   0.8581E-03   0.5296E-04   0.3414E-09
0.9135E-12   0.1334E+01   0.8883E+01    12.00   0.4247E-02   0.1478E-02   0.2873E-04   0.5832E-10
0.2877E-12   0.2550E+01   0.3808E+01    12.50   0.3754E-02   0.2477E-02   0.1516E-04   0.9691E-11
0.9060E-13   0.6367E+01   0.1490E+01    13.00   0.3018E-02   0.3957E-02   0.7627E-05   0.1536E-11
0.2853E-13   0.1842E+02   0.5335E+00    13.50   0.2075E-02   0.5846E-02   0.3549E-05   0.2251E-12
0.8986E-14   0.5659E+02   0.1779E+00    14.00   0.1139E-02   0.7720E-02   0.1476E-05   0.2947E-13
```

TABLE 6

```
   [A] =   0.10E-01
    K1 =   0.45E-06          K2 =   0.47E-10          K3 =   0.00E+00          KW =   0.10E-13

    (1)            (2)            (3)          (4)       (5)            (6)           (7)           (8)
   [H+]             X          DLN[H+]/DX      PH         T           [CO3--]       [HCO3-]       [H2CO3]

 0.1000E+00    -0.5000E+01    0.2000E+00     1.00    0.0000E+00    0.2115E-16    0.4500E-07    0.1000E-01
 0.5623E-01    -0.2812E+01    0.3557E+00     1.25    0.0000E+00    0.6688E-16    0.8002E-07    0.1000E-01
 0.3162E-01    -0.1581E+01    0.6325E+00     1.50    0.0000E+00    0.2115E-15    0.1423E-06    0.1000E-01
 0.1778E-01    -0.8891E+00    0.1125E+01     1.75    0.0000E+00    0.6689E-15    0.2531E-06    0.1000E-01
 0.9999E-02    -0.5000E+00    0.2000E+01     2.00    0.0000E+00    0.2115E-14    0.4500E-06    0.1000E-01
 0.5623E-02    -0.2811E+00    0.3556E+01     2.25    0.0000E+00    0.6689E-14    0.8002E-06    0.9999E-02
 0.3162E-02    -0.1580E+00    0.6322E+01     2.50    0.0000E+00    0.2115E-13    0.1423E-05    0.9999E-02
 0.1778E-02    -0.8878E-01    0.1123E+02     2.75    0.0000E+00    0.6688E-13    0.2530E-05    0.9997E-02
 0.9999E-03    -0.4977E-01    0.1991E+02     3.00    0.0000E+00    0.2115E-12    0.4498E-05    0.9996E-02
 0.5623E-03    -0.2771E-01    0.3507E+02     3.25    0.0000E+00    0.6684E-12    0.7997E-05    0.9992E-02
 0.3162E-03    -0.1510E-01    0.6054E+02     3.50    0.0000E+00    0.2113E-11    0.1421E-04    0.9986E-02
 0.1778E-03    -0.7628E-02    0.9853E+02     3.75    0.0000E+00    0.6673E-11    0.2525E-04    0.9975E-02
 0.9998E-04    -0.2759E-02    0.1383E+03     4.00    0.0000E+00    0.2106E-10    0.4481E-04    0.9955E-02
 0.5622E-04     0.1159E-02    0.1482E+03     4.25    0.0000E+00    0.6637E-10    0.7940E-04    0.9921E-02
 0.3162E-04     0.5436E-02    0.1177E+03     4.50    0.0000E+00    0.2086E-09    0.1403E-03    0.9860E-02
 0.1778E-04     0.1145E-01    0.7736E+02     4.75    0.0000E+00    0.6526E-09    0.2469E-03    0.9753E-02
 0.9998E-05     0.2104E-01    0.4737E+02     5.00    0.0000E+00    0.2025E-08    0.4307E-03    0.9569E-02
 0.5622E-05     0.3677E-01    0.2891E+02     5.25    0.0000E+00    0.6195E-08    0.7411E-03    0.9259E-02
 0.3162E-05     0.6214E-01    0.1828E+02     5.50    0.0000E+00    0.1852E-07    0.1246E-02    0.8754E-02
 0.1778E-05     0.1009E+00    0.1239E+02     5.75    0.0000E+00    0.5340E-07    0.2020E-02    0.7980E-02
 0.9997E-06     0.1552E+00    0.9337E+01     6.00    0.0000E+00    0.1459E-06    0.3104E-02    0.6896E-02
 0.5622E-06     0.2223E+00    0.8095E+01     6.25    0.0000E+00    0.3717E-06    0.4446E-02    0.5554E-02
 0.3161E-06     0.2937E+00    0.8246E+01     6.50    0.0000E+00    0.8732E-06    0.5873E-02    0.4126E-02
 0.1778E-06     0.3585E+00    0.9838E+01     6.75    0.0000E+00    0.1895E-05    0.7167E-02    0.2831E-02
 0.9997E-07     0.4093E+00    0.1340E+02     7.00    0.0000E+00    0.3845E-05    0.8179E-02    0.1817E-02
 0.5622E-07     0.4449E+00    0.2008E+02     7.25    0.0000E+00    0.7427E-05    0.8883E-02    0.1110E-02
 0.3161E-07     0.4677E+00    0.3182E+02     7.50    0.0000E+00    0.1387E-04    0.9331E-02    0.6555E-03
 0.1778E-07     0.4823E+00    0.5096E+02     7.75    0.0000E+00    0.2537E-04    0.9596E-02    0.3791E-03
 0.9996E-08     0.4915E+00    0.7686E+02     8.00    0.0000E+00    0.4579E-04    0.9738E-02    0.2163E-03
 0.5621E-08     0.4981E+00    0.9714E+02     8.25    0.0000E+00    0.8190E-04    0.9796E-02    0.1224E-03
 0.3161E-08     0.5040E+00    0.9224E+02     8.50    0.0000E+00    0.1455E-03    0.9786E-02    0.6874E-04
 0.1778E-08     0.5112E+00    0.6761E+02     8.75    0.0000E+00    0.2566E-03    0.9705E-02    0.3834E-04
 0.9996E-09     0.5218E+00    0.4338E+02     9.00    0.0000E+00    0.4481E-03    0.9531E-02    0.2117E-04
 0.5621E-09     0.5339E+00    0.2694E+02     9.25    0.0000E+00    0.7708E-03    0.9218E-02    0.1151E-04
 0.3161E-09     0.5660E+00    0.1716E+02     9.50    0.0000E+00    0.1294E-02    0.8700E-02    0.6111E-05
 0.1777E-09     0.6072E+00    0.1167E+02     9.75    0.0000E+00    0.2091E-02    0.7906E-02    0.3123E-05
 0.9995E-10     0.6648E+00    0.8781E+01    10.00    0.0000E+00    0.3198E-02    0.6801E-02    0.1511E-05
 0.5621E-10     0.7365E+00    0.7521E+01    10.25    0.0000E+00    0.4554E-02    0.5446E-02    0.6802E-06
 0.3161E-10     0.8148E+00    0.7350E+01    10.50    0.0000E+00    0.5979E-02    0.4021E-02    0.2824E-06
 0.1777E-10     0.8709E+00    0.7831E+01    10.75    0.0000E+00    0.7256E-02    0.2744E-02    0.1084E-06
 0.9995E-11     0.9623E+00    0.8174E+01    11.00    0.0000E+00    0.8246E-02    0.1754E-02    0.3395E-07
 0.5620E-11     0.1036E+01    0.7317E+01    11.25    0.0000E+00    0.8932E-02    0.1068E-02    0.1334E-07
 0.3160E-11     0.1127E+01    0.5327E+01    11.50    0.0000E+00    0.9370E-02    0.6301E-03    0.4425E-08
 0.1777E-11     0.1263E+01    0.3346E+01    11.75    0.0000E+00    0.9636E-02    0.3644E-03    0.1439E-08
 0.9994E-12     0.1490E+01    0.1959E+01    12.00    0.0000E+00    0.9792E-02    0.2082E-03    0.4624E-09
 0.5620E-12     0.1884E+01    0.1117E+01    12.25    0.0000E+00    0.9882E-02    0.1182E-03    0.1476E-09
 0.3160E-12     0.2579E+01    0.6307E+00    12.50    0.0000E+00    0.9933E-02    0.6679E-04    0.4691E-10
 0.1777E-12     0.3812E+01    0.3552E+00    12.75    0.0000E+00    0.9962E-02    0.3767E-04    0.1488E-10
 0.9993E-13     0.6002E+01    0.1998E+00    13.00    0.0000E+00    0.9979E-02    0.2122E-04    0.4712E-11
 0.5620E-13     0.9897E+01    0.1124E+00    13.25    0.0000E+00    0.9988E-02    0.1194E-04    0.1491E-11
 0.3160E-13     0.1682E+02    0.6320E-01    13.50    0.0000E+00    0.9993E-02    0.6719E-05    0.4718E-12
 0.1777E-13     0.2914E+02    0.3554E-01    13.75    0.0000E+00    0.9996E-02    0.3779E-05    0.1492E-12
 0.9993E-14     0.5104E+02    0.1999E-01    14.00    0.0000E+00    0.9998E-02    0.2126E-05    0.4720E-13
```

TABLE 7

```
              CATEQ7      VERSION H2/NULL     13-SEP-79

     [A] =   0.10E-01
      K1 =   0.45E-06          K2 =   0.47E-10          K3 =   0.10E+01          KW =   0.10E-13


      (1)          (2)           (3)         (4)       (5)          (6)           (7)           (8)
     [H+]           X        DLN[H+]/DX      PH         T         [CO3**]       [HCO3*]       [H2CO3]

  0.1000E+00  -0.5000E+01   0.2000E+00    1.00   0.4359E-09   0.2082E-16   0.4429E-07   0.9842E-02
  0.5624E-01  -0.2812E+01   0.3556E+00    1.25   0.8189E-09   0.6765E-16   0.8095E-07   0.1012E-01
  0.3162E-01  -0.1581E+01   0.6324E+00    1.50   0.1425E-08   0.2116E-15   0.1424E-06   0.1001E-01
  0.1778E-01  -0.8392E+00   0.1125E+01    1.75   0.2511E-08   0.6661E-15   0.2521E-06   0.9961E-02
  0.1000E-01  -0.5000E+00   0.2000E+01    2.00   0.4537E-08   0.2123E-14   0.4518E-06   0.1004E-01
  0.5624E-02  -0.2812E+00   0.3556E+01    2.25   0.8007E-08   0.6689E-14   0.8004E-06   0.1000E-01
  0.3163E-02  -0.1581E+00   0.6321E+01    2.50   0.1424E-07   0.2115E-13   0.1423E-05   0.1000E-01
  0.1779E-02  -0.8890E-01   0.1123E+02    2.75   0.2528E-07   0.6684E-13   0.2529E-05   0.9996E-02
  0.1000E-02  -0.4978E-01   0.1991E+02    3.00   0.4493E-07   0.2113E-12   0.4496E-05   0.9993E-02
  0.5624E-03  -0.2772E-01   0.3506E+02    3.25   0.7985E-07   0.6679E-12   0.7993E-05   0.9990E-02
  0.3163E-03  -0.1510E-01   0.6049E+02    3.50   0.1419E-06   0.2111E-11   0.1421E-04   0.9986E-02
  0.1779E-03  -0.7619E-02   0.9838E+02    3.75   0.2517E-06   0.6668E-11   0.2524E-04   0.9975E-02
  0.1000E-03  -0.2740E-02   0.1379E+03    4.00   0.4458E-06   0.2104E-10   0.4478E-04   0.9955E-02
  0.5625E-04   0.1195E-02   0.1473E+03    4.25   0.7871E-06   0.6631E-10   0.7935E-04   0.9919E-02
  0.3163E-04   0.5499E-02   0.1168E+03    4.50   0.1382E-05   0.2084E-09   0.1402E-03   0.9857E-02
  0.1779E-04   0.1156E-01   0.7678E+02    4.75   0.2404E-05   0.6516E-09   0.2466E-03   0.9749E-02
  0.1000E-04   0.2121E-01   0.4705E+02    5.00   0.4113E-05   0.2021E-08   0.4301E-03   0.9562E-02
  0.5625E-05   0.3705E-01   0.2876E+02    5.25   0.6840E-05   0.6180E-08   0.7397E-03   0.9247E-02
  0.3163E-05   0.6252E-01   0.1823E+02    5.50   0.1086E-04   0.1846E-07   0.1243E-02   0.8736E-02
  0.1779E-05   0.1013E+00   0.1239E+02    5.75   0.1601E-04   0.5317E-07   0.2012E-02   0.7956E-02
  0.1000E-05   0.1555E+00   0.9366E+01    6.00   0.2122E-04   0.1451E-06   0.3089E-02   0.6868E-02
  0.5626E-06   0.2223E+00   0.8134E+01    6.25   0.2445E-04   0.3694E-06   0.4422E-02   0.5529E-02
  0.3164E-06   0.2934E+00   0.8282E+01    6.50   0.2400E-04   0.8681E-06   0.5843E-02   0.4108E-02
  0.1779E-06   0.3580E+00   0.9857E+01    6.75   0.2013E-04   0.1885E-05   0.7136E-02   0.2821E-02
  0.1000E-06   0.4088E+00   0.1338E+02    7.00   0.1478E-04   0.3830E-05   0.8154E-02   0.1813E-02
  0.5626E-07   0.4445E+00   0.1999E+02    7.25   0.9825E-05   0.7405E-05   0.8865E-02   0.1108E-02
  0.3164E-07   0.4676E+00   0.3160E+02    7.50   0.6106E-05   0.1394E-04   0.9319E-02   0.6552E-03
  0.1779E-07   0.4822E+00   0.5055E+02    7.75   0.3635E-05   0.2533E-04   0.9508E-02   0.3771E-03
  0.1001E-07   0.4914E+00   0.7628E+02    8.00   0.2107E-05   0.4572E-04   0.9734E-02   0.2164E-03
  0.5627E-08   0.4980E+00   0.9659E+02    8.25   0.1199E-05   0.8180E-04   0.9793E-02   0.1225E-03
  0.3164E-08   0.5040E+00   0.9199E+02    8.50   0.6732E-06   0.1453E-03   0.9785E-02   0.6830E-04
  0.1779E-08   0.5112E+00   0.6757E+02    8.75   0.3724E-06   0.2563E-03   0.9705E-02   0.3837E-04
  0.1001E-08   0.5218E+00   0.4340E+02    9.00   0.2020E-06   0.4476E-03   0.9530E-02   0.2119E-04
  0.5627E-09   0.5387E+00   0.2696E+02    9.25   0.1062E-06   0.7699E-03   0.9217E-02   0.1153E-04
  0.3164E-09   0.5658E+00   0.1717E+02    9.50   0.5323E-07   0.1292E-02   0.8700E-02   0.6118E-05
  0.1780E-09   0.6071E+00   0.1168E+02    9.75   0.2473E-07   0.2089E-02   0.7908E-02   0.3127E-05
  0.1001E-09   0.6634E+00   0.8801E+01   10.00   0.1025E-07   0.3189E-02   0.6790E-02   0.1510E-05
  0.5628E-10   0.7358E+00   0.7528E+01   10.25   0.3707E-08   0.4547E-02   0.5445E-02   0.6809E-06
  0.3165E-10   0.8153E+00   0.7343E+01   10.50   0.1141E-08   0.5981E-02   0.4028E-02   0.2832E-06
  0.1780E-10   0.8992E+00   0.7770E+01   10.75   0.3042E-09   0.7324E-02   0.2773E-02   0.1077E-06
  0.1001E-10   0.9144E+00   0.8436E+01   11.00   0.6155E-10   0.7812E-02   0.1664E-02   0.3700E-07
  0.5628E-11   0.1035E+01   0.7321E+01   11.25   0.1430E-10   0.8931E-02   0.1069E-02   0.1337E-07
  0.3165E-11   0.1530E+00   0.6330E+01   11.50   0.0000E+00   0.0000E+00   0.0000E+00   0.0000E+00
  0.1780E-11   0.2809E+00   0.3560E+01   11.75   0.0000E+00   0.0000E+00   0.0000E+00   0.0000E+00
  0.1001E-11   0.4996E+00   0.2002E+01   12.00   0.0000E+00   0.0000E+00   0.0000E+00   0.0000E+00
  0.5629E-12   [illegible]  0.1126E+01   12.25   0.0000E+00   0.0000E+00   0.0000E+00   0.0000E+00
  0.3165E-12   0.1500E+01   0.6330E+00   12.50   0.0000E+00   0.0000E+00   0.0000E+00   0.0000E+00
```

TABLE 8

```
           CATEQ7     VERSION H2/NULL     13-SEP-79

     [A] =   0.10E-01
      K1 =   0.45E-06         K2 =   0.47E-10          K3 =   0.10E+02          KW =   0.10E-13


       (1)          (2)            (3)          (4)        (5)           (6)           (7)           (8)
      [H+]           X          DLN[H+]/DX      PH          T          [CO3**]        [HCO3*]       [H2CO3]

   0.1000E+00   -0.5000E+01     0.2000E+00     1.00    0.4497E-08    0.2114E-16    0.4498E-07    0.9996E-02
   0.5624E-01   -0.2812E+01     0.3556E+00     1.25    0.7980E-08    0.6679E-16    0.7991E-07    0.9986E-02
   0.3162E-01   -0.1581E+01     0.6324E+00     1.50    0.1425E-07    0.2116E-15    0.1424E-06    0.1001E-01
   0.1778E-01   -0.8892E+00     0.1125E+01     1.75    0.2530E-07    0.6687E-15    0.2530E-06    0.1000E-01
   0.1000E-01   -0.5000E+00     0.2000E+01     2.00    0.4500E-07    0.2115E-14    0.4500E-06    0.1000E-01
   0.5624E-02   -0.2812E+00     0.3556E+01     2.25    0.7999E-07    0.6686E-14    0.8000E-06    0.9998E-02
   0.3163E-02   -0.1581E+00     0.6321E+01     2.50    0.1422E-06    0.2114E-13    0.1422E-05    0.9997E-02
   0.1779E-02   -0.8879E-01     0.1123E+02     2.75    0.2529E-06    0.6684E-13    0.2529E-05    0.9997E-02
   0.1000E-02   -0.4976E-01     0.1990E+02     3.00    0.4494E-06    0.2113E-12    0.4497E-05    0.9995E-02
   0.5624E-03   -0.2768E-01     0.3501E+02     3.25    0.7986E-06    0.6679E-12    0.7993E-05    0.9990E-02
   0.3163E-03   -0.1503E-01     0.6026E+02     3.50    0.1418E-05    0.2111E-11    0.1420E-04    0.9983E-02
   0.1779E-03   -0.7506E-02     0.9732E+02     3.75    0.2515E-05    0.6665E-11    0.2522E-04    0.9970E-02
   0.1000E-03   -0.2541E-02     0.1343E+03     4.00    0.4451E-05    0.2103E-10    0.4475E-04    0.9946E-02
   0.5625E-04    0.1542E-02     0.1404E+03     4.25    0.7849E-05    0.6621E-10    0.7924E-04    0.9905E-02
   0.3163E-04    0.6100E-02     0.1096E+03     4.50    0.1375E-04    0.2078E-09    0.1399E-03    0.9833E-02
   0.1779E-04    0.1258E-01     0.7178E+02     4.75    0.2384E-04    0.6488E-09    0.2456E-03    0.9707E-02
   0.1000E-04    0.2208E-01     0.4425E+02     5.00    0.4053E-04    0.2006E-08    0.4270E-03    0.9492E-02
   0.5625E-05    0.3960E-01     0.2742E+02     5.25    0.6676E-04    0.6106E-08    0.7308E-03    0.9136E-02
   0.3163E-05    0.6604E-01     0.1774E+02     5.50    0.1045E-03    0.1812E-07    0.1219E-02    0.8572E-02
   0.1779E-05    0.1054E+00     0.1238E+02     5.75    0.1515E-03    0.5172E-07    0.1958E-02    0.7739E-02
   0.1000E-05    0.1588E+00     0.9601E+01     6.00    0.1974E-03    0.1400E-06    0.2980E-02    0.6625E-02
   0.5626E-06    0.2235E+00     0.8468E+01     6.25    0.2252E-03    0.3545E-06    0.4244E-02    0.5306E-02
   0.3164E-06    0.2917E+00     0.8603E+01     6.50    0.2214E-03    0.8336E-06    0.5611E-02    0.3945E-02
   0.1779E-06    0.3544E+00     0.1005E+02     6.75    0.1880E-03    0.1822E-05    0.6896E-02    0.2726E-02
   0.1000E-06    0.4048E+00     0.1329E+02     7.00    0.1405E-03    0.3734E-05    0.7948E-02    0.1767E-02
   0.5626E-07    0.4412E+00     0.1936E+02     7.25    0.9493E-04    0.7279E-05    0.8713E-02    0.1089E-02
   0.3164E-07    0.4653E+00     0.3004E+02     7.50    0.5975E-04    0.1369E-04    0.9219E-02    0.6482E-03
   0.1779E-07    0.4807E+00     0.4756E+02     7.75    0.3588E-04    0.2516E-04    0.9526E-02    0.3767E-03
   0.1001E-07    0.4905E+00     0.7179E+02     8.00    0.2091E-04    0.4555E-04    0.9697E-02    0.2156E-03
   0.5627E-08    0.4975E+00     0.9211E+02     8.25    0.1194E-04    0.8163E-04    0.9772E-02    0.1222E-03
   0.3164E-08    0.5036E+00     0.8954E+02     8.50    0.6715E-05    0.1452E-03    0.9773E-02    0.6872E-04
   0.1779E-08    0.5110E+00     0.6679E+02     8.75    0.3719E-05    0.2562E-03    0.9698E-02    0.3835E-04
   0.1001E-08    0.5217E+00     0.4321E+02     9.00    0.2018E-05    0.4475E-03    0.9527E-02    0.2119E-04
   0.5627E-09    0.5337E+00     0.2692E+02     9.25    0.1062E-05    0.7698E-03    0.9217E-02    0.1153E-04
   0.3164E-09    0.5659E+00     0.1716E+02     9.50    0.5323E-06    0.1292E-02    0.8700E-02    0.6118E-05
   0.1780E-09    0.6071E+00     0.1167E+02     9.75    0.2473E-06    0.2089E-02    0.7908E-02    0.3127E-05
   0.1001E-09    0.6646E+00     0.8785E+01    10.00    0.1029E-06    0.3195E-02    0.6802E-02    0.1513E-05
   0.5628E-10    0.7364E+00     0.7521E+01    10.25    0.3713E-07    0.4551E-02    0.5449E-02    0.6815E-06
   0.3165E-10    0.8153E+00     0.7343E+01    10.50    0.1141E-07    0.5981E-02    0.4028E-02    0.2832E-06
   0.1780E-10    0.8919E+00     0.7821E+01    10.75    0.2991E-08    0.7263E-02    0.2750E-02    0.1088E-06
   0.1001E-10    0.9414E+00     0.8286E+01    11.00    0.6546E-09    0.8057E-02    0.1716E-02    0.3815E-07
   0.5628E-11    0.9169E+00     0.7656E+01    11.25    0.1095E-09    0.7812E-02    0.9355E-03    0.1170E-07
   0.3165E-11    0.9655E+00     0.5476E+01    11.50    0.1947E-10    0.7812E-02    0.5261E-03    0.3700E-08
   0.1780E-11    0.2809E+00     0.3560E+01    11.75    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
   0.1001E-11    0.4996E+00     0.2002E+01    12.00    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
   0.5629E-12    0.8880E+00     0.1126E+01    12.25    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
   0.3165E-12    0.1530E+01     0.6330E+00    12.50    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
```

TABLE 9

```
                    CATE07      VERSION H2/NULL      13-SEP-79

        [A] =  -0.10E-01
         K1 =    0.45E-06          K2 =    0.47E-10          K3 =    0.50E+02          KW =    0.10E-13

     (1)           (2)             (3)            (4)        (5)           (6)            (7)            (8)
    [H+]            X          DLN[H+]/DX         PH          T        [CO3**]        [HCO3*]        [H2CO3]

 0.1000E+00    0.5000E+01    -0.2000E+00     1.00    0.2250E-07   -0.2115E-16   -0.4500E-07   -0.1000E-01
 0.5624E-01    0.2812E+01    -0.3556E+00     1.25    0.4001E-07   -0.6688E-16   -0.8002E-07   -0.1000E-01
 0.3162E-01    0.1581E+01    -0.6324E+00     1.50    0.7115E-07   -0.2115E-15   -0.1423E-06   -0.1000E-01
 0.1778E-01    0.8892E+00    -0.1125E+01     1.75    0.1265E-06   -0.6687E-15   -0.2530E-06   -0.1000E-01
 0.1000E-01    0.5001E+00    -0.2000E+01     2.00    0.2250E-06   -0.2115E-14   -0.4499E-06   -0.1000E-01
 0.5624E-02    0.2812E+00    -0.3556E+01     2.25    0.4000E-06   -0.6686E-14   -0.8001E-06   -0.9999E-02
 0.3163E-02    0.1582E+00    -0.6325E+01     2.50    0.7112E-06   -0.2114E-13   -0.1423E-05   -0.9999E-02
 0.1779E-02    0.8399E-01    -0.1125E+02     2.75    0.1264E-05   -0.6685E-13   -0.2530E-05   -0.9997E-02
 0.1000E-02    0.5012E-01    -0.2004E+02     3.00    0.2248E-05   -0.2113E-12   -0.4497E-05   -0.9996E-02
 0.5624E-03    0.2832E-01    -0.3581E+02     3.25    0.3994E-05   -0.6680E-12   -0.7994E-05   -0.9992E-02
 0.3163E-03    0.1617E-01    -0.6469E+02     3.50    0.7093E-05   -0.2111E-11   -0.1421E-04   -0.9986E-02
 0.1779E-03    0.9526E-02    -0.1211E+03     3.75    0.1259E-04   -0.6668E-11   -0.2524E-04   -0.9975E-02
 0.1000E-03    0.6126E-02    -0.2580E+03     4.00    0.2229E-04   -0.2104E-10   -0.4479E-04   -0.9955E-02
 0.5625E-04    0.4812E-02    -0.1231E+04     4.25    0.3937E-04   -0.6632E-10   -0.7937E-04   -0.9921E-02
 0.3163E-04    0.5137E-02     0.5065E+03     4.50    0.6915E-04   -0.2084E-09   -0.1403E-03   -0.9860E-02
 0.1779E-04    0.7210E-02     0.1841E+03     4.75    0.1203E-03   -0.6519E-09   -0.2467E-03   -0.9753E-02
 0.1000E-04    0.1173E-01     0.9325E+02     5.00    0.2060E-03   -0.2023E-08   -0.4305E-03   -0.9570E-02
 0.5625E-05    0.2017E-01     0.5104E+02     5.25    0.3429E-03   -0.6189E-08   -0.7407E-03   -0.9259E-02
 0.3163E-05    0.3517E-01     0.2882E+02     5.50    0.5451E-03   -0.1850E-07   -0.1245E-02   -0.8755E-02
 0.1779E-05    0.6076E-01     0.1685E+02     5.75    0.8056E-03   -0.5334E-07   -0.2019E-02   -0.7981E-02
 0.1000E-05    0.1017E+00     0.1069E+02     6.00    0.1070E-02   -0.1458E-06   -0.3103E-02   -0.6897E-02
 0.5626E-06    0.1605E+00     0.8199E+01     6.25    0.1234E-02   -0.3713E-06   -0.4444E-02   -0.5556E-02
 0.3164E-06    0.2331E+00     0.8498E+01     6.50    0.1212E-02   -0.8722E-06   -0.5871E-02   -0.4128E-02
 0.1779E-06    0.3077E+00     0.1169E+02     6.75    0.1015E-02   -0.1893E-05   -0.7165E-02   -0.2833E-02
 0.1000E-06    0.3721E+00     0.1881E+02     7.00    0.7435E-03   -0.3842E-05   -0.8173E-02   -0.1818E-02
 0.5626E-07    0.4202E+00     0.3211E+02     7.25    0.4932E-03   -0.7420E-05   -0.8882E-02   -0.1111E-02
 0.3164E-07    0.4526E+00     0.5504E+02     7.50    0.3060E-03   -0.1386E-04   -0.9330E-02   -0.6560E-03
 0.1779E-07    0.4732E+00     0.9004E+02     7.75    0.1820E-03   -0.2535E-04   -0.9595E-02   -0.3794E-03
 0.1001E-07    0.4861E+00     0.1285E+03     8.00    0.1054E-03   -0.4574E-04   -0.9738E-02   -0.2165E-03
 0.5627E-08    0.4949E+00     0.1410E+03     8.25    0.5999E-04   -0.8182E-04   -0.9796E-02   -0.1225E-03
 0.3164E-08    0.5020E+00     0.1141E+03     8.50    0.3367E-04   -0.1454E-03   -0.9786E-02   -0.6891E-04
 0.1779E-08    0.5097E+00     0.7578E+02     8.75    0.1862E-04   -0.2563E-03   -0.9705E-02   -0.3838E-04
 0.1001E-08    0.5203E+00     0.4665E+02     9.00    0.1010E-04   -0.4477E-03   -0.9531E-02   -0.2119E-04
 0.5627E-09    0.5368E+00     0.2861E+02     9.25    0.5313E-05   -0.7700E-03   -0.9219E-02   -0.1153E-04
 0.3164E-09    0.5626E+00     0.1823E+02     9.50    0.2662E-05   -0.1292E-02   -0.8701E-02   -0.6119E-05
 0.1780E-09    0.6014E+00     0.1251E+02     9.75    0.1237E-05   -0.2089E-02   -0.7908E-02   -0.3127E-05
 0.1001E-09    0.6547E+00     0.9636E+01    10.00    0.5146E-06   -0.3195E-02   -0.6803E-02   -0.1513E-05
 0.5628E-10    0.7186E+00     0.8685E+01    10.25    0.1856E-06   -0.4551E-02   -0.5449E-02   -0.6814E-06
 0.3165E-10    0.7830E+00     0.9573E+01    10.50    0.5693E-07   -0.5976E-02   -0.4024E-02   -0.2830E-06
 0.1780E-10    0.8346E+00     0.1398E+02    10.75    0.1492E-07   -0.7253E-02   -0.2747E-02   -0.1086E-06
 0.1001E-10    0.8623E+00     0.4462E+02    11.00    0.3427E-08   -0.8244E-02   -0.1756E-02   -0.3904E-07
 0.5628E-11    0.8577E+00    -0.2434E+02    11.25    0.7152E-09   -0.8931E-02   -0.1069E-02   -0.1337E-07
 0.3165E-11    0.8105E+00    -0.7787E+01    11.50    0.1400E-09   -0.9369E-02   -0.6309E-03   -0.4437E-08
 0.1780E-11    0.7008E+00    -0.3797E+01    11.75    0.2633E-10   -0.9635E-02   -0.3649E-03   -0.1443E-08
 0.1001E-11    0.4900E+00    -0.2044E+01    12.00    0.4835E-11   -0.9791E-02   -0.2085E-03   -0.4638E-09
 0.5629E-12    0.1057E+00    -0.1133E+01    12.25    0.8758E-12   -0.9882E-02   -0.1183E-03   -0.1490E-09
 0.3165E-12   -0.5030E+00    -0.6344E+00    12.50    0.1574E-12   -0.9933E-02   -0.6689E-04   -0.4705E-10
```

TABLE 10

```
             CATEQ7      VERSION H2/NULL      13-SEP-79

       [A] =   0.10E-01
        K1 =   0.45E-06          K2 =  0.47E-10          K3 =   0.10E+03          KW =   0.10E-13

    (1)          (2)            (3)          (4)        (5)           (6)            (7)           (8)
   [H+]           X          DLN[H+]/DX      PH          T          [CO3**]        [HCO3*]       [H2CO3]

0.1000E+00   -0.5000E+01    0.2000E+00      1.00    0.4502E-07    0.2116E-16    0.4501E-07    0.1000E-01
0.5624E-01   -0.2812E+01    0.3556E+00      1.25    0.7999E-07    0.6687E-16    0.8001E-07    0.9978E-02
0.3162E-01   -0.1581E+01    0.6324E+00      1.50    0.1423E-06    0.2115E-15    0.1423E-06    0.1000E-01
0.1778E-01   -0.8892E+00    0.1125E+01      1.75    0.2530E-06    0.6687E-15    0.2530E-06    0.1000E-01
0.1000E-01   -0.5000E+00    0.2000E+01      2.00    0.4498E-06    0.2114E-14    0.4497E-06    0.9998E-02
0.5624E-02   -0.2811E+00    0.3555E+01      2.25    0.7997E-06    0.6685E-14    0.7997E-06    0.9998E-02
0.3163E-02   -0.1580E+00    0.6318E+01      2.50    0.1422E-05    0.2114E-13    0.1422E-05    0.9996E-02
0.1779E-02   -0.8867E-01    0.1121E+02      2.75    0.2526E-05    0.6681E-13    0.2528E-05    0.9992E-02
0.1000E-02   -0.4956E-01    0.1982E+02      3.00    0.4487E-05    0.2111E-12    0.4493E-05    0.9987E-02
0.5624E-03   -0.2733E-01    0.3458E+02      3.25    0.7963E-05    0.6670E-12    0.7982E-05    0.9976E-02
0.3163E-03   -0.1440E-01    0.5807E+02      3.50    0.1411E-04    0.2105E-11    0.1417E-04    0.9958E-02
0.1779E-03   -0.6392E-02    0.8797E+02      3.75    0.2492E-04    0.6635E-11    0.2511E-04    0.9925E-02
0.1000E-03   -0.5910E-03    0.1072E+03      4.00    0.4381E-04    0.2086E-10    0.4440E-04    0.9868E-02
0.5625E-04    0.4913E-02    0.9732E+02      4.25    0.7635E-04    0.6530E-10    0.7815E-04    0.9769E-02
0.3163E-04    0.1180E-01    0.7046E+02      4.50    0.1311E-03    0.2029E-09    0.1366E-03    0.9601E-02
0.1779E-04    0.2190E-01    0.4653E+02      4.75    0.2197E-03    0.6232E-09    0.2359E-03    0.9324E-02
0.1000E-04    0.3727E-01    0.3076E+02      5.00    0.3555E-03    0.1879E-08    0.3799E-03    0.8887E-02
0.5625E-05    0.5995E-01    0.2141E+02      5.25    0.5446E-03    0.5515E-08    0.6600E-03    0.8251E-02
0.3163E-05    0.9130E-01    0.1607E+02      5.50    0.7775E-03    0.1563E-07    0.1052E-02    0.7393E-02
0.1779E-05    0.1313E+00    0.1312E+02      5.75    0.1021E-02    0.4245E-07    0.1607E-02    0.6352E-02
0.1000E-05    0.1783E+00    0.1159E+02      6.00    0.1222E-02    0.1101E-06    0.2344E-02    0.5212E-02
0.5626E-06    0.2296E+00    0.1097E+02      6.25    0.1330E-02    0.2725E-06    0.3262E-02    0.4078E-02
0.3164E-06    0.2822E+00    0.1104E+02      6.50    0.1316E-02    0.6427E-06    0.4326E-02    0.3042E-02
0.1779E-06    0.3328E+00    0.1183E+02      6.75    0.1183E-02    0.1445E-05    0.5470E-02    0.2163E-02
0.1000E-06    0.3785E+00    0.1361E+02      7.00    0.9673E-03    0.3099E-05    0.6596E-02    0.1466E-02
0.5626E-07    0.4167E+00    0.1694E+02      7.25    0.7221E-03    0.6348E-05    0.7599E-02    0.9501E-03
0.3164E-07    0.4463E+00    0.2284E+02      7.50    0.4965E-03    0.1248E-04    0.8404E-02    0.5909E-03
0.1779E-07    0.4675E+00    0.3278E+02      7.75    0.3191E-03    0.2373E-04    0.8983E-02    0.3552E-03
0.1001E-07    0.4821E+00    0.4781E+02      8.00    0.1947E-03    0.4396E-04    0.9358E-02    0.2081E-03
0.5627E-08    0.4924E+00    0.6475E+02      8.25    0.1145E-03    0.7995E-04    0.9571E-02    0.1197E-03
0.3164E-08    0.5007E+00    0.7148E+02      8.50    0.6558E-04    0.1434E-03    0.9657E-02    0.6791E-04
0.1779E-08    0.5093E+00    0.6009E+02      8.75    0.3670E-04    0.2545E-03    0.9634E-02    0.3310E-04
0.1001E-08    0.5207E+00    0.4147E+02      9.00    0.2004E-04    0.4459E-03    0.9493E-02    0.2111E-04
0.5627E-09    0.5382E+00    0.2652E+02      9.25    0.1058E-04    0.7683E-03    0.9199E-02    0.1150E-04
0.3164E-09    0.5656E+00    0.1707E+02      9.50    0.5313E-05    0.1291E-02    0.8692E-02    0.6113E-05
0.1780E-09    0.6067E+00    0.1165E+02      9.75    0.2471E-05    0.2088E-02    0.7904E-02    0.3126E-05
0.1001E-09    0.6646E+00    0.8776E+01     10.00    0.1029E-05    0.3195E-02    0.6802E-02    0.1513E-05
0.5628E-10    0.7363E+00    0.7519E+01     10.25    0.3712E-06    0.4550E-02    0.5448E-02    0.6813E-06
0.3165E-10    0.8146E+00    0.7340E+01     10.50    0.1139E-06    0.5976E-02    0.4024E-02    0.2830E-06
0.1780E-10    0.8910E+00    0.7827E+01     10.75    0.2985E-07    0.7256E-02    0.2747E-02    0.1087E-06
0.1001E-10    0.9617E+00    0.8177E+01     11.00    0.6847E-08    0.8240E-02    0.1755E-02    0.3902E-07
0.5628E-11    0.1033E+01    0.7326E+01     11.25    0.1424E-08    0.8911E-02    0.1067E-02    0.1335E-07
0.3155E-11    0.1126E+01    0.5332E+01     11.50    0.2800E-09    0.9369E-02    0.6309E-03    0.4437E-08
0.1780E-11    0.1077E+01    0.3380E+01     11.75    0.3462E-10    0.7812E-02    0.2958E-03    0.1170E-08
0.1001E-11    0.4996E+00    0.2002E+01     12.00    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
0.5627E-12    0.8833E+00    0.1126E+01     12.25    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
0.3165E-12    0.1580E+01    0.6330E+00     12.50    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
```

TABLE 11

```
          CATEQ7      VERSION H2/NULL      13-SEP-79

     [A] =   0.10E-01
      K1 =   0.45E-06          K2 =   0.47E-10          K3 =   0.25E+03          KW =   0.10E-13

     (1)           (2)            (3)          (4)        (5)           (6)            (7)            (8)
     [H+]           X          DLN[H+]/DX      PH          T          [CO3'']        [HCO3']        [H2CO3]

  0.1000E+00   -0.5000E+01    0.2000E+00     1.00    0.1125E-06    0.2115E-16    0.4500E-07    0.9999E-02
  0.5624E-01   -0.2812E+01    0.3556E+00     1.25    0.2000E-06    0.6687E-16    0.8002E-07    0.9999E-02
  0.3162E-01   -0.1581E+01    0.6324E+00     1.50    0.3557E-06    0.2115E-15    0.1423E-06    0.9999E-02
  0.1778E-01   -0.8892E+00    0.1125E+01     1.75    0.6324E-06    0.6686E-15    0.2530E-06    0.9998E-02
  0.1000E-01   -0.5000E+00    0.2000E+01     2.00    0.1124E-05    0.2114E-14    0.4498E-06    0.9997E-02
  0.5624E-02   -0.2811E+00    0.3554E+01     2.25    0.1998E-05    0.6684E-14    0.7998E-06    0.9995E-02
  0.3163E-02   -0.1579E+00    0.6314E+01     2.50    0.3551E-05    0.2113E-13    0.1422E-05    0.9991E-02
  0.1779E-02   -0.8849E-01    0.1119E+02     2.75    0.6306E-05    0.6676E-13    0.2526E-05    0.9985E-02
  0.1000E-02   -0.4922E-01    0.1969E+02     3.00    0.1119E-04    0.2109E-12    0.4487E-05    0.9973E-02
  0.5624E-03   -0.2673E-01    0.3390E+02     3.25    0.1981E-04    0.6654E-12    0.7963E-05    0.9952E-02
  0.3163E-03   -0.1336E-01    0.5484E+02     3.50    0.3497E-04    0.2096E-11    0.1411E-04    0.9916E-02
  0.1779E-03   -0.4577E-02    0.7633E+02     3.75    0.6139E-04    0.6586E-11    0.2493E-04    0.9852E-02
  0.1000E-03    0.2528E-02    0.8192E+02     4.00    0.1068E-03    0.2060E-10    0.4383E-04    0.9743E-02
  0.5625E-04    0.1015E-01    0.6743E+02     4.25    0.1827E-03    0.6389E-10    0.7647E-04    0.9558E-02
  0.3163E-04    0.2025E-01    0.4803E+02     4.50    0.3049E-03    0.1957E-09    0.1317E-03    0.9259E-02
  0.1779E-04    0.3472E-01    0.3342E+02     4.75    0.4896E-03    0.5881E-09    0.2226E-03    0.8798E-02
  0.1000E-04    0.5510E-01    0.2434E+02     5.00    0.7456E-03    0.1721E-08    0.3663E-03    0.8142E-02
  0.5625E-05    0.8203E-01    0.1911E+02     5.25    0.1063E-02    0.4873E-08    0.5832E-03    0.7291E-02
  0.3163E-05    0.1149E+00    0.1624E+02     5.50    0.1407E-02    0.1329E-07    0.8948E-03    0.6291E-02
  0.1779E-05    0.1523E+00    0.1476E+02     5.75    0.1727E-02    0.3492E-07    0.1322E-02    0.5225E-02
  0.1000E-05    0.1924E+00    0.1406E+02     6.00    0.1968E-02    0.8840E-07    0.1882E-02    0.4183E-02
  0.5626E-06    0.2338E+00    0.1391E+02     6.25    0.2090E-02    0.2161E-06    0.2586E-02    0.3233E-02
  0.3164E-06    0.2755E+00    0.1383E+02     6.50    0.2074E-02    0.5104E-06    0.3435E-02    0.2415E-02
  0.1779E-06    0.3167E+00    0.1416E+02     6.75    0.1922E-02    0.1165E-05    0.4410E-02    0.1744E-02
  0.1000E-06    0.3564E+00    0.1498E+02     7.00    0.1659E-02    0.2567E-05    0.5464E-02    0.1215E-02
  0.5626E-07    0.3931E+00    0.1667E+02     7.25    0.1329E-02    0.5447E-05    0.6521E-02    0.8153E-03
  0.3164E-07    0.4249E+00    0.1986E+02     7.50    0.9861E-03    0.1113E-04    0.7490E-02    0.5266E-03
  0.1779E-07    0.4508E+00    0.2545E+02     7.75    0.6795E-03    0.2190E-04    0.8291E-02    0.3278E-03
  0.1001E-07    0.4703E+00    0.3444E+02     8.00    0.4387E-03    0.4173E-04    0.8833E-02    0.1975E-03
  0.5627E-08    0.4847E+00    0.4627E+02     8.25    0.2686E-03    0.7743E-04    0.9269E-02    0.1159E-03
  0.3164E-08    0.4960E+00    0.5513E+02     8.50    0.1579E-03    0.1408E-03    0.9477E-02    0.6664E-04
  0.1779E-08    0.5065E+00    0.5198E+02     8.75    0.8980E-04    0.2517E-03    0.9531E-02    0.3769E-04
  0.1001E-08    0.5191E+00    0.3896E+02     9.00    0.4951E-04    0.4432E-03    0.9437E-02    0.2078E-04
  0.5627E-09    0.5373E+00    0.2589E+02     9.25    0.2629E-04    0.7659E-03    0.9170E-02    0.1147E-04
  0.3164E-09    0.5651E+00    0.1691E+02     9.50    0.1324E-04    0.1289E-02    0.8678E-02    0.6103E-05
  0.1780E-09    0.6067E+00    0.1161E+02     9.75    0.6168E-05    0.2086E-02    0.7898E-02    0.3123E-05
  0.1001E-09    0.6645E+00    0.8762E+01    10.00    0.2571E-05    0.3194E-02    0.6800E-02    0.1512E-05
  0.5628E-10    0.7363E+00    0.7514E+01    10.25    0.9278E-06    0.4550E-02    0.5448E-02    0.6813E-06
  0.3165E-10    0.8145E+00    0.7346E+01    10.50    0.2846E-06    0.5975E-02    0.4023E-02    0.2830E-06
  0.1780E-10    0.8708E+00    0.7828E+01    10.75    0.7459E-07    0.7254E-02    0.2747E-02    0.1086E-06
  0.1001E-10    0.9634E+00    0.8168E+01    11.00    0.1718E-07    0.8255E-02    0.1758E-02    0.3909E-07
  0.5628E-11    0.1033E+01    0.7326E+01    11.25    0.3560E-08    0.8911E-02    0.1067E-02    0.1335E-07
  0.3165E-11    0.1126E+01    0.5332E+01    11.50    0.6999E-09    0.9369E-02    0.6309E-03    0.4437E-08
  0.1780E-11    0.1263E+01    0.3350E+01    11.75    0.1316E-09    0.9635E-02    0.3649E-03    0.1443E-03
  0.1001E-11    0.1207E+01    0.1970E+01    12.00    0.1537E-10    0.7812E-02    0.1664E-03    0.3700E-09
  0.5629E-12    0.8803E+00    0.1126E+01    12.25    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
  0.3165E-12    0.1580E+01    0.6330E+00    12.50    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
```

TABLE 12

```
              CATEQ7      VERSION H2/NULL      13-SEP-79

      [A] =    0.10E-01
       K1 =    0.45E-06           K2 =    0.47E-10           K3 =    0.50E+03           KW =    0.10E-13


       (1)          (2)            (3)          (4)         (5)            (6)            (7)            (8)
      [H+]           X         DLN[H+]/DX       PH           T           [CO3**]        [HCO3*]        [H2CO3]

  0.1000E+00   -0.5000E+01    0.2000E+00     1.00     0.2250E-06     0.2115E-16     0.4500E-07     0.9999E-02
  0.5624E-01   -0.2812E+01    0.3556E+00     1.25     0.4001E-06     0.6687E-16     0.8002E-07     0.9999E-02
  0.3162E-01   -0.1581E+01    0.6324E+00     1.50     0.7112E-06     0.2114E-15     0.1423E-06     0.9998E-02
  0.1778E-01   -0.8891E+00    0.1125E+01     1.75     0.1265E-05     0.6686E-15     0.2530E-06     0.9997E-02
  0.1000E-01   -0.4999E+00    0.1999E+01     2.00     0.2240E-05     0.2114E-14     0.4497E-06     0.9995E-02
  0.5624E-02   -0.2810E+00    0.3553E+01     2.25     0.3994E-05     0.6681E-14     0.7994E-06     0.9991E-02
  0.3163E-02   -0.1577E+00    0.6307E+01     2.50     0.7092E-05     0.2111E-13     0.1421E-05     0.9984E-02
  0.1779E-02   -0.8817E-01    0.1115E+02     2.75     0.1258E-04     0.6660E-13     0.2523E-05     0.9972E-02
  0.1000E-02   -0.4867E-01    0.1948E+02     3.00     0.2228E-04     0.2104E-12     0.4477E-05     0.9951E-02
  0.5624E-03   -0.2576E-01    0.3284E+02     3.25     0.3931E-04     0.6628E-12     0.7932E-05     0.9913E-02
  0.3163E-03   -0.1166E-01    0.5038E+02     3.50     0.6899E-04     0.2082E-11     0.1401E-04     0.9848E-02
  0.1779E-03   -0.1667E-02    0.6338E+02     3.75     0.1199E-03     0.6500E-11     0.2463E-04     0.9736E-02
  0.1000E-03    0.7398E-02    0.6092E+02     4.00     0.2050E-03     0.2018E-10     0.4295E-04     0.9547E-02
  0.5625E-04    0.1797E-01    0.4782E+02     4.25     0.3417E-03     0.6178E-10     0.7394E-04     0.9243E-02
  0.3163E-04    0.3207E-01    0.3507E+02     4.50     0.5482E-03     0.1856E-09     0.1249E-03     0.8779E-02
  0.1779E-04    0.5113E-01    0.2642E+02     4.75     0.8349E-03     0.5431E-09     0.2055E-03     0.8125E-02
  0.1000E-04    0.7557E-01    0.2136E+02     5.00     0.1194E-02     0.1540E-08     0.3277E-03     0.7205E-02
  0.5625E-05    0.1046E+00    0.1869E+02     5.25     0.1593E-02     0.4217E-08     0.5048E-03     0.6310E-02
  0.3163E-05    0.1366E+00    0.1748E+02     5.50     0.1984E-02     0.1116E-07     0.7513E-03     0.5281E-02
  0.1779E-05    0.1700E+00    0.1712E+02     5.75     0.2318E-02     0.2861E-07     0.1083E-02     0.4281E-02
  0.1000E-05    0.2036E+00    0.1715E+02     6.00     0.2556E-02     0.7124E-07     0.1516E-02     0.3371E-02
  0.5626E-06    0.2371E+00    0.1724E+02     6.25     0.2673E-02     0.1728E-06     0.2068E-02     0.2595E-02
  0.3164E-06    0.2704E+00    0.1722E+02     6.50     0.2658E-02     0.4085E-06     0.2750E-02     0.1933E-02
  0.1779E-06    0.3040E+00    0.1712E+02     6.75     0.2512E-02     0.9418E-06     0.3565E-02     0.1409E-02
  0.1000E-06    0.3376E+00    0.1713E+02     7.00     0.2250E-02     0.2113E-05     0.4499E-02     0.1000E-02
  0.5626E-07    0.3709E+00    0.1759E+02     7.25     0.1898E-02     0.4603E-05     0.5510E-02     0.6889E-03
  0.3164E-07    0.4025E+00    0.1898E+02     7.50     0.1500E-02     0.9703E-05     0.6532E-02     0.4592E-03
  0.1779E-07    0.4310E+00    0.2186E+02     7.75     0.1105E-02     0.1975E-04     0.7475E-02     0.2956E-03
  0.1001E-07    0.4549E+00    0.2695E+02     8.00     0.7586E-03     0.3880E-04     0.8260E-02     0.1837E-03
  0.5627E-08    0.4738E+00    0.3442E+02     8.25     0.4884E-03     0.7383E-04     0.8839E-02     0.1105E-03
  0.3164E-08    0.4889E+00    0.4197E+02     8.50     0.2978E-03     0.1367E-03     0.9203E-02     0.6471E-04
  0.1779E-08    0.5021E+00    0.4330E+02     8.75     0.1735E-03     0.2475E-03     0.9368E-02     0.3704E-04
  0.1001E-08    0.5166E+00    0.3559E+02     9.00     0.9712E-04     0.4390E-03     0.9346E-02     0.2078E-04
  0.5627E-09    0.5358E+00    0.2494E+02     9.25     0.5203E-04     0.7619E-03     0.9123E-02     0.1141E-04
  0.3164E-09    0.5642E+00    0.1667E+02     9.50     0.2634E-04     0.1286E-02     0.8656E-02     0.6087E-05
  0.1780E-09    0.6062E+00    0.1154E+02     9.75     0.1230E-04     0.2084E-02     0.7889E-02     0.3120E-05
  0.1001E-09    0.6643E+00    0.8740E+01    10.00     0.5136E-05     0.3192E-02     0.6796E-02     0.1511E-05
  0.5628E-10    0.7362E+00    0.7506E+01    10.25     0.1855E-05     0.4549E-02     0.5447E-02     0.6812E-06
  0.3165E-10    0.8145E+00    0.7343E+01    10.50     0.5692E-06     0.5975E-02     0.4023E-02     0.2830E-06
  0.1780E-10    0.8907E+00    0.7827E+01    10.75     0.1491E-06     0.7253E-02     0.2746E-02     0.1086E-06
  0.1001E-10    0.9625E+00    0.8172E+01    11.00     0.3430E-07     0.8247E-02     0.1756E-02     0.3906E-07
  0.5628E-11    0.1037E+01    0.7318E+01    11.25     0.7169E-08     0.8942E-02     0.1071E-02     0.1339E-07
  0.3165E-11    0.1126E+01    0.5332E+01    11.50     0.1400E-08     0.9369E-02     0.6309E-03     0.4437E-08
  0.1780E-11    0.1263E+01    0.3350E+01    11.75     0.2633E-09     0.9635E-02     0.3649E-03     0.1443E-08
  0.1001E-11    0.1289E+01    0.1970E+01    12.00     0.3078E-10     0.7812E-02     0.1664E-03     0.3700E-09
  0.5629E-12    0.8883E+00    0.1126E+01    12.25     0.0000E+00     0.0000E+00     0.0000E+00     0.0000E+00
  0.3165E-12    0.1580E+01    0.6330E+00    12.50     0.0000E+00     0.0000E+00     0.0000E+00     0.0000E+00
```

TABLE 13

```
          CATEQ7      VERSION H2/NULL      13-SEP-79

   [A] =   0.10E-01
    K1 =   0.45E-06          K2 =    0.47E-11          K3 =   0.10E+04          KW =   0.10E-13

    (1)           (2)            (3)          (4)        (5)           (6)            (7)            (8)
   [H+]            X         DLN[H+]/DX       PH          T          [CO3°°]        [HCO3°]        [H2CO3]

0.1000E+00   -0.5000E+01    0.2000E+00      1.00    0.4499E-06    0.2115E-17    0.4500E-07    0.9999E-02
0.5624E-01   -0.2812E+01    0.3556E+00      1.25    0.8000E-06    0.6687E-17    0.8001E-07    0.9998E-02
0.3162E-01   -0.1581E+01    0.6324E+00      1.50    0.1422E-05    0.2114E-16    0.1423E-06    0.9997E-02
0.1778E-01   -0.8891E+00    0.1124E+01      1.75    0.2528E-05    0.6684E-16    0.2529E-06    0.9995E-02
0.1000E-01   -0.4998E+00    0.1999E+01      2.00    0.4491E-05    0.2113E-15    0.4495E-06    0.9991E-02
0.5624E-02   -0.2808E+00    0.3551E+01      2.25    0.7975E-05    0.6676E-15    0.7988E-06    0.9983E-02
0.3163E-02   -0.1574E+00    0.6293E+01      2.50    0.1414E-04    0.2108E-14    0.1419E-05    0.9970E-02
0.1779E-02   -0.8755E-01    0.1108E+02      2.75    0.2504E-04    0.6651E-14    0.2517E-05    0.9947E-02
0.1000E-02   -0.4758E-01    0.1909E+02      3.00    0.4416E-04    0.2095E-13    0.4458E-05    0.9907E-02
0.5624E-03   -0.2386E-01    0.3100E+02      3.25    0.7743E-04    0.6577E-13    0.7871E-05    0.9837E-02
0.3163E-03   -0.8406E-02    0.4379E+02      3.50    0.1343E-03    0.2054E-12    0.1383E-04    0.9717E-02
0.1779E-03    0.3769E-02    0.4892E+02      3.75    0.2292E-03    0.6363E-12    0.2408E-04    0.9518E-02
0.1000E-03    0.1610E-01    0.4328E+02      4.00    0.3806E-03    0.1944E-11    0.4138E-04    0.9197E-02
0.5625E-04    0.3105E-01    0.3411E+02      4.25    0.6076E-03    0.5826E-11    0.6972E-04    0.8715E-02
0.3163E-04    0.5017E-01    0.2689E+02      4.50    0.9206E-03    0.1700E-10    0.1144E-03    0.8044E-02
0.1779E-04    0.7373E-01    0.2253E+02      4.75    0.1310E-02    0.4011E-10    0.1821E-03    0.7197E-02
0.1000E-04    0.1008E+00    0.2038E+02      5.00    0.1745E-02    0.1317E-09    0.2802E-03    0.6229E-02
0.5625E-05    0.1296E+00    0.1973E+02      5.25    0.2181E-02    0.3490E-09    0.4177E-03    0.5221E-02
0.3163E-05    0.1587E+00    0.2004E+02      5.50    0.2572E-02    0.8986E-09    0.6048E-03    0.4252E-02
0.1779E-05    0.1868E+00    0.2086E+02      5.75    0.2884E-02    0.2257E-08    0.8542E-03    0.3377E-02
0.1000E-05    0.2139E+00    0.2174E+02      6.00    0.3098E-02    0.5546E-08    0.1180E-02    0.2624E-02
0.5626E-06    0.2400E+00    0.2227E+02      6.25    0.3200E-02    0.1337E-07    0.1600E-02    0.2000E-02
0.3164E-06    0.2658E+00    0.2220E+02      6.50    0.3187E-02    0.3163E-07    0.2129E-02    0.1497E-02
0.1779E-06    0.2920E+00    0.2158E+02      6.75    0.3059E-02    0.7349E-07    0.2782E-02    0.1100E-02
0.1000E-06    0.3193E+00    0.2069E+02      7.00    0.2822E-02    0.1674E-06    0.3563E-02    0.7921E-03
0.5626E-07    0.3476E+00    0.1997E+02      7.25    0.2490E-02    0.3728E-06    0.4462E-02    0.5579E-03
0.3164E-07    0.3766E+00    0.1987E+02      7.50    0.2085E-02    0.8090E-06    0.5446E-02    0.3829E-03
0.1779E-07    0.4051E+00    0.2088E+02      7.75    0.1646E-02    0.1704E-05    0.6452E-02    0.2551E-03
0.1001E-07    0.4312E+00    0.2369E+02      8.00    0.1217E-02    0.3475E-05    0.7398E-02    0.1645E-03
0.5627E-08    0.4532E+00    0.2932E+02      8.25    0.8421E-03    0.6855E-05    0.8206E-02    0.1026E-03
0.3164E-08    0.4703E+00    0.3935E+02      8.50    0.5481E-03    0.1311E-04    0.8829E-02    0.6208E-04
0.1779E-08    0.4827E+00    0.5537E+02      8.75    0.3391E-03    0.2446E-04    0.9261E-02    0.3662E-04
0.1001E-08    0.4916E+00    0.7576E+02      9.00    0.2020E-03    0.4476E-04    0.9530E-02    0.2119E-04
0.5627E-09    0.4985E+00    0.8889E+02      9.25    0.1170E-03    0.8079E-04    0.9673E-02    0.1210E-04
0.3164E-09    0.5051E+00    0.8028E+02      9.50    0.6638E-04    0.1443E-03    0.9716E-02    0.6832E-05
0.1780E-09    0.5135E+00    0.5728E+02      9.75    0.3696E-04    0.2553E-03    0.9667E-02    0.3823E-05
0.1001E-09    0.5262E+00    0.3619E+02     10.00    0.2012E-04    0.4467E-03    0.9511E-02    0.2115E-05
0.5628E-10    0.5468E+00    0.2215E+02     10.25    0.1060E-04    0.7691E-03    0.9209E-02    0.1152E-05
0.3165E-10    0.5801E+00    0.1380E+02     10.50    0.5319E-05    0.1292E-02    0.8697E-02    0.6116E-06
0.1780E-10    0.6324E+00    0.9012E+01     10.75    0.2472E-05    0.2088E-02    0.7907E-02    0.3127E-06
0.1001E-10    0.7096E+00    0.6297E+01     11.00    0.1029E-05    0.3195E-02    0.6803E-02    0.1513E-06
0.5628E-11    0.8164E+00    0.4697E+01     11.25    0.3713E-06    0.4550E-02    0.5449E-02    0.6815E-07
0.3165E-11    0.9568E+00    0.3594E+01     11.50    0.1139E-06    0.5976E-02    0.4024E-02    0.2830E-07
0.1780E-11    0.1143E+01    0.2628E+01     11.75    0.2980E-07    0.7248E-02    0.2745E-02    0.1086E-07
0.1001E-11    0.1411E+01    0.1749E+01     12.00    0.6818E-08    0.8240E-02    0.1755E-02    0.3903E-08
0.5629E-12    0.1833E+01    0.1060E+01     12.25    0.1424E-08    0.8911E-02    0.1067E-02    0.1335E-08
0.3165E-12    0.2548E+01    0.6214E+00     12.50    0.2800E-09    0.9369E-02    0.6310E-03    0.4438E-09
```

TABLE 14

CATEQ7 VERSION H2/NULL 13-SEP-79

[A] = 0.10E-01
K1 = 0.45E-06 K2 = 0.47E-10 K3 = 0.12E+04 KW = 0.10E-13

(1) [H+]	(2) X	(3) DLN[H+]/DX	(4) PH	(5) T	(6) [CO3**]	(7) [HCO3*]	(8) [H2CO3]
0.1000E+00	-0.5000E+01	0.2000E+00	1.00	0.5399E-06	0.2115E-16	0.4500E-07	0.9999E-02
0.5624E-01	-0.2812E+01	0.3556E+00	1.25	0.9599E-06	0.6687E-16	0.8001E-07	0.9998E-02
0.3162E-01	-0.1581E+01	0.6324E+00	1.50	0.1706E-05	0.2114E-15	0.1422E-06	0.9996E-02
0.1778E-01	-0.8890E+00	0.1124E+01	1.75	0.3033E-05	0.6683E-15	0.2529E-06	0.9994E-02
0.1000E-01	-0.4997E+00	0.1999E+01	2.00	0.5387E-05	0.2112E-14	0.4495E-06	0.9989E-02
0.5624E-02	-0.2807E+00	0.3550E+01	2.25	0.9563E-05	0.6674E-14	0.7985E-06	0.9980E-02
0.3163E-02	-0.1572E+00	0.6288E+01	2.50	0.1695E-04	0.2107E-13	0.1418E-05	0.9965E-02
0.1779E-02	-0.8730E-01	0.1105E+02	2.75	0.2998E-04	0.6645E-13	0.2514E-05	0.9938E-02
0.1000E-02	-0.4715E-01	0.1894E+02	3.00	0.5281E-04	0.2091E-12	0.4450E-05	0.9870E-02
0.5624E-03	-0.2311E-01	0.3035E+02	3.25	0.9235E-04	0.6557E-12	0.7847E-05	0.9807E-02
0.3163E-03	-0.7149E-02	0.4177E+02	3.50	0.1596E-03	0.2044E-11	0.1375E-04	0.9667E-02
0.1779E-03	0.5815E-02	0.4527E+02	3.75	0.2703E-03	0.6308E-11	0.2387E-04	0.9436E-02
0.1000E-03	0.1925E-01	0.3955E+02	4.00	0.4442E-03	0.1918E-10	0.4081E-04	0.9071E-02
0.5625E-04	0.3556E-01	0.3150E+02	4.25	0.6991E-03	0.5704E-10	0.6827E-04	0.8534E-02
0.3163E-04	0.5600E-01	0.2546E+02	4.50	0.1041E-02	0.1650E-09	0.1111E-03	0.7808E-02
0.1779E-04	0.8052E-01	0.2197E+02	4.75	0.1453E-02	0.4625E-09	0.1750E-03	0.6919E-02
0.1000E-04	0.1079E+00	0.2044E+02	5.00	0.1900E-02	0.1254E-08	0.2669E-03	0.5933E-02
0.5625E-05	0.1363E+00	0.2027E+02	5.25	0.2336E-02	0.3297E-08	0.3946E-03	0.4933E-02
0.3163E-05	0.1642E+00	0.2098E+02	5.50	0.2720E-02	0.8437E-08	0.5678E-03	0.3992E-02
0.1779E-05	0.1910E+00	0.2213E+02	5.75	0.3023E-02	0.2109E-07	0.7983E-03	0.3156E-02
0.1000E-05	0.2163E+00	0.2326E+02	6.00	0.3227E-02	0.5167E-07	0.1100E-02	0.2445E-02
0.5626E-06	0.2407E+00	0.2392E+02	6.25	0.3325E-02	0.1244E-06	0.1487E-02	0.1861E-02
0.3164E-06	0.2647E+00	0.2383E+02	6.50	0.3313E-02	0.2944E-06	0.1982E-02	0.1393E-02
0.1779E-06	0.2892E+00	0.2302E+02	6.75	0.3190E-02	0.6851E-06	0.2593E-02	0.1025E-02
0.1000E-06	0.3149E+00	0.2183E+02	7.00	0.2963E-02	0.1565E-05	0.3332E-02	0.7409E-03
0.5626E-07	0.3420E+00	0.2070E+02	7.25	0.2639E-02	0.3504E-05	0.4194E-02	0.5244E-03
0.3164E-07	0.3703E+00	0.2008E+02	7.50	0.2239E-02	0.7653E-05	0.5152E-02	0.3622E-03
0.1779E-07	0.3989E+00	0.2035E+02	7.75	0.1795E-02	0.1625E-04	0.6151E-02	0.2432E-03
0.1001E-07	0.4264E+00	0.2188E+02	8.00	0.1349E-02	0.3340E-04	0.7110E-02	0.1581E-03
0.5627E-08	0.4511E+00	0.2494E+02	8.25	0.9463E-03	0.6634E-04	0.7942E-02	0.9930E-04
0.3164E-08	0.4725E+00	0.2905E+02	8.50	0.6200E-03	0.1273E-03	0.8572E-02	0.6028E-04
0.1779E-08	0.4913E+00	0.3175E+02	8.75	0.3814E-03	0.2368E-03	0.8965E-02	0.3545E-04
0.1001E-08	0.5098E+00	0.2944E+02	9.00	0.2214E-03	0.4278E-03	0.9109E-02	0.2026E-04
0.5627E-09	0.5318E+00	0.2279E+02	9.25	0.1214E-03	0.7513E-03	0.8995E-02	0.1125E-04
0.3164E-09	0.5620E+00	0.1604E+02	9.50	0.6231E-04	0.1276E-02	0.8593E-02	0.6043E-05
0.1780E-09	0.6050E+00	0.1135E+02	9.75	0.2933E-04	0.2076E-02	0.7862E-02	0.3109E-05
0.1001E-09	0.6637E+00	0.8680E+01	10.00	0.1229E-04	0.3187E-02	0.6787E-02	0.1509E-05
0.5623E-10	0.7360E+00	0.7483E+01	10.25	0.4447E-05	0.4547E-02	0.5444E-02	0.6808E-06
0.3165E-10	0.8144E+00	0.7333E+01	10.50	0.1366E-05	0.5974E-02	0.4023E-02	0.2829E-06
0.1780E-10	0.8907E+00	0.7824E+01	10.75	0.3579E-06	0.7253E-02	0.2746E-02	0.1086E-06
0.1001E-10	0.9623E+00	0.8172E+01	11.00	0.8227E-07	0.8245E-02	0.1756E-02	0.3905E-07
0.5628E-11	0.1035E+01	0.7322E+01	11.25	0.1715E-07	0.8926E-02	0.1069E-02	0.1337E-07
0.3165E-11	0.1126E+01	0.5332E+01	11.50	0.3359E-08	0.9369E-02	0.6309E-03	0.4437E-08
0.1780E-11	0.1263E+01	0.3350E+01	11.75	0.6319E-09	0.9635E-02	0.3649E-03	0.1443E-08
0.1001E-11	0.1489E+01	0.1962E+01	12.00	0.1160E-09	0.9791E-02	0.2085E-03	0.4638E-09
0.5629E-12	0.1882E+01	0.1118E+01	12.25	0.2102E-10	0.9882E-02	0.1183E-03	0.1480E-09
0.3165E-12	0.2576E+01	0.6317E+00	12.50	0.3777E-11	0.9933E-02	0.6689E-04	0.4705E-10

TABLE 15

```
              CATEQ7      VERSION H2/NULL      13-SEP-79

   [A] =   0.10E-01
    K1 =   0.45E-06          K2 =   0.47E-10          K3 =   0.15E+04          KW =   0.10E-13

     (1)            (2)             (3)          (4)        (5)            (6)            (7)            (8)
    [H+]             X          DLN[H+]/DX       PH          T          [CO3**]        [HCO3*]        [H2CO3]

  0.1000E+00    -0.5000E+01     0.2000E+00      1.00    0.6748E-06     0.2115E-16     0.4499E-07     0.9999E-02
  0.5624E-01    -0.2812E+01     0.3556E+00      1.25    0.1200E-05     0.6686E-16     0.8000E-07     0.9998E-02
  0.3162E-01    -0.1581E+01     0.6324E+00      1.50    0.2133E-05     0.2114E-15     0.1422E-06     0.9996E-02
  0.1778E-01    -0.8890E+00     0.1124E+01      1.75    0.3790E-05     0.6682E-15     0.2520E-06     0.9992E-02
  0.1000E-01    -0.4997E+00     0.1998E+01      2.00    0.6731E-05     0.2112E-14     0.4493E-06     0.9986E-02
  0.5624E-02    -0.2806E+00     0.3548E+01      2.25    0.1194E-04     0.6670E-14     0.7982E-06     0.9975E-02
  0.3163E-02    -0.1570E+00     0.6279E+01      2.50    0.2116E-04     0.2105E-13     0.1417E-05     0.9956E-02
  0.1779E-02    -0.8693E-01     0.1100E+02      2.75    0.3737E-04     0.6635E-13     0.2511E-05     0.9923E-02
  0.1000E-02    -0.4650E-01     0.1872E+02      3.00    0.6567E-04     0.2086E-12     0.4438E-05     0.9864E-02
  0.5624E-03    -0.2201E-01     0.2945E+02      3.25    0.1144E-03     0.6528E-12     0.7811E-05     0.9763E-02
  0.3163E-03    -0.5311E-02     0.3918E+02      3.50    0.1964E-03     0.2028E-11     0.1365E-04     0.9594E-02
  0.1779E-03     0.8758E-02     0.4105E+02      3.75    0.3295E-03     0.6229E-11     0.2357E-04     0.9318E-02
  0.1000E-03     0.2368E-01     0.3553E+02      4.00    0.5337E-03     0.1880E-10     0.4001E-04     0.8893E-02
  0.5625E-04     0.4170E-01     0.2881E+02      4.25    0.8239E-03     0.5539E-10     0.6629E-04     0.8286E-02
  0.3163E-04     0.6370E-01     0.2406E+02      4.50    0.1199E-02     0.1584E-09     0.1066E-03     0.7496E-02
  0.1779E-04     0.8916E-01     0.2153E+02      4.75    0.1635E-02     0.4387E-09     0.1661E-03     0.6564E-02
  0.1000E-04     0.1166E+00     0.2070E+02      5.00    0.2091E-02     0.1177E-08     0.2504E-03     0.5567E-02
  0.5625E-05     0.1442E+00     0.2110E+02      5.25    0.2524E-02     0.3065E-08     0.3669E-03     0.4586E-02
  0.3163E-05     0.1708E+00     0.2229E+02      5.50    0.2896E-02     0.7786E-08     0.5241E-03     0.3684E-02
  0.1779E-05     0.1958E+00     0.2387E+02      5.75    0.3185E-02     0.1936E-07     0.7329E-03     0.2897E-02
  0.1000E-05     0.2192E+00     0.2533E+02      6.00    0.3378E-02     0.4728E-07     0.1006E-02     0.2238E-02
  0.5626E-06     0.2415E+00     0.2617E+02      6.25    0.3470E-02     0.1136E-06     0.1360E-02     0.1701E-02
  0.3164E-06     0.2634E+00     0.2605E+02      6.50    0.3458E-02     0.2690E-06     0.1811E-02     0.1273E-02
  0.1779E-06     0.2859E+00     0.2503E+02      6.75    0.3343E-02     0.6272E-06     0.2374E-02     0.9387E-03
  0.1000E-06     0.3096E+00     0.2348E+02      7.00    0.3128E-02     0.1439E-05     0.3062E-02     0.6809E-03
  0.5626E-07     0.3350E+00     0.2191E+02      7.25    0.2818E-02     0.3238E-05     0.3876E-02     0.4846E-03
  0.3164E-07     0.3621E+00     0.2078E+02      7.50    0.2428E-02     0.7128E-05     0.4799E-02     0.3374E-03
  0.1779E-07     0.3901E+00     0.2047E+02      7.75    0.1985E-02     0.1528E-04     0.5786E-02     0.2289E-03
  0.1001E-07     0.4178E+00     0.2130E+02      8.00    0.1526E-02     0.3178E-04     0.6765E-02     0.1504E-03
  0.5627E-08     0.4437E+00     0.2348E+02      8.25    0.1097E-02     0.6388E-04     0.7647E-02     0.9562E-04
  0.3164E-08     0.4667E+00     0.2671E+02      8.50    0.7349E-03     0.1240E-03     0.8347E-02     0.5870E-04
  0.1779E-08     0.4872E+00     0.2916E+02      8.75    0.4605E-03     0.2327E-03     0.8811E-02     0.3484E-04
  0.1001E-08     0.5071E+00     0.2768E+02      9.00    0.2710E-03     0.4234E-03     0.9014E-02     0.2005E-04
  0.5627E-09     0.5302E+00     0.2204E+02      9.25    0.1500E-03     0.7469E-03     0.8942E-02     0.1118E-04
  0.3164E-09     0.5610E+00     0.1580E+02      9.50    0.7741E-04     0.1272E-02     0.8567E-02     0.6024E-05
  0.1780E-09     0.6045E+00     0.1128E+02      9.75    0.3656E-04     0.2073E-02     0.7850E-02     0.3104E-05
  0.1001E-09     0.6634E+00     0.8654E+01     10.00    0.1534E-04     0.3185E-02     0.6702E-02     0.1508E-05
  0.5628E-10     0.7358E+00     0.7473E+01     10.25    0.5557E-05     0.4546E-02     0.5443E-02     0.6306E-06
  0.3165E-10     0.8144E+00     0.7329E+01     10.50    0.1707E-05     0.5974E-02     0.4022E-02     0.2329E-06
  0.1780E-10     0.8907E+00     0.7822E+01     10.75    0.4474E-06     0.7253E-02     0.2746E-02     0.1096E-06
  0.1001E-10     0.9623E+00     0.8171E+01     11.00    0.1028E-06     0.8245E-02     0.1756E-02     0.3905E-07
  0.5628E-11     0.1035E+01     0.7322E+01     11.25    0.2143E-07     0.8926E-02     0.1069E-02     0.1337E-07
  0.3165E-11     0.1126E+01     0.5332E+01     11.50    0.4199E-08     0.9369E-02     0.6309E-03     0.4437E-08
  0.1780E-11     0.1263E+01     0.3350E+01     11.75    0.7898E-09     0.9635E-02     0.3649E-03     0.1443E-08
  0.1001E-11     0.1489E+01     0.1962E+01     12.00    0.1451E-09     0.9791E-02     0.2085E-03     0.4638E-09
  0.5627E-12     0.1674E+01     0.1120E+01     12.25    0.1642E-10     0.7812E-02     0.9356E-04     0.1170E-09
  0.3165E-12     0.1590E+01     0.6330E+00     12.50    0.0000E+00     0.0000E+00     0.0000E+00     0.0000E+00
```

TABLE 16

```
          CATEQ7       VERSION H2/NULL       13-SEP-79

      [A] =   0.10E-01
       K1 =   0.45E-06          K2 =    0.47E-10          K3 =   0.20E+04          KW =    0.10E-13

        (1)           (2)            (3)           (4)        (5)           (6)            (7)           (8)
       [H+]            X         DLN[H+]/DX        PH          T          [CO3**]        [HCO3*]       [H2CO3]

    0.1000E+00   -0.5000E+01    0.2000E+00      1.00    0.8997E-06    0.2115E-16    0.4499E-07    0.9998E-02
    0.5624E-01   -0.2812E+01    0.3556E+00      1.25    0.1597E-05    0.6686E-16    0.7999E-07    0.9997E-02
    0.3162E-01   -0.1581E+01    0.6324E+00      1.50    0.2843E-05    0.2114E-15    0.1422E-06    0.9994E-02
    0.1778E-01   -0.8889E+00    0.1124E+01      1.75    0.5050E-05    0.6680E-15    0.2528E-06    0.9990E-02
    0.1000E-01   -0.4996E+00    0.1998E+01      2.00    0.8766E-05    0.2111E-14    0.4491E-06    0.9982E-02
    0.5624E-02   -0.2804E+00    0.3546E+01      2.25    0.1590E-04    0.6665E-14    0.7975E-06    0.9967E-02
    0.3163E-02   -0.1567E+00    0.6266E+01      2.50    0.2813E-04    0.2102E-13    0.1415E-05    0.9942E-02
    0.1779E-02   -0.8632E-01    0.1093E+02      2.75    0.4958E-04    0.6618E-13    0.2504E-05    0.9898E-02
    0.1000E-02   -0.4545E-01    0.1838E+02      3.00    0.8681E-04    0.2077E-12    0.4419E-05    0.9822E-02
    0.5624E-03   -0.2022E-01    0.2812E+02      3.25    0.1503E-03    0.6480E-12    0.7754E-05    0.9692E-02
    0.3163E-03   -0.2366E-02    0.3577E+02      3.50    0.2555E-03    0.2003E-11    0.1348E-04    0.9476E-02
    0.1779E-03    0.1336E-01    0.3612E+02      3.75    0.4220E-03    0.6105E-11    0.2311E-04    0.9133E-02
    0.1000E-03    0.3039E-01    0.3122E+02      4.00    0.6691E-03    0.1823E-10    0.3879E-04    0.8623E-02
    0.5625E-04    0.5062E-01    0.2608E+02      4.25    0.1005E-02    0.5298E-10    0.6341E-04    0.7926E-02
    0.3163E-04    0.7439E-01    0.2277E+02      4.50    0.1419E-02    0.1493E-09    0.1005E-03    0.7062E-02
    0.1779E-04    0.1007E+00    0.2131E+02      4.75    0.1877E-02    0.4072E-09    0.1541E-03    0.6091E-02
    0.1000E-04    0.1270E+00    0.2133E+02      5.00    0.2337E-02    0.1077E-08    0.2293E-03    0.5097E-02
    0.5625E-05    0.1542E+00    0.2243E+02      5.25    0.2758E-02    0.2775E-08    0.3321E-03    0.4152E-02
    0.3163E-05    0.1789E+00    0.2429E+02      5.50    0.3111E-02    0.6989E-08    0.4704E-03    0.3307E-02
    0.1779E-05    0.2016E+00    0.2646E+02      5.75    0.3381E-02    0.1728E-07    0.6539E-03    0.2585E-02
    0.1000E-05    0.2226E+00    0.2839E+02      6.00    0.3558E-02    0.4203E-07    0.8946E-03    0.1989E-02
    0.5626E-06    0.2424E+00    0.2948E+02      6.25    0.3642E-02    0.1008E-06    0.1207E-02    0.1509E-02
    0.3164E-06    0.2619E+00    0.2933E+02      6.50    0.3631E-02    0.2387E-06    0.1607E-02    0.1130E-02
    0.1779E-06    0.2820E+00    0.2800E+02      6.75    0.3526E-02    0.5579E-06    0.2112E-02    0.8349E-03
    0.1000E-06    0.3033E+00    0.2595E+02      7.00    0.3327E-02    0.1285E-05    0.2736E-02    0.6082E-03
    0.5626E-07    0.3265E+00    0.2376E+02      7.25    0.3038E-02    0.2912E-05    0.3486E-02    0.4358E-03
    0.3164E-07    0.3517E+00    0.2197E+02      7.50    0.2666E-02    0.6469E-05    0.4355E-02    0.3062E-03
    0.1779E-07    0.3786E+00    0.2094E+02      7.75    0.2232E-02    0.1403E-04    0.5312E-02    0.2100E-03
    0.1001E-07    0.4063E+00    0.2092E+02      8.00    0.1765E-02    0.2959E-04    0.6300E-02    0.1401E-03
    0.5627E-08    0.4332E+00    0.2208E+02      8.25    0.1308E-02    0.6042E-04    0.7233E-02    0.9044E-04
    0.3164E-08    0.4531E+00    0.2425E+02      8.50    0.9038E-03    0.1191E-03    0.8017E-02    0.5637E-04
    0.1779E-08    0.4808E+00    0.2620E+02      8.75    0.5817E-03    0.2265E-03    0.8576E-02    0.3391E-04
    0.1001E-08    0.5029E+00    0.2541E+02      9.00    0.3495E-03    0.4164E-03    0.8865E-02    0.1971E-04
    0.5627E-09    0.5275E+00    0.2097E+02      9.25    0.1962E-03    0.7398E-03    0.8857E-02    0.1108E-04
    0.3164E-09    0.5595E+00    0.1543E+02      9.50    0.1022E-03    0.1266E-02    0.8524E-02    0.5994E-05
    0.1780E-09    0.6036E+00    0.1116E+02      9.75    0.4851E-04    0.2068E-02    0.7831E-02    0.3097E-05
    0.1001E-09    0.6630E+00    0.8613E+01     10.00    0.2042E-04    0.3182E-02    0.6775E-02    0.1507E-05
    0.5628E-10    0.7357E+00    0.7457E+01     10.25    0.7404E-05    0.4544E-02    0.5441E-02    0.6804E-06
    0.3165E-10    0.8143E+00    0.7323E+01     10.50    0.2275E-05    0.5973E-02    0.4022E-02    0.2829E-06
    0.1780E-10    0.8707E+00    0.7819E+01     10.75    0.5965E-06    0.7252E-02    0.2746E-02    0.1086E-06
    0.1001E-10    0.9623E+00    0.8171E+01     11.00    0.1371E-06    0.8245E-02    0.1756E-02    0.3905E-07
    0.5628E-11    0.1035E+01    0.7322E+01     11.25    0.2858E-07    0.8926E-02    0.1069E-02    0.1337E-07
    0.3165E-11    0.1126E+01    0.5332E+01     11.50    0.5599E-08    0.9369E-02    0.6309E-03    0.4437E-08
    0.1780E-11    0.1263E+01    0.3350E+01     11.75    0.1053E-08    0.9635E-02    0.3649E-03    0.1443E-08
    0.1001E-11    0.1499E+01    0.1962E+01     12.00    0.1934E-09    0.9791E-02    0.2085E-03    0.4638E-09
    0.5629E-12    0.1674E+01    0.1120E+01     12.25    0.2190E-10    0.7812E-02    0.9356E-04    0.1170E-09
    0.3165E-12    0.1580E+01    0.6330E+00     12.50    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
```

TABLE 17

```
CATEQ7     VERSION H2/NULL     13-SEP-79

 [A] =   0.10E-01
  K1 =   0.45E-06          K2 =    0.47E-10          K3 =   0.35E+04          KW =    0.10E-13

    (1)          (2)            (3)           (4)        (5)           (6)           (7)           (8)
   [H+]           X          DLN[H+]/DX       PH          T          [CO3**]       [HCO3*]       [H2CO3]

0.1000E+00   -0.5000E+01    0.2000E+00      1.00    0.1574E-05    0.2114E-16    0.4499E-07    0.9997E-02
0.5624E-01   -0.2812E+01    0.3556E+00      1.25    0.2798E-05    0.6684E-16    0.7998E-07    0.9994E-02
0.3162E-01   -0.1581E+01    0.6323E+00      1.50    0.4970E-05    0.2113E-15    0.1422E-06    0.9990E-02
0.1778E-01   -0.8887E+00    0.1124E+01      1.75    0.8825E-05    0.6675E-15    0.2526E-06    0.9982E-02
0.1000E-01   -0.4992E+00    0.1997E+01      2.00    0.1565E-04    0.2108E-14    0.4485E-06    0.9968E-02
0.5624E-02   -0.2798E+00    0.3538E+01      2.25    0.2769E-04    0.6649E-14    0.7956E-06    0.9944E-02
0.3163E-02   -0.1556E+00    0.6227E+01      2.50    0.4882E-04    0.2094E-13    0.1409E-05    0.9901E-02
0.1779E-02   -0.8453E-01    0.1073E+02      2.75    0.8551E-04    0.6570E-13    0.2486E-05    0.9826E-02
0.1000E-02   -0.4238E-01    0.1748E+02      3.00    0.1481E-03    0.2051E-12    0.4364E-05    0.9699E-02
0.5624E-03   -0.1514E-01    0.2509E+02      3.25    0.2521E-03    0.6344E-12    0.7591E-05    0.9488E-02
0.3163E-03    0.5674E-02    0.2940E+02      3.50    0.4171E-03    0.1935E-11    0.1302E-04    0.9153E-02
0.1779E-03    0.2535E-01    0.2848E+02      3.75    0.6629E-03    0.5784E-11    0.2189E-04    0.8652E-02
0.1000E-03    0.4675E-01    0.2531E+02      4.00    0.9992E-03    0.1684E-10    0.3584E-04    0.7966E-02
0.5625E-04    0.7083E-01    0.2276E+02      4.25    0.1416E-02    0.4754E-10    0.5689E-04    0.7111E-02
0.3163E-04    0.9690E-01    0.2166E+02      4.50    0.1882E-02    0.1300E-09    0.8747E-04    0.6148E-02
0.1779E-04    0.1234E+00    0.2197E+02      4.75    0.2356E-02    0.3448E-09    0.1305E-03    0.5158E-02
0.1000E-04    0.1489E+00    0.2349E+02      5.00    0.2798E-02    0.8909E-09    0.1896E-03    0.4215E-02
0.5625E-05    0.1722E+00    0.2602E+02      5.25    0.3180E-02    0.2253E-08    0.2696E-03    0.3370E-02
0.3163E-05    0.1931E+00    0.2928E+02      5.50    0.3488E-02    0.5594E-08    0.3765E-03    0.2647E-02
0.1779E-05    0.2116E+00    0.3279E+02      5.75    0.3716E-02    0.1369E-07    0.5183E-03    0.2049E-02
0.1000E-05    0.2284E+00    0.3581E+02      6.00    0.3864E-02    0.3311E-07    0.7047E-03    0.1567E-02
0.5626E-06    0.2440E+00    0.3750E+02      6.25    0.3933E-02    0.7921E-07    0.9481E-03    0.1185E-02
0.3164E-06    0.2594E+00    0.3728E+02      6.50    0.3925E-02    0.1876E-06    0.1263E-02    0.8879E-03
0.1779E-06    0.2752E+00    0.3522E+02      6.75    0.3838E-02    0.4400E-06    0.1665E-02    0.6584E-03
0.1000E-06    0.2923E+00    0.3200E+02      7.00    0.3672E-02    0.1020E-05    0.2172E-02    0.4830E-03
0.5626E-07    0.3114E+00    0.2845E+02      7.25    0.3425E-02    0.2337E-05    0.2798E-02    0.3498E-03
0.3164E-07    0.3329E+00    0.2525E+02      7.50    0.3098E-02    0.5271E-05    0.3548E-02    0.2495E-03
0.1779E-07    0.3569E+00    0.2279E+02      7.75    0.2699E-02    0.1167E-04    0.4416E-02    0.1746E-03
0.1001E-07    0.3832E+00    0.2127E+02      8.00    0.2243E-02    0.2522E-04    0.5369E-02    0.1194E-03
0.5627E-08    0.4107E+00    0.2075E+02      8.25    0.1762E-02    0.5300E-04    0.6344E-02    0.7933E-04
0.3164E-08    0.4383E+00    0.2112E+02      8.50    0.1294E-02    0.1077E-03    0.7252E-02    0.5100E-04
0.1779E-08    0.4651E+00    0.2180E+02      8.75    0.8836E-03    0.2110E-03    0.7990E-02    0.3159E-04
0.1001E-08    0.4915E+00    0.2138E+02      9.00    0.5580E-03    0.3977E-03    0.8467E-02    0.1883E-04
0.5627E-09    0.5201E+00    0.1863E+02      9.25    0.3251E-03    0.7199E-03    0.8619E-02    0.1078E-04
0.3164E-09    0.5550E+00    0.1448E+02      9.50    0.1736E-03    0.1248E-02    0.8399E-02    0.5906E-05
0.1780E-09    0.6012E+00    0.1082E+02      9.75    0.8369E-04    0.2054E-02    0.7776E-02    0.3075E-05
0.1001E-09    0.6618E+00    0.8492E+01     10.00    0.3552E-04    0.3173E-02    0.6755E-02    0.1502E-05
0.5628E-10    0.7351E+00    0.7409E+01     10.25    0.1293E-04    0.4539E-02    0.5435E-02    0.6796E-06
0.3165E-10    0.8141E+00    0.7303E+01     10.50    0.3979E-05    0.5971E-02    0.4021E-02    0.2828E-06
0.1780E-10    0.8906E+00    0.7812E+01     10.75    0.1044E-05    0.7252E-02    0.2746E-02    0.1086E-06
0.1001E-10    0.9622E+00    0.8169E+01     11.00    0.2399E-06    0.8245E-02    0.1756E-02    0.3904E-07
0.5628E-11    0.1035E+01    0.7320E+01     11.25    0.5006E-07    0.8930E-02    0.1069E-02    0.1337E-07
0.3165E-11    0.1126E+01    0.5332E+01     11.50    0.9798E-08    0.9369E-02    0.6309E-03    0.4437E-08
0.1780E-11    0.1263E+01    0.3350E+01     11.75    0.1843E-08    0.9635E-02    0.3647E-03    0.1443E-08
0.1001E-11    0.1485E+01    0.1962E+01     12.00    0.3385E-09    0.9791E-02    0.2085E-03    0.4638E-09
0.5629E-12    0.1674E+01    0.1120E+01     12.25    0.3832E-10    0.7812E-02    0.9356E-04    0.1170E-09
0.3165E-12    0.1580E+01    0.6330E+00     12.50    0.0000E+00    0.0000E+00    0.0000E+00    0.0000E+00
```

TABLE 18

```
      CATEQ7     VERSION H2/NULL     13-SEP-79

  [A] =    0.10E-01
   K1 =    0.45E-06        K2 =    0.47E-10        K3 =   0.50E+04        KW =   0.10E-13

   (1)          (2)           (3)         (4)        (5)           (6)           (7)           (8)
  [H+]           X         DLN[H+]/DX     PH          T          [CO3""]       [HCO3"]       [H2CO3]

0.1000E+00  -0.5000E+01   0.2000E+00    1.00   0.2248E-05   0.2114E-16   0.4498E-07   0.9995E-02
0.5624E-01  -0.2812E+01   0.3556E+00    1.25   0.3995E-05   0.6683E-16   0.7996E-07   0.9992E-02
0.3162E-01  -0.1581E+01   0.6323E+00    1.50   0.7094E-05   0.2112E-15   0.1421E-06   0.9986E-02
0.1778E-01  -0.8086E+00   0.1124E+01    1.75   0.1259E-04   0.6670E-15   0.2524E-06   0.9975E-02
0.1000E-01  -0.4939E+00   0.1995E+01    2.00   0.2230E-04   0.2105E-14   0.4479E-06   0.9955E-02
0.5624E-02  -0.2792E+00   0.3531E+01    2.25   0.3937E-04   0.6634E-14   0.7938E-06   0.9920E-02
0.3163E-02  -0.1546E+00   0.6189E+01    2.50   0.6917E-04   0.2085E-13   0.1403E-05   0.9860E-02
0.1779E-02  -0.8278E-01   0.1055E+02    2.75   0.1204E-03   0.6524E-13   0.2469E-05   0.9757E-02
0.1000E-02  -0.3946E-01   0.1675E+02    3.00   0.2066E-03   0.2026E-12   0.4311E-05   0.9583E-02
0.5624E-03  -0.1045E-01   0.2298E+02    3.25   0.3460E-03   0.6218E-12   0.7441E-05   0.9300E-02
0.3163E-03   0.1279E-01   0.2587E+02    3.50   0.5595E-03   0.1875E-11   0.1262E-04   0.8868E-02
0.1779E-03   0.3525E-01   0.2497E+02    3.75   0.8620E-03   0.5519E-11   0.2089E-04   0.8255E-02
0.1000E-03   0.5930E-01   0.2297E+02    4.00   0.1252E-02   0.1577E-10   0.3357E-04   0.7462E-02
0.5625E-04   0.8517E-01   0.2174E+02    4.25   0.1707E-02   0.4367E-10   0.5227E-04   0.6533E-02
0.3163E-04   0.1117E+00   0.2179E+02    4.50   0.2188E-02   0.1172E-09   0.7890E-04   0.5546E-02
0.1779E-04   0.1375E+00   0.2309E+02    4.75   0.2652E-02   0.3061E-09   0.1158E-03   0.4579E-02
0.1000E-04   0.1613E+00   0.2557E+02    5.00   0.3070E-02   0.7808E-09   0.1662E-03   0.3694E-02
0.5625E-05   0.1825E+00   0.2908E+02    5.25   0.3421E-02   0.1955E-08   0.2339E-03   0.2924E-02
0.3163E-05   0.2009E+00   0.3337E+02    5.50   0.3698E-02   0.4819E-08   0.3243E-03   0.2280E-02
0.1779E-05   0.2171E+00   0.3790E+02    5.75   0.3900E-02   0.1174E-07   0.4442E-03   0.1756E-02
0.1000E-05   0.2315E+00   0.4178E+02    6.00   0.4030E-02   0.2829E-07   0.6021E-03   0.1339E-02
0.5626E-06   0.2449E+00   0.4394E+02    6.25   0.4090E-02   0.6758E-07   0.8089E-03   0.1011E-02
0.3164E-06   0.2580E+00   0.4366E+02    6.50   0.4082E-02   0.1601E-06   0.1078E-02   0.7576E-03
0.1779E-06   0.2715E+00   0.4103E+02    6.75   0.4007E-02   0.3761E-06   0.1424E-02   0.5629E-03
0.1000E-06   0.2863E+00   0.3691E+02    7.00   0.3861E-02   0.8754E-06   0.1864E-02   0.4143E-03
0.5626E-07   0.3030E+00   0.3233E+02    7.25   0.3641E-02   0.2016E-05   0.2413E-02   0.3018E-03
0.3164E-07   0.3221E+00   0.2810E+02    7.50   0.3347E-02   0.4583E-05   0.3085E-02   0.2169E-03
0.1779E-07   0.3440E+00   0.2466E+02    7.75   0.2978E-02   0.1025E-04   0.3881E-02   0.1534E-03
0.1001E-07   0.3687E+00   0.2220E+02    8.00   0.2544E-02   0.2247E-04   0.4783E-02   0.1064E-03
0.5627E-08   0.3956E+00   0.2071E+02    8.25   0.2066E-02   0.4802E-04   0.5748E-02   0.7188E-04
0.3164E-08   0.4239E+00   0.2009E+02    8.50   0.1577E-02   0.9950E-04   0.6698E-02   0.4710E-04
0.1779E-08   0.4527E+00   0.1992E+02    8.75   0.1121E-02   0.1989E-03   0.7530E-02   0.2977E-04
0.1001E-08   0.4819E+00   0.1926E+02    9.00   0.7349E-03   0.3819E-03   0.8130E-02   0.1808E-04
0.5627E-09   0.5134E+00   0.1712E+02    9.25   0.4416E-03   0.7020E-03   0.8404E-02   0.1051E-04
0.3164E-09   0.5507E+00   0.1374E+02    9.50   0.2412E-03   0.1230E-02   0.8282E-02   0.5824E-05
0.1780E-09   0.5987E+00   0.1053E+02    9.75   0.1179E-03   0.2039E-02   0.7722E-02   0.3054E-05
0.1001E-09   0.6605E+00   0.8377E+01   10.00   0.5043E-04   0.3163E-02   0.6735E-02   0.1498E-05
0.5628E-10   0.7346E+00   0.7363E+01   10.25   0.1843E-04   0.4534E-02   0.5429E-02   0.6789E-06
0.3165E-10   0.8140E+00   0.7283E+01   10.50   0.5690E-05   0.5969E-02   0.4019E-02   0.2827E-06
0.1780E-10   0.8906E+00   0.7804E+01   10.75   0.1491E-05   0.7251E-02   0.2746E-02   0.1086E-06
0.1001E-10   0.9622E+00   0.8167E+01   11.00   0.3427E-06   0.8244E-02   0.1755E-02   0.3904E-07
0.5629E-11   0.1035E+01   0.7320E+01   11.25   0.7151E-07   0.8930E-02   0.1069E-02   0.1337E-07
0.3165E-11   0.1126E+01   0.5332E+01   11.50   0.1400E-07   0.9369E-02   0.6309E-03   0.4437E-08
0.1780E-11   0.1263E+01   0.3350E+01   11.75   0.2633E-08   0.9635E-02   0.3649E-03   0.1443E-08
0.1001E-11   0.1489E+01   0.1962E+01   12.00   0.4835E-09   0.9791E-02   0.2085E-03   0.4638E-09
0.5629E-12   0.1892E+01   0.1118E+01   12.25   0.8730E-10   0.9882E-02   0.1183E-03   0.1480E-09
0.3165E-12   0.1580E+01   0.6330E+00   12.50   0.0000E+00   0.0000E+00   0.0000E+00   0.0000E+00
```

TABLE 19

```
        CATEQ7      VERSION H2/NULL      13-SEP-79

   [A] =    0.10E-01
    K1 =    0.45E-06          K2 =    0.47E-10          K3 =    0.10E+05          KW =    0.10E-13


    (1)          (2)            (3)           (4)        (5)           (6)            (7)            (8)
    [H+]          X          DLN[H+]/DX       PH          T          [CO3'']         [HCO3']        [H2CO3]

0.1000E+00   -0.5000E+01    0.2000E+00      1.00    0.4492E-05    0.2113E-16    0.4496E-07    0.9991E-02
0.5624E-01   -0.2811E+01    0.3556E+00      1.25    0.7976E-05    0.6677E-16    0.7989E-07    0.9984E-02
0.3162E-01   -0.1580E+01    0.6321E+00      1.50    0.1415E-04    0.2109E-15    0.1419E-06    0.9972E-02
0.1778E-01   -0.8879E+00    0.1123E+01      1.75    0.2505E-04    0.6654E-15    0.2518E-06    0.9950E-02
0.1000E-01   -0.4978E+00    0.1991E+01      2.00    0.4420E-04    0.2096E-14    0.4460E-06    0.9911E-02
0.5624E-02   -0.2773E+00    0.3509E+01      2.25    0.7754E-04    0.6583E-14    0.7877E-06    0.9844E-02
0.3163E-02   -0.1513E+00    0.6076E+01      2.50    0.1347E-03    0.2057E-13    0.1384E-05    0.9729E-02
0.1779E-02   -0.7730E-01    0.1005E+02      2.75    0.2301E-03    0.6377E-13    0.2413E-05    0.9537E-02
0.1000E-02   -0.3064E-01    0.1501E+02      3.00    0.3833E-03    0.1951E-12    0.4153E-05    0.9229E-02
0.5624E-03    0.2954E-02    0.1909E+02      3.25    0.6145E-03    0.5859E-12    0.7012E-05    0.8764E-02
0.3163E-03    0.3161E-01    0.2072E+02      3.50    0.9369E-03    0.1716E-11    0.1155E-04    0.8115E-02
0.1779E-03    0.5928E-01    0.2076E+02      3.75    0.1345E-02    0.4874E-11    0.1845E-04    0.7291E-02
0.1000E-03    0.8704E-01    0.2080E+02      4.00    0.1812E-02    0.1342E-10    0.2855E-04    0.6347E-02
0.5625E-04    0.1143E+00    0.2167E+02      4.25    0.2299E-02    0.3583E-10    0.4288E-04    0.5360E-02
0.3163E-04    0.1398E+00    0.2366E+02      4.50    0.2765E-02    0.9318E-10    0.6271E-04    0.4408E-02
0.1779E-04    0.1627E+00    0.2687E+02      4.75    0.3182E-02    0.2371E-09    0.8972E-04    0.3547E-02
0.1000E-04    0.1826E+00    0.3138E+02      5.00    0.3535E-02    0.5925E-09    0.1261E-03    0.2803E-02
0.5625E-05    0.1995E+00    0.3715E+02      5.25    0.3820E-02    0.1461E-08    0.1748E-03    0.2185E-02
0.3163E-05    0.2137E+00    0.4392E+02      5.50    0.4038E-02    0.3561E-08    0.2397E-03    0.1685E-02
0.1779E-05    0.2259E+00    0.5095E+02      5.75    0.4193E-02    0.8605E-08    0.3257E-03    0.1288E-02
0.1000E-05    0.2365E+00    0.5694E+02      6.00    0.4292E-02    0.2064E-07    0.4394E-03    0.9768E-03
0.5626E-06    0.2463E+00    0.6029E+02      6.25    0.4337E-02    0.4921E-07    0.5890E-03    0.7364E-03
0.3164E-06    0.2558E+00    0.5987E+02      6.50    0.4332E-02    0.1166E-06    0.7849E-03    0.5518E-03
0.1779E-06    0.2657E+00    0.5583E+02      6.75    0.4274E-02    0.2747E-06    0.1040E-02    0.4111E-03
0.1000E-06    0.2767E+00    0.4947E+02      7.00    0.4163E-02    0.6428E-06    0.1368E-02    0.3042E-03
0.5626E-07    0.2892E+00    0.4236E+02      7.25    0.3994E-02    0.1493E-05    0.1787E-02    0.2235E-03
0.3164E-07    0.3040E+00    0.3569E+02      7.50    0.3761E-02    0.3436E-05    0.2313E-02    0.1626E-03
0.1779E-07    0.3216E+00    0.3005E+02      7.75    0.3459E-02    0.7813E-05    0.2958E-02    0.1169E-03
0.1001E-07    0.3424E+00    0.2559E+02      8.00    0.3087E-02    0.1750E-04    0.3726E-02    0.8285E-04
0.5627E-08    0.3666E+00    0.2226E+02      8.25    0.2650E-02    0.3846E-04    0.4604E-02    0.5756E-04
0.3164E-08    0.3941E+00    0.1985E+02      8.50    0.2165E-02    0.8242E-04    0.5549E-02    0.3902E-04
0.1779E-08    0.4245E+00    0.1808E+02      8.75    0.1661E-02    0.1712E-03    0.6481E-02    0.2563E-04
0.1001E-08    0.4578E+00    0.1648E+02      9.00    0.1179E-02    0.3421E-03    0.7283E-02    0.1619E-04
0.5627E-09    0.4949E+00    0.1454E+02      9.25    0.7631E-03    0.6525E-03    0.7812E-02    0.9768E-05
0.3164E-09    0.5381E+00    0.1212E+02      9.50    0.4424E-03    0.1178E-02    0.7932E-02    0.5578E-05
0.1780E-09    0.5911E+00    0.9746E+01      9.75    0.2255E-03    0.1994E-02    0.7552E-02    0.2986E-05
0.1001E-09    0.6566E+00    0.8036E+01     10.00    0.9870E-04    0.3132E-02    0.6669E-02    0.1483E-05
0.5628E-10    0.7329E+00    0.7215E+01     10.25    0.3659E-04    0.4517E-02    0.5409E-02    0.6764E-06
0.3165E-10    0.8133E+00    0.7219E+01     10.50    0.1134E-04    0.5962E-02    0.4015E-02    0.2823E-06
0.1780E-10    0.8904E+00    0.7777E+01     10.75    0.2780E-05    0.7249E-02    0.2745E-02    0.1086E-06
0.1001E-10    0.9621E+00    0.8159E+01     11.00    0.6852E-06    0.8243E-02    0.1755E-02    0.3904E-07
0.5628E-11    0.1035E+01    0.7318E+01     11.25    0.1430E-06    0.8930E-02    0.1069E-02    0.1337E-07
0.3165E-11    0.1126E+01    0.5332E+01     11.50    0.2300E-07    0.9369E-02    0.6309E-03    0.4437E-08
0.1780E-11    0.1263E+01    0.3350E+01     11.75    0.5265E-08    0.9635E-02    0.3649E-03    0.1443E-08
0.1001E-11    0.1409E+01    0.1962E+01     12.00    0.9670E-09    0.9791E-02    0.2085E-03    0.4638E-09
0.5629E-12    0.1832E+01    0.1118E+01     12.25    0.1752E-09    0.9832E-02    0.1183E-03    0.1480E-09
0.3165E-12    0.2364E+01    0.6320E+00     12.50    0.1947E-10    0.7812E-02    0.5261E-04    0.3701E-10
```

TABLE 20