AAEC/TM411

AAEC/TM411

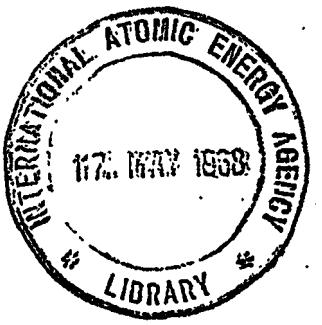
# AUSTRALIAN ATOMIC ENERGY COMMISSION

## RESEARCH ESTABLISHMENT
## LUCAS HEIGHTS

# HEAVY WATER REACTOR CHEMISTRY STUDIES
# PART 3. ROLE OF CARBON DIOXIDE

by

H.F. RYAN
L.E. SMYTHE




October 1967

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

# HEAVY WATER REACTOR CHEMISTRY STUDIES

# III - ROLE OF CARBON DIOXIDE

by

H. F. RYAN

L. E. SMYTHE

## ABSTRACT

The mechanism of the adsorption of bicarbonate ions onto both unirradiated and irradiated Amberlite XE-78 resin in the OH-form was studied using C14-tracer techniques.

The data obtained from these laboratory experiments have been related to reactor conditions in HIFAR. The mechanism of adsorption of dissolved carbon dioxide and other anionic impurities from the HIFAR moderator onto the anion exchange resin is now understood.

CONTENTS

## 1. INTRODUCTION

Analyses of exhausted mixed-bed ion-exchange resins from the A.A.E.C. reactor HIFAR (Smythe 1963, Ryan and Smythe 1967) have shown the life of the ion exchanger to be governed by the dissolved carbon dioxide in the system. In an attempt to understand the mechanism of adsorption of dissolved carbon dioxide onto the anion exchange resin, a study of the adsorption of bicarbonate ions onto Amberlite XE-78 in the OH-form was undertaken using C14-tracer techniques to determine the break-through characteristics for this ion. The uptake and release mechanism in relation to the condition of irradiated Amberlite XE-78 was also studied.

The dissolution of carbon dioxide in water is represented by

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \overset{K_1}{\rightleftharpoons} HCO_3^- + H^+ \qquad .....(1)$$

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

At 25°C, $K_1 = 4.30 \times 10^{-7}$, $K_2 = 5.61 \times 10^{-11}$ (Weast 1965).

The pH titration of standard carbonate solution shows that the neutralisation occurs in two distinct stages (Vogel 1959a), the equivalence point for the first stage being at pH 8.3. At this pH, all dissolved carbon dioxide should be present as bicarbonate. Below pH 8.3, Reaction 1 applies and equilibrium concentrations of bicarbonate and carbonic acid will be present. Above pH 8.3, Reaction 2 governs the solution equilibria.

Our experiment was carried out with a C14-labelled bicarbonate solution of pH 8.3. This pH is higher than that of the HIFAR moderator which usually lies in the range 5 to 7 at 45°C. However, below pH 8.3 it would be impossible to prepare a standard solution which would be stable for any length of time, because the carbonic acid present has a tendency to decompose, liberating carbon dioxide. The pH of the standard was adjusted to 8.3 with hydrochloric acid, so that the affinity of the resin for chloride and bicarbonate ions was actually studied.

The experiment used both unirradiated Amberlite XE-78 and a sample of irradiated Amberlite XE-78, taken from an exhausted batch of resin which had been in circuit in HIFAR for 4½ months; the aim was to determine whether any change in affinity occurred because of radiation damage to the resin. The room temperature during the experiment was approximately 22°C.

## 2. EXPERIMENTAL

### 2.1 Standard C14-labelled Bicarbonate Solution

The C14-labelled bicarbonate solution was prepared by dissolving 2.6g of A.R. sodium bicarbonate in demineralised water, adding 100 ml of C14-labelled sodium carbonate standard containing 1 mg $CO_3^{2-}$/ml and 1 μCi/ml C14 activity, and diluting to 1 litre. The pH was adjusted to 8.3 with concentrated hydrochloric acid and the solution then standardised for bicarbonate by titration with 0.1N hydrochloric acid (Vogel 1959b) and for chloride by the Mohr titration method (A.P.H.A. 1960). The standard thus contained 1.52 mg $HCO_3^-$/ml (0.0249 meq/ml) and 0.93 mg $Cl^-$/ml (0.0262 meq/ml).

### 2.2 Passage of Standard Bicarbonate Solution through Resin

A sample of Amberlite XE-78 anion resin was placed in a calibrated column, regenerated with 1N sodium hydroxide, and washed with boiled demineralised water until the effluent was neutral to phenolphthalein; then the resin volume was measured. The standard bicarbonate solution was passed through the column at a rate of 1 ml/min. Suitable aliquots of the effluent were collected and analysed to determine bicarbonate and chloride breakthrough. Liquid scintillation techniques were used to determine C14-levels and the Mohr titration method was used for the chloride analyses of the effluent aliquots.

At the completion of the run, the column was washed well with demineralised water, eluted with 2N sodium sulphate solution and the effluent analysed for chloride by Mohr titration and for carbonate/bicarbonate by titration with standard 0.1N hydrochloric acid. This enabled determination of the final distribution of anions on the resin.

The same technique was employed for the sample of irradiated Amberlite XE-78.

### 2.3 'Dead' Volume

Because the volume of standard which actually passed through the resin and not the total volume of effluent was required, the 'dead' volume or volume of water held between the swollen resin beads and in the outlet of the column had to be determined. For both the irradiated and unirradiated sample the dead volume was found to be 12.0 ± 0.5 ml.



## 3. RESULTS AND DISCUSSION

### 3.1 Mechanism of the Adsorption of Bicarbonate and Chloride onto Irradiated and Unirradiated Amberlite XE-78

The results obtained for bicarbonate and chloride breakthrough for the unirradiated Amberlite XE-78 are given in Table 1 and those for the irradiated resin in Table 2. To compare the properties of the irradiated and unirradiated resins, corrections for the difference in salt-splitting capacity (0.83, 1.05 meq/ml respectively) and for sample volume (5.3, 6.6 ml respectively) must be made. The corrected volumes shown in Table 2 represent the volume of standard which should have been added to a sample of irradiated resin of capacity equal to that of the unirradiated sample.

Figure 1 shows the percentage breakthrough of bicarbonate and chloride ions for equal capacities of unirradiated and irradiated resins. The breakthrough values have been plotted at the mid-point of the aliquot interval. It is evident that bicarbonate breakthrough is almost identical for both resin samples. However, chloride breakthrough occurs sooner for the irradiated sample than for the unirradiated one.

If adsorption of both bicarbonate and chloride ions onto the resin had resulted in the exchange of one hydroxide ion for each ion removed from the standard, breakthrough of both chloride and bicarbonate should theoretically have commenced when approximately 135 ml of standard had passed through the column. However, breakthrough of both bicarbonate and chloride commenced well before this volume, with bicarbonate breakthrough commencing first.

These phenomena can be explained if bicarbonate ions from the standard are adsorbed onto the resin as carbonate. While the resin environment is strongly basic due to the presence of a large number of OH-sites, the bicarbonate might be expected to be adsorbed as carbonate (Equation 2). That is, 1 meq of bicarbonate from the standard solution would occupy 2 meq of resin capacity. Hence the resin should be exhausted with carbonate and chloride after 91 ml of standard have passed through. This was found to be the case. Approximately 25 per cent breakthrough of bicarbonate was occurring at this point.

Anion exchange equilibrium measurements with Dowex 1, a resin very similar in structure to Amberlite XE-78, have shown its affinity for bicarbonate, chloride and hydroxide to be of the order $Cl^- > HCO_3^- > OH^-$ (Kunin 1958). Although no such data appear to be available for carbonate, being a divalent ion it should be

preferentially adsorbed to the univalent ions. That is, the order of affinity of Amberlite XE-78 for the anions present in the experiment would be expected to be $CO_3^{2-} > Cl^- > HCO_3^- > OH^-$ .

As the resin nears exhaustion of OH-sites and the interior of the resin beads reaches a pH where Equation 2 applies (pH< 11), some hydrolysis of the adsorbed carbonate ions would be expected to occur as follows:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- .$$

Both bicarbonate and chloride would then compete for the OH-sites, with chloride being preferentially adsorbed. In addition bicarbonate would tend to be replaced by chloride because of the greater affinity of the resin for chloride ions. This explains both the plateau region (Figure 1) where greater than 100 per cent breakthrough of bicarbonate was occurring, and the observation that chloride breakthrough occurred later than bicarbonate.

As chloride breakthrough became appreciable (> 50 per cent) the bicarbonate breakthrough gradually decreased to approximately 102 per cent. After 288 ml of standard had passed through, 95 per cent breakthrough of chloride was occurring. At this stage bicarbonate accounted for 20 per cent of the resin capacity, carbonate 9 per cent and chloride 71 per cent compared with the proportions in the standard of 49 per cent bicarbonate and 51 per cent chloride, and the proportions expected for exhaustion of the resin with carbonate and chloride of approximately 66 per cent $CO_3^{2-}$ and 34 per cent $Cl^-$ .

For the irradiated sample, after 266 ml of solution had passed through, 90 per cent breakthrough of chloride was occurring and the resin contained 20 per cent bicarbonate, 14 per cent carbonate and 66 per cent chloride. If a further 22 ml of standard had been passed through the irradiated sample, only about 0.05 meq of chloride would have been adsorbed since at least 90 per cent breakthrough was occurring at this stage. This would correspond to approximately 1 per cent increase in the chloride content of the resin. Hence the irradiated sample appears to have a lower affinity for chloride ions and a higher affinity for carbonate ions than the unirradiated sample.

This difference in affinity for the irradiated resin may have resulted from changes caused by radiation damage to the cross-linking and/or other parts of the resin structure. The irradiated resin is known to contain a higher concentration (25 per cent) of weakly basic exchange sites than the unirradiated sample (10 per cent) (Ryan and Smythe 1967). The dissociation of these weakly basic groups may



be represented by

$$R_sNH_3^+ \overset{K_a}{\rightleftharpoons} R_sNH_2 + H^+ ,$$

where $pK_a$ lies in the range 7 to 9 (Helfferich 1962). However, under the basic conditions which prevailed within the resin throughout the experiment, these amines would be undissociated and thus unable to take part in the exchange reactions.

Neither experiment was pursued far enough to determine whether equilibrium concentrations of chloride, carbonate and bicarbonate would eventually be reached on the resin or whether, because of the greater affinity of the resin for chloride over bicarbonate, the chloride content of the resin would gradually continue to increase until the resin was completely converted to the chloride form. In view of the above calculation on the increase of the chloride content of the irradiated resin when 90 per cent breakthrough of chloride was occurring, the latter process, if applicable, would be very gradual.

To investigate this point, a standard bicarbonate/chloride solution of pH 8.3 was prepared in a similar manner to the labelled standard used above. In this case the bicarbonate and chloride concentrations were 0.0313 meq/ml and 0.0332 meq/ml respectively, compared with those of the labelled solution of 0.0249 meq/ml and 0.0262 meq/ml the chloride/bicarbonate ratio being 1.05 in each case. Samples (4 ml) were taken of Amberlite XE-78 in the OH-form and a known volume of standard passed through each sample at a rate of 1 ml/min. The sample was then washed with water, eluted with 1N sodium sulphate and the effluent analysed for carbonate, bicarbonate and chloride. The results are given in Table 3.

Equilibrium concentrations of 72 per cent chloride, 22 per cent bicarbonate and 6 per cent carbonate were reached with the passage of 150 ml of standard. The final volume of 288 ml in the previous experiment would correspond to 137 ml in this experiment. That is, the final concentrations of 9 per cent carbonate, 20 per cent bicarbonate and 71 per cent chloride obtained in that experiment were very close to the equilibrium concentrations.

### 3.2 The Effect of Changes in Parameters (including Flow Rate and Concentration) on Breakthrough Characteristics

The mechanism of adsorption of dissolved carbon dioxide from the HIFAR moderator onto the anion exchange resin would be essentially the same as described above. In this case, however, dissolved carbon dioxide accounts for approximately

90 per cent of the anionic impurities in the system, while chloride, nitrate and sulphate ions together account for approximately 10 per cent (see Table 8).

To investigate the breakthrough characteristics and the likely equilibrium concentrations of carbonate, bicarbonate and other anions on the resin for the percentages of anions present in the reactor, a standard bicarbonate/chloride solution of pH 8.3 containing 96 per cent bicarbonate (0.031 meq $HCO_3^-$/ml) and 4 per cent chloride (0.0012 meq $Cl^-$/ml) was prepared and a study of the approach to equilibrium concentrations of chloride, bicarbonate and carbonate on the resin at a flow rate of 1 ml/min carried out in the same manner as described above. The results of this run are given in Table 4 and Figure 2. Final equilibrium concentrations of 7 per cent chloride, 67 per cent bicarbonate and 26 per cent carbonate were reached after approximately 500 ml of standard had passed through the resin. Breakthrough of bicarbonate would be expected after the passage of approximately 65 ml of standard, when the resin would be exhausted with carbonate and chloride ions. Breakthrough of chloride was observed after approximately 200 ml of standard had passed through, the chloride content of the resin then being approximately 6 per cent.

The nitrate and sulphate ions also present in the reactor moderator both have a stronger affinity for Amberlite XE-78 than does chloride (Kunin 1958). Hence, in the above experiment, breakthrough of either of these ions later than for chloride could have been expected, as well as a higher equilibrium concentration of either anion and lower equilibrium concentration of bicarbonate. However, because of the difficulties (described in detail later) of relating the results of these laboratory experiments to actual reactor operating conditions, the extent of this effect has not been fully investigated for either sulphate or nitrate. Since it is easy to analyse for chloride, the bicarbonate/chloride system has been used throughout.

In order to obtain an indication of the equilibrium values likely to be reached for other bicarbonate/chloride ratios in the standard, a series of equilibrium experiments were done in the same manner as above, with the total bicarbonate and chloride concentration in the standard kept constant at 0.031 meq/ml for chloride contents of 28, 52, 75 and 100 per cent. The equilibrium values reached in these experiments are given in Table 5. In Figure 3 the percentage chloride on the resin is plotted against percentage chloride in the standard. The factor relating the percentage of chloride present on the resin at equilibrium to the percentage of chloride in the standard was less than two



in each case and decreased with increasing chloride content of the standard.

In HIFAR, the actual concentration of dissolved impurities in the moderator, temperature, resin environment and flow rate are considerably different from those in the above experiments. The ion exchanger consists of 1 $ft^3$ of nuclear grade Amberlite XE-150 mixed-bed resin, which is made up of approximately 0.38 $ft^3$ Amberlite XE-77 cation resin and 0.62 $ft^3$ Amberlite XE-78 anion resin. This volume of anion resin is a factor of $10^3$ greater than in the above experiments. The flow rate through the unit is 5 gal/min (factor of $10^4$ higher than above) at a temperature of 45°C. The average concentration of dissolved carbon dioxide in the moderator was calculated to be approximately $3 \times 10^{-6}$M (factor of $10^4$ lower than above). At the normal pH of the moderator (5 to 7) equilibrium concentrations of both bicarbonate and carbonic acid would be present.

A number of experiments have attempted to gauge the effect of differences in concentration and flow rate on the final equilibrium conditions on the resin. The effect of concentration was studied using 50/50 bicarbonate/chloride standards of pH 8.3 at a flow rate of 1 ml/min. The equilibrium concentrations of chloride, bicarbonate and carbonate on the resin have already been found to be almost identical for chloride concentrations of 0.016 and 0.033 meq/ml in the standard (see Tables 3, 5). To determine the effects of greater concentration differences the equilibrium experiments were repeated for chloride concentrations of 0.080, 0.0033, and 0.0011 meq/ml. The results are given in Table 6. A decrease in the equilibrium chloride concentration on the resin with decreasing concentration in the standard was observed. The effect was most pronounced below the chloride concentration of 0.016 meq/ml. It is impractical to repeat the experiment at concentrations much lower than above because of the large volume of standard required to reach equilibrium. Hence it is impossible to predict the equilibrium concentrations likely to be reached for solutions of the order of $10^{-6}$M, though it appears that the ordinates of Figure 3 would be considerably less at this concentration. Breakthrough of chloride would also be expected to commence at a lower chloride content of the resin.

To investigate the effect of flow rate, equilibrium measurements were made using a 50/50 bicarbonate/chloride standard of pH 8.3 and a chloride concentration of 0.016 meq/ml, the flow rate being 60 ± 5 ml/min. The results are given in Table 7. The final equilibrium concentration on the resin appeared to be the same as for the slow run and was reached at 1500 ml compared with 150 ml at the slower rate. This shows that, as expected, the efficiency of the ion exchanger

is much less at higher flow. Under reactor conditions, however, the larger volume of resin would offset to some extent the loss of efficiency caused by the high flow rate.

For pH values less than 8.3 where both carbonic acid and bicarbonate are present, the adsorption onto the ion exchanger should be less efficient than for a similar concentration of bicarbonate alone, since conversion of carbonic acid to bicarbonate would be expected to occur before exchange could take place. The effect of temperature on the adsorption is two-fold: the rate of anion exchange is known to increase with temperature (Kunin and Myers 1947) and the acid dissociation constants of carbonic acid increase with temperature. $K_1$ equals $4.30 \times 10^{-7}$ at 25°C, and $5.13 \times 10^{-7}$ at 45°C (Weast 1965). That is, for a given concentration of dissolved carbon dioxide, a higher concentration of bicarbonate should be present at the higher temperature. The removal of dissolved carbon dioxide should thus be more efficient at 45°C than at 25°C. However, because of the uncertainties already encountered by considering only concentration and flow rate in extrapolating results of the laboratory experiments to reactor conditions, no attempt has been made to obtain data on the effect of pH and temperature on the removal of dissolved carbon dioxide at this stage.

### 3.3 Behaviour of Ion-exchange Resins in HIFAR

Although from these laboratory experiments no quantitative conclusions can be drawn concerning the levels at which breakthrough of various anions will commence under reactor conditions, the general pattern of breakthrough for the reactor ion exchanger is now clear. Whatever the ratio of dissolved carbon dioxide to other anions in the system, breakthrough of bicarbonate is expected to occur before breakthrough of the other anions present. This leads to an increase in the dissolved carbon dioxide level of the moderator and consequently an increase in the equilibrium carbon dioxide level of the gas blanket. Breakthrough of other anions will commence later.

For HIFAR the practice has been to remove the ion exchanger from the circuit when the carbon dioxide level of the gas blanket increases from the normal level of 200-500 v.p.m. to 2000-3000 v.p.m. during an operating period of approximately 28 days. A slight rise in conductivity of the moderator over this period (average 0.3 µmho/cm) has usually been observed and often, but not always, a slight decrease in pH occurs. However, no analyses have been carried out to determine whether breakthrough of the other anions had already commenced when the ion exchanger is removed from circuit and it is impossible from the existing routine analyses of the moderator to make any predictions.



Table 8 shows the results of analyses for four batches of exhausted anion-exchange resin from HIFAR and an estimate of the average percentages of dissolved carbon dioxide and other anions in the moderator for each batch. The percentages of the other anions on the resin are all less than half the values which would be predicted from Figure 3. However, as discussed previously, the concentration at which breakthrough of these anions is likely to commence at concentrations present in the reactor is less than indicated in Figure 3. Hence no conclusions about breakthrough can be drawn from these figures either.

Nevertheless, in view of the general breakthrough pattern, for reactors of this type where a significant conductivity increase alone (say 1 µmho/cm) is used to indicate exhaustion of the ion-exchange unit, it is obvious that a high level of carbon dioxide must also be present in the gas blanket. This is confirmed by analyses of the HIFAR gas circuit over a large number of operating periods.

## 4. ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance given by Mrs Y. J. Farrar in the execution of the experimental work for this report.

## 5. REFERENCES

American Public Health Assoc. (1960). - Standard Methods for the Analysis of Water and Waste Water, 11th Ed. p.78.

Helfferich, F. (1962). - Ion Exchange, p.86. McGraw Hill.

Kunin, R. and Myers, R. J. (1947). - J. Phys. and Colloid Chem., 51 : 5.

Kunin, R. (1958). - Ion Exchange Resins, p.60-62. John Wiley and Sons.

Ryan, H. F. and Smythe, L. E. (1967). - Heavy water reactor chemistry studies. Pt. II. A.A.E.C. report in preparation.

Smythe, L. E. (1963). - Chemical monitoring of heavy water moderated research reactors. Progress in Nuclear Energy. Pergamon Series IX (3) : Ch. 5.

Vogel, A. I. (1959a). - A Text-book of Quantitative Inorganic Analysis. 2nd Ed. 67. Longmans Green and Co.

Vogel, A. I. (1959b). - ibid. p.243.

Weast, R. C. Ed. (1965). - Handbook of Chemistry and Physics, 46th Ed. Chemical Rubber Publishing Co.

TABLE 1

ADSORPTION OF BICARBONATE AND CHLORIDE IONS

ONTO UNIRRADIATED AMBERLITE XE-78 IN THE OH-FORM

Volume of Resin = 6.6 ml

Salt-splitting Capacity = 1.05 meq/ml

| Total Volume of Effluent * | Midpoint of Interval | Bicarbonate | | Chloride | |
|---|---|---|---|---|---|
| | | Concentration (meq/ml x $10^2$) | Percentage Breakthrough ‡ | Concentration (meq/ml x $10^2$) | Percentage Breakthrough ‡ |
| 13 ml | 0.5 ml | - | - | - | - |
| 38 ml | 25.5 ml | - | - | - | - |
| 63 ml | 50.5 ml | - | - | - | - |
| 88 ml | 75.5 ml | 0.09 | 4 | - | - |
| 98 ml | 93 ml | 0.59 | 24 | - | - |
| 108 ml | 103 ml | 1.24 | 50 | - | - |
| 118 ml | 113 ml | 2.16 | 87 | 0.07 | 3 |
| 128 ml | 123 ml | 2.93 | 118 | 0.12 | 5 |
| 138 ml | 133 ml | 3.23 | 130 | | |
| 148 ml | 143 ml | 3.26 | 131 | 0.40 | 15 |
| 158 ml | 153 ml | 3.27 | 131 | | |
| 168 ml | 163 ml | 3.30 | 132 | 0.79 | 30 |
| 178 ml | 173 ml | 3.10 | 125 | | |
| 188 ml | 183 ml | 3.07 | 123 | 1.30 | 50 |
| 198 ml | 193 ml | | | | |
| 208 ml | 203 ml | 2.78 | 112 | 1.75 | 67 |
| 218 ml | 213 ml | | | | |
| 228 ml | 223 ml | 2.54 | 102 | 2.07 | 79 |
| 238 ml | 233 ml | | | | |
| 248 ml | 243 ml | 2.41 | 97 | 2.28 | 87 |
| 258 ml | 253 ml | | | | |
| 268 ml | 263 ml | 2.53 | 102 | 2.37 | 91 |
| 278 ml | 273 ml | | | | |
| 288 ml | 283 ml | 2.56 | 103 | 2.45 | 94 |
| Standard | | 2.49 | 100 | 2.62 | 100 |

* Volume corrected for 'dead' volume of the column.

‡ Percentage breakthrough of anion $X^-$ = $\frac{[X^-] \text{ in effluent}}{[X^-] \text{ in standard}}$ x 100

TABLE 2

ADSORPTION OF BICARBONATE AND CHLORIDE IONS

ONTO IRRADIATED AMBERLITE XE-78 IN THE OH-FORM

Volume of Resin = 5.3 ml

Salt-splitting Capacity = 0.83 meq/ml

| Total Volume of Effluent * | Corrected Volume ‡ | Midpoint of Interval | Bicarbonate | | Chloride | |
|---|---|---|---|---|---|---|
| | | | Concentration (meq/ml x $10^2$) | Percentage Breakthrough | Concentration (meq/ml x $10^2$) | Percentage Breakthrough |
| 13 ml | 21 ml | 1 ml | - | - | - | - |
| 38 ml | 60 ml | 40 ml | 0.01 | 0.6 | - | - |
| 48 ml | 76 ml | 68 ml | 0.02 | 1 | - | - |
| 58 ml | 92 ml | 84 ml | 0.31 | 13 | 0.10 | 4 |
| 68 ml | 108 ml | 100 ml | 1.09 | 44 | 0.12 | 5 |
| 78 ml | 123 ml | 115 ml | 2.68 | 108 | 0.30 | 12 |
| 88 ml | 139 ml | 131 ml | 3.15 | 127 | 0.54 | 20 |
| 98 ml | 155 ml | 147 ml | 3.24 | 130 | 0.85 | 33 |
| 108 ml | 171 ml | 163 ml | 3.17 | 127 | 1.21 | 46 |
| 118 ml | 187 ml | 179 ml | 3.03 | 122 | 1.56 | 60 |
| 128 ml | 202 ml | 195 ml | 2.85 | 114 | 1.83 | 70 |
| 138 ml | 218 ml | 210 ml | 2.81 | 113 | 2.00 | 76 |
| 148 ml | 234 ml | 226 ml | 2.68 | 108 | | |
| 158 ml | 250 ml | 242 ml | 2.65 | 107 | 2.26 | 86 |
| 168 ml | 266 ml | 258 ml | | | 2.36 | 90 |
| Standard | | | 2.49 | 100 | 2.62 | 100 |

* Volume has been corrected for the 'dead' volume of the column.

‡ Corrected for the difference in volume and capacity between this sample and the unirradiated sample. The corrected volume now represents the volume of the standard bicarbonate solution which would have been added to an irradiated resin sample of capacity equal to that of the unirradiated sample (6.9 meq) used in the previous run.

TABLE 3

ADSORPTION OF ANIONS ONTO AMBERLITE XE-78 IN THE OH-FORM FROM A SOLUTION COMPOSED OF 49 PER CENT BICARBONATE AND 51 PER CENT CHLORIDE

Standard contains 0.033 meq $Cl^-$/ml, 0.031 meq $HCO_3^-$/ml

| Volume of Standard Bicarbonate/Chloride Solution Passed Through (ml) | Effluent Analysis | | |
|---|---|---|---|
| | Chloride (%) | Bicarbonate (%) | Carbonate (%) |
| 85 | 55 | 27 | 18 |
| 100 | 63 | 24 | 13 |
| 130 | 69 | 23 | 8 |
| 150 | 71 | 23 | 6 |
| 300 | 72 | 22 | 6 |
| 350 | 72 | 22 | 6 |

TABLE 4

ADSORPTION OF ANIONS ONTO AMBERLITE XE-78 IN OH-FORM FROM A SOLUTION COMPOSED OF 96 PER CENT BICARBONATE AND 4 PER CENT CHLORIDE

| Volume of Standard Passed Through (ml) | Effluent Analysis | | |
|---|---|---|---|
| | Chloride (%) | Bicarbonate (%) | Carbonate (%) |
| 80 | 3.5 | 12.2 | 84.2 |
| 130 | 4.2 | 48.8 | 47.0 |
| 180 | 4.9 | 60.7 | 34.3 |
| 250 | 6.0 | 63.1 | 30.9 |
| 300 | 6.6 | 63.7 | 29.7 |
| 400 | 7.2 | 66.0 | 26.8 |
| 500 | 7.5 | 67.2 | 25.3 |
| 650 | 7.4 | 66.5 | 26.2 |
| 800 | 7.0 | 67.0 | 26.2 |

TABLE 5

EQUILIBRIUM CONCENTRATIONS OF CHLORIDE, BICARBONATE AND CARBONATE ON RESIN FOR VARIOUS BICARBONATE/CHLORIDE RATIOS IN STANDARD

| Composition of Standard | | | | Equilibrium Concentrations on Resin | | |
|---|---|---|---|---|---|---|
| Bicarbonate (meq/ml) | Chloride (meq/ml) | Bicarbonate (%) | Chloride (%) | Bicarbonate (%) | Carbonate (%) | Chloride (%) |
| 0.031 | 0.0012 | 96 | 4 | 67 | 26 | 7 |
| 0.023 | 0.009 | 72 | 28 | 36 | 18 | 46 |
| 0.015 | 0.016 | 48 | 52 | 21 | 7 | 72 |
| 0.008 | 0.024 | 25 | 75 | 7 | 5 | 88 |
| 0 | 0.032 | 0 | 100 | - | - | 100 |

TABLE 6

EFFECT OF CONCENTRATION FOR 50/50 BICARBONATE/CHLORIDE STANDARDS ON EQUILIBRIUM CONCENTRATIONS ON RESIN

| Composition of Standard | | Equilibrium Concentrations on Resin | | |
|---|---|---|---|---|
| Bicarbonate (meq/ml) | Chloride (meq/ml) | Bicarbonate (%) | Carbonate (%) | Chloride (%) |
| 0.079 | 0.080 | 22 | 2 | 76 |
| 0.031 | 0.033 | 22 | 6 | 72 |
| 0.015 | 0.016 | 21 | 7 | 72 |
| 0.0031 | 0.0033 | 25 | 13 | 62 |
| 0.0011 | 0.0011 | 36 | 12 | 51 |

TABLE 7

ADSORPTION OF ANIONS ONTO AMBERLITE XE-78 AT A FLOW RATE OF 60 ml/min

Standard contains 0.016 meq $Cl^-$/ml, 0.016 meq $HCO_3^-$/ml

| Volume of Standard Passed Through (ml) | Flow Rate (ml/min) | Concentration of Anions on Resin | | |
|---|---|---|---|---|
| | | Bicarbonate (%) | Carbonate (%) | Chloride (%) |
| 600 | 57 | 18 | 20 | 62 |
| 900 | 59 | 19 | 14 | 67 |
| 1200 | 55 | 21 | 9 | 70 |
| 1500 | 57 | 21 | 8 | 71 |

TABLE 8

IMPURITIES IN THE HIFAR CIRCUIT

| Resin Batch Number | Anionic Impurities on Resin | | | Estimated Ratio of Anionic Impurities in the Moderator | |
|---|---|---|---|---|---|
| | $HCO_3^-$ (%) | $CO_3^{2-}$ (%) | Other Anions (%) | Dissolved $Co_2$ (%) * | Other Anions (%) ‡ |
| 11 | 46 | 45 | 9 | 89 | 11 |
| 12 | 48 | 45 | 7 | 90 | 10 |
| 13 | 45 | 52 | 3 | 95 | 5 |
| 14 | 47 | 45 | 8 | 90 | 10 |

* Calculated from $HCO_3^-$, $CO_3^{2-}$ content of anion resin + increase in dissolved $CO_2$ and $CO_2$ level of gas space after exhaustion.

‡ Calculated from $NO_3^-$, $SO_4^{2-}$, $Cl^-$ content of anion resin.

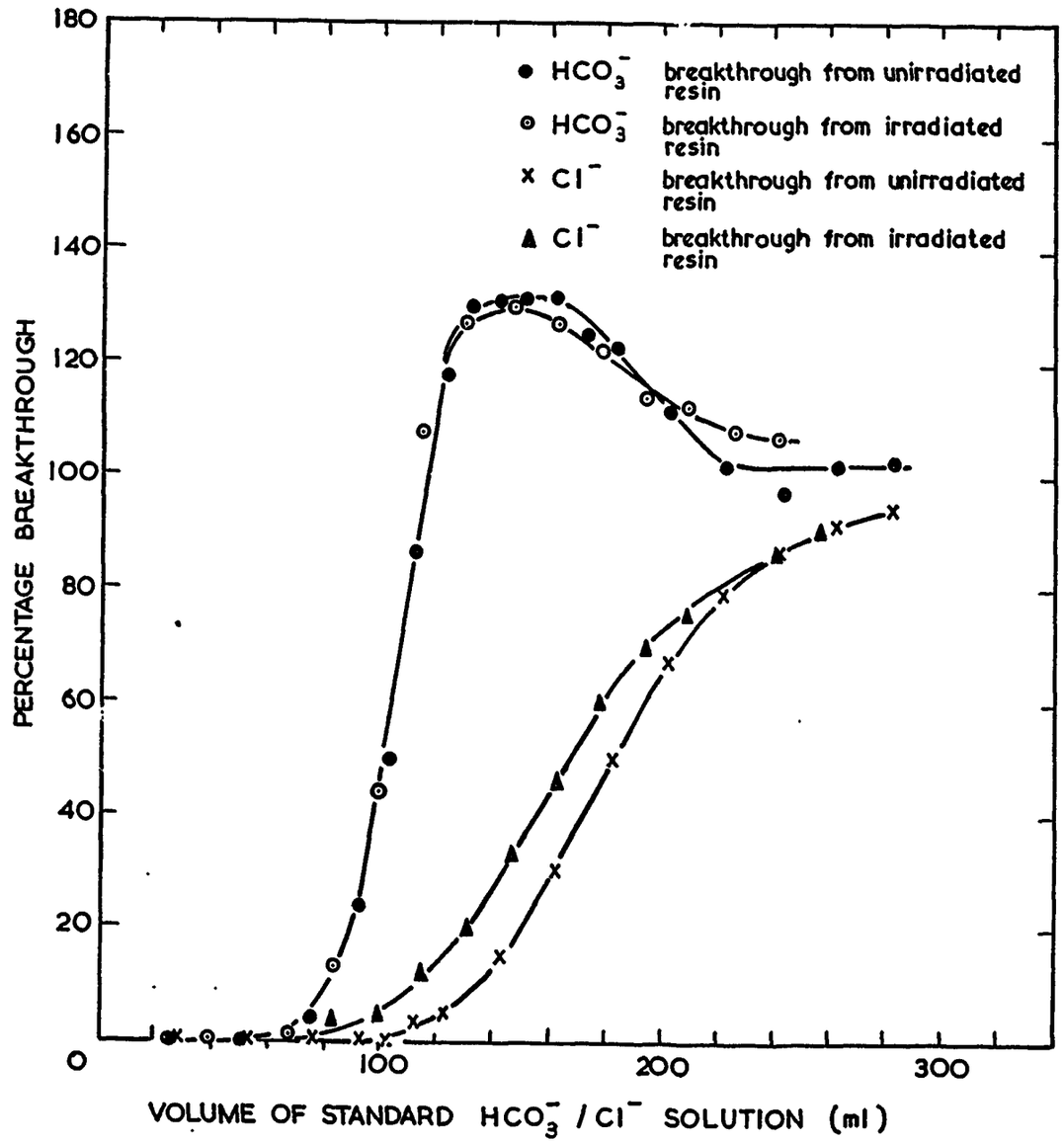



FIGURE 1. BICARBONATE AND CHLORIDE BREAKTHROUGH FROM IRRADIATED AND UNIRRADIATED AMBERLITE XE-78

P1226

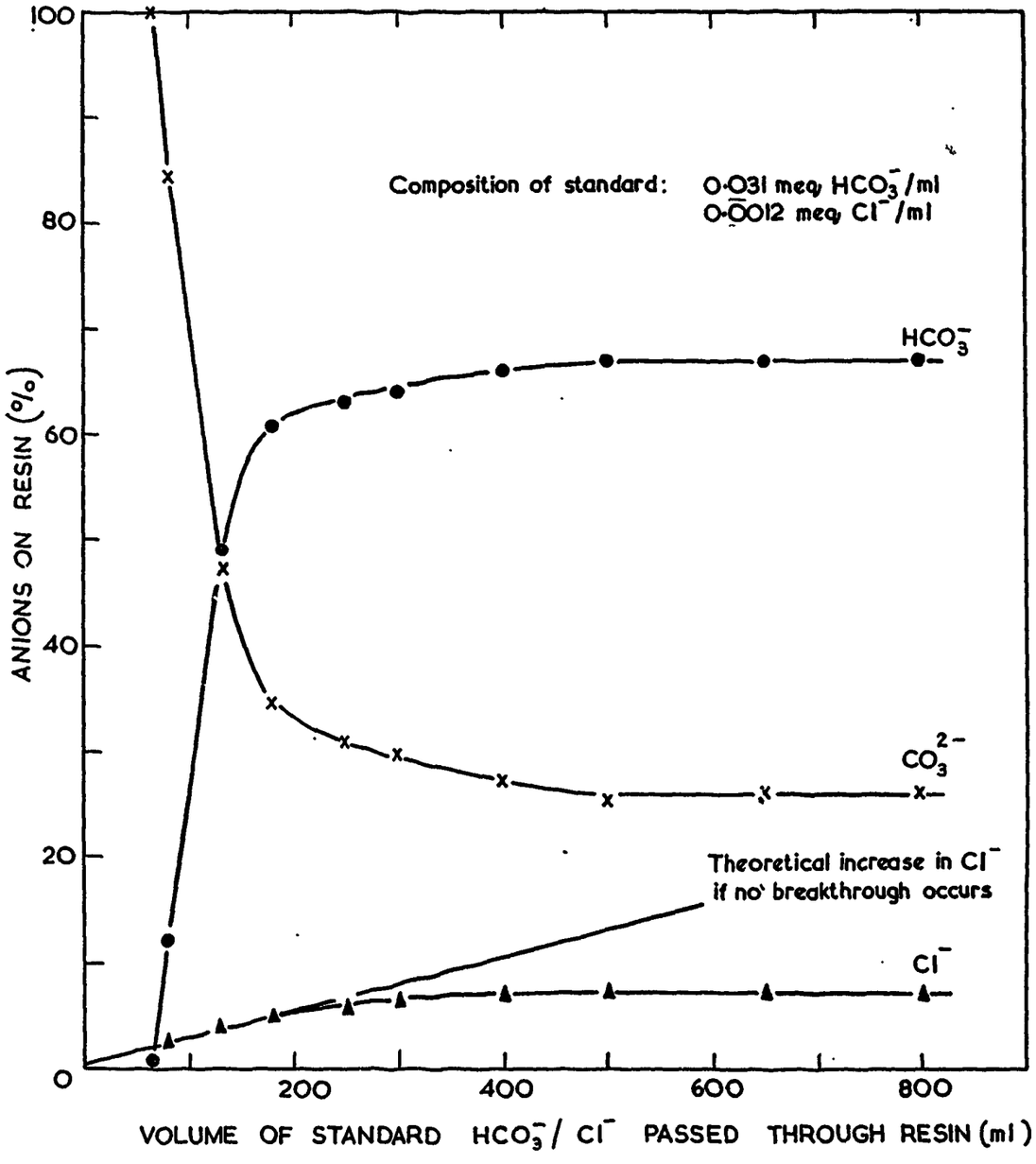



FIGURE 2. VARIATION IN CHLORIDE, CARBONATE, AND BICARBONATE CONTENT OF RESIN WITH VOLUME OF STANDARD PASSED THROUGH

P1226

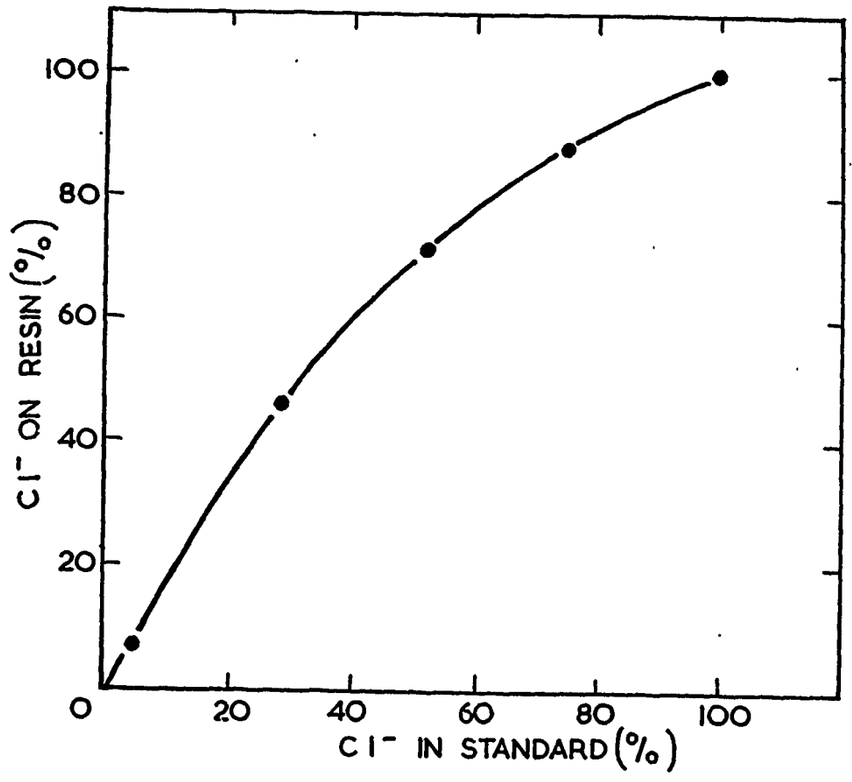



FIGURE 3. RELATION BETWEEN EQUILIBRIUM CHLORIDE CONTENT AND CHLORIDE CONTENT OF STANDARD SOLUTION

P1226