

THE EFFECT OF SOME INORGANIC IONS
ON THE RATE OF OXYGEN EXCHANGE
BETWEEN CARBON DIOXIDE AND WATER

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by
James Eric Dexter
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to my parents

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in the form of a teaching assistantship.

A handwritten signature in cursive script, appearing to read "James Dexter", written in dark ink. The signature is positioned above the printed name.

J.E. Dexter

ABSTRACT

The rate of oxygen exchange between carbon dioxide and water was determined using oxygen-18 as a tracer.

It was found that zinc(II) in the presence of an ammonia buffer catalyses the exchange rate markedly. This was explained by a mechanism involving $\text{Zn}(\text{NH}_3)_4^{2+}$. Copper(II) under similar conditions had a barely observable catalytic effect, while cobalt(II) showed no apparent effect on the exchange rate. The variation in the catalysis by these ions was explained by structure differences between $\text{Zn}(\text{NH}_3)_4^{2+}$, $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Co}(\text{NH}_3)_6^{2+}$.

A number of experiments were also performed where some metal-EDTA complexes were added. No dramatic increase in exchange rate was observed, and in the case of a number of the metals tried, no catalysis was apparent.

The rate of exchange between carbon dioxide and water was determined in solutions 0.1 M in Na_2CO_3 with various amounts of uranyl ion added. From the decrease in the exchange rate as the ratio of uranyl ion concentration to total carbonate concentration increased, evidence was obtained for the presence of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{CO}_3)_2(\text{OH})_2]^{4-}$ in solution.

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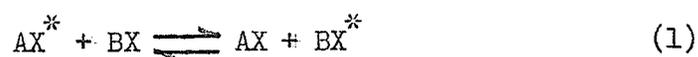
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1 - 1 ISOTOPE EXCHANGE REACTIONS

An isotope exchange reaction may be defined as the spontaneous reciprocal substitution of an atom (which may be neutral or charged, stable or radioactive) in a molecule by another atom of the same atomic number (of mass equal to or different from that of the other atom) from another molecule.

In general, an exchange reaction can be represented as follows:



where X is the exchanging atom. The chemical identity of isotopes makes possible an investigation of reaction kinetics in systems at chemical equilibrium. In other words, this exchange reaction is observable if one of the exchanging species, AX or BX, is "tagged", that is, if X* does not have the same mass as X. X*, the isotope used to tag the system may be either stable or radioactive, as was mentioned earlier, and it will be referred to simply as the tracer isotope. The rate of the establishment of isotopic equilibrium may be measured in a system in a steady state except for the distribution of isotopes. Such a system labelled with a tracer isotope is regarded as being homogeneous, with the tracer isotope merely serving as an indicator. Thus, it is assumed that the rates of exchange are the same for all isotopic atoms, regardless of their mass. This is not quite true, of course, but except for hydrogen isotopes the error associated with this assumption is small.

Ordinary chemical equilibrium is concerned with the number of ions and molecules present, whereas isotopic equilibrium is concerned

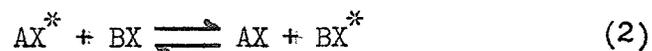
with the distribution of isotopes in the ions and molecules. The constants for isotopic equilibrium are very near unity (except for hydrogen and deuterium), with the result that at isotopic equilibrium there is virtually a uniform distribution of isotopes amongst the molecules involved in the exchange process. Since in order to establish isotopic equilibrium each molecule or ion must come to equilibrium with all other molecules and ions involved in the exchange process, the time required to reach isotopic equilibrium is far longer than that required to reach ordinary chemical equilibrium. This very often makes isotopic exchange a convenient method of studying fast reactions.

In order to conduct a kinetic study of an exchanging system, the chemical species, one of which is initially labelled with a tracer isotope, are mixed, and after a suitable period of time are separated by some chemical or physical means in order that the isotopic composition of the species may be determined. It is of utmost importance to recognize the possibility of separation induced exchange (the exchange brought about by the process of separating the exchanging species). If, after a certain period of time, the exchange process has not gone to completion, it is always possible to determine the magnitude of the separation induced exchange by extrapolating the data back to zero time. For any homogeneous exchange reaction the rate of appearance of tracer atoms in the initially untagged reactant follows a simple first order rate law. This result is always true, regardless of the mechanism by which the exchange occurs, except for those systems in which the tracer atom is at high concentration and the kinetic order is two or greater. It is still possible to determine the order of reaction, however, by varying the concentrations of the exchanging

molecules and comparing the resulting difference in the exchange rate. Kinetic studies have shown that the rate of isotopic exchange may be very fast, medium, or near zero, depending on the particular system being studied and the experimental conditions. From such studies one is able to consider the effect of various factors (such as temperature, ionic strength, pH, concentration of exchanging molecules, etc.) on the velocity of exchange processes, and, hopefully, this information will lead to the mechanisms involved in the reaction. The method of isotopic exchange offers the advantage of studying a system while it is at chemical equilibrium, with the velocity of the exchange process demonstrating the importance of all processes responsible for exchange.

1 - 2 MATHEMATICS OF EXCHANGE REACTIONS

Consider a system where two molecular entities AX and BX are in dynamic equilibrium. One of the entities, say AX, is labelled with an isotopic tracer.



In the above process, X^* is a tracer isotope which can exchange with the "normal" isotope X. The overall rate of exchange, R, may be defined as the velocity with which X atoms (whether a tracer atom is involved or not) are exchanged between AX and BX. Since the system is at chemical equilibrium throughout the exchanging process, this will also be the rate of the reverse reaction. This rate, R, will not vary so long as experimental conditions are not altered (although it will be a function of such variables as pH, temperature, ionic strength, etc.). In order to derive an expression for R, it is necessary to define the following variables:

$[AX^*] = x =$ the concentration of AX which is labelled with a tracer isotope at a given time (moles/liter)

$[BX^*] = y =$ the concentration of BX which is labelled with a tracer isotope at a given time (moles/liter)

$x_0 =$ the value of x at zero time

$y_0 =$ the value of y at zero time

$x_\infty =$ the value of x at isotopic equilibrium

$y_\infty =$ the value of y at isotopic equilibrium

$[AX^*] + [AX] = a =$ the total concentration of the species AX (moles/liter)

$[BX^*] + [BX] = b =$ the total concentration of the species BX (moles/liter)

$[AX] = a - x =$ the concentration of AX which is not labelled with a tracer isotope (moles/liter)

$[BX] = b - y =$ the concentration of BX which is not labelled with a tracer isotope (moles/liter)

It is assumed that R is independent of the isotopic masses, i.e., that there is no isotope effect. This approximation is more than adequate except where hydrogen isotopes are being considered. The rate at which X in BX exchanges with X* in AX* will be proportional to both the fraction of AX* and AX which is in the form AX* and the fraction of BX* and BX which is in the form BX, regardless of the mechanism involved in the exchange. Similarly, the rate of the reverse exchange will be proportional to the fraction of BX* and BX in the form BX* and the fraction of AX* and AX in the form AX. The overall rate of exchange is the difference between these quantities:

$$\frac{dx}{dt} = -\frac{dy}{dt} = R\left(\frac{y}{b}\right) \left[\frac{a-x}{a}\right] - R\left(\frac{x}{a}\right) \left[\frac{b-y}{b}\right] \quad (3)$$

$$\frac{dx}{dt} = R \left[\frac{ay-bx}{ab}\right] \quad (4)$$

The law of conservation of mass requires:

$$x + y = x_{\infty} + y_{\infty} \quad (5)$$

$$y = x_{\infty} - x + y_{\infty} \quad (6)$$

Also, at isotopic equilibrium:

$$\frac{x_{\infty}}{y_{\infty}} = \frac{a}{b} \quad (7)$$

$$x_{\infty} b = y_{\infty} a \quad (8)$$

By substituting equation (6) into equation (4):

$$\frac{dx}{dt} = R \left[\frac{ax_{\infty} - ax + ay_{\infty} - bx}{ab} \right] \quad (9)$$

By substituting equation (8) into equation (9):

$$\frac{dx}{dt} = R \left[\frac{ax_{\infty} - ax + bx_{\infty} - bx}{ab} \right] \quad (10)$$

Rearranging equation (10) results in the following differential equation:

$$\frac{dx}{(x_{\infty} - x)} = R \frac{(a+b)}{ab} dt \quad (11)$$

Integrating equation (11) gives the following result:

$$-\ln(x_{\infty} - x) = R \frac{(a+b)}{ab} t + \text{constant} \quad (12)$$

The constant is easily determined by substituting $t = 0$ and $x = x_0$ into equation (12), and turns out to be $-\ln(x_{\infty} - x_0)$:

$$-\ln \frac{(x_{\infty} - x)}{(x_{\infty} - x_0)} = R \frac{(a+b)}{ab} t \quad (13)$$

F, the fraction of exchange at time t is defined as:

$$F = \frac{x - x_0}{x_{\infty} - x_0} \quad (14)$$

$$Rt = - \frac{ab}{(a+b)} \ln(1-F) \quad (15)$$

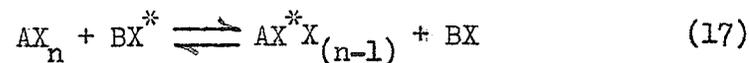
This expression predicts that a plot of $-\ln(1-F)$ against time should give a straight line passing through the origin. Thus, no matter what the form of R, whether the reaction is unimolecular, bimolecular, termolecular, or something more complicated, the redistribution of the tracer isotope follows the rate expression for a reversible first order reaction. This particularly simple result was originally demonstrated by H.A.C. McKay⁽¹⁾, consequently equation (15) is often referred to as the McKay equation.

It is particularly useful to introduce $t_{\frac{1}{2}}$, the time required for exchange to be half completed (the half-life of the exchange reaction), into equation (15). Now,

$$R = \frac{ab}{(a+b)t_{\frac{1}{2}}} 0.693 \quad (16)$$

The preceding derivation holds where there is only one equivalent site in each of the exchanging species for the exchanging atom. This is quite often not the case.

For the more general case



the equivalent expression for equation (15) is:

$$Rt = - \frac{nab}{(na+b)} \ln(1-F) \quad (18)$$

1 - 3 OXYGEN-18 AS A TRACER IN EXCHANGE STUDIES

Oxygen-18 has been widely used as a tracer in isotope exchange reactions. It has found a great deal of use in the study of hydration reactions, and is ideally suited for the study of the reactions between carbon dioxide and water.

The problem of measuring F, the fraction of exchange, is solved through the use of a dual collector mass spectrometer which can give the concentration of oxygen-18 in the sample relative to the amount of oxygen-16 it contains. This is most convenient, since an arbitrary and variable amount of product may be used rather than requiring an exact known amount.

Let us consider the case where the sample to be analyzed is in the form of carbon dioxide. The mass spectrometer compares the ratio of mass 46 (made up virtually entirely of $C^{12}O^{16}O^{18}$) to the sum of mass 44 ($C^{12}O^{16}O^{16}$), mass 45 ($C^{12}O^{16}O^{17}$ and $C^{13}O^{16}O^{16}$), mass 47 ($C^{13}O^{16}O^{18}$ and $C^{12}O^{17}O^{18}$) and mass 48 ($C^{12}O^{18}O^{18}$ and $C^{13}O^{17}O^{18}$). Mass 49 ($C^{13}O^{17}O^{18}$) is much too rare to be considered. Also, in most cases, except where there is an exceptionally large enrichment of oxygen-18, mass 47 and mass 48 may be neglected. This ratio is the so-called "p-factor" from the mass spectrometer. Theoretically the p-factor for "normal" carbon dioxide would be expected to be 0.00405. In practice, however, the Varian Mat GD 150 isotope ratio mass spectrometer used in our analyses gave a ratio of 0.00368. This 10% deviation from the expected value appears to arise from the $\pm 10\%$ uncertainty in resistance values of resistors in the pre-amplifiers and is not of importance for our application. It was also found that in order to

get optimum results, it is advisable to attempt to maintain reasonably consistent sample pressures. Since there is only one oxygen of mass 18 in carbon dioxide of mass 46, and two oxygens of mass 16 in carbon dioxide of mass 44, clearly the $\frac{0^{18}}{0^{16}}$ ratio is 0.5 p.

When a non-radioactive tracer such as oxygen-18 is employed it is necessary to take into account the naturally occurring tracer. Thus, F, the fraction of exchange, may be expressed in terms of p-values from the sample recovered from the exchanging species:

$$F = \frac{p_t - p_o}{p_\infty - p_o} \quad (19)$$

$$1-F = \frac{p_\infty - p_t}{p_\infty - p_o} \quad (20)$$

where p_o is the initial value of p at zero time, p_t is the value of p at time t, and p_∞ is the value of p at isotopic equilibrium. p_∞ may either be calculated, or obtained directly by a measurement after isotopic equilibrium has been reached (about nine half-lives).

Quite often it is necessary to determine the p-factor of enriched water. Since placing a sample of water in the mass spectrometer would require baking out the instrument after each analysis, and since oxygen gas reacts with the filament, neither of these forms is convenient. However, by equilibrating a known amount of carbon dioxide with a known amount of water, the enrichment of the water can be determined. The carbon dioxide is added to the water in a vessel, frozen in liquid nitrogen, and sealed off in vacuum. The vessel is then shaken at room temperature until isotopic equilibrium is reached. The % oxygen-18 in the water can then be determined from the measured value in the carbon dioxide.

In following the reaction between carbon dioxide and water using oxygen-18 as a tracer, we have several alternatives:

- (1) label water and follow the oxygen-18 content of water with time.
- (2) label water and follow the oxygen-18 content of carbonate (through liberated carbon dioxide) with time.
- (3) label carbonate and follow the oxygen-18 content of water with time.
- (4) label carbonate and follow the oxygen-18 content of carbonate with time.

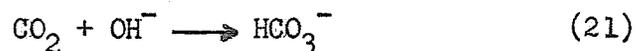
In most cases the concentration of carbonate will be less than one molar, i.e., there will be no more than three gram-atoms of oxygen per liter present in the carbonate. By comparison there will be about fifty-five gram-atoms of oxygen per liter of water. From these figures it is obvious that method (2) and method (4) will be far more accurate than the others. It is usually found most convenient (and economical of tracer) to label the salt and follow its oxygen-18 level with time, and most of the work described here was done in this way.

1 - 4 PREVIOUS STUDIES IN THE CARBON DIOXIDE-WATER SYSTEM

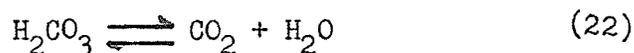
The hydration of carbon dioxide, because of its great importance industrially and biologically, as well as its interesting properties, has been the object of a great many intensive studies by a wide variety of techniques. A detailed description of investigations into the hydration of carbon dioxide before 1958 is given by Kern⁽²⁾.

It was noticed very early⁽³⁾ that the neutralization of base by carbon dioxide is not instantaneous. This led to the suggestion that

only a small fraction of aqueous carbon dioxide exists in the hydrated form H_2CO_3 , so-called metacarbonic acid. If a base is added to an aqueous carbon dioxide solution it was suggested that only that fraction equivalent to the amount of H_2CO_3 present is neutralized immediately, the remainder of the carbon dioxide reacting via the process:



For the equilibrium



$$K = \frac{(\text{CO}_2)}{(\text{H}_2\text{CO}_3)} \cong 600 \quad (23)$$

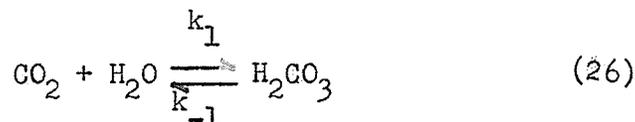
H_2CO_3 is presumably highly ionized because of its small concentration. Hence, its true dissociation constant, K_a , must be much greater than the ordinarily determined first dissociation constant, K_1 , often called the apparent first dissociation constant (although K_1 is nevertheless a real constant).

$$K_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{CO}_2 + \text{H}_2\text{CO}_3)} = 4.45 \times 10^{-7} \quad (24)$$

$$K_a = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} \cong 2.5 \times 10^{-4} \quad (25)$$

This much larger value for the true dissociation constant of metacarbonic acid is also consistent with its structure, since a comparison of the structure of H_2CO_3 with that of simple organic acids leads one to predict a much higher ionization for this acid than is actually observed in carbon dioxide solutions.

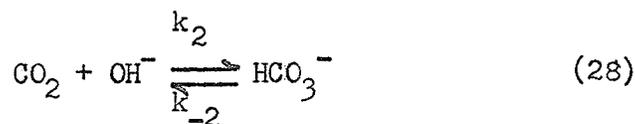
It is now generally accepted that the hydration of carbon dioxide proceeds primarily through two processes. (4, 5, 16) At $\text{pH} < 8$, the predominant pathway is via direct hydration.



This is a pseudo first order process.

$$R_1 = k_1' (\text{H}_2\text{O})(\text{CO}_2) = k_1(\text{CO}_2) \quad (27)$$

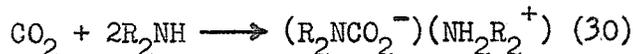
At a pH ≥ 10 , the predominant process is a direct reaction with OH^- :



$$R_2 = k_2(\text{CO}_2)(\text{OH}^-) \quad (29)$$

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

The importance of pH on the reaction process was first recognized by Faurholt⁽⁴⁾ in 1924. The values he found for the rates and equilibration constants of the $\text{CO}_2 - \text{H}_2\text{O}$ system, when recalculated using presently accepted constants rather than the rather unreliable values he had at his disposal, have hardly been improved in later works employing more elaborate techniques. Faurholt's procedure was ingeniously simple, although it involved painstaking experimentation. His method relied on the fact that alkyl amines react extremely rapidly with unhydrated carbon dioxide to form carbamates:



H_2CO_3 is neutralized by the amine at the same time, being converted to HCO_3^- and CO_3^{2-} . As a result, the interconversion $\text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$ is instantly quenched in both directions. Thus, by adding an excess of amine to a solution of carbon dioxide or carbonate (for the forward or reverse reactions respectively) mixed with a buffer of known pH

after the desired reaction time, the reaction is stopped. Faurholt was studying the dissipation of carbon dioxide in buffers of various pH, which, of course, determines the rate of hydration. He mixed various solutions with a buffer, and after the desired reaction time the process was quenched. Barium chloride precipitated the carbonate fraction, leaving carbamate in solution. Heating decomposed the carbamates which precipitated as the barium salt, and were analyzed by titration against standard acid. Thus, Faurholt was able to determine the concentrations of hydrated and unhydrated carbon dioxide at any instant during the reaction. He was very fortunate in his choice of pH (6-8 and 10.3-10.8) since in these areas only one hydration reaction was dominant, enabling him to sort out the two mechanisms and establish their rate laws. Despite the crudeness of his technique, when his results are recalculated with the aid of modern values for the required constants, his results are in excellent agreement with currently accepted values.

The biochemist Roughton and his co-workers have made an invaluable contribution to the knowledge of the kinetics of carbon dioxide hydration. In 1933 Brinkman, Margaria and Roughton⁽⁵⁾ pioneered the use of an elementary yet powerful manometric technique in the investigation of carbon dioxide hydration. To measure $k_1(\text{CO}_2)$ they shook basic buffers in a carbon dioxide atmosphere in a thermostatted vessel connected to a manometer. They assumed that Henry's law applied at all times, *i.e.*, the concentration of unhydrated carbon dioxide in solution is proportional to the partial pressure of gaseous carbon dioxide. The reverse process was studied by carbon dioxide evolution experiments with bicarbonate-acid buffers. The major drawback encountered in this procedure was that the establishment of equilibrium between gaseous

carbon dioxide and that in solution was far from instantaneous. Even when vigorous mechanical shaking was employed they were restricted to half-lives larger than forty-five seconds (pH range 6-10). They confirmed the validity of Faurholt's overall mechanism, although they could not get quantitative agreement with his values. They suspected this discrepancy to be due to some sort of interference by a phase boundary, but a flow technique gave them comparable results. (It was eventually discovered that Faurholt had omitted the logarithmic factor 2.303 from his calculations.) The manometric method has been greatly refined, and despite the need for a significant correction to compensate for the slowness of diffusion between the gaseous and liquid phases, the method has yielded very consistent results. It was found by Roughton and Booth⁽⁶⁾ that the hydration of carbon dioxide is catalyzed by the basic constituents of most of the buffers used in studies of the system, although they found no evidence for catalysis by carbonate and bicarbonate. Dennard and Williams⁽⁷⁾ conducted a manometric investigation into the catalytic properties of many inorganic bases and also concluded that there was no catalytic effect in carbonate-bicarbonate buffers. Roughton and co-workers^(8, 9), despite a number of difficulties, managed to attain a value for k_2 manometrically in a carbonate-bicarbonate buffer, although other methods prove to be more useful.

A variety of flow techniques has also been applied in the kinetic study of the hydration of carbon dioxide, meeting with excellent success. Once again Roughton and co-workers⁽⁵⁾ pioneered in the application of flow techniques in the field of carbon dioxide hydration, employing a rapid flow apparatus. In this method the reactant solutions are

forced at high speed through multiple jets into a small mixing chamber, and from there into an observation tube. Mixing is complete in a few milliseconds, and the time elapsed after mixing is directly proportional to the distance travelled along the tube. To apply this process to the carbon dioxide system, solutions of bicarbonate or carbon dioxide were mixed with solutions of various pH and examined at various distances from the mixing chamber by means of a photoelectric cell. An acid-base indicator was employed to color the solution. The rate at which H_2CO_3 entered or left the solutions was estimated by the pH change. Results comparable to those obtained by a crude manometric approach were obtained.

Roughton improved on the rapid flow application, and in 1941⁽¹⁰⁾ he conducted a detailed study of the system. By means of a movable thermocouple junction inserted into the observation tube of the rapid flow apparatus the course of the reaction between HCl and NaHCO_3 was followed as a function of the temperature change in the essentially adiabatic system. Roughton had perfected his apparatus over a number of years to the point where he was able to achieve great accuracy. He was able to learn a great deal about the dehydration of H_2CO_3 by examining the increase in temperature associated with the mixing of HCl and NaHCO_3 . He found that there was a virtually instantaneous evolution of heat corresponding to the combination of H^+ and HCO_3^- ions to form H_2CO_3 , followed by a slower temperature rise due to the dissociation of H_2CO_3 into CO_2 and H_2O . Thus, in addition to attaining values for the dissociation velocity constant of H_2CO_3 , he obtained heats of reaction for each of the two processes rather than their sum.

He also obtained a good value for the true first ionization constant of carbonic acid (2.5×10^{-4} @ 0°C).

More recently the method of stopped flow has been applied to the study of carbon dioxide hydration. This method originally found applications as a convenient method for studying reactions too slow to be studied by fast flow, yet too fast to be studied by conventional techniques. The mixing procedure is unchanged, but the flow is no longer continuous. Instead the flow is stopped and the progress of the reaction is followed by continual observation at a fixed point on the observation tube. A typical stopped flow apparatus is described by Spencer and Sturtevant⁽¹¹⁾. Time is counted from the instant the flow of liquid is stopped by the stopping syringe hitting an adjustable stop. The stopped flow technique has met with excellent success in a number of studies using a variety of detection methods.⁽¹²⁻¹⁴⁾ The great advantage it holds over continuous flow is the very small volume of solution required.

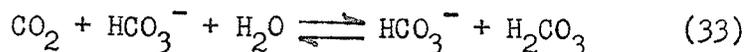
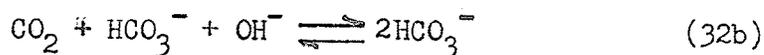
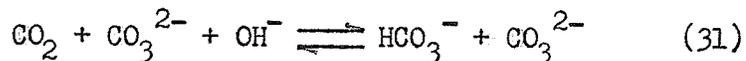
Mills and Urey applied the isotope exchange method to the study of carbon dioxide hydration in 1940⁽¹⁵⁾. They prepared some carbon dioxide enriched in carbon-13 as well as some carbon dioxide and Na_2CO_3 enriched in oxygen-18. A solution of sodium bicarbonate and carbon dioxide will establish chemical equilibrium fairly quickly. Mills and Urey mixed a solution of carbon dioxide enriched with carbon-13 with a solution of ordinary sodium bicarbonate. Following the rapid establishment of chemical equilibrium there was a fairly slow process tending to establish a uniform distribution of carbon isotopes. By drawing off samples of carbon dioxide from the solution at various times and making an isotopic analysis, Mills and Urey observed the rate

of change of the $\frac{C^{13}}{C^{12}}$ ratio in the carbon dioxide. They were then able to relate the rate of reaction between carbon dioxide and water to the rate of isotopic scrambling. Exchange also occurs between the oxygen of carbon dioxide, bicarbonate ion, carbonate ion and water. Mills and Urey studied the hydration reaction by observing the rate of depletion of oxygen-18 in enriched carbon dioxide dissolved in water. Oxygen exchange in solutions of carbonates or bicarbonates was measured by studying the rate of change of oxygen-18 content in the carbon dioxide liberated from solution at various times. Mills and Urey interpreted the rate of change of oxygen-18 content in the carbon dioxide liberated in terms of the processes normally occurring. They found that the exchange between carbon dioxide and water was due to the reversible hydration only. Sodium bicarbonate exchanged its oxygens only through the reversible formation of carbon dioxide by simple hydration when the pH was less than 8. They also found that sodium carbonate exchanged its oxygens slowly with water, although the rate was far faster than would be anticipated from simple hydration of the carbon dioxide present. This increased rate was interpreted as a reaction between carbon dioxide and hydroxyl ion, although a high concentration of hydroxyl ion retarded the exchange rate since only a very small concentration of carbon dioxide was present. The value Mills and Urey obtained for the rate of simple hydration of carbon dioxide was in excellent agreement with the previously discussed manometric study of Roughton and Booth.

Poulton and Baldwin⁽¹⁶⁾ used oxygen-18 exchange in order to study the reaction of carbon dioxide with water and hydroxide ions as a function of pH, ionic strength and carbonate-bicarbonate concentration. Sodium carbonate enriched in oxygen-18 was prepared and dissolved in

water of normal isotopic abundance at the desired pH. The rate of oxygen-18 depletion was followed by taking a series of samples at various time intervals and placing them in a flask connected to a vacuum line. Each aliquot was frozen and degassed. Immediately upon melting 0.5 ml. concentrated sulfuric acid was added through a side arm sealed with a rubber syringe. After refreezing the sample in a dry ice-methanol bath the carbon dioxide was transferred to an evacuated sample tube cooled in liquid nitrogen. By double sublimation of the carbon dioxide sample between dry ice-methanol and liquid nitrogen traps trace amounts of water were removed. The sample was then analyzed on a double collector type mass spectrometer similar to that described by Nier⁽¹⁷⁾.

Poulton and Baldwin conducted a series of experiments in which the total concentration of carbonate and bicarbonate was constant at various ionic strengths. They found a general decrease in rate with ionic strength. They also discovered that the rate of exchange increased with increasing carbonate and bicarbonate concentrations at a rate greater than would be expected from the simple first order hydration processes. They thus postulated three additional processes second order in carbonate plus bicarbonate concentration to account for this:



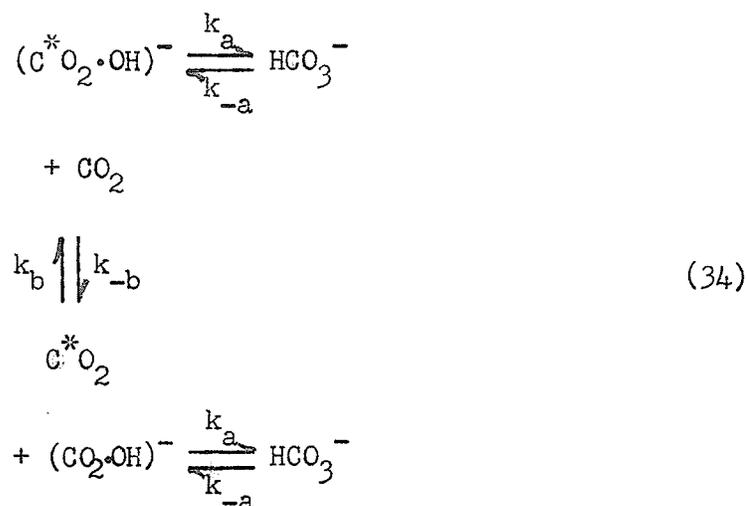
Processes (32a) and (32b) would be indistinguishable experimentally in their effect on isotope exchange, so Poulton and Baldwin just consider-

ed reaction (32a). They claimed that the earlier reports by Roughton and Booth⁽⁶⁾ as well as Dennard and Williams⁽⁷⁾ which had claimed to find no catalysis in carbonate-bicarbonate buffers were in error because the manometric method they employed was not sensitive enough to note the effect, whereas the low concentrations of carbon dioxide and consequent high ratios of concentration of carbonate and bicarbonate to carbon dioxide under the conditions of chemical equilibrium used in the isotope exchange method permitted the evaluation of the catalytic effects of these species.

Welch, Lifton and Seck⁽¹⁸⁾ have recently completed a study of the exchange between carbon dioxide and water using radioactive oxygen-15 as a tracer. Oxygen-15 has a two minute half-life and decays by positron emission, and therefore was simply detected by γ -counting of the 511 KeV annihilation radiation. The authors decided to use oxygen-15 since only a very small amount of tracer is required for a study, making it possible to study a wide range of temperature and pH without the presence of a large amount of species (including buffers) which may catalyze or inhibit the reactions. Their studies reached over a range of pH from 0.5 to 11.5, while temperature ranged from 1°C to 55.5°C. Using the 2 minute half-life tracer meant accurate measurement of k_2 from equation (28) was not possible, although a value for k_{-2} was found. They also were able to determine k_1 of equation (26). They found that their value for k_1 was higher than the accepted value, although it agreed well with Poulton and Baldwin's value⁽¹⁶⁾ at 25°C when ionic strength differences were taken into consideration. Also, their value for k_{-2} was in excellent agreement with those predicted from the values of k_2 determined by Poulton

and Baldwin as well as by Pinsent and co-workers⁽⁸⁾.

It is of interest to note the amazing reproducibility of the results obtained in the many studies which have been conducted, despite the wide variety of techniques employed. The only gross discrepancy appears to be the work of Himmelblau and Babb⁽¹⁹⁾ using a carbon-14 tracer. They obtained a value for k_1 in agreement with previous workers, but their value for k_2 is 50-100 times larger than that of other workers. An attempt has been made to explain their results:⁽²⁰⁾



where $(\text{CO}_2 \cdot \text{OH})^-$ is a new species and $k_b(\text{CO}_2) \gg k_a$. Assuming this mechanism is the cause of this discrepancy the true value of k_2 should be obtained by using an oxygen tracer, since the oxygen isotopes would not be exchanged in this mechanism.

1 - 5 THE CATALYSIS OF CARBON DIOXIDE HYDRATION AND ITS IMPORTANCE IN SCIENCE AND INDUSTRY

In 1928 Henriques⁽²¹⁾ found that the rate at which carbon dioxide was evolved from the blood was much greater than could be expected from Faurholt's⁽⁴⁾ data. The catalytic agent was soon isolated and turned out to be the enzyme carbonic anhydrase which is found in blood corpuscles. Since then a great many papers have been published discussing the chemistry and physiology of this catalysis⁽²²⁻²⁷⁾. This interest in the catalysis of H_2CO_3 dehydration in the blood also did a great deal to spur on measurements of the uncatalyzed reaction.

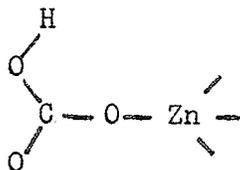
The dehydration of carbonic acid proceeds sufficiently slowly near pH neutrality, so as to require enzymic catalysis if the reaction is to be of physiological consequence. It is now generally accepted that human erythrocyte carbonic anhydrase occurs in three forms⁽²⁷⁻³⁰⁾. Nyman's group⁽²⁸⁾ separated the three forms by column electrophoresis, Laurent et al⁽³¹⁾ in Derrien's laboratory used chromatography on Amberlite GD-50, while Rickli and Edsall⁽³²⁾ positively identified two forms by hydroxylapatite chromatography with phosphate buffers. The three forms have been designated as types A, B and C. Of the three forms, all of which are active, one (type C) is more active than the others but is in relatively small concentration^(28, 31). Type B is by far the most common of the three fractions. All three forms are soluble, stable and colorless proteins with a molecular weight near 30,000^(27, 29). One zinc atom is firmly bound to each enzyme and is necessary for the activity⁽²⁹⁾. Rickli et al⁽²⁷⁾ quote turn-over values for carbonic anhydrase forms B and C at 25°C and above pH 7 as 20,000 moles (mole enzyme)⁻¹sec.⁻¹ and greater than 600,000 moles

(mole enzyme)⁻¹ sec.⁻¹ respectively. It is uncommon to find more than one enzyme which works on the same substrate but with such different activities, and the reason is not understood. From spectral properties of different cobalt(II) carbonic anhydrases (zinc(II) replaced by cobalt(II)) it appears that the metal co-ordination is essentially the same in all human forms of the enzyme. There appears to be a very low α -helical content in the enzyme^(27,33,34). It is known that sulphonamides are strong and specific inhibitors of all animal forms of the enzyme.

Fridborg et al⁽³⁴⁾ have elucidated the molecular structure of carbonic anhydrase C and an enzyme inhibitor complex at 5.5 Å resolution. They were able to draw some conclusions about the molecular shape, the tertiary structure, the chain ends, the α -helical content, the zinc environment and the position of cysteine and inhibitors. They found that the zinc atom is situated near the centre of the molecule. At the zinc atom there is a large cavity in the molecule, and one slit points from the neutral atom to the surface of the enzyme. The slit from the zinc atom to the surface of the enzyme is rather narrow requiring the inhibitor (a mercury derivative of a sulphonamide inhibitor) to be almost vertically orientated. One of the ends of the main chain appears to be quite close to the zinc atom. They found that the distance between the zinc atom and the only S-H group of the enzyme was 14 Å, ruling out the suggestion that cysteine is one of the zinc ligands⁽³⁵⁾.

The necessity of zinc for the activity of carbonic anhydrase leads to speculation if a carbonate complex of zinc(II) has any part in the overall hydration-dehydration equilibrium of carbon dioxide

and water⁽³⁶⁾. Infrared evidence has been found for bicarbonate coordination with the zinc in a study attempting to gain information on the mechanism of carbonic anhydrase catalysis⁽³⁷⁾. The carbonyl oxygen and the hydroxyl oxygen of the co-ordinated bicarbonate ion



are assumed to be held in the hydrophobic cavity of the enzyme in the hydration, and $\text{O}=\text{C}=\text{O}$ in the dehydration reactions.

Because of the great rapidity of carbonic anhydrase catalyzed carbon dioxide hydration its use for isotope enrichment has been investigated. However, its use in enrichment of carbon-13 in the CO_2 - HCO_3^- system⁽³⁸⁾ and oxygen-18 in the CO_2 - H_2O exchange⁽³⁹⁾ show little promise. Taylor et al⁽³⁹⁾ have found that some amines, especially monoethanolamine, catalyze the oxygen-18 exchange between carbon dioxide and water bringing the half time of exchange down to 2.4 seconds at room temperature. They also found that selenous acid, complex ions, ion exchange resins and a variety of solids were also catalysts. However, even though monoethanolamine catalyzed the reaction, experiments in an exchange column showed that it alone is not active enough to render the carbon dioxide hydration process practical for the enrichment of oxygen-18. It has been shown that $\text{Zn}(\text{NH}_3)_4^{2+}$ catalyzes the hydration of carbon dioxide⁽⁴⁰⁾, while $\text{Cu}(\text{NH}_3)_4^{2+}$ also shows some catalysis⁽⁴¹⁾. Taylor et al⁽⁴²⁾ thus decided to try complexes of monoethanolamine with copper(II) and zinc(II) as catalysts in the hydration of carbon dioxide in an exchange column. Both complexes were of comparable activity, and both exceeded that of monoethanolamine

itself. The copper(II) complex was most useful since it did not precipitate from solutions saturated in carbon dioxide, while the zinc (II) complex did. Taylor et al have found greatest success where a compound arising from the reaction of acetone and monoethanolamine is employed, although further improvement is required. They found that mixtures of this catalyst and copper co-ordination compounds in monoethanolamine gave comparable results.

Roughton and Booth⁽⁶⁾ and Kiese and Hastings⁽⁴³⁾ studied the catalysis of reaction (26) because of its physiological importance. They found that a number of anions of weak acids, such as selenite, arsenite, tellurate, hypochlorite, hypobromite, etc. possessed a high catalytic power.

Sharma and Danckwerts⁽⁴⁴⁾, using a manometric method similar to that of Roughton and Booth⁽²³⁾, undertook to throw more light on the catalytic effect of various types of anions, and also to search for catalysts of possible industrial value. They suggested that a linear relationship might exist between the acid dissociation constant of the acid, HB, and the catalytic constant of the base for a related series of bases.

Dennard and Williams⁽⁷⁾, using a manometric technique not unlike that of Roughton and Booth⁽⁶⁾, studied the effect of simple anions on the rate of reaction between carbon dioxide and water as well, but did not observe the relationship suggested by Sharma and Danckwerts. They suggest that the individual geometry and electronic structure of the bases are of over-riding importance. They found that the best catalysts are those oxyanions of lower oxidation states of non-metals which have at least one lone pair of electrons (e.g., sulfite, selenite,

arsenite, hypochlorite, hypobromite). They also found that if an oxyanion is of the highest oxidation state of a non-metal, there must be no equivalent oxygen atom in the anion to that from which the proton has been removed (e.g., $\text{OTe}(\text{OH})_5^-$, $\text{OGe}(\text{OH})_3^-$ and $\text{OSi}(\text{OH})_3^-$). The reason for this may be that put forward by Bell and Higginson⁽⁴⁵⁾. They pointed out that spread of charge over $(n+1)$ oxygens on ionization of an acid $\text{XO}_n(\text{OH})_m$ is likely to lead to a low effective charge on any oxygen essential for catalysis. Dennard and Williams put forth two possible catalytic pathways:

- a) direct attack of the anion on carbon dioxide
- b) attack of the anion on water adjacent to carbon dioxide.

Mechanism (b) would be expected to give a Brønsted plot, while mechanism (a) may or may not do so, depending on whether OX^- is a good leaving group or not. The authors do not present enough evidence to determine which of the two mechanisms is favored. In actual fact, it is likely that different anions would act in different ways.

Dennard and Williams also investigated catalysis by the neutral species imidazole, pyridine, 2-methyl-, 2,6-dimethyl-, and 2,4,6-trimethyl-pyridine. Only imidazole showed activity, but this was weak. Addition of metal ions to imidazole solutions apparently caused some increase in catalysis comparable with that by the zinc(II) and copper(II) amines and glycinate complexes.

1 - 6 EFFECT OF TEMPERATURE AND IONIC STRENGTH ON THE IONIZATION OF CARBONIC ACID AND BICARBONATE ION

While conducting a kinetic study of the oxygen exchange between carbon dioxide and water, it is necessary to examine the dependence of pH on the relative amounts of the various species present in solution. These species are: CO_3^{2-} , HCO_3^- and CO_2 (where CO_2 also includes any carbonic acid present).

The following expressions are required for calculation of the relative amounts of each species at a given pH:

$$C_{\text{IV}} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (35)$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (36)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (37)$$

The following fractions are now easily determined:

$$\frac{[\text{CO}_3^{2-}]}{C_{\text{IV}}} = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \quad (38)$$

$$\frac{[\text{HCO}_3^-]}{C_{\text{IV}}} = \frac{[\text{H}^+] K_1}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \quad (39)$$

$$\frac{[\text{CO}_2]}{C_{\text{IV}}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \quad (40)$$

In order to perform an accurate calculation of these ratios it is necessary to have accurate values for K_1 and K_2 . In almost all cases

the work described in this thesis was done at 24.7°C with solutions of ionic strength about 0.5. K_1 and K_2 both vary considerably over ranges of temperature and ionic strength, and this must be taken into account. Two independent studies of the variation of K_1 with ionic strength at 25°C arrive at virtually the same value for pK_1 at an ionic strength of 0.5^(46, 47), that value being 6.02. The reason for the change in the value of K_1 over a range of ionic strength and temperature is the change in activity of the various species, i.e.,

$$K_1 = \frac{\gamma_{+}(H^{+}) \gamma_{-}(HCO_3^{-})}{\gamma(CO_2)} \quad (41)$$

Since γ for CO_2 is known to be 1.12 at an ionic strength of 0.5⁽⁴⁸⁾, and pK_1 at 25°C extrapolated to zero ionic strength is known to be 6.352⁽⁴⁹⁾, if 6.02 is in fact the correct value for pK_1 at 25°C and an ionic strength of 0.5, then γ^{+} for $H^{+}HCO_3^{-}$ would be 0.721, which is certainly not unreasonable.

It is still necessary to find an appropriate value for pK_2 at 25°C where the ionic strength is 0.5. Hastings and Sendroy⁽⁵⁰⁾ conducted a study at 38°C and established the following relationship:

$$pK_2 = 10.22 - 1.1\sqrt{\mu} \quad (42)$$

where μ is the ionic strength, and 10.22 is the value for pK_2 extrapolated to zero ionic strength. This relationship predicts a value of 9.45 for pK_2 at $\mu = 0.5$. A study by Bruchenstein and Nelson⁽⁵¹⁾ claims pK_2 equals 9.37 at $\mu = 1.0$ and $T = 38^\circ C$. Harned and Scholes⁽⁵²⁾ give values at zero ionic strength for pK_2 of 10.220 at 40°C and 10.329 at 25°C. From all these values, it is reasonable to conclude that pK_2 at 25°C and $\mu = 0.5$ must be very close to 9.60.

The fraction of each species present over a range of pH may be calculated from equation (38), equation (39) and equation (40), at $\mu = 0.5$ and $T = 25^{\circ}\text{C}$ using the values determined for K_1 and K_2 . The results are listed in Table I.

Table I

The relative amounts of each of the species present in the Carbon Dioxide-Water System over the pH range 6-13

pH	$\frac{[\text{CO}_2]}{C_{\text{IV}}}$	$\frac{[\text{HCO}_3^-]}{C_{\text{IV}}}$	$\frac{[\text{CO}_3^{2-}]}{C_{\text{IV}}}$
6	5.10×10^{-1}	4.87×10^{-1}	1.94×10^{-4}
6.5	2.49×10^{-1}	7.51×10^{-1}	9.45×10^{-4}
7	9.43×10^{-2}	9.01×10^{-1}	3.58×10^{-3}
7.5	3.16×10^{-2}	9.56×10^{-1}	1.20×10^{-2}
8	1.00×10^{-2}	9.55×10^{-1}	3.80×10^{-2}
8.5	2.93×10^{-3}	8.86×10^{-1}	1.11×10^{-1}
9	7.46×10^{-4}	7.13×10^{-1}	2.84×10^{-1}
9.5	1.47×10^{-4}	4.43×10^{-1}	5.57×10^{-1}
10	2.10×10^{-5}	2.01×10^{-1}	7.98×10^{-1}
10.5	2.44×10^{-6}	7.37×10^{-2}	9.27×10^{-1}
11	2.56×10^{-7}	2.45×10^{-2}	9.74×10^{-1}
11.5	2.61×10^{-8}	7.89×10^{-3}	9.92×10^{-1}
12	2.62×10^{-9}	2.51×10^{-3}	9.97×10^{-1}
12.5	2.62×10^{-10}	7.94×10^{-4}	9.98×10^{-1}
13	2.62×10^{-11}	2.51×10^{-4}	9.98×10^{-1}

FRACTION OF EACH CARBONATE SPECIES

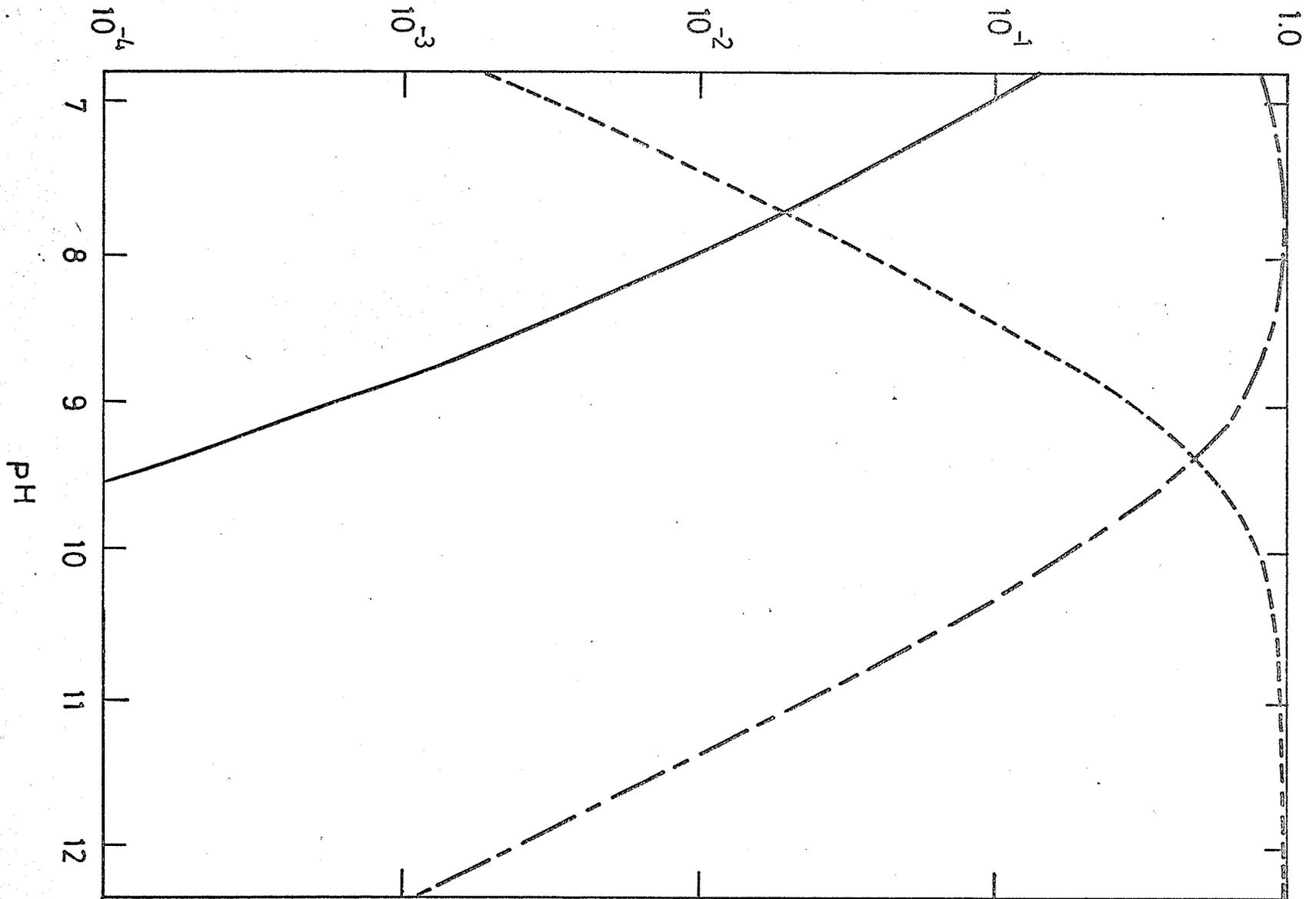


FIGURE I

The fraction of each of the carbonate species present in the $\text{CO}_2\text{-H}_2\text{O}$ system as a function of pH.

————— fraction present as CO_2
- - - - - fraction present as HCO_3^-
----- fraction present as CO_3^{2-}

The fractions of each species at each pH listed in Table I are shown graphically in Figure I. The fraction of CO_2 present in the system becomes less as the pH rises. The rate of decrease increases as the pH rises, to a point where it attains a second order relationship to pH in the range 10-13. The fraction of HCO_3^- present is relatively constant between pH 7 and 9, and diminishes as the pH continues to rise. There is a first order relationship between the fraction of HCO_3^- present and pH in the range of pH 10-13. The fraction of CO_3^{2-} present increases as the pH rises, reaching almost unity over the range of pH 11-13.

From the values listed in Table I and shown in Figure I it is possible to test out various exchange mechanisms, determine their rate constants, and predict their importance at any given pH in the range 6-13. Any postulated mechanisms must be able to predict the rate of exchange at a given pH by implementing the values in Table I.

1 - 7 PURPOSE OF THE INVESTIGATION

Despite the great number of extensive investigations into the reaction between carbon dioxide and water some doubt persists as to the exact mechanism of the hydration process⁽¹⁶⁾. Thus a thorough investigation of the process over a pH range of about 7 to 11 was undertaken in an attempt to clarify the mechanism.

A study of the catalysis of the hydration of carbon dioxide was also conducted. Since a zinc(II) atom appears to be essential for the activity of carbonic anhydrase, the enzyme which catalyzes carbon dioxide hydration in the blood, it was decided to begin by investigating the

catalytic properties of zinc(II) in a solution of ammonium hydroxide. The resulting complex, $\text{Zn}(\text{NH}_3)_4^{2+}$ is well known to have catalytic properties⁽⁴⁰⁾. It was hoped to learn more about the mechanism of the catalysis. Some metal EDTA complexes were also investigated for any catalytic activity.

The effect of UO_2^{2+} ions on the rate of reaction between carbon dioxide and water was also investigated. From this study a great deal was learned about the properties of a uranyl carbonate complex.

2 - 1 MATERIALS

Water enriched to approximately 1.6 atom % oxygen-18 (Yeda Research and Development Co. Ltd.) was distilled once from alkaline KMnO_4 . Water of normal isotopic abundance (approximately 0.2 atom % oxygen-18) was doubly distilled.

The following reagents were used without any further treatment:

NH_4Cl (Shawinigan Reagent), $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Baker's C.P. Analyzed), NaCl (certified A.C.S. Fisher), NaHCO_3 (Analar Analytical Reagent), Na_2CO_3 (Baker Analyzed Reagent), KOH (Shawinigan Reagent), hydrochloric acid (12M, C.P. Reagent, C.I.L.), ZnCl_2 (Fisher Certified Reagent), sulfuric acid (18M, C.P. Reagent, C.I.L.) and standard buffer solutions (pH 7.00 ± 0.02 , Fisher; pH 4.01 ± 0.01 , Harlew).

The preparation of oxygen-18 enriched Na_2CO_3 was as follows:

Approximately three grams of NaHCO_3 was dissolved in twenty ml. of oxygen-18 enriched water. The solution was set aside for at least twelve hours to equilibrate. After equilibration, the solution was frozen in liquid nitrogen (-196°C), and the equilibration flask was evacuated. The flask was allowed to warm up, and the water was then removed to a side arm immersed in a liquid nitrogen bath. This distillation process was made more rapid by repeatedly heating the equilibration flask with a heat gun. Upon the removal of virtually all the solvent water, the salt was removed and heated under vacuum in an oven at 200°C . This process also converted any bicarbonate present into carbonate. The oxygen-18 water was recovered from the side arm for further use as required. The purity of the oxygen-18 enriched

salt was checked by comparing its infrared spectrum with that of sodium carbonate containing a normal isotopic abundance of oxygen-18. The salts were examined as Nujol mulls on a Perkin Elmer Model 337 grating infrared spectrophotometer in the region $400-4000\text{ cm}^{-1}$ (25 to 2.5 microns). The spectra both appeared to be identical, and agreed well with reported spectra⁽⁵³⁾. A spectrum of a mixture of sodium bicarbonate and sodium carbonate was also obtained for comparison, and a strong absorption around 10 microns, attributable to sodium bicarbonate was found as would be expected from reported spectra⁽⁵³⁾. There was no sign of any absorption in this region in the spectrum of the oxygen-18 enriched salt, proving it was virtually entirely converted to sodium carbonate. If any water were present an absorption should occur in the vicinity of 3 microns⁽⁵⁴⁾. This also was not present in the spectrum of the oxygen-18 enriched salt, proving all the water had been removed.

2 - 2 SAMPLE PREPARATION AND ISOTOPIC ANALYSIS

In order to make a kinetic study of the system, the change in oxygen-18 content of the sodium carbonate was followed. In all but a few cases the salt was initially enriched in oxygen-18, and the water was of normal isotopic abundance. Hence, the rate at which the oxygen-18 content of the salt decreased with time was followed. Twenty ml. of water was measured by pipette and placed in the reaction vessel. All reagents except the sodium carbonate were then added to the water. The resulting solution was then placed in a constant temperature bath (24.7°C) and given ample time to achieve thermal equilibrium with the bath. A weighed amount of O^{18} -labelled sodium carbonate was then added

to the solution (sufficient to make 0.1 M. Na_2CO_3), and once the salt was completely dissolved (about fifteen seconds) timing commenced. A four ml. aliquot of the exchanging solution was withdrawn, and its pH was measured by an Orion Model 801 digital pH meter equipped with a Corning glass pH-electrode (No. 476022) and a Fisher calomel reference electrode (No. 13-639-62). For preliminary runs the ionic strength of the solutions was adjusted with sodium chloride. It was found, however, that the pH of the solutions increased with time, which was obviously undesirable, since the exchange rate depends on pH. This was easily rectified by using ammonium chloride in place of sodium chloride. The pH of the solutions was now well buffered over the entire range at which the exchange process was studied, and the ammonium ion proved to have no appreciable effect on the exchange rate. The exchange process was studied over a pH range of from 7.1 to 10.9. In order to get the desired pH for a given trial, sufficient concentrated hydrochloric acid or potassium hydroxide was added to the solution along with the ammonium chloride prior to the addition of the sodium carbonate.

The oxygen-18 content of the salt in solution during the exchange process was found by a method similar to that employed by Poulton and Baldwin⁽¹⁶⁾. (The induced exchange resulting from this procedure will be discussed in the appendix.) At various timed intervals aliquots of the exchanging solution were removed by means of a Plastipak disposable syringe (Becton, Dickinson, and Co.) to a bulb equipped with a ground glass joint and an unsealed side arm. The side arm was sealed by a rubber serum cap, and the bulb placed on a vacuum line. The aliquot was then frozen by immersing the bulb in

a dry ice-acetone bath (-77°C), and then degassed. As soon as the aliquot began to melt, 1 ml. of concentrated sulfuric acid was introduced through the serum cap covering the side arm by means of a Plastipak disposable syringe. The sample was once again cooled in the dry ice-acetone bath for several minutes. The carbon dioxide liberated upon addition of the acid was then permitted to pass through a trap (n-pentane slush, -130°C) and was condensed into a previously evacuated bulb cooled to liquid nitrogen temperature (-196°C). After 10 seconds the transfer of carbon dioxide was virtually complete, and the trapped carbon dioxide was opened to the vacuum line in order to remove any non-condensable gases.

The isotopic ratio of the resulting sample was determined by measuring the ratio of the mass 46 peak ($\text{C}^{12}\text{O}^{16}\text{O}^{18}$) to the mass 45 and mass 44 peaks ($\text{C}^{12}\text{O}^{17}\text{O}^{16}$, $\text{C}^{13}\text{O}^{16}\text{O}^{16}$, $\text{C}^{12}\text{O}^{16}\text{O}^{16}$) on a Varian-Mat GD 150 isotope ratio mass spectrometer. This ratio, read directly by the double collector procedure, is referred to as the p-factor of the sample. It was found that in order to generate enough carbon dioxide to result in a dependable p-factor reading, the required size of the aliquot was $1\frac{1}{2}$ ml.

2 - 3 TREATMENT OF DATA

The fraction of exchange, F, and the p-factor may be related as below

$$F = \frac{p_t - p_0}{p_{\infty} - p_0} \quad (19)$$

where p_t is the p-factor at a time t during the reaction, p_0 is the p-factor at time zero, and p_{∞} is the p-factor at infinite time when

isotopic equilibrium has been reached. If $-\log_{10}(1-F)$ is plotted against time for any given run, a straight line plot results. The slope, intercept, and uncertainty in the slope and intercept, were then determined by a least-squares program on the Hewlett-Packard Calculator Model 9100 A.

The half-time ($t_{\frac{1}{2}}$) for the exchange reaction is defined as the length of time required for the fraction of exchange to equal 0.5. Ordinarily, then, the half-life would be obtained by reading the time (on the x-axis) corresponding to $-\log_{10}0.5$ (0.301 on the y axis). However, this would apply only when the intercept is zero, which is not usually the case in actual practice. Because of induced exchange, a zero-time intercept generally in the range of 0.01 must be allowed for. Thus the half-life of the reaction is actually that time corresponding to a value on the y-axis of the sum of 0.301 plus the zero-time intercept. However, the slope of the line is not affected by the zero-time intercept, and a convenient way to obtain the half-life is to divide the slope by $-\log_{10}0.5$, which was done in all cases. A more complete discussion of induced exchange may be found in the Appendix.

The rate of exchange for each reaction was calculated by the following previously derived relation:

$$R = \frac{ab}{(a+b)t_{\frac{1}{2}}} \quad 0.693 \quad (16)$$

where a is the number of gram-atoms oxygen per liter of water (55.55 gram-atoms oxygen liter⁻¹), b is the number of gram atoms oxygen in the carbonate per liter (three times the molarity of the

carbonate) giving R the units of gram-atoms oxygen liter⁻¹ time⁻¹.

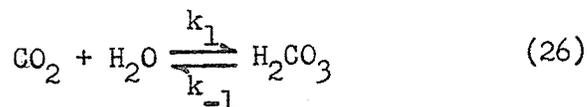
It is easily shown that the magnitude of R remains unchanged when its units are converted to moles of carbonate liter⁻¹ time⁻¹. Typically six to eight samples were taken for each run over a period of time corresponding to between one and two half-lives.

3 - 1 THE EXCHANGE BETWEEN CARBON DIOXIDE AND WATER IN THE ABSENCE OF A CATALYST

Prior to studying the effect of catalysis on the rate of oxygen exchange between carbon dioxide and water, it was necessary to conduct a series of experiments to determine the rate of oxygen exchange in the absence of any deliberately added catalysts. The results are shown in Table II and Table III. The rate of exchange between carbon dioxide and water was measured by following the decrease in the oxygen-18 content of enriched sodium carbonate dissolved in water of normal isotopic abundance (except where indicated). All trials were performed at 24.7°C and enough sodium carbonate was added to make up a 0.1 M solution. For the results shown in Table II enough ammonium chloride was dissolved to raise the ionic strength to 0.5. Table III lists a number of trials performed at an ionic strength of 1.0. In these cases the solutions were made up in exactly the same fashion as for trials done at an ionic strength of 0.5, except for the addition of an amount of sodium chloride sufficient to raise the ionic strength to 1.0.

Figure II shows a plot of the exchange rates listed in Table II and Table III against pH. Although there is a decrease in exchange rate at high ionic strength, the effect is not large.

As was mentioned in Section 1 - 4, it has long been acknowledged that the following processes are of major importance in the hydration of carbon dioxide: (4, 5, 16)



$\frac{N - N_{\infty}}{t}$, mol/l s

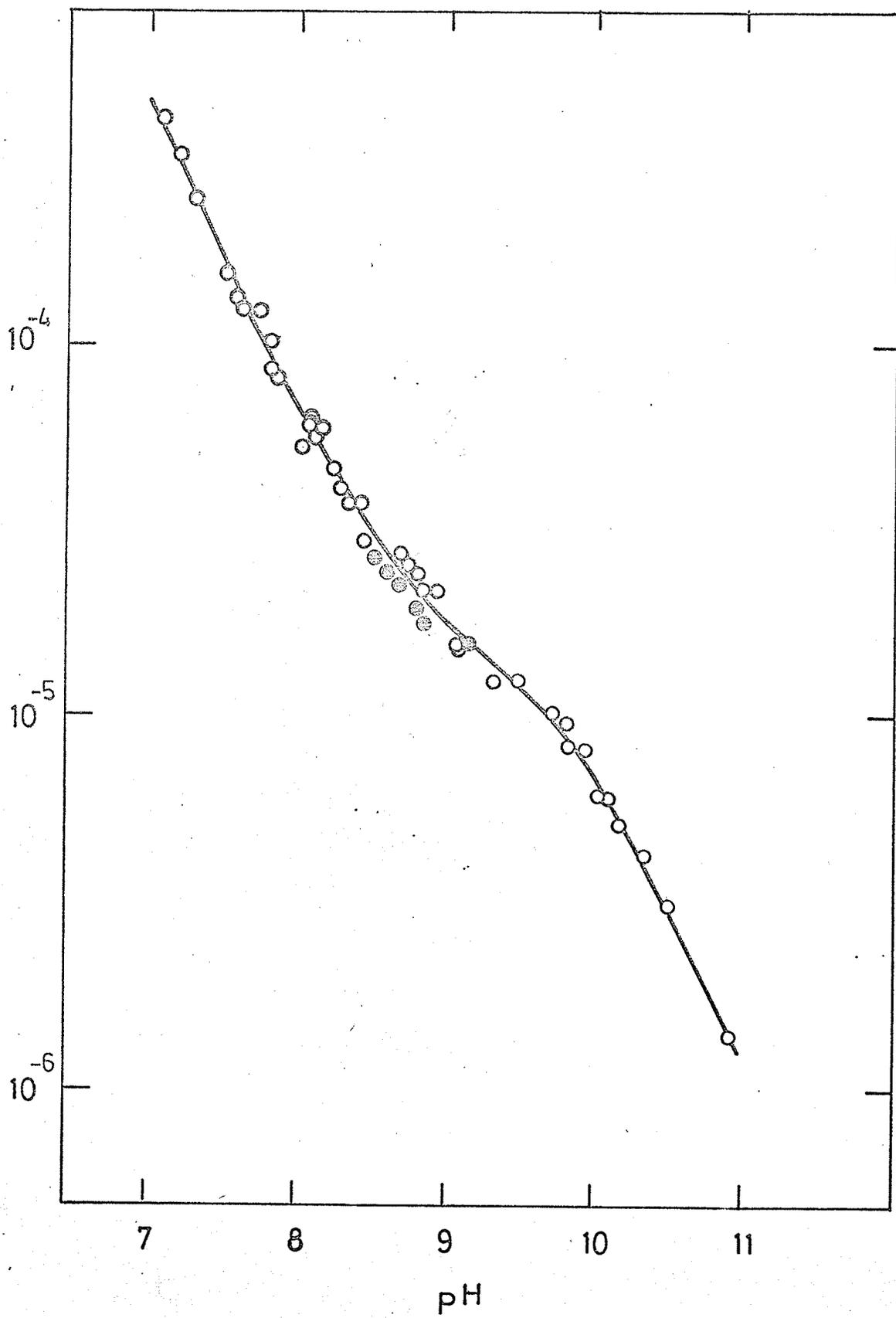


FIGURE II

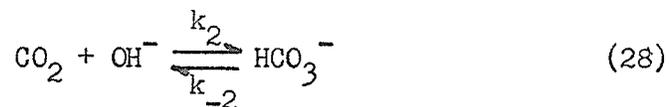
The pH dependence for carbon dioxide-water
exchange in 0.1 M Na_2CO_3 solution at 24.7°C.

- $\mu = 0.5$
- $\mu = 1.0$

Table II

The Rate of Oxygen Exchange Between Carbon Dioxide and Water at 24.7°C and Ionic Strength 0.5 Total Carbonate Concentration 0.1 M			
Rate		Rate	
pH	(moles liters ⁻¹ seconds ⁻¹)	pH	(moles liters ⁻¹ seconds ⁻¹)
7.103	4.053 x 10 ⁻⁴	8.713	2.714 x 10 ⁻⁵
7.241	3.275 x 10 ⁻⁴	8.768	2.572 x 10 ⁻⁵
7.339	2.461 x 10 ⁻⁴	8.838	2.372 x 10 ⁻⁵
7.568	1.560 x 10 ⁻⁴	8.896	2.186 x 10 ⁻⁵
7.616	1.330 x 10 ⁻⁴	8.934	2.151 x 10 ⁻⁵
7.662	1.283 x 10 ⁻⁴	*9.1	1.561 x 10 ⁻⁵
7.777	1.247 x 10 ⁻⁴	9.124	1.568 x 10 ⁻⁵
7.845	1.003 x 10 ⁻⁴	*9.15	1.554 x 10 ⁻⁵
7.856	8.632 x 10 ⁻⁵	9.365	1.229 x 10 ⁻⁵
7.900	8.368 x 10 ⁻⁵	9.509	1.260 x 10 ⁻⁵
8.071	5.370 x 10 ⁻⁵	9.743	1.008 x 10 ⁻⁵
8.097	6.017 x 10 ⁻⁵	9.822	9.428 x 10 ⁻⁶
8.100	6.172 x 10 ⁻⁵	9.873	8.262 x 10 ⁻⁶
8.149	5.626 x 10 ⁻⁵	9.968	8.160 x 10 ⁻⁶
8.173	5.942 x 10 ⁻⁵	10.060	6.003 x 10 ⁻⁶
8.273	4.689 x 10 ⁻⁵	10.096	6.049 x 10 ⁻⁶
8.310	4.118 x 10 ⁻⁵	10.197	5.187 x 10 ⁻⁶
8.378	3.735 x 10 ⁻⁵	10.357	4.224 x 10 ⁻⁶
8.435	3.767 x 10 ⁻⁵	10.530	3.074 x 10 ⁻⁶
8.484	2.983 x 10 ⁻⁵	10.940	1.386 x 10 ⁻⁶

* - normal isotope abundance Na₂CO₃ in oxygen-18 enriched H₂O



Both of these processes are first order with respect to carbon dioxide concentration:

$$R_1 = k_1^i (\text{CO}_2)(\text{H}_2\text{O}) = k_1(\text{CO}_2) \quad (27)$$

$$R_2 = k_2(\text{CO}_2)(\text{OH}^-) \quad (29)$$

Previous studies⁽²⁾ have suggested that process 1 is dominant for pH less than 8, while process 2 becomes predominant where the pH exceeds 10. In the pH range 8-10 both processes should contribute to the overall reaction between carbon dioxide and water.

Table III

The Rate of Oxygen Exchange Between Carbon Dioxide and Water at 24.7°C and Ionic Strength 1.0. Total Carbonate Concentration 0.1 M			
Rate		Rate	
pH	(moles liters ⁻¹ seconds ⁻¹)	pH	(moles liters ⁻¹ seconds ⁻¹)
8.545	2.672 x 10 ⁻⁵	8.828	1.992 x 10 ⁻⁵
8.630	2.438 x 10 ⁻⁵	8.873	1.868 x 10 ⁻⁵
8.700	2.338 x 10 ⁻⁵		

If this two-process mechanism is correct it should be possible to explain Figure II qualitatively by examining the effect of pH on the rates of the two processes both individually and collectively. In order to do this it is required that the concentration of carbon dioxide in solution be known as a function of pH. In Section 1 - 5 the fraction of the species present as carbon dioxide over the range of pH 6-13

was calculated for an ionic strength of 0.5 and a temperature of 25°C. Using this information, the concentration of carbon dioxide may be determined for conditions where the total concentration of all carbonate species is 0.1 M. Since the conditions imposed on the calculation of the concentrations of carbon dioxide at various pH correspond almost exactly to the experimental conditions under which the data in Table II were obtained, it should be possible to explain the trend observed in Figure II qualitatively by means of the calculated carbon dioxide concentrations, the rate law for process 1 (equation(27)) and the rate law for process 2 (equation(28)). If it is assumed that process 1 is the principal exchange route where the pH is less than 8, since its rate law shows a first order dependence on the concentration of carbon dioxide, at pH less than 8 the exchange rate should vary with pH in the same manner as the concentration of carbon dioxide. Since the rate of decrease of the concentration of carbon dioxide is slightly less than first order with respect to pH in this region, the overall exchange rate should also show close to a first order dependence on pH. The rate law for process 2 shows a first order dependence on carbon dioxide concentration. The rate of decrease of carbon dioxide concentration is nearly second order with respect to pH where the pH exceeds 10. Thus, if process 2 dominates in this region, the overall exchange rate should be nearly first order with respect to pH. In the pH 8-10 region where both processes are involved to a measurable degree, the exchange rate should show less than a first order dependence on pH since process 2 would have less than a first order dependence on pH in this region. An examination of Figure II shows that all these conditions are met. Thus, there is qualitative agreement with the proposed two-process

Table IV

The Concentration of Carbon Dioxide at 25°C and Ionic Strength 0.5 where Total Carbonate Concentration is 0.1 M			
pH	[CO ₂] (M.)	pH	[CO ₂] (M.)
6.5	2.49 x 10 ⁻²	9.5	1.47 x 10 ⁻⁵
7	9.43 x 10 ⁻³	10	2.10 x 10 ⁻⁶
7.5	3.16 x 10 ⁻³	10.5	2.44 x 10 ⁻⁷
8	1.00 x 10 ⁻³	11	2.56 x 10 ⁻⁸
8.5	2.93 x 10 ⁻⁴	11.5	2.61 x 10 ⁻⁸
9	7.46 x 10 ⁻⁵	12	2.62 x 10 ⁻¹⁰

Table V

Data for Determination of k ₁ & k ₂ from Equation (44)				
pH	R (ml ⁻¹ s ⁻¹)	[CO ₂] (M.)	$\frac{R}{[CO_2]}$ (s ⁻¹)	[OH ⁻] x 10 ⁷ (M.)
7.000	4.8 x 10 ⁻⁴	9.43 x 10 ⁻³	0.051	1.0
8.000	7.0 x 10 ⁻⁵	1.00 x 10 ⁻³	0.070	10
9.000	1.95 x 10 ⁻⁵	7.46 x 10 ⁻⁵	0.261	100
9.301	1.5 x 10 ⁻⁵	2.91 x 10 ⁻⁵	0.515	200
9.500	1.25 x 10 ⁻⁵	1.47 x 10 ⁻⁵	0.850	316
9.602	1.1 x 10 ⁻⁵	1.01 x 10 ⁻⁵	1.09	400
9.699	1.0 x 10 ⁻⁵	7.01 x 10 ⁻⁶	1.43	500
9.778	9.2 x 10 ⁻⁶	4.99 x 10 ⁻⁶	1.84	600
9.845	8.5 x 10 ⁻⁶	3.97 x 10 ⁻⁶	2.14	700
9.903	8.0 x 10 ⁻⁶	3.13 x 10 ⁻⁶	2.56	800
9.954	7.4 x 10 ⁻⁶	2.53 x 10 ⁻⁶	2.92	900
10.000	6.8 x 10 ⁻⁶	2.10 x 10 ⁻⁶	3.24	1000

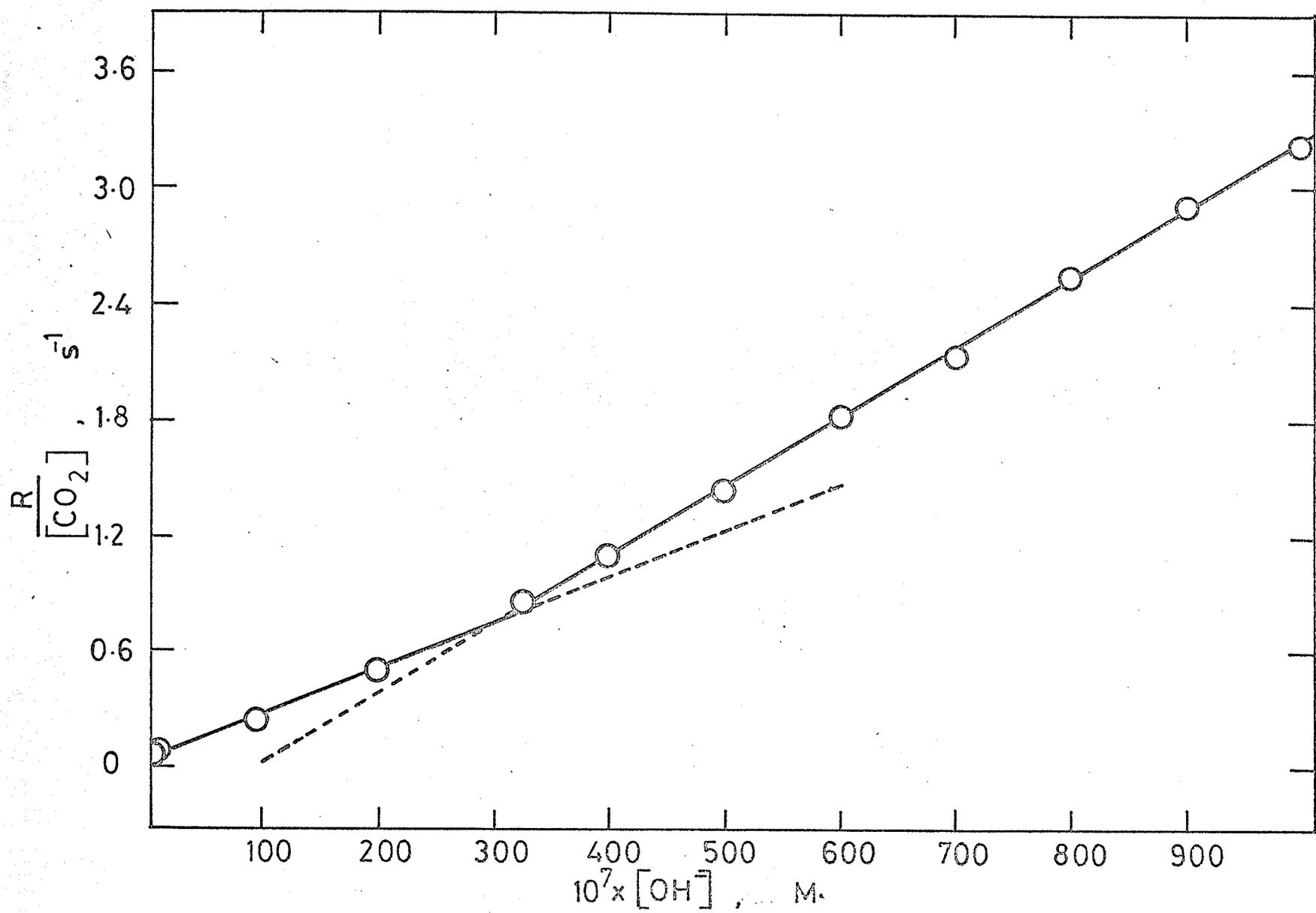


FIGURE III

Plot of $\frac{R}{[\text{CO}_2]}$ against $[\text{OH}^-]$ for determination
of k_1 and k_2 from equation (44).

mechanism.

If these two processes are the only ones involved in the overall mechanism, then

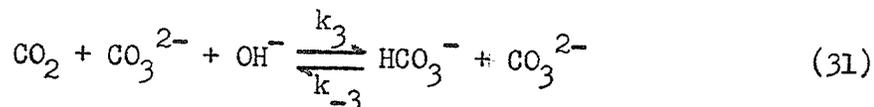
$$R_{\text{TOTAL}} = R_1 + R_2 = k_1(\text{CO}_2) + k_2(\text{CO}_2)(\text{OH}^-) \quad (43)$$

$$\frac{R_{\text{TOTAL}}}{(\text{CO}_2)} = k_1 + k_2(\text{OH}^-) \quad (44)$$

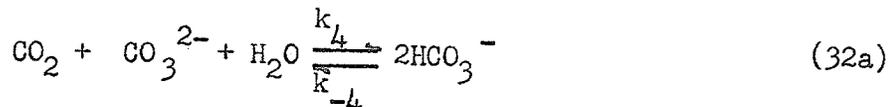
Thus, a plot of the quantity shown on the left hand side of Equation (44) against $[\text{OH}^-]$ should give a straight line of slope k_2 and intercept k_1 . Data for a plot of this type may be found in Table V. The values for R were taken from Figure II, while the concentration of carbon dioxide at each pH was calculated in the usual way. In previous studies⁽²⁾ using a monometric technique which appears to uphold the two-process mechanism, values of about $8.5 \times 10^3 \text{ l m}^{-1} \text{ s}^{-1}$ for k_2 and 0.03 sec^{-1} for k_1 have been established. A plot of the data in Table V is shown in Figure III. Examination of Figure III shows that the expected straight line relationship does not hold. The slope appears to be increasing with increasing hydroxide ion concentration, levelling off as the hydroxide ion concentration exceeds $3 \times 10^{-5} \text{ M}$ (pH 9.5). This trend suggests that there are other processes of importance to the overall reaction between carbon dioxide and water in addition to the two already considered. These additional processes appear to be gaining in relative importance as the pH is increased.

Poulton and Baldwin⁽¹⁶⁾ studied the reaction between carbon dioxide and water using oxygen-18 exchange. They examined the dependence of

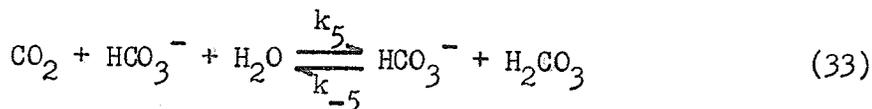
the overall exchange rate on the concentration of carbon dioxide and found it to be somewhat greater than first order (about 1.2). They thus postulated three processes in addition to the two already considered. Their data led to values of $3.64 \times 10^{-2} \text{sec}^{-1}$ for k_1 and $8.5 \times 10^3 \text{lm}^{-1} \text{sec}^{-1}$ for k_2 . The other three processes they postulated follows:



$$R_3 = k_3(\text{CO}_2)(\text{CO}_3^{2-})(\text{OH}^-) \quad (45)$$



$$R_4 = k_4(\text{CO}_2)(\text{CO}_3^{2-}) \quad (46)$$



$$R_5 = k_5(\text{CO}_2)(\text{HCO}_3^-) \quad (47)$$

Poulton and Baldwin give values of $1.6 \times 10^5 \text{l}^2 \text{m}^{-2} \text{sec}^{-1}$ for k_3 , $1.3 \text{lm}^{-1} \text{sec}^{-1}$ for k_4 , and $4.8 \times 10^{-2} \text{lm}^{-1} \text{sec}^{-1}$ for k_5 . The values given above for k_1 , k_2 , k_3 , k_4 and k_5 are for $T = 25 \text{C}$ and ionic strength (μ) 0.5, which is nearly identical to the conditions under which the data in Table II were accumulated. Thus, using the rate laws and rate constants above it should be possible to get quantitative agreement with Figure II through calculation, providing the concentration of each of the carbonate species is known. The relative amounts of each of the species present at $T = 25^\circ \text{C}$ and $\mu = 0.5$ were found in Section 1 - 6 over the pH range of Figure II. The results of the calculations are shown in Table VI and Table VII.

- 46 -
Table VI

The rate of each reaction process second order in total carbonate calculated from the rate constants of Poulton and Baldwin⁽¹⁶⁾ at 25°C and $\alpha = 0.5$. Total carbonate concentration 0.1 M.

pH	R_3 (ml ⁻¹ s ⁻¹)	R_4 (ml ⁻¹ s ⁻¹)	R_5 (ml ⁻¹ s ⁻¹)	Total Second Order Contribution
7	5.40×10^{-8}	4.39×10^{-6}	4.08×10^{-5}	4.52×10^{-5}
7.5	1.92×10^{-7}	4.93×10^{-6}	1.45×10^{-5}	1.94×10^{-5}
8	6.08×10^{-7}	4.94×10^{-6}	4.58×10^{-6}	1.01×10^{-5}
8.5	1.67×10^{-6}	4.23×10^{-6}	1.25×10^{-6}	7.15×10^{-6}
9	3.39×10^{-6}	2.75×10^{-6}	2.55×10^{-7}	6.40×10^{-6}
9.5	4.14×10^{-6}	1.06×10^{-6}	3.13×10^{-8}	5.23×10^{-6}
10	2.68×10^{-6}	2.18×10^{-7}	2.03×10^{-9}	2.90×10^{-6}
10.5	1.14×10^{-6}	2.94×10^{-8}	8.62×10^{-11}	1.17×10^{-6}
11	3.99×10^{-7}	3.24×10^{-9}	3.01×10^{-12}	4.02×10^{-7}
11.5	1.31×10^{-7}	3.37×10^{-10}	9.88×10^{-14}	1.31×10^{-7}
12	4.18×10^{-8}	3.40×10^{-11}	3.16×10^{-15}	4.18×10^{-8}

Table VII

The rate of each reaction process first order in total carbonate calculated from the rate constants of Poulton and Baldwin⁽¹⁶⁾ at 25°C and $\alpha = 0.5$. Total carbonate concentration 0.1 M. The total of all processes is also shown.

pH	R_1 (ml ⁻¹ s ⁻¹)	R_2 (ml ⁻¹ s ⁻¹)	Total First Order Contribution	Total Exchange Rate
7	3.43×10^{-4}	7.92×10^{-6}	3.51×10^{-4}	3.96×10^{-4}
7.5	1.15×10^{-4}	8.39×10^{-6}	1.23×10^{-4}	1.42×10^{-4}
8	3.64×10^{-5}	8.40×10^{-6}	4.48×10^{-5}	5.49×10^{-5}
8.5	1.07×10^{-5}	7.78×10^{-6}	1.85×10^{-5}	2.57×10^{-5}
9	2.72×10^{-6}	6.27×10^{-6}	8.99×10^{-6}	1.54×10^{-5}
9.5	5.35×10^{-7}	3.90×10^{-6}	4.44×10^{-6}	9.67×10^{-6}
10	7.65×10^{-8}	1.76×10^{-6}	1.84×10^{-6}	4.74×10^{-6}
10.5	8.88×10^{-9}	6.48×10^{-7}	6.57×10^{-7}	1.83×10^{-6}
11	9.32×10^{-10}	2.15×10^{-7}	2.16×10^{-7}	6.18×10^{-7}
11.5	9.50×10^{-11}	6.93×10^{-8}	6.94×10^{-8}	2.00×10^{-7}
12	9.54×10^{-12}	2.20×10^{-8}	2.20×10^{-8}	6.38×10^{-8}

RATE OF OXYGEN EXCHANGE, $\text{mol l}^{-1} \text{s}^{-1}$

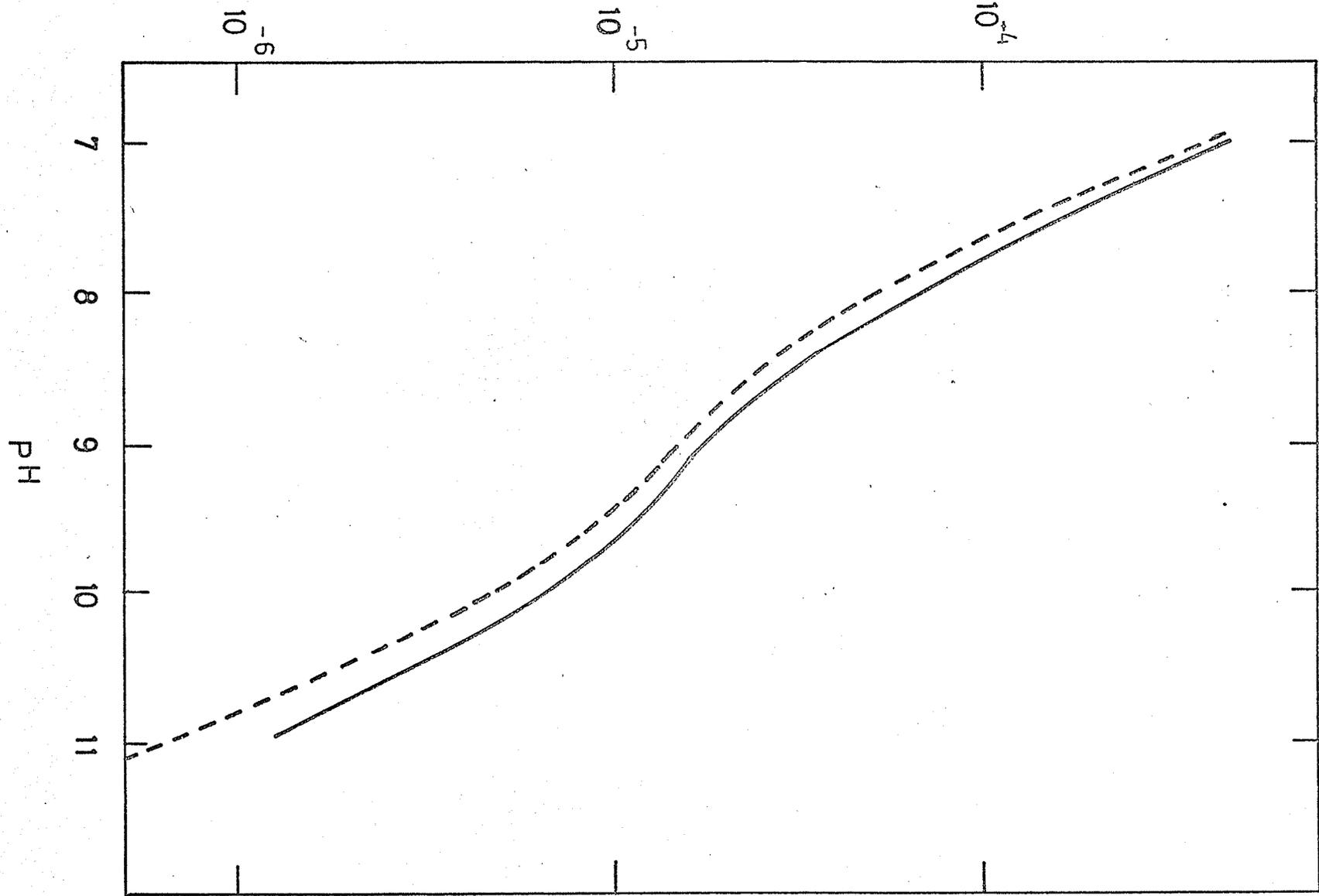


FIGURE IV

Comparison of data from this work for the rate of oxygen exchange between CO_2 and H_2O with results calculated from the data of Poulton and Baldwin⁽¹⁶⁾.

————— this work
----- calculated from data of Poulton and Baldwin for $\mu = 0.5$, $T = 25^\circ\text{C}$ and total carbonate 0.1 M.

RATE OF OXYGEN EXCHANGE, $\text{mol l}^{-1} \text{s}^{-1}$

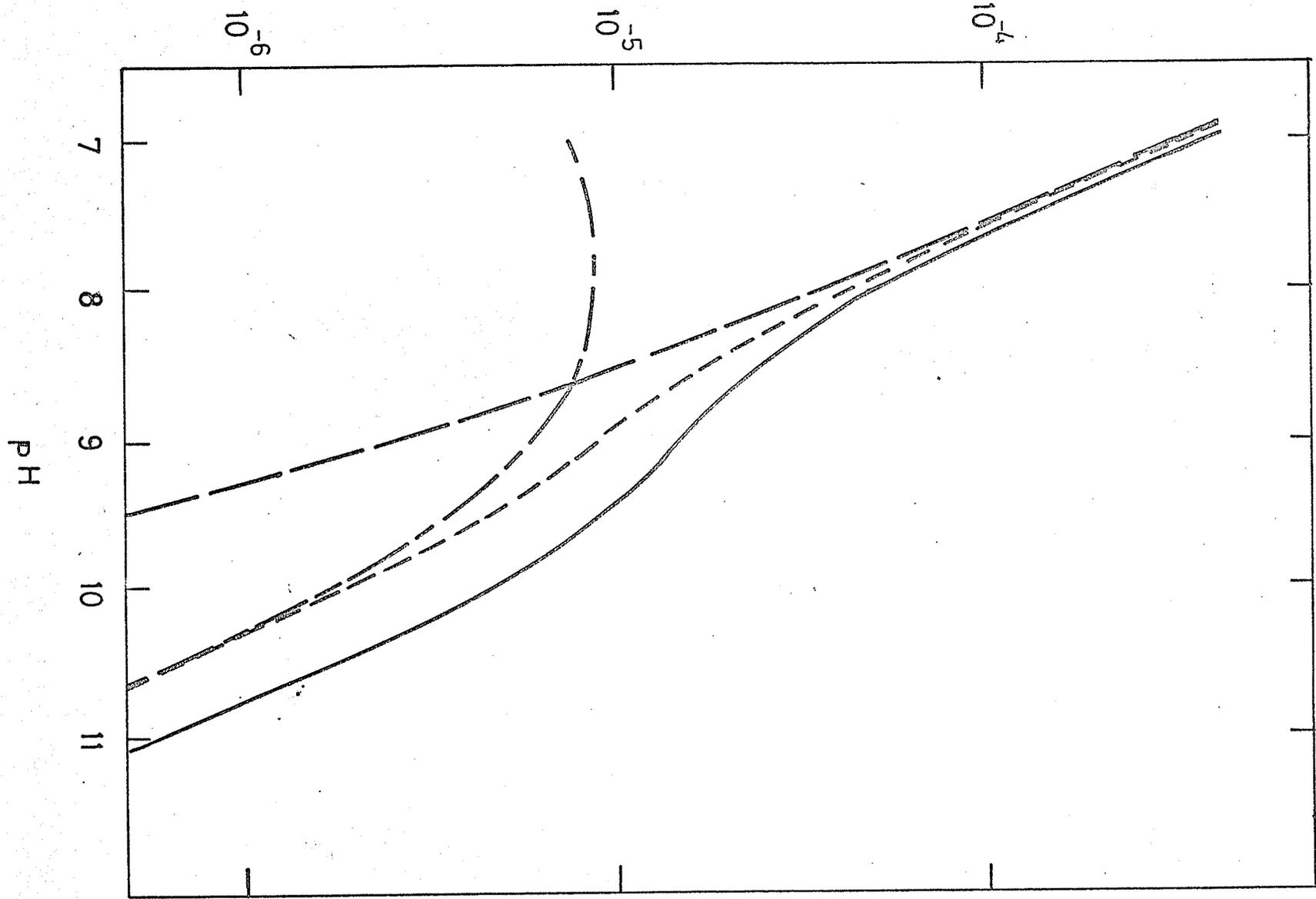


FIGURE V

The pH dependence of exchange processes first order in $[\text{CO}_2]$. All curves were calculated from the data of Poulton and Baldwin⁽¹⁶⁾, for $T = 25^\circ\text{C}$, $\mu = 0.5$ and total carbonate 0.1 M.

————— total exchange rate
----- total first order contribution
to the overall exchange rate
—— ——— $R_1 = k_1 [\text{CO}_2]$
- - - - - $R_2 = k_2 [\text{CO}_2] [\text{OH}^-]$

RATE OF OXYGEN EXCHANGE, $\text{mol l}^{-1} \text{s}^{-1}$

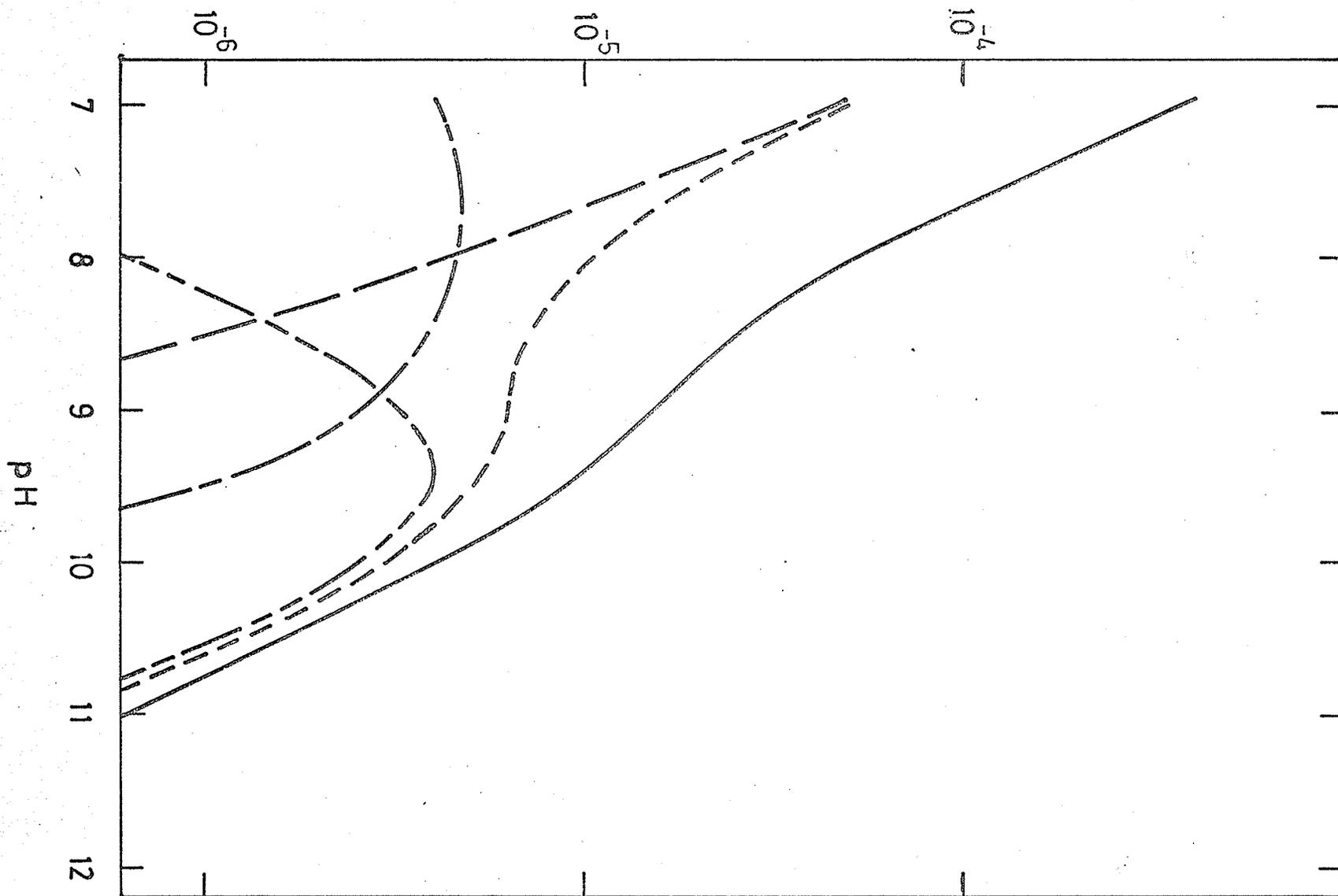


FIGURE VI

The pH dependence of exchange processes second order in $[\text{CO}_2]$. All curves were calculated from the data of Poulton and Baldwin⁽¹⁶⁾, for $T = 25^\circ\text{C}$, $\mu = 0.5$ and total carbonate 0.1 M.

- _____ total exchange rate
- total second order contribution to the overall exchange rate
- - - - - $R_3 = k_3 [\text{CO}_2] [\text{CO}_3^{2-}] [\text{OH}^-]$
- — — — — $R_4 = k_4 [\text{CO}_2] [\text{CO}_3^{2-}]$
- — — — — $R_5 = k_5 [\text{CO}_2] [\text{HCO}_3^-]$

RATE OF OXYGEN EXCHANGE, $\text{mol l}^{-1} \text{s}^{-1}$

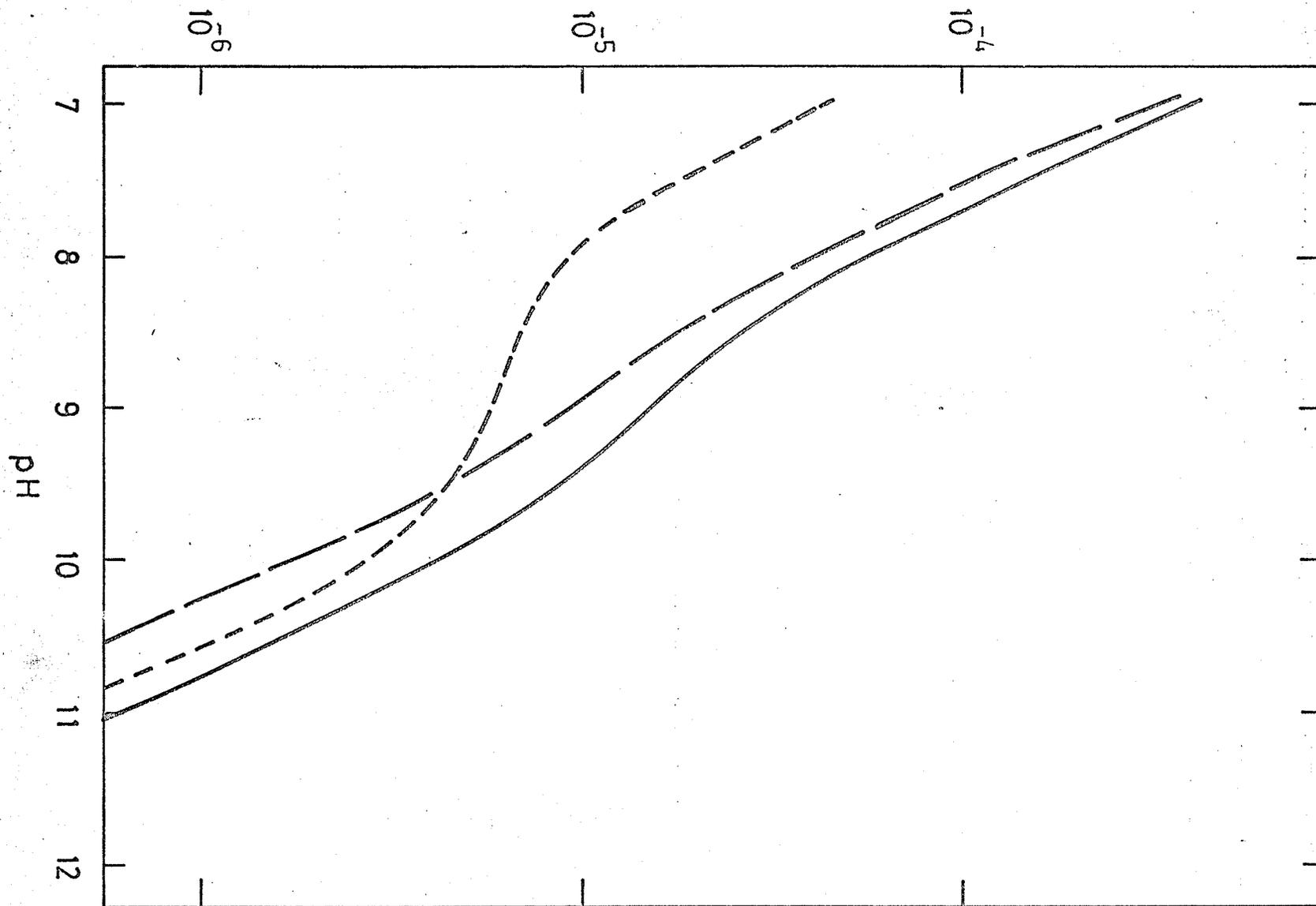


FIGURE VII

Comparison of the contribution by processes first order in $[\text{CO}_2]$ with the contribution of processes second order in $[\text{CO}_2]$ to the overall exchange process. All curves calculated from data of Poulton and Baldwin⁽¹⁶⁾, for $T = 25^\circ\text{C}$ $\mu = 0.5$, and total carbonate 0.1 M.

————— total exchange rate
- - - - - first order contribution
----- second order contribution

Figure IV compares the result of calculations using the mechanism and rate constants proposed by Poulton and Baldwin with the results of this work (previously shown in Figure II). The dependence of exchange rate on pH is nearly identical in both instances. The results of this work would seem to indicate a slight increase in the exchange rate relative to that found by Poulton and Baldwin. This is perhaps not surprising since ammonium chloride was used as a buffer and some amines are known to catalyze the hydration of carbon dioxide.⁽³⁹⁾ This mechanism would thus appear to be consistent with the data obtained in this work.

Figure V shows the contributions of process 1 and process 2 both individually and collectively. They behave exactly as was predicted in the earlier discussion when a simple two process mechanism was considered. However, there is obviously another contribution to the total rate, especially at pH greater than 9.

Figure VI shows the contributions by second order processes. In the region above pH 9 process 3 (equation (31)) is important among the processes second order in total carbonate.

Figure VII gives a comparison between the importance of processes first order in total carbonate and that of the processes second order in total carbonate. Above pH 9.5, the second order processes actually become more important than the first order terms. It is easily seen that R_3 , the process mainly responsible for the second order contribution in this range has a first order dependence on pH (since $[\text{CO}_3^{2-}]$ is virtually constant in this region) explaining why it would appear qualitatively that Figure II supports the simple two process mechanism.

As was explained earlier in Section 1 - 4, previous works which had claimed a simple two process mechanism^(6,7) were in error because

the manometric methods they employed were not sensitive enough to note the effect of the second order processes, while the low concentrations of carbon dioxide and consequent high ratios of concentration of carbonate and bicarbonate to carbon dioxide under the conditions of chemical equilibrium used in the isotope exchange method permit the evaluation of the catalytic effect of these species.

It is necessary to perform a complete study of the oxygen exchange between carbon dioxide over a range of pH at several different total carbonate concentrations in order to extract values for the various rate constants involved in Poulton and Baldwin's mechanism. Since this has not been done in this work, it is not possible to extract values for the various rate constants for comparison against the values given by Poulton and Baldwin. Nevertheless, the extraordinary fit demonstrated in Figure IV is strong evidence in support of the reaction scheme they have proposed.

3 - 2 THE EFFECT OF SOME METAL(II)-AMMONIA COMPLEXES ON THE RATE OF OXYGEN EXCHANGE BETWEEN CARBON DIOXIDE AND WATER.

The enzyme carbonic anhydrase which catalyses the process " $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ " contains a zinc atom which is necessary for its activity⁽²⁹⁾. Other zinc complexes have been shown to have some catalytic effect. Grønvald and Faurholt⁽⁴⁰⁾ explained the catalysis of the process "carbamate \rightleftharpoons carbonate" by the catalysis of $\text{Zn}(\text{NH}_3)_4^{2+}$ on the hydration of carbon dioxide. Taylor et al⁽⁴²⁾ demonstrated that a complex of monoethanolamine and zinc(II) catalyses the hydration of carbon dioxide.

In this study Zn(II) in the form of various known amounts of

RATE OF OXYGEN EXCHANGE, mol l⁻¹ s⁻¹

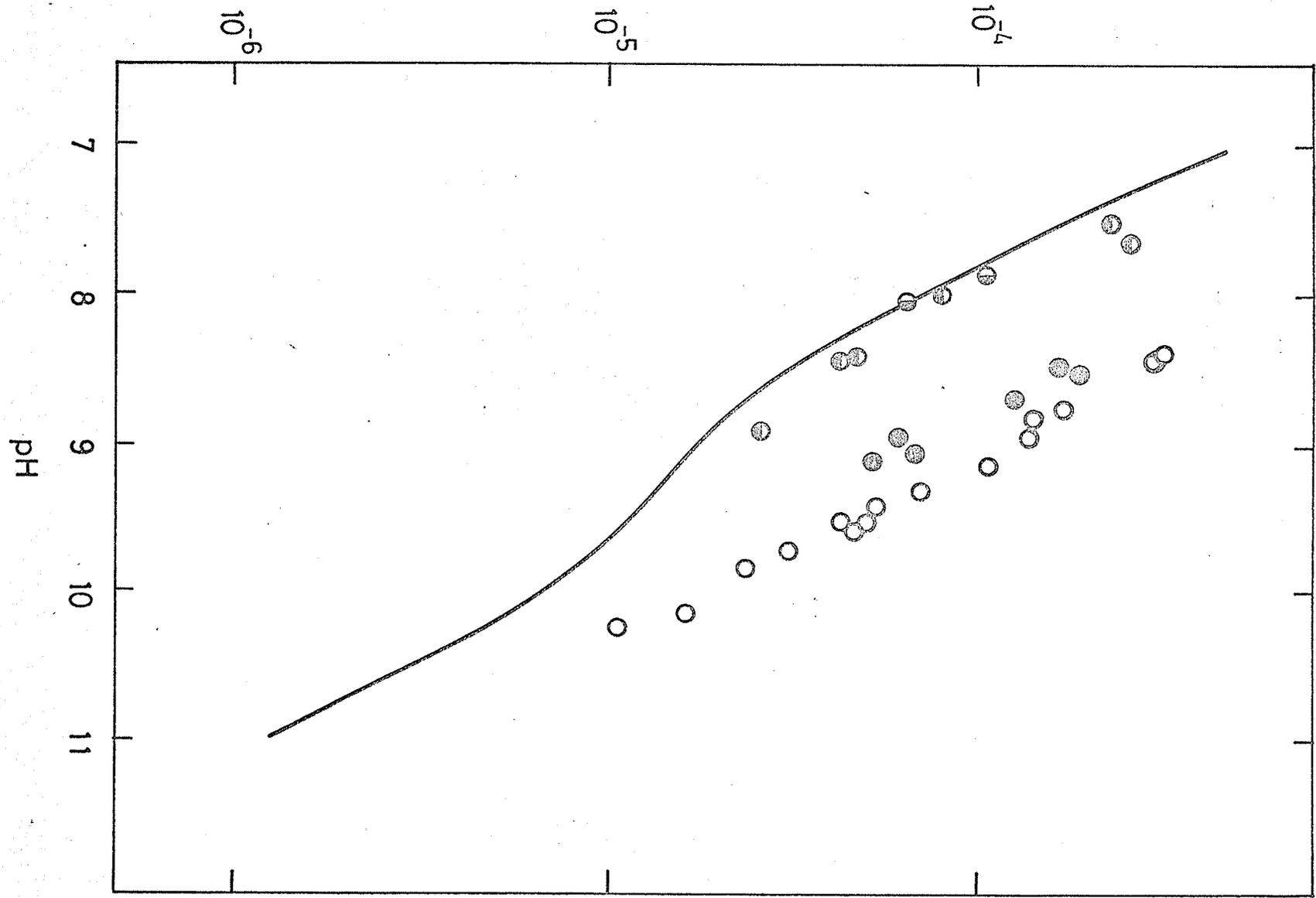


FIGURE VIII

The rate of oxygen exchange between carbon dioxide and water at 24.7°C , $\mu = 0.5$ and total carbonate 0.1 M in the presence of some metal-ammonia complexes.

○ 0.020 M $\text{Zn}(\text{NH}_3)_4^{2+}$

● 0.010 M $\text{Zn}(\text{NH}_3)_4^{2+}$

◐ 0.010 M $\text{Co}(\text{NH}_3)_6^{2+}$

◑ 0.012 M $\text{Cu}(\text{NH}_3)_4^{2+}$

— data from this work for

exchange rate at 24.7°C , $\mu = 0.5$ and total carbonate 0.1 M where no catalyst has been added.

FIGURE IX

The dependence in pH of that portion of the overall exchange rate attributable to

the catalytic power of $\text{Zn}(\text{NH}_3)_4^{2+}$



0.02 M $\text{Zn}(\text{NH}_3)_4^{2+}$

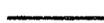


0.01 M $\text{Zn}(\text{NH}_3)_4^{2+}$



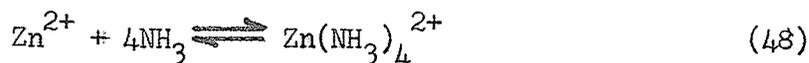
data for 0.01 M $\text{Zn}(\text{NH}_3)_4^{2+}$

doubled



plot of first order dependence on pH.

ZnCl₂ was added to basic 0.1M carbonate solutions containing 0.4M NH₄Cl. In a basic ammonia medium such as exists here a complex Zn(NH₃)₄²⁺ is formed. (44)



$$K = \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^4} = 10^9 \quad (49)$$

Thus, in excess ammonia virtually all the zinc(II) in solution should form Zn(NH₃)₄²⁺.

Marked catalysis was observed in the exchange rate for carbonate solutions containing Zn(NH₃)₄²⁺. Results are shown in Table VIII. Figure VIII gives a comparison between the rate of exchange between carbon dioxide and water in the presence of Zn(NH₃)₄²⁺ and the exchange rate in the absence of any added zinc(II). That portion of the overall exchange attributable to the catalytic power of Zn(NH₃)₄²⁺, R'-R, has also been calculated by subtracting the exchange rate expected in the absence of zinc(II) from the total rate with zinc(II) added at comparable pH. Values for this quantity for each run are shown in Table VIII.

Figure IX shows a plot of the contribution to the total exchange rate from Zn(NH₃)₄²⁺ catalysis plotted against pH for each trial listed in Table VIII. From Figure IX it would appear that the amount of catalysis is first order in Zn(II) concentration, and decreases with a first order dependence of hydrogen ion concentration.

The first order dependence on zinc(II) concentration is illustrated by doubling the values for R'-R where the concentration of zinc(II) is about 0.01M. The resulting values are in close agreement with values for R'-R where the concentration of zinc(II) is about 0.02M at comparable pH.

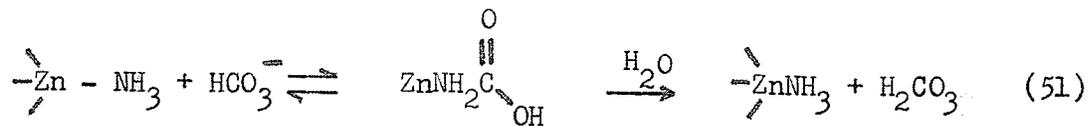
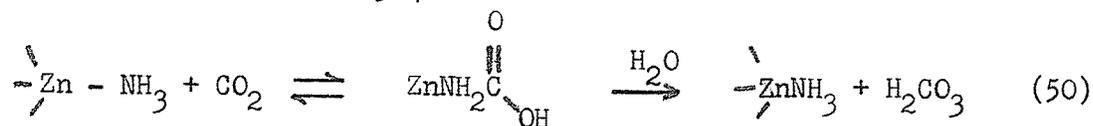
Table VIII

R' is the rate of oxygen exchange between carbon dioxide and water in 0.1 M Na_2CO_3 and 0.4 M NH_4Cl in the presence of zinc(II).

R is the exchange rate in the absence of zinc(II) (from Figure II, Section 3 - 1) $T = 24.7^\circ\text{C}$, $\mu \approx 0.5$.

pH	ZnCl_2 (M.)	R ($\text{ml}^{-1}\text{s}^{-1}$)	R ($\text{ml}^{-1}\text{s}^{-1}$)	$R' - R$
8.411	.01875	3.094×10^{-4}	3.8×10^{-5}	2.7×10^{-4}
8.441	.01893	2.937×10^{-4}	3.6×10^{-5}	2.6×10^{-4}
8.777	.02040	1.691×10^{-4}	3.5×10^{-5}	1.3×10^{-4}
8.866	.01998	1.391×10^{-4}	2.3×10^{-5}	1.2×10^{-4}
8.988	.02179	1.347×10^{-4}	2.0×10^{-5}	1.2×10^{-4}
9.182	.02142	1.037×10^{-4}	1.7×10^{-5}	8.7×10^{-5}
9.330	.02168	6.952×10^{-5}	1.5×10^{-5}	5.5×10^{-5}
9.446	.02142	5.225×10^{-5}	1.3×10^{-5}	3.9×10^{-5}
9.524	.02143	4.918×10^{-5}	1.2×10^{-5}	3.7×10^{-5}
9.525	.02060	4.194×10^{-5}	1.2×10^{-5}	3.0×10^{-5}
9.577	.02116	4.312×10^{-5}	1.1×10^{-5}	3.2×10^{-5}
9.746	.02142	3.037×10^{-5}	9.8×10^{-6}	2.1×10^{-5}
9.884	.02032	2.320×10^{-5}	8.5×10^{-6}	1.5×10^{-5}
10.096	.02130	1.656×10^{-5}	6.2×10^{-6}	1.0×10^{-5}
10.274	.01935	1.054×10^{-5}	4.4×10^{-6}	6.1×10^{-5}
10.955	.02198	3.573×10^{-6}	1.3×10^{-6}	2.3×10^{-5}
8.503	.009428	1.611×10^{-4}	3.6×10^{-5}	1.3×10^{-4}
8.573	.01021	1.807×10^{-4}	3.2×10^{-5}	1.5×10^{-4}
8.702	.01049	1.213×10^{-4}	2.75×10^{-5}	9.4×10^{-5}
8.979	.01064	6.020×10^{-5}	2.1×10^{-5}	3.9×10^{-5}
9.094	.01101	6.077×10^{-5}	1.9×10^{-5}	4.2×10^{-5}
9.227	.009318	5.082×10^{-5}	1.6×10^{-5}	3.5×10^{-5}

Two possible catalytic pathways for hydration of carbon dioxide in the presence of $\text{Zn}(\text{NH}_3)_4^{2+}$ are:



Since the intermediate carbamate would be expected to be very unstable, and thus in low concentration, the first order dependence on zinc(II) concentration would be expected if these mechanisms are involved in the catalysis. The first order dependence in pH is not as easily explained. Around pH 8.0 the dependence on pH of CO_2 concentration is in slight excess of first order, and increases to a second order dependence by pH 11. At pH greater than 10 the concentration of bicarbonate ion decreases with a first order dependence on pH, while at lower pH its dependence on pH is considerably less than first order. However, if the two processes go on simultaneously, with the former predominating at low pH and the latter at high pH, a first order dependence could result.

Some runs were also performed with Cu(II) and Co(II) under comparable conditions to those runs using Zn(II). Results are shown in Table IX for Cu(II) and Table X for (Co(II)). The catalysis from $\text{Cu}(\text{NH}_3)_4^{2+}$ is quite small while $\text{Co}(\text{NH}_3)_6^{2+}$ seems to have no effect at all. The data in Table IX and Table X are plotted in Figure VIII. This lessening of catalysis could be due to the difference in structure of the metal amino complexes. $\text{Zn}(\text{NH}_3)_4^{2+}$ is tetrahedral⁽⁵⁶⁾ while

Table IX

The rate of oxygen exchange between carbon dioxide and water in 0.1 M Na ₂ CO ₃ and 0.4 M NH ₄ Cl in the presence of copper(II). T = 24.7°C, $\mu = 0.5$		
pH	CuCl ₂ ·2H ₂ O	R
7.549	0.01255	2.268 x 10 ⁻⁴
7.683	0.01176	2.511 x 10 ⁻⁴
7.970	0.004223	7.739 x 10 ⁻⁵
8.022	0.01205	7.877 x 10 ⁻⁵
8.085	0.02587	7.225 x 10 ⁻⁵
8.410	0.01314	4.713 x 10 ⁻⁵
8.435	0.01261	4.380 x 10 ⁻⁵
8.952	0.01176	2.610 x 10 ⁻⁵

Table X

The rate of oxygen exchange between carbon dioxide and water in 0.1 M Na ₂ CO ₃ and 0.4 M NH ₄ Cl in the presence of cobalt(II). T = 24.7°C, $\mu = 0.5$		
pH	CoCl ₂ ·6H ₂ O	R
7.857	0.01063	1.027 x 10 ⁻⁴
7.042	0.01063	6.233 x 10 ⁻⁵

$\text{Co}(\text{NH}_3)_6^{2+}$ is octahedral⁽⁵⁷⁾. $\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ has a distorted octahedral structure⁽⁵⁸⁾, with the two waters not being closely bound.

$\text{Cu}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and $\text{Cu}(\text{NH}_3)_6^{2+}$ are known but not easily formed except in very concentrated ammoniacal solutions. They also have a distorted octahedral structure⁽⁵⁸⁾. The tetrahedral $\text{Zn}(\text{NH}_3)_4^{2+}$ would be expected to have the least steric hindrance for a mechanism such as has been proposed, while $\text{Co}(\text{NH}_3)_6^{2+}$ would be expected to have the most. This may be partly responsible for the observed differences in catalytic power for the three metal(II)-ammonia complexes considered. Johansen and Faurholt⁽⁴¹⁾ have shown in a previous investigation that $\text{Cu}(\text{NH}_3)_4^{2+}$ has some catalytic effect, although much less than $\text{Zn}(\text{NH}_3)_4^{2+}$, whereas $\text{Co}(\text{NH}_3)_6^{2+}$ was found to have no effect, in agreement with the results of this work.

3 - 3 THE EFFECT OF METAL-EDTA COMPLEXES ON THE RATE OF OXYGEN EXCHANGE BETWEEN CARBON DIOXIDE AND WATER

In Section 3 - 2 catalysis of the oxygen exchange between carbon dioxide and water in carbonate solutions containing ammonia and either zinc(II) or copper(II) was studied. The observed increase in exchange rate in these systems was explained by the catalytic action of $\text{Zn}(\text{NH}_3)_4^{2+}$ and $\text{Cu}(\text{NH}_3)_4^{2+}$ on the hydration of carbon dioxide. It was decided to determine whether any catalysis was observable in the presence of metal-EDTA complexes for which the inner co-ordination sphere of the metal is markedly different.

In preparation for a study on the catalytic effect of metal-EDTA complexes on the rate of oxygen exchange between carbon dioxide and water, a series of runs were performed in sodium carbonate solutions

RATE OF OXYGEN EXCHANGE, $\text{mol l}^{-1} \text{s}^{-1}$

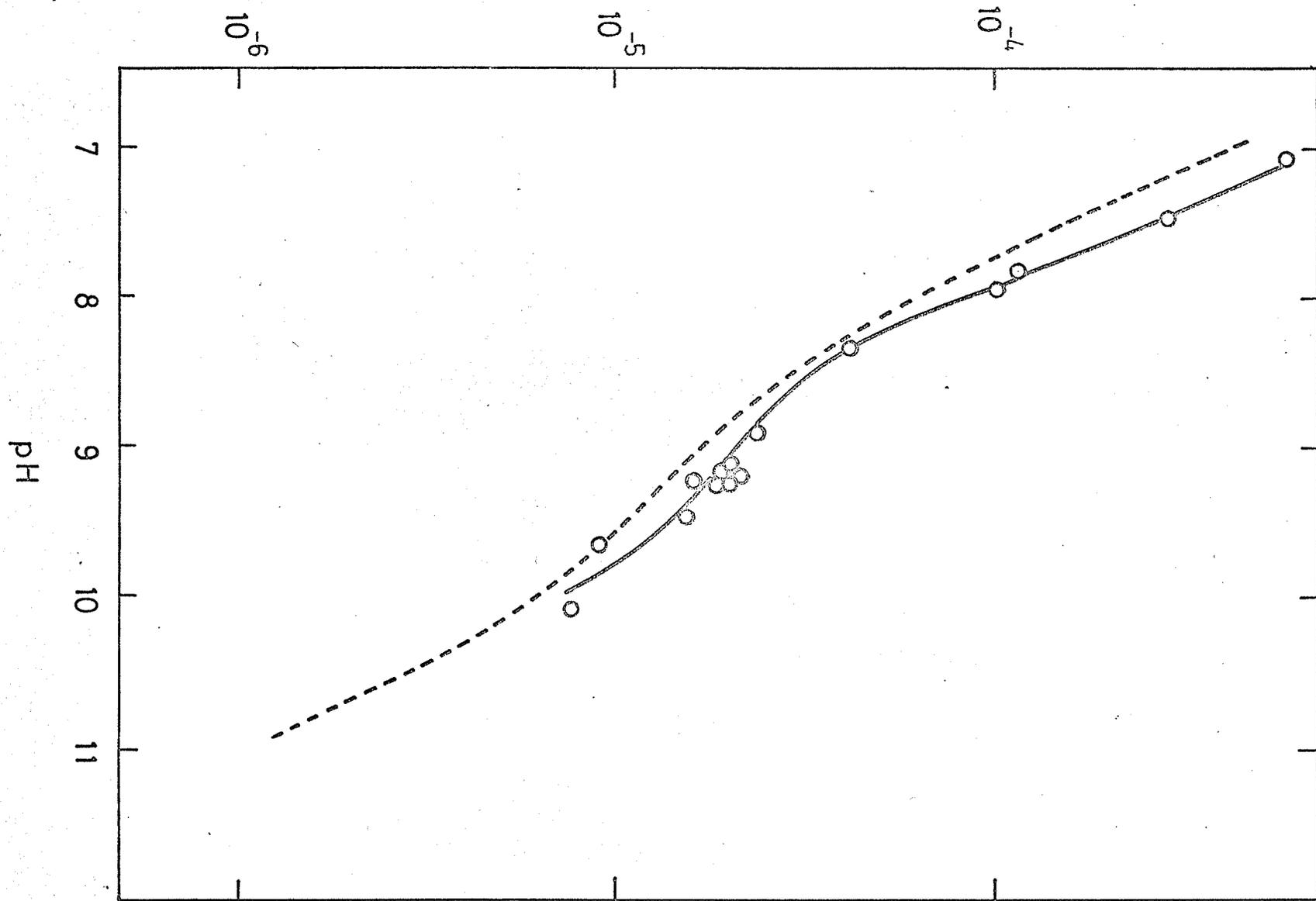


FIGURE X

Rate of oxygen exchange between CO_2 and water at 24.7°C in $0.1 \text{ M Na}_2\text{CO}_3$ solution with $0.1 \text{ M Na}_2\text{EDTA}$ (μ in the vicinity of 0.5) compared with comparable results from this work with no Na_2EDTA added.

○ Na_2EDTA added
----- no Na_2EDTA added

in the presence of Na_2EDTA . In all cases the solutions were 0.1 M in Na_2CO_3 and 0.1 M in Na_2EDTA . In a few cases 0.15 M NH_4Cl was added as a pH buffer but since the pH was already well buffered because of the presence of Na_2EDTA , it was not added in all cases. No particular care was taken to maintain a constant ionic strength (although variations from trial to trial would be small) since it has been shown that the rate of oxygen exchange does not vary greatly with small variations in ionic strength (Figure II, Section 3 - 1). Results are shown in Table XI.

Figure X shows a comparison of the exchange rate in the presence of Na_2EDTA (Table XI) with the data in Table II, Section 3 - 1 where no deliberately added catalyst was present. It would appear that there is some barely observable catalysis at $\text{pH} \leq 8$, but none at higher pH. Perhaps this is an indication that simple hydration is catalyzed slightly while the base catalyzed process which predominates at higher pH is not. It is best not to place any importance on this apparent catalysis however, since its magnitude is so small as to approach the experimental error involved in the rate determinations.

The first metal-EDTA complex considered was that of zinc(II). As is the case for most metal-EDTA complexes, the zinc(II) complex is extremely stable (formation constant 2×10^{16} (60)). Thus, in the presence of excess Na_2EDTA it is apparent that all the zinc(II) present is complexed. The rate of oxygen exchange in solutions 0.1 M in Na_2CO_3 and 0.1 M in Na_2EDTA containing 0.05 M ZnCl_2 was studied over a range of pH as shown in Table XII. Comparison of the rates attained in this study with the data in Table XI shows that the increase in exchange rate is merely about 10%. This amount of change in the rate

Table XI

The rate of oxygen exchange between carbon dioxide and water in 0.1 M Na ₂ CO ₃ solution with 0.1 M Na ₂ EDTA added. Temperature 24.7°C, is not controlled.			
pH	R(ml ⁻¹ s ⁻¹)	pH	R(ml ⁻¹ s ⁻¹)
7.105	5.891 x 10 ⁻⁴	9.190	2.067 x 10 ⁻⁵
7.534	2.872 x 10 ⁻⁴	9.195	1.931 x 10 ⁻⁵
* 7.831	1.156 x 10 ⁻⁴	* 9.230	1.654 x 10 ⁻⁵
* 7.965	1.006 x 10 ⁻⁴	9.260	1.843 x 10 ⁻⁵
* 8.320	4.110 x 10 ⁻⁵	9.474	1.500 x 10 ⁻⁵
* 8.914	2.324 x 10 ⁻⁵	9.765	9.841 x 10 ⁻⁶
* 9.104	2.003 x 10 ⁻⁵	10.108	7.534 x 10 ⁻⁶
9.152	1.947 x 10 ⁻⁵		

* -0.15 M NH₄Cl added

Table XII

The rate of oxygen exchange between carbon dioxide and water in 0.1 M Na ₂ CO ₃ solution with 0.1 M Na ₂ EDTA and 0.05 M ZnCl ₂ added. Temperature 24.7°C, is not controlled			
pH	R(ml ⁻¹ s ⁻¹)	pH	R(ml ⁻¹ s ⁻¹)
7.769	1.596 x 10 ⁻⁴	9.328	1.382 x 10 ⁻⁵
8.270	5.535 x 10 ⁻⁵	9.377	1.885 x 10 ⁻⁵
8.578	4.074 x 10 ⁻⁵	9.611	1.768 x 10 ⁻⁵
8.974	2.682 x 10 ⁻⁵	9.623	1.726 x 10 ⁻⁵
9.174	2.534 x 10 ⁻⁵		

RATE (CuII-EDTA) — RATE (EDTA only)
(mol l⁻¹ s⁻¹)

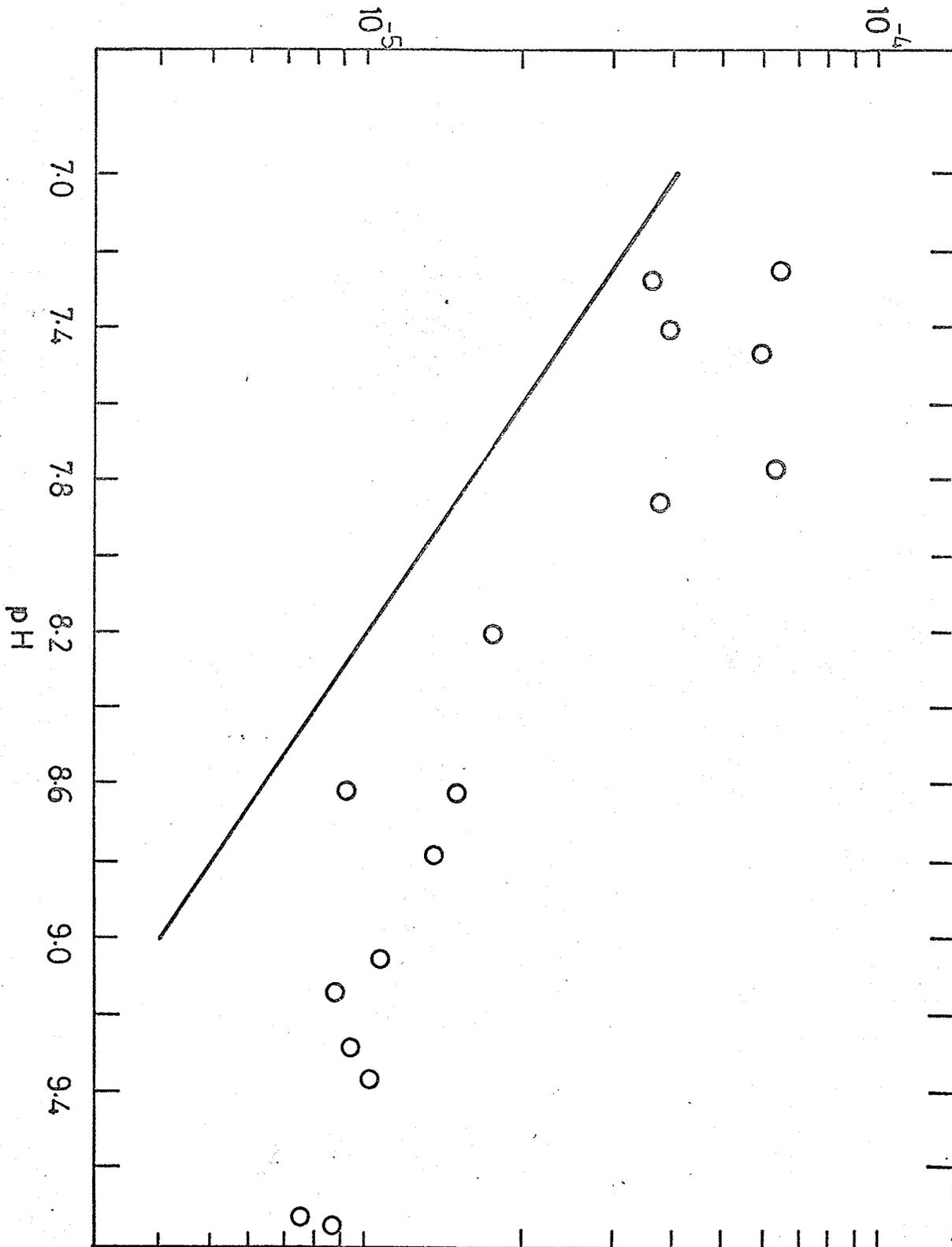


FIGURE XI

Dependence on pH of that portion of the overall exchange rate attributable to catalysis by Cu(II)-EDTA at 24.7°C, 0.1 M Na₂CO₃.



0.05 M Cu(II),
0.1 M Na₂EDTA



plot of half-order dependence
on pH

is hardly significant, and it is probably best to consider the exchange rate to be unchanged.

The rate of oxygen exchange between carbon dioxide and water in 0.1 M Na_2CO_3 solutions containing 0.1 M Na_2EDTA and 0.05 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was also determined over a range of pH. The copper(II)-EDTA complex is extremely stable (formation constant 6×10^{18} (60)) and thus all the copper(II) present may be assumed to be complexed. Results are shown in Table XIII. The catalysis in this case is of the order of 50%, large enough to be considered real, although not large enough to be of great interest. When the rate of exchange between carbon dioxide and water in the absence of copper(II) but in the presence of 0.1 M Na_2EDTA (Figure X) is subtracted from the total rates (at the same pH) listed in Table XIII, and the resulting difference is plotted against pH (Figure XI), it turns out that the catalytic contribution from the presence of the Cu(II)-EDTA complex has a half order dependence on the concentration of hydrogen ion. Because of the low magnitude of the catalysis no attempt was made to establish whether there was any dependence on complex concentration.

A few trials were also performed in 0.1 M Na_2CO_3 , 0.1 M Na_2EDTA , and 0.05 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The Co(II)-EDTA complex is extremely strong (formation constant 2×10^{16} (60)) and all the cobalt(II) present may be assumed to be complexed. Results are shown in Table XIV. There is no measurable increase in the exchange rate in these trials.

One run was done where 0.05 M HgCl_2 was added to a solution 0.1 M in sodium carbonate and 0.1 M in Na_2EDTA at pH 8.530 (formation constant $\text{Hg(II)-EDTA} = 10^{22}$ (60)). The rate obtained for oxygen

Table XIII

R is the rate of oxygen exchange between carbon dioxide and water in 0.1 M Na₂CO₃ solution with 0.1 M Na₂EDTA and 0.05 M CuCl₂·2H₂O added.
R' is the rate in the absence of CuCl₂·2H₂O from Figure X.

pH	R(ml ⁻¹ s ⁻¹)	R'(ml ⁻¹ s ⁻¹)	R - R'
7.147	6.045 x 10 ⁻⁴	5.4 x 10 ⁻⁴	6.5 x 10 ⁻⁵
7.172	5.560 x 10 ⁻⁴	5.2 x 10 ⁻⁴	3.6 x 10 ⁻⁵
7.311	4.270 x 10 ⁻⁴	3.9 x 10 ⁻⁴	3.7 x 10 ⁻⁵
7.365	3.999 x 10 ⁻⁴	3.4 x 10 ⁻⁴	6.0 x 10 ⁻⁵
7.675	2.385 x 10 ⁻⁴	1.75 x 10 ⁻⁴	6.4 x 10 ⁻⁵
7.759	1.782 x 10 ⁻⁴	1.4 x 10 ⁻⁴	3.8 x 10 ⁻⁵
8.102	8.378 x 10 ⁻⁵	6.6 x 10 ⁻⁵	1.8 x 10 ⁻⁵
8.533	4.201 x 10 ⁻⁵	3.3 x 10 ⁻⁵	9.0 x 10 ⁻⁶
8.538	4.811 x 10 ⁻⁵	3.3 x 10 ⁻⁵	1.5 x 10 ⁻⁵
8.634	4.461 x 10 ⁻⁵	3.1 x 10 ⁻⁵	1.4 x 10 ⁻⁵
8.939	3.421 x 10 ⁻⁵	2.35 x 10 ⁻⁵	1.1 x 10 ⁻⁵
9.064	3.063 x 10 ⁻⁵	2.2 x 10 ⁻⁵	8.6 x 10 ⁻⁶
9.181	2.998 x 10 ⁻⁵	2.05 x 10 ⁻⁵	9.5 x 10 ⁻⁶
9.267	2.758 x 10 ⁻⁵	1.75 x 10 ⁻⁵	1.0 x 10 ⁻⁵
9.613	1.985 x 10 ⁻⁵	1.25 x 10 ⁻⁵	7.4 x 10 ⁻⁶
9.643	2.125 x 10 ⁻⁵	1.25 x 10 ⁻⁵	8.8 x 10 ⁻⁶

Table XIV

The rate of oxygen exchange between carbon dioxide and water in 0.1 M Na₂CO₃ solution with 0.1 M Na₂EDTA and 0.05 M CoCl₂·6H₂O added.

pH	R(ml ⁻¹ s ⁻¹)
7.518	2.135 x 10 ⁻⁴
7.999	9.883 x 10 ⁻⁵
8.531	3.446 x 10 ⁻⁵
9.081	2.123 x 10 ⁻⁵
9.591	1.385 x 10 ⁻⁵

exchange was $6.11 \times 10^{-5} \text{ ml}^{-1} \text{ s}^{-1}$ which is an increase of about 30% from the rate at the same pH taken from Figure X.

Two runs were performed with solutions 0.095 M in $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M in Na_2CO_3 and 0.1 M in Na_2EDTA (formation constant for Ni(II)-EDTA = 4×10^{18} (60)). At pH 7.668 the rate of exchange was $1.56 \times 10^{-4} \text{ ml}^{-1} \text{ s}^{-1}$ and at pH 8.241 the rate was $5.889 \times 10^{-5} \text{ ml}^{-1} \text{ s}^{-1}$. These results would seem to indicate no appreciable catalysis by Ni(II)-EDTA.

Thus, from the results discussed in this section, it would appear that the presence of metal-EDTA complexes results in, at most, only a moderate increase in the rate of exchange of carbon dioxide and water. In many cases there appears to be no catalysis at all.

3 - 4 THE EFFECT OF URANYL-CARBONATO COMPLEXES ON THE RATE OF OXYGEN EXCHANGE BETWEEN CARBON DIOXIDE AND WATER

Uranyl compounds are well known to be very soluble in carbonate solutions, indicating the formation of stable complex ions. (61-66) Haldar (62) observed discontinuities in conductometric titrations of uranyl nitrate with carbonate solutions at points corresponding to carbonate:uranyl mole ratios of 3:1 and 2:1. Blake et al (63), from solubilities and spectrophotometric measurements have obtained evidence for the existence of $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, with an estimate of the stability of the latter, as well as for an additional complex ion having the molar ration $\text{CO}_2:\text{U}$ of 0.5. A recent review article on the chemistry of metal carbonate complexes by Krishnamurty et al (36) lists a number of uranyl-carbonato complexes including $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{CO}_3)_2(\text{OH})_2]^{4-}$. According to this review article, the stability constants of the former two complex ions were

determined by Babko and Kodenskaya⁽⁶⁴⁾ from a solubility study in which they account for the solubility of $\text{UO}_2(\text{OH})_2$ ($K_{\text{sp}} = 1.8 \times 10^{-22}$) in aqueous carbonate solutions at pH 7 - 9 in terms of $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, while evidence for $[\text{UO}_2(\text{CO}_3)_2(\text{OH})_2]^{4-}$ was obtained from a polarographic study by Strabrovskii⁽⁶⁵⁾.

In order to study the effect of different uranyl:carbonate ratios on the rate of oxygen exchange between carbon dioxide and water, various amounts of uranyl nitrate were introduced into solutions 0.1 M in sodium carbonate. The sodium carbonate used in these solutions was initially enriched in oxygen-18; while the water was of "normal" isotopic abundance. Carbon dioxide samples for analysis were obtained in the usual manner by adding concentrated sulfuric acid to aliquots of the solution at various timed intervals. Ammonium chloride (about 0.4 M) was also present in solution in order to buffer the pH. The desired pH was attained by adding the required amount of concentrated hydrochloric acid or potassium hydroxide.

Results are shown in Table XV. As the amount of uranyl ion in solution is increased with respect to total carbonate concentration, the half-life for exchange at a particular pH increases (i.e., the rate of oxygen exchange between carbon dioxide and water decreases). From Figure VII in Section 3 - 1, the rate of oxygen exchange between carbon dioxide and water should be largely due to processes first order in total carbonate concentration in the pH range 7 - 9, which is the pH range in which the effect of uranyl carbonate complex ions on the oxygen exchange rate was studied. Thus, one would expect little change in the half-life for oxygen exchange in this pH region as the total carbonate concentration decreases, since $t_{\frac{1}{2}}$ should be independent of

Table XV

Comparison of $t_{1/2}$ for oxygen exchange between carbon dioxide and water in sodium carbonate solutions in the presence of uranyl ions and in the absence of uranyl ions. The number of carbonates per uranyl ion, calculated from these half-lives, is also shown.
Temperature 24.7°C.

pH	$[UO_2^{2+}]$ M.	$[Na_2CO_3]$ M.	$t_{1/2}$ (minutes)	$t_{1/2}$ (minutes)		
				no UO_2^{2+} added	$[CO_3^{2-}]$ COM.	$\frac{[CO_3^{2-}]_{COM.}}{UO_2^{2+}}$
8.474	0.01001	0.1007	145	96	0.0341	3.41
8.494	0.01023	0.9764	160	99	0.0359	3.51
8.678	0.01070	0.09987	199	124	0.0377	3.53
8.691	0.01063	0.09982	234	128	0.0450	4.24
8.697	0.01014	0.1038	192	126	0.0380	3.75
8.778	0.01027	0.09741	213	142	0.0363	3.54
8.794	0.01003	0.1015	200	144	0.0298	2.97
9.045	0.01055	0.09940	296	200	0.03179	3.01
7.705	0.02028	0.1016	116	29	0.07549	3.72
7.985	0.02065	0.1027	172	48	0.97465	3.62
8.096	0.02101	0.1010	206	57	0.07346	3.50
8.267	0.02106	0.1042	260	75	0.07553	3.59
8.379	0.02050	0.1016	291	83	0.07326	3.57
8.450	0.02058	0.1001	285	94	0.06718	3.26
8.487	0.02006	0.09925	290	96	0.06599	3.29
7.573	0.03190	0.09869	311	22	0.09149	2.87
7.828	0.02970	0.1008	465	44	0.09125	3.07
8.395	0.03185	0.1008	1390	89	0.09442	2.97

$[CO_3^{2-}]_{COM.}$ is the concentration of carbonate associated with UO_2^{2+} in the uranyl carbonate complex calculated from the half-lives above. $t_{1/2}$ in the absence of uranyl carbonate complex ions is calculated from Figure II, Section 3 - 1.

carbonate concentration. However, contrary to the expected results, a large increase in the half-life for exchange is observed. This leads to the following postulates:

- (1) assume that those carbonate ions involved in a uranyl-carbonato complex ion are inert to oxygen exchange with water.
- (2) assume that those carbonate ions involved in the uranyl-carbonato complex ions exchange freely with the remaining carbonate ions in solution, i.e., over a finite period of time each carbonate ion in the system is involved in a uranyl-carbonato complex ion for the same length of time as any other carbonate ion.

Using the above postulates, and assuming that the oxygen exchange between carbon dioxide and water is carried out chiefly by processes first order with respect to total carbonate concentration (equations (26) and (28), Section 1 - 4), the following derivation is valid. Recall

$$R = -\ln(1-F) \frac{nab}{(na+b)t} \quad (18)$$

In our system a is the number of moles of carbonate per liter (0.1), b is the number of moles of water per liter (55.5), and n equals 3. Since $b \gg a$, equation (18) becomes

$$R' = -3\left(\frac{1}{t} [\text{CO}_3^{2-}]_T \ln(1-F)\right) \quad (52)$$

where $[\text{CO}_3^{2-}]_T$ is the total carbonate concentration. Also, if the exchange between carbon dioxide and water occurs through processes first order in total carbonate concentration, in the presence of uranyl ions the following relationship holds:

$$R' = k_1 [\text{CO}_2]_F + k_2 [\text{CO}_2]_F [\text{OH}^-] + k_3 [\text{UO}_2^{2+} \dots] \quad (53)$$

where $[\text{CO}_2]_F$ is the concentration of carbon dioxide in solution (which is proportional to the amount of uncomplexed carbonate ion in solution), and $k_3 [\text{UO}_2^{2+} \dots]$ is the rate of exchange of the oxygens in the carbonate

ions involved in the uranyl-carbonato complex ions with water. Since $k[\text{UO}_2^{2+} \dots]$ has been assumed to be zero

$$R' = k_1[\text{CO}_2]_F + k_2[\text{CO}_2]_F[\text{OH}^-] \quad (54)$$

In the absence of uranyl ion:

$$R = -3\left(\frac{1}{t} [\text{CO}_3^{2-}]_T \ln(1-F)\right) \quad (55)$$

$$R = k_1[\text{CO}_2]_T + k_2[\text{CO}_2]_T[\text{OH}^-] \quad (56)$$

where $[\text{CO}_2]_T$ is proportional to the total amount of carbonate present in the system. Divide equation (54) into equation (56)

$$\frac{R}{R'} = \frac{[\text{CO}_2]_T (k_1 + k_2[\text{OH}^-])}{[\text{CO}_2]_F (k_1 + k_2[\text{OH}^-])} \quad (57)$$

Where the pH is the same in each case,

$$\frac{R}{R'} = \frac{[\text{CO}_2]_T}{[\text{CO}_2]_F} = \frac{[\text{CO}_3^{2-}]_T}{[\text{CO}_3^{2-}]_F} \quad (58)$$

Dividing equation (52) into equation (55) gives

$$\frac{R}{R'} = \frac{t'}{t} \quad (59)$$

for the same value of F. Equating equation (58) and equation (59)

$$\frac{t'}{t} = \frac{[\text{CO}_3^{2-}]_T}{[\text{CO}_3^{2-}]_F} \quad (60)$$

where t' is the exchange time in the presence of uranyl ion and t is the time required for the same fraction of exchange in the absence of uranyl ion.

From equation (60) it is possible to compute the amount of carbonate involved in the uranyl carbonate complex ions where the

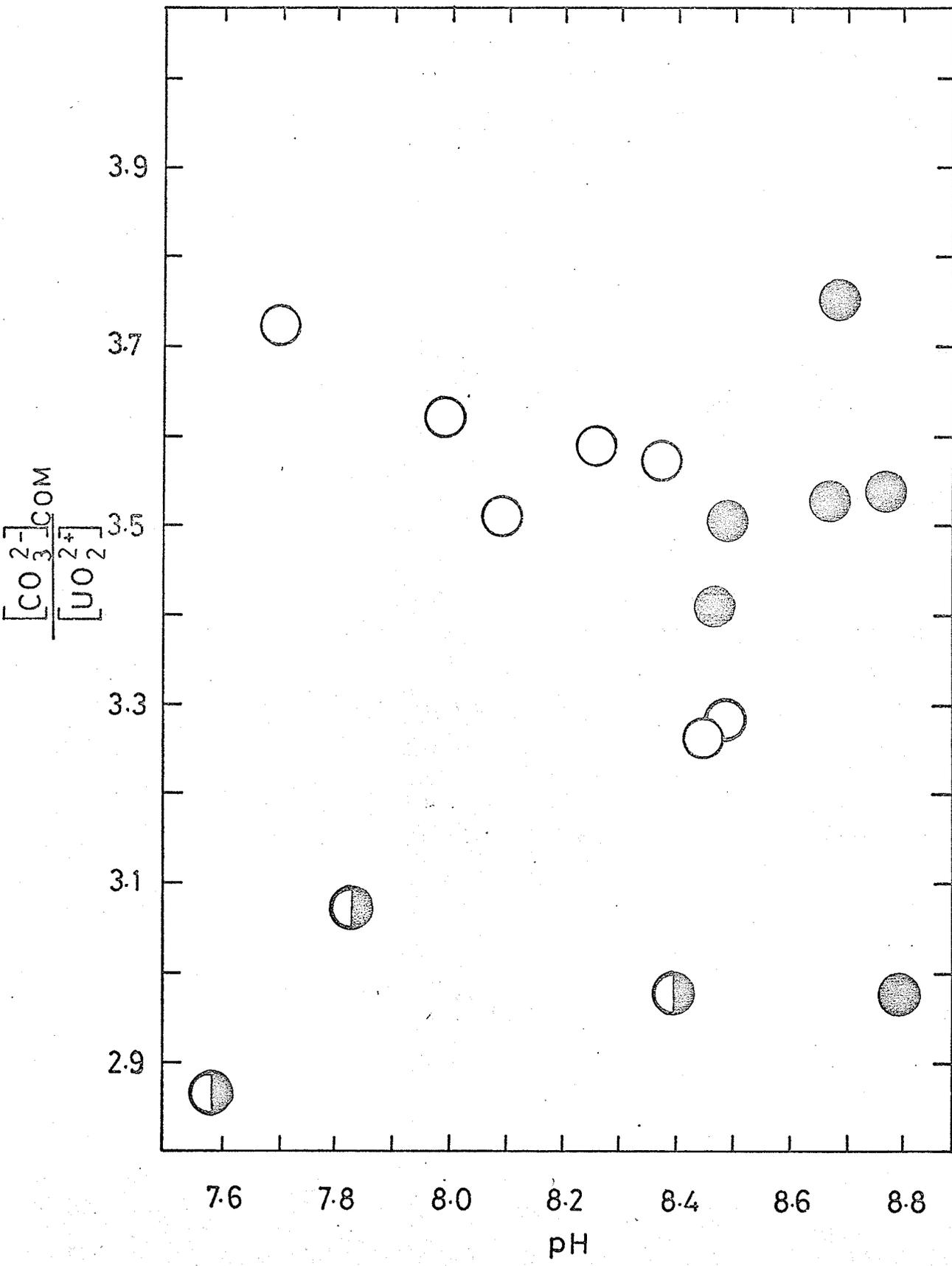


FIGURE XII

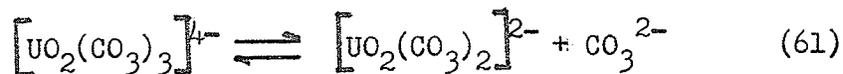
The dependence on pH of the number of carbonate ligands per uranyl ion involved in the uranyl carbonate complexes.

$T = 24.7^{\circ}\text{C}$, $[\text{Na}_2\text{CO}_3] = 0.1 \text{ M}$

- 0.01 M UO_2^{2+} ($\text{UO}_2^{2+}:\text{CO}_3^{2-} = 1:10$)
- ◐ 0.03 M UO_2^{2+} ($\text{UO}_2^{2+}:\text{CO}_3^{2-} = 1:3.3$)
- 0.02 M UO_2^{2+} ($\text{UO}_2^{2+}:\text{CO}_3^{2-} = 1:5$)

half-life for exchange in the presence of uranyl ion is known as well as the half-life for exchange in the absence of uranyl ion, all other experimental conditions being equal. From this value the average number of carbonate ligands associated with each uranyl carbonate complex ion may be readily computed. Results are shown in Table XV.

Figure XII shows a plot of the number of carbonate ligands per uranyl-carbonato complex ion, against pH for various uranyl ion concentrations, the concentration of total carbonate being held constant at 0.1 M. Despite the scattering prevalent in this plot, it is quite apparent that at a given pH, as the uranyl:carbonate ratio increases the average number of carbonate ligands involved in the uranyl carbonate complex ions decreases. There would thus appear to be more than one type of complex ion present, in equilibrium with each other, in solution. Blake et al⁽⁶³⁾ established the existence of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ in aqueous solution. For the equilibrium

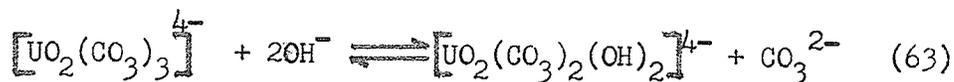


they claim

$$K = \frac{[\text{UO}_2(\text{CO}_3)_2]^{2-} [\text{CO}_3^{2-}]}{[\text{UO}_2(\text{CO}_3)_3]^{4-}} = 3 \times 10^{-4} \quad (62)$$

where K is the stability constant for $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ at ionic strength 2 and 25°C.

Although a definite trend is difficult to establish, it does not appear too unreasonable to postulate from Figure XII that as the pH of the solution increases, the average number of carbonate ligands associated with the uranyl-carbonato complex ions decreases. If this apparent trend is real, it may be due to the displacement of a carbonate ligand by hydroxide ions:



Evidence for the existence of $\left[\text{UO}_2(\text{CO}_3)_2(\text{OH})_2 \right]^{4-}$ has been obtained by Stabrovskii⁽⁶⁵⁾ using polarography. It was found in this laboratory that the addition of uranyl ion in excess of that required to give a uranyl:carbonate ratio of 1:3 caused a sharp drop in pH, consistent with the formation of $\left[\text{UO}_2(\text{CO}_3)_2(\text{OH}^-)_2 \right]^{4-}$ from $\left[\text{UO}_2(\text{CO}_3)_3 \right]^{4-}$.

The number of carbonate ligands per uranyl-carbonato complex ion was consistently calculated to be greater than three. There would appear to be two possible reasons for this. One possible explanation is that in addition to the three carbonate ions associated with the complex ion, other carbonate ions positioned in close proximity to the complex may be sufficiently altered in nature to also be unable to exchange their oxygens with water. An alternate explanation, which is really just an extreme case of the previous one, is that a uranyl-carbonato complex ion containing more than three carbonate ligands may exist in solution in equilibrium with $\left[\text{UO}_2(\text{CO}_3)_3 \right]^{4-}$.

It would appear from the data accumulated in this work that the mechanism for oxygen exchange between carbon dioxide and water must include some pathways to exchange in addition to simple hydration and base catalyzed hydration over the pH range 7-11. The three processes second order in total carbonate postulated by Poulton and Baldwin⁽¹⁶⁾, when combined with the two previously mentioned processes, have been found to adequately predict the exchange rate over this pH range.

The catalysis of the oxygen exchange between carbon dioxide and water by $\text{Zn}(\text{NH}_3)_4^{2+}$, $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Co}(\text{NH}_3)_6^{2+}$ was examined. $\text{Zn}(\text{NH}_3)_4^{2+}$ was found to have the greatest catalytic power, while $\text{Co}(\text{NH}_3)_6^{2+}$ did not alter the exchange rate noticeably and $\text{Cu}(\text{NH}_3)_4^{2+}$ proved to be a weak catalyst. The differences in the catalytic effect of these complexes may be related to their differing structures.

A number of metal-EDTA complexes were also examined as possible catalysts for the oxygen exchange between carbon dioxide and water. In a few cases slight catalysis was observed, but in all cases the effect was very small.

UO_2^{2+} was dissolved in various known amounts in 0.1 M Na_2CO_3 solutions in order to determine how the resulting carbonate complexes would alter the exchange rate. It was found that the rate of exchange was made much slower, and this was interpreted by assuming that the carbonate ions involved in the uranyl-carbonate complexes were inert to oxygen exchange, although interchanging freely with the carbonate ions unassociated with these complexes. From the magnitude of the slowdown in the exchange rate the stoichiometry of these complexes was determined.

APPENDIX

Table XVI

Data for a representative run from Section 3 - 1. Temperature was 24.7°C, pH 10.53, $[\text{CO}_3^{2-}]_T$ 0.1 M, and $\mu \approx 0.5$.				
Aliquot No.	Time (min.)	p-factor	1-F	$-\log_{10}(1-F)$
1	101	.02155	0.9246	0.0341
2	244	.02016	0.8518	0.0697
3	366	.01905	0.7936	0.1004
4	518	.01770	0.7229	0.1410
5	1472	.01153	0.3997	0.3982
6	1721	.01046	0.3436	0.4640

Data for one of the trials listed in Table II, Section 3 - 1 are shown in Table XVI above. Recall that F, the fraction of exchange is given by

$$F = \frac{p_t - p_o}{p_{\infty} - p_o}$$

Thus

$$1-F = \frac{p_t - p_{\infty}}{p_o - p_{\infty}}$$

where p_o is the initial p-factor for the labelled sodium carbonate (0.02299 in this case), and p_{∞} is the p-factor for the sodium carbonate at isotopic equilibrium (measured to be 0.00390 after nine half-lives). A plot of $-\log_{10}(1-F)$ against time is shown in Figure XIII. An analysis of the data by a least-squares program in the Hewlett-Packard Calculator Model 9100A gave a slope of $2.679 \pm 0.015 \times 10^{-4}$ and an intercept of $4.4 \pm 1.0 \times 10^{-3}$. The half-life for the exchange process was determined

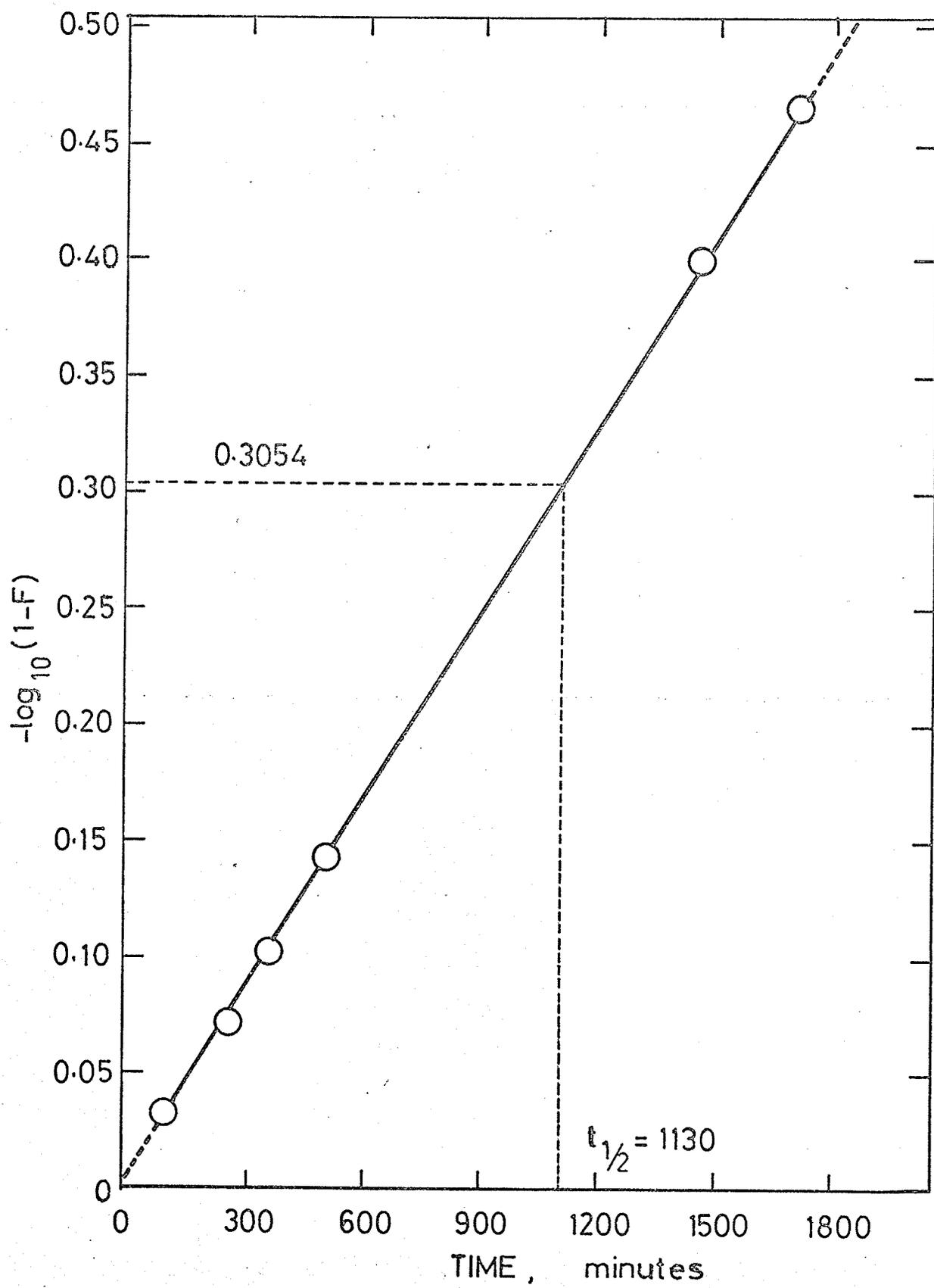


FIGURE XIII

The plot of $-\log_{10}(1-F)$ vs. time for a
representative run from Section 3 - 1.

pH = 10.53, $\mu = 0.5$, $[\text{Na}_2\text{CO}_3] = 0.1 \text{ M}$.

by dividing the slope into $-\log_{10}(1 - 0.5)$, and was found to be 1130 minutes. This method is valid providing that induced exchange arising from the separation procedure does not affect the slope of the plot. Even when the cause of the induced exchange is not understood Prestwood and Wahl⁽⁵⁹⁾ have shown that when the effects are reproducible and consistent techniques are employed throughout, the effects may be eliminated. Defining F as the fraction of exchange at time t prior to separation, F' as the fraction of exchange at time t after separation, F_0 as the fraction of exchange after separation at time zero, p_t as the p -factor at time t , p_0 as the p -factor at zero time, and p_{∞} as the p -factor at isotopic equilibrium, they show that:

$$F = \frac{p_t - p_0}{p_{\infty} - p_0} = \frac{F' - F_0}{1 - F_0} \quad (64)$$

During experiment, F' and F_0 are the quantities actually being measured. F_0 may be obtained by a separation immediately after mixing. If a value for F_0 is found and F is calculated as above, the points will be on an exchange curve passing through $(1-F) = 1$ at time zero. Recall

$$Rt = \frac{-ab}{(a+b)} \ln(1-F) \quad (15)$$

Substituting the expression for F into this equation gives the following result:

$$\ln(1-F) = \frac{a+b}{ab} Rt + \ln(1-F_0) \quad (65)$$

which is the expression which results when uncorrected points are used. By comparing this expression with equation (15) it is evident that the slopes for the corrected and uncorrected curves would be unchanged, vindicating the method used in this work for computing $t_{\frac{1}{2}}$.

It is usual to use uncorrected curves (as was done in this study) with the extent of the induced exchange being found by the magnitude of the intercept on the vertical axis. By substituting the value for the half-life and the value for $\ln(1-F)$ at the half-life into equation (15) the rate of exchange is found.

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