PRELIMINARY INVESTIGATIONS OF $CaCO_3$ NUCLEATION IN PRECIPITATION REACTIONS FROM QUASI-HOMOGENEOUS SOLUTION

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TO JENNY
WITH EQUAL PARTS
OF LUST AND LOVE

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ABSTRACT

An analysis of reported and theoretical methods of precipitating calcium carbonate from aqueous solution is presented, with emphasis on methods that generate the anion in the presence of Ca(++) ion.

A new $CaCO_3$ precipitation method referred to as precipitation from quasi-homogeneous solution and suitable for digital processor control is developed. This technique is then used to investigate the effects of ionic strength and Mg(++) ion on calcium carbonate nucleation.

A minicomputer based interactive information system, capable of automatic data logging and processing of experimental results in studies using processor controlled precipitation of $CaCO_3$ from quasi-homogeneous solution, is implemented and tested.

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PART I

INTRODUCTION

The factors controlling the crystallization of calcium carbonate are of considerable importance in industrial, geochemical and metabolic processes. For instance:

1. In heat exchange technology (6) the formation of calcium carbonate scale on heat transfer surfaces can occasion a change in flow pattern and/or heat exchange efficiency. This applies directly to desalination and water cooled systems.
2. Though surface sea waters are supersaturated with calcium carbonate (42,50), the only marine calcium carbonate precipitated is that which originates from shell forming organisms. Calcium carbonate is 100 times more soluble in sea water than in pure water.
3. The conditions leading to the formation of dolomite ($CaMg(CO_3)_2$) are unknown (43). The transformation of aragonite to calcite (both are $CaCO_3$ polymorphs) may play a role in the dolomitization process. Dolomitization generates a carbonate rock with improved capillary properties; this rock is commonly an oil reservoir or host for ore mineral deposits.
4. Agronomically, $CaCO_3$ precipitation, while reducing the total salt load of the water, can increase the sodium hazard of the water when used for irrigation purposes (15).

5. The conditions controlling the deposition and solution of the mineral matter of tooth and bone (17,26) involve supersaturation as well as the adsorption of various ions upon an underlying crystal lattice.

A simple interpretation of calcification in terms of solubility is not sufficient; What is the effect of divalent metal ions other than Ca^{++} upon calcification?

I.A. Previous Work

Efforts to study the effect of foreign ions on calcification have centered around two approaches:

(i) Interactions with the formation or growth of the solid phase.
(ii) Interactions with calcium carbonate in the solution phase.

I.A.1. Solid Phase Studies

Calcium carbonate was the first substance discovered to exhibit the phenomena of existing in different crystal forms.† Subsequent studies established the existence of three distinct crystal structures which bear the mineralogical names calcite, aragonite and vaterite. The occurrence of the latter is very rare in nature but calcite and aragonite are found

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† In 1788 Klaproth (see Mellor, 1923, p. 814) suggested that calcite and a new mineral from Spain had identical chemical compositions. This was in conflict with the law of constancy of interfacial angles derived from the work of Steno in 1669 and that of de L'isle in 1772 (see Phillips, 1956) which stated that "in all crystals of the same substance the angles between corresponding faces have a constant value".

both as pure phases and in intimate mixtures with each other in sedimentary rocks, cave deposits and marine shells.

The awareness of polymorphism brought about many early studies in which the goal was to develop recipes for growing each of the polymorphs in its pure phase. The task was arduous because in the presence of the mother solution a quick distribution of the crystal habits would occur. It has only been recently that pure large vaterite crystals were finally formed (54).

The voluminous writings on calcite and aragonite date back to the end of the 18th century. Dedik (1966) provides an extensive bibliography in his book dealing with studies on $CaCO_3$ during the period 1819 to 1956. Goto (1961), Ingerson (1962) and Curl (1962) review much of the literature in their studies concerning the calcite-aragonite problem. A brief sketch of the more significant work follows.

Rose (1837) first recognized that precipitating $CaCO_3$ at temperatures above 30°C favored the formation of aragonite. Credner (1870) observed that solutions containing strontium, barium and plumbous ion also had a similar tendency. Leitmeier (1910) first recognized the influence of magnesium ion in favoring the formation of aragonite. Weyl (1961) concluded that Mg^{++} inhibits calcium carbonate formation by interactions at the solid-liquid interface. Kitano (1962) found that solutions of the alkali halides and nitrates, bicarbonate ion and calcium ion favored calcite formation. Pytkowitz (1965) reported that aragonite nucleation rates were decreased by the presence of magnesium ion. Akin and Lagerwerff (1965) reported an enhancement of the solubility of $CaCO_3$ precipitating from supersaturated solutions in the presence of Mg^{++}. Bischoff (1966) found that Mg^{++} inhibited the diagenetic aragonite to calcite transformation by reacting with calcite nuclei. Packter (1968) determined $CaCO_3$ nucleation and growth rates as a function of supersaturation. Silk (1970) elucidated the factors which control phase formation and growth in the calcium carbonate system. Nancollas and Reddy (1971) studied the crystallization kinetics of calcium carbonate.

I.A.2. Solution Phase Studies

The formation of ion pairs by foreign ions with $CO_3^{=}$, HCO_3^{-} and OH^{-} ions would increase the amount of $CaCO_3$ which could dissolve and lessen the amount which would precipitate when compared to a system without such ion pairs. Nakayama (1968), using specific ion electrodes, found that in saturated $CaCO_3$ solutions under atmospheric conditions, 20% of the Ca^{++} ion in solution exists as ion-pair, with $CaCO_3^{\circ}$ being the predominant species. Greenwald (1941), Garrels and Christ (1965), Davies (1962) and others have also shown that Mg^{++} ion can react to form ion pairs having the same effect on carbonate equilibria as the Ca^{++} ion pairs. In contrast, however, Hasegawa _et al._ (1970) using a liquid-liquid distribution method reported that the concentration of carbonate complexes in $CaCO_3$ solutions is negligibly small.

I.A.3. Analysis of Precipitation Methods

The manner in which $CaCO_3$ is formed places limitations on the scope of the possible nucleation experiments. The limiting factors associated with a precipitation method are solution temperature, whether or not the presence of solid $CaCO_3$ is needed to induce precipitation, and the ability to control the level of supersaturation with respect to calcium carbonate. A survey of the methods used in the representative works mentioned in section I.A.1 shows that four main precipitation techniques are encountered:

1. Precipitation brought about by direct mixing of two solutions separately containing the cation or anion.
2. Precipitation as a result of seeding stable supersaturated $CaCO_3$ solutions.
3. Transformation of aragonite to calcite.
4. Precipitation from homogeneous solution.†

The direct mixing technique was used by Packter in his studies. Pytkowicz used a variation of this approach by adding Na_2CO_3 solutions to natural and artificial sea waters and determining the time lapsed before the onset of precipitation. This approach is subject to local inhomogeneities and provides little real time control during an experiment. The final concentrations in the working solution are fixed by the stock parent solutions. Reconciling experimental results with classical nucleation theory is not possible, for the latter assumes that supersaturation is built up homogeneously and slowly so that clusters of ions are always in a steady state (35).

Nancollas and Reddy prepared stable supersaturated solutions of $CaCO_3$ and then followed the crystallization kinetics -- after the addition of calcite seed crystals -- by monitoring calcium and hydrogen ion con-

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† PFHS is a technique whereby the precipitant is generated _in situ_ and uniformly throughout the precipitation solution.

centrations. This technique relies on the introduction of the solid phase.

In his experiments, Bischoff (3) studied the kinetics of calcite crystallization from dilute $MgCl_2$ solutions equilibrated with aragonite and atmospheric CO_2 at 108°C. (At room temperature the transformation would require from months to years to reach completion.) From graphs of per cent calcite versus time and Mg^{++} concentration Bischoff was lead to conclude that Mg^{++} ion inhibits the rate of calcite nucleation and in so doing is incorporated into the calcite nuclei. Can the same inhibition be expected to take place without the presence of solid aragonite?

The use of PFHS in calcium carbonate studies has been limited due to the lack of control over the precipitation process. In a study of coprecipitation of cations with $CaCO_3$, A. Tsusue and H. D. Holland (1965) precipitated calcite from aqueous solution by the hydrolysis of a calcium-organic-acid salt (trifluoroacetic, trichloroacetic or propionic acid). This method introduces foreign ions into the solution and is temperature bound as the hydrolysis occurs appreciably only at 50°C or higher.

Of keen interest is Kitano's use of PFHS in his minearological studies. Kitano pulverized calcium carbonate and suspended it in distilled H_2O while CO_2 gas was bubbled through the suspension for one day's time after which he filtered the solution and once more bubbled CO_2 through it for one hour. Subsequently, $CaCO_3$ formed from this calcium bicarbonate solution as CO_2 gas escaped -- a reaction which is typical in the formation of $CaCO_3$ by inorganic processes in the hydrosphere such as in thermal springs. Any attempt to control the state of $CaCO_3$ saturation would be complex indeed since this method depends on a process of non-equilibrium.

None of the described methods offers the capability of bringing about precipitation in the absence of a solid $CaCO_3$ phase and at the same time giving the experimentalist control over the solution temperature and its level of supersaturation. If control over these three variables could be made not to be mutually exclusive some interesting experiments would become feasible. One such experiment motivated the development of this desired method and is described in Part II. The experiment incorporates the use of specific ion electrodes to monitor Ca^{++} ion activity prior to the onset of precipitation.

The proper choice of precipitation method would then allow both solid phase and solution phase aspects of $CaCO_3$-Mg^{++} ion interactions to be integrated into one experiment. Solid phase aspects deal with the dehydration of reactants on the surface of the growing crystal; solution phase aspects deal with the formation of Ca^{++} and Mg^{++} ion carbonate complexes.

I.B. Statement of the Problem

Of considerable significance to precipitation studies of the calcification process is the mechanism used to bring about $CaCO_3$ precipitation. The development of a method which generates carbonate ions *in situ* at a controllable rate and temperature would greatly enhance such studies. The goal of this project was to develop such a method.

I.C. Nucleation

Precipitation involves two distinct processes: nucleation and crystal growth. Nucleation is that process which results in the formation of the first particles of precipitate capable of continued growth. These centers of crystallization may occur spontaneously (homogeneous nucleation) or form upon minute foreign contaminants (heterogeneous nucleation). Subsequent deposition of ions from the supersaturated solution onto these nuclei gives rise to observable crystals. The number and size of these will be largely determined by the initial nucleation step.

As is evidenced by a solution's ability to exist in a state of supersaturation without crystal formation taking place, a barrier to the nucleation process must exist. Classical nucleation theory associates with this barrier the work required to form the interface between the two new phases.

In the development of classical nucleation theory it is assumed that supersaturation is built up homogeneously and extremely slowly until a critical supersaturation is reached; that is, steady-state concentrations of clusters of various sizes are always present in the solution (35). These clusters are generally considered to arise as a result of ions or molecules associating in a series of step-wise equilibria. For singly-charged species this may be pictured as follows:

$$A^+ + B^- \rightleftarrows AB$$

$$AB + A^+ \rightleftarrows (A_2B)^+$$

$$\vdots$$

$$A_iB_{j-1}^{(i-j+1)} + B^- \rightleftarrows A_iB_j^{(i-j)}$$

In a state of supersaturation the solution's tendency to deplete itself of soluble ions will cause a certain size embryo, A_iB_j, to change from the liquid-like state to the solid-like state.

The transformation of ions in a supersaturated solution to a critical nucleus capable of continued solid growth requires the prior formation of extremely small clusters of ions whose free energy is greater than that of the saturated solution. For the simple case of spherical clusters, the free energy change accompanying the formation of an embryo can be modeled in terms of the surface area and number of molecules in the embryo using equation 1 (40).

$$\Delta G = 4\pi r^2\sigma + \frac{4\pi r^3}{3V} \cdot \Delta G_B \tag{1}$$

where σ is the interfacial free-energy per unit area between the forming phase and the "mother" phase, V is the volume of a single molecule of the forming phase, r is the radius of the embryo, and ΔG_B is the difference in free energy between one molecule in the macro-crystalline state and one molecule in the supersaturated phase.

Because ΔG is a function of two terms of opposite sign ($\Delta G_B < 0$) and each depends differently on r, the free energy difference accompanying the formation of an embryo will reach a maximum value at some critical value of r (see Fig. 1a).

The critical value of r, r(c), can be evaluated by setting

$$\frac{\partial \Delta G}{\partial r} = 0 \tag{2}$$

The resulting equation for r(c), as denoted by equation (3), shows that the size of the critical nucleus is inversely proportional to the difference ΔG_B. That is, as the level of supersaturation in a solution is increased the number of unit species required to form a critical nucleus decreases.

$$r(c) = \frac{2\sigma V}{\Delta G_B} \tag{3}$$

Therefore, raising the supersaturation of a solution increases the probability of a nucleation event taking place.

The concept of critical nucleus formation is analogous to that of the formation of an activated state in a chemical reaction. In a free energy diagram relating the transformation of ions in a solution to a macrocrystal the critical nucleus will occupy the highest energy position (see Fig. 1b). Although the chances for dissolution of small embryos leading to the formation of the critical nucleus will be greater than their chances for growth, statistical fluctuations will allow some to reach the critical size. Beyond this point, the critical nucleus can grow to an observable crystal.

I.C.1 Critical Nucleus Size Determination

In the stepwise formation of embryos described in Section I.C. A_iB_j is the critical nucleus; that is, it is equally likely to gain another ion as it is to lose one. All reactions leading to the critical nucleus are considered steady state processes. If all nuclei (or a constant fraction of them) grow to observable size then,

$$dN/dt = k(A^+)^i(B^-)^j \tag{4}$$

where N is the number of nuclei formed, t is the time, and k is a constant. When i = j,

$$dN/dt = k(IP)^n \tag{5}$$

where IP is the ion product of $(A^+)(B^-)$ and n is $(i+j/2)$. Then,

$$N = k\int(IP)^n dt \tag{6}$$

If the nucleation process is homogeneous, n represents the number of AB units in the homogeneous nucleus. The value of n may be obtained as the slope of a plot of log dN/dt against log IP.

$$(\text{e.g.} \quad \log dN/dt = n \log IP + \log k) \tag{7}$$

The rate of heterogeneous nucleation may be written (32),

$$dN/dt = k(N°-N)(IP)^n \tag{8}$$

where N° is the number of foreign particles originally present, so that (N°-N) is the number of foreign particles available to act as nuclei. In this case, if precipitant is generated at a constant rate, at any time "t", then before an appreciable amount of precipitation takes place, $(N°-N \cong N°)$ the ion product is directly proportional to time. The above equation becomes:

$$dN/dt = k't^n \tag{9}$$

integrating,

$$\int dN = \int k't^n dt; \quad N = k't^{n+1} \tag{10}$$

taking logs,

$$\log N = (n+1) \log t + \log k' \tag{11}$$

So that a plot of log N against log t will yield a slope having the value n+1.

The above expression has been used to correlate data from experiments using PFHS. No attempt is made in classical theory, to incorporate the induction period[†] as a parameter in equation (8). It is important to note that both the induction period and the nuclei number are determined by the rates of both growth and nucleation during this period.

In direct-mixing type experiments (38), the Christiansen-Nielsen theory (8) has been used to calculate the number of units in the critical size nucleus by means of the relation

$$K = Co^{(p-1)}\tau \tag{12}$$

where K is a constant, p is the number of ions in the critical nucleus, Co is the concentration of the supersaturated solution and τ is the induction period. Christiansen-Nielsen theory assumes that the supersaturated solution initially does not contain clusters of any size, but that a steady state distribution of these in various sizes rapidly occurs.

Classical theory predicts a nucleus size which is dependent on supersaturation and that the rate of nucleation depends very drastically upon supersaturation. In contrast, the Christiansen-Nielsen theory predicts a constant nucleus size and a nucleation rate which is much less dependent upon supersaturation, implying a small nucleus.

Thus there are two ways of arriving at the critical size nucleus. It has not been possible to support either one of these two views (35) because the theories have been derived to fit essentially different experi-

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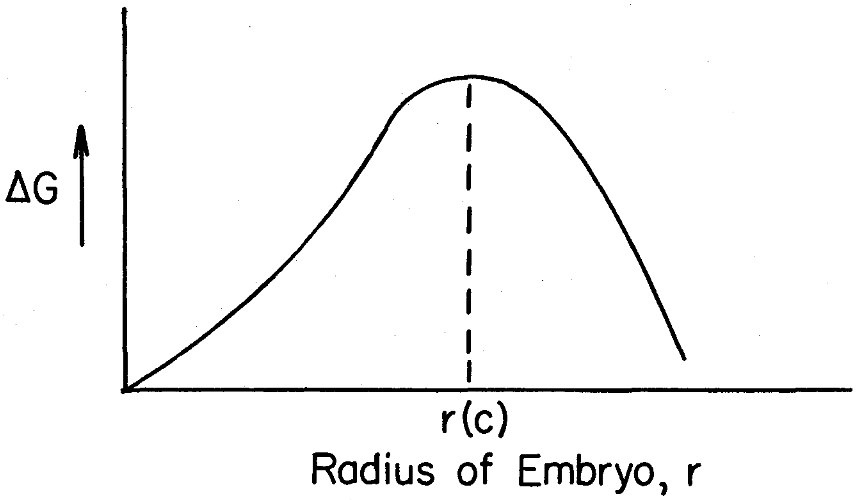
[†] The induction period can be interpreted as the time required to build up clusters of size X_n, corresponding to the critical nuclei or in direct mixing-type experiments as the time lapsed between mixing of the reactants and the onset of precipitation.

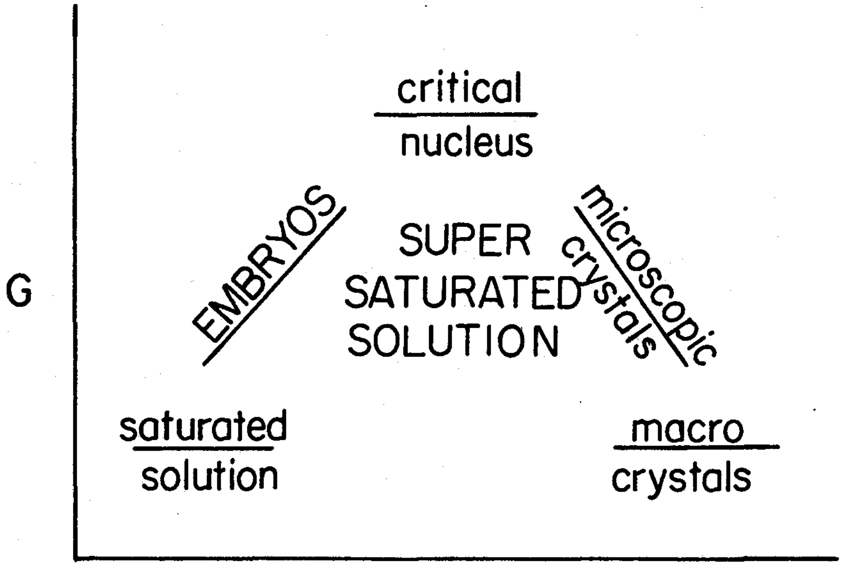
mental cases.

The method developed in this project to generate precipitant should allow one to stop generation at will. The experiments designed in Module 2. of Part II would make feasible a comparison of the critical size nucleus using both approaches on one experimental technique closely resembling PFHS. Perhaps integration of induction time into the classical expression would be possible.

Fig. 1.(a) Variation of ΔG as a function of r

Fig. 1.(b) Free energy relationships in nucleation and growth of crystals


ΔG
r(c)
Radius of Embryo, r


G
critical
nucleus
EMBRYOS
SUPER
SATURATED
SOLUTION
microscopic
crystals
saturated
solution
macro
crystals

I.D. Precipitation Factors

A simple study of the effects of Mg^{++} ion on $CaCO_3$ crystallization would entail measuring the induction period and critical supersaturation[†] associated with $CaCO_3$ precipitation as a function of Mg^{++} ion concentration in the mother solution. Any such experiment would have to consider the effects of the following factors upon the precipitation process.

1. the number of heterogeneous sites
2. the pH of the solution
3. the ionic strength, μ, of the solution
4. the presence of other ions able to complex with $CO_3^{=}$ or affecting the pH

I.D.1. Nucleation Sites

Changes in the number of heterogeneous nuclei in the Mg^{++}-$CaCO_3$ system can alter the critical supersaturation independently of the Mg(++) ion present. Impurities can be introduced by the water used, the reagents used and contamination from the air. Other sites of crystallization such as electrode and thermometer surfaces and the container walls themselves may change from one experiment to the other. These factors must be taken into account and standardized when comparing results from different runs. In certain studies (58) this problem has been handled by assuring

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[†] critical supersaturation $=(K_{I.P.}/K_{S.P.})^{1/2}$ where $K_{I.P.}$ is the ion product (e.g., total concentrations, free and complexed) at the onset of precipitation and $K_{S.P.}$ is the solubility product in terms of activities.

homogeneous nucleation through use of the droplet technique (59).

I.D.2. Thermodynamic Equilibria

It is easily concluded that the solubility of $CaCO_3(s)$ will increase as a result of lowering the pH of the solution in contact with it. The effect of this from equilibrium considerations is to lower the $CO_3^=$ concentration present in solution due to the formation of HCO_3^- and H_2CO_3. This results in a shift to the right in the last of the following equilibrium equations controlling the solution and precipitation properties of $CaCO_3$ (5):

$$CO_2(gas) \rightleftharpoons CO_2(aq); \qquad K_1 = \frac{ACO_2(aq)}{PCO_2(gas)} = 3.4 \times 10^{-2} \tag{13}$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3; \qquad K_2 = \frac{AH_2CO_3}{ACO_2(aq)} = 2.6 \times 10^{-3} \tag{14}$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+; \qquad Kd_1 = \frac{AH^+ \cdot AHCO_3^-}{AH_2CO_3} = 1.7 \times 10^{-4} \tag{15}$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+; \quad Kd_2 = \frac{AH^+ \cdot ACO_3^=}{AHCO_3^-} = 5.6 \times 10^{-11} \tag{16}$$

$$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^=; \qquad Ksp = \frac{ACa^{++} \cdot ACO_3^=}{ACaCO_3(s)} = 1.6 \times 10^{-8} \tag{17}$$

The equilibria involving CO_2 gas and carbonic acid are of particular interest. Only a small fraction of the carbon dioxide dissolved in water exists as the diprotic acid H_2CO_3. As a result the first ionization constant of carbonic acid is usually given as 4.4×10^{-7} and corresponds to the overall reaction arising from the equilibria (14) and (15).

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-; \qquad Kd_1' = \frac{AH^+ \cdot AHCO_3^-}{ACO_2} \tag{18}$$

A calculation of the percentage distribution of $CO_3^=$, HCO_3^-, H_2CO_3 and CO_2(aq) as a function of pH shows equation (18) to be valid. Carbonic acid can dissociate via reactions (14), (15) or (16). Assuming that all CO_2 formed remains in solution the mass balance equation on carbonate is:

$$CO_2(aq) + H_2CO_3 + HCO_3^- + CO_3^= = C \tag{19}$$

where C is the analytical concentration of carbonic acid (total carbonate). Equation (19) can be rewritten as (using concentrations in place of activities)

$$\frac{[H^+]\cdot[HCO_3^-]}{Kd_1 \cdot K_2} + \frac{[H^+]\cdot[HCO_3^-]}{Kd_1} + [HCO_3^-] + \frac{Kd_2[HCO_3^-]}{[H^+]} = C \tag{20}$$

or

$$\text{total carbonate} = [HCO_3^-]\cdot\left[\frac{[H^+]}{Kd_1 \cdot K_2} + \frac{[H^+]}{Kd_1} + 1 + \frac{Kd_2}{[H^+]}\right] \tag{21}$$

Therefore at a constant pH

$$\text{total carbonate} = [HCO_3^-]\cdot M, \quad \text{where M is a constant,} \tag{21a}$$

and the

$$\text{fraction of carbonate as } HCO_3^- = \frac{[HCO_3^-]}{[HCO_3^-]\cdot M} = \frac{1}{M} \tag{22}$$

$$\text{fraction as } H_2CO_3 = \frac{[H^+][HCO_3^-]}{Kd_1[HCO_3^-]M} = \frac{[H^+]}{Kd_1 \cdot M} \tag{23}$$

$$\text{fraction as } CO_3^= = \frac{Kd_2 \cdot [HCO_3^-]}{[H^+][HCO_3^-]M} = \frac{Kd_2}{[H^+]\cdot M} \tag{24}$$

$$\text{fraction as } CO_2(aq) = \frac{[H^+][HCO_3^-]}{Kd_1 \cdot K_2[HCO_3^-]M} = \frac{[H^+]}{Kd_1 \cdot K_2 \cdot M} \quad (25)$$

From Table I it becomes apparent that $[H_2CO_3]$ is always less than 0.3% of the $[CO_2]$ present in a solution and is therefore negligible in any mass balance. Figure 2 shows the percentage distribution of carbonate species in a solution as a function of pH.

It is well to note that in calculations involving the solubility of $CaCO_3$ one must be aware that the mass balance equation holds true only so long as all CO_2 formed remains in solution. In an open vessel the partial pressure of CO_2 above the solution (PCO_2) determines the amount of equilibrium CO_2 in solution. This is quantified by Henry's law:

$$[CO_2] = 3.43 \times 10^{-2} \cdot PCO_2 \quad (26)$$

where PCO_2 is in atmospheres and $[CO_2]$ is in moles/litre. Solubility equilibrium will be reached only when the CO_2 pressure above the solution equals about 10^{-3} atm. Any subsequent loss of CO_2 from the solution would increase the apparent solubility of the carbonate.

The corrected mass balance would be

$$C = [CO_3^=] + [HCO_3^-] + 3.43 \times 10^{-2}\, PCO_2 + G \quad (27)$$

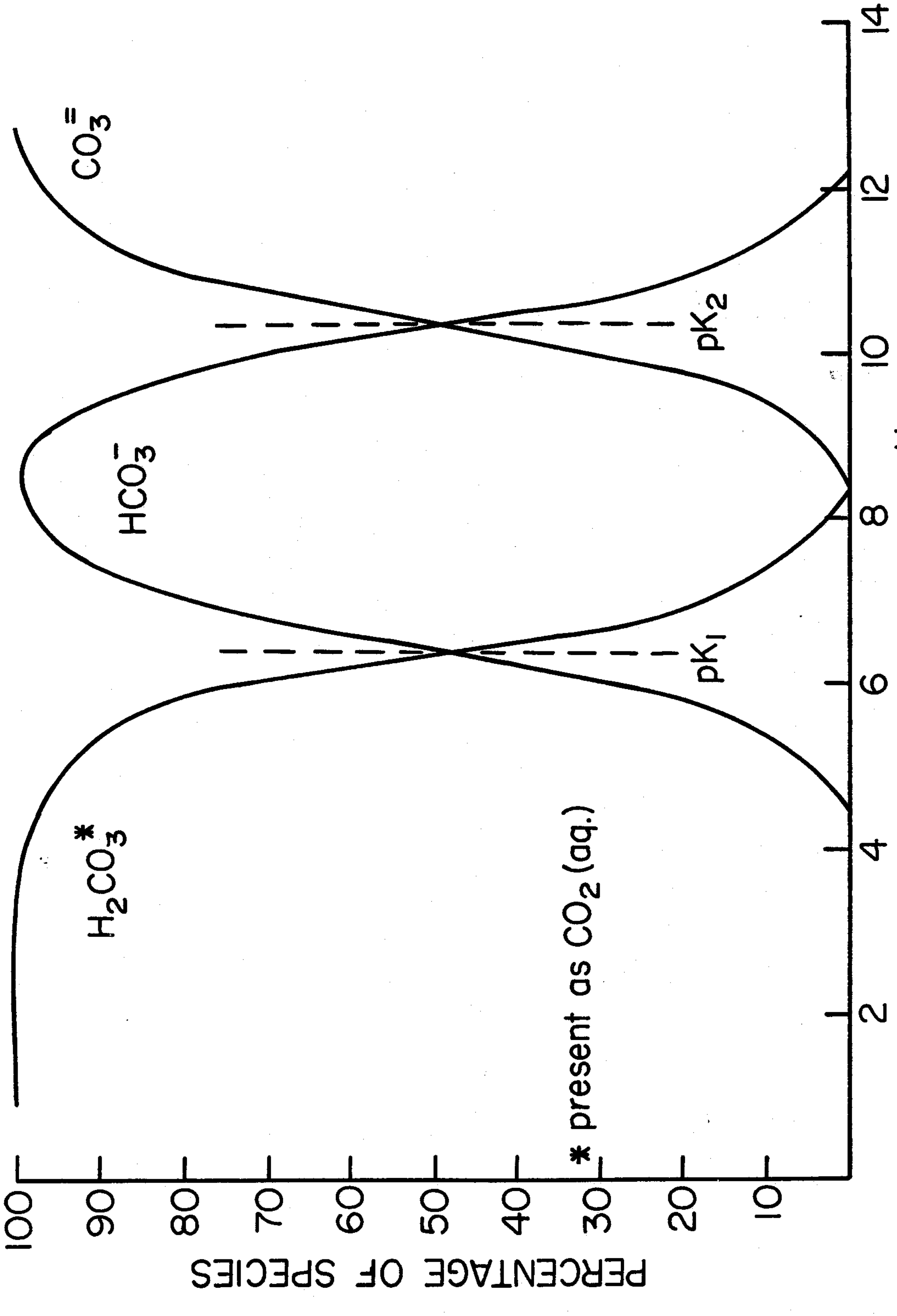
where G is the no. of moles of CO_2 that escape from one litre of solution under the conditions of the reaction.

TABLE I

Fractional distribution of carbonate species vs. pH

pH	CO_2	H_2CO_3	HCO_3^-	$CO_3^=$
1.0	0.997	2.58 E-03	4.39 E-06	2.46 E-15
1.5	0.997	2.53 E-03	1.39 E-05	2.46 E-14
2.0	0.997	2.58 E-03	4.39 E-05	2.46 E-13
2.5	0.997	2.58 E-03	1.39 E-04	2.46 E-12
3.0	0.996	2.58 E-03	4.39 E-04	2.46 E-11
3.5	0.996	2.58 E-03	1.39 E-03	2.45 E-10
4.0	0.993	2.57 E-03	4.37 E-03	2.45 E-09
4.5	0.984	2.55 E-03	1.37 E-02	2.42 E-08
5.0	0.955	2.47 E-03	4.20 E-02	2.35 E-07
5.5	0.876	2.27 E-03	0.122	2.16 E-06
6.0	0.693	1.79 E-03	0.305	1.71 E-05
6.5	0.418	1.08 E-03	0.581	1.03 E-04
7.0	0.185	4.78 E-04	0.814	4.56 E-04
7.5	6.69 E-02	1.73 E-04	0.931	1.65 E-03
8.0	2.21 E-02	5.72 E-05	0.972	5.45 E-03
8.5	2.01 E-03	1.81 E-05	0.976	1.73 E-02
9.0	2.15 E-03	5.56 E-06	0.945	5.29 E-02
9.5	6.10 E-04	1.58 E-06	0.849	0.150
10.0	1.46 E-04	3.77 E-07	0.641	0.359
10.5	2.59 E-05	6.71 E-08	0.361	0.639
11.0	3.44 E-06	8.91 E-09	0.152	0.848
11.5	3.84 E-07	9.94 E-10	5.35 E-02	0.947
12.0	3.99 E-08	1.03 E-10	1.75 E-02	0.982
12.5	4.04 E-09	1.04 E-11	5.62 E-03	0.994
13.0	4.05 E-10	1.05 E-12	1.78 E-03	0.998
13.5	4.06 E-11	1.05 E-13	5.64 E-04	0.999

Fig. 2. Percentage distribution of carbonate species as a function of pH


PERCENTAGE OF SPECIES
100
90
80
70
60
50
40
30
20
10
pH
2
4
6
8
10
12
14
$H_2CO_3^*$
HCO_3^-
$CO_3^=$
pK_1
pK_2
* present as CO_2 (aq.)

I.D.2.a Ionic Strength

The K_{SP} equation describing the equilibrium of reaction (17) takes into account the fact that the solubility of $CaCO_3$ will change upon the addition of a salt without a common ion to the solution in contact with the $CaCO_3$. The activity concept is used to describe effective concentrations in the following manner:

$$A_i = f_i[C_i] \tag{28}$$

where f_i is the activity coefficient of the ionic species "i". Debye and Huckel (13) derived a quantitative relationship between activity coefficient and ionic concentration for the simple model in which the ions are treated as point charges, and the solvent as a continuous medium of uniform dielectric constant.

The equation they derived for the activity coefficient of a single ionic species is

$$\log f_i = -AZ_i^2\sqrt{\mu} \tag{29}$$

where the

$$\text{constant } A = \left(\frac{2\pi\eta\varepsilon^6}{1000(D\kappa T)^3}\right)^{1/2} \cdot (2.303)^{-1}$$

and

Z_i = charge on the ions i

μ = ionic strength = $1/2 \sum_i C_i Z_i^2$

η = Avogadro's number

ε = charge on the electron

D = dielectric constant of the medium

κ = Boltzmann constant

T = absolute temperature

A equals 0.5091 in water at 25°C.

The concept of the activity of a single kind of ion, as distinct from a salt, has no strict thermodynamic significance. It is impossible to transport a weighable quantity of positive ions without an accompanying equivalent quantity of negative ions, or at best, transporting another kind of positive ion in the opposite direction.

Thus, $f_{Ca^{++}}$ ions cannot be measured nor can $f_{CO_3^{=}}$ but the product of these, $f_{Ca^{++}} \cdot f_{CO_3^{=}}$, can be measured. It is customary to define a mean activity coefficient:†

$$f\pm \text{ for } CaCO_3 = (f_{Ca^{++}} \cdot f_{CO_3^{=}})^{1/2} \tag{30}$$

Equation (29) then, the limiting Debye-Huckel equation, should be read as

$$\log f\pm = -A(Z+)(Z-)\sqrt{\mu} \tag{31}$$

A more accurate equation takes into account the radii of the ions and the lowering of the dielectric constant of the solvent by the electric force between the ions.

$$\log f\pm = \frac{-(Z+)(Z-)\cdot A\sqrt{\mu}}{1 + B\sqrt{\mu}} + Q\mu \tag{32}$$

B depends on the ionic radii and is 0.3288 Å at 25°C in water, Å being the mean distance of closest approach of the 2 ions in Angstrom units. Since Å is usually about 3 it is convenient to set B = 1 for approximate calculations. Q is a small constant which depends on the nature of the salt. Equation (32) with B = 1 and Q = 0 works well up to $\mu \cong 0.1$

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† In general for a salt $A_X B_Y$ which ionizes to XA^{+Y} and YB^{-X}

$$f\pm = (f_A^{X} f_B^{Y})^{1/X+Y}$$

particularly if allowance is made for the slight degree of ionic association that usually exists.

The activity of a dissolved substance depends both on the concentration of its own ions as well as the concentration of all other ions in solution. It will be noted that the activity coefficients are smaller the greater the charges on the ions concerned. Thus an increase in ionic strength lowers the activity coefficient and raises the effective concentration of Ca^{++} and $CO_3^=$ which can be in equilibrium with the solid phase. In order to make a comparison of the induction times associated with $CaCO_3$ precipitation as a function of Mg^{++} concentration, the ionic strength of the solutions would have to be equivalent.

I.D.3. Complexation Reactions

The activities of Ca^{++} and $CO_3^=$ ions can be lowered by ion pair associations as well as by electrostatic attractions in solution. Ionic strength effects were seen to affect the mean activity coefficient for $CaCO_3$. Undissociated $CaCO_3$ molecules and the formation of complexes involving Ca^{++} or $CO_3^=$ ions lower the concentration of these species in solution and therefore their activities. As indicated in Section I.A.2., Greenwald (21) showed that both Ca^{++} and Mg^{++} interact with HCO_3^- and $CO_3^=$ to form soluble complexes.

The important equilibria are listed below

$$CaCO_3^\circ \rightleftharpoons Ca^{++} + CO_3^=; \quad \frac{MCa^{++}MCO_3^=}{MCaCO_3^\circ} = 1 \times 10^{-3} \tag{33}$$

$$MgCO_3^\circ \rightleftharpoons Mg^{++} + CO_3^=; \quad \frac{MMg^{++}MCO_3^=}{MMgCO_3^\circ} = 4.3 \times 10^{-3} \tag{34}$$

$$Ca(HCO_3)^+ \rightleftharpoons Ca^{++} + HCO_3^-; \quad \frac{MCa^{++} \cdot MHCO_3^-}{MCaHCO_3^+} = 1.6 \times 10^{-1} \tag{35}$$

$$Mg(HCO_3)^+ \rightleftharpoons Mg^{++} + HCO_3^-; \quad \frac{MMg^{++}MHCO_3^-}{MMgHCO_3^+} = 1.7 \times 10^{-1} \tag{36}$$

Greenwald determined apparent constants based on molarities rather than activities at nearly constant ionic strength ($\mu = 0.15$) and at 22°C.

Garrels and Christ (18) calculated the thermodynamic dissociation constants (based on activities) for Mg^{++} and Na^+ carbonate complexes to be as follows:

$$\frac{AMg^{++} \cdot ACO_3^=}{AMgCO_3} = 4.0 \times 10^{-4} \tag{37}$$

$$\frac{ANa^+ACO_3^=}{ANaCO_3^-} = 5.4 \times 10^{-2} \tag{38}$$

Their calculations showed that of the total $CO_3^=$ in sea water as determined by titration and not including HCO_3^-, about 75 percent was $MgCO_3°$, 15 percent $NaCO_3^-$ and 10 percent free $CO_3^=$.

In addition both Ca^{++} and Mg^{++} can associate with hydroxide ions.

$$Ca(OH)^+ \rightleftharpoons Ca^{++} + OH^- \tag{39}$$

$$Mg(OH)^+ \rightleftharpoons Mg^{++} + OH^- \tag{40}$$

The effect of the presence of ion pairs is to increase the amount of $CaCO_3$ which would dissolve and to decrease the amount which would precipitate compared to a system without ion-pairs. The equilibrium condition

($K_{SP} = ACa^{++} \cdot ACO_3^{=}$) would still hold but the analytical concentration of Ca^{++} and $CO_3^{=}$ (i.e., concentrations of ion and complex) in solution would increase.

I.E. Methods of $CaCO_3$ Precipitation

Several methods have been used previously to precipitate $CaCO_3$ by generation of $CO_3^{=}$ ion. These along with other theoretically possible methods are now described.

CO_2 Evolution

Pulverized $CaCO_3$ is suspended in a solution through which CO_2 gas is bubbled for 24 hours. The solution is then filtered and CO_2 bubbled through once more for one hour. $CaCO_3$ will form from this calcium bicarbonate solution as CO_2 gas escapes. This technique was used by Kitano (1962).

Urea Decomposition

Urea decomposition has been used in PFHS studies (62) as a means of generating $OH^{\ominus}$ to precipitate Al, Sn, Bi and Fe in the form of metal hydroxides.

$$(NH_2)_2CO + 3H_2O \rightleftharpoons CO_2 + 2NH_4^{\oplus} + 2OH^- \qquad (41)$$

It would seem possible that CO_2 produced in the presence of Ca^{++} ion could bring about precipitation of $CaCO_3$ through the hydrolysis of CO_2 and its subsequent reaction with base to produce $CO_3^{=}$.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (14)$$

$$H_2CO_3 + 2OH^- \rightleftharpoons CO_3^= + 2H_2O \qquad (42)$$

Cyanate Decomposition

Upon heating, potassium cyanate solutions should behave similarly to those of urea, this time producing $CO_3^=$ directly.

$$KOCN + 2H_2O \xrightarrow{\Delta} K^+ + NH_4^+ + CO_3^= \qquad (43)$$

Trichloroacetate Hydrolysis

The hydrolysis of rare earth trichloroacetates in a homogeneous phase reaction has been used satisfactorily to yield a pure crystalline carbonate (52).

$$2Nd(C_2Cl_3O_2)_3 + 3HOH \rightarrow 3CO_2 + 6CHCl_3 + Nd_2(CO_3)_3 \qquad (44)$$

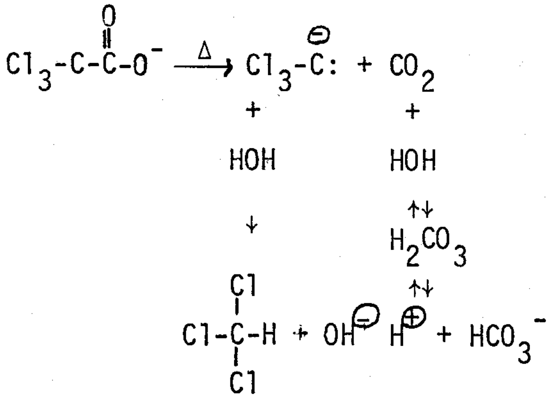
Trichloroacetate hydrolysis is also mentioned very briefly in an obscure unclassified U.S. Government Progress report (AT(30-1)2266) as having been used as a reaction for $CaCO_3$ precipitation at 100°C in a study of coprecipitation of metallic ions with $CaCO_3$.

$$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^= + H_2O \qquad (45)$$

The hydrolysis of trichloroacetate in the presence of Ca^{++} ions should result in $CaCO_3$ precipitation. Such a reaction was initiated in Section III.B. by neutralization of a trichloroacetic acid solution with a $Ca(OH)_2$ solution prior to its hydrolysis.

$$Ca(OH)_2 + 2Cl_3CCOOH \rightarrow 2Ca^{++} + 2Cl_3CCOO^- + 2H_2O \qquad (46)$$

The reaction mechanism for the hydrolysis of trichloroacetate and the subsequent precipitation may be modeled as follows:



(47)

The bicarbonate ion dissociation,

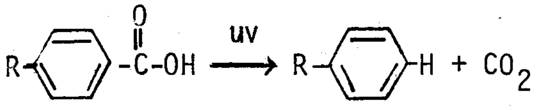
$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (16)$$

is minimal (pH dependent) until the K_{SP} of $CaCO_3$ is exceeded, at which time the formation of $CaCO_3$ results in a pH drop.

$$Ca^{++} + HCO_3^- \rightarrow CaCO_3\downarrow + H^{\oplus} \qquad (48)$$

Photodecarboxylation

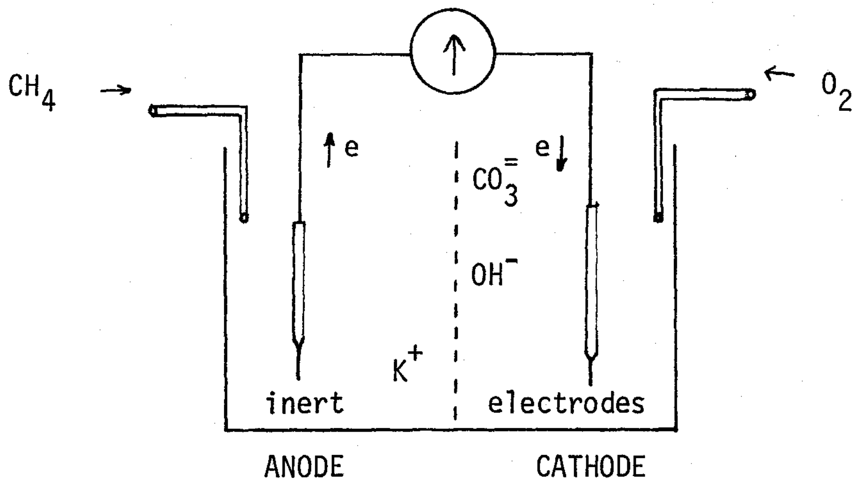
The uv decomposition of certain organic acids (24) should result in the production of CO_2 which again should result in the formation of carbonic species.



(49)

Fuel Cell By-Product

Of academic interest is the formation of $CO_3^=$ as a by-product in the operation of a fuel cell (37).



anode $CH_4(g) + 10\ OH^- \rightarrow CO_3^= + 7H_2O + 8e;\quad E_{ox} = 0.73\ V$ (50)

cathode $2O_2 + 4H_2O + 8e \rightarrow 8OH^-;\quad E_{red} = 0.40\ V$ (51)

cell $CH_4(g) + 2O_2(g) + 2OH^- \rightarrow CO_3^= + 3H_2O;\quad E = 1.13\ V$ (52)

According to the reaction mechanism, methane is oxidized to methanol, to formaldehyde, to formic acid and finally to carbonate ion. It would be possible to start with methanol at the anode.

Electrolytic Generation

The following abstract of Voreux's work (60) on Kolbe's electrolysis provides the basis for a method of $CO_3^=$ generation.

An aqueous solution of acetic acid does not conduct current very well and to demonstrate the interesting anodic oxidation of the acetate ion, an equimolar mixture of NaOAc and AcOH is used, 1 mole/l of each. With 10-30 V, a gas is evolved at the anode containing 50% CO_2, no O_2 and 50% of a gas which burned with a luminous flame. The volume of the anodic gas is 50-200% of the H_2 volume at the cathode, depending on the current. The OH^- produced at the cathode reacts with the CO_2 evolved at the anode to produce $CO_3^{=}$, since CO_2 is quite soluble in H_2O.

$$2OH^- + CO_2 \rightarrow CO_3^{=} + H_2O \tag{53}$$

The flammable gas is C_2H_6.

I.F. Outline of the Method of Study

Once developed, the new analytical method described in Section III was used in preliminary studies to determine its suitability to carry out a more extensive research of the interactions of Mg^{++} ion on $CaCO_3$ nucleation. A systems analysis on this research proposal is delineated in the following section and in many ways governed the development of the electrolytic method developed for the precipitation of calcium carbonate. Also, in this present work the behavior of specific ion electrodes and a computer based data gathering system to be used in conjunction with the proposed research were tested and evaluated.

PART II

A SYSTEMS ANALYSIS OF A $CaCO_3$ NUCLEATION STUDY PROPOSAL

II.A. Preface

The general objective of this proposal is two-fold:

1. To acquire meaningful data pertaining to the nucleation step of precipitate formation and leading to its representation in terms of a physical model;
2. To realize a computer based information system as an alternative to a set of manual and mechanical procedures needed to collect and process this data.

Overall the proposal consists of three modules. Modules one and two form the essence of the experimental section and consist of basic building blocks or processes some of which are common to both of them. Module three is the data acquisition system which would act upon certain blocks of modules one and two.

Conceptually, reference is made to modules and their blocks to allow flexibility in the integration of these elements into the final system, therefore allowing variable depth of study and ease of design.

II.B. Analysis Outline

II.C. Analyses

1. Introduction

a. Problem Recognition

Specifically this study would concern itself with the influence of magnesium ion on calcium carbonate nucleation. Previous studies by Bischoff (4) of the transformation of aragonite to calcite in the presence of an aqueous solution near 100°C have shown that Mg^{++} ion has an inhibiting effect on the transformation and in the process is incorporated into the calcite nuclei.

Nancollas and Purdie (45) indicate that the dehydration of reactants on the surface of a growing crystal is often a rate controlling step in crystallization processes. Thus, from a statistical standpoint, a strongly hydrated Mg^{++} ion drawn to calcite growth sites will remain for a relatively long time, preventing growth until dehydration and final incorporation into the lattice.

Another possibility is that magnesium adsorption makes necessary a larger critical nucleus, or Mg^{++} could inhibit the precipitation of $CaCO_3$ not by interacting directly in the nucleation process but instead by tying up $CO_3^=$ in the form of $MgCO_3$ complexes, as suggested by Pykowitz (50). These ideas are not mutually exclusive.

Bischoff's findings apply only to calcite that has formed from aragonite and may not necessarily extend to calcite precipitating directly from solution.

b. Formulation of Objectives

Given that a way can be found to precipitate $CaCO_3$ from aqueous solution at a controlled rate and at room temperature modules one and two respectively aim to gain insight into:

Module 1

- i) The effect and nature of the Mg^{++} ion interaction on $CaCO_3$ nucleation .
- ii) The effect of ionic strength on $CaCO_3$ nucleation.

Module 2

- i) The size of the $CaCO_3$ critical nucleus and how Mg^{++} affects it
- ii) Nucleation theory, per se.

Data will arise as a result of:

Part 1 (modules one and two)

- A) While generating $CO_3^=$ at a constant rate, the critical supersaturation will be measured as a function of:
  - 1) magnesium ion concentration
  - 2) ionic strength
- B) At varying $[Ca^{++}]\cdot[CO_3^=]$ ion products, induction time will be measured as a function of:
  - 1) magnesium ion concentration
  - 2) ionic strength

Part 2 (module two)

The information required for a determination of the number of units in the nucleus will be:

1. The number of particles formed vs. time.
2. The concentration of calcium and carbonate ions as a function of time.

In all experiments the onset of precipitation will be determined potentiometrically, at which time the Ca^{++} and divalent $(Ca^{++} + Mg^{++})$ ion activities will be measured with specific ion electrodes, and an indirect determination of the $CO_3^{=}$ activity will be made.

Having recognized the significance of the problem and documented its objectives it remains to outline the variables and processes likely to be involved, which in turn will define the specifications for an appropriate method of $CaCO_3$ precipitation.

The analysis as follows was conceived for Module 1 prior to any experimental testing. These subsystems are expanded in Parts I, II, III and IV of this work.

2. Systems Definition

a. Significant Variables

1. calcium concentration
2. magnesium concentration
3. temperature
4. foreign nuclei in solution
5. nucleating surfaces
6. solution - ambient air interface

b. Dynamic Processes Required

1. A process (resembling PFHS) which precipitates $CaCO_3$ from aqueous solution. This process must allow calculation of the critical supersaturation.
2. A process which determines the onset of precipitation.

3. A process which minimizes and standardizes foreign nuclei in solution.
4. A process which standardizes the amount of CO_2 in solution.
5. A Ca^{++} activity monitoring process.
6. A Mg^{++} activity monitoring process.
7. An information system - data acquisition.

3. Analysis

a. Processes Specifications

1. Since there are no methods available to measure low concentrations of $CaCO_3$ on a real time basis, the design of 2.b.1 above will imply that $CaCO_3$ will be precipitated as a result of $CO_3^{=}$ generation at a constant rate in the presence of Ca^{++}.
2. The ability to stop $CO_3^{=}$ generation at any time must exist.
3. The $CO_3^{=}$ generation process must not generate extraneous substances which can affect the solubility of $CaCO_3$ independently of the Mg^{++} ion.
4. The ability must exist to carry out the precipitation at a constant temperature which in turn can be varied.
5. The specific ion electrodes to be used for Ca^{++} and Mg^{++} activity monitoring are liquid membrane electrodes; their operation must take place at temperatures below 50°C.

b. Feasibility

1. $CaCO_3$ Precipitation
   a) decarboxylation
   b) urea decomposition
   c) cyanate decomposition
   d) trichloroacetate hydrolysis
   e) photodecarboxylation
   f) fuel cell by-product
   g) electrolytic generation

2. Determination of Critical Supersaturation
   a) pH correlation
   b) specific ion electrodes
   c) Weyl saturometer
   d) kinetic indirect determination

3. Determination of the Onset of Precipitation
   a) pH drop
   b) turbidimetry
   c) conductance

4. Minimization of Foreign Nuclei in Solution
   a) use of de-ionized distilled water
   b) millipore filtration
   c) pre-precipitation

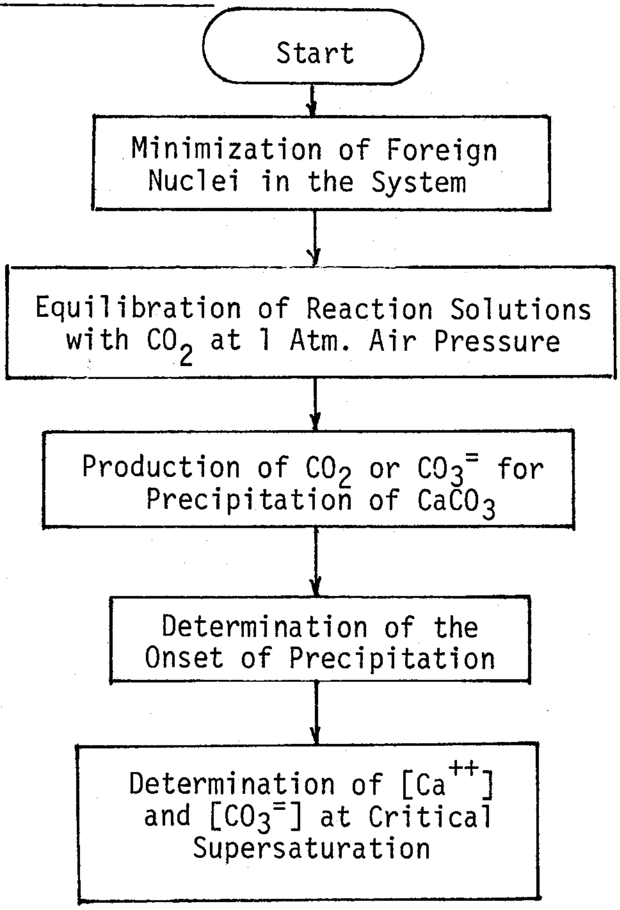
5. Standardization of CO_2 in Solution
    a) Equilibration of reaction solutions with atmospheric CO_2.

6. Determination of Mg^{++} Ion
    a) Ca^{++} and divalent specific ion electrodes.

7. Data Acquisition
    a) mechanical
    b) semi-automated
    c) processor controlled

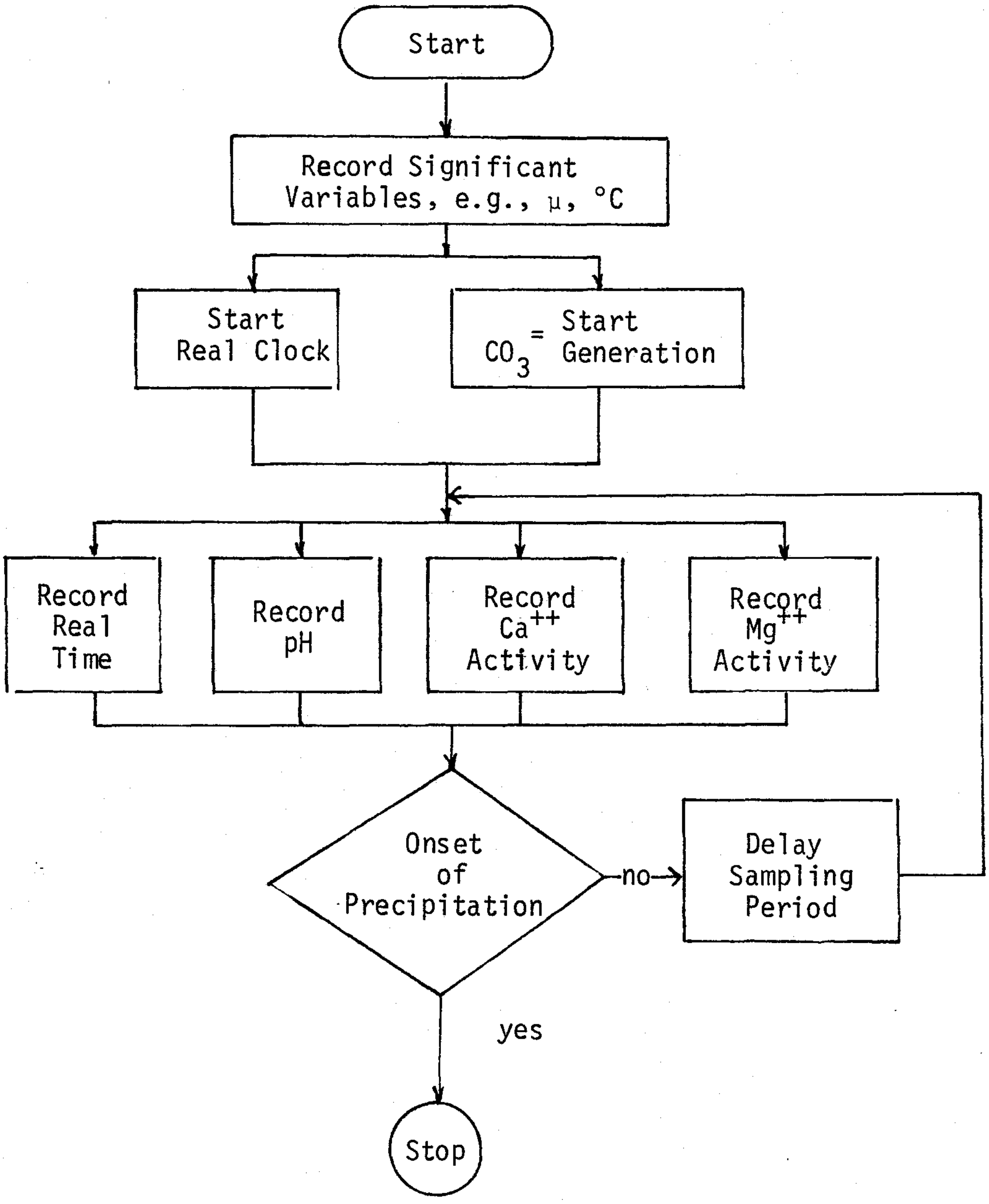
4. Design

a Experimental Flow

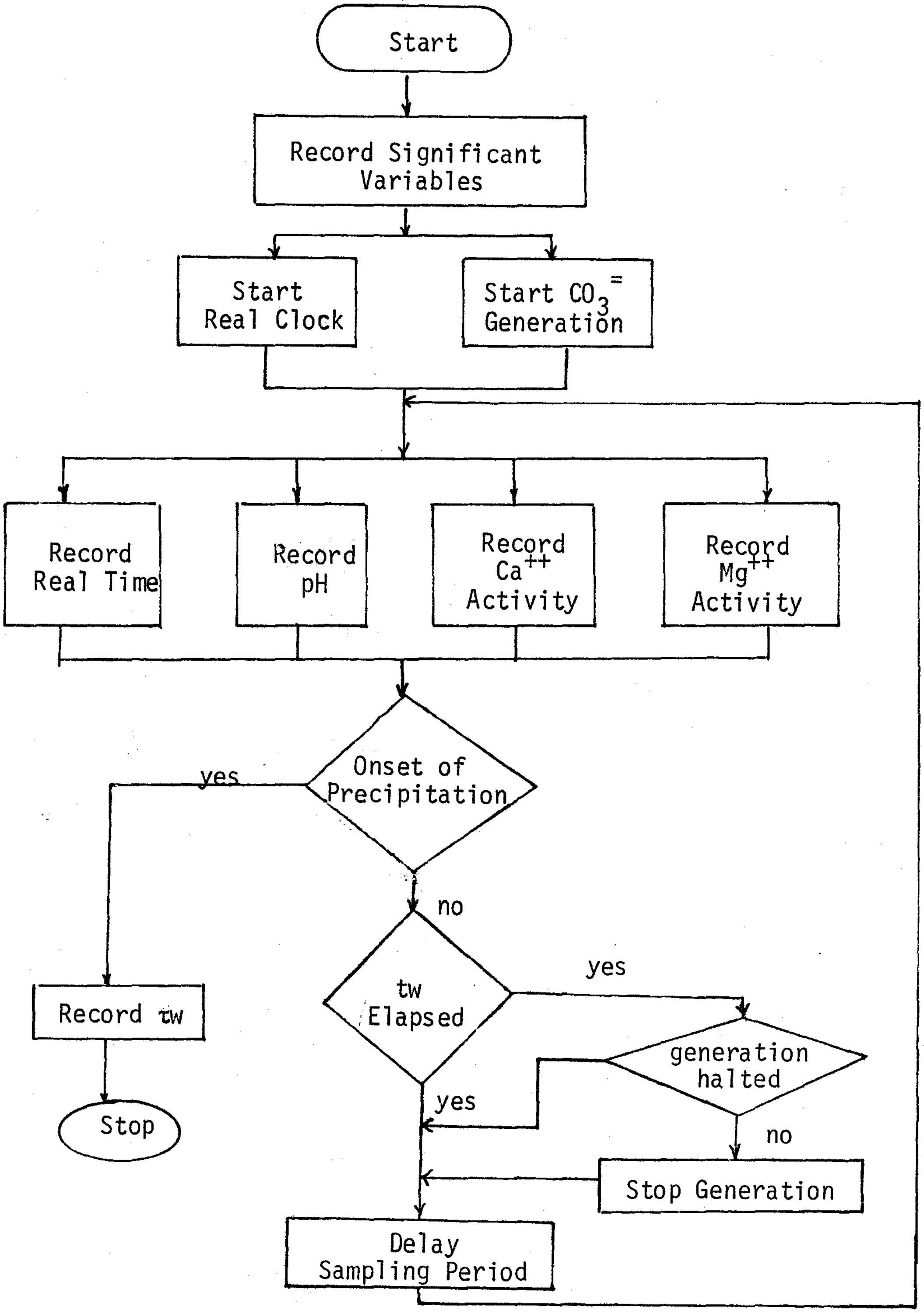


b Data Flow

1. Part 1 (Method A)



2. Part 1 (Method B)



tw = time needed to reach a certain supersaturation
τw = induction period (excludes tw).

5. System Implementation

Experimental details are to be found in Sections III and IV.

Following is the analysis for Module Two.

Module 2. Nucleation Theory

1. Introduction

a. Problem Recognition

In experiments where PFHS has been used, the precipitant is generated very slowly and continuously until precipitation is observed. The critical supersaturation can be described by the ratio $((I.P.)/K_{SP})^{1/2}$ where K_{sp} is determined thermodynamically. $I.P. = [A^+]\cdot[B^-]$ and $[A^+]$ and $[B^-]$ refer to total concentrations, i.e., concentrations of ions and complexes. Time is not considered a factor here.

Consider the following experiment involving Systems A and B.

System A

Generate B^- at a constant rate, R, in the presence of a fixed concentration of A^+ until precipitation of AB occurs; at which time, t_1, the critical ion product needed to cause precipitation ($I.P._1$) is $[A^+] \times R \times t_1$.

Repeating the above experiment but this time stopping generation of B^- at a time tw, $tw < t_1$, one would after a time τ_W observe precipitation and calculate I.P. as $[A^+] \times R \times tw$ with the conclusion that $I.P._1$ was not critical at all when time is considered.

At which time tw ($= t_{SP}$) will cessation of precipitant generation cause $\tau_W \rightarrow \infty$? The activity product of the ions A^+ and B^- in solution at this time should define the solubility product, $K_{S.P.}$. Therefore, generating

B^- for some time t_o such that $t_o > t_{SP}$, will in fact give rise to a critical I.P.° and cause observable precipitation after a time T°. By how much does I.P.° exceed K_{SP}?

System B

If one now mixes solutions of A^+ and B^- (where all other variables are identical to system A) so that the ensuing solution had an I.P. equal to I.P.° will precipitation occur? How will the induction period compare to τ°? In using PFHS how much nucleation and growth occur during the period t_o?

Can a missing link be established between PFHS and direct mixing type experiments? Can a general theory of nucleation be developed which encompasses classical theory and the Nielsen-Christiansen approach? Should not the critical-size nucleus of a salt AB be independent of how supersaturation is achieved? Must the critical-size nucleus develop from prior nuclei of smaller radius? Is the stepwise formation of clusters a reasonable mechanism for the formation of the critical nucleus? Is the size of the critical nucleus dependent on the level of supersaturation?

b. Formulation of Objectives

The goal of this study would be to acquire meaningful data on the interacting and/or interrelated variables and the dynamic processes of interaction among these system components in the nucleation step of precipitate formation. Specifically, the data will arise as a result of comparing the critical-size nucleus calculated by using both classical and Christiansen-Nielsen theory on $CaCO_3$ nucleation brought about using one experimental technique closely resembling PFHS but allowing induction-type measurements to be made.

2. Systems Definition

a. Significant Variables

1. foreign nuclei in solution
2. solution-ambient air interphase
3. temperature
4. stirring rate
5. initial Ca^{++} concentration
6. $CO_3^=$ generation rate

b. Dynamic Processes Required

1. A process which will build up saturation quasi-homogeneously and in such manner that generation of the precipitant can be stopped prior to precipitation. This process must allow calculation of the I.P. as a function of time.
2. A process which will allow detection of the onset of precipitation.
3. A Ca^{++} activity monitoring process-specific ion electrode.
4. A process which will allow calculation of the number of nuclei formed as a function of time. Therefore this process must count particles and determine their size.
5. A process which will normalize and minimize the number of foreign nuclei in solution.
6. A direct mixing-type precipitation system.
7. Information system.

3. Analysis

a. Processes Specifications

1. Process 1 above should be one allowing close reproduction to be made using direct mixing-type experiments (e.g., minimization of extraneous species).
2. Since there are no methods available to measure $CO_3^=$ concentration on a real time basis, the design of process one above will imply that $CaCO_3$ will be precipitated as a result of $CO_3^=$ generation at a constant rate.
3. The specific ion electrode must operate at temperatures below 50°C.
4. The ability should exist to carry out the precipitation at a constant temperature which in turn can be varied.
5. The amount of CO_2 dissolved in solution must be standardized.
6. The nuclei counting process must be able to count at moderate frequencies nuclei formed.

b. Feasibility

1. $CaCO_3$ precipitation (see Module 1, section 3.b.)

2. Detection of precipitation onset (see Module 1, section 3.b)
3. Ca^{++} activity monitoring
4. Heterogeneous nuclei minimization
5. Particle count
   a) Microscopic
   b) Electronic particle counter
6. Direct mixing-type precipitation system
   a) $CaCl_2 + NaHCO_3$
   b) $CaCl_2 + Na_2CO_3$

4. Design

The experimental and data flows of Module 2 would be similar to those of Module 1 except that in place of measuring Mg^{++} concentration a particle count vs. time would be made. Inclusion of the Mg^{++} measurement would allow its effect on the critical nucleus to be made.

A direct mixing-type precipitation system would then be used to carry out the system B experiment described under section I.A. of Module Two's analysis.

5. System Implementation

As presented here the analysis is minimum. At this time its main purpose is to record certain ideas. No attempts were made to carry out preliminary investigations into the feasibility of the particle counting process.

Following is an outline of how the data acquisition system was first envisioned after development of the electrolytic method of $CO_3^=$ generation.

Module 3. Information Systems

1. Introduction

a. Problem Recognition

The combined design of Modules 1 and 2 entail a number of function measurements. How can one automate and facilitate data acquisition and processing?

b. Objectives

1. To realize a computer based information system as an alternative to a set of manual and mechanical procedures needed to collect the data and produce meaningful results from it while obtaining increased accuracy and speed and minimizing human intervention.

2. To develop this PILOT information model as an academic exercise for the system does not warrant the expense involved.

2. System Definition

a. Significant Variables (initially fixed)

1. initial $[Ca^{++}]$
2. initial $[Mg^{++}]$
3. initial $[HCO_3^-]$
4. ionic strength, μ_o
5. constant current (m amps)
6. solution temperature
7. concentration of spectator ions
8. $CO_3^=$ generation rate
9. pH (dependent variables)

b. Logged data

1. real clock time, t
2. Ca^{++} ion activity vs. t
3. divalent ion activity vs. t
4. pH vs. t
5. t for current on
6. t for current off
7. number of particles vs. t
8. size distribution of particles

c. Derived variables (cpu processing)

1. final ionic strength
2. coulombs passed
3. time, t_o, at precipitation onset

4. induction time (System B)
5. distribution of species at time t_o according to activities and molalities
   a) Ca^{++}
   b) Mg^{++}
   c) HCO_3^-
   d) $CO_3^=$
   e) H^+
   f) OH^-
6. I.P., $[Ca^{++}]\cdot[CO_3^=]$, at t_o
7. critical supersaturation as a function of Mg^{++}
8. critical supersaturation as a function of initial μ
9. nucleation rate
10. number of units in the critical-size nucleus
    a) using Christiansen-Nielsen theory
    b) using classical theory
11. generation time
12. ratio of generation time to induction time
13. Mg^{++} activity (from divalent and Ca^{++} measurements)

d. Instrumentation

1. Sensors
   a) real clock
   b) Ca^{++} specific ion electrode
   c) divalent ion specific electrode
   d) electronic particle counter
   e) thermometer
   f) glass, and reference electrodes
2. Process interacting components
   a) constant current source-coulometer
   b) constant temperature-water bath
3. Amplifiers and others
   a) expanded scale pH meters
   b) strip chart recorders
   c) A/D converters

3. Analysis

a. Process specifications

1. The initial Ca^{++}, Mg^{++}, HCO_3^- and spectator ions concentrations can be varied at will by solution preparation.
2. The temperature will be adjusted using a constant temperature bath
3. The current passed will be controlled using a coulometer.
4. The Ca^{++} and divalent ion activities can be measured using specific ion electrodes, a common reference electrode and an expanded scale pH meter. Simultaneous reading of both the Ca^{++} and divalent species concentration can be accomplished using two meters.

5. Since detection of the onset of precipitation is signaled by a drop in pH, an expanded scale pH meter will increase detection sensitivity. The reference electrode used by the specific ion electrodes can be shared as well by the glass electrode to be used for pH measurements.
6. Solution temperature will be maintained constant by use of a special reaction cell with water jackets attached to a constant temperature-water bath.
7. Calibration procedures for the electronic counter entail special solution preparation. Aliquots will have to be removed from the reaction solution and counted. This counting procedure must be such so that the instrument will be free to record another count at a specified frequency.

b. Feasibility

1. Data Logging

a. Mechanical

All real time variable readings can be recorded manually by examination of values on instrument panels.

b. Semi-automated

pH, Ca^{++} ion activity and divalent ion activity can be recorded automatically using strip chart recorders.

Output from the electronic particle counter can be transferred into a multi-step channel analyzer and then dumped onto tape for later examination.

c. Digital-computer controlled

All real time variable readings can be entered into the memory of a digital computer by conversion of the voltage outputs into digital values using analog/digital converters. Alternatively, pH meters can be chosen with digital outputs.

All other pertinent information (initially fixed variable values and source programs) can be entered into the computer with subsequent processing and output of all derived variables (meaningful results).

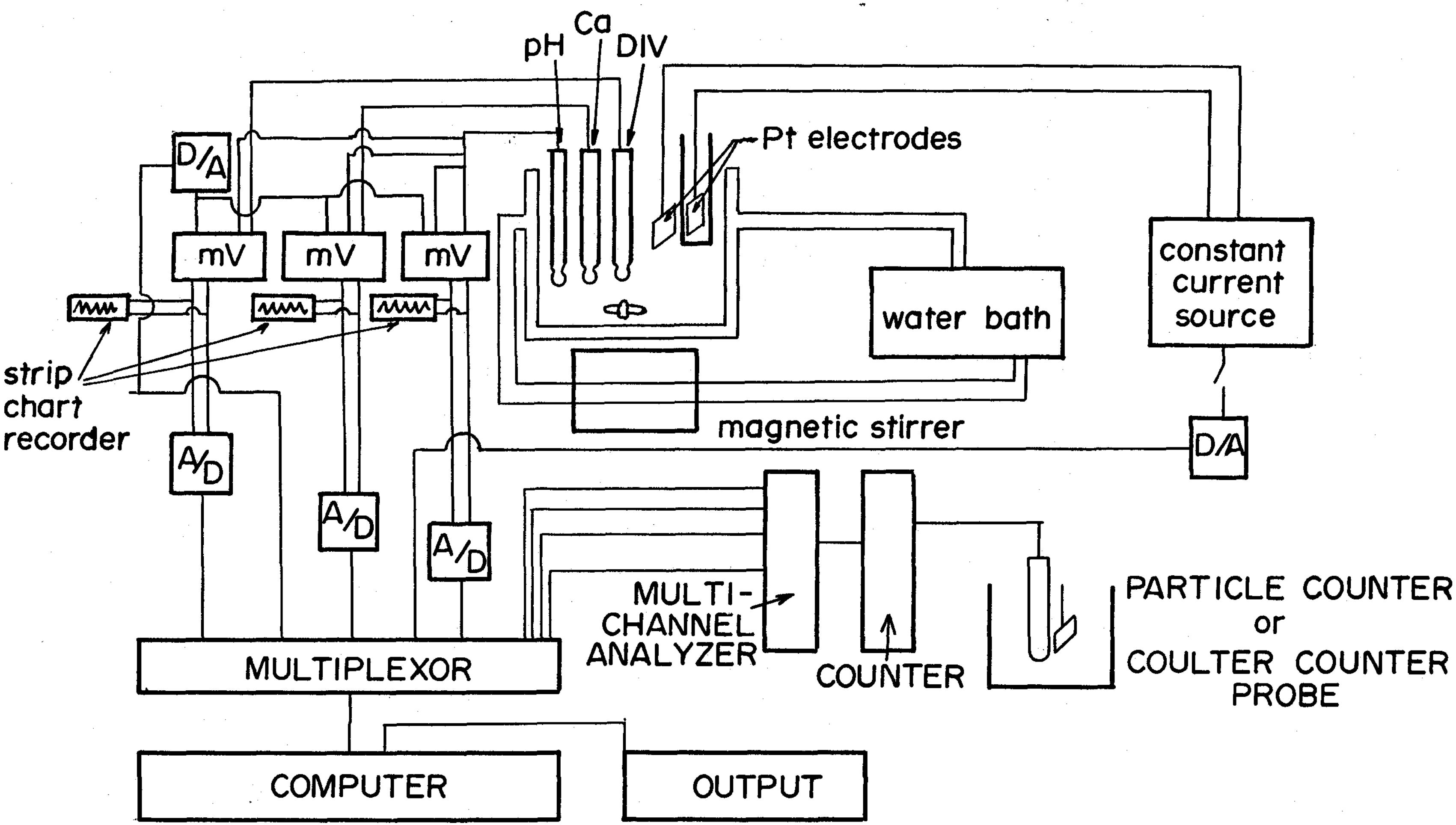
4. Design

An attempt will be made to place all phases of system control and data acquisition under control of a processor based real time operating system. A user-machine interactive executive program will allow the user to specify control parameters, enter information pertinent to the electrolytic sample solution and initiate control actions at will. A possible layout of the hardware configuration could be as shown in Fig. 3.

5. System implementation

A Data General Nova minicomputer operating under its Real Time Disk Operating System was used to implement the information system. The extent to which this was done is described in Section VI.

Fig. 3. Hardware configuration for computer controlled experiment


pH
Ca
DIV
Pt electrodes
D/A
mV
mV
mV
strip chart recorder
A/D
A/D
A/D
water bath
constant current source
magnetic stirrer
D/A
MULTI-CHANNEL ANALYZER
COUNTER
PARTICLE COUNTER or COULTER COUNTER PROBE
MULTIPLEXOR
COMPUTER
OUTPUT

PART III

DEVELOPMENT OF THE PRECIPITATION METHOD

III.A. Introduction

Certain requirements were deemed necessary for the successful development of a $CaCO_3$ precipitation method suitable for the type of study described in Section II. This investigation would examine the effects of Mg^{++} ion on $CaCO_3$ nucleation. The experiments involved make the following assumptions about the nature of the desired precipitation method:

1. That $CaCO_3$ can be precipitated from aqueous solution as a result of $CO_3^{=}$ generation.
2. That the generation process does not introduce extraneous substances which could affect the solubility of $CaCO_3$ independently of the Mg^{++} ion.
3. That the user be able to control the rate and duration of $CO_3^{=}$ generation.
4. That the precipitation process can take place below 50°C and preferably at room temperature.
5. That the onset of precipitation can be determined.
6. That the $CO_3^{=}$ concentration at such time can be derived.

None of the methods described in Section I fulfill the specifications of the proposed method. This of course was not apparent at the development stage. Two methods were chosen successively as possible approaches:

1) trichloroacetate hydrolysis and
2) Kolbe's electrochemical reaction.

Experimentation with these methods soon led to a new idea on how to achieve the desired precipitation. The events leading to this new method now follow chronologically.

III.B. Preliminary Approaches

1. Trichloroacetate Hydrolysis

a. Introduction

As referred to in Section I.E., the hydrolysis of trichloroacetate should result in the formation of $CO_3^=$ and if this reaction takes place in the presence of Ca^{++} ions, $CaCO_3$ should precipitate.

b. Experimental

50 Mls of a 'combined solution' made by mixing equal volumes of 0.05 N Cl_3CCOOH and 0.5 N $Ca(OH)_2$ in a temperature equilibrated beaker was held overnight at 40°C with continuous stirring in a constant temperature water bath. This procedure was repeated at 60°C and at 85°C.

c. Results and Discussion

No obvious reaction took place at 40°C or 60°C. $CaCO_3$ precipitation was finally seen to occur at 85°C. Figure 4 shows pH and temperature changes following placement of the 'combined reaction solution' into a temperature equilibrated beaker at 85°C. Fourteen minutes lapsed before the temperature reached 80°C. The onset of visible precipitation occurred at 63 minutes, leading to copious precipitation 40 minutes later.

Overall temperature equilibration of the system was not found to be reproducible and was too slow. As the amount of $CO_3^=$ generated would be temperature-dependent the rate of hydrolysis would vary with time. This can be seen from Figure 5 which shows the pH and temperature changes following placement of 50 mls of trichloroacetic acid solution into a temperature equilibrated beaker at 85°C in a constant temperature water bath. It took 20 minutes for the solution temperature to reach 80°C and at 27 minutes the temperature was 83.5°C.

The high temperatures needed to carry out a trichloroacetate hydrolysis would exclude the possibility of the use of specific ion electrodes, and $CO_3^=$ generation would not be under user control. This method was found inappropriate.

Fig. 4. pH vs. time during the hydrolysis of trichloroacetate in the presence of Ca^{++} ion

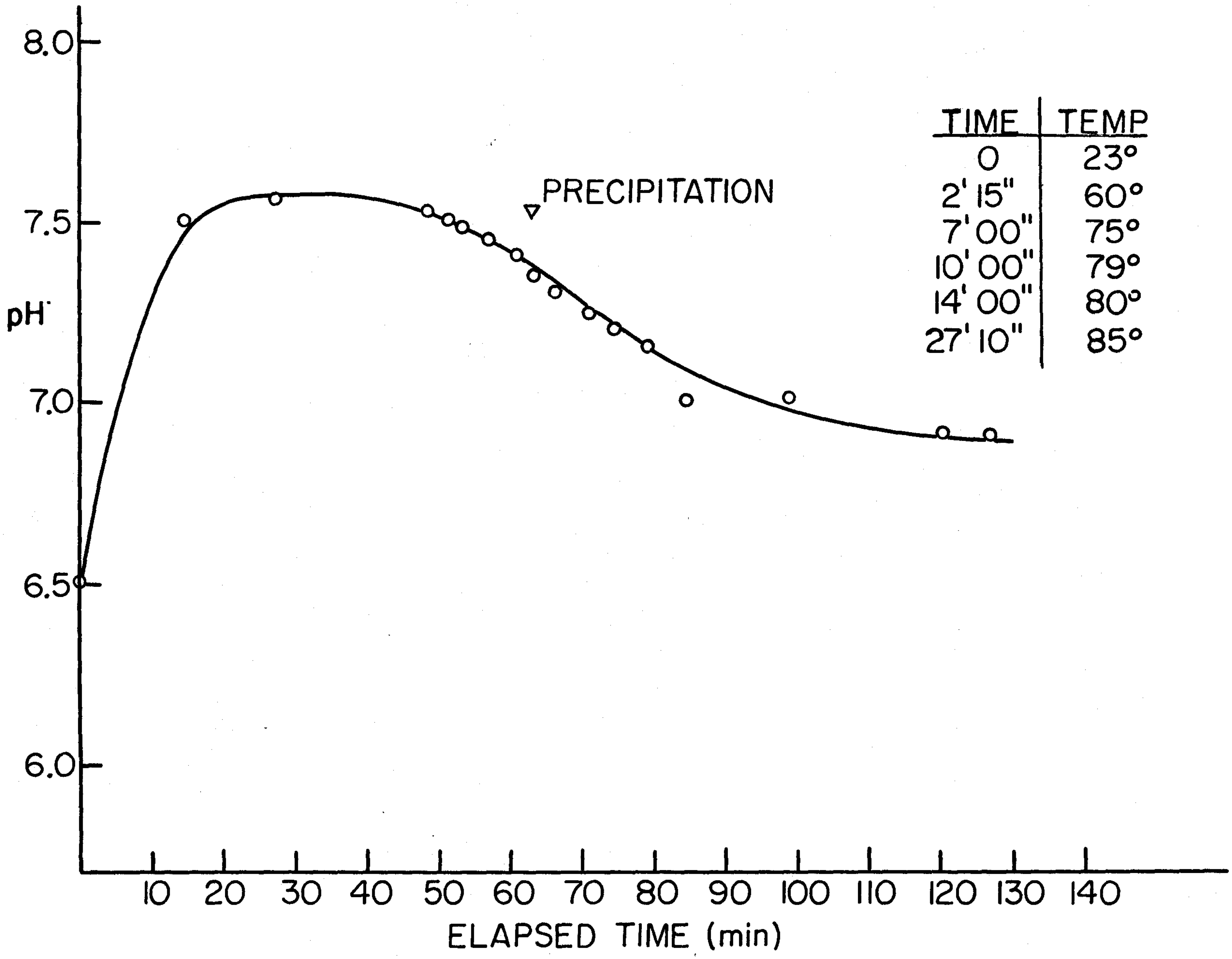
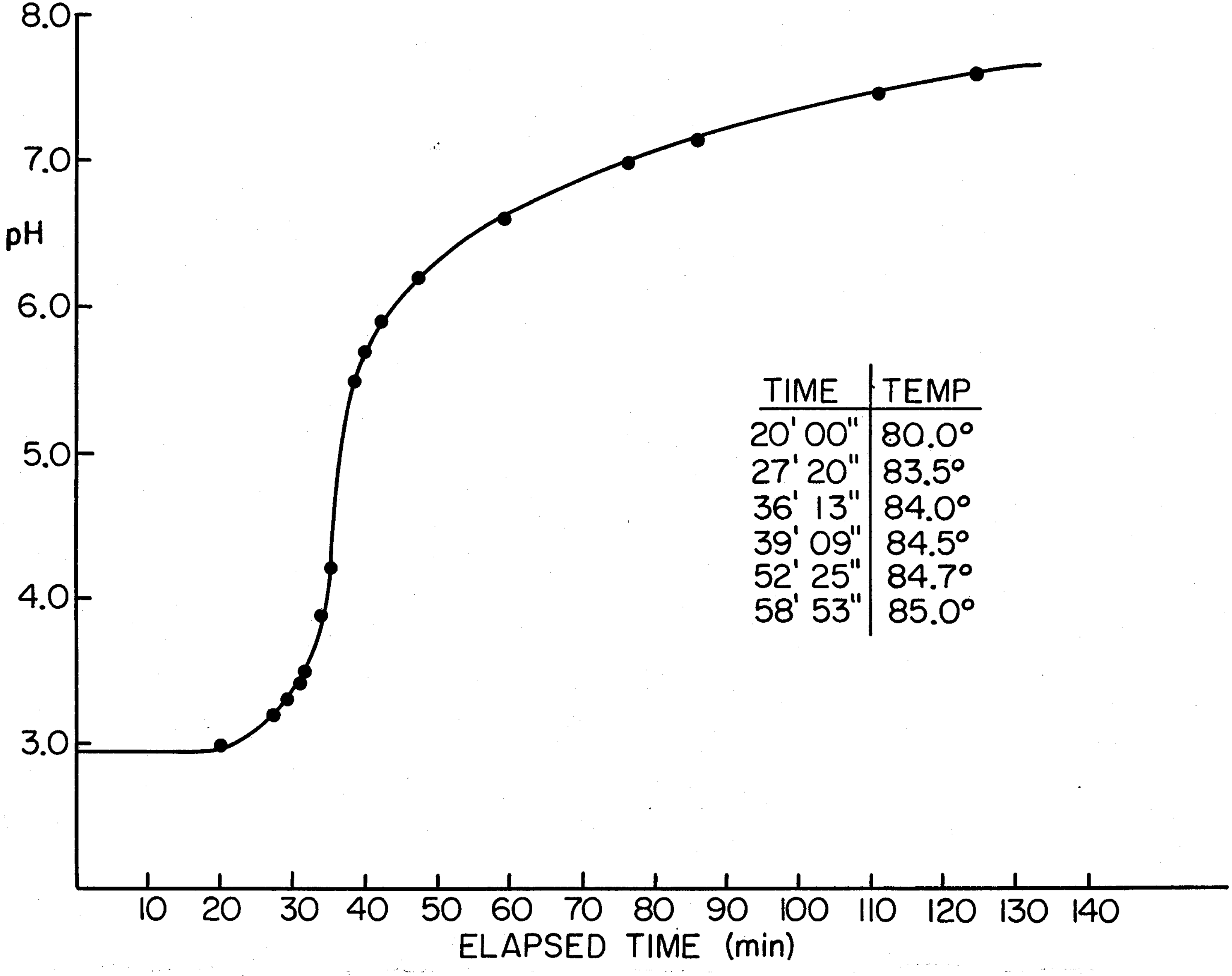

8.0
7.5
pH
7.0
6.5
6.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
ELAPSED TIME (min)
PRECIPITATION
TIME
TEMP
0
23°
2' 15"
60°
7' 00"
75°
10' 00"
79°
14' 00"
80°
27' 10"
85°

Fig. 5. pH vs. time during the hydrolysis of a 0.05 F trichloroacetic acid solution



TIME	TEMP
20' 00"	80.0°
27' 20"	83.5°
36' 13"	84.0°
39' 09"	84.5°
52' 25"	84.7°
58' 53"	85.0°

III.B.2. Kolbe Type Electrolysis

As reviewed in Section I.E., Kolbe's electrochemical reaction was used as a basis for an electrolytic method of $CO_3^=$ generation. The voltage source was a modified Sargeant (Model N) coulometric constant current source as a constant current level would be essential for the indirect determination of the amount of $CO_3^=$ formed.

a) Experimental Details

Run 06-27-1300

One hundred mls of a solution 1 M in acetic acid, 1 M in sodium acetate and 0.05 M in $CaCl_2$ were placed in a beaker so as to form the electrolyte in an electrolytic cell. The cathode was isolated in a small tube fitted with a fritted disk at one end. The solution inside this compartment was 1 M acetic acid and 1 M in sodium acetate. Both electrodes were platinum. A current of 4.825 milliamperes was passed for 30 minutes through the solution which was magnetically stirred. The reaction was repeated using 9.65 milliamps of current.

Run 06-28-1300

50 Mls of (1 M acetic acid and 1 M Na acetate and 0.05 M $CaCl_2$) were neutralized to a pH of 7 using 59 mls of 1 M NaOH. One-tenth gram of $CaCl_2$ was added to bring the final solution to about 0.05 M in Ca^{++}. An electrolysis was carried out as in run 06-27-1300 using a current of 9.65 mamps. After 20 minutes generation was halted.

Run 06-28-1445

The experiment described in run 06-28-1300 was repeated but without use of the fritted disk, both electrodes now being immersed in the same electrolytic solution.

Run 06-28-1645

Ca^{++} ion was added to the fritted glass compartment of run 06-28-1300 and the electrodes reversed, so that the isolated electrode in the electrolytic cell was now the anode. An electrolysis was carried out using 9.65 mamps of current.

Run 06-29-1340

50 Mls each of 0.01 F $NaHCO_3$ and 0.1 F $CaCl_2$ were combined in a 250 ml beaker which was then capped with a drilled out rubber stopper through which a combination electrode and two platinum electrodes could then be inserted and immersed in the electrolytic solution. The anode was placed inside a fritted disk compartment which was then filled with an acetate-acetic acid electrolyte. The solution in the cathode compartment was stirred magnetically. The Pt electrodes were connected to a constant current source and 9.65 milliamps of current passed for 829 seconds.

b) Results and Discussion

Bubbles were seen to rise from both electrodes during the electrolyses of run 06-27-1300. It was hoped that the $OH^{\ominus}$ produced in the cathode compartment would migrate to the anode compartment and react there with CO_2 forming $CO_3^{=}$. (CO_2 is soluble to some extent in the electrolyte.) At 25°C and 0.05 M Ca^{2+}, the carbonate concentration needed to exceed the $K_{S.P.}$ of $CaCO_3$ would have been approximately 10^{-7} molar; however, no precipitation occurred in either trial.

The pH of the anodic solution was measured to be 4.5. It would have taken a considerable amount of base to exhaust this buffer solution. It appeared that $OH^{\ominus}$ was not reacting with the anodic CO_2 but rather being neutralized in the highly acidic electrolytic medium. The pH of the reaction solution must rise to about 9 before an appreciable amount of the CO_2 in solution is in the form of $CO_3^{=}$.

In run 06-28-1300 the electrolytic solution was neutralized prior to the electrolysis. The only goal here was to achieve precipitation. Again gases evolved at both electrodes but no precipitate formed. The final pH of the anodic solution was 6.9. In contrast, the pH inside the fritted disk compartment was 11.5! Apparently the $OH^{\ominus}$ was not the anticipated current carrier through the physical barrier between the two electrode compartments.

A neutralized electrolytic solution was again used in run 06-28-1445 but without isolation of either electrode. After the electrolysis the electrolytic solution pH read 6.9 and no precipitate was observed. Perhaps the $OH^{\ominus}$ produced at the cathode was not reacting with the CO_2 or else both species were reacting in equivalent amounts giving rise to a HCO_3^- H_2CO_3 buffer.

$$CO_2(g) \text{ produced at anode} + H_2O \rightleftharpoons H_2CO_3 \tag{54}$$

$$OH^{\ominus} \text{ produced at cathode} + H_2CO_3 \rightleftharpoons HCO_3^- + HOH \tag{55}$$

In the electrolysis of run 06-28-1645 the anode was isolated in the presence of a basic (pH $\cong$ 11) Ca^{++}/OAc^- ion solution. The CO_2 produced there would dissolve in the electrolyte and hence form $CO_3^=$ in the basic solution. This in fact was the case and precipitation of $CaCO_3$ took place after 17 minutes.

III.C. Conception of a New Idea

The described experiments brought to light two new approaches for the precipitation of $CaCO_3$. A way had now been found to produce CO_2 and $OH^{\ominus}$ and keep either species in contact with a reaction solution and isolated from the other by the use of a fritted disk compartment. Therefore, an electrolysis with either of the following solutions and electrode arrangements would result in $CaCO_3$ precipitation.

Method 1. ($OH^{\ominus}$ reacting with HCO_3^-)

The cathode is placed in contact with a $NaHCO_3$-$CaCl_2$ solution. The anode is isolated.

Method 2. (CO_2 reacting with $OH^{\ominus}$)

The anode is placed in a basic Ca^{++} ion solution. The cathode is isolated.

After some preliminary experimentation it was found that a solution formed by combining equal parts of 0.01 F $NaHCO_3$ and 0.1 F Ca^{++} did not form a precipitate upon standing in a closed container for a a four-hour period. Such a solution was used in the electrolysis of run 06-29-1340.

The idea behind method 1 proved valid. Two minutes after having completed the electrolysis precipitation was first observed.

TABLE II

pH vs. time during the electrolysis of a $Ca(HCO_3)_2$ solution (Run 06-29-1340)

Run Time (Secs)	pH	Observations
50	7.6	
600	7.8	
815	7.7	
829		Stopped Generation
860	7.2	pH drop due to electrical perturbation
949	7.1	precipitation visible
1271	7.1	solution cloudy

Table II shows the pH values recorded during the run. It had been previously observed that upon turning the coulometer on or off the pH meter would become unstable for a period of time. In this run the pH meter was turned on after generation had commenced. Turning the coulometer off resulted in an offset pH measurement upon meter re-stabilization (e.g., from 7.7 to 7.2). However, prior to any visible precipitation the pH dropped. This property of the system could be used to detect the onset of precipitation.

Although method 2 was shown to be effective as a means of generating

$CaCO_3$ in the electrolysis of run 06-28-1645, its use would require high concentrations of $OH^{\ominus}$. Method 1 seemed more suitable to satisfy the six basic requirements which were set forth previously in Section III.A, and as such was chosen as the technique to be used in subsequent experimentation.

III.D. $CaCO_3$ Precipitation from Quasi-Homogeneous Solution

To say that in run 06-29-1340 $CaCO_3$ precipitation occurred from "homogeneous solution" would be inappropriate. Precipitation could just as likely be brought about by addition of a very dilute base to a calcium bicarbonate solution. This certainly would not be PFHS. However, electrolytic $CO_3^{=}$ formation is simpler and provides control not inherent in the direct mixing technique. No additional cation is added to the reaction solution and a certain homogeneity of solution is achieved, in contrast to the sudden gradients that must arise from the mixing of two solutions. The $OH^{\ominus}$ is produced from inside the solution at the electrode surface.

Electrolysis as a method of precipitant generation has been used sparingly; as for example, in the precipitation of magnesium hydroxide (33) and in the precipitation of barium sulphate (32). Klein makes the same remarks about this type of method bearing similarities to PFHS and coins the term 'quasi-homogeneous' for this precipitation technique.

Electrolysis as a method of $CaCO_3$ precipitation has not been cited previously in the literature. In fact this process could just as well be used to precipitate any salt where previously the $OH^{\ominus}$ produced from urea decomposition was used as a method of raising the pH of a solution and thereby causing precipitation (63).

The procedure consists in passing an electric current through an electrolytic cell containing an electrolyte of $CaCl_2$, $NaHCO_3$ and dissolved CO_2 from the atmosphere, in contact with the electrode surface of the cathode. The anode electrode is immersed in this solution but at the same time isolated from it by means of a glass compartment sealed at one end with a fritted disk. The anode solution originally consisted of an equimolar (1M) mixture of sodium acetate and acetic acid. However, any electrolyte will do including the reaction solution.

The essential process is the reduction of H_2O at the cathode producing the OH^- needed to form $CO_3^=$.

$$2H_2O + 2e \rightarrow H_2 + 2OH^-; \quad \varepsilon_{red^\circ} = -0.8277 \text{ V} \tag{56}$$

By controlling the amount of current passed, one can control the amount of $CO_3^=$ produced. This process can be carried out at any temperature by using as the cell a vessel with water jackets attached to a constant temperature bath.

III.D.1 Preliminary Nucleation Experiments

Before this newly developed method was refined a set of experiments was carried out to examine the effects of NaCl and Mg^{++} ion on $CaCO_3$ formation and to further develop the technique.

a. Experimental

For each of several electrolyses a 'matrix' electrolyte solution was made by combining 45 mls each of 0.1 F $CaCl_2$ and 0.01 F $NaHCO_3$. To these matrix solutions ten mls of either NaCl or $MgCl_2$ solutions of varying concentration were added. All water used was de-ionized and no attempt was made to equilibrate any of the stock solutions or the final combined solutions.

After combining the solutions inside a 250 ml electrolytic cell the latter was capped with a sealed four-hole rubber stopper through which a thermometer, two platinum electrodes and a combination pH electrode were inserted. The anode was isolated in a fritted disk compartment filled with reaction solution. For each run the time lag between mixing of the solutions and start of electrolysis was fixed at 15 minutes. After passing 9.65 milliamps of current for 150 seconds at ambient temperature, the induction period needed to observe precipitation was measured.

b. Results and Discussion

Table III shows the effect upon induction time caused by varying the Ca^{++} to Mg^{++} ratio from 50 to 1 and by the addition of NaCl. The onset of precipitation was determined by a drop in pH which normally preceeded visual observation from about 15 to 50 seconds.

These preliminary studies pointed to NaCl catalysis and Mg^{++} ion inhibition of $CaCO_3$ formation. These results were very encouraging and efforts were now made towards refining and standardizing the precipi-

TABLE III

Induction time vs. Ca^{++} to Mg^{++} ratio and added NaCl

Matrix Sol. + 10 mls of	μ	Ca/Mg	secs t (induction time)
H_2O	0.140	---	135
0.01 F $MgCl_2$	0.143	50	95
0.1 F $MgCl_2$	0.161	5	365
0.5 F $MgCl_3$	0.290	1	∞
0.03 F NaCl	0.143	---	30
0.015 F NaCl	0.141	---	80

tation procedure so as to minimize as much as possible all other variables besides the ones being studied. The use of specific ion electrodes had not yet been incorporated into these first runs. Their use is described in Section IV.B.

III.D.2 Refinement of the Method

Three important variables determining the reproducibility of these experiments will be the number of foreign nuclei in solution, the amount of CO_2 in solution and the extent to which the solution is stirred. Experiments showed that upon continuous stirring, matrix-based solutions (a 'matrix' solution + 10 mls H_2O) would give rise to spontaneous precipitation within 15 to 20 minutes with the pH fixed at about 7.57 until the onset of precipitation. It was also observed that upon bubbling air through matrix-based solutions the pH rose gradually and precipitation was initiated.

The runs in Appendix A are representative of attempts leading to the development of a final acceptable matrix solution. From those runs it is seen that the addition of a Ca^{++} ion solution to a HCO_3^- solution lowers the pH considerably when compared to a similar portion of added H_2O. This seems to be an indication of complexation occurring between Ca^{++} and HCO_3^- and $CO_3^=$ to form $CaHCO_3^+$ and $CaCO_3^\circ$.

More important is the observation that unless the final system is in equilibrium with atmospheric CO_2, carbon dioxide will enter or escape from the solution. When the matrix solution was left opened to the air the pH rose, indicating that CO_2 had left the solution. As shown in Section I.D.2 the fraction of HCO_3^- in the form of $CO_3^=$ is dependent on the pH which is dependent on the CO_2 equilibrium.

Table IV shows the rise in pH occasioned by preparing HCO_3^- solutions of different concentrations and letting them equilibrate with atmospheric CO_2 overnight. All solutions were prepared with de-ionized distilled H_2O which had been boiled with N_2 bubbled through it and cooled inside glass bottles void of CO_2. The solutions were placed in 100 ml beakers and to avoid large volume losses due to evaporation, each was partially covered with parafilm.

The concentration of CO_2 in a solution in equilibrium with air at atmospheric pressure ($PCO_2 = 10^{-3.5}$ atm.) can be calculated to be 1.1×10^{-5} M using equation (26). In the last column of Table IV, approximate values are listed for the initial experimental CO_2 concentration arising as a result of the bicarbonate equilibria (reactions 13-16). Using equation (18) and assuming that $[HCO_3^-]_i$ is equal to its analytical composition[†]

$$[CO_{2_i}] = \frac{[H_o^+][HCO_{3_i}^-]}{4.4 \times 10^{-7}} \tag{18}$$

As the solutions equilibrated, the excess CO_2 in the solutions escaped, with a subsequent shift in the carbonate equilibrium reactions (reactions 13-16) to the left resulting in a rise in solution pH.

The task of finding the proper matrix solution took into account these factors in aiming for reproducibility:

1. That the system be in equilibrium with atmospheric CO_2.
2. That the ionic strength of the solution be kept as low as possible for better specific ion electrode response.
3. That the number of foreign particles be normalized.
4. That stirring of the solution should not be a factor in itself to bring about precipitation.
5. That there would be enough $CaCO_3$ produced in the system after $CO_3^=$ generation to bring about visible precipitation.

The final matrix solution arrived at combined 45 mls of air equilibrated 0.005 F $KHCO_3$ with 45 mls of 0.025 F $CaCl_2$. The HCO_3^- solution was made with de-ionized-distilled CO_2 free water and then equilibrated with atmospheric CO_2 by bubbling air through it until the

---

[†] From Table I it is seen that in the pH range 8.0 to 8.5 carbonate is present mostly in the form of HCO_3^-.

pH was constant. The Ca^{++} solution was made using the water produced by a mixed-bed ion exchanger.

Upon dilution with ten mls of water the pH of the matrix solution is in the neighborhood of 8.1. The analytical Ca^{++} and initial HCO_3^- concentrations are as follows:

$$[Ca^{++}] = 0.0113 \text{ F}$$

$$[HCO_3^-] = 0.0023 \text{ F}$$

Neglecting ion pair formation one can roughly estimate the fraction present as $CO_3^=$:

$$\alpha CC_3^= = \frac{Kd_2}{[H^+]M} \tag{57}$$

where

$$M = \left[\frac{[H^+]}{Kd_1 \cdot K_2} + \frac{[H^+]}{Kd_1} + 1 + \frac{Kd_2}{[H^+]}\right]$$

At a pH of 8.1, $\alpha CO_3^= = 6.87 \times 10^{-3}$ of the total HCO_3^-. And at an ionic strength of 0.036 the mean activity coefficient for $CaCO_3$ in solution is 0.41, so that the $Ca^{++} \times CO_3^=$ ion activity product in a matrix-based solution is:

$$\begin{aligned} ACO_3^= \cdot ACa^{++} &= fCO_3^= \cdot \alpha CO_3^= \cdot [HCO_3^-] \cdot fCa^{++} \cdot [Ca^{++}] \\ &\cong 3 \times 10^{-8} \end{aligned} \tag{58}$$

The $K_{S.P.}$ for $CaCO_3$ is in the order of 1.6×10^{-8}. It was found that when matrix-based solutions were prepared and placed in 125 ml sealed polyethylene containers no precipitation would ensue, even after prolonged shaking.

TABLE IV

pH vs. time for HCO_3^- solutions equilibrating with air at atmospheric pressure

$[HCO_3^-]$	pH_0	pH_1	pH_2	CO_{2_i}
0.010	8.51	8.97	9.12	7.0 E-05
0.020	8.48	9.10	9.31	1.5 E-04
0.050	8.42	9.12	9.41	4.3 E-04
0.100	8.34	9.09	9.41	1.0 E-03

(a) potassium bicarbonate solutions

$[HCO_3^-]$	pH_0	pH_1	pH_2	CO_{2_i}
0.010	8.49	8.94	9.11	7.3 E-05
0.020	8.41	9.07	9.29	1.8 E-04
0.050	8.35	9.09	9.39	5.1 E-04
0.100	8.26	9.02	9.35	1.2 E-03

(b) sodium bicarbonate solutions

H_2O-CO_2 free $pH_0 = 6.44$ $pH_1 = 6.33$

pH_0 = initial pH upon mixing

pH_1 = pH after 24 hrs equilibration

pH_2 = pH after 72 hrs equilibration

CO_{2_i} = Experimental approximation of initial $[CO_2]$

Two other components considered in the final system are now briefly described.

Minimization of Foreign Nuclei in Solution

When the matrix-based solution was pressure filtered, electrolysis failed to produce a precipitate. Filtration was therefore not used and large enough batches of solution were prepared to allow completion of a set of experiments using the same solvent throughout. The low levels of supersaturation attainable seem to require heterogeneous nucleation as a necessary mechanism for precipitate formation.

Determination of the Onset of Precipitation

pH Drop

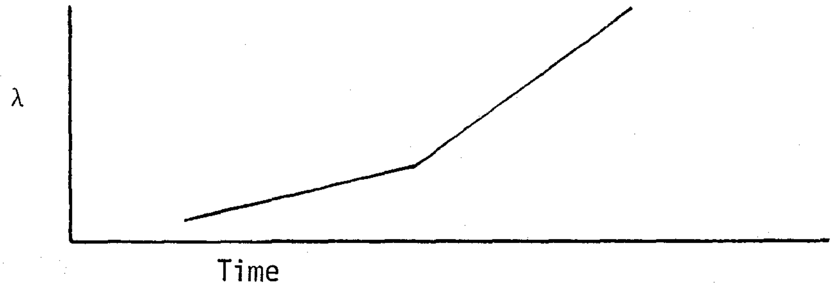
Upon $CaCO_3$ forming, $CO_3^=$ is removed from the system and the equilibration shift ensuing results in H^+ being generated. This pH drop was used satisfactorily to detect the onset of precipitation in all runs and always preceeded visual observation of precipitation. pH Drop was chosen over two other possible approaches.

Turbidimetry

The appearance of solid $CaCO_3$ can interact with light in various ways to signal the onset of precipitation.

Conductance

In the reduction of H_2O, OH^- is produced which reacts with HCO_3^- to produce $CO_3^=$. At the onset of precipitation Ca^{++} and $CO_3^=$ are removed from the system but $H^{\oplus}$ is produced. Considering what the equivalent conductances of the ions involved are (Table V) it would seem likely that a plot of solution conductance vs. time would be represented as depicted by the following curve:



The abscissa value of the point of intersection of the two straight lines would correspond to the onset of precipitation.

TABLE V

Ionic equivalent conductances at infinite dilution at 25°C (39)

Ion	λ°, mho-cm^2/g. equivalent
HCO_3^-	44.5
$CO_3^=$	69.3
H^+	349.0
OH^-	198.0
Ca^{++}	59.5

In the next section studies were carried out to evaluate the suitability of the method to accomplish the goals set forth in Section II.

PART IV

APPLICATION OF THE PRECIPITATION METHOD

IV.A. Introduction

The method developed for quasi-homogeneous precipitation of $CaCO_3$ (see Section III.D) seemed suitable at first to carry out nucleation studies as outlined in Section II. These experiments would consist of calculating the critical ion product of $CaCO_3$ as a function of Mg^{++} ion concentration and ionic strength using two approaches:

> The first approach would measure the critical supersaturation while generating precipitant at a constant rate.
>
> The second approach would entail stopping $CO_3^{=}$ generation prior to the onset of precipitation and then measuring the critical supersaturation after an induction period "τ_o".

IV.A.1 Electrical Interferences

It was pointed out previously that turning on the current source of the coulometer had an adverse effect on the stability of the pH meter. It had been hoped that use of a grounded platinum shield around the glass and calomel electrodes, as suggested by Klein (34), would do away with the interference. Considerable experimentation with this problem offered no solution; neither shielding the generating electrodes nor use of a combination electrode in place of the glass and calomel electrodes helped.

Different grounding schemes were attempted, assuring that all grounds were at the same potential to avoid ground loops. The interference persisted even when using an isolation transformer to isolate line voltage. If the electrodes were inserted into the solution after having turned on the coulometer or having the electrodes in the solution but turning them on only after generation had commenced the initial pH readings still oscillated in a pH range of 6 to 10. This effect was much more noticeable when using digital pH meters.

In previous experiments using a meter with an analog readout, the inertia of the pH needle had apparently dampened the shock much more. The final problem arose when it was observed that turning on the coulometer affected pH readings when the sensing electrodes were placed in a different beaker than those of the electrolysis circuit. Shielding of the cables leading to the platinum electrodes did not solve the problem.

Initial fluctuations of pH readings combined with a prolonged bias from the actual pH proved to be an obstacle to carrying out preliminary investigations based on the first approach. Use of a light scattering detector for the onset of precipitation would eliminate the presence of these electrical interferences.

IV.B. In Conjunction with Specific Ion Electrodes

It would be of great interest to monitor the activities of Ca^{++} and Mg^{++} ions prior and up to the onset of precipitation. In this section an evaluation of the use of specific ion electrodes to accomplish this task is presented.

IV.B.1. Experimental

Calibration standards were prepared by dilution of an Orion supplied 0.1000 F $CaCl_2$ stock solution. Orion specific ion electrodes model 92-20 (Ca^{++} ion) and 92-32 (divalent cations) were calibrated separately after immersion in each respective calibration solution for a period of one minute after which time mv readings were taken every 15 seconds for 2 minutes using a Fisher Model 420 digital pH meter on the expanded scale. A saturated calomel electrode served as the reference electrode.

The experimental set-up illustrated in Fig. 6 was used to record H^+ ion, Ca^{++} ion and divalent ion activities after halting $CO_3^=$ generation and prior to the onset of precipitation in matrix-based solutions of varying Mg^{++} to Ca^{++} ratios. The signal from the reference electrode was tapped so as to produce 3 outputs, with one lead going to each of the pH meters. The specific ion electrodes were normally immersed at a 20° angle with respect to the vertical to avoid having bubbles lodge themselves in the concave tip of the electrode, therefore causing electrode fluctuations. In order to eliminate that possibility altogether the specific ion electrodes were also introduced into the solution after generation had stopped. (At this time gas production ceases.)

IV.B.2. Results and Discussion

Both specific ion electrodes exhibit Nernst potential behavior as given by the following equations:

$$ECa = Ex + 2.3 \frac{RT}{2F} \log_{10} (ACa^{++} + CxAx^{++}) \qquad (59)$$

$$Ediv = Ea + 2.3\,\frac{RT}{2F}\,\log_{10}\,(ACa^{++} + AMg^{++} + KxAx^{++}) \qquad (60)$$

where: ECa and Ediv = the measured total potential for the Ca^{++} and divalent electrode systems respectively

Ex and Ea = the portion of the total potential due to choice of internal and external reference electrodes and internal solutions

$2.3\,\frac{RT}{2F}$ = Nernst factor (29.58 mv at 25°C)

ACa^{++} = the calcium ion activity in the sample solution

AMg^{++} = the magnesium ion activity in the sample solution

Cx = selectivity constant for the divalent cation X^{++} (0.014 for Mg^{++})

Kx = selectivity constant for a third divalent cation

Monovalent cations are also detected by the electrodes. The error is larger with Na^+ than with K^+. The highest concentration of K^+ used in any of the runs was 0.03 M. For the Ca^{++} electrode the error introduced is negligible. For the divalent electrode the positive error introduced would be under 1% (47).

Table VI Part "a" shows the electrode potentials developed by the calibration solutions. Table VI Part "b" shows recalibration readings after 25 minutes on two of the standards calibrated in Table VI Part "a". From the range and σ values in Table VII Part "b" it is seen that the stability of the calibration readings varied from solution to solution. Overall the divalent electrode responded better. Figure 7 shows the calibration curves for the mean mv readings vs. ion activity given on Table VII.

From Tables VII Parts "b" and "c", the Ca^{++} electrode mean mv readings can be seen to have changed by +10% and +4.1% respectively for the 0.0050 and 0.010 F standards during a 25 minute period. From Table VI it is actually seen that for the 0.010 F standard, the values of the Ca^{++} readings taken before and after recalibration form two non-overlapping sets. Readings taken on the calibration solutions drift with time. It is well to note that under the same conditions pH readings were very stable.

Table VIII shows calibration data preceeding and following an electrolysis in a matrix-based sample solution with an initial Mg^{++}/Ca^{++} ratio of 0.5 and a total ionic strength of 0.07. Recalibration showed (Table IX) that half an hour after the original calibration, meter readings on the 0.010 and 0.020 standards with both electrodes had changed substantially. Table IX also shows the Ca^{++} and Mg^{++} activities of the sample solution as calculated using the Debye-Hückel Limiting Law and as initially measured. The calculated values are an approximation and are high as they only account for ionic strength effects but not for ion-pair formation.

Table X shows the actual electrode readings measured after generating 195 mamps of current for 15 seconds. Forty-five seconds after halting generation the Ca^{++} and divalent electrodes read 26.6 mv and 19.6 mv respectively. Based on the calibration curve made at the beginning of the run (Fig. 8) these values correspond to activities of 5.2×10^{-3} and 5.3×10^{-3} for the Ca^{++} and divalent ($Ca^{++} + Mg^{++}$) ions respectively. The Ca^{++} reading seems high.

The Ca^{++} readings dropped steadily with time prior to precipitation. The divalent electrode readings did stay essentially unchanged at

19.6 mv. Because particles forming in solution contribute noise to the electrode signal, readings were stopped when the solution became cloudy.

The actual difficulty with the electrodes involved the inconsistencies in readings (due to electrode wander) and the drift inherent in the potential developed by the calibration solutions. This latter property calls for frequent recalibrations which in this system are not possible during the analysis. These two properties of the electrodes compound themselves, making the electrode readings difficult to interpret. Response time and the stability of measurements were not found to be within the tolerances required to determine on a real time basis the Ca^{++} and divalent (Ca^{++} + Mg^{++}) ion activities and to subsequently calculate the Mg^{++} ion activity.

TABLE VI

Mv readings on $CaCl_2$ standards using Ca^{++} and divalent ion specific ion electrodes

		Elapsed Time Secs								
		0	15	30	45	60	75	90	105	120
$[Ca^{++}]$ moles/l	Electrode	mv Reading								
0.0050	CA	13.0	13.5	13.8	14.0	14.1	14.2	14.5	14.5	14.6
0.0050	DIV	8.7	9.9	9.0	9.1	9.2	9.2	9.2	9.2	9.3
0.010	CA	21.7	21.6	21.7	21.8	21.9	22.3	22.1		
0.010	DIV	15.5	15.5	15.6	15.5	15.5	15.4	15.4		
0.020	CA	29.7	29.9	30.4	30.6	30.8	31.1	31.2	31.4	31.5
0.020	DIV	22.1	22.1	22.0	21.9	21.9	21.8	21.8	21.8	21.7
0.025	CA	32.6	32.8	33.3	33.4	33.7	33.1	32.8	32.8	32.7
0.025	DIV	24.0	24.0	24.0	23.9	23.9	24.0	24.0	24.0	23.9

(a)

0.0050	CA	15.0	14.9	15.2	15.2	15.3	15.8	15.7	15.7	15.7
0.0050	DIV	9.4	9.2	9.2	9.1	9.1	9.1	9.1	9.1	9.1
0.010	CA	22.6	22.9	23.0	23.0	22.9	22.8	22.8	22.8	22.9
0.010	DIV	15.8	15.5	15.4	15.4	15.3	15.3	15.2	15.3	15.2

(b)

(a) initial calibration

(b) recalibration after 25 minutes

TABLE VII

Mean mv readings on $CaCl_2$ standards vs. Ca^{++} activity
(from raw data on Table VI)

$[CaCl_2]$	μ_T	λCa^{++}	ACa^{++}	$\log ACa^{++}$
0.0050	0.015	0.56	2.8×10^{-3}	-2.55
0.010	0.030	0.44	4.4×10^{-3}	-2.36
0.020	0.060	0.32	6.4×10^{-3}	-2.19
0.025	0.075	0.28	7.0×10^{-3}	-2.15

(a)

$[Ca^{++}]$	ACa^{++}	CA $\overline{X}$ (MV)	CA RANGE (MV)	σ	DIV $\overline{X}$ (MV)	DIV RANGE (MV)	σ
0.0050	2.8×10^{-3}	14.0	1.6	0.52	9.1	0.6	0.19
0.010	4.4×10^{-3}	21.9	0.6	0.20	15.5	0.2	0.17
0.020	6.4×10^{-3}	30.7	1.8	0.64	21.9	0.4	0.14
0.025	7.0×10^{-3}	33.0	1.1	0.37	24.0	0.1	0.15

(b)

0.0050	2.8×10^{-3}	15.4	0.9	0.34	9.1	0.3	0.10
0.010	4.4×10^{-3}	22.8	0.4	0.12	15.4	0.6	0.19

(c)

(a) Calculation of Ca^{++} activities in standard solutions where

$$-\log \lambda Ca^{++} = 0.51 Z_i^2 \sqrt{\mu_T}$$

(b) Calibration mean mv readings, range and σ values.

(c) Recalibration values after 25 minutes.

TABLE VIII

Specific ion electrodes calibration data before and after an electrolysis

		Elapsed Time (Secs)								
		0	15	30	45	60	75	90	105	120
$[Ca^{++}]$	Electrode	mv Reading								
0.010	CA	22.4	22.8	22.7	22.8	22.7	22.7	21.9	21.9	21.9
0.010	DIV	16.5	16.7	16.7	16.5	16.4	16.9	16.4	16.3	16.2
0.020	CA	30.5	31.4	31.8	32.0	32.4	30.8	30.2	30.0	29.8
0.020	DIV	28.2	23.1	23.1	23.0	22.9	22.9	22.9	22.9	22.9
Sol #5	CA	19.3	18.8	18.6	--	18.8	19.4	18.9	18.8	18.7
Sol #5	DIV	20.0	20.0	20.0	--	20.0	19.9	19.8	19.8	19.8

(a)

0.010	CA	26.3	25.3	24.9	24.6	24.4	24.1	23.8	23.8	23.8
0.010	DIV	15.9	15.9	15.9	15.8	15.8	15.7	15.6	15.6	15.6
0.020	CA	27.2	28.5	29.2	29.6	29.6	29.1	28.0	27.9	27.8
0.020	DIV	21.3	21.3	21.2	21.6	21.3	21.3	21.2	21.3	2.13

(b)

(a) initial readings on standards and sample solution #5

(b) recalibration readings on standards after electrolysis

TABLE IX

Mean mv calibration data before and after an electrolysis
(From raw data on Table VIII)

Ca^{++}	ACa^{++}	Ca^{++} $\overline{X}$ (MV)	Ca^{++} RANGE (MV)	Ca^{++} σ	DIV $\overline{X}$ (MV)	DIV RANGE (MV)	DIV σ
0.010	4.4×10^{-3}	22.4	0.9	0.4	16.5	0.7	0.22
0.020	6.4×10^{-3}	30.9	2.6	0.94	22.9	0.3	0.11
Sol #5[1]		18.9 [2]	0.7	0.29	19.9	0.2	0.1
				(a)			
0.010	4.4×10^{-3}	24.5	2.5	0.84	15.7	0.3	0.13
0.020	6.4×10^{-3}	28.5	2.4	0.87	21.3	0.4	0.12
				(b)			

---

[1]

	Analytical $[Ca^{++}]$	Theoretical ACa^{++}	Measured ACa^{++}	Analytical $[Mg^{++}]$	Theoretical AMg^{++}	Measured AMg^{++}
Sol #5	0.0112	6.0×10^{-3}	3.6×10^{-3}	0.0056	6.0×10^{-3}	1.8×10^{-3}

[2] $\overline{X}_{corr} = 18.8$; at $(AMg^{++}/ACa^{++}) = 0.5$, a 0.7% error

(a) mean mv readings at initial calibration time

(b) mean mv readings 30 minutes later

TABLE X

Electrodes readings vs. time after the electrolysis of solution 5

			MV	
Time (secs)	pH	Time (secs)	CA	DIV
30	8.82	45	26.6	19.6
60	8.81	75	28.8	19.6
100	8.81	90	27.1	19.6
120	8.81	120	24.7	19.6
185	8.80	170	22.6	19.6
240	8.78	250	20.7	19.6
280	8.76	300	21.1	19.6
315	8.74	405	19.7	19.5
345	8.70		(b)	
370	8.68			
390	8.65			
450	8.56			
510	8.47			
(a)				

(a) pH vs. time after current generation

(b) specific ion electrode readings vs. time after current generation

Fig. 6. Experimental set up for induction time studies using electrolytic precipitation of $CaCO_3$

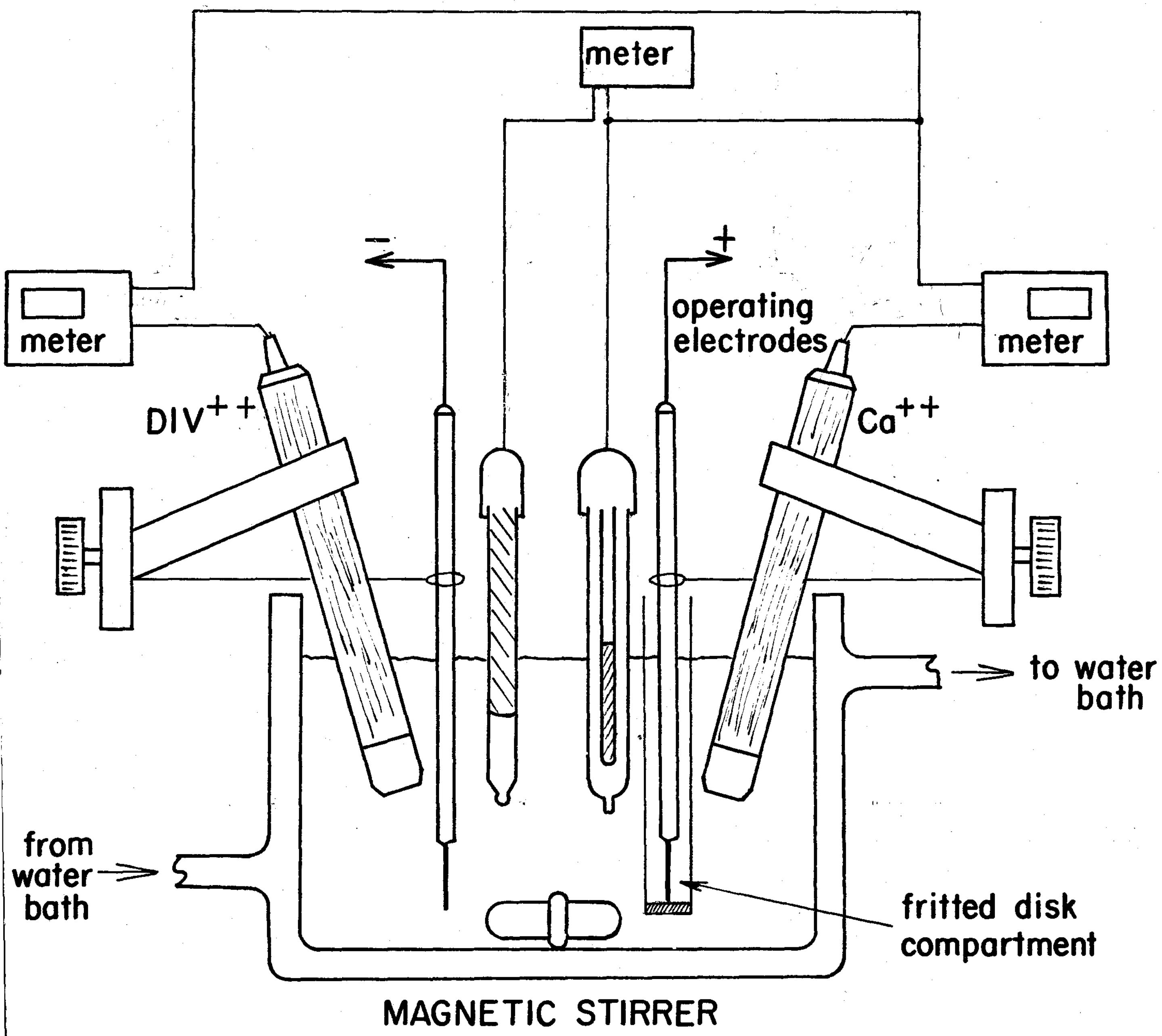

meter
meter
meter
−
+
operating electrodes
DIV^{++}
Ca^{++}
to water bath
from water bath
fritted disk compartment
MAGNETIC STIRRER

Fig. 7. Electrode potential vs. log of Ca^{++} activity (using values from Table VII part "b")

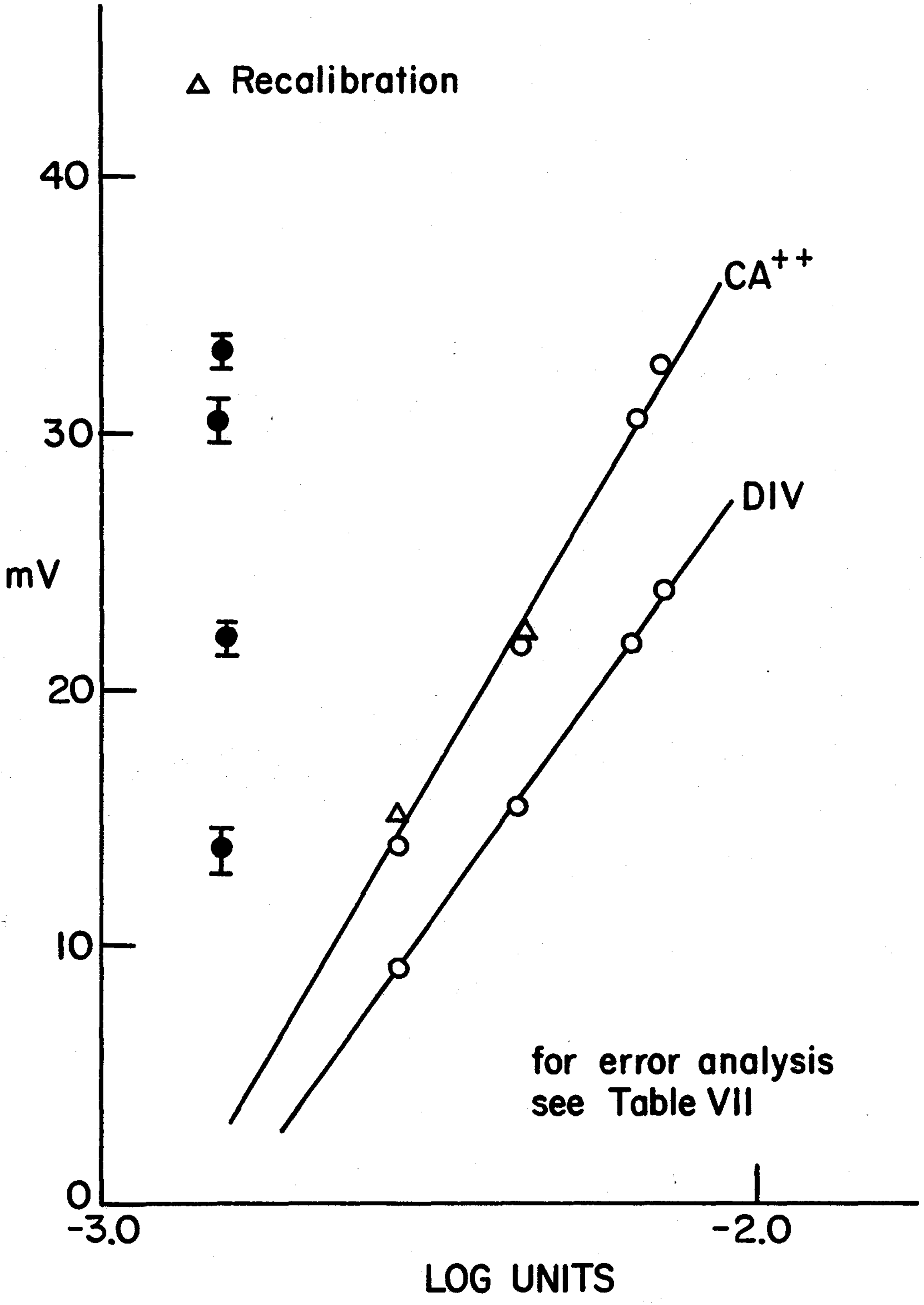
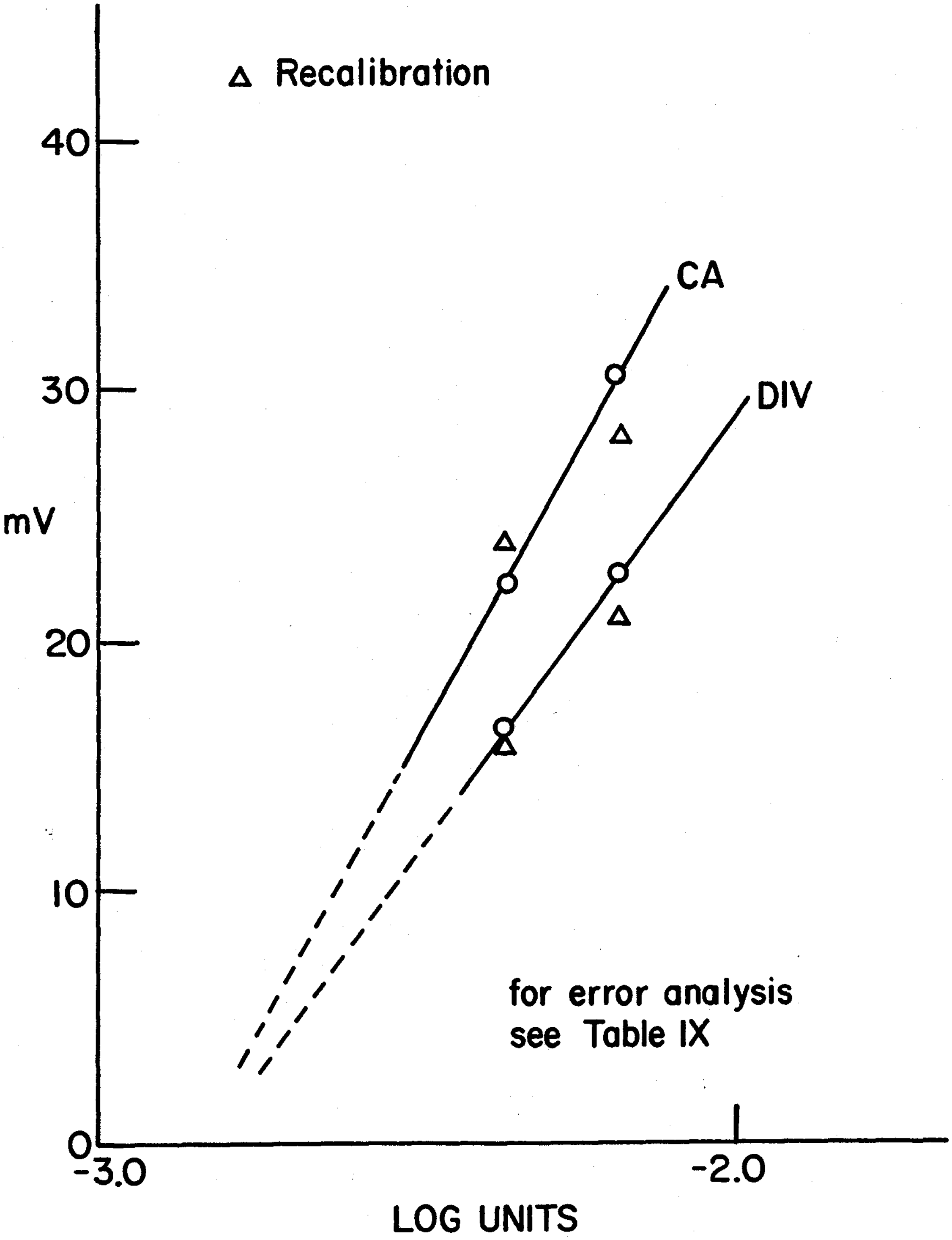

△ Recalibration
40
30
mV
20
10
0
-3.0
-2.0
LOG UNITS
CA⁺⁺
DIV
for error analysis
see Table VII

Fig. 8. Electrode potential vs. log of Ca^{++} activity (using values on Table IX parts "a" and "b")


△ Recalibration
40
30
20
10
0
mV
CA
DIV
for error analysis
see Table IX
-3.0
-2.0
LOG UNITS

IV.C. Induction-time studies of $CaCO_3$ nucleation

Based on the results gathered from using the specific ion electrodes, the decision was made not to measure critical supersaturation but to clearly limit the scope of the nucleation experiments to measurements of induction times.

IV.1. Experimental

Two sets of experiments labelled IA and IB were designed to measure induction time in precipitation reactions from quasi-homogeneous solution as a function of Mg^{++} ion concentration and ionic strength respectively. Group IA varied the Mg^{++}/Ca^{++} ratio from 0.1 to 1 in 0.1 incremental steps. Total ionic strength was kept constant at 0.07 for all samples in this group by adding KCl. Group IB varied the ionic strength from 0.01 to 1.0 as a result of adding either KCl or NaCl. Four sets of group IA experiments and 3 sets of group IB experiments were carried out.

Reagent grade chemicals were used throughout the experiments. All bicarbonate solutions were prepared with de-ionized distilled CO_2-free water and left to equilibrate with atmospheric CO_2 overnight as air was passed through a gas dispenser in the solutions. $CaCl_2$, $MgCl_2$, KCl and NaCl solutions were prepared with de-ionized distilled H_2O as obtained from an ion exchanger.

The experiments were run in a 250 ml glass container with a water jacket connected to a constant temperature bath held at 25°C. All solutions were stirred magnetically at a constant rate. The reaction cell was opened to the ambient air. pH Measurements were made with glass and saturated calomel electrodes using a Beckman 540 research digital meter and standardized to ± 0.01 pH units with both 6.86 and 9.17 buffers. A Sargent (Model N) coulometric constant current source supplying 195 mamps to two Pt electrodes was used to carry out the electrolyses.

Solutions were normally prepared by combining 45 mls of 0.0050 F $KHCO_3$ and 45 mls of 0.025 F $CaCl_2$ along with solutions of $MgCl_2$ and KCl to make 100 mls of final solution. These solutions were added directly to 125 ml polyethylene containers which were then capped and left equilibrating for at least 24 hours.

At run time the platinum electrodes were placed in position and then a sample solution transferred to the reaction cell. Sample solution was then pipetted into the anode compartment and the solution pH taken leaving the glass and calomel electrodes in place. The pH meter was then turned off and solution stirring started a minute prior to current generation. After stopping generation a stopwatch was started and pH readings were taken vs. time.

Electrode surfaces and container surfaces were washed with dilute HCl and distilled H_2O between runs. The reaction cell and anode compartment were dried using a high power hot air drier.

The results of the experiments are given in Tables XI, XII and XIII. The sample solutions referred to within any one table were prepared from the same batch of matrix solutions but three different batches were used to prepare the samples associated with each of the tables.

IV.2. Results and Discussion

Induction Period

The induction period preceeding the onset of precipitation is analyzed in terms of two variables: lag time and induction time. These two parameters are illustrated in Figure 9 in which plots of pH vs. time lapsed after electrolysis are shown for 2 runs in set 2 of group IA. Table XV contains the raw data for these 2 experiments and shows for each sample solution the time interval between each successive pH unit drop. As can be seen, the pH values for a sample solution would drop quickly to a steady value within half a minute after which a period of time would follow without a drop in pH or with the pH fluctuating between a high and low value. At some time later the pH would drop again but it would then continue to do so in a well-defined manner (without fluctuations) at smaller and smaller time intervals. Although not shown on Table XV these time intervals between successive unit pH drops would go through a minima and then increase again as the precipitation process became complete at which time the pH would stabilize.

The first handle, lag time, corresponds to the absolute time after stopping generation when the pH dropped from its steady value. The second handle, induction time, refers to the time of the subsequent pH drop. Nucleation must occur during the lag time and the induction time probably signals that steady state growth has commenced.

IV.C.2.b. Mg^{++} ion effects

In Table XI the composition of each sample solution used in the IA group is defined. Table XI also contains the pH values for each sample solution in set 1 after the addition of each of its components. It is readily observed (pH_3) that upon adding Ca^{++} ion to the HCO_3^- solutions a substantial drop in pH occurred. Though the subsequent drop in pH due to the addition of Mg^{++} ion was much smaller it can be seen that with increasing Mg^{++} ion the drop was larger. A comparison of final pH in solution #0 (pH_3) and solution #10 (pH_4) indicates that ion pair formation must be occurring between the carbonate species and Mg^{++} ion as well as with Ca^{++} ion.

pH_5 and pH_6 correspond respectively to the pH of the sample solutions immediately before and after the electrolysis. These two values along with lag time and induction time are given for each of the remaining experimental sets. In all sample solutions the final Ca^{++} and HCO_3^- ion concentrations were 0.0112 and 0.0022 respectively. Total ionic strength was standardized to 0.07 by the addition of KCl.

On Fig. 10 a plot of induction time vs. the Mg^{++} to Ca^{++} ratio is shown for set 1 of group IA. The effect of Mg^{++} ion on $CaCO_3$ nucleation seems to be one of inhibition. The observation was verified by the experiments of set 2†(Table XII). However it became apparent that inconsistencies might arise as a result of differences in nucleation sites in sets 2 and 3. Solution 8 (with more Mg^{++} ion) had given rise to precipitation whereas solution #6 had not.

In Table XIV values for the slope and y-intercept constants (a_1 and a_0) are given which will fit the induction period data for each of the sets in Tables XI and XII to a linear function of the form

$$\tau = a_1 \cdot \frac{[Mg^{++}]}{[Ca^{++}]} + a_0 \qquad (61)$$

For each of the sets, Table XIV also shows the coefficient of determination, d^2, which is an indication of how close the resulting equation fits the experimental data. Its value ranges between 0 and 1 with the closer d^2 is to 1, the better the fit.

Sets 3 and 4 aimed at examining the reproducibility of the induction period by carrying out an electrolysis of 15 seconds duration on solutions of similar composition prepared from the same stock solutions. The results are shown in Table XII, Parts b and c. The data can hardly be labelled reproducible. The lag times however do show a general trend of Mg^{++} ion inhibition of $CaCO_3$ nucleation. It is likely that solution handling could have contributed a large variability in the number

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† The current generation time in set 2 was reduced by 3 seconds from that used in set 1 in order to minimize further the ratio of the generation time to the induction time.

of foreign particles present in each solution.

IV.C.2.c. Ionic strength effects

It was pointed out that the solubility of a compound will increase in a solution to which a salt without a common ion has been added. Is there any reason to believe that this same salt would promote catalysis of the reverse process? Could the added salt make it easier for a precipitate to form by tying up water molecules and therefore reducing the number of hydration forces acting on newly formed $CO_3^=$ molecules?

Table XIII shows the data for the IB ionic strength experiments. Contrary to the findings made earlier (Table III) there seemed to be no marked catalysis by increasing the ionic strength of the precipitation solutions. In fact, results from Part A indicate the contrary. In all cases raising the ionic strength to 1.0 inhibited precipitation. The lag times in Part "c" do show a trend of catalysis and a similar effect to a lesser degree can be seen in the NaCl experiment (Part b). In Fig. 11 a graph plotting lag time vs. ionic strength for sets 1 and 3 of group IB is shown.

The inconsistencies in these runs could well be due to changes in the number of nuclei in solution either brought about during solution preparation, by the changing condition of the reaction cell and electrode surfaces or by particle contamination from the air. Stirring rate was roughly controlled by leaving the stirrer in a preset power position and turning the line power off or on.

These preliminary investigations indicate that much more attention in the standardization of experimental conditions is needed to achieve reproducible results.

TABLE XI

pH and induction period data as a function of Mg^{++} ion concentration (IA experiments, set 1)

Sol #	$[Mg^{++}]$	Mg^{++}/Ca^{++}	mls added 0.337 KCl	pH 1	pH 2	pH 3	pH 4	lag time	(secs) induction time	pH 5	pH 6
0	0.0000	0.0	10	8.88	8.67	8.11	--	60	138	8.15	8.77
1	0.0011	0.1	9	8.87	8.67	8.11	8.10	--	136	8.18	8.76
2	0.0022	0.2	8	8.88	8.67	8.10	8.09	105	187	8.11	8.73
3	0.0034	0.3	7	8.88	8.69	8.09	8.07	--	123	8.21	8.78
4	0.0045	0.4	6	8.88	--	8.09	8.06	68	189	8.19	8.76
5	0.0056	0.5	5	8.87	8.72	8.08	8.05	93	240	8.21	8.78
6	0.0068	0.6	4	8.88	8.74	8.08	8.04	215	354	8.19	8.75
7	0.0079	0.7	3	8.88	--	8.08	8.03	271	449	8.03	8.67
8	0.0090	0.8	2	8.88	--	8.08	8.02	310	426	8.18	8.72
9	0.0100	0.9	1	8.88	--	8.07	8.01	402	471	8.16	8.67
10	0.0110	1.0	0	8.88	--		8.01	430	489	8.15	8.64
0	0.0000	0.0	10	8.88	--	8.13	--	--	114	8.17	8.79

where:

pH_1 = pH after addition of HCO_3^-

pH_2 = pH after KCl addition

pH_3 = pH after addition of Ca^{++}

pH_4 = pH after addition of Mg^{++}

pH_5 = pH after equilibration with air gap inside 125 ml polyethylene bottles

pH_6 = pH after generating current (195 mamps) for 15 seconds

and the subscript numbers correspond to the order of mixing (in solutions 0-3 stirring not standardized)

TABLE XII

pH and induction period data as a function of Mg^{++} ion concentration (IA experiments, sets 2, 3 and 4)

Gen. Time	Sol #	pH_5	pH_6	lag time	induction time	Comments
12.0	0	8.32	8.90	85	145	
12.0	2	8.24	8.73	150	207	
12.0	4	8.26	8.72	247	295	
12.1	6	8.28	8.71			No vis. ↓, pH = 8.65 @ 73 min
12.0	8	8.17	8.62	875	990	
12.2	10	8.24	8.62			No vis. ↓, pH = 8.64 @ 54 min
12.2	Basic + 10 mls H_2O	8.06		63	223	
(a)						
14.9	0	8.32	8.87		220	
15.5	2	8.28	8.81	180	330	
15.0	4	8.19	8.74	200	248	
15.2	6	8.14	8.72	186	462	No vis. ↓, pH = 8.55 @ 115 min
15.0	8	8.21	8.72	465	1054	Vis. @ 34 min
15.1	10	8.06	8.62	505	790	Vis. @ 17 min
(b)						
15.0	Basic	8.12	8.67	117	150	
15.0	0	8.32	8.87	97	132	
14.9	2	8.25	8.84	115	143	
15.1	4	8.25	8.81	129	194	
15.2	6	8.15	8.72	170	283	
15.0	8	8.28	8.74	200	515	
14.9	10	8.11	8.62	522		No vis. ↓
(c)						

TABLE XIII

pH and induction period data as a function of ionic strength (IB experiments, sets 1, 2, and 3)

Sol. #†	KCl g	Volume (mls)	of Chloride	Added μ	Lag time	(secs) Induction p.	pH_5	pH_6	Gen. Time
0	--	--	--	0.000	72	160	8.07	8.50	12.0
1	--	10	0.10	0.010	90	165	8.08	8.61	12.1
2	--	5	0.50	0.025		100	8.11	8.67	12.0
3	--	10	0.50	0.050		202	8.10	8.68	11.9
4	--	10	1.00	0.100	267	324	8.18	8.75	12.0
5	3.72	--	--	0.050	300	657	8.17	8.75	12.0
6	7.45	--	--	1.000	No ↓		8.15	8.72	12.1

(a)

Sol. #†	KCl g	Volume (mls)	of Chloride	Added μ	Lag time	(secs) Induction p.	pH_5	pH_6	Gen. Time
1	--	10	0.10	0.010		82	8.12	8.65	14.9
2	--	5	0.50	0.025	99	200	8.20	8.78	15.2
3	--	10	0.50	0.050	109	233	8.20	8.79	14.9
4	--	10	1.00	0.100	270	474	8.14	8.77	15.0
5	2.92	No ↓		0.500	97	1292	8.09	8.72	14.9
6	5.83	No ↓		1.000	76	146			15.0

(b)

Sol. #†	KCl g	Volume (mls)	of Chloride	Added μ	Lag time	(secs) Induction p.	pH_5	pH_6	Gen. Time
1	--	10	0.10	0.010	95	340	8.23	8.80	15.0
2	No ↓	5	0.50	0.025	240	556	8.27	8.82	14.9
3	--	10	0.33	0.033	197	233	8.26	8.84	15.1
4	--	10	1.00	0.050	180	312	8.24	8.84	15.0
5	1.49	--	--	0.200	153	366	8.24	8.85	15.0
6	5.59	No ↓		0.750	157		8.19	8.81	15.0

(c)

(a) Set 1, added salt: KCl; (b) Set 2, added salt: NaCl; † all solutions made to

TABLE XIV

Curve Fitting Parameters[†] for the induction period data in Tables XI and XII

	Set 1	Set 2	Set 3	Set 4	
a_0	- 10.83	- 14.60	32.70	32.57	y intercept
a_1	402.25	1011.00	457.50	345.86	slope $\frac{\text{secs}}{\text{unit ratio}}$
d^2	0.84	0.90	0.79	0.66	coefficient of determination

(a) τ = lag time

	Set 1	Set 2	Set 3	Set 4	
a_0	88.41	70.80	143.33	72.20	y intercept
a_1	337.18	1038.43	748.00	453.00	slope $\frac{\text{secs}}{\text{unit ratio}}$
d^2	0.85	0.88	0.70	0.82	coefficient of determination

(b) τ = induction time

$$\tau = a_1 \cdot \frac{[Mg^{++}]}{[Ca^{++}]} + a_0$$

TABLE XV

pH vs. time during induction time period in Type IA experiments

Time (secs)	pH_6	Δt/pH unit
4	8.62	---
12	8.61	8
875	8.60	863
990	8.59	115
1028	8.58	38
1065	8.57	37
1091	8.56	26
1109	8.55	18
1126	8.54	17
1144	8.53	18

(a) Sol. #8

Time (secs)	pH_6	Δt/pH unit
5	8.72	---
12	8.71	7
32	8.70	20
236 → 247	8.69 ↔ 8.70	215
295	8.68	48
317	8.67	22
338	8.66	21
346	8.65	18
362	8.64	16

(b) Sol. #4

Fig. 9. pH vs. lapsed time after electrolysis
(from values on Table XV)

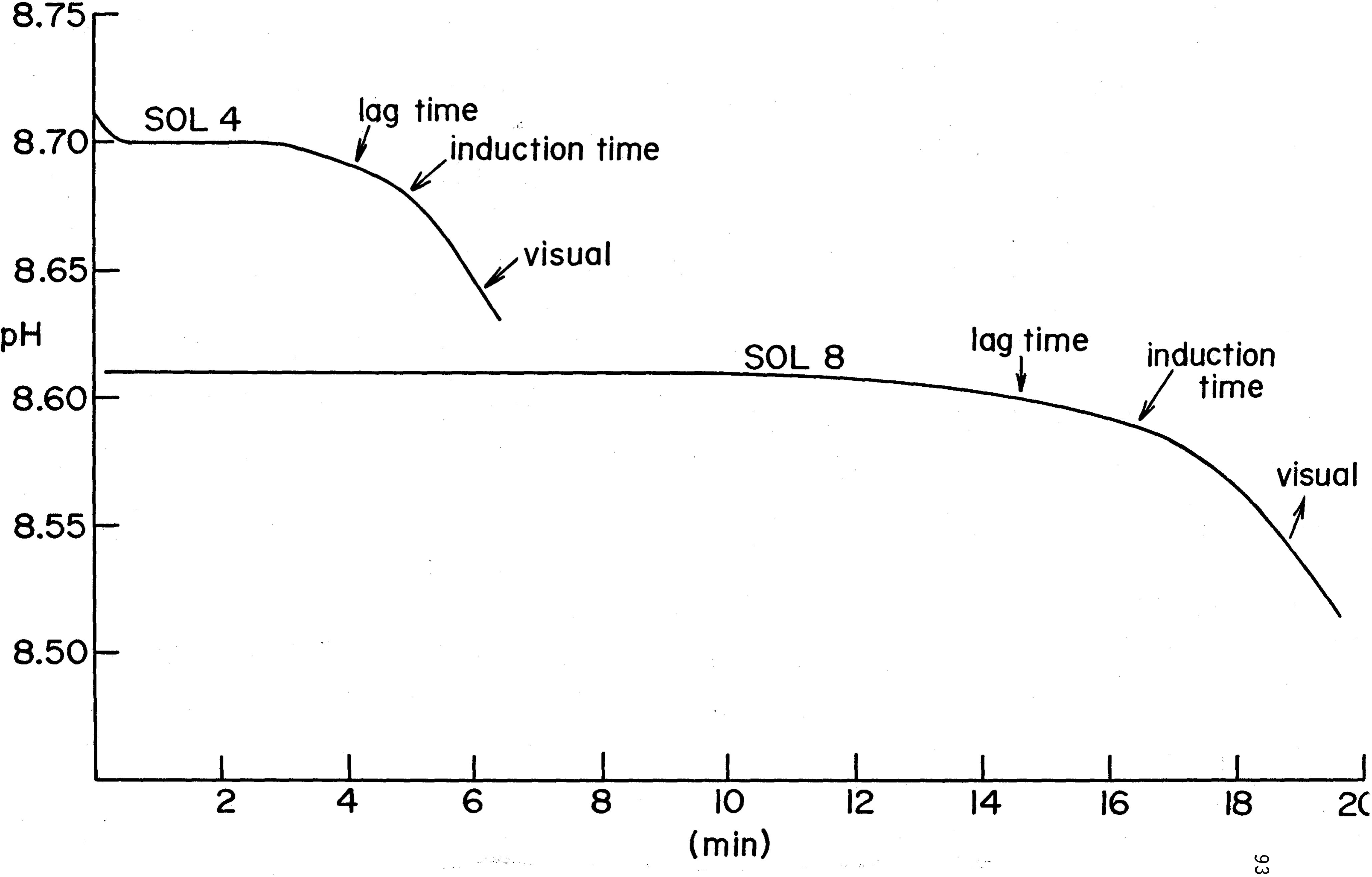

8.75
8.70
8.65
pH
8.60
8.55
8.50
SOL 4
lag time
induction time
visual
SOL 8
lag time
induction
time
visual
2
4
6
8
10
12
14
16
18
20
(min)

Fig. 10. Induction time vs. Mg^{++}/Ca^{++}
(IA experiment, set 1)

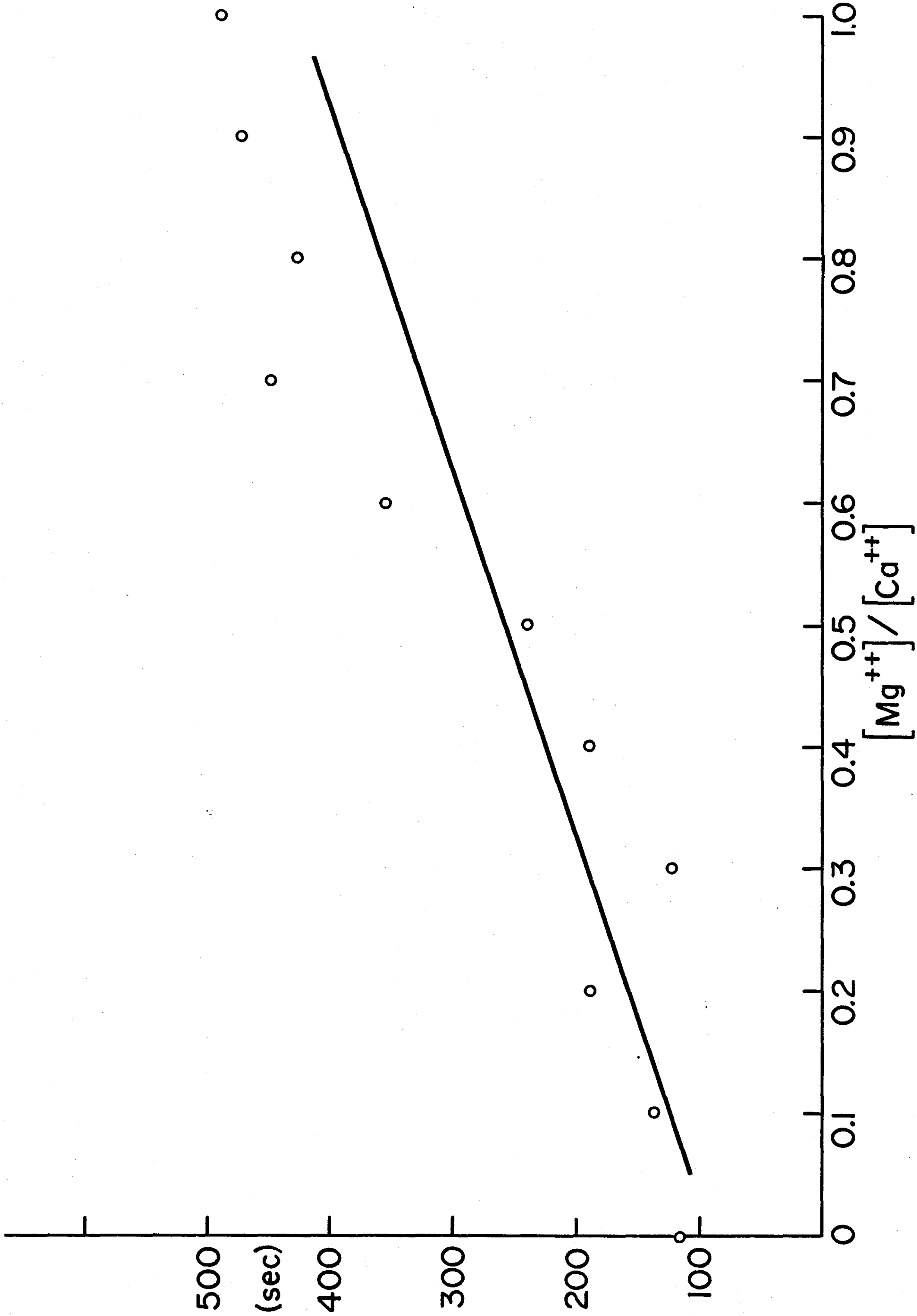
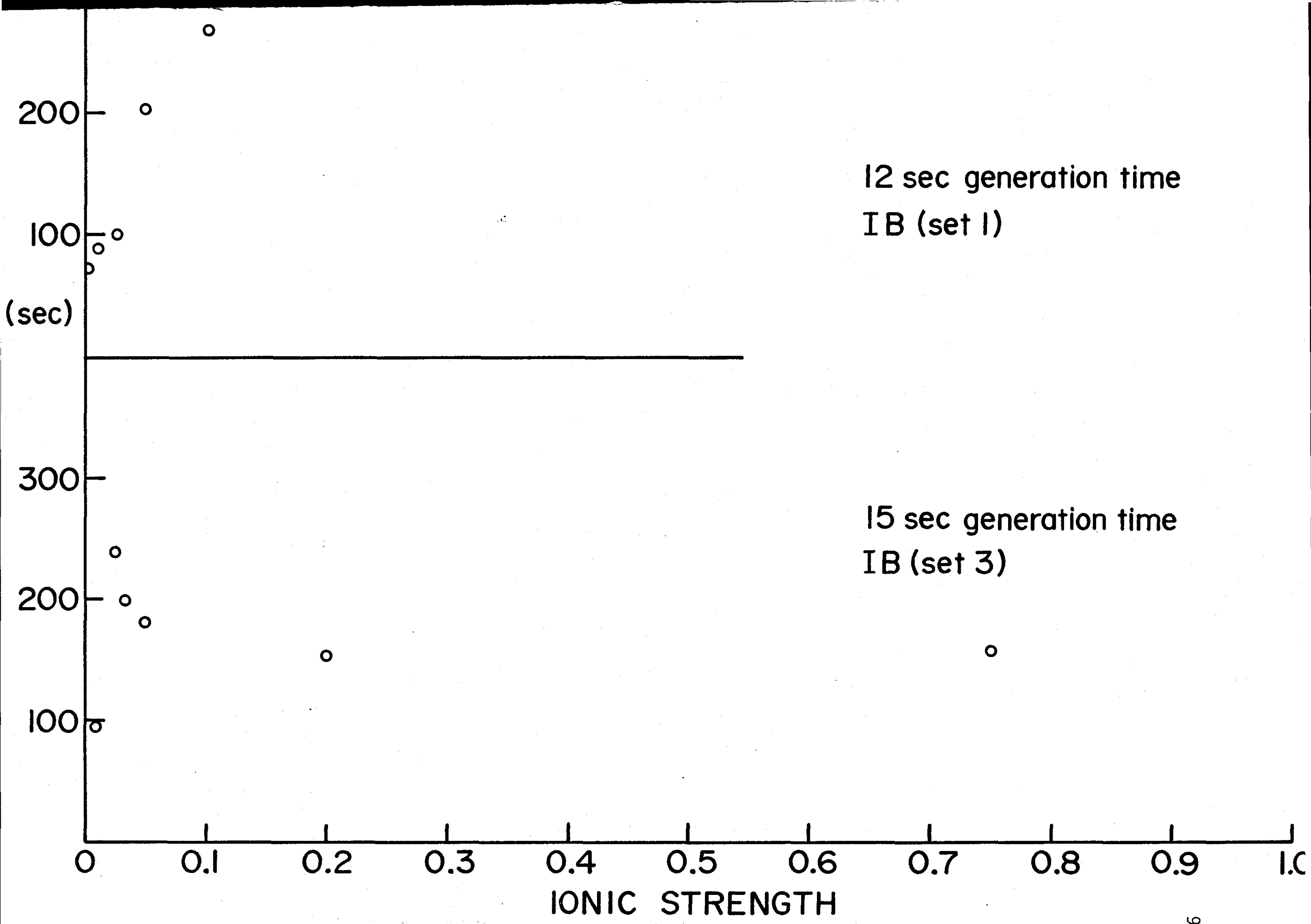

(sec)
100
200
300
400
500
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
$[Mg^{++}]/[Ca^{++}]$

Fig. 11. Lag time vs. ionic strength
(IB experiments, sets 1 and 3)


200
100
(sec)
300
200
100
12 sec generation time
IB (set 1)
15 sec generation time
IB (set 3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.C
IONIC STRENGTH

PART V

DIVALENT ION-BICARBONATE SOLUTION INTERACTIONS

Solution Interactions

Throughout the length of this study it was noticed that upon addition of either a Ca^{++} or Mg^{++} ion solution to a HCO_3^- solution the pH would drop. This was attributed to the formation of soluble complexes between both Ca^{++} and Mg^{++} and HCO_3^- and $CO_3^=$ as reported by Greenwald (21) and also by Garrels and Christ (18). The following experiments were to be part of a larger whole involving Ca^{++} and divalent specific ion electrodes. As presented here they do not involve measurements of Ca^{++} and Mg^{++} ion activities directly but are relevant to this aspect since ion pair formation would lower the activities of the cations. The study concentrates on the effect of $MgCl_2$, $CaCl_2$ and NaCl salts on the pH of HCO_3^- solutions of the same total ionic strength. An empirical determination of the HCO_3-$CO_3^=$ distribution is also made on some of the solutions.

V.1. Experimental

pH Measurements were made with glass and saturated calomel electrodes using a Fisher Accumet 420 Model digital meter standardized to ± 0.01 pH units on both 6.86 and 9.17 buffers. Reagent grade chemicals were used throughout. The 0.005 F bicarbonate solution was made using distilled de-ionized CO_2 free water and afterwards equilibrating it with atmospheric CO_2 by bubbling air through it until the pH was stable. All stock solutions were prepared and pH measured as described in the preceeding section for the IA group experiments. A series of sample solutions were prepared having a total ionic strength of 0.07 and containing 45.0 mls of the air equilibrated 0.005 F $KHCO_3$ solution. Varying amounts of Mg^{++}, Ca^{++} and Na^+ were added individually to the HCO_3^- solutions by adding proportionally stock solutions of 0.225 F $CaCl_2$, 0.225 F $MgCl_2$ and 0.70 F NaCl respectively. All solutions were brought to a final 100.0 ml total volume with H_2O and then the pH was measured.

Three of the solutions were prepared a second time and used to carry out an empirical determination of the HCO_3^--$CO_3^=$ distribution. The analysis consisted of measuring the equivalents of the two components in 25.0 ml aliquots by titration with 0.0103 F HCl using 2 drops of bromocresol green as an indicator. Acid was added until the solution just began to change from blue to green. The solution was then carefully boiled for 2 minutes to drive CO_2 out, and cooled to room temperature under a flow of tap water. The heating would return the solution to a blue color. The titration would then be quickly finished.

The bicarbonate concentration was then determined in a second 25.0 ml aliquot by the addition of 10.0 mls of 0.00977 F NaOH and 10.0 mls of 10% $BaCl_2$. Precipitation of the carbonate ion from the original salt as well as that formed by reaction of the bicarbonate with the base leaves only the excess NaOH which was then determined by a back titration with the standard acid and 2 drops of phenolpthalein indicator. A blank correction was made by titrating 25.0 mls H_2O, 10.0 mls of the $BaCl_2$ solution and 10.0 mls of base with acid. Tables XVI, XVII and XVIII show the results from these experiments.

V.2. Results and Discussion

The data from Table XVI indicate that as the amount of Ca^{++} or Mg^{++} ion added to a HCO_3^- solution increases the pH decreases. This observation can be explained in terms of the complexation reactions described in Section I.D.3. From Table XVII it is also observed that upon adding KCl or NaCl to a HCO_3^- solution the pH decreases when compared to solutions in which 55.0 ml of H_2O were added. This effect would be largely attributable to a lowering of the activity coefficient ratio of eq. (16) as a result of the solution's higher ionic strength. In addition, a certain amount of ion pair formation may be occurring between the monovalent ions and $CO_3^=$ resulting in a release of H^+ ions as the $HCO_3^- \rightleftharpoons CO_3^= + H^{\oplus}$ equilibrium shifts to the right. This effect is more pronounced with Na^+ than with K^+ (Greenwald).

Table XVIII displays the results of analyzing the HCO_3^--$CO_3^=$ distribution in three bicarbonate solutions. To solution 1 enough KCl was added to bring its total ionic strength to 0.07. Similarly solution 2 was made to have an ionic strength of 0.07 but this time as a result of adding Ca^{++}. Solution 3 was the parent bicarbonate solution used to prepare the previous two. All three had a final volume of 100.0 ml.

Analyses showed that although the total equivalents of $CO_3^=$ and HCO_3^- were the same in solution 1 as in solution 2 (see Table XVIII-b), there was a marked difference in the distribution of the 2 components of interest.

The column labelled $[CO_3^=]_{exp}$ in Table XVIII, Part a, shows that empirically solution no. 2 had 5.6 times as much total $CO_3^=$ (complexed or not) as solution 1. The bicarbonate concentration of solution 1 is essentially equal to its analytical composition. Solution 2, however, only has 0.38 as much bicarbonate. Even when accounting for the extra amount of $CO_3^=$ present, the empirical amount of total carbonate (HCO_3^- + $CO_3^=$) in solution 2 was only 0.70 of its analytical composition. The 0.0050 HCO_3^- solution (#3) was empirically determined to be 0.0049 F.

A model explaining the considerably higher concentration of total $CO_3^=$ in solution 2 is as follows:

Ca^{++} complexing with $CO_3^=$ in the form of a soluble $CaCO_3^\circ$ complex would remove this free $CO_3^=$ and shift the equilibrium

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \tag{16}$$

to the right with a subsequent drop in pH. During the addition of $BaCl_2$

it was noticed that precipitation was considerably slower to occur with solution 2 than with either of the other two. This could be caused by a considerable lock up of the $CO_3^{=}$ in the form of ion pairs with Ca^{++}.

The reduced amount of total carbonate in solution 2 implies that as a result of adding Ca^{++} ion to a HCO_3^- solution some form of this latter ion is lost from the system, most likely as CO_2. A mechanism consistent with this observation would involve complexation between Ca^{++} and $CO_3^{=}$ and/or OH^-. The subsequent dissociation of HCO_3^- or H_2O would give rise to a surplus of H^+ which would drive reaction (15) to the left with a subsequent shift to the right in the $CO_2(aq) \rightleftharpoons CO_2(gas)$ equilibrium.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad (15)$$

$$H_2CO_3 \rightleftharpoons CO_2(aq) + H_2O \qquad (14)$$

$$CO_2(aq) \rightleftharpoons CO_2(gas) \qquad (13)$$

The results of these experiments provide evidence for the existence of soluble complexes between Ca^{++} ion and the carbonate species and presents an interesting problem relating to the carbonate mass equilibria in a Ca^{++}-bicarbonate solution.

TABLE XVI

pH vs. $[Ca^{++}]$ and $[Mg^{++}]$ in HCO_3^- solutions

$H_2O^\dagger$ (mls)	$KCl^\dagger$ (mls)	$Stock^\dagger$ (mls)	pH^0 (Ca^{++})	pH^1 (Mg^{++})
45.00	10.00	0.00	8.52	8.57
45.00	9.00	1.00	8.41	8.47
45.00	8.00	2.00	8.28	8.40
45.00	7.00	3.00	8.18	8.35
45.00	6.00	4.00	8.12	8.29
44.90	5.10	5.00	8.07	8.25
44.90	4.10	6.00	8.02	8.21
44.80	3.20	7.00	7.98	8.17
44.80	2.20	8.00	7.94	8.14
44.75	1.25	9.00	7.91	8.11
44.70	0.30	10.00	7.88	8.08

where:

$[KCl] = 0.70$ F
pH^0 = pH when stock was 0.225 F Ca^{++}
pH^1 = pH when stock was 0.225 F Mg^{++}

† volume of reagent added to 45.0 mls of 0.005 F HCO_3^- whose pH was 8.81 for the Ca^{++} tests and 8.83 for the Mg^{++} tests. (upon addition of 55.0 mls of H_2O to 45.0 mls of the HCO_3^- solution the pH dropped to 8.80).

TABLE XVII

pH vs. [Na^+] and [K^+] in HCO_3^- solutions

Sol. #	KCl† (mls)	NaCl† (mls)	pH
0	10.0	0.0	8.58
1	9.0	1.0	8.58
2	8.0	2.0	8.56
3	7.0	3.0	8.56
4	6.0	4.0	8.56
5	5.0	5.0	8.56
6	4.0	6.0	8.55
7	3.0	7.0	8.55
8	2.0	8.0	8.55
10	0.0	10.0	8.54

where [KCl] = [NaCl] = 0.70 F

† Volume of reagent added to 45.0 mls of 0.005 F HCO_3^- solution. Each sample was made up to 100.0 ml total volume.

TABLE XVIII

HCO_3^--$CO_3^=$ empirical determinations

Sol #	Mls 0.0050 $KHCO_3$	Mls 0.337 KCl	Vol_t	μ	Mls 0.225 Ca^{++}	$[HCO_3^-]_i$	$[Ca^{++}]_i$	pH_i	$[HCO_3^-]_{exp}$	$[CO_3^=]_{exp}$	Mass Balance	% loss
1	45.0	10.0	100.0	0.07	0.0	0.0022	0.0	8.52	0.0020	1.4×10^{-4}	-6.0×10^{-5}	1.0
2	45.0	0.30	100.0	0.07	10.0	0.0022	0.022	7.88	7.6×10^{-4}	7.8×10^{-4}	-6.6×10^{-4}	30
3	100.0	0.00	100.0	0.005	0.0	0.0050	0.0	8.81	4.8×10^{-3}	NIL		

(a) Solution Composition‡

	1st Aliquot Titration		Back Titration		
Sol. #	Mls 0.0103 F HCl	Total meq $HCO_3^- + CO_3^=$	Mls 0.0103 F HCl	meq HCO_3^-	CO_3^{2-} (by differences)
1	5.62	0.0579	4.10	0.0510	0.0069
2	5.62	0.0579	7.20	0.0190	0.0389
3	11.78	0.1210	6.70†	0.1220	NIL
Blank			9.05	0.0044	

(b) HCO_3^--$CO_3^=$ Determinations

‡ [ ] = F

† added 20.0 ml 0.00977 NaOH

PART VI

COMPUTER BASED INFORMATION SYSTEM

VI.A. Introduction

After initial development of the electrolytic method of $CaCO_3$ precipitation it became obvious that the nature of the method and experiments planned made the system suitable for implementation of a computer based information system. This would entail control of current generation, automatic logging[†] and processing of all data. Such a system is outlined in Module Three of Section II.

Program SS205 is an executive program incorporating a subset of the specifications as first envisioned in Module Three. Data reduction routines were not incorporated into the software due to further work required in the process interfacing and use of the specific ion electrodes. Maximum emphasis was placed on the development and testing of software to accomplish the control and data acquisition functions. Hardware development did not reach the stage where meaningful data was acquired from the transducers. However, trial runs were made with the system using a multiplexed 10-bit analog-to-digital converter (ADC) to receive signals from glass and calomel electrodes and 2 other inputs. A brief description now follows of program SS205 and multitask programming and its use in a $CaCO_3$ precipitation experiment.

[†] Feedback from the pH electrode would allow the processor to use a previously specified pH value as a setpoint at which data acquisition should stop.

VI.A.1. Multitask Programming

In a single task environment the processor idles while an I/O operation is in progress. Efforts to use processor time more efficiently led to the concept of multitask operating systems. This is especially important in real time systems where processed results must be made available in time to affect the process or its environment. The contrast between a single task environment and a multitask environment is shown in Figure 12.

In the latter environment a task scheduler is needed to decide which of several programs will be allocated cpu control. In essence then the multitask program consists of a network of single tasks.

In program SS205 all task activity is under control of a system executive program referred to as RDOS (Real Time Disk Based Operating System). The user tasks can signal RDOS to perform desired actions through use of either system or task calls. System calls generally deal with I/O operations or in defining interrupt servicing routines. Task calls involve task management functions such as task initiation, suspension, activation and termination. System calls in effect transfer subroutine parameters to the operating system which then decides what action should be taken. In addition to processing system and task calls the RDOS executive provides routines to process interrupts and dispatch them to device interrupt servicing modules as well as getting or changing the time of day or date. Figure 13 depicts the flow of interaction between the user tasks, RDOS and hardware.

Initialization of the program starts execution of the first task.

To create other tasks the first task initiates the second and subsequent tasks by issuing the appropriate task monitor calls. At the time of task initiation each task is assigned a starting address and a priority, with priority 0 being the highest. This allows the scheduler to decide which task will have cpu control. The scheduler runs after the completion of any system call and after servicing external interrupts.

Tasks within RDOS can be either in an idle or active state. If the task is idle (dormant) the system has no knowledge that the task exists even though the code remains part of the program. Tasks can exist in one of four states.

EXECUTING	The task has control of the central processor unit (cpu).
READY	The task is ready and available for execution but cannot gain control of the cpu until all higher priority tasks existing in the READY or EXECUTING state are completed or go into a SUSPENDED state.
SUSPENDED	The task is awaiting the occurrence or completion of some system call or other real time operation.
DORMANT	The task has not been initiated (made known to RDOS) or its execution was completed and it is now idle.

The scheduler keeps status information about each active task within an information structure called a TASK CONTROL BLOCK (TCB). Tasks in the TCB are linked together in chains in order of decreasing task priority. Figure 14 depicts task state transitions.

Though tasks operate asynchronously under scheduler control, tasks have the ability to communicate with each other and therefore transmit messages which can act as synchronizing elements. This allows a task to halt temporarily (SUSPENDED) until RDOS receives word from another task that the suspended task can again be brought to the ready state. It is also possible to transmit a message directly from an interrupt service routine to a user task therefore providing the basis for task activation based on the occurrence of external events as indicated by interrupts. A task can also issue a system call which will cause itself to suspend for a specified time period that is a multiple of the real time clock frequency.

Figure 15 shows flow chart conventions for a multitask programming environment. Appendix B shows the flow chart for program SS205. Table XIX shows a summary of task calls used in SS205.

VI.A.2. Computer Program Scope

SS205 is a multitask program (Appendix E) operating under version III of Data General Nova's Real Time Disk Operating System on a Nova 2 minicomputer. Upon program initialization a user-machine interactive executive task is set up which gives the user total control over the state of the system. Program initialization consists of a set of questions regarding concentration values for the different ions in the precipitation solution, solution temperature, current amps, generation time and the sampling frequency with which to record three electrode readings during the induction period.

Control over the system is attained by pressing simultaneously the CRTL and A keys on the system console (e.g., teletype) and entering a number corresponding to one of the following actions: (user is queried)

0 - System initialization

This command is to be used whenever changing component concentrations in the sample solution. This instruction generates a series of 9 questions and waits for an answer for each before proceeding with the next question. If a return is entered without a preceeding value the previous value for this variable is retained. It is important to note that SS205 can be run in conjunction with the debug editor therefore allowing the capacity to change the value of any variable individually without going through a series of questions. A breakpoint would be inserted at the CTRL A interrupt location. This enables the user then to have access at will to the editing capabilities of the debug editor by entering CTRL A. (When an exit is made from the debug editor processing resumes with the instruction at the breakpoint location. In program SS205 the user is asked to "enter the number corresponding to the action desired.")

1 - Electrode verifications

To facilitate electrode standardizations and verify proper functioning of data acquisition this command is used to get a listing of the electrode readings on the line printer.

2 - Proceed with experiment, Module 1, Part 1

This command initiates current generation for the user specified period and then gives rise to concurrent sampling of the transducer outputs.

3 - Continue with data processing

This command would be used with a set of user subroutines to calculate pertinent information for the system using component and system values entered during system initialization along with the recorded data.

Meaningful results would then be listed at the end.

4 - Turn off the electrodes

This command controls the relays which would turn the pH meters from operate to standby.

5 - Wait for CTRL-A

This command deletes all tasks from the TCB except one and has the effect of a system shutdown. CTRL-A must be entered subsequently to bring the program to an active state.

The normal sequence of events taking place during an experimental run would be as follows:

With the RDOS system running the user enters the file name SS205 from the teletype. This command gives rise to execution of the program. SS205 begins by printing a few comments on the teletype describing the system's capabilities and giving proper instructions as to the format of the answers to be entered for the system initialization questions.

After all questions have been answered a line prompt will appear on the system console instructing the user to hit the return key when ready to verify the electrode readings. At this point the user would place the electrodes in a standard solution(s) and hit the return key. A listing of the values read would then appear on the line printer and the user can verify that the system is recording values correctly.

A line prompt then appears on the teletype instructing the user to enter the number corresponding to the action desired. If the system is working properly the user can then proceed to set up his precipitation system. A reply of 2 on the teletype will record the initial time and electrode values and then actuate current generation for the user specified period of time.

After current generation has ended sampling of the transducer readings at the user specified frequency will occur with concurrent storage of the data (time and values) in memory and a real time listing of these values on the line printer. This will continue until such a time that the operator enters CTRL A or until the pH equals the setpoint value specified by the variable OVER (accessible with debug III).

The user could now enter a reply of 3 which would give rise to data processing and a report of meaningful information and derived results.

VI.B. Experimental Work

In order to test out the software, trial runs were made using an analog voltage supply connected to an analog to digital converter and multiplexed to the two channels corresponding to the columns pH and pDIV in Appendix D. A digital millivolt meter was attached across the voltage supply and measurements taken visually while the voltage to the A/D was varied. These values are shown on the fifth column of Appendix D. The values as seen by the program are listed under pDIV times a factor of 10^4. A conversion factor to pH units was arbitrarily assigned. The channel corresponding to pCa was left floating.

The sequence of commands in Appendix C produced the line printer responses shown in Appendix D which shows two runs programmed to stop when the pH dropped below 6.80. The first run was sampled at 1 sec. intervals. The second run was sampled at 2 second intervals. This change was made using DEBUG by entering octal 24 for the variable SAMPL. DEBUG is called by pressing CTRL-A which gives rise to a listing of the contents of the four arithmetic registers.

Each time a heading line appears in Appendix D, a 1 was entered as a user response except for the very first time which corresponds to having hit the return key. The first electrode readings occur 15 seconds after having entered a response of 2. In this case generation time was 10 seconds and a 5 second delay was allowed before sampling, for electrode stabilization.

Program SS205 was used to carry out actual $CaCO_3$ precipitations using the electrolytic method described previously. Connections for remote control were made on the back of the coulometer and attached in series with a relay operated by the computer. Because remote turning on and off of the pH meters would have entailed modifications to the meters this function was done manually. That is, during the five second delay following the end of current generation the meters would be switched from standby to operate.

VI.C. Discussion

No details are given here of the $CaCO_3$-precipitation runs since use of the specific ion electrodes had not proved satisfactory before (Section IV). The recorder output from a pH meter using glass and calomel electrodes in the induction-type experiments showed considerable random noise after X1000 signal amplification preceeding input to the A/D (± 0.2 pH units). An optimized system would have allowed for digitization of the voltage values at the transducer back end before transmitting them to the computer. The digital meters used had in fact a binary coded decimal output. The processor required an ASCII input thus optimization of transmission would have required incorporation of a BCD to ASCII conversion interphase board.

Current generation time became more reproducible from run to run as the processor would turn off the relay to the current source after exactly the same interval each time whereas with operator control of the on-off switch, generation time varied from -0.1 to +0.2 seconds.

Program SS205 provides the software for an efficient processor controlled data information system that can be tailored to suit more specific needs and on-going developments. A satisfactory breadboard level of hardware interfacing was not pursued.

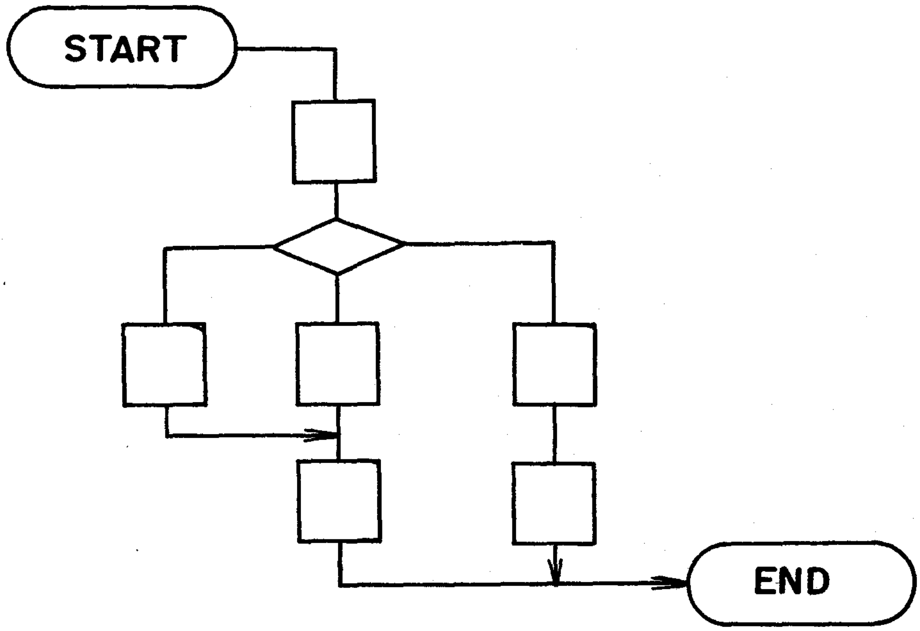
TABLE XIX

TASK calls used in SS205

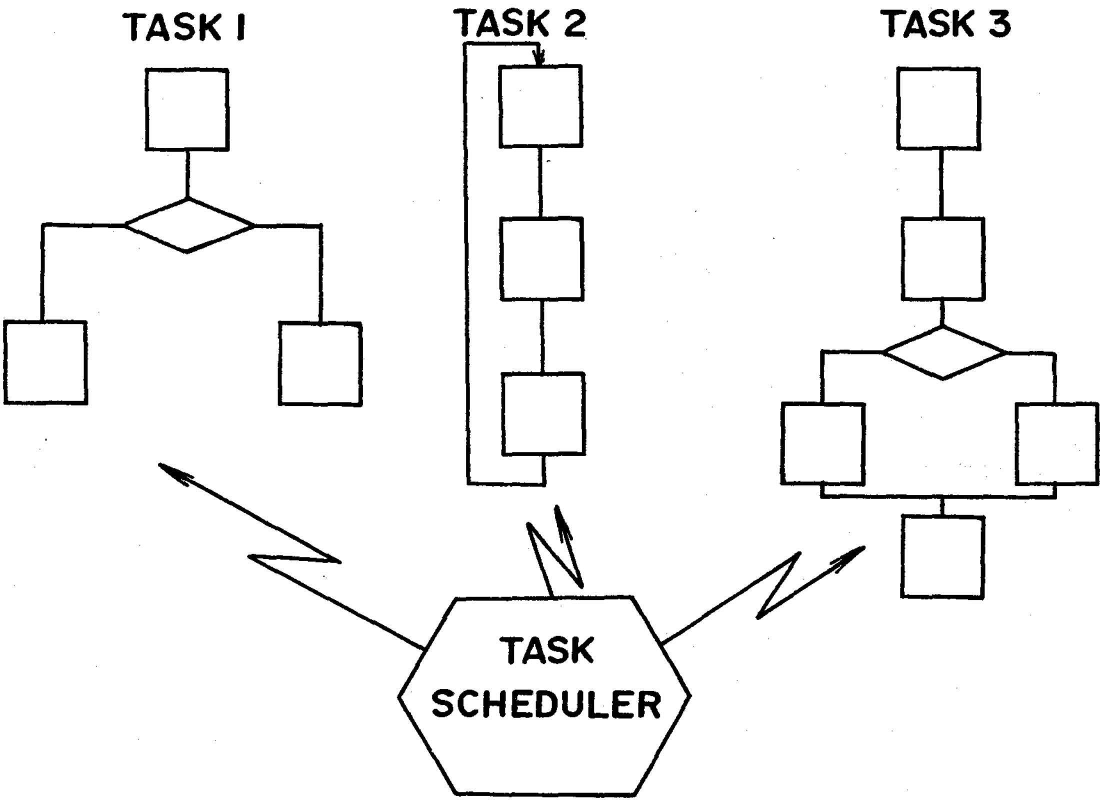
.TASK;	initiate a task
.KILL;	delete the calling task
.XMT;	transmit a message
.IXMT;	transmit a message from an INTERRUPT routine
.REC;	receive a message
.OCEX;	exit from a user clock routine
.PRI;	change the calling task's priority
.TIDK;	delete task specified by ID
.ABORT;	ABORT task with ID in accumulator 1
.TIDP;	change the priority of task with ID

Fig. 12

Single task - multitask environments

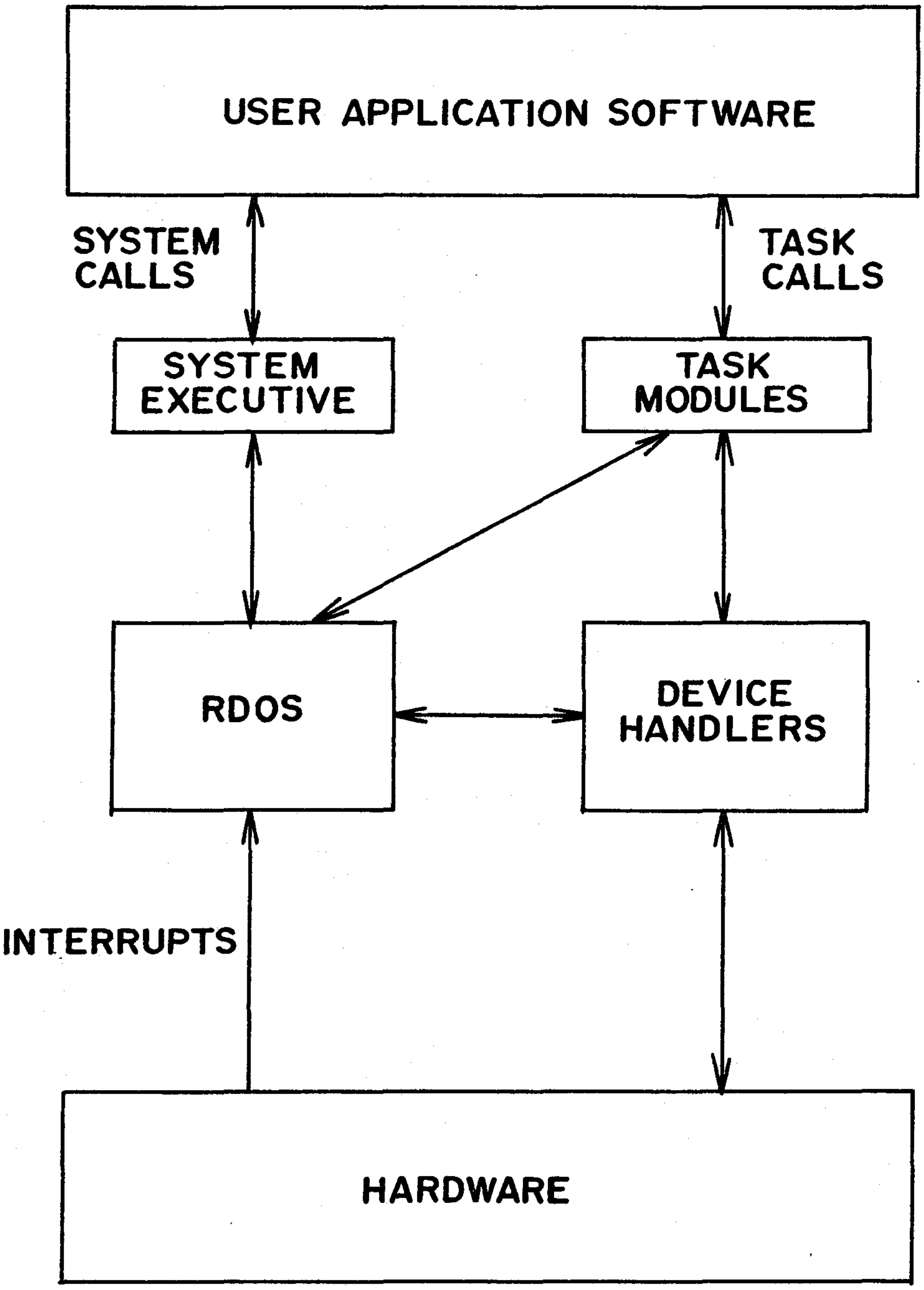


SINGLE TASK ENVIRONMENT



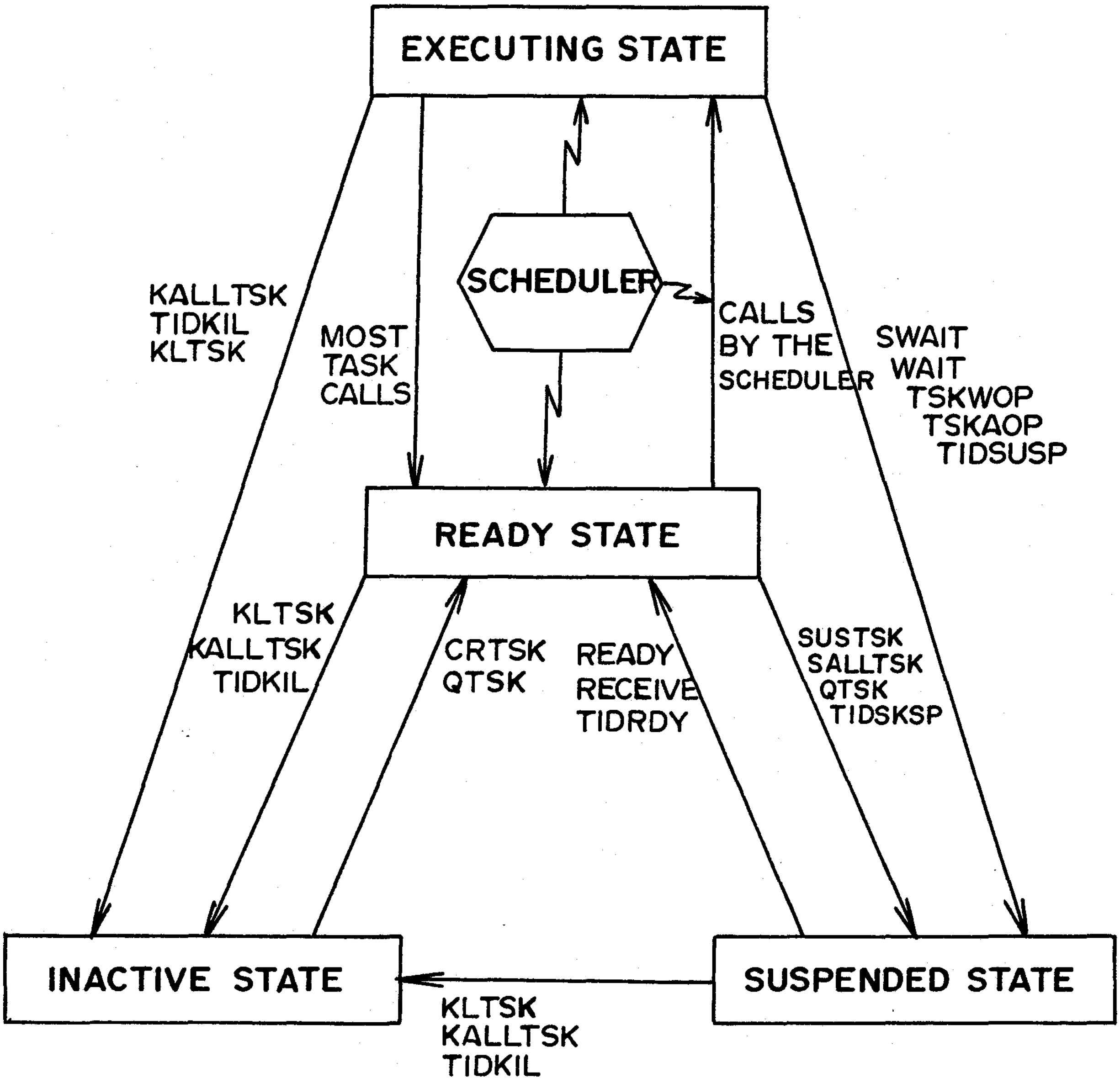
MULTITASK ENVIRONMENT

Fig. 13 Program Execution Flow



PROGRAM EXECUTION FLOW

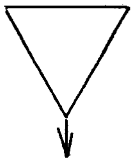
Fig. 14 Task State Transitions



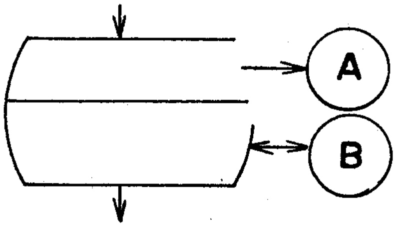
TASK STATE TRANSITIONS

Fig. 15 Flowcharting Symbols for Multitasking Programs (from Ref. 65)

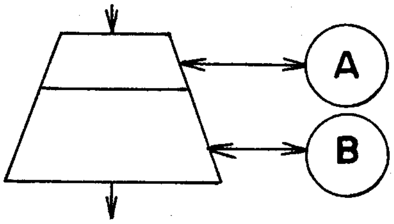
MULTITASKING AND SYSTEM SYMBOLS



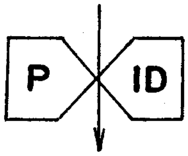
Entry point to the real time operating system from the first user task or program.



System call. Call word or macro-comment is put in the top section, arguments or qualifiers below. Error return (if any) goes to entry point A. Communications (if any) are to or fro another system or task call at entry point B.

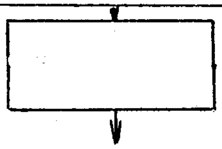


Task call. Call work or macro-command is put in the top section, arguments or qualifiers bel Error return (if any) goes to entry point A. Communications (if any) are to or from another system or task call at entry point B.

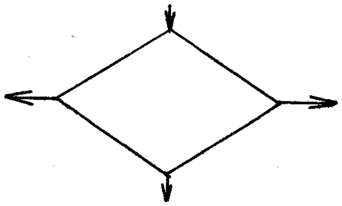


Task priority, (P), and identification, (ID). This symbol should appear at least once on each on-going task logic path. It would normally follow any task call which changes or establish P or ID.

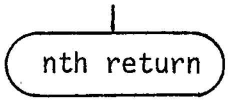
SIMPLIFIED USER PROGRAM SYMBOLS



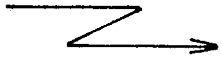
Normal user task processing, programming or log



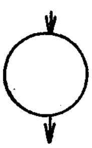
Decision.



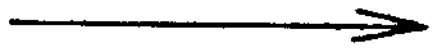
Subroutine retur



Communications Link.



Connector.



Program path lin

CONCLUSIONS

A newly developed method for precipitating $CaCO_3$ from aqueous solution consists in passing an electrolytic current through a calcium-bicarbonate solution. In effect, the electrolysis of the solvent produces OH^- ions which then react with HCO_3^- to yield $CO_3^=$ ions. The duration and strength of the current will determine the amount of $CO_3^=$ produced. Temperature control is derived by carrying out the reaction in a thermostatted cell. The onset of precipitation is detected by a drop in pH.

Preliminary studies based on the above technique showed that Mg^{++} ion has an inhibiting effect on $CaCO_3$ nucleation in precipitation reactions. It was found that as the Mg^{++} ion concentration in solution increased so did the induction period preceeding the onset of precipitation. This is partly attributable to the fact that Mg^{++} forms water soluble complexes with $CO_3^=$ therefore reducing the activity of this latter ion.

In general results from one set of experiments to another varied considerably. This lack of reproducibility arises as a result of the number of nucleating surfaces and particles in solution. Experiments involving ionic strength effects on $CaCO_3$ nucleation showed no conclusive evidence of catalysis as shown previously by Bischoff (4). Tests involving Ca^{++} and divalent specific ion electrodes showed that their response time and stability were not within the tolerances required to determine Ca^{++} and Mg^{++} ion activities on a real time basis in a dynamically changing system.

The technique of electrolytic precipitation of $CaCO_3$ was found suitable for implementation of a computer based interactive information system entailing control of current generation, logging and processing of all experimental and user entered data.

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APPENDIX A

Pre-matrix solution development runs

RUN 03-13-7510

45 Mls of 0.1 F $CaCl_2$ + 45 mls 0.01 F $NaHCO_3$ and 10 mls H_2O were placed in a thermostatted reaction cell at 25°C and covered. The solution was stirred magnetically.

Time (Min)	pH	
0	7.57	
5	7.58	
10	7.56	
12	7.57	
14	7.53	▽ precipitation visible
16	7.47	
25	7.23	

APPENDIX A (continued)

RUN 03-13-1300

Solution	pH	Comment
45 mls. 0.01 F $KHCO_3$	8.92	solution was air equilibrated
+ 10 mls. H_2O	8.96	
+ 10 mls. 0.1 F $CaCl_2$	8.22	
+ 35 mls. 0.1 F $CaCl_2$	7.89	

This solution was kept covered overnight and the next day a precipitate was observed to have formed. The pH was 7.29.

RUN 04-03-2000

Solution	pH	Comment
45 mls. 0.05 F $KHCO_3$	8.44	solution was not air equilibrated
+ 25 mls. 0.025 $CaCl_2$	8.01	
+ 20 mls. 0.025 $CaCl_2$	7.90	
+ 10 mls. H_2O	7.95	

Upon stirring copious precipitation occurred.

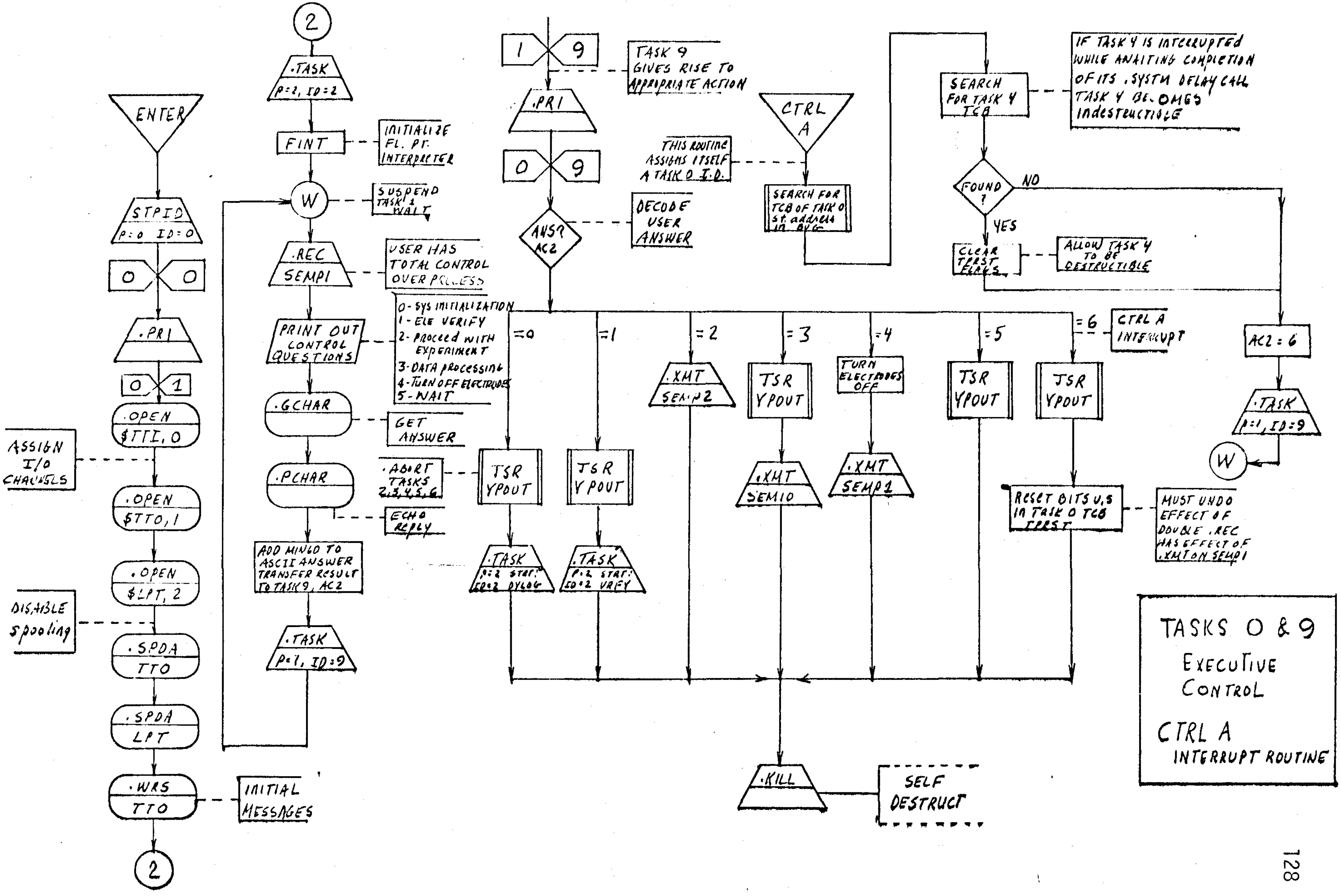
RUN 04-04-1600

Solution	pH	Comment
45 mls. 0.01 F $KHCO_3$	8.53	solution was not air equilibrated
+ 0.10 mls H_2O	8.59	
+ 45 mls. 0.0025 $CaCl_2$	8.38	

When left standing opened to the air the pH had risen to 8.76 after 79 minutes. At 85 minutes the pH was 8.60 and precipitate was visible. After 24 hours the pH was 8.40.

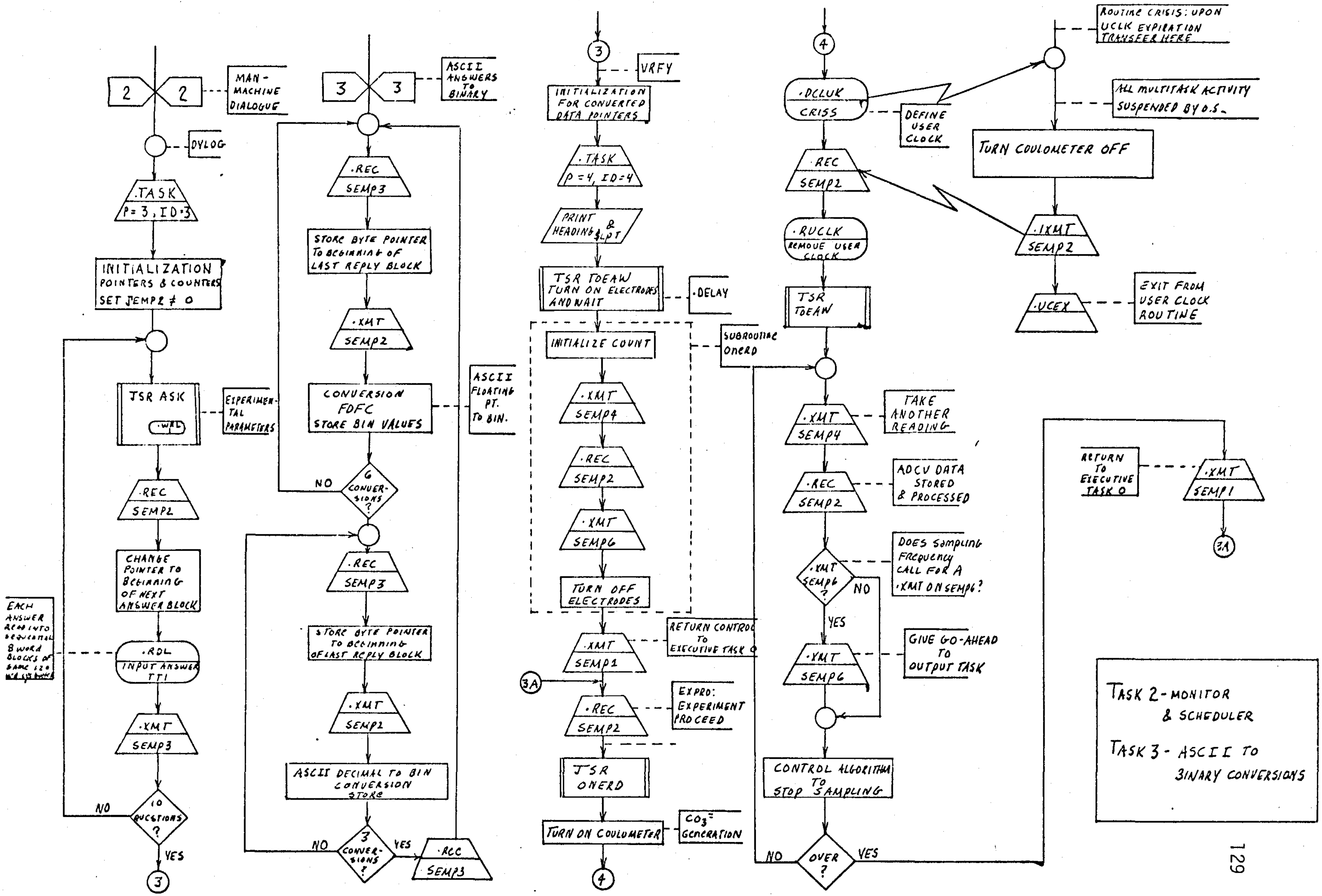
APPENDIX B

Flowchart for System Program SS205



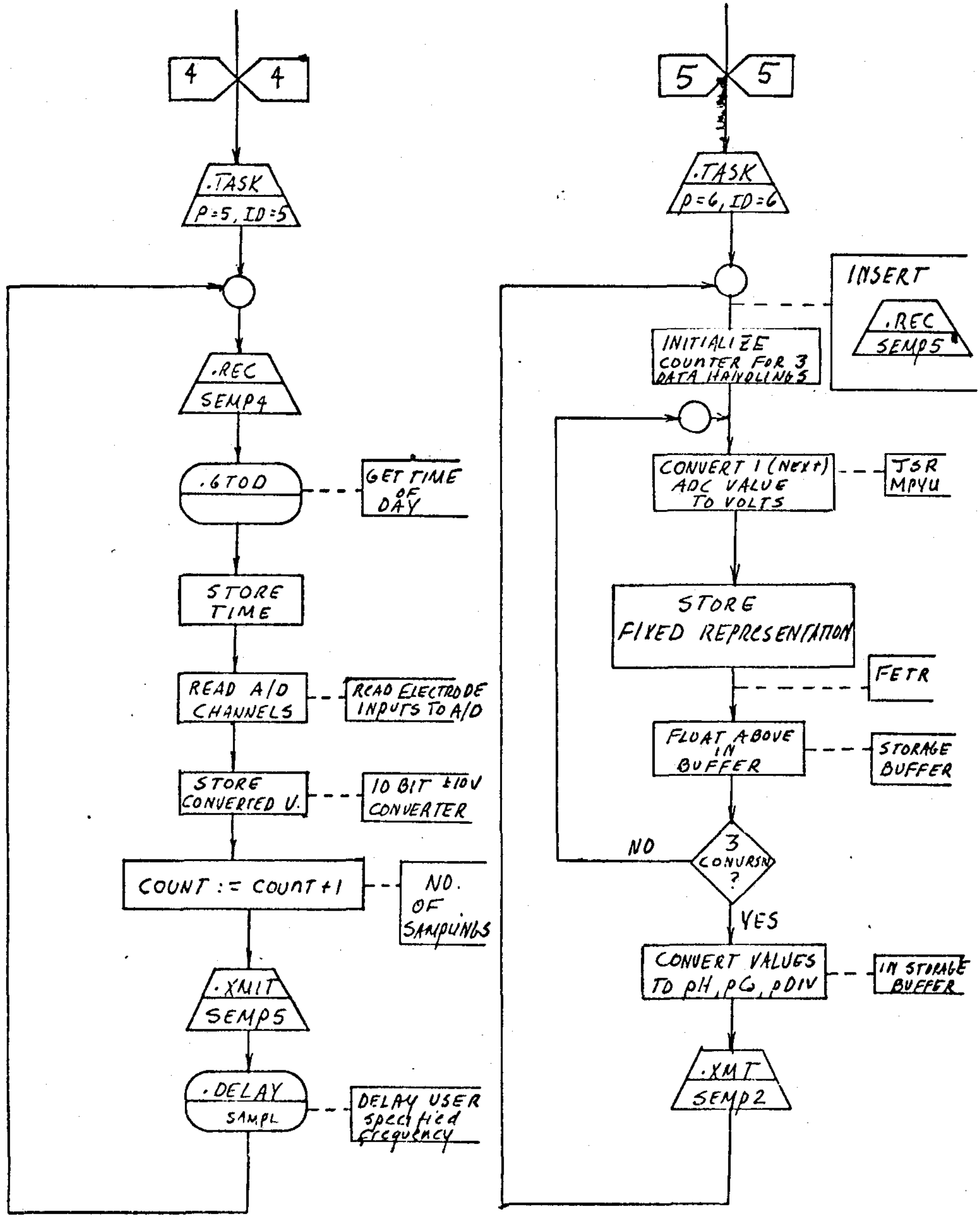
TASKS 0 & 9
EXECUTIVE
CONTROL

CTRL A
INTERRUPT ROUTINE

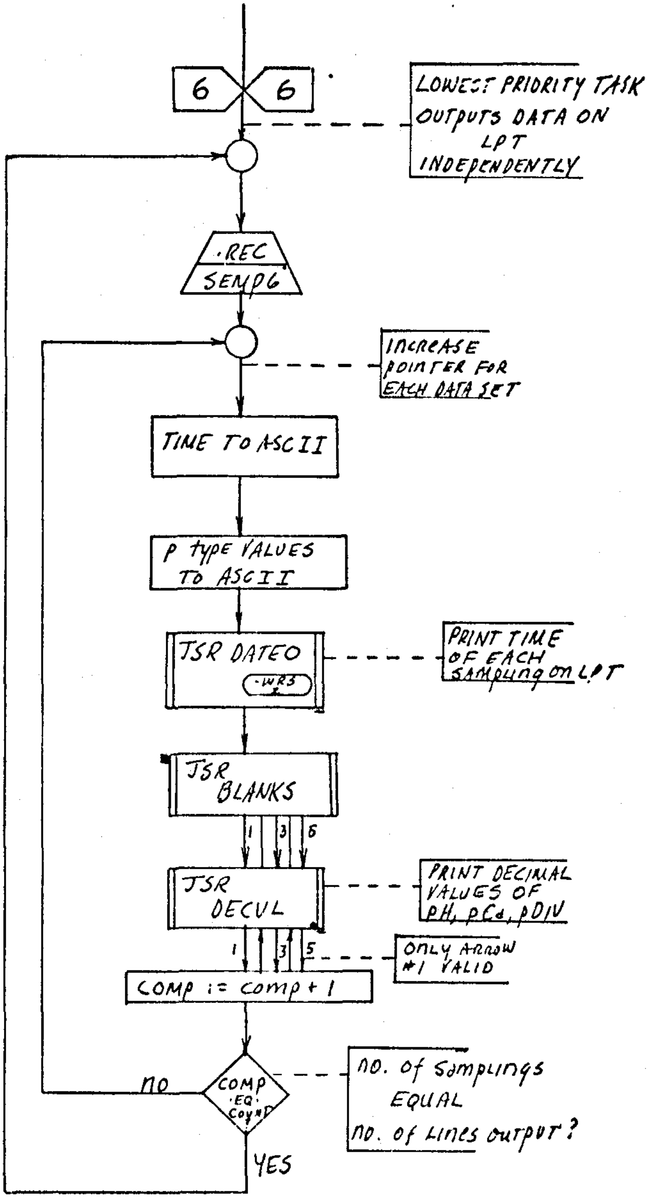


TASK 2 - MONITOR & SCHEDULER

TASK 3 - ASCII TO BINARY CONVERSIONS

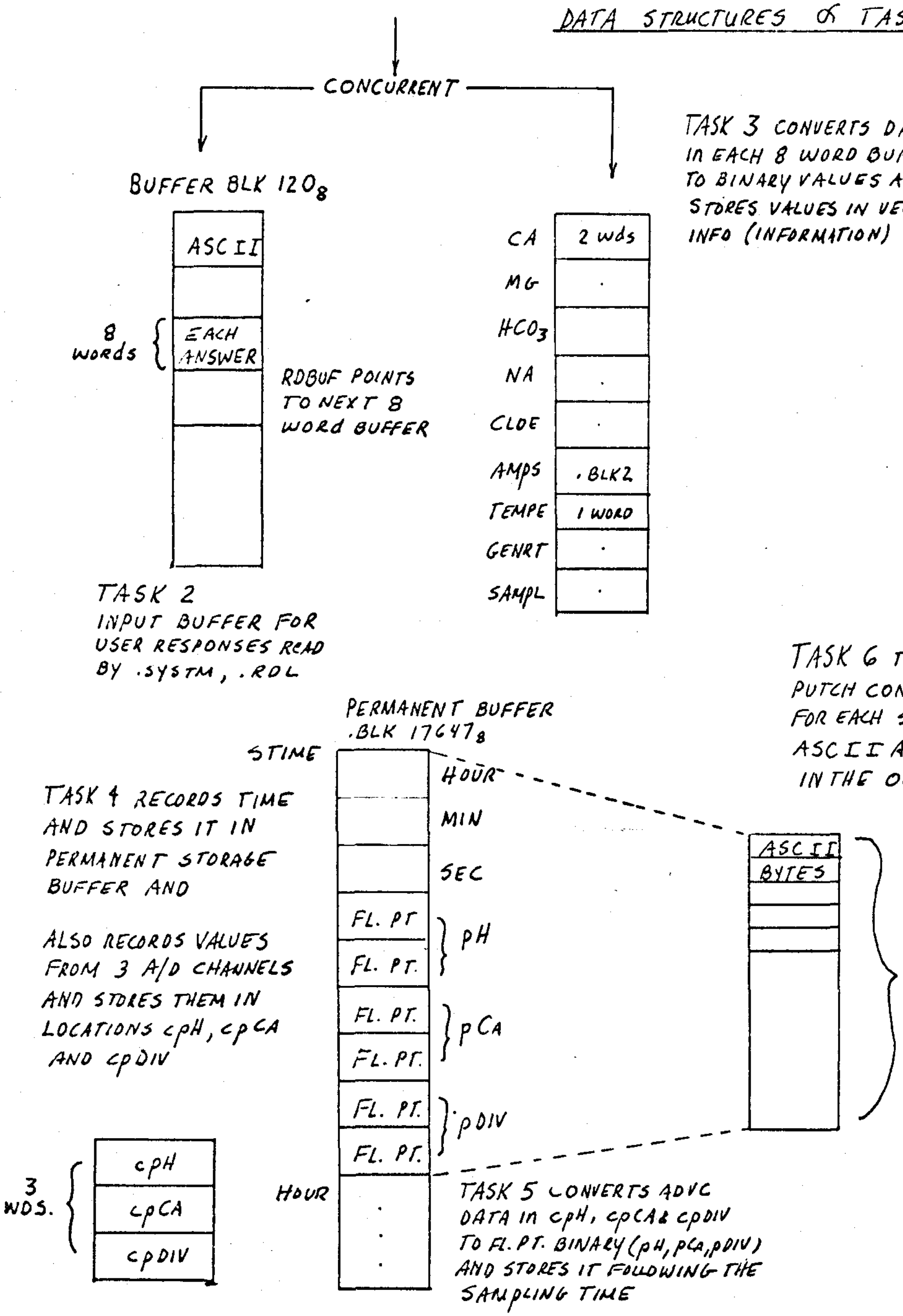


TASKS 4 & 5 - DATA LOGGING



TASK 6 - OUTPUT on LPT

DATA STRUCTURES & TASK INTERACTIONS



TASK 3 CONVERTS DATA IN EACH 8 WORD BUFFER TO BINARY VALUES AND STORES VALUES IN VECTOR INFO (INFORMATION)

RDBUF POINTS TO NEXT 8 word BUFFER

TASK 2
INPUT BUFFER FOR USER RESPONSES READ BY .SYSTM, .RDL

TASK 6 TOGETHER WITH PUTCH CONVERTS THE DATA FOR EACH SAMPLING TO ASCII AND PLACES IT IN THE OUTPUT BUFFER.

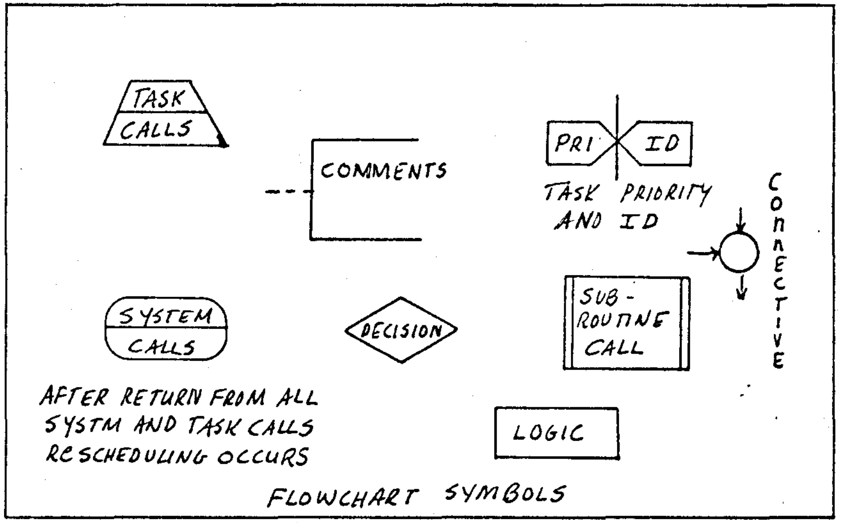
TASK 4 RECORDS TIME AND STORES IT IN PERMANENT STORAGE BUFFER AND

ALSO RECORDS VALUES FROM 3 A/D CHANNELS AND STORES THEM IN LOCATIONS cpH, cpCA AND cpDIV

33_8 WDS.

only one BUFFER USED FOR ALL DATA OUTPUT

TASK 5 CONVERTS ADVC DATA in cpH, cpCA & cpDIV TO FL. PT. BINARY (pH, pCa, pDIV) AND STORES IT FOLLOWING THE SAMPLING TIME



AFTER RETURN FROM ALL SYSTM AND TASK CALLS RESCHEDULING OCCURS

FLOWCHART SYMBOLS

APPENDIX C

Sequence of SS205 Commands

```
DEB SS205.←

SS205%
TKOVRSB
$R

F. DURANZA
CHM ENG 760

                     GREETINGS FROM SS205

                      PROJECT CACO3-MGII
A STUDY ON CALCIUM CARBONATE NUCLEATION AND MAGNESIUM ION INTERACTIONS

ANSWER THE FIRST 6 QUESTIONS USING E FORMAT
(+.NNNNNNNE+MM)

ANSWER THE LAST 3 WITH FIXED PT. (BASE 10)

END ALL ANSWERS WITH A RETURN

NOTE: USER HAS UNCONDITIONAL ACCESS
     TO CONTROL QUESTIONS
TO DO THIS ENTER CTRL A ON TTI

FOLLOWING ARE THE CONTROL ACTIONS AVAILABLE
 0 - SYSTEM INITIALIZATION
 1 - ELECTRODE VERIFICATIONS
 2 - PROCEED WITH EXP., MOD.1,PART 1
 3 - CONTINUE WITH DATA PROCESSING
 4 - TURN OFF ELECTRODES
 5 - WAIT FOR CTRL A

P.S USER CAN USE DEBUG DURING RUN TIME
    WITHOUT LOSING CONTROL EXECUTIVE

    VARIABLES OF INTEREST:
    PULSE: METER TIME DELAY IN HZ
    GENRT: CO3 GENERATION TIME IN HZ
    SAMPL: SAMPLING FREQUENCY DURING DATA LOGGING
    AMPS:  COULOMETER AMPS
    CPH:   ADCV DATA LOC FOR PH READING

    ENTER 177777 IN LOC 411 FOLLOWED BY CTRL A
    TO RETURN TO THE CLI


INITIAL CALCIUM(++) CONCENTRATION (M) ?
.36E-02
INITIAL MAGNESIUM++ CONCENTRATION(M) ?
0
INITIAL BICARBONATE CONCENTRATION (M) ?
.35E-02
INITIAL SODIUM CONCENTRATION (M) ?
.50E-04
```

```
INITIAL CHLORIDE CONCENTRATION (M) ?
.50E-04
CONSTANT CURRENT (AMPS) ?
9.85E-03
SOLUTION TEMPERATURE ?
25
CARBONATE GENERATION TIME (HZ; 10 HZ/SEC) ?
100
SAMPLING FREQUENCY DURING INDUCTION PERIOD (HZ) ?
10
HIT RETURN KEY TO VERIFY ELECTRODE MEASUREMENTS


     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?2

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?1

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?1

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?5
```

```
  DATA LOGGING WAS SET TO STOP WHEN THE PH DROPPED BELOW 6.80

 THE VOLTAGE INPUT EQUIVALENT FOR TEST MODEL IS 4.85

  THE VOLTAGE INPUT TO THE A/D IS SHOWN UNDER PDIV TIMES E+04
```

OFF-LINE
NOTE

```
7B TKOVR
0 000123  1 001466  2 000005  3 000000
$P

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?
7B TKOVR
0 003552  1 000076  2 000006  3 000000
SAMPL/000012 000024
$P

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?1

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?2

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?1

     ENTER THE NO. CORRESPONDING TO THE ACTION DESIRED
?
7B TKOVR
0 003552  1 000076  2 000001  3 000000
411/000671 177777
INT
R
```

APPENDIX D

Program SS205 Logged Data

```
  TIME              FH                 FCA                FDIV
19:47:56      +.1340966E+02      +.1274228E+05      +.9555000E+05
19:48:11      +.1338235E+02      +.3315000E+04      +.9555000E+05
19:48:26      +.1338235E+02      +.2613000E+05      +.9574500E+05
19:48:27      +.1338235E+02      +.4563000E+05      +.9555000E+05
19:48:28      +.1338235E+02      +.5850000E+05      +.9574500E+05
19:48:29      +.1340966E+02      +.6766500E+05      +.9574500E+05
19:48:30      +.1338235E+02      +.7410000E+05      +.9574500E+05
19:48:31      +.1338235E+02      +.7897500E+05      +.9594000E+05
19:48:32      +.1340966E+02      +.8267999E+05      +.9574500E+05
19:48:33      +.1338235E+02      +.8521500E+05      +.9555000E+05
19:48:34      +.1338235E+02      +.8716500E+05      +.9555000E+05
19:48:35      +.1338235E+02      +.8872500E+05      +.9555000E+05
19:48:36      +.1338235E+02      +.8989500E+05      +.9555000E+05
19:48:37      +.1338235E+02      +.9067500E+05      +.9574500E+05
19:48:38      +.1343697E+02      +.9126000E+05      +.9574500E+05
19:48:39      +.1338235E+02      +.9165000E+05      +.9555000E+05
19:48:40      +.1338235E+02      +.9184499E+05      +.9555000E+05
19:48:41      +.1338235E+02      +.9243000E+05      +.9613500E+05
19:48:42      +.1338235E+02      +.9262500E+05      +.9555000E+05
19:48:43      +.1338235E+02      +.9262500E+05      +.9574500E+05
19:48:44      +.1338235E+02      +.9282000E+05      +.9574500E+05
19:48:45      +.1335504E+02      +.9301500E+05      +.9574500E+05
19:48:46      +.1338235E+02      +.9301500E+05      +.9574500E+05
19:48:47      +.1338235E+02      +.9301500E+05      +.9574500E+05
19:48:48      +.1335504E+02      +.9301500E+05      +.9574500E+05
19:48:49      +.1338235E+02      +.9320999E+05      +.9574500E+05
19:48:50      +.1340966E+02      +.9320999E+05      +.9555000E+05
19:48:51      +.1338235E+02      +.9320999E+05      +.9555000E+05
19:48:52      +.1338235E+02      +.9340500E+05      +.9535500E+05
19:48:53      +.1340966E+02      +.9340500E+05      +.9555000E+05
19:48:54      +.1338235E+02      +.9340500E+05      +.9574500E+05
19:48:55      +.1338235E+02      +.9340500E+05      +.9574500E+05
19:48:56      +.1338235E+02      +.9340500E+05      +.9555000E+05
19:48:57      +.1338235E+02      +.9340500E+05      +.9574500E+05
19:48:58      +.1338235E+02      +.9320999E+05      +.9574500E+05
19:48:59      +.1335504E+02      +.9340500E+05      +.9555000E+05
19:49:00      +.1338235E+02      +.9340500E+05      +.9555000E+05
19:49:01      +.1338235E+02      +.9340500E+05      +.9555000E+05
19:49:02      +.1338235E+02      +.9340500E+05      +.9574500E+05
19:49:03      +.1338235E+02      +.9340500E+05      +.9574500E+05
19:49:04      +.1332773E+02      +.9301500E+05      +.9516000E+05
19:49:05      +.1319118E+02      +.9243000E+05      +.9340500E+05
19:49:06      +.1289075E+02      +.9106500E+05      +.9204000E+05
19:49:07      +.1294537E+02      +.9067500E+05      +.9262500E+05
19:49:08      +.1305462E+03      +.9106500E+05      +.9340500E+05
19:49:09      +.1291807E+02      +.9028500E+05      +.9204000E+05
19:49:10      +.1250840E+02      +.8872500E+05      +.8950499E+05
19:49:11      +.1250840E+02      +.8833500E+05      +.8950499E+05
19:49:12      +.1163445E+02      +.8404500E+05      +.8307000E+05
19:49:13      +.1166176E+02      +.8365499E+05      +.8365499E+05
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19:49:15      +.1166176E+02      +.8248500E+05      +.8326500E+05
19:49:16      +.1166176E+02      +.8209500E+05      +.8326500E+05
19:49:17      +.1163445E+02      +.8190000E+05      +.8307000E+05
19:49:18      +.1163445E+02      +.8170500E+05      +.8326500E+05
19:49:19      +.1163445E+02      +.8131500E+05      +.8307000E+05
19:49:20      +.1160714E+02      +.8131500E+05      +.8307000E+05
19:49:21      +.1163445E+02      +.8092500E+05      +.8326500E+05
19:49:22      +.1163445E+02      +.8092500E+05      +.8307000E+05
19:49:23      +.1163445E+02      +.8092500E+05      +.8307000E+05
19:49:24      +.1163445E+02      +.8092500E+05      +.8326500E+05
19:49:25      +.1166176E+02      +.8092500E+05      +.8307000E+05
```

```
  19:49:26        +.1166176E+02        +.8092500E+05        +.8307000E+05
  19:49:27        +.1166176E+02        +.8092500E+05        +.8307000E+05
  19:49:28        +.1163445E+02        +.8092500E+05        +.8287500E+05
  19:49:29        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:30        +.1160714E+02        +.8092500E+05        +.8326500E+05
  19:49:31        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:32        +.1163445E+02        +.8092500E+05        +.8287500E+05
  19:49:33        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:34        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:35        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:36        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:37        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:38        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:39        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:40        +.1163445E+02        +.8092500E+05        +.8346000E+05
  19:49:41        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:42        +.1166176E+02        +.8092500E+05        +.8326500E+05
  19:49:43        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:44        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:45        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:46        +.1163445E+02        +.8092500E+05        +.8346000E+05
  19:49:47        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:48        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:49        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:50        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:51        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:52        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:53        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:54        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:55        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:56        +.1166176E+02        +.8092500E+05        +.8326500E+05
  19:49:57        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:49:58        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:49:59        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:50:00        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:50:01        +.1163445E+02        +.8092500E+05        +.8326500E+05
  19:50:02        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:50:03        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:50:04        +.1163445E+02        +.8092500E+05        +.8346000E+05
  19:50:05        +.1163445E+02        +.8092500E+05        +.8307000E+05
  19:50:06        +.8684874E+01        +.6825000E+05        +.6259500E+05
  19:50:07        +.5981091E+01        +.5479500E+05        +.4270499E+05
    TIME                FH                  FCA                 FDIV
  19:50:50        +.6063024E+01        +.3763500E+05        +.4348500E+05
    TIME                FH                  FCA                 FDIV
  19:51:39        +.1321849E+02        +.5635500E+05        +.9457500E+05
    TIME                FH                  FCA                 FDIV
  19:55:41        +.1259033E+02        +.9165000E+04        +.8989500E+05
  19:55:51        +.1259033E+02        +.2964000E+05        +.9009000E+05
  19:56:06        +.1256302E+02        +.4075500E+05        +.8989500E+05
  19:56:08        +.1261764E+02        +.5362500E+05        +.8989500E+05
  19:56:10        +.1261764E+02        +.6240000E+05        +.8950499E+05
  19:56:12        +.1256302E+02        +.6844500E+05        +.8989500E+05
  19:56:14        +.1259033E+02        +.7273499E+05        +.8989500E+05
  19:56:16        +.1259033E+02        +.7624500E+05        +.8989500E+05
  19:56:18        +.1259033E+02        +.7858500E+05        +.8989500E+05
  19:56:20        +.1256302E+02        +.8053500E+05        +.8989500E+05
  19:56:22        +.1259033E+02        +.8190000E+05        +.8989500E+05
  19:56:24        +.1259033E+02        +.8287500E+05        +.8989500E+05
  19:56:26        +.1259033E+02        +.8365499E+05        +.8989500E+05
  19:56:28        +.1256302E+02        +.8443500E+05        +.8989500E+05
  19:56:30        +.1256302E+02        +.8482500E+05        +.9009000E+05
  19:56:32        +.1261764E+02        +.8521500E+05        +.9009000E+05
  19:56:34        +.1253571E+02        +.8521500E+05        +.8989500E+05
  19:56:36        +.1259033E+02        +.8560500E+05        +.8989500E+05
  19:56:38        +.1253571E+02        +.8560500E+05        +.8989500E+05
  19:56:40        +.1259033E+02        +.8560500E+05        +.8989500E+05
  19:56:42        +.1259033E+02        +.8599500E+05        +.8989500E+05
  19:56:44        +.1261764E+02        +.8599500E+05        +.8989500E+05
  19:56:46        +.1259033E+02        +.8599500E+05        +.8989500E+05
  19:56:48        +.1198949E+02        +.8346000E+05        +.8560500E+05
  19:56:50        +.9586134E+01        +.7273499E+05        +.6844500E+05
  19:56:52        +.7974789E+01        +.6415500E+05        +.5713500E+05
  19:56:54        +.6609243E+01        +.5596500E+05        +.4758000E+05
    TIME                FH                  FCA                 FDIV
  19:57:11        +.6636554E+01        +.4777500E+05        +.4738500E+05
```

APPENDIX E

Program SS205 Code

```
        .TITL   SS205
; PROGRAM SS205 FORMS MODULE THREE OF RESEARCH PROJECT
  ;CACO3-MGII - A STUDY ON CALCIUM CARBONATE NUCLEATION
  ; AND MAGNESIUM (++) INTERACTIONS
; THIS MODULE PROVIDES A COMPUTER BASED INFORMATON SYSTEM
 AS AN ALTERNATIVE TO A SET OF MANUAL AND MECHANICAL PROCEDURES
; NEEDED TO COLLECT AND PROCESS THE DATA FROM MODULE ONE, PART 1.
;

;MOD ONE, PART 1:
; AT VARYING CA(++) X CO3(-2) ION PRODUCTS, INDUCTION TIME
; WILL BE MEASURED AS A FUNCTION OF (1) MG ION CONCENTRATION
; (2) IONIC STRENGTH

;
;EXPERIMENTALLY CACO3 WILL BE PRECIPITATED FROM QUASI-HOMOGENEOUS
; SOLUTION USING ELECTROLYTIC GENERATION OF CO3(-2) IN THE PRESENCE
; OF CALCIUM ION.
;ELECTRODE MEASUREMENTS TAKEN WILL BE PH; PCA AND PDIV(CA+MG)
; USING LIQUID MEMBRANE SPECIFIC ION ELECTRODES

;
;BECAUSE READINGS CANNOT BE TAKEN ACCURATELY SIMULTANEOUSLY
 WITH CURRENT GENERATION - THESE PROCESSES MUST BE MUTUALLY EXCLUSIVE
; THE REACTION FLASK IS THEREFORE A CRITICAL REGION WITH RESPECT
; TO THE LATTER TWO PROCESSES
;
;SS205 IMPLEMENTS THIS CRITICAL REGION, LOGS AND PROCESSES ALL DATA
; AND SETS UP A USER MACHINE INTERACTION EXECUTIVE GIVING THE
; FORMER TOTAL CONTROL
;
;                       MULTITASK ENVIRONMENT
;TASK 0 -OPENS AND ASSIGNS I/O DEVICE CHANNELS
 ;      -SETS UP CTRL A INTERRUPT ROUTINE ADDRESS
 ;      -INITIATES TASK 2
;        -WAITS FOR CUE TO PRINT OUT CONTROL QUESTIONS
 ;      -CREATES TASK 9
;
;TASK 2 -CREATES AND INITIATES TASK 3
;        -SETS UP INITIAL SYSTEM CONFIGURATION DIALOGUE
 ;       INCLUDING RUN-TIME CONTROL VARIABLES
;        -ACTS AS A SCHEDULER TO INITIATE SYNCHRONIZATION
 ;       OF THE REST OF THE TASKS
;        -ACTS AS A MONITOR TO CONTROL RELAYS AND SENSORS AND
 ;       TRANSFER CONTROL TO EXECUTIVE TASK 0
;
;TASK 3 -OPERATES CONCURRENTLY WITH TASK 2 TO CONVERT(PREVIOUS ANSWER)
;         FROM DEC. ASCII TO BIN WHILE TASK 2 AWAITS COMPLETION
;         OF USER RESPONSE TO CURRENT DIALOGUE QUESTION
 ;
;TASK 4 -CREATES AND INITIATES TASK 5
;        -GETS TIME OF DAY, STORES TIME, READS ELECTRODES
 ;       STORES ADCV DATA, DETERMINES NEXT SAMPLING TIME
 ;
;TASK 5 -CONVERTS AND STORES (PERMANENTLY) ALL ADCV
;         VALUES (AS FIXED POINT EQUIVALENT VOLTS INPUT)
 ;      -CONVERTS VOLTS TO EQUIVALENT P TYPE MEASUREMENTS (F FORMAT)
;
;TASK 6 -OPERATES INDEPENDENTLY, AT LOWEST PRIORITY
 ;       TO CONVERT FL. PT. LOGGED DATA TO ASCII STRINGS
;
          AND PRINT RESULTS ON THE $LPT
;
;TASK 9 -DECIPHERS ANSWER TO CONTROL QUESTIONS AND GIVES RISE
;         TO APPROPRIATE ACTION
```

```
                           ;SYSTEM VARIABLES
;        .EXTD    .CMSK    ;CURRENT MASK
;        .EXTD    USTP     ;USER STATUS TABLE POINTER
                           ;RTOS TASK MODULES
         .EXTN    .TASK    ;INITIATE A TASK
         .EXTN    .KILL    ;DELETE THE CALLING TASK
         .EXTN    .XMT     ;TRANSMIT A MESSAGE
         .EXTN    .IXMT    ;XMT A MESSAGE FROM AN INTERRPT ROUT.
         .EXTN    .REC     ;RECEIVE A MESSAGE
         .EXTN    .UCEX    ;EXIT FROM A USER CLOCK ROUT
         .EXTN    .PRI     ;CHANGE THE CALLING TASK'S PRIORITY
         .EXTN    .TIDK    ;DELETE TASK SPECIFIED BY ID
         .EXTN    .ABORT   ;ABORT TASK WITH ID IN AC1
         .EXTN    .TIDP    ;CHANGE THE PRIORITY OF TASK W ID
                           ;LIBRARY ROUT
         .EXTN    .DBIN    ;DECIMAL ASCII TO BIN (S.P.)
         .EXTN    .BIND    ;BINARY TO ASCII DECIMAL (S.P.)
         .EXTN    .MPYU    ;MULTIPLY AC1 X AC2
         .EXTN    FENT     ;FLOATING PT. INTERPRETER ENTER
         .EXTN    FINT     ;INITIALIZE INTERPRETER
                           ;FOR USE BY LIB. ROUT
         .ENT     .GTCH .PTCH
                           ;FOR USE W INTERPRT I/O
         .ENT     GETC PUTC
         .ENT     WSA      ;WSA POINTS TO INTERPRT WRITEABLE AREA
         .ENT     START    ;BEG OF PROGRAM FOR LOADER MAP
         .TXTM 1           ;PACK ALL STRINGS FROM L/R
         .ZREL
.GTCH:            GETCH
GETC:             GETCH    ;USER ROUTINE REF TO BY FDFC,.DBIN
.PTCH:            PUTCH
PUTC:             PUTCH    ;USER ROUT REF TO BY FFDC,.BIND
WSA:     WRBLK             ;WORK BLOCK FOR INTERPRT
BIND:    .BIND
DBIN:    .DBIN
ERR:     JMP      .        ;ERROR RETURN FOR MOST SYSTM AND
                           ; TASK CALLS: (AC3)=ERR CALL LOC + 1
         .NREL

; * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 0

START:   LDA      0,ALARM  ;CONSOLE INTRRPT CRTL A
                           ; WILL TRANSFER CONTROL TO TKOVR
         LDA      2,USTP   ;CALCULATE USTIT ADDRESS
         STA      0,11,2   ;STA IN USER STATUS TABLE INTERRUPT ADD
         LDA      0,ONE    ;TSK 0 WILL HAVE PRIORITY ONE
         .PRI
         LDA      0,.TTI
         SUB      1,1
         .SYSTM            ;OPEN $TTI ON CHN 0
         .OPEN    0
         JSR      ERR
         LDA      0,.TTO
         .SYSTM            ;OPEN $TTO ON CHN 1
         .OPEN    1
         JSR      ERR
         LDA      0,.LPT
         .SYSTM            ;OPEN $LPT ON CHN 2
         .OPEN    2
         JSR      ERR
         LDA      0,.TTO
         .SYSTM            ;DISABLE SPOOLING ON $TTO
         .SPDA
```

```
        JSR     ERR
        LDA     0,.LPT
        .SYSTM          ;DISABLE SPOOLING ON $LPT
        .SPDA
        JSR     ERR
        LDA     @0,HELO ;INTRODUCTORY MESSAGE
        LDA     @1,BYE.
        SUB     0,1     ;CALCULATE LENGTH OF MESSAGE
        .SYSTM
        .WRS    1
        JSR     ERR
        LDA     0,TASK2
        LDA     1,NTSK2
        .TASK           ;TASK 2 INITIALIZES DIALOGUE
        JSR     ERR     ; WITH USER
TSS1:   FINT            ;INTITIALIZE INTERPRETER
WAIT:   LDA     0,SEMP1
        .REC            ;USER ASSUMES CONTROL AT ANY TIME
                        ;BY ENTERING CTRL A
SUSPA:  LDA     @0,.WNXT        ;BYTE POINTER TO CONTROL QUESTIONS
        LDA     @1,.LMIT        ;CALC NO. OF CHARACTERS
        SUB     0,1     ; TO BE PRINTED
        .SYSTM
        .WRS    1       ;PRINT OUT CONTROL QUESTONS
        JSR     ERR
        .SYSTM
        .GCHAR          ;GET RESPONSE
        JSR     ERR
        .SYSTM
        .PCHAR          ;ECHO USER RESPONSE
        JSR     ERR
        LDA     1,MIN60
        ADD     1,0     ;AC0 CONTAINS BIN EQUIV OF ANSW
        MOV     0,2     ;MESSAGE TO TASK NINE
CTRLA:  LDA     0,TASK9 ;TASK 9 DECIPHERS ANSWER
        LDA     1,NTSK9 ; AND GIVES RISE TO APPROPRIATE ACTION
        .TASK
        JSR     ERR
        JMP     WAIT
TKOVR:  LDA     3,ONE
        LDA     1,MIN4
        LDA     2,USTP
        LDA     2,15,2  ;START OF ACTIVE TCB CHAIN
SERCH:  LDA     0,12,2  ;AC0 = ID OF TCB
        MOV     0,0,SNR ;VERY HARD TO EXPLAIN
        STA     2,BUG   ;NOTE THIS TASK JUMPS BACK TO ITSELF
        ADD     #1,0,SNR        ;IS THIS TCB NO. 4?
        JMP     TIDR    ;YES, TCB 4 FOUND
        LDA     2,7,2   ;AC2= START OF NEXT ACTIVE TCB
        ADD     #3,2,SNR        ;IS THIS LAST TCB IN CHAIN
        JMP     GO      ;YES, STOP SERCH
        JMP     SERCH   ;SERCH MORE
TIDR:   LDA     1,MSK9  ;CLEAR STPRT FLAGS
        STA     1,5,2
GO:     LDA     2,SIX   ;CTRL A INTERRPT MESSAGE
        LDA     0,TASK9
        LDA     1,NTSK9
        .TASK           ;CREATE TASK 9
        JSR     ERR
        JMP     WAIT    ;TKOVR ASSUMED THE ID OF PREVIOUS ZERO
```

```
; * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 2

DYLOG:  LDA     0,TASK3 ;TASK 3 CONVERTS USER'S ASCII DEC
        LDA     1,NTSK3 ; ANSWERS TO FX OR FL PT BINARY
        .TASK
        JSR     ERR
        LDA     0,MIN10 ;INITIALIZE VALUE IN NEG10, FOR NO.
        STA     0,NEG10 ; OF QUESTIONS TO BE MADE
        LDA     0,MIN6  ;INIT VAL IN NEG6 FOR NO. OF FL PT
        STA     0,NEG6  ; CONVERSIONS TO BE MADE
        LDA     0,MIN3  ;INIT VAL IN NEG3 FOR NO OF FX PT
        STA     0,NEG3  ; CONVERSIONS TO BE MADE
        LDA     0,BUF16 ;BUF16 HOLDS INIT VALUE
        STA     0,RDBUF ;FOR THE READ BUFFER BYTE POINTER
        LDA     0,INFOI ;INFOI HOLDS INITIAL LOC
        STA     0,INFO  ; FOR CONVERTED DATA STORAGE
        STA     @0,SEMP2        ;ENABLE FIRST PASS THRU QUESTIONS
        LDA     @2,.QUSP        ;BYTE POINTER TO FIRST QUESTION
TALKF:  JSR     ASK     ;ASK USER FOR INPUT PARAMT
        LDA     0,SEMP2 ;WAIT FOR TRANSFER OF BYTE POINTER
        .REC            ; OF LAST ANSWR TO TASK 3
        LDA     0,RDBUF ;ALLOW FOR AN EIGHT WORD BUFFER
        LDA     1,DEC16 ; FOR EACH REPLY
        ADD     1,0
        STA     0,RDBUF ;NEXT REPLY GOES INTO NEXT BUF
        .SYSTM
        .RDL    0       ;READ RESPONSE
        JMP     EXPRO
        SUBZL   1,1     ;NON ZERO MESSAGE
        LDA     0,SEMP3 ;XMIT ON SEMAPHORE 3
        .XMT            ; THAT IS, ASCII TO BIN CON MAY BEG
        JSR     ERR     ; FOR USER INPUT JUST READ
        ISZ     NEG10   ;TEN QUESTS ASKED? YES, SKIP
        JMP     TALKF   ;NO, RETN TO QUESTIONING
VRFY:   LDA     0,DECP1
        STA     0,DECP2 ;INIT FOR DEC CONVTD DATA POINTERS
        STA     0,DECP3
        LDA     0,ZERO  ;INIT SAMPLING COUNTER
        STA     0,COUNT
        STA     0,COMP  ;INIT COUNTER FOR OUTPUT OF SMPLED DATA
        LDA     0,TASK4 ;TSK4 GTOD, ST TIME, READS ELECTRODES,
        LDA     1,NTSK4 ;ST ADCV DATA, WAITS FOR NXT SMPLING
        .TASK
        JSR     ERR
        LDA     @0,.HEDP        ;BYTE POINTER TO HEADING
        .SYSTM          ;PRINT HEADING ON $LPT
        .WRL    2
        JSR     ERR
        JSR     TOEAW   ;TURN ON ELECTRODES AND WAIT
        JSR     ONERD   ;DO ONE READ
        LDA     0,SEMP1
        SUBZL   1,1
        .XMT            ;RETURN CONTROL TO TASK 1
        JSR     ERR
EXPRO:  LDA     0,SEMP2 ;PROCEED W EXPT
        .REC
        LDA     0,ZERO  ;INITIALIZE CONTROL LOOP VAR
        STA     0,DUMMY
        JSR     ONERD
        LDA     0,COUL  ;TURN ON COULOMETER
        DOA     0,25
        LDA     0,GENRT
        LDA     1,CRISS
        .SYSTM          ;SET USER CLOCK TO GENERATION TIME
        .DUCLK
        JSR     ERR
        LDA     0,SEMP2 ;SIGNAL FROM USER CLOCK EXPIRED
```

```
        .REC
        .SYSTM          ;REMOVE USER CLOCK
        .RUCLK
        JSR     ERR
        JSR     TOEAW
RPEET:  LDA     0,SEMP4 ;TAKE ANOTHER READING
        SUBZL   1,1     ;NON ZERO MESSG
        .XMT
        JSR     ERR
        LDA     0,SEMP2 ;ADCV DATA STORED AND PROCESSED
        .REC
        LDA     0,COMP  ;SYNCHRONIZATION OF TASK 6 IS
        INC     0,0     ; DEPENDENT ON SAMPLING FREQUENCY
        LDA     1,COUNT ; E.G. IF COMP = COUNT - 1 TASK
        SUB     1,0,SZR ; SIX IS WAITING FOR A .XMT TO PROCEED
        JMP     .+4     ; WITH OUTPUT
        LDA     0,SEMP6
        .XMT
        JSR     ERR
                        ;CONTROL ALGORITH TO STO SAMPLING
        FENT
        FLDA    1,OVER
        FLDA    2,PH
        FSUB    1,2,FSGT        ;SKP IF PH .GT. OVER
        FISZ    DUMMY           ;DUMMY WILL EQ ONE
        FEXT
        LDA     1,DUMMY
        MOV     1,1,SNR         ;PH .LT. OVER, SKP
        JMP     RPEET
        LDA     0,SEMP1
        .XMT                    ;RETURN TO CONTROL
        JSR     ERR
        JMP     EXPRO
ASK:    STA     3,16    ;SAVE RTN ADDRESS
        LDA     0,0,2   ;LOAD AC0 WITH BYTE POINTER
        .SYSTM
        .WRL    1
        JSR     ERR
        INC     2,2     ;UPDATE BYTE PNTR FOR NEXT MESSG
        JMP     0,3     ;RETURN TO CALL+1

TOEAW:  STA     3,16
        LDA     0,ELEON ;TURN ELECTRODES ON
        DOA     0,25
        LDA     1,PULSE
        .SYSTM
        .DELAY
        JSR     ERR
        JMP     0,3

ONERD:  STA     3,16
        SUBZL   1,1     ;NON ZERO MESSAGE
        LDA     0,SEMP4 ;SIGNAL TSK 4 TO START READING
        .XMT
        JSR     ERR
        LDA     0,SEMP2 ;WAIT FOR SIGNAL INDICATING ONE
        .REC            ; RD HAS BEEN DONE
        LDA     0,SEMP6 ;GIVE GO-AHEAD TO OUTPUT
        SUBZL   1,1     ;NON ZERO MESSAGE
        .XMT
        JSR     ERR
        LDA     0,ELEOF ;TURN ELECTRODES OFF
        DOA     0,25
        JMP     0,3
```

```
CRISS:  .+1
        STA     3,16    ;CRISIS
        LDA     0,COLOF ;TURN COULOMETER OFF
        DOA     0,25
        LDA     0,SEMP2 ;SCHEDULER WILL RETURN TO TASK2
        SUBZL   1,1     ;NON ZERO MESSAGE
        .IXMT
        JSR     ERR
        LDA     3,16    ;.IXMT DESTROYS ALL ACCUMULATORS
        .UCEX

; * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 3

CONVF:  LDA     0,SEMP3 ;WAIT TILL USER HAS ENTRD
        .REC            ; REPLY, PROC WITH CONVR
        LDA     0,RDBUF ;ST BYTE POINTER TO BEG
        STA     0,READB ; OF LAST REPLY IN READB
        LDA     0,SEMP2 ;BYTE POINTER CAN NOW BE CHANGED
        .XMT            ; FOR NEXT ANSWR LOC BY TASK2
        JSR     ERR
                        ;CONVERSION IS MADE BY WAY OF GETCH
                        ; WHICH USES READB AS A POINTER
        FENT
        FDFC    1       ;FAC1 HAS CONVERTED VAL (FL PT)
        FSTA    @1,INFO ;ST CONVRTD VAL IN VECTOR INFO
        FEXT
        ISZ     INFO    ;EACH FL PT PARMT OCC 2 WORDS IN INFO
        ISZ     INFO
        SUBZL   1,1     ;NON ZERO MESSAGE
        ISZ     NEG6    ;SIX CONVERSIONS MADE?
        JMP     CONVF   ;NO, GET READY FOR NEXT
FXDPT:  LDA     0,SEMP3 ;PROCEED WITH LAST THREE ASCII TO
        .REC            ; BIN FX PT CONVERSIONS
        LDA     0,RDBUF
        STA     0,READB
        LDA     0,SEMP2 ;BYTE POINTER CAN NOW BE CHANGED
        .XMT            ; FOR NEXT ANSWR LOC BY TASK2
        JSR     ERR
        JSR     @DBIN   ;ASCII DECIMAL TO BIN
        STA     @1,INFO ;BIN RETRND IN AC1
        ISZ     INFO    ;LAST 3 ANSWRS OCCUPY ONE WRD
        ISZ     NEG3
        JMP     FXDPT
        LDA     0,SEMP3 ;WAIT FOR .XMT SIGNAL FROM ANSWER
        .REC            ; TO TENTH QUESTION
        JMP     CONVF

                        ;GETCH AND PUTCH USE A BYTE POINTER
                        ;BITS 0-14 OF THE BPA CONTAIN THE
                        ;ADDRESS OF THE MEMORY LOCATION
                        ;THAT CONTAINS OR WILL CONTAIN THE
                        ;BYTE, BIT 15 SPECIFIES WHICH HALF
                        ;(0 LEFT, 1 RIGHT)

                        ;GETC CHOOSES CHARACTERS FROM L/R
GETCH:  LDA     2,READB ;GET BYTE POINTER
        ISZ     READB   ;INCREMENT POINTER
        MOVZR   2,2     ;PUT ADDRESS IN RIGHT PLACE
                        ;(LEFT/RIGHT BIT TO CARRY
        LDA     0,0,2   ;BRING MEMORY WORD TO AC0
        LDA     2,C377  ;GET EIGHT BIT MASK
        MOV     0,0,SNC ;TEST CARRY FOR WHICH HALF
        MOVS    0,0     ;SWAP BYTE FROM LEFT TO RIGHT
        AND     2,0     ;MASK OUT UNWANTED BYTE
        JMP     0,3     ;RETURN
C377:           377
```

```
                        ;PUTCH PACKS TWO 8 BIT ASCII BYTES
                        ; IN A WORD AND STORES IT AWAY IN
                        ; THE OUTPUT BUFFER
PUTCH:  LDA     2,STPT2 ;BYTE POINTER TO NEXT LOC OF
                        ; OUTPUT BUFF USED FOR RESULTS
        ISZ     STPT2   ;INC POINTER
        MOVZR   2,2,SNC ;PUT ADDRESS IN RIGHT PLACE
                        ;(LEFT/RIGHT BIT TO CARRY)
        MOVS    0,0,SZC ;SWITCH LEFT AND RIGHT BYTES
        JMP     RIGHT   ;C IS 1, DEALING W RIGHT BYTE
        STA     0,TEMP  ;STORE LEFT BYTE IN LEFT BYTE OF TEMP
        JMP     0,3
RIGHT:  LDA     1,TEMP
                        ;INCLUSIVE OR OF AC1 AND AC0
                        ;WILL CONTAIN THE 2 BYTES IN PROPER PLACE
        COM     0,0     ;NOT B
        AND     0,1     ;NOT B .AND. A IN AC1
        ADC     0,1     ;NOT(NOT B) + NOT B .AND. A=B+NOTB.AND. A IN AC1
        STA     1,0,2   ;ST IN NEXT LOC OF OUTPUT BUFFER
        JMP     0,3     ;RETURN TO F


; * * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 4

SMPLN:  LDA     0,TASK5 ;TSK 5 CONVERTS ADCV VALUES TO
        LDA     1,NTSK5 ; FL PT DEC VALUES
        .TASK
        JSR     ERR
LOOP:   LDA     0,SEMP4 ;MAKE READY FOR ONE COMPLETE
        .REC            ; LOGGING PASS
        .SYSTM
        .GTOD           ;GET TIME OF DAY
        JSR     ERR
        LDA     3,DECP2
        STA     2,0,3   ;ST HOUR
        STA     1,1,3   ;ST MIN
        STA     0,2,3   ;ST SEC
        LDA     @0,.CMSK        ;AC0 W CURRENT MASK
        STA     0,CMSK  ;SAVE CURRENT MASK
        LDA     0,MASK1 ;DISABLE INTERRUPT FOR EVERYTH BUT CLOCK AND TTI
        STA     @0,.CMSK        ;CLOCK INTRRPT WILL NOT CHANGE MASK
        MSKO    0
RDELE:  LDA     0,PHCHN ;PH CHANNEL
        DOAS    0,ADCV  ;PH READ
        SKPDN   ADCV    ;WAIT FOR END OF CONVERSION
        JMP     .-1
        DICS    0,ADCV  ;ST PH IN AC0, RD PCA
        SKPDN   ADCV    ;WAIT FOR END OF CONVERSION
        JMP     .-1
        DICS    1,ADCV  ;ST PCA IN AC1, RD PDIV
        SKPDN   ADCV
        JMP     .-1
        DICC    2,ADCV  ;ST PDIV IN AC2
        LDA     3,CMSK
        STA     @3,.CMSK        ;RESTORE LAST USED INTERRRPT MASK
        LDA     3,ZERO  ;CLEAR ALL DISABLE FLAGS
        MSKO    3
STCND:  STA     0,CPH
        STA     1,CPCA
        STA     2,CPDIV ;ST CONVERTED DATA
        ISZ     COUNT   ;COUNT SAMPLING LOOPS
        SUBZL   1,1     ;NON ZERO MESSAGE
        LDA     0,SEMP5 ;TASK 5 MAY BEGIN CONVRSN
        .XMT            ; OF ADCV DATA
        JSR     ERR
        LDA     1,SAMPL
        .SYSTM
        .DELAY          ;DELAY USER SPECIFIED SAMPLING FRE
        JSR     ERR
        JMP     LOOP
```

```
; * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 5

C2FDV:  LDA     0,TASK6 ;TSK 6 DOES OUTPUT
        LDA     1,NTSK6 ; OF SAMPLED DATA VALUES
        .TASK
        JSR     ERR
PRECV:  LDA     0,SEMP5
        .REC
        LDA     0,MIN3  ;INIT COUNTER FOR 3 DATA MANIPULTNS
        STA     0,NEG3
        LDA     0,NPMS1 ;INIT ADCV DATA POINTER
        STA     0,NPMS2
NEXCV:  LDA     @1,NPMS2
        LDA     2,VPER  ;VOLTAGE VALUE FOR LSB OF ADCV DATA
        JSR     @MPYU   ;THE DECIMAL EQUIVALENT TIMES
                        ;10,000 OF THE VOLTAGE INPUT TO THE
                        ;ADCV WILL APPEAR IN AC0 AND AC1
        LDA     2,DECP2 ;DECIMAL POINTER
        STA     0,3,2   ;SAVE FX PT REPRESENTATION
        STA     1,4,2   ; OF INPUT VOLTAGE
        FENT
        FFLO    3,2     ;FX PT DOUBLE PRE TO FL PT
        FEXT
        ISZ     DECP2   ;EACH FL PT REP OCCUP TWO WRDS
        ISZ     DECP2
        ISZ     NPMS2   ;POINT TO NEXT ADCV DATA LOC
        ISZ     NEG3    ;3 ELECTRODE MEAS CONVRTD?
        JMP     NEXCV   ;NO, REPEAT
        JSR     VALUE   ;CALCULATE PH, PCA AND PDIV
        LDA     0,DECP2 ;ALLOW FOR CORRECT INSERTION
        LDA     1,THREE ; OF NEXT SAMPLING TIME
        ADD     1,0
        STA     0,DECP2
        SUBZL   1,1     ;NON ZERO MESSAGE
        LDA     0,SEMP2 ;SIGNAL TSK 2, WHICH DECIDES
        .XMT            ; TO ACTIVATE OR NOT, ANOTHER
        JSR     ERR     ; DATA LOGGING PASS
        JMP     PRECV   ;WAIT FOR SIGNAL FROM TASK 4
VALUE:  STA     3,SAVE  ;SAVE RTN ADDR
        FENT
        FLDA    1,-1,2  ;(FAC1)=VOLTAGE INPUT TO A/D *E+04
        FLDA    2,PHFAC ;PHFAC = VOLTS/PH *E-04
        FDIV    2,1
        FSTA    1,PH    ;LOAD PH IN CONTROL LOOP REGISTER
        FSTA    1,-1,2  ;PLACE BACK IN STORAGE BUFFER
        FEXT
        JMP     @SAVE

; * * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 6

OUTWT:  LDA     0,SEMP6 ;GO AHEAD WITH OUTPUT OF DATA LOGGED
        .REC
AUTPT:  LDA     0,STPT1 ;BYTE POINTER TO OUTPUT BUFFER
        STA     0,STPT2 ;BYTE POINTER USED BY PUTCH TO PLACE
                        ; ASCII IN OUTBU
        LDA     2,DECP3 ;POINTER TO NEXT SAMPLED DATUM
        LDA     0,STPT4 ;INIT POINTER FOR DECVL
        STA     0,STPT5
        LDA     0,STPT3 ;INIT POINTER FOR DATA BYTE CALC
        STA     0,STPT6
        LDA     1,0,2   ;HOUR TO ASCII DEC
        JSR     @BIND
```

```
        LDA     1,1,2   ;MIN TO ASCII
        JSR     @BIND
        LDA     1,2,2   ;SEC TO ASCII
        JSR     @BIND
        FENT
        FLDA    1,3,2
        FFDC    1       ;CONVERT PH FLO PT REPRESENTATION
                        ; TO ASCII STRING
        FLDA    1,5,2
        FFDC    1       ;REPEAT (WITH PCA)
        FLDA    1,7,2
        FFDC    1       ;REPEAT (WITH PDIV)
        FEXT
        LDA     1,NINE
        ADD     1,2
        STA     2,DECP3 ;POINTS TO (NEXT) SAMPLING DATUM
        JSR     DATEO   ;HOUR OUT
        JSR     KOLON   ;COLON
        JSR     DATEO   ;MIN OUT
        JSR     KOLON   ;COLON
        JSR     DATEO   ;SECS OUT
        JSR     BLANK   ;SKP 10 SPACES
        JSR     DECVL   ;DECIMAL PH VALUE OUT
        JSR     BLANK
        JSR     DECVL   ;DEC PCA VALUE OUT
        JSR     BLANK
        JSR     DECVL   ;DEC PDIV VALUE OUT
        LDA     0,CRLF  ;CARRIAGE RETURN,LINE FEED
                        ;BYTE POINTER
        LDA     1,TWO
        .SYSTM          ;CR,LF ON LINE PRINTER
        .WRS    2
        JSR     ERR
        ISZ     COMP    ;CONTROL ALGORITH FOR DATA OUTPUT
        LDA     0,COUNT ;NO. OF SAMPLINGS OUTPUT =
        LDA     1,COMP  ;NO. OF SAMPLINGS DONE?
        SUB     1,0,SZR
        JMP     AUTPT   ;NO, DO MORE OUTPUT
        JMP     OUTWT   ;WAIT FOR FURTHER OUTPUT INST

DATEO:  STA     3,16    ;SAVE RTN ADD
        LDA     0,STPT6 ;USED TO CALC EFF BYTE POINTER
        LDA     1,SEVEN ; OF NEXT PART OF THE TIME
        ADD     1,0
        STA     0,STPT6 ;PRINT OUT HR OR MIN OR SEC
        LDA     1,TWO   ;TWO CHARACTERS
        .SYSTM
        .WRS    2
        JSR     ERR
        JMP     0,3

KOLON:  STA     3,16
        LDA     0,COLON
        LDA     1,ONE
        .SYSTM
        .WRS    2       ;PRINT OUT A COLON
        JSR     ERR
        JMP     0,3

BLANK:  STA     3,16
        LDA     0,SPACE
        LDA     1,TEN
        .SYSTM
        .WRS    2       ;TAB 10 SPACES
        JSR     ERR
        JMP     0,3
```

```
DECVL:  STA     3,16
        LDA     0,STPT5
        LDA     1,DEC14
        ADD     1,0
        STA     0,STPT5
        .SYSTM          ;PRINT OUT NEXT DECIMAL PTYPE VALUE
        .WRS    2
        JSR     ERR
        JMP     0,3

; * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * TASK 9

FORK:   LDA     0,ZERO  ;TASK 9 HAS ABSOLUTE PRIORITY
        .PRI            ; CONTROL SYS BY TRYING TO INTERR TSK9
        LDA     1,MIN1
        MOV     2,2,SNR ;DETERMINE USER RESPONSE
        JMP     SYSIN   ;0 - SYS INITIALIZATION
        ADD     1,2,SNR
        JMP     SYVRF   ;1 - ELECTRODE VERIFY
        ADD     1,2,SNR
        JMP     SYPRO   ;2 - SYS PROCEED
        ADD     1,2,SNR
        JMP     DATAP   ;3 - DATA PROCESS
        ADD     1,2,SNR
        JMP     SYOFF   ;4 - TURN OFF ELECTRODES
        ADD     1,2,SNR
        JMP     SYSHT   ;5 - SHYSTEM SHUTDOWN
        ADD     1,2,SNR
        JMP     RAND.   ;6 - CONSOLE CTRAL A INTERRPT
        LDA     2,ILLGL ;OTHERWISE ILLEGAL ANSWER
        JSR     @.ASK   ;PRINT MESSAGE TO THAT EFFECT
RAND.:  JSR     YPOUT   ;WIPE OUT TASKS 2,3,4,5,6
NOBUG:  LDA     1,ONE
        LDA     2,BUG   ;MUST UNDO THE DOUBLE .REC
        STA     1,5,2   ;RESET S AND U BITS IN TASK 0 STPTR
SUICD:  .KILL           ;SELF -DESTRUCT

SYSIN:  JSR     YPOUT   ;WIPE OUT TASKS 2,3,4,5,6
        LDA     0,TASK2
        LDA     1,NTSK2
        .TASK
        JMP     ERR
        JMP     SUICD
SYVRF:  JSR     YPOUT
        LDA     0,TASK2
        LDA     1,ENTR2
        .TASK
        JSR     ERR
        JMP     SUICD
SYPRO:  LDA     0,SEMP2
        .XMT
        JSR     ERR
        JMP     SUICD
DATAP:  LDA     0,SEM10
        .XMT
        JSR     ERR
        JMP     SUICD
SYOFF:  LDA     0,ELEOF
        DOA     0,25
        SUBZL   1,1     ;NON ZERO MESSAGE
        LDA     0,SEMP1 ;ASK FOR FURTHER INSTRUCTIONS
        .XMT
        JSR     ERR
SYSHT:  JSR     YPOUT   ;KEYBOARD WILL BE WAITING
        JMP     SUICD   ; FOR CTRL A TO PROCEED
```

```
YPOUT:  STA     3,16
        LDA     2,MIN5
        STA     2,NEG5
        LDA     1,TWO
        LDA     0,SEMPI
        STA     0,SEMPB ;INITIALIZE SEMPB
        LDA     0,ZERO
TIDK:   STA     @0,SEMPB        ;RESTORE ALL SEMAPHORE LOC TO 0
        .ABORT          ;TERMINATE TASKS 2,3,4,5,6
        JMP     .+1     ;SOME TASK IS DORMANT
        ISZ     SEMPB
        ISZ     SEMPB   ;SEMPB POINTS SUCCESIVELY TO SEMAPHORES
        INC     1,1
        ISZ     NEG5
        JMP     TIDK
        JMP     0,3


; * * * * * * * * * * * * DATA STRUCTURES * * * * * * * * * * * * *

        .ZREL
USTP:   400     ;SYMBOL NOT LISTED BY SYSTEM
.CMSK:  010     ;SYMBOL NOT LISTED BY SYSTEM
CMSK:   000
MSK9:   004     ;FOR TPRST
BUG:    000     ;STORAGE FOR TCB POINTER OF TASK 0
ALARM:  TKOVR
.TTI:   .+1*2
        .TXT @$TTI@
.TTO:   .+1*2
        .TXT @$TTO@
.LPT:   .+1*2
        .TXT @$LPT@

;+ + + + + + + + + + + + + TASK IDENTIFICATIONS + + + + + +
                        ;LEFT BYTE = ID; RIGHT BYTE = PRIORITY

TASK1:          0401
TASK2:          1002
TASK3:          1403
TASK4:          2004
TASK5:          2405
TASK6:          3006
TASK9:          4401

;+ + + + + + + + + + + + + STARTING ADDRS FOR NEW TASKS + +

NTSK2:  DYLOG
NTSK3:  CONVF
NTSK4:  SMPLN
NTSK5:  C2FDV
NTSK6:  OUTWT
NTSK9:  FORK
ENTR2:  VRFY

;+ + + + + + + + + + + + + SEMAPHORE LOCATIONS + + + + + + +

SEMPI:  .+5     ;FOR CLEARING OF SEMP'S
SEMPB:  000
SEMP1:  .+1
        000
SEMP2:  .+1
        000
SEMP3:  .+1
        000
SEMP4:  .+1
        000
```

```
SEMP5:   .+1
         000
SEMP6:   .+1
         000
SEM10:   .+1
         000
;+ + + + + + + + + + + + + NUMERICAL CONSTANTS + + + + + + +

SAVE:    000       ;SAVE REGISTER
PHFAC:   7.14E+03
TEMP:    000       ;TEMPORARY FOR PUTCH
MIN60:   -060
MIN5:    -005
NEG5:    000
MIN4:    -004
MIN1:    -001
ZERO:    000
ONE:     001
TWO:     002
THREE:   003
FOUR:    004
FIVE:    005
SIX:     006
SEVEN:   007
NINE:    011
TEN:     012
DEC14:   016
DEC16:   020

;+ + + + + + + + + + + + + POINTERS FOR TXT MESSG GROUPS
;                                         AND OTHERS + + + +

HELO:    HELLO     ;POINTER TO INTRO MESSAGE
BYE.:    BYE       ;BYTE CALCULATION
.WNXT:   WNEXT     ;POINTER TO CONTROL QUESTS
.LMIT:   LIMIT     ;POINTER TO CTROL QUEST BOUNDARY
.QUSP:   QUESP     ;POINTER TO USER PARMTR QUESTS
.HEDP:   HEADP     ;POINTER TO HEADING
.ASK:    ASK       ;POINTR TO ASK SUBROUTINE
.DYLG:   DYLOG     ;POINTER TO BEG. OF TASK 2
;+ + + + + + + + + + + + + INITIALIZATION PARAMETERS AT BEG
;                              OF TASK 2 + + + + + + + + + + + + +

MIN10:   -012
NEG10:   000
MIN6:    -006
NEG6:    000
MIN3:    -003
NEG3:    000
BUF16:   BUFER*2-20
RDBUF:   000       ;FOR TASK 2
READB:   000       ;FOR TASK 3
INFOI:   CA
INFO:    000
DECP1:   STIME
DECP2:   000
DECP3:   000
COUNT:   000
DUMMY:   000
COMP:    000
```

```
; + + + + + + + + + + + + + RELAY DATA WORDS + + + + + + + +

COUL:    000
COLOF:   000
FLEON:   000
FLEOF:   177777
         .NREL
HEADP:   .+1*2
         .TXT @  TIME                      PH
                     PCA                          PDIV<15><12>@
         .ZREL
;+ + + + + + + + + + + + + CONTROL LOOP VARIABLES TO STOP
;                              DATA LOGGING + + + + + + + + + + +
OVER:    6.80     ;'SET POINT' SIGNAL
PH:      0.0

         .RDX 10           ;10 HZ
PULSE:   50       ;5 SECONDS FOR METER STABILIZATION
VPER:    195      ;19.5 MV/BIT ON ADCV DATA
         .RDX 8
PHCHN:   000      ;CHANNEL ASSIGNED TO PH
MASK1:   17771
MASK:    000200
NPMS1:   CPH               ;P MEASUREMENT POINTER
NPMS2:   000
NPMS3:   000
;+ + + + + + + + + + + + + STORAGE LOCS FOR ADCV DATA + + + +

CPH:     000
CPCA:    000
CPDIV:   000
MPYU:    .MPYU
;+ + + + + + + + + + + + + POINTERS TO STORED P TYPE DATA + +

STPT1:   2*OUTBU           ;BYTE POINTER TO OUTPUT BUFFER LPT
STPT2:   000               ;REST OF THESE ARE USED FOR
STPT3:   2*OUTBU-3         ; EFFECTIVE MANIPULATION OF STACKED
STPT4:   2*OUTBU+7         ; CHARACTERS, E.G. SKIPPING OVER
STPT5:   000               ; ZEROS, CREATING LOOPS
STPT6:   000
;+ + + + + + + + + + + + + TASK 6 OUTPUT FUNCTIONS + + + + + +

CRLF:    .+1*2
         .TXT @<15><12>@
SPACE:   .+1*2
         020040   ;TEN BLANKS
         020040
         020040
         020040
         020040
COLON:   .+1*2
         .TXT @<072>@
;+ + + + + + + + + + + + + STORAGE LOCATIONS FOR USER RESPONSES +

CA:      .BLK 2
MG:      .BLK 2
HCO3:    .BLK 2
NA:      .BLK 2
CLDE:    .BLK 2
AMPS:    .BLK 2
TEMPE:   000
GENRT:   000               ;GENERATION TIME
SAMPL:   020               ;SAMPLING FREQUENCY

         .NREL
ILLGL:   .+1
         WARN*2
WARN:    .TXT @UNDEFINED ANSWER, TRY AGAIN <15><12>@
WNEXT:   .+1*2             ;WHAT NEXT?
         .TXT @<15><12><12>      ENTER THE NO. CORRESPONDING TO THE
ACTION DESIRED <15><12><077>@
LIMIT:   .*2
```

```
QUESP:  .+1
        MESS0*2         ;BYTE POINTERS FOR MESSAGES
        MESS1*2
        MESS2*2
        MESS3*2
        MESS4*2
        MESS5*2
        MESS6*2
        MESS7*2
        MESS8*2
        MESS9*2
;+ + + + + + + + + + + + + TEXT MESSAGES + + + + + + + + + + + + 

MESS0:  .TXT @INITIAL CALCIUM(++) CONCENTRATION (M) <077><15><12>@
MESS1:  .TXT @INITIAL MAGNESIUM++ CONCENTRATION(M) <077><15><12>@
MESS2:  .TXT @INITIAL BICARBONATE CONCENTRATION (M) <077><15><12>@
MESS3:  .TXT @INITIAL SODIUM CONCENTRATION (M) <077><15><12>@
MESS4:  .TXT @INITIAL CHLORIDE CONCENTRATION (M) <077><15><12>@
MESS5:  .TXT @CONSTANT CURRENT (AMPS) <077><15><12>@
MESS6:  .TXT @SOLUTION TEMPERATURE <077><15><12>@
MESS7:  .TXT @CARBONATE GENERATION TIME (HZ; 10 HZ/SEC) <077><15><12>@
MESS8:  .TXT @SAMPLING FREQUENCY DURING INDUCTION PERIOD (HZ)
        <077><15><12>@
MESS9:  .TXT @HIT RETURN KEY TO VERIFY ELECTRODE MEASUREMENTS@
HELLO:  .+1*2
        .TXT @<15><12>
F. DURANZA <15><12>
CHM ENG 760 <15><12>
<12><12>
                        GREETINGS FROM SS205<15><12><12>
                         PROJECT CACO3-MGII<15><12>
A STUDY ON CALCIUM CARBONATE NUCLEATION AND MAGNESIUM ION INTERACTIONS
<15><12><12>
ANSWER THE FIRST 6 QUESTIONS USING E FORMAT<15><12>
(+.NNNNNNNE+MM)<15><12><12>
ANSWER THE LAST 3 WITH FIXED PT. (BASE 10)<15><12><12>
END ALL ANSWERS WITH A RETURN<15><12><12>
NOTE: USER HAS UNCONDITIONAL ACCESS<15><12>
     TO CONTROL QUESTIONS<15><12>
TO DO THIS ENTER CTRL A ON TTI<15><12>
<12>
FOLLOWING ARE THE CONTROL ACTIONS AVAILABLE
        <15><12> 0 - SYSTEM INITIALIZATION
        <15><12> 1 - ELECTRODE VERIFICATIONS
        <15><12> 2 - PROCEED WITH EXP., MOD.1,PART 1
        <15><12> 3 - CONTINUE WITH DATA PROCESSING
        <15><12> 4 - TURN OFF ELECTRODES
        <15><12> 5 - WAIT FOR CTRL A <15><12><12>
P.S USER CAN USE DEBUG DURING RUN TIME<15><12>
    WITHOUT LOSING CONTROL EXECUTIVE<15><12><12>
    VARIABLES OF INTEREST:
<15><12>    PULSE: METER TIME DELAY IN HZ
<15><12>    GENRT: CO3 GENERATION TIME IN HZ
<15><12>    SAMPL: SAMPLING FREQUENCY DURING DATA LOGGING
<15><12>    AMPS:  COULOMETER AMPS
<15><12>    CPH:   ADCV DATA LOC FOR PH READING<15><12><12>
    ENTER 177777 IN LOC 411 FOLLOWED BY CTRL A <15><12>
    TO RETURN TO THE CLI<15><12><12><12>@
BYE:    .*2
;+ + + + + + + + + + + + + STIME BEGINS BINARY STORAGE BUFFER
;                              FOR TIME AND P VALUES OF EACH
;                              MEASUREMENT DURING SAMPLING + + + + +
STIME:  000
MIN:    000
SEC:    000
        .BLK 17644
WRBLK:  .BLK 144
OUTBU:  .BLK 033        ;OUTPUT LOGGED DATA BUFFER (ASCII)
BUFER:  .BLK 120        ;INPUT BUFFER FOR USER RESPONSES
        .END START
```