RATE OF DISSOLUTION OF CARBONATE MINERALS AND AGRICULTURAL LIMESTONES

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ABSTRACT

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The rate of solution of carbonates in several acid systems was investigated using different techniques. The most satisfactory method was solution in 0.05 normal acetic acid and weighing the carbon dioxide evolved after absorption in Ascarite.

The influence of the type of mineral, particle size, surface area as determined by N_2 adsorption, and acid strength on the rate of solution of three calcites, aragonite, two dolomites and magnesite was studied. The chemical composition of the carbonate mineral was found to influence the reaction rate more than any other factor. The surface area became more important as the acid concentration was decreased which suggested that diffusion inside the mineral particles was becoming more important. The reaction appeared to follow a first order kinetic equation; however, with some samples there was a deviation from this equation. The deviation could not be explained satisfactorily with an equation that was developed from the data and theory.

A number of limestones were investigated. The chemical composition, surface area and rates of solution in acetic acid and H-resin were studied. The presence of calcite, dolomite or a mixture of both greatly influenced the rate of solution.

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by

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INTRODUCTION

Soils that have an acid reaction occur in the humid regions of the Earth. Acidity or its side effect is responsible for inhibiting growth of many agricultural crops; thus, it is important if these crops are to be grown that the acidity be neutralized. Several compounds have been used as neutralizing agents and it has been noted in field studies that various neutralizers may react with a given soil at varying rates.

There is an optimum soil pH at which best yields can be obtained and it is important that this optimum be maintained during the growth of the plant. Thus an attempt must be made to predict how acidity may be neutralized in a certain time period.

In the neutralizing reaction there are three basic components: the neutralizing agent, the soil and the soil moisture. Each of these must be fully studied if there is to be an understanding of the reaction so that an accurate prediction can be made of the quantity of neutralizer to be added to the soil to produce the required acidity in a stated time.

It has been shown in previous studies that various neutralizing agents have different rates of reaction, depending on chemical composition, the particle size distribution, the porosity and the hardness. The Federal cost sharing program for liming materials approves one ton of standard ground limestone containing at least 80 percent calcium carbonate equivalent, and ground sufficiently fine so that 85 percent, including all of the finer particles obtained in the grinding process, will pass through a U. S. Standard No. 8 sieve, and 25 percent through a U. S. Standard No. 100 sieve. But it is possible that a coarse, porous, soft calcitic limestone that barely meets these standards may react faster than a fine, crystalline, hard dolomitic limestone which easily meets the standards since porosity and chemical composition may be more important than particle size distribution.

It is the purpose of this study to review the knowledge gained thus far concerning the relevant properties of the reacting components and to study the effect of chemical composition, particle size, porosity and hardness on the rate of solution of pure carbonates and agricultural limestones in acid systems.

LITERATURE REVIEW

Liming Materials

Neutralizing agents that are most commonly used are calcite and dolomite. Also used are the hydroxides and oxides of calcium and magnesium, marble, coral, marl, chalk and blast furnace slag. These agents are usually ground to particles of specified size. It is possible that calcium orthosilicate, aragonite, magnesite and other rhombohedral divalent carbonates are used intentionally as liming agents or are present as impurities.

Crystal Structure

Bragg (4) in a classical study determined the crystal structure of pure calcite ($CaCO_3$) and showed that the unit cell was face-centered rhombohedral. It was similar to the cubic sodium chloride structure but distorted to accommodate the large, planar, carbonate (CO_3^{--}) group. This group consisted of a carbon ion at the center of an equilateral triangle formed by oxygen atoms. Alternate CO_3^{--} triangles, in fact, pointed in opposite directions. Consequently, the unit cell contained 32 $CaCO_3$. The primitive cell actually contained 2 $CaCO_3$. The C-O distance has been calculated to be 1.32 Å and 1.29 Å by two different authors. Wyckoff and

Merwin (55) showed that dolomite [$CaMg(CO_3)_2$] had a similar structure to calcite but the symmetry of the space group was lower, being $R\bar{3}$ instead of $R\bar{3}c$. Bradley, et al. (3), with powder diffraction methods, proposed a model combining one layer of $CaCO_3$ from calcite and one layer of $MgCO_3$ from magnesite. This also had a planar CO_3^{--} group. Steinfink and Sans (48) confirmed this structure and calculated the interatomic distances as: Ca-O = 2.390 Å, Mg-O = 2.095 Å and C-O = 1.283 Å. The structure of magnesite was assumed to be similar to that of calcite. The substitution of Mg by Ca caused an increase in cell size. The Mg-C distance for synthetic magnesite was 1.67 Å. Bragg (5) showed that aragonite had four molecules of $CaCO_3$ per unit cell and the space group was Pmcn. Deer, Howie and Zussman (12) have described the differences in structure between calcite and aragonite:

> Wyckoff determined the structure in more detail, the calcium atoms are approximately in the positions of a hexagonal close-packed structure which has been deformed by compression along the hexagonal axis. In calcite the CO_3 groups occur half-way between Ca layers, and each oxygen has two calciums as nearest neighbours, whereas in aragonite the CO_3 groups do not lie midway between Ca layers and are rotated 30° to right or left so that each oxygen atom has three neighbouring calcium atoms.

Occurrence

Pettijohn (36) has stated: "Calcite is a crystalline or microcrystalline aggregate of calcareous substances, shells or calcareous fossils formed by biochemical and chemical precipitation of calcium carbonate in the hydrosphere." Dolomite is not primary in formation but it is thought to be formed by the replacement of calcium ions in precipitated calcium carbonate, with magnesium ions from sea or ground water.

Many impurities may be present in calcite or dolomite; silica is commonly present and feldspar is a usual minor constituent. Ferrous iron is also common in dolomite (12).

Neutralizing Value

If pure $CaCO_3$ is given a neutralizing value of 100 then pure $MgCO_3$ has a value of 119, pure calcium hydrate 135, pure magnesium hydrate 172, pure calcite 100, and pure dolomites 108. This is important economically to the farmer who buys limestone by the ton, since he can obtain more neutralizing power per ton from a dolomite than a calcite if all the limestone reacts. But, dolomites are usually slower to react with the soil than calcites (13).

Solubility

Many authors have observed different rates of solution of the divalent carbonates in acids. Morgan and Slater (31) measured rate of solubility of several natural calcites and dolomites in 2N acetic acid. They also studied various physical properties but could show no apparent relationship between these properties and the rate of solubility. Ferrari and Sessa (15) observed the rate of solution of six carbonates in hydrochloric acid (HCl). Calcite was dissolved in eight percent acid and the rate of solution doubled with each 12°C rise in temperature. Magnesite and dolomite were less soluble, dissolving in concentrated acid at 70°C or in 50 percent acid at 90°C. The relative velocities of solution for samples of the same surface area were calcite 100,000, synthetic calcite 100,000, synthetic magnesite $\sim$ 670, dolomite 650, and magnesite 9. The velocity of solution was shown to diminish with decrease in cation radius. They suggested that the velocity was proportional to the ease of rupture of the metal-carbonate bond. This gives a sequence of reactions as follows:

$$MCO_3 \longrightarrow M^{++} + CO_3^{--}$$

$$2H^+ + CO_3^- \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

where M is a divalent cation.

They used the equation:

$$\frac{-dv}{dt} = kS$$

to describe the dissolution of carbonates when controlled by the surface area S, where v is the volume, t is time, and k is the rate constant. It can be shown that

$$Wf^{\frac{1}{3}} - (Wf-Wt)^{\frac{1}{3}} = Kt$$

where Wf, Wt are the final weight and weight after time t, and K is 1/3 $M^{\frac{1}{3}}$ kh. Some of their results are:

	K	Mol Vol	M^{++}
Calcite	1.0000	61.27 Å^3	1.06 Å
Dolomite	.0349		0.92 Å (Mean of Ca and Mg)
Magnesite	.0005	46.60 Å^3	0.78 Å

Teodorovich and Shvedova (49) investigated the solubility of some carbonate minerals in HCl. They found that in 10 percent HCl at 16-20°C, calcite and aragonite dissolved in 6 — 20 seconds, dolomite in 20-30 minutes and magnesite in 48 — 65 hours; at 100°C dolomite dissolved in 3-60 seconds and magnesite dissolved in 10-20 minutes. Calcite, dolomite and magnesite were dissolved in acids of different concentrations by Yurgranov and Zimov'ev (57), who were interested in determining calcite in sedimentary rocks. Magnesite and dolomite dissolved in 0.1 N acid in 40 minutes; whereas, calcite dissolved in 10 minutes. Skinner _et al_. (46) were interested in determining the amount of calcite and dolomite in soils and limestones and made use of the fact that calcite was rapidly dissolved in 4N hydrochloric acid whereas dolomite was slowly soluble. They manometrically measured the increase in pressure of the system as carbon dioxide was evolved. Their results obeyed a first order rate equation where $\log(h_\alpha - h_t)$ was a linear function of time (h_α and h_t were the final height of mercury and height after time t). When calcite and dolomite were present the curve consisted of two straight lines. Gortikov and Panteleeva (18) studied the rate of solvation of calcium carbonate (marble) in dilute aqueous solutions of acids and found that the reaction obeyed the following equation:

$$\frac{dx}{dt} = KS\ (c-x)$$

where c was the initial acid concentration, x the amount reacted, S the surface area and K a proportionality constant. They found the rate was proportional to the degree of ionization and to the concentration of the acid (c-x). In buffer solutions it was proportional to the degree of ionization and the ratio of acid to salt. In all cases the reaction rate was proportional to the rate of stirring; thus, they came to the conclusion that the reaction was a diffusion process.

Many authors have used different acid media for the purpose of evaluating activities of agricultural limestones. Thomas and Gross (50) hoped to simulate the reaction in the soil by using many acids and salts on different limestone sizes. They found no test equally suitable for two limestones. Shaw and Robinson (45) and others (43) have steam distilled limestone samples in ammonium chloride solution and found that there was some similarity between this reaction rate and the acid soil-limestone reaction rate with certain limestones. Gibaly and Axley (17) described a method using disodium ethylenediaminetetraacetate (EDTA) which formed a complex with calcium and magnesium from limestone. They felt that this method was better than using HCl because the CO_3^{--} combined with sodium, carbon dioxide was not released and there were no diffusion problems. They obtained highly significant correlation between the EDTA rating and the reaction of the same limestones with soil suspensions. However, diffusion of ions undoubtedly is still a large factor since many Na_2CO_3 molecules would be dissociated and this would affect the reaction. Hunter et al. (20) used this method to evaluate 39 different liming materials and results obtained in 12 laboratories showed the rating was positively correlated with percent $CaCO_3$ in the sample, percent passing 60-, 100-, and 200-mesh sieves and pH of suspensions when limestone, soil and water were shaken together for 100 minutes. The correlation between the ratings and percent $MgCO_3$ were significant and negative. However, in the incubation they did not use a constant $CaCO_3$ equivalent of limestone but a constant weight. Therefore some correlation with percent $CaCO_3$ and $MgCO_3$ present would be expected. Further, they did not use limestone particles of the same size.

In a second series of experiments they evaluated twelve limestones with the di- and tri-sodium salts of EDTA and incubated them with twelve soils in both water and calcium chloride suspensions. Changes in pH and residual carbonate were measured after one and six months. It should be noted that the soils were limed at constant $CaCO_3$ equivalent with a weight equivalent to 1.2 times the exchange acidity of the soil. It was found that pH and limestone decomposition were highly correlated with activity ratings of the limestones with both EDTA reagents and percent $CaCO_3$. However, they found variation in limestone reactivity that could not be accounted for by ratings or percent $CaCO_3$ (52).

Fineness and Surface Area

Bear and Allen (2) postulated that limestones reacting with soil dissolve such that the diameters of all particle sizes are reduced by the same amount. The diameter reduction was called the "a" value and was determined by measuring residual carbonate in an average soil-limestone mixture after a definite time. Thus the degree of decomposition of large sizes of limestone particles could be calculated.

$$R = \left(\frac{d-a}{d}\right)^3$$

where R is the proportion of the material in each sieve fraction remaining after the diameter d has been reduced by a. Using the above, a chart was constructed by Schollenberger and Slater for evaluating limestone efficiencies at various times after application (42). Assumptions were made as to size distribution but the method avoided the calculations of reaction rates. This method has been used extensively in Ohio with success, but its development requires initial incubations lasting up to 3 years.

Ferrari's concept that surface area was a controlling factor in the solution of carbonates was shared by Barnes (1) who developed a method for estimating surface area. In this method a coating of calcium oxalate was formed on the surface of calcium carbonate particles, dissolved in sulphuric acid and titrated with potassium permanganate.

Meyer and Volk (28) in incubation studies showed that finer particles reacted faster and calcite was initially more effective than dolomite, but after 9 months the reverse was true. Barnes' method was thought to be ineffective for dolomite since the magnesium oxalate coating was soluble. Thomas and Gross (50), however, found weaker oxalic acid was more satisfactory. They titrated the unreacted oxalic acid. They found fine particles were very reactive and in some cases dolomites were as reactive as calcites. But in other cases calcites were more reactive. A different incubation method using a five percent H-saturated clay was developed by Webster _et al_. (51), who followed the reaction with pH measurements. The surface area was also measured by Barnes' method and they again found chemical composition of the sample was influencing the measurement. Particles of calcite were found to react faster than those of dolomite.

The BET method (described under Methods of Area Determination) has been used to measure the surface area of limestones and their reactivity has been estimated with ammonium chloride by Love and Whittaker (26). The surface area was also calculated for each sieve fraction using the mean sieve size diameter and assuming the particles were spherical. The calculated area was smaller than the BET area in each case.

The variation in BET area for the same sieve fraction of different samples was thought to be due to the variation in average size and the degree of bonding of elementary particles in the aggregates. With the smaller fractions, where the BET area was closer to the geometric area, elementary particles were present and interstitial space disappeared. From their experiments they concluded that the rate of reaction was proportional to the reacting surface which was the BET surface area less the interior surface. Miner (30) measured the surface area of limestones using the BET continuous flow method and then evaluated the reactivity of the samples by incubating them with soil. He concluded that the rate of reaction was largely dependent on the external surface area which was calculated assuming the particles to be spherical. However, he found with dolomite that an equation similar to that of Ferrari and Sessa was probably obeyed.

Schollenberger and Whittaker compared methods for evaluating activities of limestones and concluded that computed reaction rate was preferable to chemical methods and that the calculation could be avoided by using the chart (44). Hunter _et al_. (20), and Whittaker _et al_. (52), in subsequent work, also measured surface area using a Blaine air permeability tester (47). The method depends on the fact that the time of diffusion of air through the sample is proportional to the square of the surface area--all things being equal. Brydon and Rice used their results and samples and estimated activity with the intercept method (9,46). Their values for $CaCO_3$ equivalent were low, probably due to the presence of CO_2 affecting the reaction equilibrium. They found that the change in pH of a soil-limestone suspension when plotted against surface area gave a linear relationship for calcites; whereas dolomites were slower to react and more grouped together. However, it appears there was variation in sample size as all sieve fractions were present. They also showed that percent calcite and dolomite affected the reaction. Samples with greater than 10 percent and less than 90 percent calcite had reaction rates intermediate between those of dolomites and calcites. They did not mention the soil and time of incubation.

Chemical Composition

Foote and Bradley (16) have shown that calcite and dolomite crystallize together. Since they react at different rates, the proportion of each in a limestone would influence its reaction. Whittaker et al. (52) measured the proportion of each by chemical analysis; Brydon and Rice (9) used the intercept method. Both showed that composition was important. Differential thermal analysis (DTA) has been used by Rowland and Beck (39) to estimate chemical composition.

Conclusion

The rate at which a pure limestone dissolves is a function of the particle size distribution, surface area, chemical composition, degree of ionization, crystallinity and hardness. However, surface area is a function of the last two.

Soil Acidity

Soil acidity, the hydrogen (H^+) ions in soil solution, is controlled by H^+ which are associated with the clay surface or carboxyl groups of organic matter. Aluminum (Al^{+++}) is present in the crystal lattice of clay minerals and can also be adsorbed onto the clay surface. Schofield (41), Chernov (10), and others (22) have described soil acidity as Al^{+++} adsorbed onto the clay surface yet being coordinated with a number of water molecules in an octahedral distribution. Some of the water molecules dissociate into H^+ and hydroxyl (OH^-) ions, the latter remain coordinated with aluminum. Acidity from the dissociation of H^+ from carboxyl groups is similar to the acidity of a weak organic acid. The pH-neutralization characteristics can be described by the equation

$$pH = pK + n \log \left(\frac{s}{1-s}\right)$$

where K is the intrinsic ionization constant, n is an integer, usually about 2, and s is the degree of neutralization (11).

Considerable quantities of CO_2 are released in the soil by respiration of plant roots and decay of organic matter. Carbon dioxide combines with water to form H^+ and bicarbonate (HCO_3^-) ions. Hydrogen ions effectively replace other cations from the clay exchange surface, which are then taken up by plants or leached from the soil. These forces cause a soil to become acid. They are often accelerated by removing vegetation, which provides cover, and by adding certain fertilizers. Ammonium sulfate ($(NH_4)_2SO_4$) particularly, and also ammonium nitrate (NH_4NO_3), anhydrous ammonia and urea, tend to increase soil acidity through the development of mineral acids (14,29).

From tests using acid nutrient solutions it has been shown that H^+ concentration alone is not harmful to many plants, but rather it is the accompanying conditions that exist in an acid soil. Several workers (25,27,28,32,34) have attributed the detrimental effect of acid soils to Al and manganese (Mn) toxicity, and deficiency of phosphorus (P), Ca and Mg. These effects can be removed by the addition of a suitable quantity of limestone. Potassium (K) may also be involved (32,34). McVickar (27) has stated that the availability of Ca and K to the plant depends on the Ca/K ratio. Calcium cannot be assimilated rapidly enough in the presence of high K concentrations and thus deficiency may result. In the case of Mg deficiency some dolomite or Mg containing limestone should be added. Limestone also promotes microbial activity which is sensitive to changes in acidity. As acidity is decreased, release of organic nitrogen (N) is increased (13,29).

Soil acidity can be effectively neutralized with limestone; however, it is difficult to determine how much limestone to add to the soil to give a desired soil pH. Woodruff developed a buffered solution which he used in conjunction with a glass electrode to determine the exchangeable H^+ in a soil (54). However, it has been shown that this was not accurate for all soils, particularly those containing extractable Al. Schoemaker et al. (40) developed the SMP buffer which indicated a liming rate that correlated very well with values obtained by incubation with pure $CaCO_3$. Keeney and Corey (23) also found good agreement when using Wisconsin soils. However, this method in no way indicates how quickly the soil will react with the lime. Ross et al. (38) in a study using nine Michigan soils evaluated the lime requirement of the soils by incubation with a limestone. They determined cation exchange capacity, organic matter content, exchangeable H^+ and lime requirement (using the SMP buffer) and found that factors other than pH affecting lime requirement were: cation exchange capacity, organic matter, exchangeable H^+ and clay content, in order of increasing importance.

As has already been indicated the soil moisture contains H^+ in an acid soil. There are also many other ions in solution and particles in suspension. When lime is added to a soil some of the ions on the surface will probably dissociate and the CO_3^{--} will react with the H^+ to form water and CO_2. Some of the H^+ will reach the lime surface and react there. Subsequently there must be a diffusion of products--Ca^{++}, Mg^{++}, CO_2--away from the particle to allow more to react. Longnecker and Merkle (25) showed there was little movement of Ca and concluded that the soil and lime should be well mixed to ensure efficient reaction. But Ririe et al. (37) found that leaching with distilled water caused a downward movement of lime and the cations Ca^{++}, Mg^{++} and K^{+}. In work mentioned above (2,17,18) it was stated that diffusion was an important or controlling factor. This in turn is controlled by amount and movement of water, temperature and placement of limestone.

Methods of Area Determination

Area by Calculation

The surface area of limestone particles can be calculated if the shape and density of the particles are known. In this case, the particles are assumed to approximate spheres, the diameter of which is taken to be the arithmetic average of the larger and smaller sieve opening. This gives the lowest possible area since area due to pore space is neglected (30). However, at the submicroscopic level many "crevasses" and "minature ziggurats" appear due to imperfections, growth and fracture.

Area by Nitrogen Adsorption

When a gas becomes concentrated at an interface in a gas-solid system, the process is called adsorption. The gas is referred to as the adsorbate and the solid as the adsorbent. There are two principal types of adsorption: physical adsorption and chemical adsorption. Physical adsorption is due to the operation of forces between the adsorbate and adsorbent surface that are similar to the van der Waals forces between molecules--forces which are undirected and non-specific. Chemical adsorption is the result of much stronger binding forces, comparable with those leading to the formation of chemical compounds.

An atom in the plane of the surface of a solid is subjected to unbalanced forces, the inward pull being greater than the outward forces. This results in a tendency to decrease the surface, and the solid may be thought of as having a surface tension. Any process that tends to decrease the free surface energy occurs spontaneously. A gas molecule adsorbed by the solid saturates some of the unbalanced forces of the surface and decreases surface tension. Thus, all adsorption phenomena are spontaneous and result in a decrease of the free energy of the system.

The adsorbed particles are either held rigidly, or are free to move over the surface in two dimensions. Before adsorption the gas molecules move in three dimensions; adsorption therefore, must be accompanied by a decrease in entropy (ΔS). The change in heat content of the system is $\Delta H = \Delta F + T\Delta S$, where ΔF is the change in free energy and T is the absolute temperature. Since ΔF and ΔS are negative, ΔH must also be negative. Thus the adsorption process is exothermic and the decrease in heat content is called the heat of adsorption. In physical adsorption it is of the same order of magnitude as heats of condensation of gases and in chemical adsorption, the same magnitude as heats of chemical reactions. In the case of the adsorption of nitrogen (N_2) on an iron catalyst, it is probably adsorbed in the molecular form by physical adsorption, but with chemical adsorption it dissociates into atoms. In the latter case N_2 and iron atoms saturate each other's valency but in the former case N_2 molecules on the iron surface are still able to adsorb a second layer of N_2 molecules, these in turn a third layer, and so on. When the surface can only take up one layer of gas, or a monolayer, it is called unimolecular adsorption, with more than one layer it is multimolecular adsorption.

For a given gas and unit weight of a given adsorbent, the amount of gas adsorbed at equilibrium is a function of the final pressure and temperature only. When the pressure is varied and the temperature kept constant, the plot of the amount adsorbed against pressure is called the adsorption isotherm (8).

The first fundamental theory of adsorption of gases on solids was proposed by Langmuir in 1916. He assumed that the adsorbed molecules could form a monolayer after which there was no further adsorption. The isotherm that he derived fits most cases of chemical adsorption. With physical adsorption there were many physical isotherms which could not be fitted to a Langmuir-type expression. There are in fact four other isotherms for physical adsorption. In 1938 and 1940 Brunauer et al. (6,7) propounded the multimolecular adsorption theory which gave a general equation that included all five isotherm types, through the entire range of adsorption from zero pressure to saturation pressure. The theory was based on the assumption that the same forces that produced condensation were also chiefly responsible for the binding energy of multimolecular adsorption. The isotherm equation obtained was:

$$V = \frac{V_m c p}{(p_o - p)\ [1 + (c-1)\frac{p}{p_o}]}$$

The equation could be tested by using the following form known as the Brunauer, Emmet and Teller (BET) equation:

$$\frac{p}{V(p_o - p)} = -\frac{1}{V_m c} + \frac{c-1}{V_m c} \cdot \frac{p}{p_o}$$

where
p is the pressure of adsorbate
p_o is the saturation pressure of adsorbate
V is the volume of adsorbate
V_m is the volume occupied by a monolayer of adsorbate
c is a constant expressing net absorption energy.

This was a linear equation and a plot of $\frac{p}{V(p_o-p)}$ against $\frac{p}{p_o}$ gives a straight line. The intercept of the straight line is $\frac{1}{V_m c}$, the slope was $\frac{c-1}{V_m c}$; thus one could obtain V_m and c from experimental data. The number of adsorbate molecules in one milliliter could be found using Avogadro's number. The cross sectional area of a nitrogen molecule was determined by assuming the packing of adsorbed molecules was the same as that in liquid nitrogen. Thus, one could determine the specific surface area of a solid.

The method had an advantage in that it was accurate and the sample was not destroyed. However, Brunauer said the method was limited to finely divided particles because large dead space corrections must be applied to small adsorption values. He stated the method was inaccurate for particles larger than 20 μ yet he found that an area of 0.16 m^2g^{-1} for -40+100 mesh $CuSO_4 \cdot 5H_2O$ was acceptable (8).

In the above method the amount of adsorbed gas was usually determined by measuring pressure differences in a calibrated high-vacuum apparatus, which was fragile and complex. A new method was developed by Nelsen and Eggertsen (33) which was based on gas adsorption and used the BET equation, but which involved a continuous flow system. As in the previous method N_2 was used as the adsorbate at a temperature close to the boiling point of the gas. However, here helium (He) was used as an inert carrier gas which passed with the N_2 in known quantities over the sample. When the sample was cooled in liquid nitrogen, nitrogen was adsorbed by the sample. This caused a change in thermal conductivity of the effluent gas stream which was monitored by thermal conductivity cells and a recording potentiometer. After adsorption, equilibrium was obtained and the recorder pen returned to the base line. On warming the sample the N_2 was desorbed and produced a peak in the opposite direction. The peak areas were a measure of the volume of N_2 adsorbed and could be calibrated by introducing a known volume of N_2 into the gas stream. Normally the desorption peak was used as this reduces tailing effects (35).

It was necessary to remove adsorbed air and other impurities from the sample before the determination was made. Wise and Lee (53) outgassed the sample for one hour at 300°C using a He stream; Nelsen and Eggertsen (33) used He at a flow rate of 20 milliliters a minute at 500°C for an hour. The temperature of the liquid N_2 must be measured in order to determine the saturation vapour pressure of N_2 and the area covered by one milliliter of N_2. The liquid oxygen (O_2) thermometer described by Laing (24) was used.

A relative pressure ($\frac{p}{p_o}$) for N_2 in the range 0.05 to 0.3 should be used since at higher pressures (0.4 to 0.95), nitrogen may be adsorbed by pores.

EXPERIMENTAL PROCEDURES

Samples

Samples of thirteen agricultural limestones (see Table 1) were dry sieved and five sieve fractions were collected. These were -20+40, -40+60, -60+80, -80+100, and finer than 100 mesh. They were washed with distilled water in Erlenmeyer flasks to remove any fine particles that adhered to the limestone surface. The supernatant liquid was decanted and the procedure repeated until the supernatant liquid was clear. The samples were then dried in an oven at 105°C. The -60+80 mesh fraction was chosen for a comparison of the properties and reactions of the limestones. A number of pure minerals were obtained for the purpose of dealing with a system relatively free of impurities. Specimens of calcite, dolomite, magnesite, aragonite, and chalk were crushed with a pestle and mortar and dry sieved; -18+35, -35+60, -60+140, and -140+200 sieve fractions were collected and then treated as above. In addition, two relatively pure agricultural limestones were sieved with both the above sets of sieves and similarly purified. They were limestone 5 (Afton, Michigan) and limestone 6 (Waukesha, Wisconsin). The calcium carbonate equivalent of the samples was determined by dissolving one gram of the limestone in excess standardized hydrochloric acid (HCl) and back titrating the excess with standardized sodium

Table 1. Source of the limestones used in the study.

Limestone Number	Source
1	Woodville, Ohio (1963)
1a	Woodville, Ohio (1961)
2	McCook, Illinois
3	Parma, Michigan
4	Bellevue, Michigan (1963)
4a	Bellevue, Michigan (1961)
5	Afton, Michigan
6	Waukesha, Wisconsin (Waukesha Lime and Stone Company)
7	Drummond, Michigan
8	Waukesha, Wisconsin (Rockwell Lime Company)
9	Cedarville, Michigan
10	Bay Port, Michigan
11	Maple City, Michigan

hydroxide (NaOH) (21). Magnesium and Ca were determined by dissolving one gram of the limestone in excess HCl, diluting to a suitable concentration and measuring the Mg or Ca with a model 303 Atomic Absorption Spectrophotometer against a series of standard solutions.

Surface Area Determination

The surface area was determined by two methods.

1. Calculation. Particles were assumed to be spherical. The particles were placed in a mixture of n-decanol and 1,1,2,2-tetrabromoethane such that they were suspended. The density was then determined by weighing two milliliters of the liquid mixture.

2. Continuous flow method described by Nelson and Eggertsen. The samples were outgassed in a stream of He for four hours at 150°C in tubes of known weight. The tubes were sealed with rubber policemen and reweighed when cool. They were then fitted to a Perkin-Elmer-Shell model 212B Sorptometer which was being flushed with He at a known flow rate. Nitrogen was then introduced, as the adsorbate, and the rate of flow determined. The tube was immersed in liquid N_2 , the boiling point being measured with an O_2 thermometer. Nitrogen in the gas stream was adsorbed onto the sample, resulting in a change of thermal conductivity of the gas which was recorded as a curve by a potentiometric recorder. The sample was then warmed to 60°C by surrounding the tube with a water bath, which caused the N_2 to be desorbed into the gas stream and a curve was recorded. This curve was more reproducible than the adsorption curve. The area under the desorption peak was then compared with the curve produced from introducing a known volume of N_2 into the system. The procedure was repeated at three other N_2 pressures. The volume of gas adsorbed, the pressure of the adsorbate and the saturation pressure of the adsorbate at the temperature of liquid N_2 were determined. From these data a plot of the BET equation was made. The reciprocal

of the sum of the slope of the line and intercept on the ordinate gave the volume occupied by a monolayer of N_2. This was converted to the specific surface by multiplying by the area covered per unit volume and dividing by the sample weight.

Differential Thermal Analysis

Differential thermal analyses were made on all samples of the -60+80 sieve fraction. The samples were not treated further, prior to DTA. In addition, a five milliequivalent sample of each of the dolomites was analyzed under one atmosphere of carbon dioxide (CO_2). The CO_2 was introduced at a pressure of one pound per square inch for three minutes, part of the CO_2 passing through the sample, and then the chamber was evacuated for one minute. This was repeated, and then CO_2 was introduced again for 45 minutes, before the temperature reached 500°C. Samples of 250 milligrams of calcite and dolomite and known mixtures of these minerals were also analyzed to standardize the procedure.

X-ray Analysis

Samples 2, 3 and 9 were finely ground and X-rayed on a sample holder. The deflections of copper radiation were recorded with a scanning goniometer, utilizing a Geiger-Muller counter tube in conjunction with a scaler-ratio meter with an automatic recorder. The calcite, dolomite, chalk, aragonite and magnesite were also crushed and X-rayed.

Rate of Reaction with H-bentonite

The incubation method of Webster *et al*. (51) was criticized by Schollenberger and Whittaker (43) on the ground that a large excess of limestone was used and thus the attack on the particles was shallow. In this incubation 80 milliliters of 0.5 percent H-bentonite was mixed with sufficient of limestones, 1a, 2, 4a, and 10, to just neutralize the acidity; thus, from 10 to 20 milligrams of limestone were used. The solution was shaken in a Burrell wrist action shaker in preference to using a magnetic stirrer which appeared to crush the particles. The reaction was followed by measuring the pH of the suspension.

In an adaptation of this method, the carbon dioxide evolved in the reaction was measured with a water manometer.

Rate of Reaction with Hydrochloric Acid

Fifty milliliters of 0.1 N HCl were added to a 500 milliliter Erlenmeyer flask. Samples of limestone, with neutralizing value equivalent to 0.2 grams $CaCO_3$, were placed in a plastic cup and floated on the acid. The flasks were stoppered and connected to mercury manometers. The reaction was begun by emptying the cup and then the change in mercury level with time was noted. A final pressure of approximately seven centimeters of mercury was obtained.

A second method with HCl was used which involved weighing the CO_2 produced by absorbing it in "Ascarite." A stream of N_2 was used to remove the products. The N_2 was purified by passing it through potassium hydroxide (KOH) pellets, concentrated sulfuric acid (H_2SO_4), anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) and Ascarite. After passing through the reaction vessel, a 500 milliliter Erlenmeyer flask in a water bath (at 25^oC), the gasses were dried with concentrated H_2SO_4 and $Mg(ClO_4)_2$. A three-way tap then directed the gases to one of two Ascarite columns while the other could be easily removed and weighed. The flow rate of N_2 used was 28 to 35 milliliters per minute as determined with a soap bubble flow meter. Two-hundred milliliters of 0.1 N HCl was slowly added from a graduated funnel to limestone in the reaction flask; this was sufficient to just neutralize the limestone (i.e., the equivalent of one gram $CaCO_3$). The experiment was repeated with different volumes of differing acid strengths and using a Burrell wrist action shaker. In the latter case the limestone was again placed in a plastic cup and floated on the acid.

Rate of Reaction with Acetic Acid

The above experiment was repeated using 400 milliliters of 0.05 N acetic acid. The shaker was set at shaking speed one on the Burrell shaker scale (250 cycles per minute) so that the reactants were constantly swirled. In this thesis, these results are presented as a graph of $\log[W_\infty - Wt]$ against time which was a plot of a first order rate of reaction. Also, the results could be shown as $(W_\infty - Wt)^{\frac{1}{3}}$ against time which, according to Ferrari and Sessa (15), assumes that the particles are spherical and the surface area is controlling the rate of reaction. W_{∞} is the final weight of CO_2 evolved (theoretically 0.4400 g). Wt is the weight of CO_2 evolved at time t. Thus, W_{∞}-Wt is proportional to the amount of unreacted limestone or unreacted acid.

Rate of Reaction with H-resin

One-hundred cubic centimeters of acid washed sand, 13 cubic centimeters of H-resin (Amberlite I R 120) and limestone equal to one gram $CaCO_3$ were mixed well in a 250 milliliter flask which was then fitted into the system described above. Readings were taken every 12 hours. The results were plotted using the above method.

RESULTS AND DISCUSSION

Analysis of Minerals

Differential thermal analysis showed that all samples except aragonite were pure. The aragonite showed three peaks, the two exotherms at 480°C and 950°C were expected but the shoulder at 1,010°C may have been due to calcite impurity. The -60+140 mesh aragonite was crushed and analyzed by X-ray which showed both calcite and aragonite were present. Chalk powdered very easily so the crystallinity was checked by X-ray. It showed that the chalk was crystalline and in fact had the calcite crystal structure. The chemical analysis of the minerals is given in Table 2. The purity of the samples was found to be the following:

Sample	Percent
Calcite	98.0
Limestone 5	94.7
Chalk	96.0
Dolomite	98.3
Limestone 6	91.8
Magnesite	96.3
Aragonite($CaCO_3$ content)	98.5

These results were calculated from percent CO_3 content and $CaCO_3$ equivalent which agreed to ± 0.5 percent.

Determination of Surface Area

Table 3 gives the surface areas of all samples as determined by N_2 adsorption. The samples calcite, dolomite

Table 2. Chemical analysis of minerals.

Mineral	Mg Content[1] (Percent)	Ca Content[1] (Percent)	CO_3 Content[2] (Percent)	$CaCO_3$ Equivalent (Percent)
Calcite	0.3	40.3	58.7	98.0
Limestone No. 5	0.4	34.3	57.3[3]	95.5
Chalk	0.1	34.7	57.6	96.0
Dolomite	12.1	21.6	63.5	105.5
Limestone No. 6	10.7	17.5	59.7[3]	98.5
Magnesite	26.0	1.8	68.6[3]	114.2
Aragonite	0.1	38.6	59.4	98.5

[1] Accurate to ± 5% of result.

[2] Determined from CO_2 evolved.

[3] Calculated from $CaCO_3$ equivalent.

Table 3. Surface area of minerals as measured by nitrogen adsorption.

Mineral	Sieve Size			
	-18+35	-35+60	=60+140	=140+200
	m^2g^{-1}			
Calcite	0.17	0.15	0.15	0.18
Limestone 5	0.62	0.59	0.68	----
Chalk	1.52	1.68	1.66	----
Dolomite	0.12	0.12	0.08	0.09
Limestone 6	1.03	1.05	1.08	----
Magnesite	2.56	2.83	2.92	2.97
Aragonite	0.11	0.12	0.14	0.25

and aragonite were hard and crystalline. The surface areas were all small, of the order of 0.1 m^2g^{-1}. The main source of error was in determining the area of the desorption peak. The peak had the following shape:

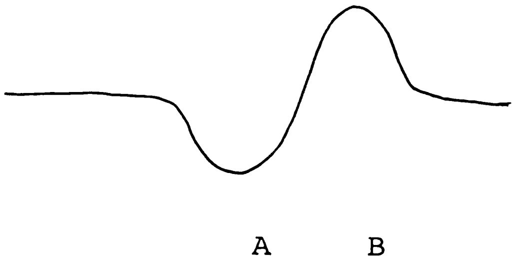


Figure 1. Desorption curve of calcite (-18+35).

The first deflection (A) was observed to occur when adsorption and desorption of the carrier gas (He) alone was attempted. This means that an impurity, such as hydrogen (H_2) as suggested by Wise and Lee (53), may be present in the He. The second deflection (B) is due to the adsorption of N_2 and the uncertainty of its measurement is estimated to be ±20 percent. Thus, the areas of these three samples can vary by ±0.02 m^2g^{-1}. But, the areas of the other samples are known with greater certainty. The uncertainty in determining the area of limestone 5 is estimated to be ±0.02 m^2g^{-1}, of chalk ±0.1 m^2g^{-1}, limestone 6 ±0.1 m^2g^{-1} and magnesite ±0.05 m^2g^{-1}. This is because the H_2 deflection is increasingly dominated by that due to N_2.

On comparing the calculated areas (Table 4) with the N_2 adsorption areas, it can be seen that the former are

Table 4. Surface area of minerals.[1]

Mineral	Sieve Size -18+35	 -35+60	 -60+140	 -140+200
	$m^2g^{-1}x10^3$			
Calcite	2.88	5.77	12.20	24.20
Chalk	3.00	6.00	12.70	---
Dolomite	2.79	5.56	10.80	23.40

[1] Determined by calculation assuming diameter is mean of sieve size.

several times smaller and increase with decrease in particle size. However, the latter increases little, if at all, with decrease in particle size. This agrees with the work of Miner (30) and Love and Whittaker (26) who suggest the calculated area is a measure of the external or reacting surface, and the measured area consists largely of internal area.

Examination of Methods

Reaction with H-bentonite

In the review of literature several papers were mentioned where the authors hoped to develop a quick test for evaluating limestone. Schollengerger and Whittaker (44) reviewed these attempts and concluded that results based on field incubation were preferable. However, this procedure requires months and even years. It was thought that a reaction involving acid clay should be much quicker, yet many of the properties of the soil-limestone mixture would be retained. Limestones 1a and 4a were used to investigate this reaction since they had been well characterized by Miner (30). The results showed that this reaction was faster than a soil-limestone reaction, in fact it was completed in one to five days. When pH was plotted against time, definite sigmoid shaped curves were obtained for the rate of reaction of limestones 1a and 4a (Figure 2a). It was noted that the calcite reacted faster than the dolomite and reached equilibrium earlier, as would be expected. The experiment was repeated several times but the results were not reproducible. This was probably due to the fact that the magnetic stirrer was crushing the limestone particles. Therefore, the experiments were performed using a Burrell shaker (Figure 2b). This gave poor results since the mixture was not agitated sufficiently and clay tended to settle out around the limestone particles. It was probably for the same reasons that the experiments with water manometers failed.

Reaction with Hydrochloric Acid

The rate of reaction with HCl was followed in order to study more closely the mechanism of the reaction. Samples 1a and 4a were again used. The Canadian workers used mercury manometers to follow the reaction and obtained good results (46); however, when this procedure was attempted the results were not reproducible, probably because the small amounts of

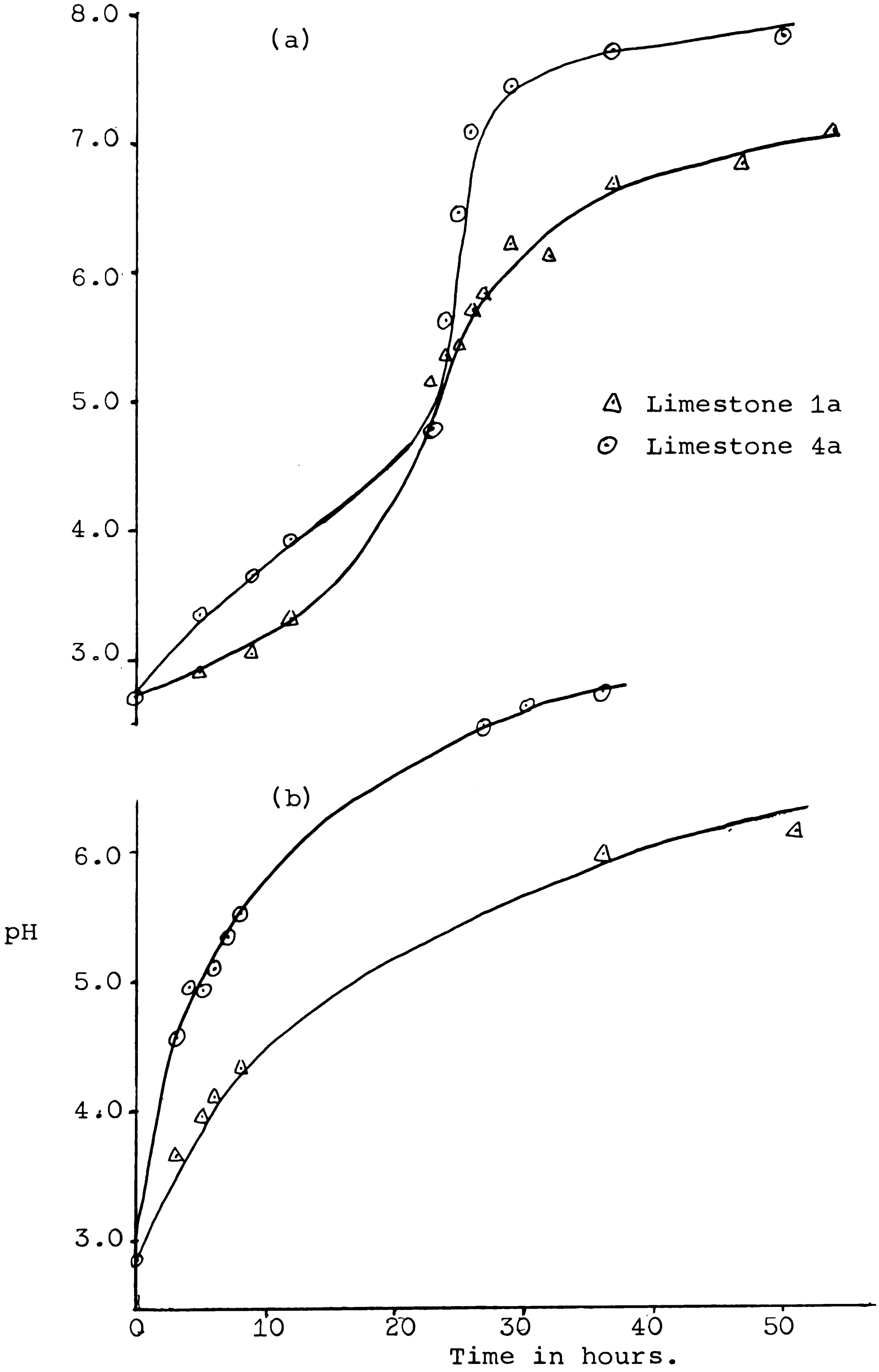


Figure 2. Incubation of limestones 1a and 4a with H-bentonite.
a. Using magnetic stirrer. b. Using Burrell shaker.

limestone did not produce enough CO_2. It was noted that after the reaction slowed down some $CaCO_3$ remained, yet it quickly dissolved when the manometer was disconnected, suggesting that the pressure of CO_2 was acting as a constraint on the reaction.

A more quantitative method was then developed where the reaction was followed by weighing the CO_2 evolved, after it had been adsorbed by Ascarite. As with all the above reactions enough acid was used to just dissolve the limestone. Although this may remove the possibility of ignoring the H^+ activity when considering the kinetics of the reaction, the reaction is more like the neutralization of the soil.

The reactions gave straight lines when the results were plotted according to a first order kinetic equation, and the method appeared more satisfactory than using a second order equation, or Ferrari and Sessa's equation. Therefore, the experiment was repeated with -18+35 mesh samples of calcite and chalk. Since the calcite was hard and crystalline and the chalk was soft and porous, the chalk dissolved slightly faster (Figure 3a). But when -60+140 mesh samples were used, no difference in reaction rate was noted. It was observed that CO_2 bubbles adhered to the particles' surface and even lifted them to the surface of the solution. This meant that some of the surface was being blocked by CO_2 and could not react; thus, diffusion of CO_2 from the surface and diffusion of H^+ to the surface were important controlling factors.

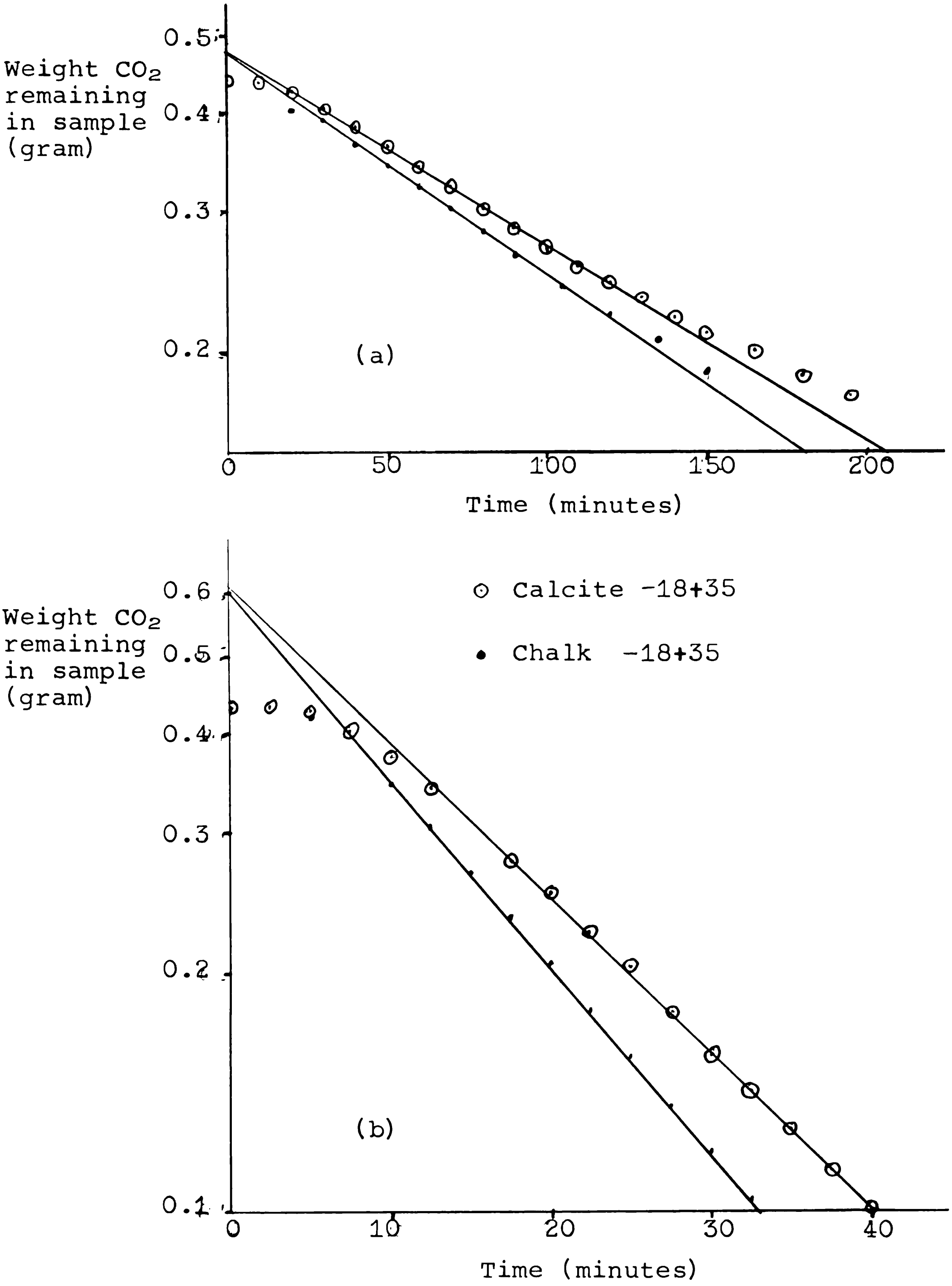


Figure 3. Rate of solution of calcite and chalk (-18+35) in 200 milliliters 0.1 N HCl.
a. Unshaken. b. Shaken.

To test this, the solution was shaken and different strengths of HCl were used (Figure 3b). When the shaker was used at setting one (250 cycles per minute) the reaction with chalk (-18+35) was half completed in 18 minutes, instead of 120 minutes. There was a definite difference between the rates of reaction of the calcite (-18+35) and chalk, the chalk being faster. With more concentrated HCl (40 ml 0.5 N) this was less pronounced than with dilute HCl (400 ml 0.05 N). With excess HCl (400 ml 0.1 N) again there was little difference in rates of reaction. This was also true with 400 milliliters of 0.05 N HCl and the -60+140 fraction. It was observed from these results that as the reaction rate was increased (either with more concentrated acid, excess acid or smaller sieve size) the difference between chalk and calcite decreased. Yet with less concentrated acid and larger sieve size the difference was more pronounced.

Reaction with Acetic Acid

Therefore, reactions with a weaker acid--acetic acid--were followed. Four-hundred milliliters of 0.05 N acetic acid were used with the same shaker speed as above. The results showed chalk reacted faster than calcite for all sieve sizes. Thus, this volume and normality of acetic acid was suitable for estimating differences in reaction rate between calcite and chalk.

Evaluation of Minerals

The rate of solution was determined for all minerals listed in Table 2. The first order kinetic plot used by

Skinner et al. (46) was preferable to the plot of Ferrari and Sessa (15). The two plots are compared in Figure 4.

In Figure 5 the rate of solution of the different sieve sizes of calcite are compared. The calculated surface areas of the different particle sizes are given in Table 4. As can be seen in Figure 5 the smaller particles reacted faster than the larger particles. Therefore, it is shown that the calculated or "external" surface area is influencing the reaction rate. This also is true for all the minerals examined. It may be noted that there are smaller differences in reaction rate for the three sizes of chalk (Figure 7) than with the calcite or limestone 5 (Figure 6). It is probable that at this fast rate of reaction some other factor is becoming rate controlling. In Figure 7 the reaction rates for the four sizes of aragonite are plotted. Although aragonite has the same formula as calcite, its crystal structure differs--as previously described on page 4. In aragonite it is more difficult for a H^+ to come close to a CO_3^{--} group than in calcite because of the different position of CO_3^{--} groups with respect to Ca^{++} ions. Thus, aragonite is slower to react than calcite.

In Figure 10 the rates of reaction of the -60+140 fraction of all the minerals are plotted. Thus, the external surface area of the samples should be approximately the same. It can be seen that the chalk reacts faster than limestone 5 and this is faster than the calcite. The surface area of each

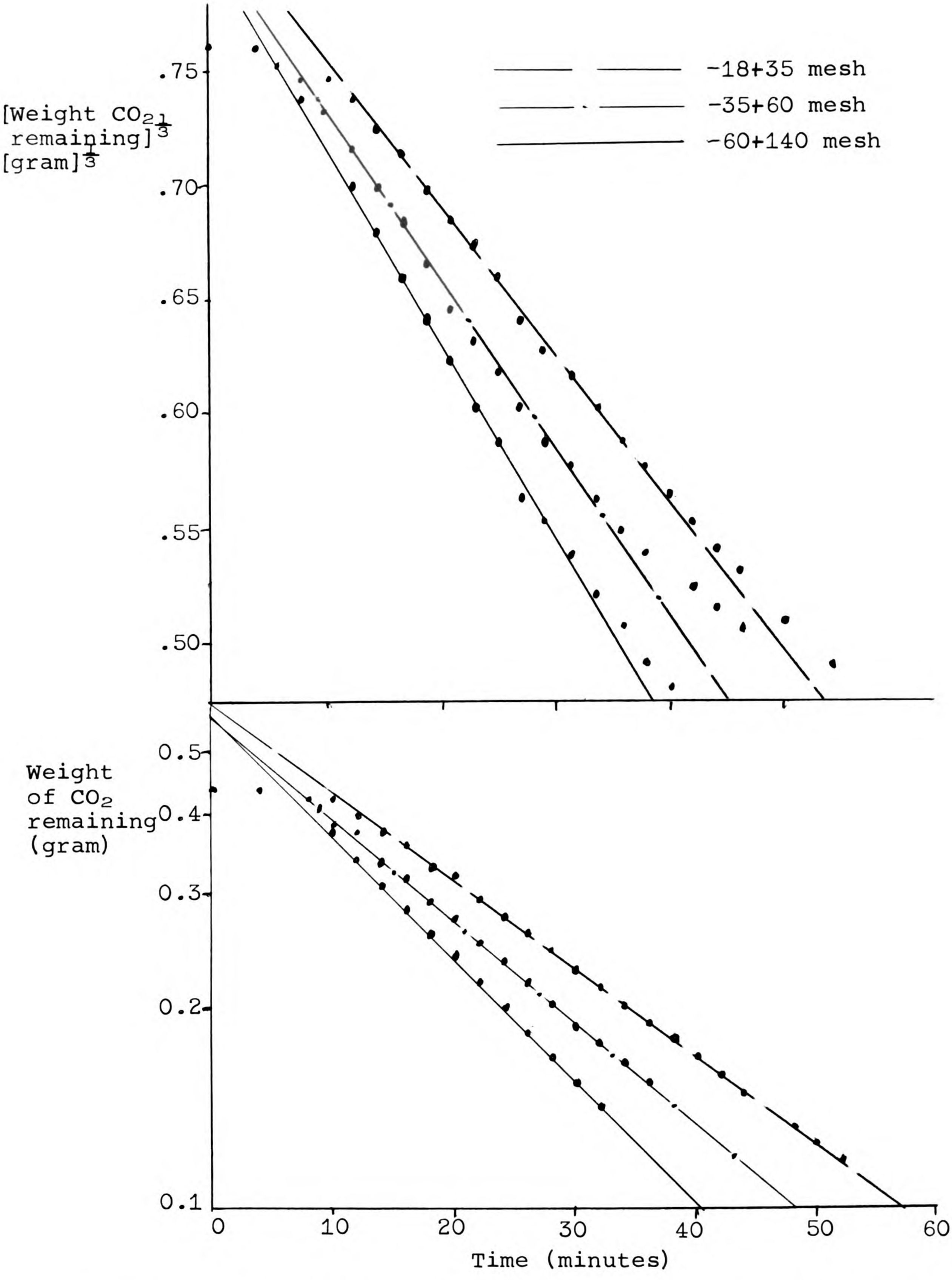


Figure 4. Rate of solution of chalk in acetic acid plotted:
a. According to Ferrari and Sessa. b. First order.

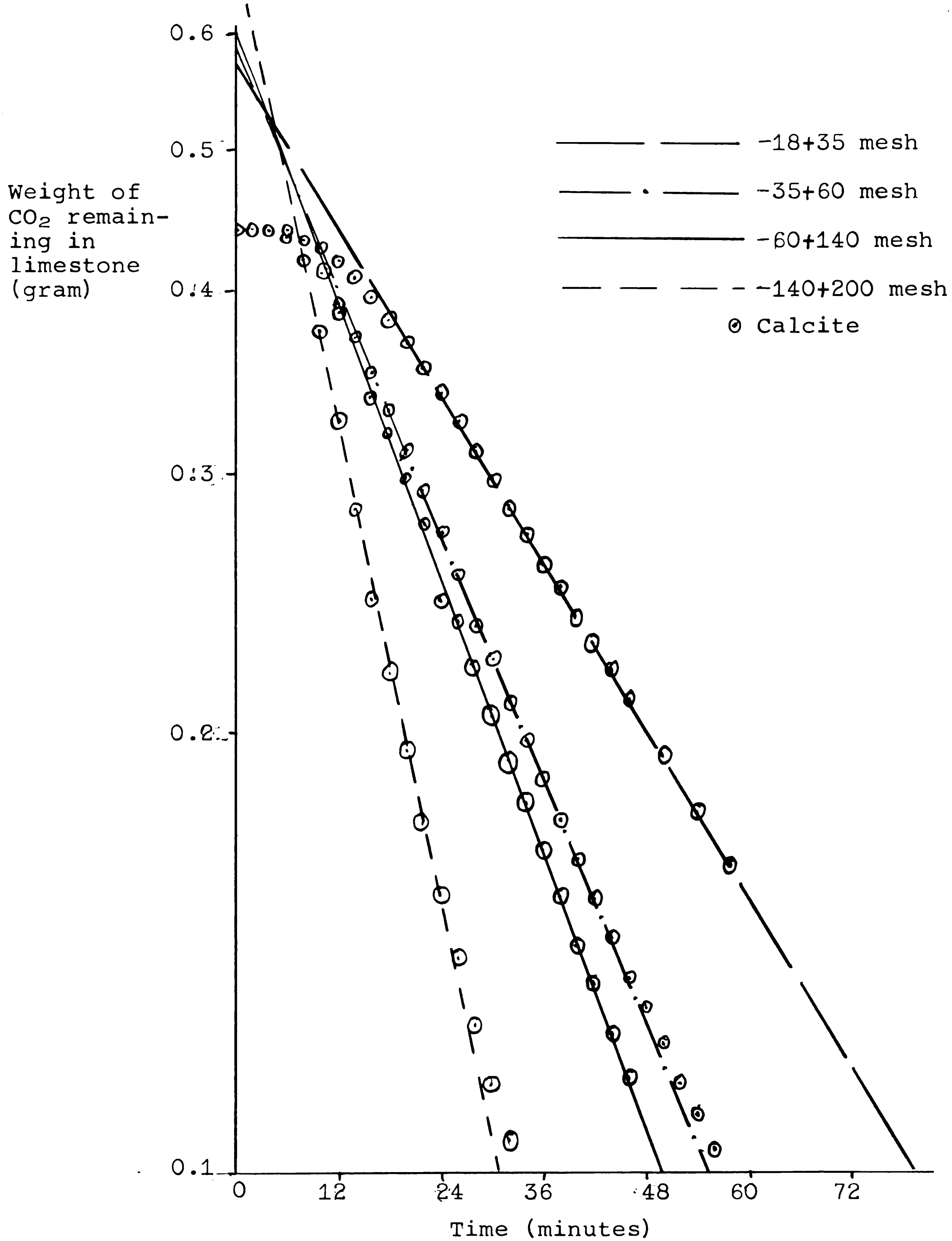


Figure 5. Rate of solution of different size fractions of calcite in acetic acid.

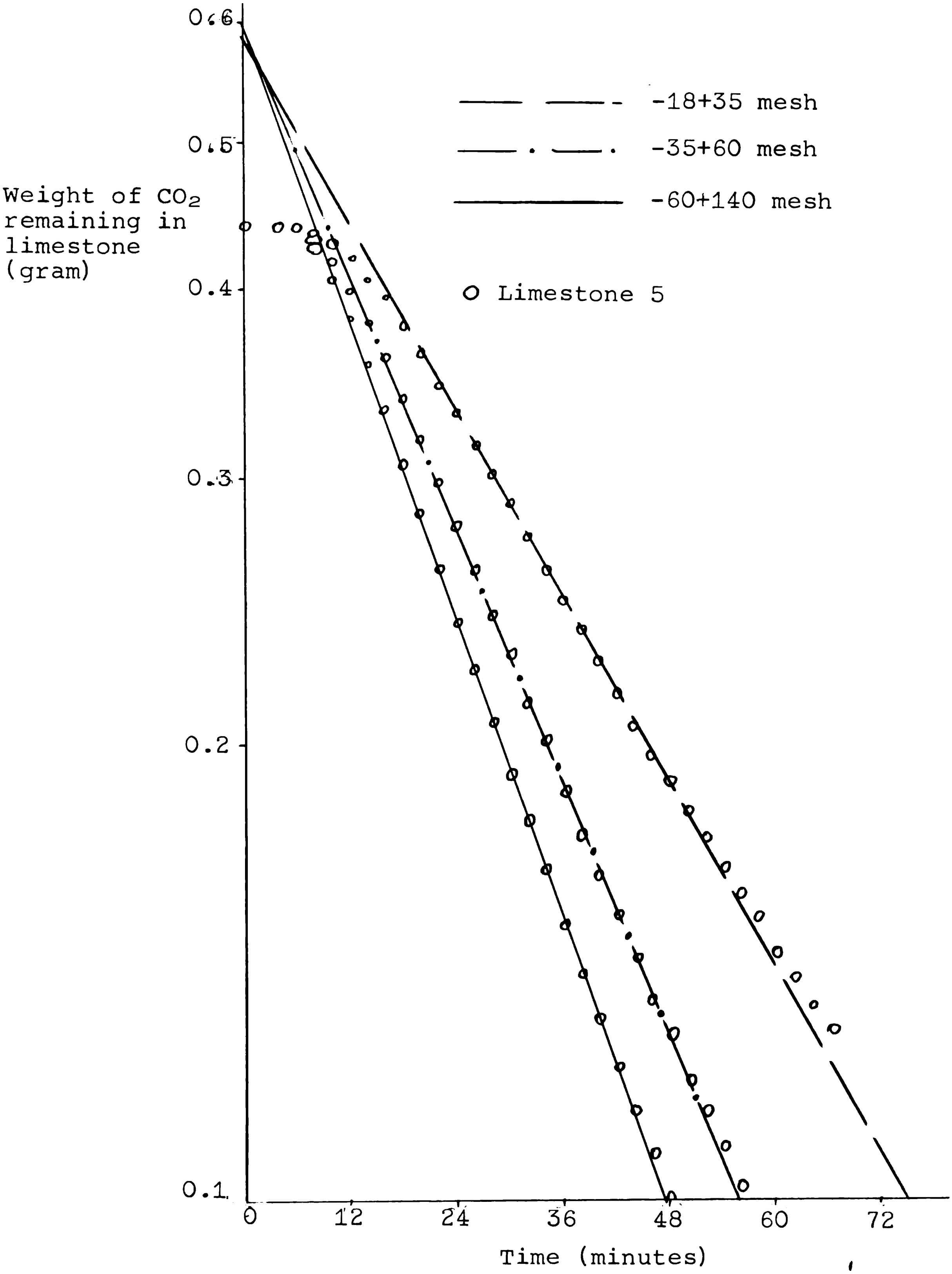


Figure 6. Rate of solution of different size fractions of limestone 5 in acetic acid.

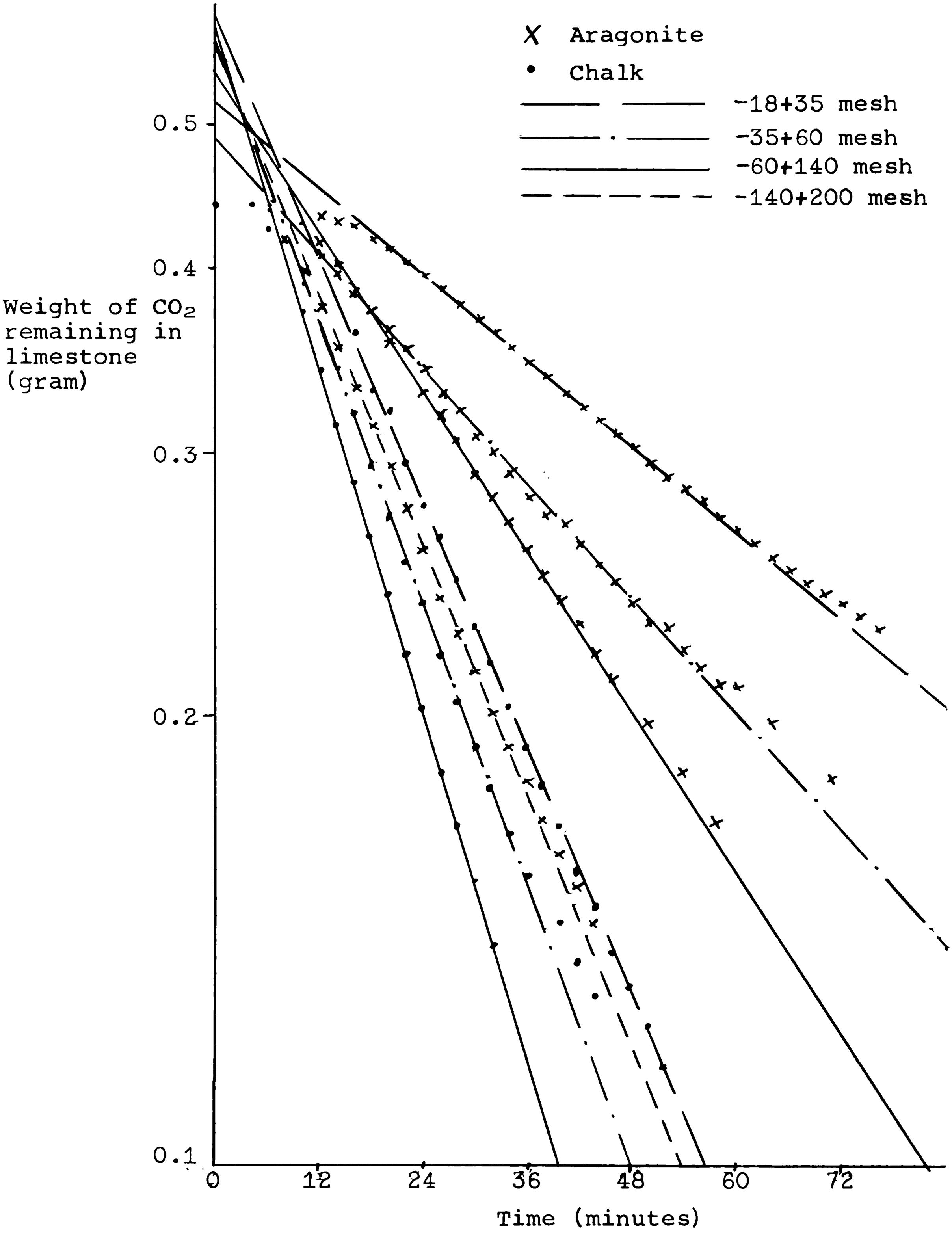


Figure 7. Rate of solution of different size fractions of chalk and aragonite in acetic acid.

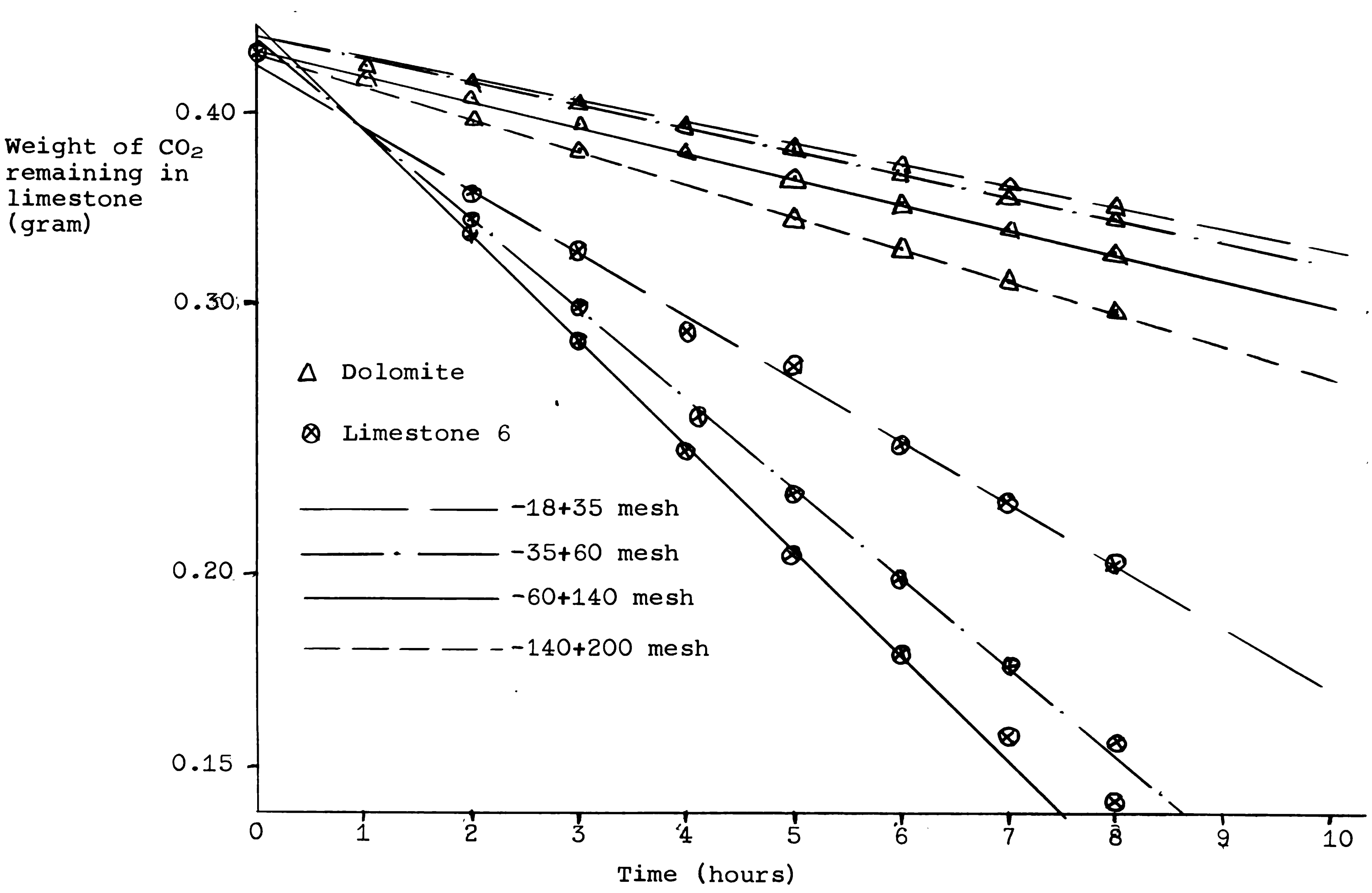


Figure 8. Rate of solution of different size fractions of the dolomites in acetic acid.

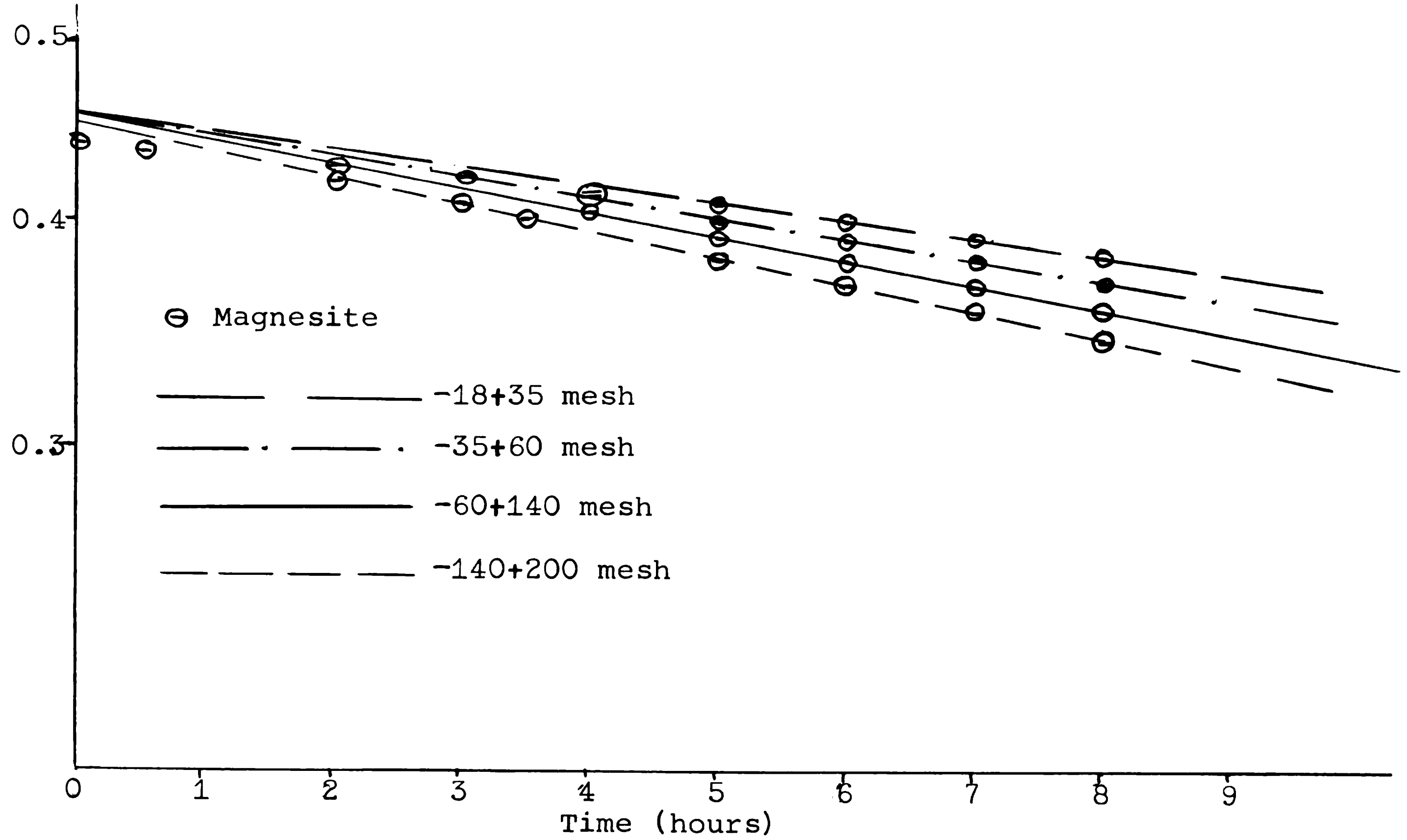


Figure 9. Rate of solution of different size fractions of magnesite in acetic acid.

as measured by N_2 adsorption is 1.66, 0.68 and 0.15 m^2g^{-1} respectively. Thus this "internal" surface area is also influencing the reaction.

However, if the differences between slopes for $CaCO_3$ in Figure 10 are compared with the differences between slopes in Figure 5, particle size or external surface change is controlling the reaction rate more than change in internal surface. But for the two dolomites changes in the internal surface area appear to be more important than changes in the external area (Figure 8). The N_2 surface areas are 1.08 and 0.08 m^2g^{-1} for limestone 6 and the pure dolomite; the dolomite being slower to react. Thus, as the reactions become slower (from calcites to dolomites), internal surface area is playing a larger part.

The reaction rates for magnesite are given in Figure 9.

Another important difference is that the reaction rate decreases as Mg is substituted for Ca in limestones. Thus, the order is $MgCO_3 < CaMg(CO_3)_2 < CaCO_3$; this was also shown by Ferrari and Sessa (15), who said that the ease of rupture of the metal carbonate bond was controlling the rate. In their equation

$$MCO_3 \longrightarrow M^{++} + CO_3^{--}$$

they implied that the mineral dissociated first as if being dissolved by water but the solubility product of calcite is less than that of magnesite which would suggest that the magnesite should dissolve faster. In fact where there is an

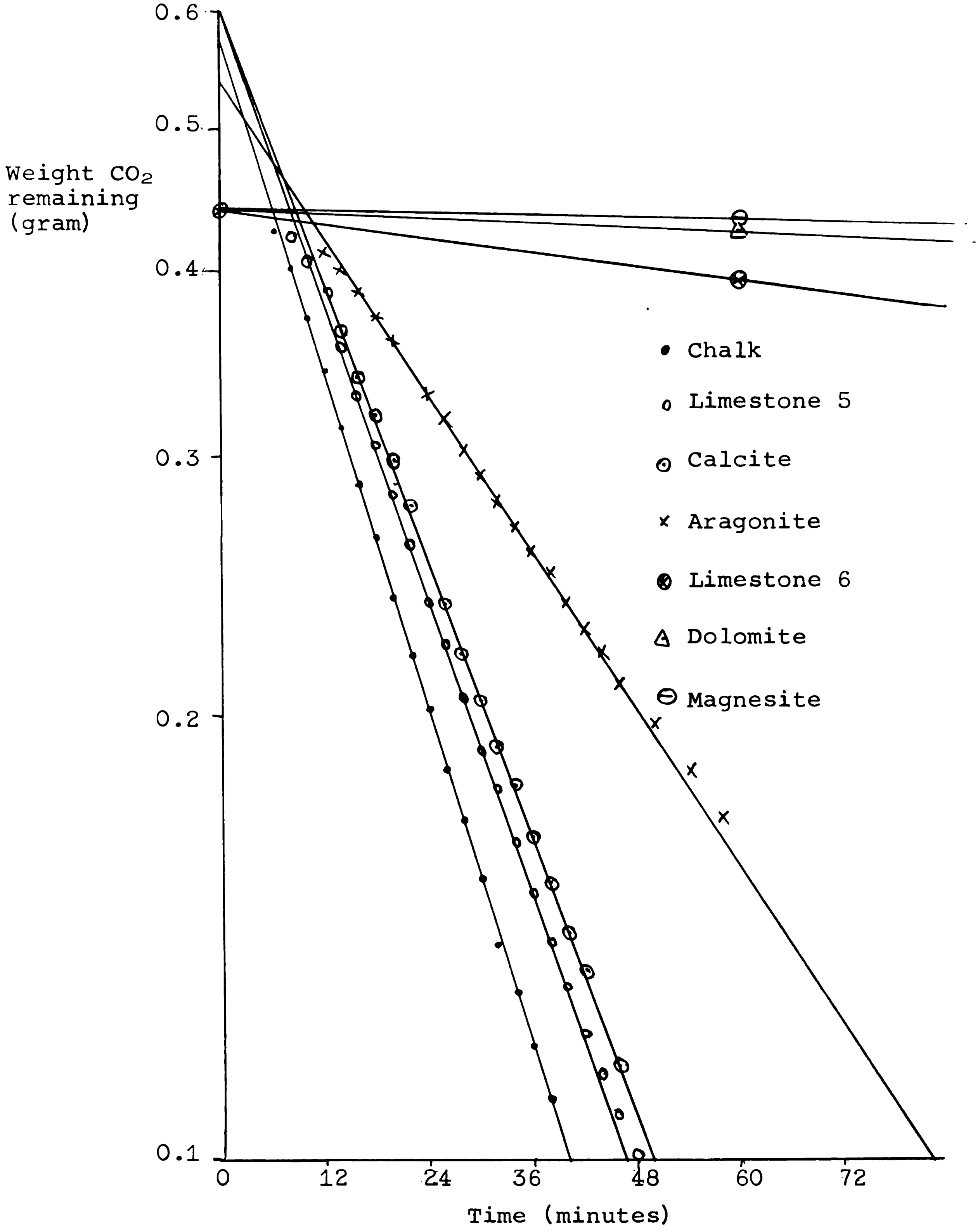


Figure 10. Rate of solution of -60+140 fraction of all minerals in acetic acid.

excess of H^+ ions, the H^+ will directly attack the mineral. The difference in rates is due to the ease with which the H^+ can polarize the CO_3^{--} group. Since the Mg is smaller than Ca, its influence is harder to overcome and thus the magnesite is slower to react; the dolomite contains both Ca and Mg and thus its reaction rate is intermediate between the two.

Perhaps the most important distinction that can be made between limestones is that they are either calcitic or dolomitic or mixtures of both. This will be dealt with in the section on limestones.

By comparison with heterogeneous reactions in the gaseous and solid phases, there is a diffusion of H^+ to the crystal surface, a reaction at the surface and then a diffusion of the products (CO_2, H_2O, Ca^{++}) away from the surface. From the earlier experiments it was concluded that the rate determining step is the diffusion of CO_2 away from the particles' surface. It was observed that the smaller sieve sizes reacted faster and, further, on shaking the suspension, a much increased reaction rate was obtained. Use of excess H^+ did not greatly increase the reaction rate. Thus, without shaking, the diffusion of CO_2 from the particle surface was rate determining and this was contolled by the external surface or sieve size.

On shaking, the diffusion of CO_2 was no longer rate controlling. Differences were observed between the same sieve fraction of calcite and chalk. When the reaction was slowed down using a lower temperature or more important, using a weaker acid, these differences became more pronounced. Thus, the total surface area became more rate controlling. In fact when the dolomites are considered the difference in rate between the pure dolomite and limestone 6 is greater than between pure calcite and limestone 5. In this case the dolomites are approximately ten times slower in reacting than the calcites.

These results have been expressed very much in a qualitative way. They can also be expressed quantitatively by the following procedure:

The rate of reaction can be described by the following equation:

$$R = f\,(M,\ S_E,\ S_I,(H^+),\ T,\ P.) \qquad (1)$$

Where R is the rate of disappearance of H^+, M is the particular carbonate mineral, S_E and S_I are the external and internal surface areas respectively, (H^+) is the hydrogen ion activity, T is the temperature and p is the partial pressure of CO_2. If T and p are kept constant as they were in the experiments and the H^+ ion activity approximates to the concentration of H^+ then (1) becomes:

$$R = f(M,\ S_E,\ S_I,\ [H^+]) \qquad (2)$$

Thus for calcite, the total differential is:

$$dR = \left(\frac{\partial R}{\partial S_E}\right)_{S_I,H} dS_E + \left(\frac{\partial R}{\partial S_I}\right)_{S_E,H} dS_I + \left(\frac{\partial R}{\partial H}\right)_{S_E,S_I} dH \quad (3)$$

Now $\left(\frac{\partial R}{\partial S_E}\right)_{S_I H}$, $\left(\frac{\partial R}{\partial S_I}\right)_{S_E H}$ and $\left(\frac{\partial R}{\partial H}\right)_{S_E S_I}$

can all be evaluated empirically from the preceding experiments. In these experiments the reaction was shown to be first order where R is the rate, t is time and c and k are constants

$$-\frac{dM}{dt} = k\ M \quad (4)$$

On integration 4 becomes

$$\ln M = -kt + C \quad (5)$$

When $t = 0$, $M = M_I$ where M_I is the initial sample weight.

$$\therefore C = \ln M_I$$

$$\therefore M = M_I\ e^{-kt} \quad (6)$$

On differentiation of 6

$$\frac{dM}{dt} = -k\ M_I\ e^{-kt} = -R$$

At $t = 0$, the initial rate is given:

$$R = k\ M_I \quad (7)$$

From this equation R can be determined if k and M_I are known. Using Figure 5, ln(CO_2 remaining) is plotted against time and thus the slope is k for any specific sieve size. The intercept at $t = 0$ is the initial weight of CO_2 in the sample which is directly proportional to the initial weight of the sample. However, due to the design of the apparatus there was a lag time of four minutes between the evolution and measurement of CO_2 so the intercept was taken at t = 4.

Now to determine $(\frac{\partial R}{\partial S_E})_{S_I H}$ R must be plotted against S_E and S_I and $[H^+]$ kept constant. Therefore, R was determined for each of the sieve sizes of pure calcite and was plotted against S_E as given in Table 4. S_I for the four fractions of calcite was approximately constant and $[H^+]$ was the same initially. This graph is presented in Figure 11. The bars on the graph represent the possible range in the external surface area where the range is limited by the sieve sizes. The method of least squares was used to determine the best straight line through the points. This procedure was repeated with limestone 5, chalk and aragonite. A straight line was the best fit that could be obtained with the aragonite and the chalk. There is some theoretical justification for this. If a single particle is considered where the H^+ surrounding it is in excess then the reaction may be thought of as occurring at specific sites. Therefore, the rate of reaction is proportional to the number of sites, σ per unit surface area.

$$R \propto \sigma \cdot S_E$$

However, microscopic examination indicates that CO_2 is evolved at the surface and this causes some of the reacting surface to be obstructed. Assuming that this fraction of the surface remains constant during the reaction, it may be represented

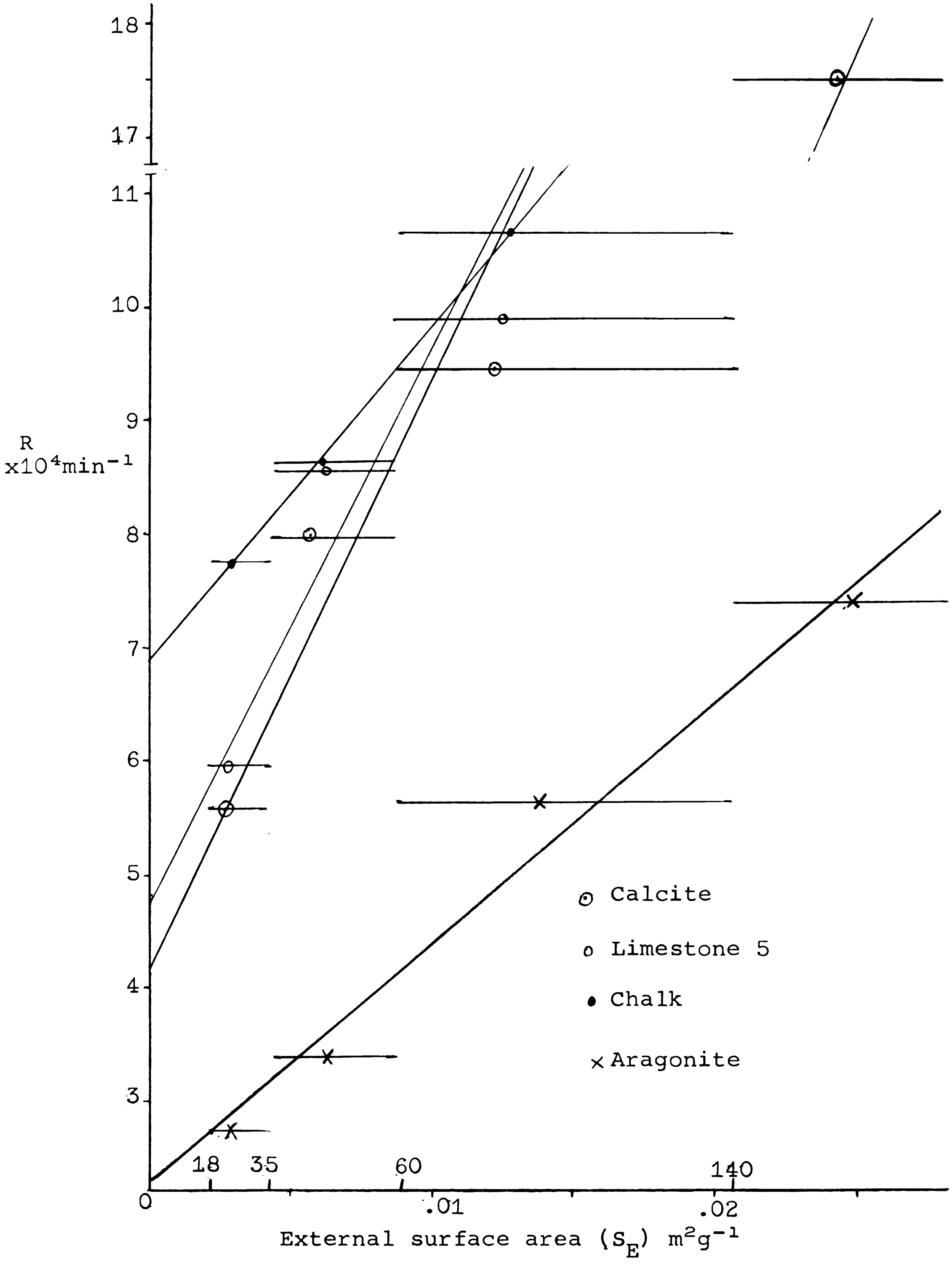


Figure 11. Rate of solution of calcites as a function of external surface area.
* The lines represent the range of S_E present between sieves.

by Θ, where Θ is a function of surface tension, depth of particles, density of fluids, surface contours and agitation of the particles. Then

$$R = (1-\Theta)\ \sigma\ S_E$$

$$\left(\frac{\partial R}{\partial S_E}\right)_{S_I, H.} = (1-\Theta)\ \sigma$$

Thus, it was assumed that a straight line should be drawn for the pure calcite and limestone 5. Each line passed through the bar of each point, but the uncertainty was probably due to error in measuring CO_2 evolved rather than an unlikely sieve distribution. Thus, the equation for pure calcite, say, is:

$$R = a\ S_E + b$$

where a is the slope and b the intercept. Therefore

$$\left(\frac{\partial R}{\partial S_E}\right)_{S_I, H} = a \qquad (8)$$

Similarly, $\left(\frac{\partial R}{\partial S_I}\right)_{S_E, H}$ was found from $R = f(S_I)$. Here the external sieve surface area was kept constant by using one sieve size from the calcite, the chalk and limestone 5. From theoretical considerations the term $\left(\frac{\partial R}{\partial S_I}\right)_{S_E H}$ is going to be a function of the ease with which H^+ enter the particle and products leave the particle. Such factors as the radius of the pores, pore volume and concentration, pressures and pH inside and outside the pore will be important.

Using Henry's law to describe the solution of CO_2 in water we obtain the following:

$$K = P/\frac{n}{n+N}$$

where P is the partial pressure of CO_2 above the solution, n is the number of moles dissolved, and N the number of moles of water per liter.

$$1.23 \times 10^{-6} = \frac{P/n}{n + 55.6}$$

If $n \ll 55.6$

$$n = P.\ 4.52 \times 10^{-5}$$

In the solution the partial pressure of CO_2 is small since the CO_2 formed in the reaction is swept away. However, in the pores there will be some CO_2 produced, but the pressure will not be great enough to force much of the CO_2 into solution. Therefore, the diffusion of CO_2 out of the pore will be controlling the rate of solution of the $CaCO_3$ forming the pore. The rate of diffusion will be controlled by the pressure difference inside and outside the pore (P_2-P_1).

$$R = D(P_2-P_1)S_I$$

$$\left(\frac{\partial R}{\partial S_I}\right)_{S_E H} = D(P_2-P_1)$$

Where D is a constant involving the pore dimensions. Now P_2-P_1 can be considered to be a constant throughout the reaction and the plot will be a straight line.

The results indicated a straight line was the best fit through the three points and the equation was determined by the method of least squares. The procedure was repeated with two other sieve sizes and the results are shown in Figure 12.

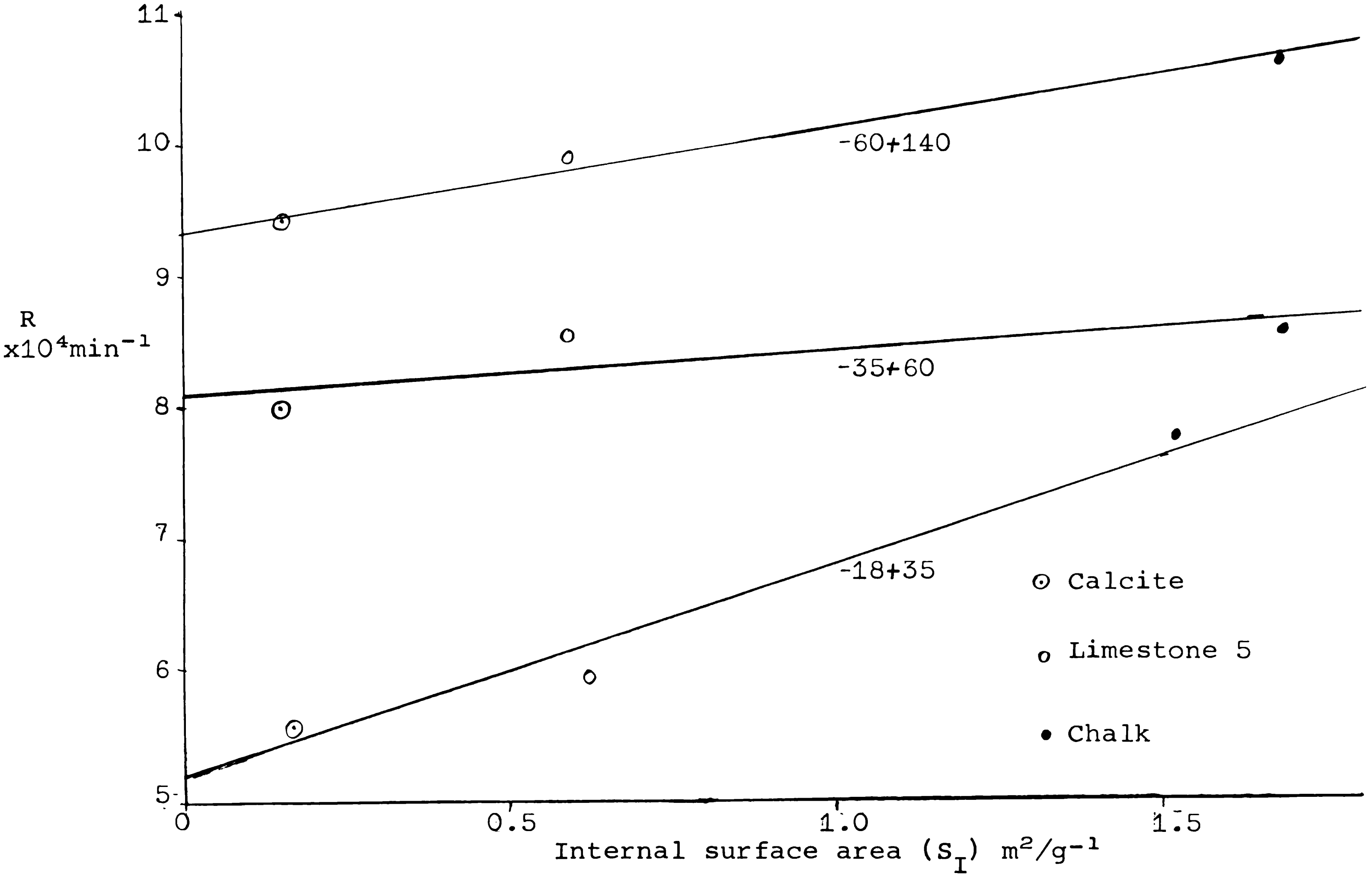


Figure 12. Rate of solution of calcites as a function of internal surface area.

The equation for one sieve size is

$$R = cS_I + f$$

where c is the slope and f the intercept. Thus

$$\left(\frac{\partial R}{\partial S_I}\right)_{S_E, H} = c \qquad (9)$$

If the slopes in Figures 11 and 12 are compared, those in Figure 11 are greater than those in Figure 12. Thus, external surface area is influencing the reaction more than internal surface area. As was mentioned earlier the aragonite was slower to react than the calcites due to different crystal structure.

$\left(\frac{\partial R}{\partial H}\right)_{S_E S_I}$ was determined by dissolving pure calcite (+18-35) in HCl of different concentrations but where the number of equivalents of acid was the same. The rate R was determined from Figure 13 and plotted against initial H^+ concentration. This also gave a straight line Figure 14, that goes through the origin; the equation was:

$$R = g\ H$$

where g is the slope. Therefore

$$\left(\frac{\partial R}{\partial H}\right)_{S_E S_I} = g \qquad (10)$$

Substituting equations 8, 9 and 10 in equation 3 we obtain

$$dR = a\ dS_E + c\ dS_I + g\ dH$$

On integrating this gives:

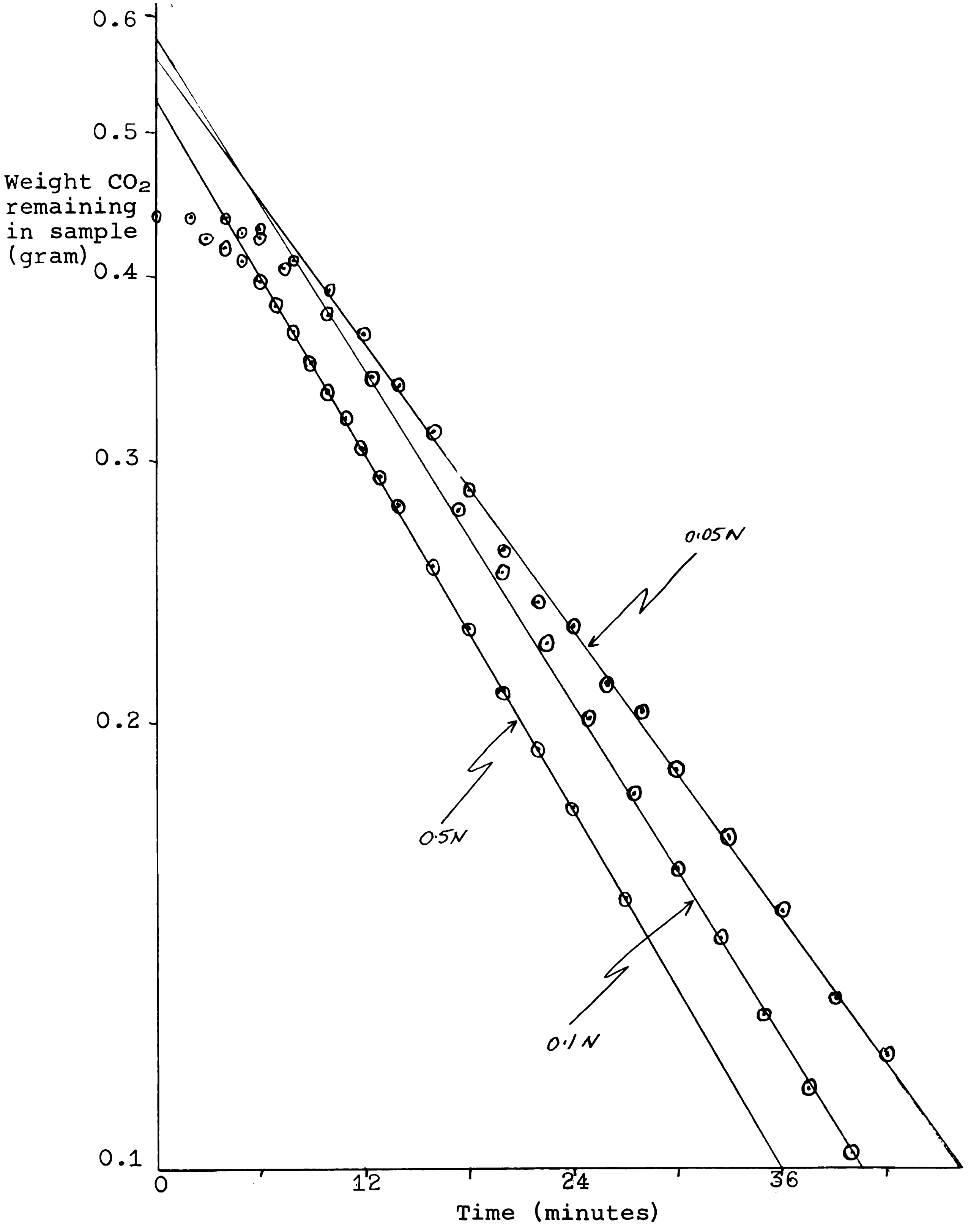


Figure 13. Rate of solution of-18+35 fraction of calcite in different concentrations of hydrochloric acid.

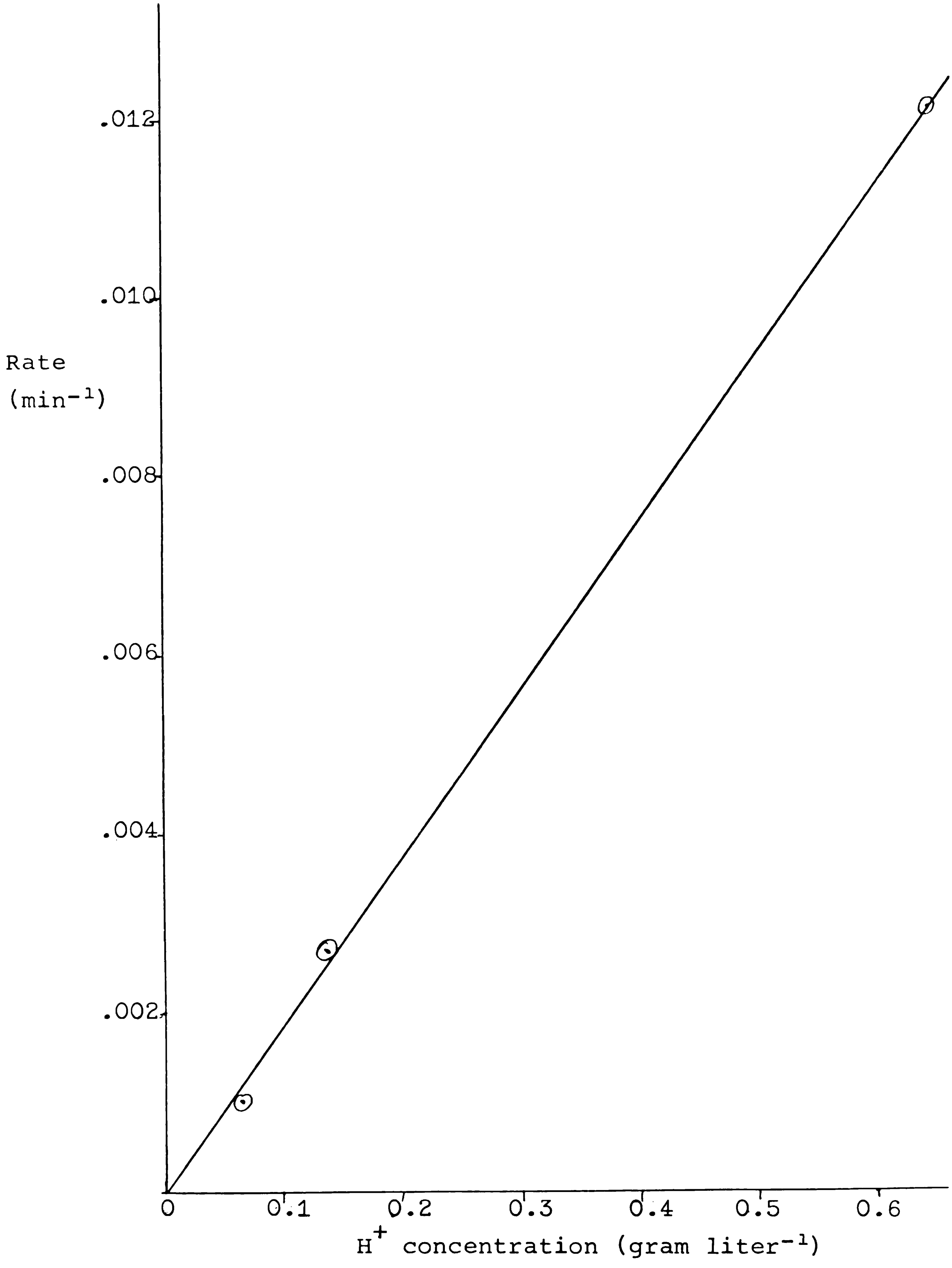


Figure 14. Rate of solution of calcite as a function of hydrogen ion concentration.

$$R = a\ S_E + c\ S_I + g\ H + h \tag{11}$$

where h is a constant.

Now if initial $[H^+]$ is kept constant this becomes

$$R = a\ S_E + c\ S_I + i\ .$$

The values determined previously for R, S_E and S_I are given in Table 5, and best results for a, c and h can be calculated using the multiple regression technique of statistics. The calculations were performed on a computer giving:

$$a = 4.88 \times 10^{-2}$$

$$c = 5.45 \times 10^{-5}$$

$$i = 4.50 \times 10^{-4}$$

The multiple regression coefficient was calculated to be 0.934 which is highly significant. This procedure gave an accurate method for determining the slopes of the lines in Figures 11 and 12 for the calcites. However, the assumption is made that the three slopes in Figure 11 are the same, and also in Figure 12. These slopes are given as a and c. This assumption is justified if nothing other than the respective surface area is controlling the reaction rate.

Now to determine whether the constant of integration, h, is required the unreal conditions can be imposed on equation 11 where we have a hard crystalline particle with zero internal surface placed in a solution of zero hydrogen ion concentration. In this case the rate of solution will be

Table 5. Rate of solution of calcite, limestone 5 and chalk in 400 ml 0.05 N acetic acid.

Material	Sieve Size	$Rx10^4$ min^{-1}	S_I m^2g^{-1}	S_E m^2g^{-1}	$[H^+]_2$ g/l
Calcite	-18+35	5.57	0.17	0.0029	0.059
	-35+60	7.98	0.15	0.0058	0.058
	- 60+140	9.44	0.15	0.0122	0.058
	-140+200	17.50	0.18	0.0242	0.061
Limestone 5	-18+35	5.95	0.62	0.0029	0.059
	-35+60	8.55	0.59	0.0058	0.060
	-60+140	9.90	0.68	0.0122	0.059
Chalk	-18+35	7.75	1.52	0.0030	0.058
	-35+60	8.58	1.68	0.0060	0.055
	- 60+140	10.65	1.66	0.0127	0.056

zero. If a one gram particle is used it will have a very small external surface area (approximately 0.0002 m^2g^{-1}); thus, R, S_I and H will all be zero and S_E will approximate to zero. Then h will also be small and almost insignificant. Therefore, h is neglected in the calculations.

Equation 11 becomes:

$$R = a\ S_E + c\ S_I + g\ H\ . \qquad (12)$$

Turning to theoretical consideration, if we assume that one particle is a perfect sphere and n is the number of particles taken, then $S_E = n4\pi r^2$ where r is the radius of the sphere. This is a fairly good approximation for the external surface area. The mass of carbonate M is $n\frac{4}{3}\pi r^3\rho$ where ρ is the density. Substituting for r this gives

$$S_E = n4\ \left(\frac{3M}{n4\pi\rho}\right)^{\frac{2}{3}}\ . \qquad (13)$$

The total surface area is measured by nitrogen adsorption and is S_T m^2g^{-1}. Therefore,

$$S_TM = S_E + S_I \quad .$$

But experimentally it has been shown that:

$$S_E \ll S_I$$

$$\therefore S_I \simeq S_TM \quad . \qquad (14)$$

Consider the equation:

$$CaCO_3 + 2H^+ \longrightarrow Ca^{++} + H_2O + CO_2 \quad .$$

M grams $CaCO_3$ react with $\frac{M}{50}$ grams H^+, therefore,

$$\frac{M}{50} \cdot \frac{1}{V} = [H^+] \qquad (15)$$

where V is the volume of solution in liters.

Substituting 13, 14, and 15 in 12 we obtain

$$R = an4\pi\left(\frac{3}{n4\pi\rho}\right)^{\frac{2}{3}} M^{\frac{2}{3}} + c\ S_TM + g\,[H^+]$$

$$= an4\pi\left(\frac{3}{n4\pi\rho}\right)^{\frac{2}{3}} M^{\frac{2}{3}} + c\ S_TM + \frac{g}{50V} \cdot M$$

where $an4\pi\left(\frac{3}{n4\pi\rho}\right)^{\frac{2}{3}}$ is i and $c\ S_T + \frac{g}{50V}$ is j.

This becomes

$$R = i\ M^{\frac{2}{3}} + j\ M \quad .$$

Therefore, $$-\frac{dM}{dt} = i\ M^{\frac{2}{3}} + j\ M$$

$$\frac{dM}{j\left(\frac{i}{j}\ M^{\frac{2}{3}} + M\right)} = -dt \quad .$$

Making the substitution $M = x^3$; then $dM = 3x^2dx$.

Then

$$\frac{3x^2dx}{j(\frac{ix^2}{j} + x^3)} = - dt.$$

Integrating

$$\frac{3}{j} \ln(\frac{i}{j} + M^{\frac{1}{3}}) = -t + k'$$

Where $t = o$, $M = M_I$. $\therefore k' = \frac{3}{j} \ln(\frac{i}{j} + M_I^{\frac{1}{3}})$

or $\ln(\frac{i}{j} + M^{\frac{1}{3}}) = - \frac{j}{3} t + \ln (\frac{i}{j} + M_I^{\frac{1}{3}})$.

This equation may be compared with the others derived for the solution of divalent carbonates

$$\frac{dx}{dt} = KS(c-x) \qquad (A)$$

$$- \frac{dV}{dt} = kS \text{ which gives } W_f^{\frac{1}{3}} - (W_f - W_t)^{\frac{1}{3}} = Kt \qquad (B)$$

$$- \frac{dM}{dt} = KM \text{ which gives } M = M_I e^{-kt} \qquad (C)$$

and

$$- \dot{y} = Ay (1 - k \int_o^t ydt)^2 \qquad (D)$$

where y is the difference between saturated and actual concentration of aqueous CO_2 solution and A and k are constants.

The first equation (A) that was developed was derived theoretically but no attempt was made to show that it was quantitatively obeyed. However, it was the first attempt to show that acid strength and surface area were involved (18). The second equation (B) assumed that the rate of reaction was proportional to the external surface area where the particles were considered to be solid spheres (15). But it has been shown that some carbonates are porous and the internal surface area must also be considered. In fact when the particle size is held constant different calcites react at different rates; therefore, something other than the surface area of the sphere is influencing the reaction rate. This equation is an oversimplification of the reaction, but it is a fair approximation for the initial rate of solution of hard crystalline particles. The third equation (C) is an empirical equation which fits the results very well (46). However, the experimental points deviate from a straight line in the latter part of the reaction with some limestones. This deviation has been explained by saying that particle size distribution within a sieve fraction was having an effect. In fact, the external surface area was changing during the reaction; thus the second equation should be used in conjunction with the first order rate equation. It was shown that the difference between the equations could account for the curvature. But it would seem that the assumption that Ferrari and Sessa's equation was correct, was in fact an error.

Brydon and Rice (9) used the equation of Skinner _et al_. and stated that differences in slope for various limestones was due to differences in surface area as measured by the Blaine air permeability tester. This was qualitatively true for the samples that they mention but they were using four normal HCl and diffusion of CO_2 from the particles' surface was probably rate controlling. However, the method is very useful in determining calcite in the presence of dolomite.

The fourth equation (D) was derived assuming that the particles were rhombohedral. This is probably true for small, hard crystalline particles. It was found the equation held in some of the samples that were tested (19).

The equation derived in this thesis was tested by plotting $\ln(\frac{i}{j} + M^{\frac{1}{3}})$ against t. Several values of i and j were assumed. Where $\frac{i}{j}$ is small compared with $M^{\frac{1}{3}}$, the equation approximates to the first order plot since $\ln M^{\frac{1}{3}}$ is $\frac{1}{3} \ln M$. It was thought that the concave curvature of some of the lines would be corrected by assuming values of $\frac{i}{j}$. However, this tended to alter the whole curve rather than the last portion.

PROPERTIES OF AGRICULTURAL LIMESTONES

Chemical Analysis

The percent composition of the -60+80 mesh fraction of the agricultural limestones is given in Table 6. The uncertainty in the measurements is the same as for the minerals. There is agreement to within four percent between the purity as determined by summing the Mg, Ca and CO_3 content and that determined from the $CaCO_3$ equivalent. This was probably due to differences in sampling and impurities that neutralized some of the acid used to determine $CaCO_3$ equivalent. Sample 3 gave the most error and this will be discussed later.

Surface Area

The surface area as determined by N_2 adsorption is given in Table 7. The uncertainty of this measurement on samples 1, 1a and 9 is ± 0.02 m^2g^{-1} and this has been discussed in the section on the minerals. The uncertainty of the surface area measurement of the other samples is less than five percent. Sample 3 had an exceptionally high surface area. It was observed that the particles were coated with a reddish-brown powder which was thought to be amorphous iron compounds. This was removed by treatment with dithionite-citrate solution buffered with sodium bicarbonate as

Table 6. Chemical analysis of the -60+80 mesh fraction of agricultural limestones.

Compound	Mg Content (Percent)	Ca Content (Percent)	Carbonate Content (Percent)	Purity[1] (Percent)	$CaCO_3$ Equivalent
Calcites					
4	0.4	16.8	26.0	43.2	43.3
4a	0.1	25.8	41.4	67.3	69.0
10	0.5	25.1	43.3	68.9	72.2
11	1.1	31.0	53.8	85.9	89.6
Dolomites					
1	11.4	18.1	62.8	92.3	104.6
1a	10.7	18.6	62.2	91.5	103.7
2	11.7	17.9	54.6	84.2	91.0
3	7.5	19.6	57.2	84.3	95.4
9	12.5	20.5	61.0	94.0	101.6

[1] Estimated by the sum of Mg, Ca and CO_3.

Table 7. Surface area of limestones as determined by nitrogen adsorption.

Limestone number	Surface area	Iron free surface area
	m^2g^{-1}	
4	1.20	0.77
4a	3.20	1.34
10	2.40	1.90
11	0.64	----
1	0.21	----
1a	0.20	----
2	2.30	----
3	4.50	0.80
9	0.10	----

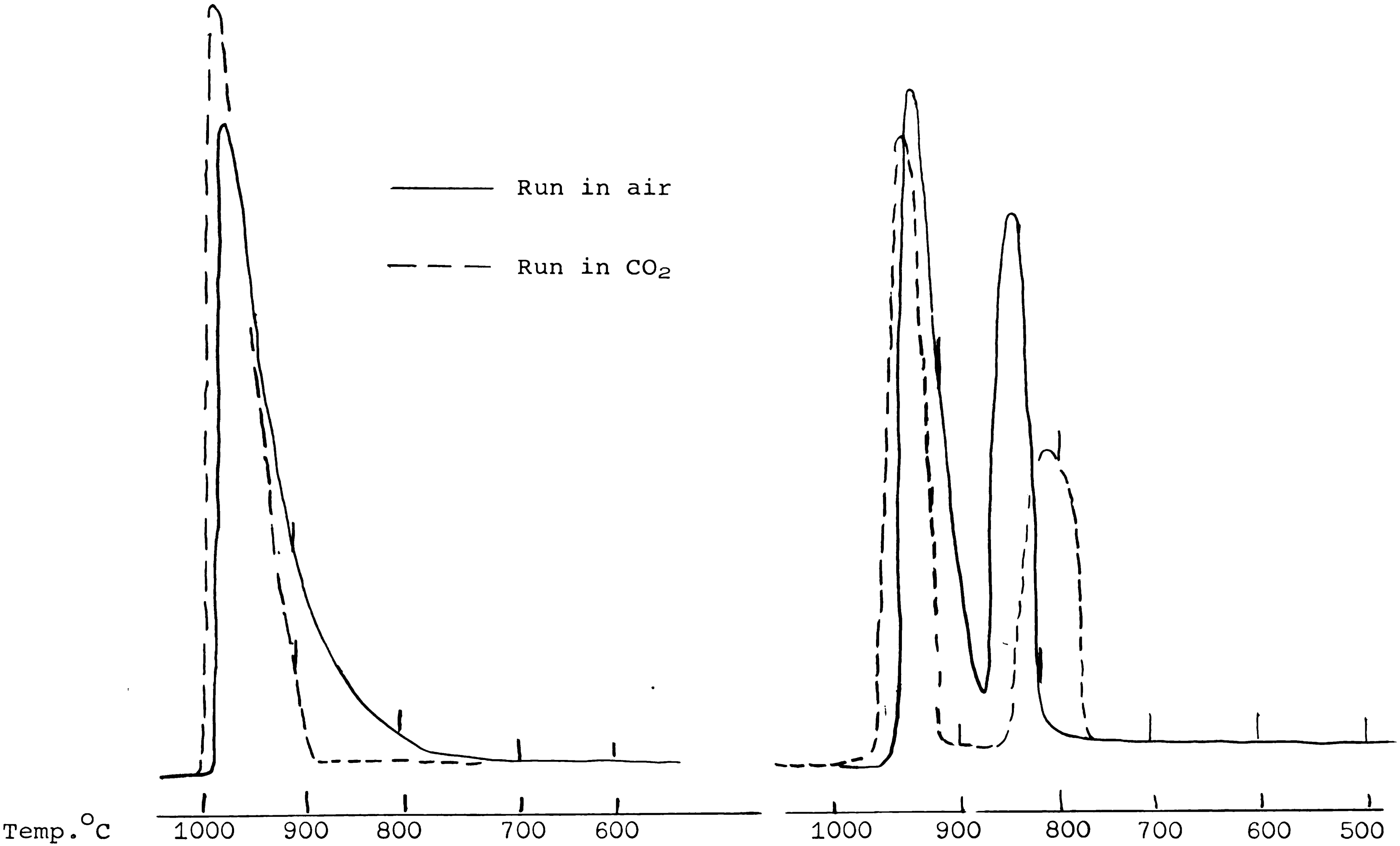
described by Jackson (21). The surface area was then determined and was found to be 0.80 m^2g^{-1}. Other samples also appeared to be coated with iron compounds: these were similarly treated and the surface areas were again reduced. The results are given in Table 7.

Characterization of Agricultural Limestones

Agricultural limestones have often been characterized by their neutralizing value or $CaCO_3$ equivalent. Sometimes calcium oxide (CaO) and magnesium oxide (MgO) content are given (1,20,45,50) and other authors have categorized the limestones as calcitic or dolomitic from these contents (28, 51). But this is strictly a classification based on chemical analysis. Some geologists identify calcites and dolomites by their different rates of solution in acids. Skinner et al. (46) used 4 N HCl to determine calcite and dolomite in soils and limestones.

Differential thermal analysis (DTA) has been used to investigate carbonate minerals. The curves of calcite and dolomite are very distinctive. A calcite has a large endotherm from 940-980°C, and dolomites have two endotherms, one at 800-850°C and one at 940-980°C. When DTA is run under CO_2 the calcite peak is considerably sharpened, the dolomite peaks are also sharpened and are separated (Figure 15).

The agricultural limestones were all analyzed by DTA, the dolomite containing limestones were analyzed under CO_2



a. Calcite

b. Dolomite

Figure 15. Differential thermal analyses curves of calcite and dolomite.

in order to estimate the percentage calcite, if any, that was present. The deflection and peak temperatures for all the limestones are given in Tables 8 and 9. None of the analyses gave perfect dolomite curves, often there were shoulders on the expected curves and sometimes there were additional peaks. These could have been due to salt impurities which are known to alter the positions and shapes of peaks. However, all soluble salts should have been removed by the washing process. If may be that some of the shoulders were due to iron carbonate ($FeCO_3$, $Fe_2(CO_3)_3$) impurities and some peaks due to magnesium carbonates ($MgCO_3$).

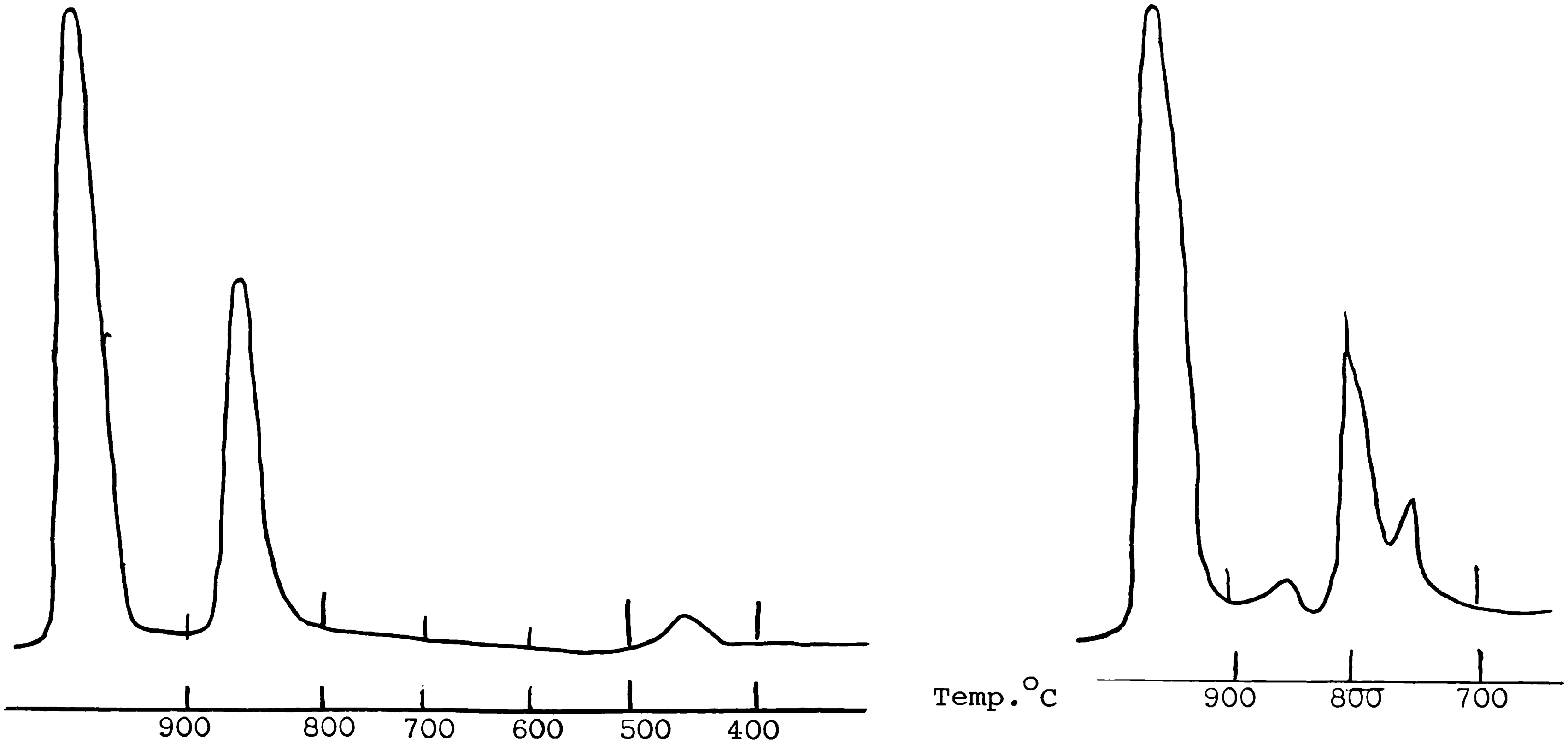
If the chemical analysis is considered by itself, samples 1, 1a, 2, 6, 7, 8 and 9 would be considered as dolomites. When the results of DTA are examined then it is confirmed that 1, 1a, 6, 7 and 8 are dolomites. However, sample 2 showed a typical magnesite peak in addition to the two dolomite peaks, the first of these appeared to be smaller than from a typical dolomite (Figure 16). In order to quantitatively determine the percentage of dolomite in the mixture, the samples were analyzed under CO_2. Samples of neutralizing value equal to 250 milligrams of $CaCO_3$ were taken and the area of the first dolomite curve was determined. This curve is present for all dolomites and is due to the initial decomposition of the mineral whereas the second curve is due to the decomposition of $CaCO_3$ and can be enlarged if calcite is also present. Mixtures of pure calcite and

Table 8. Differential thermal analysis--deflection and peak temperatures of endotherms of -60+80 mesh fraction of agricultural limestones run in air.

Lime- stone number	Peak 1		Peak 2[*]		Peak 3		Peak 4		Peak 5		Peak 6	
	Deflec- tion	Peak	Deflec- tion	Peak	Deflec- tion	Peak	Deflec- tion	Peak	Deflec- tion	Peak	Deflec- tion	Peak
	°C											
1					540	shoulder	740	850			870	960
1a					640	shoulder	700	840			870	950
2	350	430					700	850			870	940
3			460	480			640	810		850	900	960
4			410	550							880	950
4a			430	460							750	950
5											800	990
6							700	850			880	960
7					560	700	750	840			870	960
8					550	shoulder	740	830			800	960
9					450	640	730	810			840	945
9[**]					400	650	710	820			850	960
10											800	960
11							540	830			860	970

[*] Exotherm

[**] Ground



a. Limestone 2.

b. Limestone 3

Figure 16. Differential thermal analyses curves of dolomitic limestone run under CO_2.

dolomite were analyzed to give a standard curve which is shown in Figure 17. The percent of dolomite in sample 2 was shown to be 55 percent. This is very different from what was found from the chemical analysis if all the Mg is assumed to be present as dolomite. This would give an analysis of 89.7 percent dolomite. There will also be some $CaCO_3$ present which will not be combined with $MgCO_3$; thus, the sample should react faster than a true dolomite. X-ray analysis confirmed that calcite and dolomite were both present.

From the chemical analysis of sample 3 it would be expected that dolomite and calcite are both present. DTA showed that there was 54 percent dolomite in the sample (Figure 16), and X-ray again confirmed the presence of the two. The DTA also indicated that there was a small amount of ankerite ($FeMgCa_2(CO_3)_4$) present. Samples 1, 1a, 2, 3, 6, 9, and 11 were all investigated using DTA and the percent dolomite measured. The results are given in Table 10 together with the percentage dolomite calculated from the Mg content assuming that all the Mg is present as dolomite. There is close agreement for all samples except number 2. It should be noted that the areas of peaks 2 and 4 were determined for sample 3 and it was assumed that the decompositions shown by these peaks had the same heat of reaction and the reactants had the same thermal conductivity. This was also assumed for the shoulders in samples 1 and 1a.

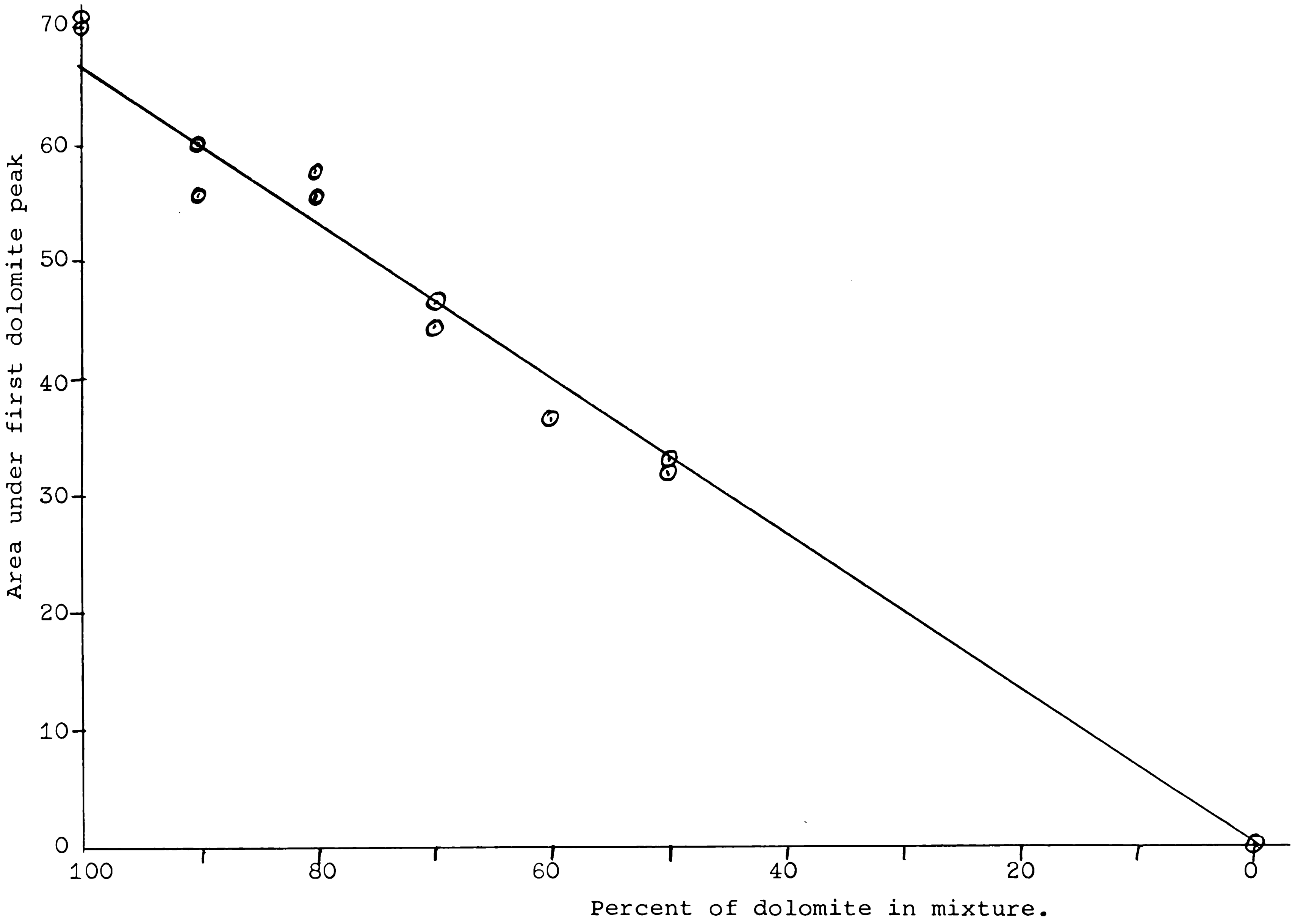


Figure 17. Calibration curve for determining the fraction of dolomite in a calcite/dolomite mixture.

Table 9. Differential thermal analysis--deflection and peak temperatures of endotherms of −60+80 mesh fraction of dolomitic limestones run in CO_2.

Limestone number	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5		Peak 6	
	Deflection	Peak	Deflection	Peak	Deflection	Peak	Deflection	Peak	Deflection	Peak	Deflection	Peak
	C°											
1					580	shoulder	740	830			905	955
1a					570	shoulder	740	820			905	955
2	430	460					710	810			910	970
3					700	720	750	800	840	860	905	960
6							700	830			900	955
9					540	660	760	790			900	960
9*					540	shoulder	750	820			910	960
11							750	815			905	960

*Ground and washed

Table 10. Determination of percent dolomite in limestone and standardization of method.

Standards Percent dolomite	Area of curve[1]	Sample	Area of curve	Percent dolomite	
				DTA	Chem. Anal.
0	0.0	1	62.1	90	87.4
50	32.5	1a	68.8	100	82.0
60	36.4	2	37.7	55	89.7
70	45.2	3	37.4	54	57.5
80	56.5	6	61.3	89	82.1
90	58.0	9	59.3	97	95.8
100	70.1	11	9.4	14	8.4

[1] Mean of two determinations

Sample 9 appeared to be a mixture of calcite and magnesite if one considered the DTA and chemical analysis; however, X-ray analysis showed it to be a pure dolomite. But 0.01 percent sodium chloride or other alkali and alkali earth halides and carbonates is sufficient to alter the first dolomite peak by up to 100°C (12). Therefore, sample 9 (-60+80) was crushed with a pestle and mortar and washed with distilled water. The DTA curve of the powder then changed considerably and the two peaks of dolomite were observed (Figure 18). Therefore it was assumed that there were soluble salts included in the structure which had affected the DTA. It was also noted that the finer than 100 mesh fraction of this sample appeared as a dolomite initially when examined by DTA; thus, the composition of various sieve fractions was chemically different.

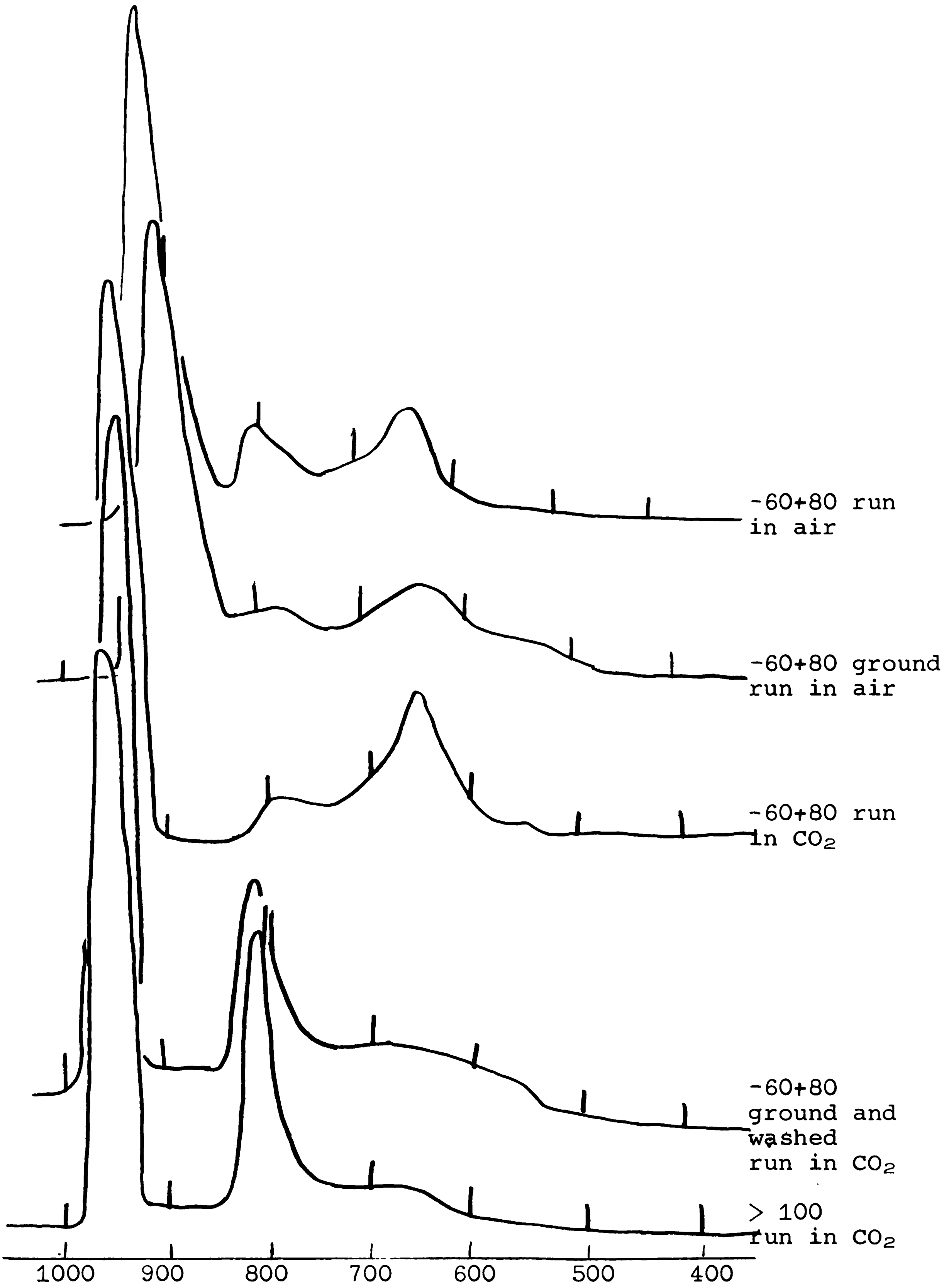


Figure 18. Differential thermal analyses curves of limestone 9.

Rate of Reaction with Acetic Acid

It was thought that the rate of reaction of the limestone could be compared with the surface area or the percent calcite and dolomite or both of these; therefore, the rate of solution of the -60+80 sieve fraction in acetic acid was studied. The calcitic limestones were found to react much faster than the dolomitic limestones.

a. Calcitic limestones

The results are shown in Figure 19. The fastest to react were 4a, 5 and 11, number 10 being the next fastest and sample 4 was the slowest. Although sample 10 had the largest surface area, it was slower to react than 4a, 5 and 11. The curve for sample 4 was not a straight line and this may have been due to the large percentage of impurity. The determination on sample 5 was performed twice and the weight of CO_2 evolved was reproducible to within four percent after a time of 16 minutes had elapsed.

b. Dolomitic limestones

The dolomitic limestones were much slower to react than the calcitic limestones (Figure 20). Samples 2 and 3 were different from the other dolomites in that the initial reaction was much faster. This was due to the presence of calcite in the limestone as was shown by DTA and X-ray analysis, although for sample 2 this was not shown by chemical analysis. Thus chemical analysis alone should not be used to characterize limestones. The samples reacted in the order 6>1>9>1a>

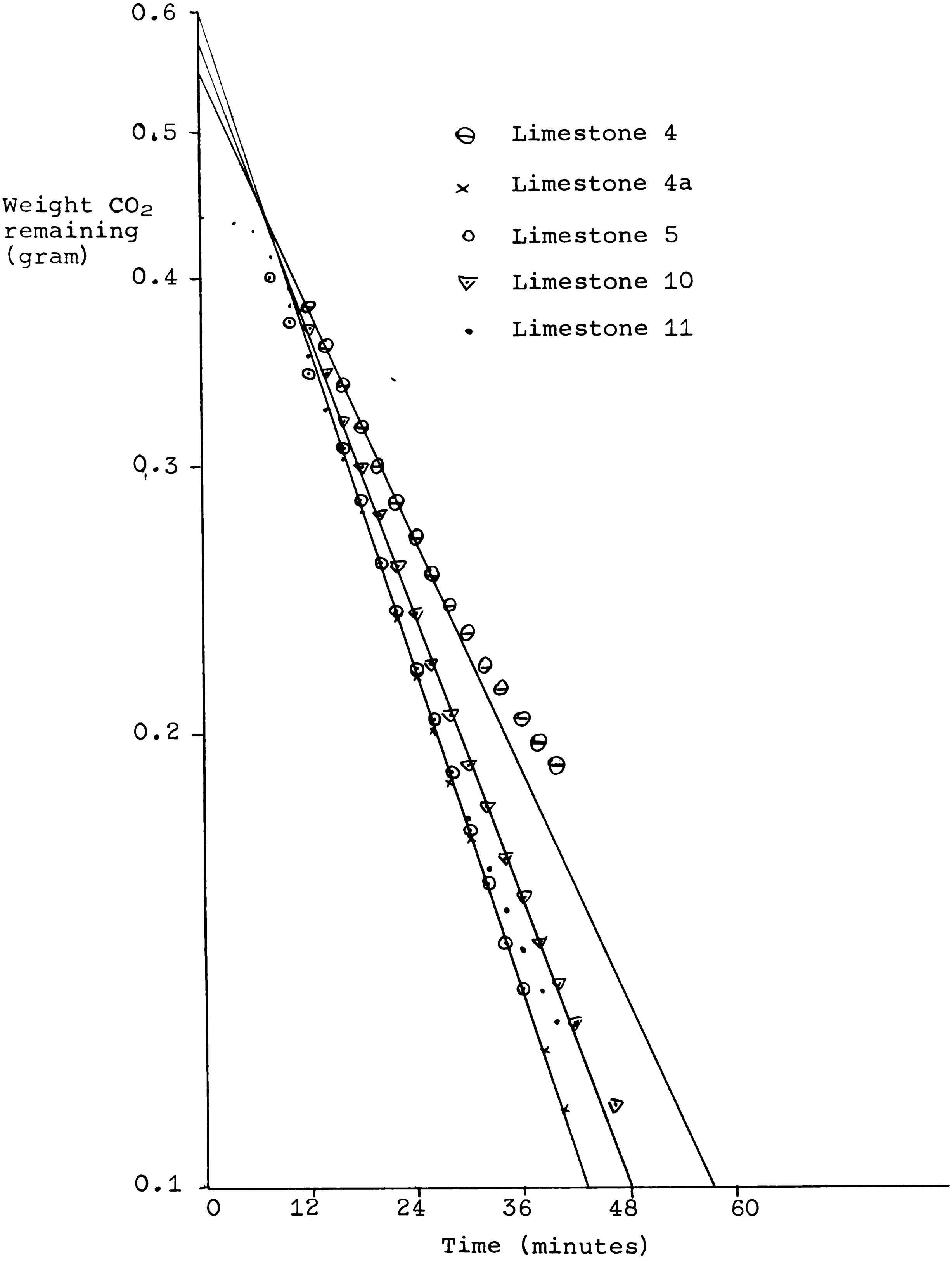


Figure 19. Rate of solution of -60+80 fraction of calcitic limestones in acetic acid.

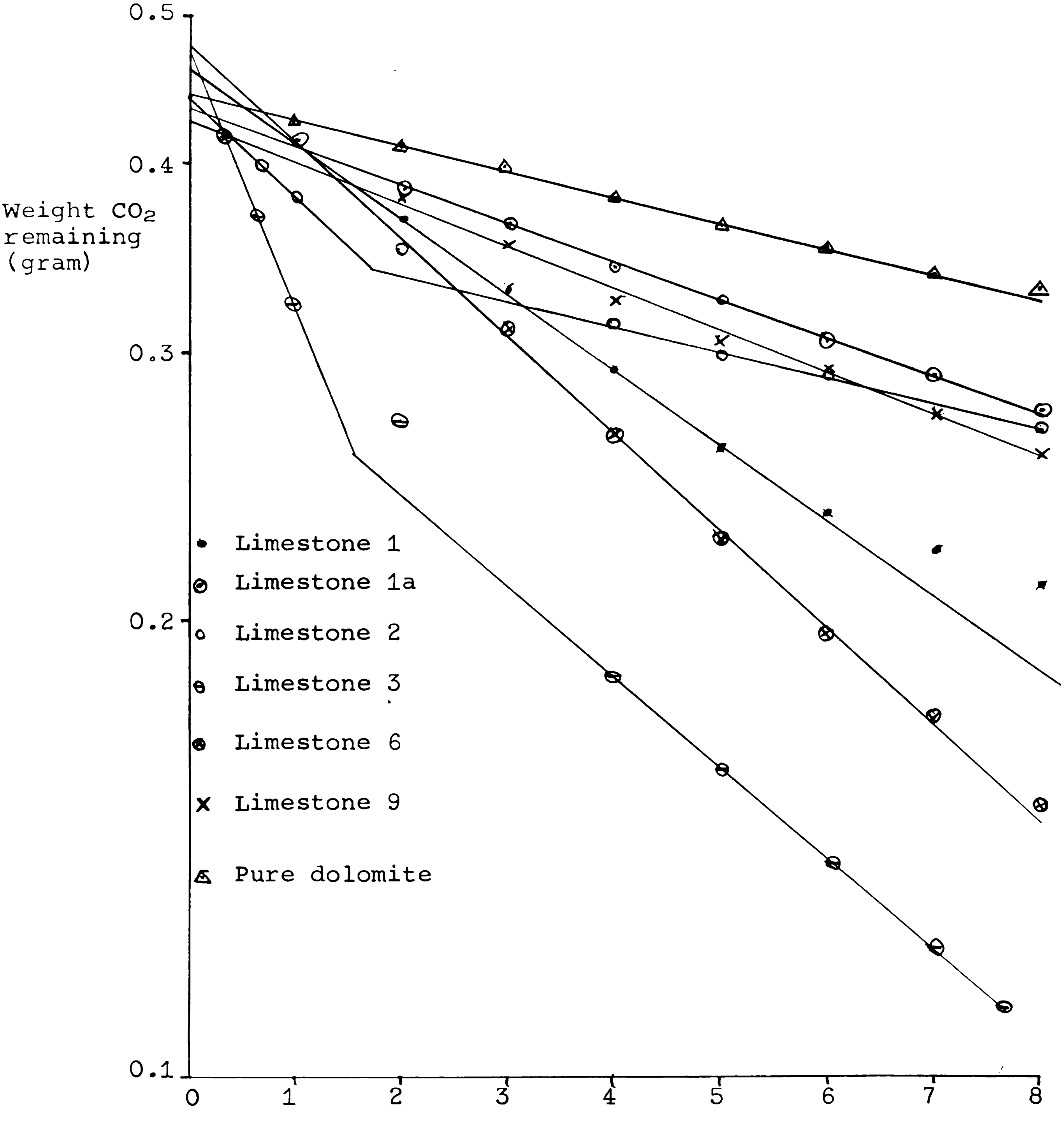


Figure 20. Rate of solution of −60+80 fraction of dolomitic limestones in acetic acid.

pure dolomite. Sample 6 had the largest surface area and the pure dolomite the smallest; whereas, samples 1, 1a and 9 had similar properties. Thus there is some correlation between surface area and reaction rate.

Rate of Reaction with H-resin

On comparing Figures 19 and 20, there was a greater difference in reaction rate between the dolomites than the calcites due to the much slower reaction of the dolomites. A system was required where the reaction was slower than in acetic acid, where diffusion was becoming more rate limiting and where there was similarity with the acid soil-limestone reaction. Therefore a H^+ saturated resin mixed with sand was used. In this case the calcites were faster to react than the dolomites, except that some dolomites reacted faster than the pure calcite, which was the slowest calcitic limestone.

a. Calcitic limestones

Half of the reaction was completed in one to four days. This was slower than the reaction in acetic acid, although the same number of equivalents of H^+ were present, because diffusion was playing a larger role and a buffered system was used. There were large differences in the rate of reaction, the order being chalk >10>5>4 = 4a>pure calcite (Figure 21). Sample 4a was out of place in the order that would be expected from surface area measurements; therefore, the experiment was repeated with this sample and the results showed agreement to within five percent. There may have been some uncertainty in

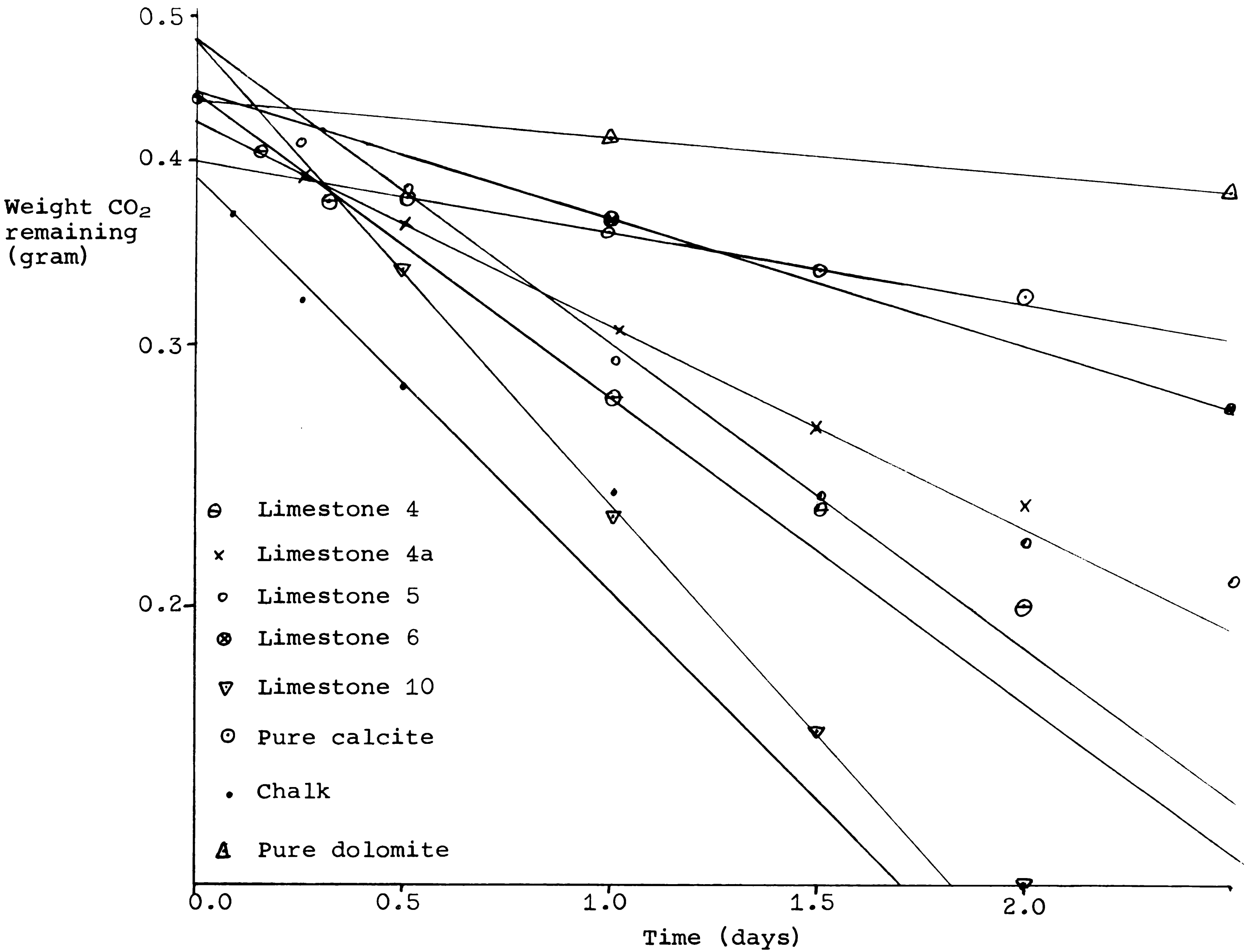


Figure 21. Rate of solution of -60+80 fraction of calcitic limestones in H-resin.

the results due to inadequate mixing of the reactants. All the curves were concave suggesting that diffusion of H^+ to the limestone was becoming rate limiting as the reaction proceeded.

b. <u>Dolomitic limestones</u>

The reactions were half completed in three or four days with most samples (Figure 22). During the first two days samples 2 and 3 were again faster to react than the other limestones; thereafter it was difficult to find any logical reason for the order of the rates of reaction unless it was that they were poorly mixed. The pure dolomite was the slowest to react as would be expected.

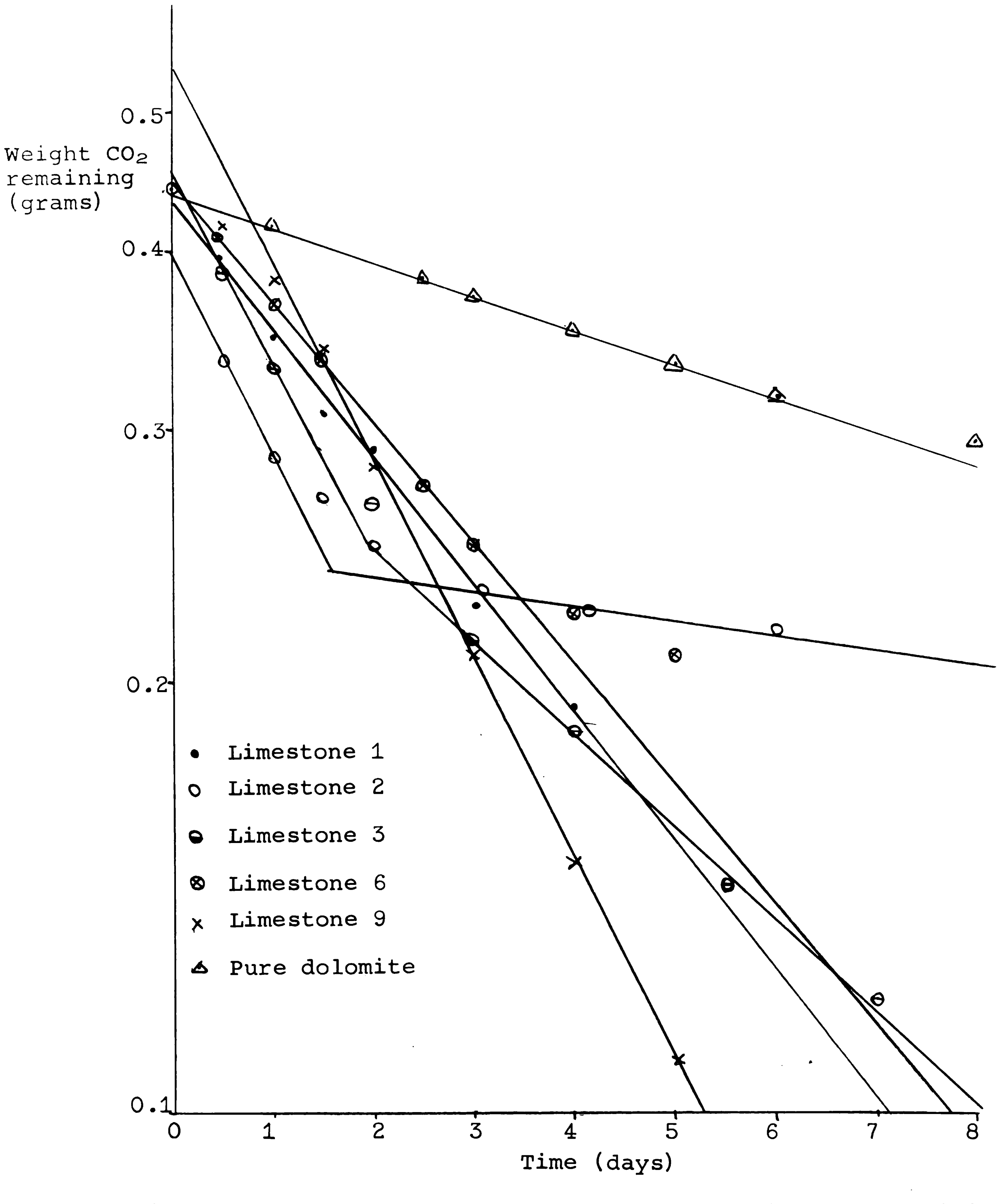


Figure 22. Rate of solution of −60+80 fraction of dolomitic limestones in H-resin.

SUMMARY AND CONCLUSIONS

Methods of following the solution of carbonate minerals in acid solutions were investigated. The rate of solution of these minerals in acid was determined by weighing the CO_2 evolved. A study of the effects of particle size, surface area as determined by N_2 adsorption and H^+ ion concentration on the rate of solution was carried out. The properties and rates of solution of agricultural limestones in various media were also studied.

The results of these studies are summarized as follows:

1. The rate of solution of carbonate minerals was best followed by using 0.05 normal acetic acid and then absorbing the CO_2 evolved in Ascarite, weighing the Ascarite, and using a first order rate equation.

2. The diffusion of CO_2 away from the mineral was rate limiting; therefore, the suspension was always shaken.

3. The most important factor influencing the rate of solution of the minerals was the chemical composition. The order of reaction rate was: calcite > aragonite > dolomite > magnesite.

4. For the three calcites studied change in particle size influenced the reaction rate more than N_2 surface area, but for the two dolomites where the reaction was slower the

reverse was true. Thus, as the rate of solution was decreased, diffusion in the pores of the mineral was becoming rate limiting.

5. The rate of reaction increased as surface area and H^+ ion concentration was increased and as particle size decreased.

6. The rate of solution of the calcitic limestones in acetic acid was too fast to evaluate them satisfactorily but there were clear differences for the dolomitic limestones. Of particular importance was the fast initial rate of the dolomites that contained some calcite.

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