# PART II

## CHEMICAL ETCHING OF CALCITE CLEAVAGES

# CHAPTER III

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## 3.1 INTRODUCTION:

When a crystal is attacked by an appropriate solvent which chemically or physically dissolves it, the initial dissolution begins at certain preferential points. This phenomenon is known as etching, which is as old as the art and science of metallography. It gives rise to various types of geometrical features on a crystal surface. It is well known that single crystals are anisotropic. The rate of attack on the crystal surface is anisotropic, being different along different directions. This anisotropy usually gives rise to the production of conical depressions with regular geometrical outlines on crystal surfaces. They are usually known as etch pits, etch marks or etch figures. The form and symmetry of etch pits were used by mineralogists to determine crystal planes and their orientation with one another. At that time, production of etch pits on a crystal surface was not understood satisfactorily. Dissolution of crystal surface is now thought to occur by retreat of monomolecular steps, being reverse to that of growth, which takes place due to the motion of steps on a surface. It is believed that when a crystal face is exposed to a solvent, dissolution usually begins by the nucleation of unit pits of one molecular depth at relatively weak spots on the surface. These unit pits grow as steps retreat across the crystal surface through the action of kinks.

The understanding of etch phenomenon was enhanced by the recognization of various types of imperfections in a crystal. The defect points are not bound with the surface as strongly as the other points of the crystal. They need less energy to dissociate than that required by points (atoms) in the regular structure. If chemical or physical change gives sufficient energy to dissociate imperfections from the exposed surface, etch pits or etch figures are observed on it. It is not necessary that solvent should be present at the time of etching, other appropriate physical conditions such as ionic bombardment, temperature etc. also help to form etch pits at preferential points on a crystal surface. Following are the ways of obtaining preferential dissolution on a crystal surface (i) Chemical etching (ii) Thermal etching (iii) Ionic etching (iv) Electrolytic etching and (v) Etching by dehydration. The etch patterns obtained by any one of the above methods are studied by high resolution optical techniques, or by X-ray microscopy or by electron microscopy. The behaviour of materials towards a given method of etch depends upon the nature of the material and other environmental conditions. For example, it is presumed that the first step in the dissolution process of metallic crystals is the oxidation of the metal followed by the removal of the oxide film.

Chemical etching produces usually a few or all features on a crystal surface mentioned below:-
(1) Etch spirals (2) Etch pits, terraced, flat-bottomed

and point-bottomed, (3) Linear etch rows (4) Polygonized etch figures (5) Tunnels and dendritics etch figures and (6) Shallow pits, pits with beaks, etch hillocks etc.

Though etching has become an important technique for study of dislocation properties of solids, the basic mechanism of chemical etch pitting process is not yet well understood. This is indicated by the use of trial and error methods by which all the known dislocation etch pitting solutions have been developed and more often than not, the occurrence of an accidental contamination of some trial solution leads to the successful etch pitting solution. Substantial work on etching of different crystals is now available in literature and is reviewed from time to time by researchers. (Regal et al., 1960; Johnston, 1962; Robinson, 1968). Some important salient features associated with chemical etching are given here with special reference to etching of ionic crystals.

## 3.2 THEORY OF ETCH PIT FORMATION AT DISLOCATIONS:

The formation of etch figures may be divided into two stages (a) nucleation of pits (b) formation of visible pits. The first is a sufficient condition for etch pit formation while other is a necessary condition of etching. Detailed understanding about the formation of dislocation etch pits is of vital importance for developing new etchants with specific characteristics which in turn are likely to promote better understanding of the mechanism of chemical etch pitting process.

Daniell (1816) who was a pioneer in etching work tried to correlate the nature of etch figures with the molecular structure of the crystalline solids. Increasing interest in the phenomenon of etching is attributed mainly to the efforts of German scientists, in the later half of nineteenth century. The first attempt to explain, several aspects of chemical process of etching is due to Goldschmidt (1904). According to him the chemical reaction between the corrosive and surfaces gives rise to currents, some of which are directed towards, and some are away from the surfaces, the interference of the ascending with the descending currents tends to form eddies, each of which is a starting point of a pit. He reported the occurrence of preferential etching along fine scratches, impurities, inclusions, dust particles etc. Further interest was created in the etching method with the discovery of X-rays and the development of the X-ray analysis of the crystal structure. The importance of chemical etching was increasingly felt when it was used for revealing dislocations and other kinds of structural defects.

In order to explain the discrepancy between the calculated and real yield stress of crystals, the concept of dislocation was introduced by Taylor (1934), Orowan (1934) and Polanyi (1934). A dislocation model was proposed by Burger (1940), for the boundary between crystals of different orientation as well as the relation between $\theta$ the angle of inclination of the crystal, b the magnitude of Burgers vector and the dislocation spacing D, viz.; $D = b/\theta$. Vogel et al. (1953) confirmed this identity of the disorientation measured at a sub-boundary by X-ray diffraction and inferred from the spacing D of dislocations revealed by etch pits. This was the first proof giving correlation between etch pits and dislocations in a lineage boundary as well as for isolated edge dislocations.

The first extensive theoretical treatment of the nucleation of etch pits at dislocations was given by Cabrera (1956), Cabrera and Lavine (1956). They postulated that the strain energy localized in the vicinity of a dislocation, lowered the free energy required for the nucleation of a cavity of unit depth at the site of intersection of dislocation with a crystal surface. This leads to preferred dissolution of the surface at the dislocation sites. Gilman (1960) has criticized the above model because elastic strain energy of a pure screw dislocation is zero at the surface and both types of dislocations (having some finite energy at the surface) seem to be etched in almost identical fashion. He has suggested that the dislocation core energy is more important than the elastic strain energy for the nucleation of etch pits. This is supported by the observations: (i) The dislocations in metals are more difficult to etch than those in ionic or covalent crystals. The core energies of dislocations in metals are less than in other types of materials while the elastic strain energies of dislocations are about the same for all materials. (ii) Since overlapping strain fields of dislocations closed together tend to cancel out, it would be expected on the basis of Cabrera's model that widely separated dislocations would etch at different rates than ones closely spaced; contrary to this, it is observed that the etch pits at isolated dislocations within subgrains of a crystal are of the same size as the etch pits in the subboundaries. (iii) Dislocations having quite different core structures in a given crystal etch at quite different rates (Gotas and Lavine, 1960). Schaarwachter (1965) has modified Cabrera's treatment taking due care of core energy suggested by Gilman. He distinguished three cases depending on the relative importance of the contributions of the dislocation core and elastic strain energy. (a) Only the core energy is important in lowering G (change in free energy of a two dimensional nucleus formed at a dislocation). This is probably the case for metals. (b) Both the core and strain energy contribute to lowering of G; this is possibly the case for ionic and covalent crystals with small Burgers vector. (c) Only the strain energy of the dislocation is significant, and Cabrera's model is valid. This case applies to materials having large Burgers vectors e.g. organic materials.

## 3.3 FORMATION OF VISIBLE ETCH PITS:

The necessary condition for the formation of visible etch pits is governed by the kinetics of dissolution ledges as they move across the crystal surface during dissolution. Successive monomolecular ledges usually sweep across close-packed surface. In order for an etch pit to be visible under an optical microscope,the slope of the etch planes should be at least about 3° with respect to a close-packed surface. Experimentally measured pit slopes for several successful dislocation etching solutions have indeed, been found to lie in the range of 5-12°. In order for the etch pit to have a sufficiently steep slope, the ratio of dissolution velocity $V_n$ (normal) to $V_l$ (lateral or ledge dissolution velocity) must be greater than a certain value, 0.1. Second condition is that the dissolution velocity at the dislocation be greater than the average vertical dissolution velocity $V_s$ of a dislocation free portion of the surface. These necessary conditions can thus be written as:

$$V_n/V_l \geqslant 0.1 , \quad V_n > V_s .$$

For a symmetrical pit, all planes forming a pit are equally inclined, while slopes of these planes are different for asymmetric pits. A detailed study of slopes of etch pits was systematically done by Ives and Mcausland (1968). They have classified pits into three categories, depending upon the various ranges of slopes of pits on (0001) surface of zinc crystals. They reported that planes of the etch pits were vicinal faces.

Impurity may segregate around dislocations in impure crystals. Impurity may enhance greater chemical reactivity, giving rise to preferential two-dimensional nucleation in metal crystals. It is normally observed that etch pitting solutions for most of the metals and semiconductors studied so far are strong oxidizing agents. It is presumed that the first step in the dissolution process is an oxidation of crystal surface. This is followed by the removal of oxide layer. It was observed that oxide nuclei were formed on pure Cu crystals (Young, 1960) and on Ge crystals (Faust, 1963). However, these oxide nuclei were not related to dislocations. The influence exerted by impurities on and around dislocations has been discussed in detail by Gilman et al. (1958) on LiF crystal which was etched by water with the addition of impurities such as $FeF_3$, $AlF_3$ etc. They found that nature of etch pits was dependent on the concentration of $FeF_3$ in solution. The function of $FeF_3$ is to inhibit the ledge motion. It means that $V_1$ depends upon $Fe^{+++}$ concentration. The $Fe^{+++}$ ion (and such others in about

30 compounds) retards the step motion, apparently by adsorption on the steps, but does not seem to effect $V_n$. Cations ($Fe^{+++}$, $Al^{+++}$ etc.) are believed to have strong tendency to form ($FeF_6$), ($AlF_6$) complexes and that is why they play a major role and anions do not effect the pit formation. Cabrera (1956) examined theoretically the conditions for the formation of etch pits and oxide nuclei at dislocations. He observed that the energy associated with the dislocations having large Burgers vector, is sufficient to cause etch pit or oxide nuclei. Sears (1960) reviewed theory of Cabrera and modified it by including the effect of solution poison. Step poison increases the rate of two-dimensional nucleation at fixed supersaturations but markedly decreases the rate of step motion or of spreading of newly formed layers. Ives and Hirth (1960) studied the etch pit profile as a function of concentration of LiF and $FeF_3$ in the etching solution. The results were consistent with a mechanistic theory involving dissociation of LiF from unimolecular steps on it and subsequent diffusion into solution if a time-dependent adsorption of $FeF_3$ poison at the receding unimolecular steps was involved. The above theory deals with 'part diffusion part inhibitor

control of ledge kinetics'. It explains very well other results except slopes of etch pits. According to this theory, the slope of a dislocation pit should decrease with decreasing undersaturation of Lithium fluoride. Experiment showed the pit slope to be essentially independent of LiF concentration. The explanation given for the discrepancy was that the accumulation of an inhibitor on a given ledge increased as the distance between ledge and surface increased i.e. it is a time-dependent process. Westwood et al. (1961) used aqueous solutions of long chain fatty acids to reveal the point of emergence of dislcations in LiF. This shows that fatty acid may provide a ready source of potential inhibitors for a variety of crystal-etchant systems. Chemisorption and complex formation in this process is likely to affect the core energy available for the nucleation of kinks. Ives and Ramchandran (1967) studied the morphology of etched LiF surface with an electron microscope. It reveals complex structure of surface ledges on (100) cleavage face of this crystal. The ledge structure is complex due to irregular inhibition by the ferric ions. Haribabu and Bansigir (1969) after studying the role of poison and undersaturation of the etching mechanism, concluded that the stability of the complexes formed at the kink site and those formed in the solvent layer very close to the crystal surface played a very important role in the formation of etch pit.

It is known that the optical resolution of a microscope is inadequate to observe the atomic steps or the small bunches of steps in the pit nucleation and early stages of growth. How do steps move during the etching of a crystal? Where does it (poison) act? How does it act for inhibiting the nature of steps? What is the exact role of poison? The present theory is not yet developed to the extent of answering convincingly these questions.

## 3.4 ETCH PITS AND THEIR CHARACTERISTICS:

The most noticeable feature on a chemically etched surface consists of etch pits. They represent the early stages of crystal dissolution and subsequent information concerning the origin, distribution and other important aspects of pits have been sought by many workers. Etch pits are used to locate dislocations terminating on a crystal surface. Density of dislocation etch pits usually remains constant for different periods of etching. Generally it is higher in metal crystals ($10^5$ to $10^7/cm^2$), than in ionic crystals ($10^3$ to $10^5/cm^2$). Crystals with low dislocation density are desirable for study of individual dislocations by etch pit technique. Whether all etch pits reveal dislocations or all dislocations give rise to etch pits is a question, which is not yet fully answered. Dislocation etch pits are usually of same size and shape but may be of different depth. The difference in depth may be due to inclination of dislocation line or energy of a dislocation. Patel and Ramnathan (1964) observed oppositely oriented triangular etch pits as well as hexagonal etch pits on octahedral cleavages of diamond. They explained these observations by assuming different energies of various dislocations inside the crystal. It is well known that dislocation line never ends within a crystal. However, if it remains inside the crystal it must form a closed loop. The distance between the positions of depth points of a pair of point bottomed etch pits produced on a dislocation loop are varying with etching time and when the loop is exhausted pits coalesce with each other and form a single pit. Due to non-existence of dislocation line it becomes shallower on further etching.

The different types of dislocation etch pits (symmetric and asymmetric) were produced on cleavage surface of NaCl and LiF by Amelinckx (1954) and Gilman and Johnston (1956) respectively. This is found to be due to different inclinations of edge and screw dislocations. Gilman and Johnston (Loc.cit.) have shown that edge dislocation lines lie normal to the plane of observation in LiF crystals; hence symmetric pits arise after heavy etch by CP-4 etchant, while screw dislocations lie 45° to the plane of observation and etching of the screw dislocations gives rise to asymmetric etch pits though symmetrical etchant was used in both cases. They could also distinguish between aged and fresh dislocations. Etch pits formed at aged dislocations are shallower than those formed at fresh dislocations. The different types of etch pits (edge and screw) terminating on grain boundaries were distinguished by their varying depths on surface of NaCl crystals by Amelinckx (1956). Livingston (1962) developed etching technique to distinguish between positive and negative edge dislocations in copper. He found two different types of pits (light and dark) on the

(111) surface of copper single crystals. Marukuwa (1967) also observed dark and light pits on Cu (111) surface. He concluded that pits at screw dislocations had dark appearance.

It is now known that shapes of etch pits are functions of concentration of etchant, etching time, temperature and other condition of etching. The shapes of pits produced by various etchants of different concentrations on calcite cleavage surface were studied by Honess and Jones (1937), Keith and Gilman (1960), Patel and Goswami (1962), Pandya and Pandya (1961), Mehta (1972). The bounding side of a pit may be rectilinear or curvilinear depending upon the energy of an etchant. Tolansky and Patel (1957) observed rectilinear etch pits when etching was carried out on octahedral faces of diamond by fused potassium nitrate at a temperature below 475°C, while at 525°C, etching was much faster and the sides of pits become rounded. Pandya (1969) had also studied the aspects of curvilinearity of etch pits for various crystals, such as calcite and mica.

The present author has made a detailed systematic study of different shapes of pits produced at different temperatures by different concentrations of various etchants on cleavage faces of calcite.

Etch pits are usually of three types i.e. (i) Flat-bottomed, (ii) Point-bottomed and (iii) Terraced etch pits. The third type may further be subdivided into (a) Flat-bottomed with terrace structure (b) Point-bottomed and terraced with closed layers or with spiral formation. Flat-bottomed pits occur on etched surfaces at the sites of point defects. This is due to formation of chemically highly resistant layers after certain dislocation at point defects, where $V_n$ has extremely small value, nearing zero. However rate of surface dissolution $V_s$, does not become zero thereby increasing shallowness of flat-bottomed pits. Point-bottomed pits are observed at line defects intersecting the plane of observation. Depth of a point bottomed etch pit usually increases with etching time. There is also variation of normal velocity of dissolution $V_n$ with etching time. Hanke (1961) observed different slopes of the same etch pits for different periods of etching by the same etchant. Terraced etch pits are formed at the dislocations associated with the impurities (Gilman, 1960). Sometimes the distance, between any two successive layers of terraces are unequal. This was explained on the basis of unequal distribution of impurities around dislocations. Hanke (loc.cit.) has also observed stepped structure of etch pits on cleavage faces of calcite crystals etched by low concentration of glacial acetic acid. He explained that dissociation constant of the etchant at low concentration was more, while reaction product was considerably less. This gives rise to a stepped structure of etch pits.

The eccentricity of an etch pit arises due to the non-coincidence of geometrical centre with the depth point, in the plane figure of etch pit. It is reported in many cases (e.g. on NaCl by Amelinckx, 1956), on diamond by Patel (1961), on calcium fluoride by Patel and Desai (1965), on gypsum by Patel and Raju (1967). They had explained the formation of the eccentric pits at the seat of inclined dislocations ending on the surface and found no effect due to the concentration of an etchant. on the eccentricity of an etch pit. Recently Mehta (1972) showed very clearly that besides other factors concentration of an etchant does affect the eccentricity of an etch pit on calcite cleavage faces.

## 3.5 REACTIVITY OF SOLIDS:

A detailed understanding of the reactivity of solids is possible only when the following conditions are met: (i) The morphology of the reacting surface is understood. (ii) The mechanism of the reaction is known. (iii) The kinetics of all processes occurring at the surface are established. In order to understand the complex reactions occurring on the surface during etching process, one has to consider Laidler's theory of heterogeneous reactions which deals with the dissolution of a solid in a liquid, forming products. According to this theory a reaction occurring at a surface may, in general, be separated into five steps, the slowest of which will determine the rate of the overall process. The successive stages are:

1. Volume diffusion of the reacting species to the surface.
2. Adsorption of the species on the surface.
3. Reaction on the surface.
4. Desorption of the reaction products.
5. Volume diffusion of the products from the surface.

The surface reactions generally have activation energies of the order of 30 K cal, whereas for the diffusion processes the values are very small 10 K cal. Diffusion is also frequently the rate-determining step in the case of solid-liquid reactions, owing to its relatively slow rate in solution. In general the processes 2 and 4 may be expected to be the slow steps in a heterogeneous reaction, provided the activation energy of adsorption or desorption is high. Because of low activation energy the surface reaction 3 is rapid. Such a rapid reaction is generally to be expected if the adsorbed particles are atoms, the combination of which requires little or no activation energy. According to the proposed mechanism, it is very probable that the actual combination of atoms on the surface will be rapid, and hence the slow stage in the reaction should be adsorption of the reactant or desorption of product.

Several workers have developed dislocation etchants for calcite crystal but the present author has not come across any systematic study on kinetics of the entire etching process, which determine the shape of the pits. Hence an attempt is made to relate reaction rates and facet formation.

Faust (1969) studied the reactivity of germanium in various oxidizing and complexing agents and suggested that the shape of the pit was controlled by the oxidizing agent and the complexing agent controlled the rate of attack. Vaghari and Shah (1974) studied the effect of different etchants containing different concentrations of oxidizing agents on Bi-single crystals and suggested that the shape of the etch pits was dependent on the strength of the defects and reactivity of etchants. In contrast to them Bhatt et al. (1974) observed that the shape of the etch pits was neither dependent on the type of oxidant used in the etchant nor on the apparent activation energy associated with the etching process.

Baranova and Nadgornyi (1969) calculated the activation energies for the dissolution process along dislocations ($E_n$) and the tangential movement of steps ($E_t$) in glacial acetic acid and acetic acid containing water. They have concluded that the activation energy is determined by the composition of the etchant. Haribabu and Bansigir (1970) calculated the values of $E_t$ and $E_s$ for NaCl crystals employing several etchants. They showed that $E_t$ is always more than $E_s$. The present work reports a systematic study of the activation energies for the dissolution of the surace

$E_s$ and for the tangential movement of the steps away from the source $E_t$ for calcite crystals in different etchants.

In addition to the above work it also reports a detailed study of the effect of, temperature of etching on the characteristics of etch patterns and, catalytic action of d.c. electric field on shape, size, orientation and eccentricity of etch pits on cleavage faces of natural calcite crystals. It presents a detailed analysis of the rates of, surface dissolution, tangential dissolution and normal dissolution on calcite cleavages.

# CHAPTER IV

# EFFECT OF TEMPERATURE ON ETCH PIT SHAPE

# CHAPTER IV

## EFFECT OF TEMPERATURE ON ETCH PIT SHAPE

### 4.1 INTRODUCTION:

With the recognisation of imperfections in nearly perfect crystals (Seitz, 1952) and their vital role in controlling various structure sensitive properties, the etch technique has assumed greater importance. It is nowadays widely used to detect and study dislocations in crystals. Several workers have reported dislocation etchants for calcite cleavages and the present author has carried out a detailed systematic optical study of a few characteristic features of etch patterns on a cleavage surface of calcite.

The shape of an etch figure is dependent on the nature, concentration, composition and temperature of an etchant. Thus the earlier workers reported the occurrence of different shapes on cleavage faces of calcite due to various types of etchants. Even with the same etchant, the change in concentration had a significant effect on the shape of etch pits (Watt, 1959; Stanley, 1959; Pandya and Pandya, 1961; and recently Mehta, 1972 etc.). In all cases the diluent used to change the concentration of an etchant is distilled water in which calcite is very sparingly soluble (0.008 gm/lit at 20°C). It is thus clear that with the same etchant, either concentrated or diluted, the chemical reaction is not materially changed. However, the rate of reaction on a cleavage face of calcite changes and this gives rise to production of etch pits of various shapes. This obviously points to the unusual characteristics of calcite cleavages. It was also reported that even with the same concentration of an etchant, the rate of stirring of the solution has a marked effect on the shape of etch figures (Hanke, 1961; Mehta, 1972). In most of the cases earlier workers have used acetic acid and hydrochloric acid as etchants which are optically inactive. To facilitate comparison with their etching work, the present study was made by using the above two etchants only. The shapes of the etch figures produced by these etchants as a function of temperatures and concentrations are discussed in this chapter.

## 4.2 EXPERIMENTAL:

Natural crystals of calcite were obtained from various localities in India (Sivarajpur, Pawagarh, Broach (Gujarat State); Rajasthan State etc.). The crystals are fairly big with their sizes ranging from 1 cm to 15 cm with cross sectional area of the order of 3 cm x 3 cm. A big crystal was selected and etching work was carried out on small pieces obtained by cleaving such a crystal. Calcite crystal was cleaved in the usual way i.e. by giving a sharp blow with a hammer on a razor blade kept in contact with the crystal along the cleavage direction. The cleavage surface was fully immersed in a still etchant of known concentration for desired time of etching at constant temperature. The temperature of etchant was maintained to within ±0.5°C by a regulator attached to constant temperature water bath for studies at higher temperatures and by ice for studies at lower temperatures. The concentration is usually expressed by quantity (volume) of acid contained, in total volume of 100 cc. After etching the crystal for a given period, it was kept in running distilled water for sometime. It was then dried by the hot air blower. The contrast in the etch pattern under high magnification and resolution is usually poor. This is therefore, enhanced by depositing silver film on the etched surface by thermal evaporation technique described in Chapter II. High resolution microscopic technique with a variety of illuminations was used to study the etch patterns on the cleavage faces. In all the cases the central region of the cleavage surfaces was investigated in detail. This was necessitated by the fact that the edges from which the cleavage had propagated, were regions of high distortion.

## 4.3 OBSERVATIONS AND RESULTS:

Change in shape of etch pits with change in temperature of different etchants:

### 4.3.1 Etchant A : (1% hydrochloric acid, A.R. quality,10N).

It is known that calcite reacts very strongly with concentrated inorganic acids. Strong hydrochloric acid

FIG. 4.1a X110

FIG. 4.1b X110

reacts violently with calcite to form highly soluble reaction products, calcium chloride, water and gaseous carbon dioxide. The later goes to the atmosphere.

In order to assess the influence of various factors on shape of etch pits, it is desirable to vary systematically one factor, by keeping all other factors constant. In the present work, the effect of temperature on the etch pit shape is investigated by keeping all other factors including time of etching constant. Fig. 4.1a (X110) shows a photomicrograph of a freshly cleaved surface etched by 1% hydrochloric acid for 20 seconds at room temperature whereas its counterpart was etched by the same etchant for the same period at 5°C [Fig.4.1b (X110)].

Certain characteristic features of these photomicrographs of oppositely matched cleavage faces of calcite are as follows:-

(i) The cleavage lines on fig. 4.1a and 4.1b are affected by etching, showing clear shift in accordance with the observations reported by earlier workers (Patel and Tolansky, 1957; Pandya and Pandya, 1959). Further there is no correspondence for cleavage line B (Fig. 4.1b) with that on Fig. 4.1a. This shows that the rate of etching of surface shown in Fig.4.1a must be fairly high compared to that in Fig. 4.1b. This is supported by the fact that though the period of etching is same for both counterparts almost all pits (Fig.4.1a) have bigger sizes than those in Fig.4.1b. Room temperature (35°C) etching has produced pits with outlines of almost regular pentagons (Fig. 4.1a) whereas low temperature etching (5°C) has produced curvilinear quadrilateral pits (Fig.4.1b). The eccentricity of regular pentagon pits is practically zero whereas the pits with curvilinear quadrilateral outlines are eccentric. The sloping planes producing quadrilateral and pentagonal outlines are of unequal sizes. The tangent at the central point of the curved line in quadrilateral pits is perpendicular to the line of symmetry [110] .

(ii) There is a good correspondence for the rows of etch pits in both the photomicrographs. The number of pits per unit length of the row in Fig.4.1a is less than that on Fig. 4.1b. Hence the pits are more closely spaced in Fig.4.1b. This appears to be due to the fact that many pits in such a row, unlike the row pits in Fig.4.1a, are having terraced structure.

(iii) Although the thermal condition of etching is different in both the cases, there is a fairly one to one correspondence of etch pit position in both the photomicrographs. However, there is not complete correspondence of etch pits on Figs. 4.1a and 4.1b so far as the characteristics of these patterns are concerned.

(iv) Flat-bottomed pits 3, 15 and 17 (Fig.4.1a) match with the point-bottomed pits in the corresponding positions. Similarly point-bottomed pits 2, 10,13, 14, 16 and 19 (Fig. 4.1a) correspond with identically numbered pits (Fig.4.1b). In this correspondence there are subtle differences:

(a) Pit no.15 is surrounded by point-bottomed pits 14 and 16 (Fig.4.1a) whereas the point-bottomed pit no.15 (Fig.4.1b) is flanked by flat-bottomed pits 14 and 16.

(b) Flat-bottomed pit no.3 (Fig.4.1a) has correspondence with a point-bottomed pit no.3 (Fig.4.1b). The adjoining pit no.2 in Fig.4.1a is point-bottomed whereas in Fig.4.1b is found at the corresponding place a flat-bottomed pit. Further the order of pits (Fig.4.1a) viz. flat-bottomed pit followed by point-bottomed pits is different from that in Fig.4.1b which shows at the centre a staunted flat-bottomed pit with point-bottomed pits on either side. Also note that a few sloping faces of point-bottomed pits no.2 and 11 (Fig.4.1a) are not clear.

(c) For a group of pits no.17, besides the characteristics mentioned for pit no.15 (Fig.4.1a), it is of interest to note that the flat-bottomed pit (Fig.4.1a) has a correspondence with a terraced pit (Fig.4.1b).

(v) (a) Flat-bottomed pit no.10 followed by point-bottomed pits no.11 and 12 (Fig.4.1b) has a correspondence with point-bottomed pit no.10 associated with point-bottomed pits no.11 and 12.

(b) Point-bottomed pits13 and 19 (Fig.4.1a) correspond with flat-bottomed pit 13 and 19 (Fig.4.1b). It is interesting to note that flat-bottomed pitsno.13 (Fig.4.1b) has a terraced structure whereas such structure is absent in pits no.13 and 19 (Fig.4.1a)

(vi) For pit no.8 (Fig.4.1a) the corresponding pit position in Fig.4.1b is missing.

(vii) It is quite significant to note that non-terraced pits no. 9, 10, 11, 13, 17 and 20 (Fig. 4.1a) match with the identically numbered terraced pits (Fig.4.1b). Most of these pits in both these photomicrographs possessed sharp point of maximum depth.

(viii) A terraced pit no.18 (Fig.4.1a) matches with a pit no.20 of similar structure (Fig.4.1b).

It should be remarked that the present author had carefully studied several matched cleavage counterparts and almost all characteristics mentioned above were observed. Further curvilinear quadrilateral outline of etch pits (Fig.4.1b) could be observed upto etching temperature 0°C to 10°C. As the temperature of etching increases from 0°C to 10°C, the pit shape remains practically of the same type. However, with fixed time of etching the lateral area of pits on the cleavage surface increases with temperature. Further the author could not conclusively establish the linear relationship between the area of a pit and temperature.

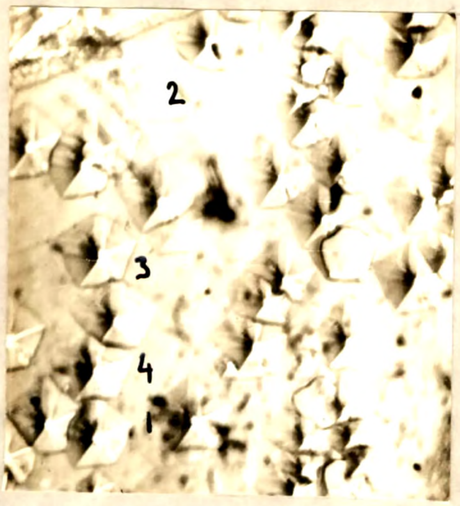


FIG. 4·2a X100

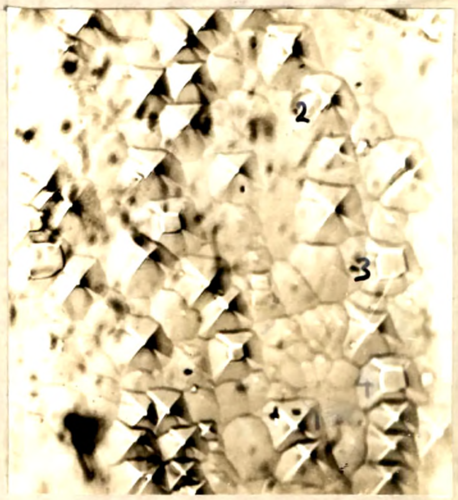


FIG. 4·2b X100

It should be noted that the quadrilateral pits have only one side curved and the convexity of this curved side is towards the corner where the crystal edges making obtuse angles with one another meet.

It was also observed that the curvilinear quadrilateral pits can also be produced on calcite cleavage faces by A.R. quality hydrochloric acid with concentration ranging from 2.0% to 4.0% at room temperature. This shows that low temperature etching by 1% hydrochloric acid is equivalent to room temperature etching of calcite cleavages by 2.0% to 4.0%.

Figures 4.2a and 4.2b (X100) represent photomicrographs of oppositely matched cleavage faces etched by 1% hydrochloric acid for 20 seconds at room temperature and at 55°C respectively. It is clear that the geometrical outlines of pyramidal and flat-bottomed etch pits on the cleavage surfaces are nearly regular pentagons (Fig.4.2a) and hexagons with fairly less eccentricity (Fig.4.2b). The outlines of hexagons are not regular and sharp; the quality or texture of the surface (Fig.4.2b) is more rough than that of Fig. 4.2a. In addition to several features mentioned above for photomicrographs (Figs.4.1a and 4.1b) e.g., correspondence of point-bottomed pits (3 and 4 in Fig.4.2a)

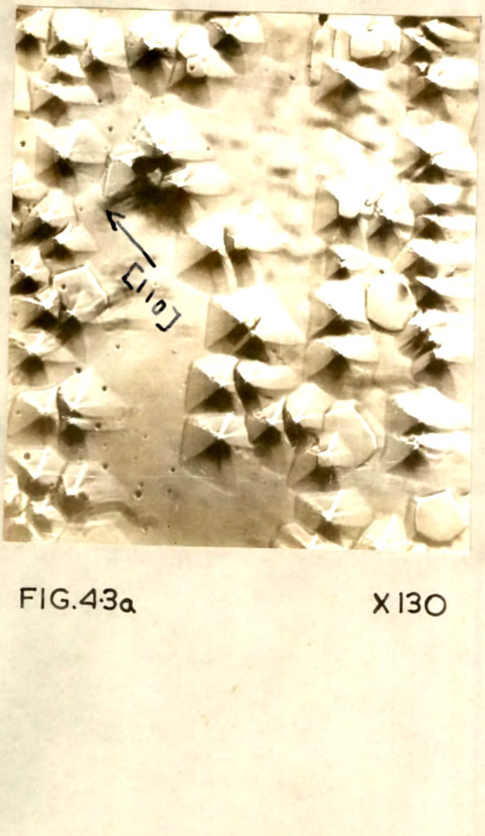


FIG.4·3a X130

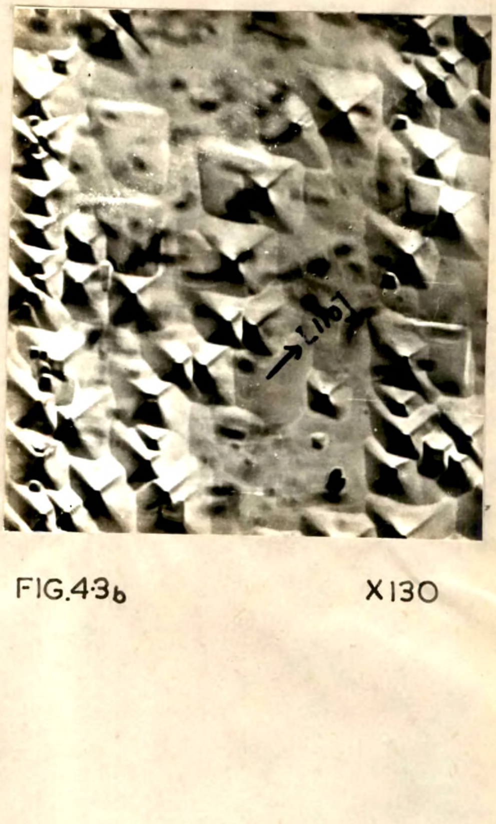


FIG.4·3b X130

with the flat-bottomed pits (3 and 4 in Fig.4.2b); correspondence of flat-bottomed pits (like 2 in Fig.4.2a) with point-bottomed pits (like 2 in Fig.4.2b), matching of a point-bottomed pit (1 in Fig.4.2a) with the corresponding point-bottomed pit (1 in Fig.4.2b), the densities of pits on both the surfaces are almost equal.

Figs. 4.3a and 4.3b (X130) exhibit another pair of matched cleavage faces etched by 1% hydrochloric acid for 20 seconds at room temperature and at a temperature of 75°C respectively. The general features mentioned above (Fig.4.1a , 4.1b and 4.2a, 4.2b) are reproduced in these photomicrographs. However the temperature has greatly affected the shape of etch pits in Fig.4.3b; the geometrical outlines of etch pits is rhombic with shorter diagonal along the direction [110] .

### 4.3.2 Etchant B : (0.45% double distilled glacial acetic acid)

In order to study the change in morphology of etch pits and the change in order of shape cycle of pits, it is felt that the use of other etchants of entirely different chemical nature is likely to throw more light on these interesting facets of etching. From the work

FIG.4·4a X 110

FIG.4·4b X 110

of previous researchers in the field of crystal dissolution in general and on the etching of calcite cleavages in particular (e.g. see Mehta, 1972) a judicious choice of etchant is made viz. diluted glacial acetic acid at different temperatures. The present author had selected etchant glacial acetic acid of 0.45% concentration, the diluent being pure distilled water. It was shown (Mehta, 1972) that this etchant gave rise to well defined rhombic etch pits. Fig. 4.4a (X110) and 4.4b (X110) show photomicrographs of oppositely matched cleavage faces etched by 0.45% glacial acetic acid for 30 seconds at temperatures of 30°C and 60°C respectively. These pairs exhibit features which are different from those observed in the previous figures. The matching of pits is excellent with almost identical densities of pits on both the faces. Further unlike the characteristics of previous figures, a point-bottomed pit on one face corresponds with a point-bottomed pit on the other; similar is the case for flat-bottomed pits. The cleavage line on Fig.4.4b corresponding to the line AB in Fig.4.4a is eaten away by fast etching at comparatively high temperature. A little increase in temperature of etching viz. from

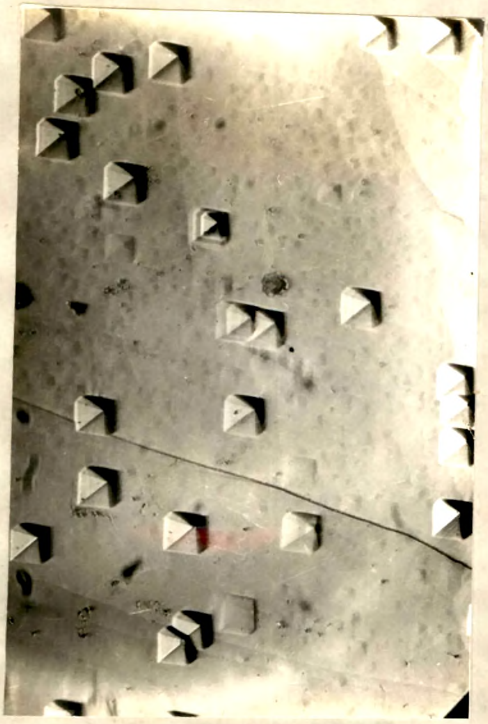


FIG.4·5a X110

FIG.4·5b X110

FIG.4·6a X125

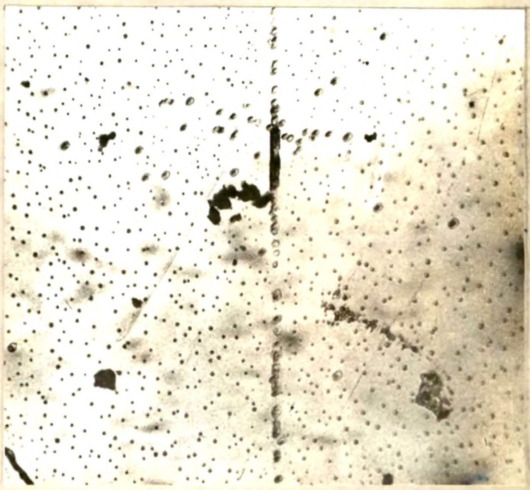


FIG.4·6b X125

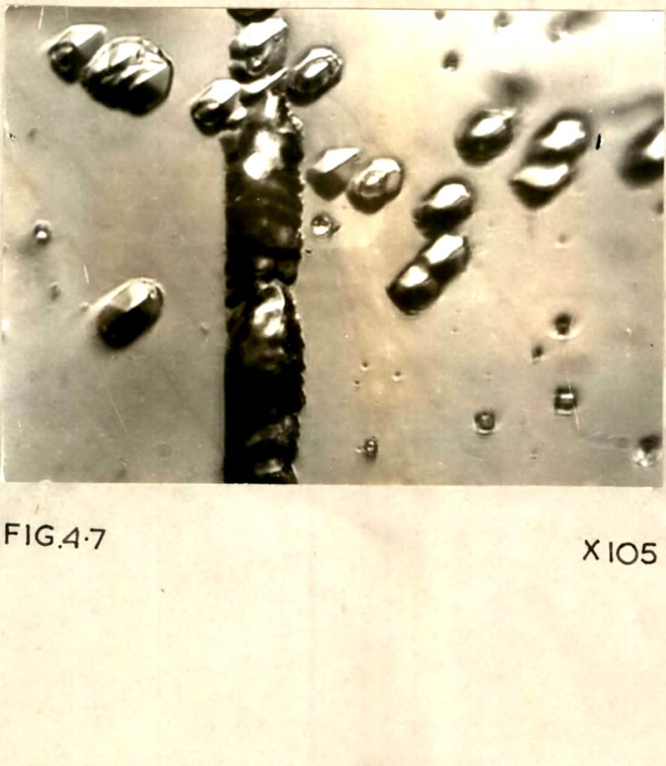


FIG. 4·7 X 105

30°C to 35°C (Fig.4.5a X110), changes the shape of etch pits with a clear tendency for the complete development of hexagonal pits. The corresponding region on the matched face is shown by Fig.4.5b (X110). There is complete matching of hexagonal etch pits on both these counterparts.

### 4.3.3 Etchant C : (60% double distilled glacial acetic acid)

It was found from experiments conducted at low temperatures that when the temperature of the etchant was lowered than 3°C the etchant 'C' was unable to produce visible etch pits on the specimen observed under very high optical magnification and resolution. However, the cleavage surface was found to be covered with dots. When the etching was carried out at a temperature of 5°C for 7 minutes by 60% glacial acetic acid, the visible etch pits could be observed on the cleavage surface (Fig.4.6b X125). It is seen from the photomicrograph that the shape of etch pits is not clear within the optical limit of the microscope. Fig.4.7 (X105) represents a part of the region of the specimen (Fig.4.6b) under high optical magnification and resolution. It is

FIG.4.8a X90

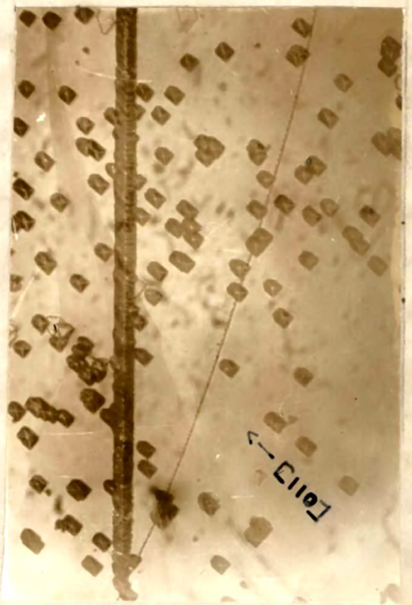


FIG.4.8b X90

FIG.4.9a X105

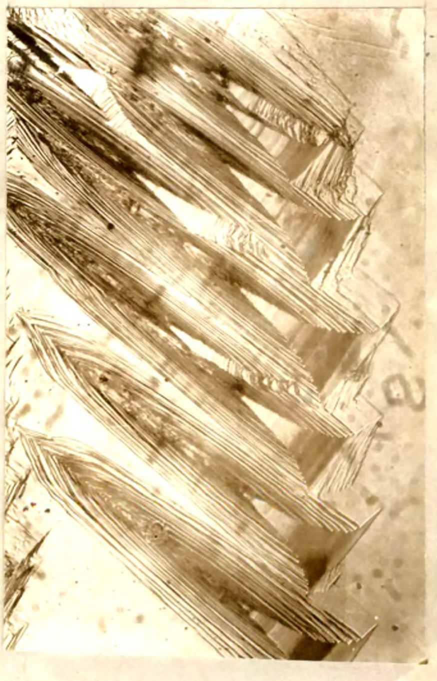
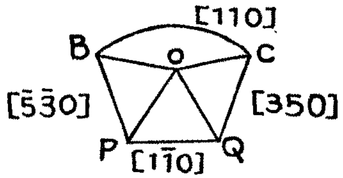
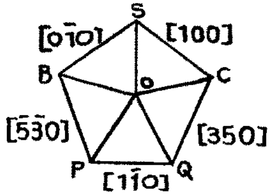
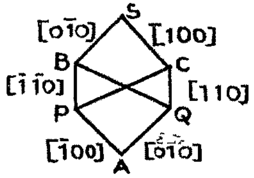
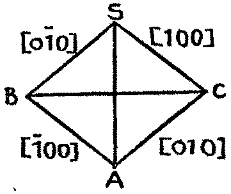
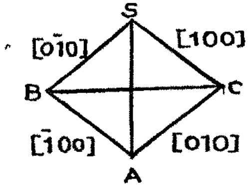


FIG.4.9b X105

clear from both the figures the effect of the chemical reaction and a preferential attack of the etchant on the cleavage surface. Etch pits with regular geometrical outlines may be produced on prolonged etching. Fig.4.6a(X125) is the cleavage counterpart etched by the same etchant for same period at room temperature. The shape of the pits is elongated pentagons with base perpendicular to direction [110].

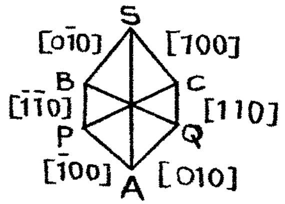
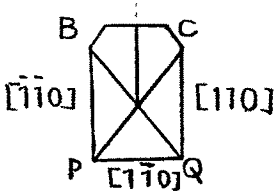
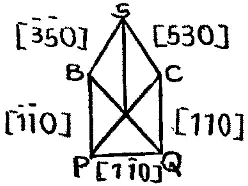
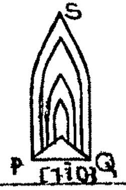
Fig. 4.8a and Fig.4.8b (X90) show photomicrographs of matched cleavage faces etched by 60% glacial acetic acid for 7 minutes at room temperature (35°C) and at 20°C respectively. The geometrical outlines of etch pits are elongated pentagons and rectangles respectively. Further, pits on both these figures have one to one correspondence except for the difference in their surface areas. The effect of temperature on reaction rate is more along [110] than in a perpendicular direction, viz. $[1\bar{1}0]$. Hence elongation of pits is due to change in temperature of etching. This is shown very clearly by photomicrographs (Figs. 4.9a and 4.9b, X105) which exhibit pits having elongated pentagonal and javelin outlines on the cleavage faces. These pits are produced on etching the oppositely matched cleavage faces by 60% glacial acetic acid for 7 minutes at room temperature and 85°C respectively. Besides this the pits with pentagonal outlines are

## SHAPES OF ETCH FIGURES WITH CHANGE IN TEMPERATURE OF ETCHANTS (A,B,C)

| Sr. No. | Etchant | Temperature range | Shape of etch pit | Quality of pit shape |
|---|---|---|---|---|
| 1. | A<br>(A.R. quality HCl 1%) | 0°C to 10°C |  | 1. Curvilinear quadrilateral<br>2. Fairly clear outlines<br>3. High eccentricity |
| 2. | " | 10°C to 50°C |  | 1. Nearly regular pentagon<br>2. Sharp outline<br>3. Zero eccentricity |
| 3. | " | 50°C to 70°C |  | 1. Hexagon<br>2. Poor outlines<br>3. Zero eccentricity |
| 4. | " | 70°C to 90°C |  | 1. Rhombic<br>2. Poor outlines<br>3. Some pits are eccentric |
| 5. | B<br>(Doubly distilled glacial acetic acid 0.45%) | 20°C to 35°C |  | 1. Well-defined rhombic<br>2. Clear outlines<br>3. Finite eccentricity |

contd....

TABLE 4.1 (Contd.)

| Sr. No. | Etchant | Temperature range | Shape of etch pit | Quality of pit shape |
|---|---|---|---|---|
| 6. | B<br>(Doubly distilled glacial acetic acid 0.45%) | 35°C to 90°C |  | 1. Well-defined hexagon<br>2. Almost zero eccentricity<br>3. Development of sides with 110 direction is very little. |
| 7. | C<br>(Doubly distilled glacial acetic acid 60%) | 0°C to 10°C | | 1. Pits with irregular outlines |
| 8. | " | 10°C to 22°C |  | 1. Rectangular outlines<br>2. Clear tendency to develop into pentagon pits |
| 9. | " | 22°C to 60°C |  | 1. Elongated pentagon<br>2. Clear outlines |
| 10. | " | 60°C to 90°C |  | 1. Terraced pits<br>2. Javelian outlines<br>3. Line centre. |

point-bottomed whereas pits with javelin outlines are terraced with line centre. This indicates that all planes forming a pit meet in a line instead of a point. The line is in the direction [11K] whose projection on the observation plane gives line of symmetry [110] .

## 4.4 DISCUSSION:

On going through the various shapes of etch pits produced on freshly cleaved surfaces of calcite crystals by etchants A, B and C with temperatures ranging from 0°C to 90°C; it is clear that a complete cycle of etch pit shapes is depicted and all shapes are symmetrical about the direction [110] which is usually passing through the centre of plane figure of a pit, projected on a cleavage surface. Further for a given range of temperature all pits usually exhibit same geometrical outlines irrespective of their origin on the cleavage surface. All these observations regarding shapes of etch pits produced by different concentrations of various etchants at different temperatures are summarised in Table 4.1.

It is worthwhile to discuss the following characteristic features of etch pits revealed by all etchants (A, B and C):-

1. (a) Observation of fixed shape at certain temperature (range) of an etchant.
   (b) Change of shape with change in temperature (range) of an etchant.
   (c) Production of identical shapes on a cleavage surface by different etchants at different temperatures (e.g. see Figs. 4.3b & 4.4a; Figs. 4.2b and 4.4b; Figs. 4.1a and 4.6a).

2. (a) Characteristics of etchant A.
   (b) Characteristics of etchant B.
   (c) Characteristics of etchant C.

These features will now be subjected to close scrutiny and detailed discussion in the following pages:-

### 4.4.1 (a) Observation of fixed shape at certain temperature (range) of an etchant:

Different shapes of etch pits are produced due to different chemical reaction rates along various directions on a crystal surface. Chemical reaction rates on a crystal surface during the process of etching may change their magnitudes or directions or both due to several ~~features~~ factors such as composition of an etchant, concentration of an etchant, etching period, condition of etching (static or dynamic), temperature of an etchant and a crystal, anisotropic character of a crystal surface, surface imperfections, imperfections terminating on the surface and the nature and strength of imperfections and their interactions. With reference to the cleavage surface of calcite crystals, the first four factors were studied in much detailed in this laboratory (Mehta, 1972). The remaining factors are given serious consideration in the present report.

It is obviously difficult to predict the dominant directions of reaction rates at a particular temperature of an etchant on a crystal surface. The observations presented above clearly indicate that the change in magnitude of reaction rates within a definite range of temperature does not change the shape of an etch pit, it simply accelerates or retards the growth of pits without introducing a change in shape. Further the present author has a definite experimental evidence (cf. Chapter VI) to show that in a given range of temperature, the energy involved during the chemical reactions between an etchant having a definite concentration and crystal surface under certain conditions does not noticeably alter the direction of reaction rates and, therefore, does not induce a change in the shape of etch pits. This appears to be due to the fact that changes in energy with a change of temperature within a given range are so small that they do not produce any significant effect on the etch pit morphology. If the temperature changes are beyond a given range, the energy changes are experimentally recognizable. These in turn affect the directions of reaction rates with a consequent change in etch pit morphology.

### 4.4.1 (b) Change of shape with change in temperature (range) of an etchant:

From the whole spectrum of etch pit shapes it is clear that pits are usually bound by directions of low indices. Since the shapes (plane geometrical outlines) of etch pits remain nearly same, when they are produced at line defects or at point defects, the normal rate of dissolution for those pits does not affect the shape noticeably. The factor governing the shape of etch pits is the lateral (tangential motion of steps) rate of dissolution, $V_t$ along different directions on the surface. From the study of changes of shapes of pits with progressive change in the temperature of an etchant, it can be conjectured that there is a systematic change in the direction of reaction rates on the surface. This in turn suggests creation of new directions of reaction rates and elimination or modification of old directions. This view is supported by the fact that when the pit shape changes from quadrilaterals to pentagons, produced by an etchant (1% hydrochloric acid in the present case), when etching temperature changes from one temperature range (0°C to 10°C) to another temperature range (10°C to 50°C), the fourth curvilinear side is modified into two distinct directions of reaction rates in addition to the reaction rates along those direction for quadrilateral pits, and has consequently given rise to development of two new planes BSO and SCO (Table 4.1) resulting into a pit with pentagonal outline on the surface. Similarly hexagon etch pits change into pits with rhombic outlines by elimination of sides along $[\bar{1}\bar{1}0]$ and $[110]$. This means that the reaction rates shown by the motion of ledges along $[\bar{1}\bar{1}0]$ and $[110]$ are reduced to zero. It should be noted that directions of reaction rates which are making equal angles with the line of symmetry [110] are simultaneously eliminated or produced by a systematic change in temperature of an etchant. Due to production or annihilation of pairs of reaction rates around [110] , the point-bottomed (pyramidal) pit or flat-bottomed pit with any geometrical outline on the surface remains symmetrical about the line of symmetry of a crystal face [110] .

### 4.4.1 (c) Production of identical shapes on a cleavage surface by different etchants at different temperatures:

Identical shapes of etch pits are obtained by using glacial acetic acid and hydrochloric acid in appropriate concentration and temperature range. Rhombic etch pits are obtained by using 0.45% glacial acetic acid at 30°C and by 1% hydrochloric acid at 75°C. This suggests that directions of reaction rates are similar for both acids but their magnitudes are more for hydrochloric acid than for glacial acetic acid. This can be inferred from the fact that for equal period of etching the average lateral area of a pit produced by 1% hydrochloric acid is more than that of a pit produced by

0.45% glacial acetic acid. This is also true for hexagonal pits which are obtained by etching the cleavage surfaces by 0.45% glacial acetic acid and 1% hydrochloric acid at 60°C and 55°C respectively.

Further the quality of etch pits produced by 0.45% glacial acetic acid is better than that of pits produced by 1% hydrochloric acid e.g. rhombic etch pits produced by 0.45% glacial acetic acid (Fig.4.4a) and by 1% hydrochloric acid (Fig.4.3b); similarly hexagonal etch pits produced by 0.45% glacial acetic acid (Fig. 4.4b) and by 1% hydrochloric acid (Fig.4.2b) .

Of the two acids 1% hydrochloric and 0.45% glacial acetic acid, the hydrochloric acid reacts comparatively violently with the cleavage surface. Hence the surface dissolution and the tangential dissolution of a pit are fairly high.

In order to support this statement it is desirable to have quantitative measurements of these rates. The rate of surface dissolution is measured by step plate technique (Ives and Plews, 1965) and/or weight loss method by using a semimicrobalance. The

TABLE 4.2

| chant | Shape of etch pits | Temp. in °C | Average tangential dissolution rate $V_t$ $\times 10^{-4}$ cm/sec. | Average surface dissolution rate $V_s$ $\times 10^{-4}$ cm/sec. | $\frac{V_t}{V_s}$ | Remarks |
|---|---|---|---|---|---|---|
| 'A'<br>% HCl) | Rhombic etch pits | 70 | 6.6 | 0.26 | 25.3 | |
| | | 80 | 6.6 | 0.28 | 23.6 | |
| | | 90 | 6.9 | 0.58 | 11.9 | |
| 'B'<br>.45%<br>ĀC) | Rhombic etch pits | 25 | 0.88 | - | - | $V_s$, not detectable |
| | | 30 | 1.3 | - | - | " |
| | | 35 | 1.9 | 0.017 | 113.3 | Estimated value of $V_s$ |
| 'A'<br>% HCl) | Hexagon etch pits | 50 | 6.2 | 0.20 | 31.0 | |
| | | 60 | 6.6 | 0.24 | 27.5 | |
| | | 70 | 6.6 | 0.26 | 25.3 | |
| 'B'<br>.45%<br>ĀC) | Hexagon etch pits | 50 | 2.6 | 0.053 | 50.0 | Estimated value of $V_s$ |
| | | 60 | 3.3 | 0.067 | 50.0 | " |
| | | 70 | 4.0 | 0.100 | 40.0 | " |
| 'A'<br>% HCl) | Pentagon etch pits | 30 | 4.5 | - | - | $V_s$, not reliable |
| | | 35 | 5.0 | 0.17 | 30.0 | |
| | | 50 | 6.2 | 0.20 | 31.0 | |
| 'C'<br>0%<br>ĀC) | Pentagon etch pits | 30 | 0.16 | - | - | $V_s$, not dedectable |
| | | 35 | 0.21 | - | - | " |
| | | 50 | 0.52 | 0.015 | 35.0 | Estimated value of $V_s$ |

TABLE 4.3

| Shape of etch pits | Temp. in °C | $V_{t_A}$ $\times 10^{-4}$ cm/sec | $V_{t_B}$ or $V_{t_C}$ $\times 10^{-4}$ cm/sec | $\frac{V_{t_A}}{V_{t_B}}$ or | $\frac{V_{t_A}}{V_{t_C}}$ |
|---|---|---|---|---|---|
| Rhombic | 70 (A) | 6.6 | 0.88 | 7.50 | |
| | 25 (B) | | | | |
| | 80 (A) | 6.6 | 1.30 | 5.07 | |
| | 30 (B) | | | | |
| | 90 (A) | 6.9 | 1.90 | 3.63 | |
| | 35 (B) | | | | |
| Hexagon | 50 (A,B) | 6.2 | 2.60 | 2.38 | |
| | 60 (A,B) | 6.6 | 3.30 | 2.00 | |
| | 70 (A,B) | 6.6 | 4.00 | 1.65 | |
| Pentagon | 30 (A,C) | 4.5 | 0.16 | | 28.12 |
| | 35 (A,C) | 5.0 | 0.21 | | 23.81 |
| | 40 (A,C) | 6.2 | 0.52 | | 11.92 |

rate of tangential (lateral) dissolution of a pit is measured by a filar micrometer eyepiece. The details of these methods are given in Chapter VI. These measurements on rates of dissolutions are given in Table 4.2. It is thus clear quantitatively from these measurements (Table 4.2) that for obtaining good quality pits - well defined and sharp pits - by an etchant the ratio of lateral rates of dissolution to the surface dissolution rate must have a large value; the Table 4.3 prepared from Table 4.2 also indicates that for obtaining highly symmetrical good quality etch pits the widening rate of pits should be less and that for given etchants producing pits of identical shapes those pits with comparatively low widening rates and greater value of $V_t/V_s$ are of better quality than the pits of high widening rates produced by another etchant.

It is known that the conditions for the formation of visible etch pits on a crystal surface subjected to etching, are (i) $V_n/V_t \quad 0.1$ (ii) $V_n/V_s \quad 1$ (Robinson, 1968). The conditions can also be understood by taking into consideration the above statement regarding the widening rates ($V_t$) and surface dissolution rates ($V_s$).

It is estimated by using light profile and interference techniques (including multiple beam interferometry) that there is not much noticeable variation in the normal rate of dissolution ($V_n$) with the change in temperature. Hence when the rates of tangential dissolution and surface dissolution are more than these prescribed by the above conditions, the pit shape will be of a poor quality. Assuming the simultaneous validity of the above two conditions, their combination yields $(V_t/V_s) \geqslant 10$. A critical study of Table 4.2 will show that for obtaining pits of fairly good quality at various temperatures the ratio $(V_t/V_s)$ must be much greater than 30 consistent with magnitudes of reaction rates at different temperatures. Further from a study of $V_t/V_s$ for etchants B and C (Table 4.2) it is very clear that, higher is the value of $V_t/V_s$, better is the quality of etch pits. In view of the limitations of the optical microscope (step plate technique) and the semi-microbalance (weight loss method), it is difficult to place an upper limit on the value of $(V_t/V_s)$ for obtaining pits of excellent quality produced by an etchant on a crystal surface.

### 4.4.2 Requirements of a good etchant:

It is well-known that an etchant should possess the following characteristics:-

(i) It should be of such a composition that it will give good all round results and reveal the greatest number and variety of structural defects, characteristics and irregularities present. At the same time, it should be able to distinguish its effect from those produced by any of the etchants which can attack only definite types of defects. Thus this selective etching should enable one to study only specific defects.

(ii) It should be simple in composition and stable so that its concentration will not change appreciably upon standing or during use at room temperature and also if possible at moderately higher or lower temperatures.

(iii) It should have constant characteristics at a particular temperature so that the conditions of etching can be easily reproduced. The important conditions of etching are as follows:-

(a) Temperature of etching:

The rate at which an etchant attacks a specimen depends upon the temperature at which etching takes place.

The precise influence of temperature, however, varies according to the composition (amount of impurity present and previous history of the specimen). It is, therefore, desirable for reproducible results to carry out etching experiments only at definite constant temperature.

(b) Time of etching:-

The time of etching is perhaps one of the important factors contributing to successful etching and attendant appearance of the structure enabling their detailed study possible with the help of optical techniques. For example, if the time of etching is short as compared to that appropriate for a particular material, the etch structure will not be completely developed nor will there be sufficient details revealed to permit accurate interpretation of the etched area. However, too long a time of etching is just as unsatisfactory as one too short, owing to details of the surface structure being thereby obscured to varying degrees and frequently some parts of the structure being completely obliterated. The time of etching depends upon the conditions of the surface (freshly cleaved surface, heat treated surface etc.) and the temperature and the nature of etchant.

(iv) While etching a specimen it (etchant) should not form products which will precipitate on the surface of the specimen considered, but must have such a composition that reaction products are immediately dissolved chemically or physically in the solution. They must possess closer affinity with the etchant than with the specimen.

(v) It should be non-injurious and non-toxic to the person conducting the work.

(vi) For orientation determination, the etchant should develop etch pits or facets with plane faces accurately parallel to the crystallographic planes of low indices.

The above presents, in general, the requirements for the development of a good etchant. In view of these requirements and the discussion of the following points the characteristics of the etchants used in the present investigation will now be considered:

(i) Matching of etch patterns on oppositely matched cleavage faces of calcite.

(ii) Internal structure of etch pits, on matched faces.

(iii) Quality of pits.

(iv) Change of shapes due to change from one etching temperature range to another.

(v) Dependence of shape of etch pits on time of etching.

(vi) Time of etching.

(vii) Background micropitting.

In addition to these there are also a few noticeable features of each etchant, which will also be presented. Further, it should be remarked here that the three etchants A,B and C used by the author are proved to be dislocation etchants.

### 4.4.2 (a) Characteristics of Etchant A:

The observations reported earlier on the etching of calcite cleavages by this etchant clearly indicate that so far as the location of etch pits is concerned, there is a perfect matching. However, the internal structures of pits on either cleavage counterparts are not fully reflected. Since this etchant is shown to be a dislocation etchant, the correspondence of a flat-bottomed pit on one face with that of point-bottomed pit on another, or the correspondence of two point-bottomed pits adjoining a flat-bottomed pit on one face with that of two flat-bottomed pits flanked by a point-bottomed pit or the matching of a point-bottomed or flat-bottomed pit on one face with a missing place etc. can be explained on the basis of the nature, geometry and motion of dislocations. However one feature which stands out prominently is the correspondence of terraced pits - a number of terraced pits - on one cleavage face with non-terraced pits on the other face. Since all factors except temperature are kept constant during etching, temperature of etching is going to be a deciding factor in resolving this anomaly of mismatching of internal structures of etch pits on the matched cleavage faces. Thus low temperature etching (Fig. 4.1b) produced a terraced structure of pits, whereas comparatively high temperature etching (Fig. 4.2b) gave rise to a large number of non-terraced etch pits. The obvious conclusion is the effect of temperature in inducing different internal structures of etch pits on matched cleavage faces. However it is difficult to jump to this conclusion in view of the fact that the use of one etchant at comparatively low and high temperatures cannot decisively lead to this rationalization. Hence it is necessary to study the effect of temperature of etching by many other known dislocation etchants.

The quality of pits includes consideration of the shape, size and symmetrical nature of pits. The earlier observations show that at a given temperature the sizes of etch pits are more or less identical and that the sizes of pits, in general, and their lateral areas in particular increase with temperature when all other factors affecting etching are maintained constant. Low temperature etching produces fairly good quality pits so far as the size and shape are concerned; however the pits do not reflect the symmetry of the calcite crystal or the symmetry of the cleavage face. High temperature etching produces pits with inappropriate orientation of their sloping faces, affecting the sharpness of edges of pits on a cleavage face. It is observed that the shapes of etch pits change with a change in the temperature range of an etchant; the transition temperature is not sharply well-defined. As a matter of fact at the transition temperature pits having plane figures of both the types are usually found. It is also noted that with the increase of etching period, the geometrical shape of an etch pit changes. In the present case it changes from quadrilateral outline to a pentagonal outline with the increase of etching time. Since the etchant A (1% HCl) reacts fairly violently with calcite crystal, the etching is very rapid; hence it is difficult to control the reaction rates. Attempts were made in the present investigation to control this rate by reducing etching time, which is 20 seconds. This is indeed too short a time of etching. Further rapid etching during etching period of 20 seconds, has created a large amount of background micropitting. These factors indicate the poor quality of the etchant.

### 4.4.2 (b) Characteristics of Etchant B:

The observations (Figs. 4.4a and 4.4b; Figs. 4.5a and 4.5b) exhibit perfect matching of etch pits on oppositely matched cleavage faces. Even the internal features have a good correspondence on either cleavage faces. These features can be explained elegantly on the basis of the nature, geometry and motion of dislocations. The pits are well-defined, sharp, and exhibit the symmetry of the cleavage face of calcite crystal. Their geometrical shapes are not dependent on time of etching. The etching time is 30 seconds which is indeed little low. The geometrical outlines of pits and their eccentricities to a certain extent are highly sensitive to small changes in temperature. The transition temperature is therefore more definite than the corresponding one in the previous case (etchant A). Background micropitting is very less. This shows that although the etching time is small (30 seconds) the preferential attack of this etchant is more and well located than that of the previous etchant A.

### 4.4.2 (c) Characteristics of Etchant C:

The photomicrographs (Figs. 4.6a, 4.6b and 4.7) show vividly the mismatching of etch patterns on the oppositely matched cleavage faces. Further the etching at low temperatures is highly irregular and non-selective. As the temperature increases, the preferential etching ~~attack~~ is more than the general dissolution. Hence pits are formed at definite spots. The figs. 4.8a and 4.8b indicate the matching of etch pits. However internal structures are not evenly reflected on matched faces. The quality of etch pits, reflected by size, shape and symmetry is similar to the one discussed in 4.4.2(a) etchant A. The temperature at which the change of etch pit shapes takes place is not well-defined. The geometrical shapes of etch figures in the present case are dependent on the time of etching which is seven minutes. This is indeed a comfortable time of etching because little error in judging the time will not be magnified in the increasing size and shape of etch pits. The background micropitting is also low. As the temperature of etching increases, the lateral areas of etch pits increase considerably; they are accompanied by the formation of terraced structures (Fig. 4.9b).

### 4.4.3 Determination of coefficient of linear expansion along [110] :

If temperature is the only factor responsible for the increase of lateral dimensions of etch pits produced

TABLE 4.4

| Sr. No. | Temp. in °C | Average length of pit in 110 direction in cm $\times 10^{-4}$ |
|---|---|---|
| 1. | 20 | 38 |
| 2. | 30 | 65 |
| 3. | 35 | 90 |
| 4. | 50 | 220 |
| 5. | 60 | 420 |
| 6. | 75 | 530 |
| 7. | 85 | 590 |
| 8. | 90 | 650 |

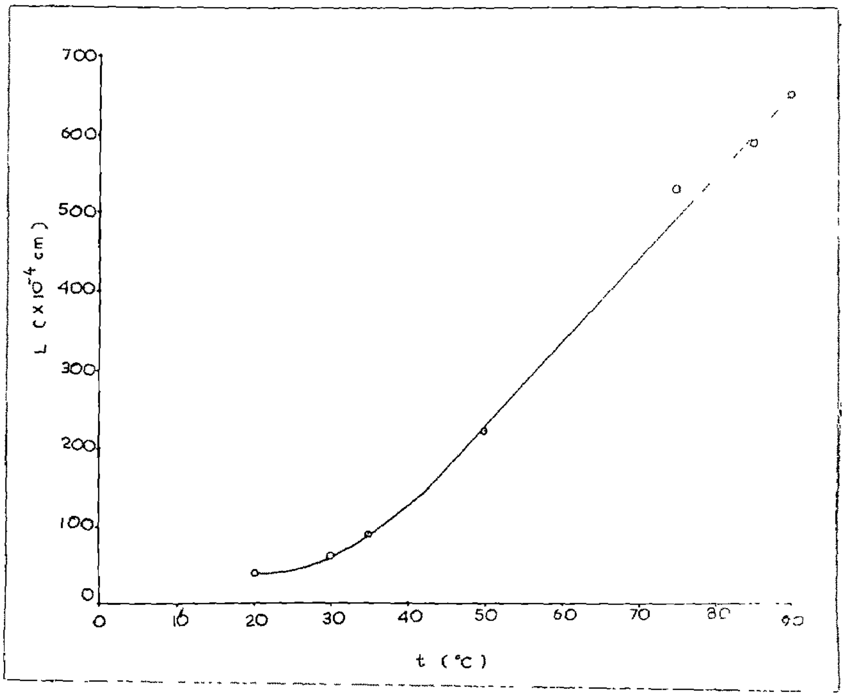

700
600
500
400
300
200
100
0
L ( x 10$^{-4}$ cm )
0
10
20
30
40
50
60
70
80
90
t ( °C )

FIG.4·10

by an etchant on a cleavage surface by etching it for a constant period of etching at all temperatures it is possible to determine the coefficient of linear and superficial expansions of the crystal as a whole along definite directions. This can be done conveniently and with the introduction of less errors in measurement by measuring the lengths of etch pits along the directions [110] and $[1\bar{1}0]$. There is also a change (contraction) of dimension along the direction $[1\bar{1}0]$ ; however this change is not of a large value for a given change of temperature, hence errors will be magnified in the measurement of length along the direction [110] . It is therefore decided to determine the coefficient of linear expansion along [110] . The measurements are made at various temperatures and are shown in Table 4.4. They are also graphically exhibited. The graph can be divided into the following regions: (i) curved region AB up to a temperature of 45°C (ii) straight line part BC beyond the temperature 45°C. The curvilinear and straight portions of the graph clearly indicate that the relations between l and t are in the beginning non-linear and after a certain temperature (45°C in the present work) become linear. In the non-linear portion of the graph, the strength of a line defect-dislocation—is playing a vital role in the overall development of a pyramidal etch pit, and the ratio $(V_n/V_s)$ has significant effect in the formation of pyramidal etch pits. The linear portion of the graph suggests that temperature of etching becomes a dominent partner in enlarging the lateral dimensions of etch pits; hence the ratio $(V_t/V_s)$ assumes greater importance; whereas $V_n$ does not appear to change significantly. The linear portion therefore should provide a reliable value for the coefficient of linear expansion. Using the formula

$$[\alpha]_{\text{along } [110]} = \frac{l_2 - l_1}{l_1(T_2 - T_1)}$$

where $l_2$ and $l_1$ are average lengths of etch pits along [110] at temperatures $T_2$ and $T_1$ respectively and $[\alpha]_{\text{along } [110]}$ - represents coefficient of linear expansion along the direction [110] . The value thus obtained is 0.06001 per °C. The value reported in the literature is 0.0426 per °C along direction [111] . The projection of this direction on (100) plane is [110] and the angle between the directions [111] and [110] is 45°23.5'. Hence the value will be 0.06001 X Cos45°23.5'= 0.04213 per °C along [110] . There is a close agreement between the value reported in literature and the one obtained from the present study.

## 4.5 CONCLUSIONS:

(1) Etch pit morphology is not much affected by changes in chemical energy with a change of temperature within a given range of temperature of etching.

(2) There is a systematic change in the direction of reaction rates on a crystal surface of calcite with a change from one range of temperature to another.

(3) Due to production or annihilation of pairs of reaction rates around the line of symmetry [110] of calcite cleavage faces , a point-bottomed (pyramidal) or a flat-bottomed pit with ~~which~~ any geometrical outline on the surface remains symmetrical about the direction [110] .

(4) Etch pits of identical shapes are produced on a cleavage surface of calcite etched by etchants of different characteristics at different temperatures.

(5) A good etchant produces pits having well-defined shape, size and reveal symmetry of etched surface.

(6) For obtaining pits of good quality the ratio of velocity of tangential dissolution to the velocity of surface dissolution ($V_t/V_s$) must be much greater than ten; higher is the value of $V_t/V_s$, better is the quality of etch pits.

(7) Under suitable conditions of etching it is possible to determine the coefficient of linear expansion along a direction [110] on the cleavage face of calcite crystal from a change in the lateral dimensions of etch pits with a change of temperature of etching.

# CHAPTER V

# CATALYTIC ACTION OF ELECTRIC FIELD ON ETCH PIT SHAPES

# CHAPTER V

# CATALYTIC ACTION OF ELECTRIC FIELD ON ETCH PIT SHAPES

## 5.1 INTRODUCTION:

Gilman et al. (1958) from their dissolution studies on LiF crystqls have concluded that the cation of poison is of major importance in forming stable complexes at the kink sites with the anions of the crystal and the role of the anion is a minor one though not completely negligible. Bhagavan Raju and Bansigir (1971) conducted experiments on the etching of NaCl crystals to reveal the role and nature of the inhibiting ion. In view of the interesting observations on the variation of shapes of etch pits with temperature by

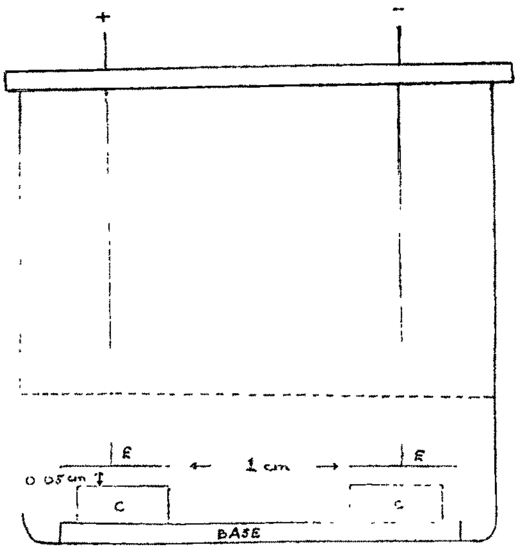


FIG - 5 1

using etchants of different chemical characters and ~~the~~ composition, the present author had performed a series of experiments on etching of the cleavage surfaces of calcite crystals by the etchant 'C' in the presence of steady d.c. electric field of different values. It should be remarked here that the terminology 'presence of electric field' is not used in the conventional sense. Here the etching of a crystal cleavage is carried out under the effect of a charged electrode below which is kept the crystal surface under etching and the distance between the two electrodes is too large to effect the etching process of this crystal surface. Further the larger plate area - electrode area - covers the crystal face whereas the cross-sectional areas of the electrodes, separated by a comparatively large distance, face each other in the etching solution.

## 5.2 EXPERIMENTAL:

A stabilized d.c. voltage was applied across identical stainless steel plates (electrodes) with dimensions 1 cm x 0.5 cm immersed in the etchant (Fig.5.1). The distance between the upper surface of a sample and the lower surface of an electrode was of the order of

FIG. 5·2a X 85

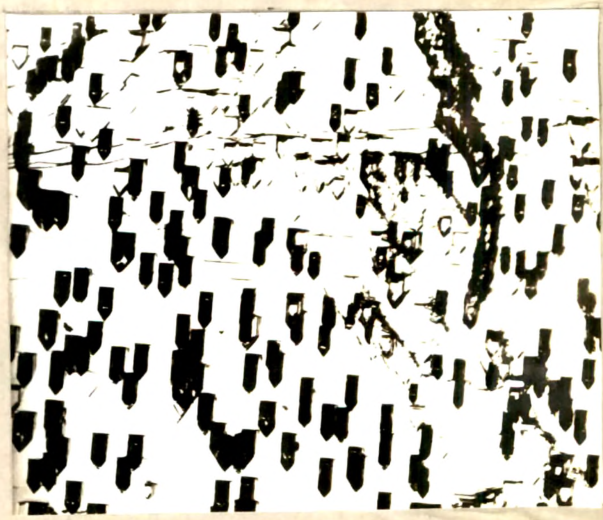


FIG. 5·2b X 85

0.05 cm, and the distance between the vertical cross-sectional faces of the electrodes was 1 cm. About 20 ml of etchant was taken in a beaker of 100 ml, capacity in order to maintain a constant height of the liquid (etchant) layer. It is clear from the entire ser of observations on etching of calcite cleavages by etchants 'A' and 'B' reported in the previous chapter that the period of etching for obtaining optically well defined etch patterns is of the order of a few seconds. Hence the action of these etchants on the cleavage face of calcite in the presence of a d.c. electric field cannot be studied with enough reliable accuracy. The etching period for etchant 'C' is of the order of a few minutes. Hence the etchant 'C' was used in the present investigation.

## 5.3 OBSERVATIONS AND RESULTS:

Fig. 5.2a and Fig. 5.2b (X85) show photomicrographs of matched calcite cleavage faces kept under anode and cathode respectively and immersed in 60% glacial acetic acid for 7 minutes etching at room temperature, and the electric field between electrodes was 5 volts. It is clear from both the figures that the plane shape of pits are elongated pentagons but the sizes of pits are different

FIG.5·3a X 85

FIG.5·3b X 85

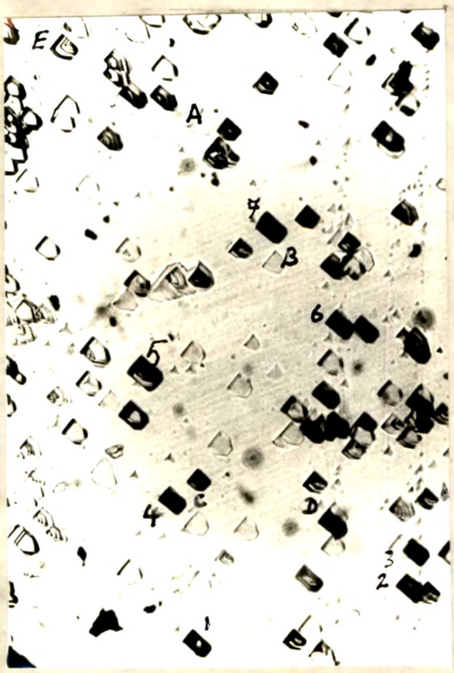


FIG.5·4a X100

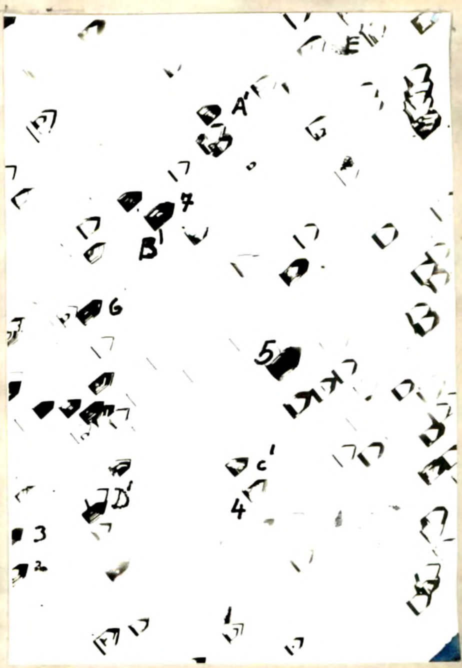


FIG.5·4b X100

in different regions. Further there is a complete one to one correspondence of etch pits on both the figures with their bases perpendicular to the direction [110]; this observation is similar to the one observed on etching a cleavage face by the same etchant in the absence of electric field.

Fig. 5.3a and Fig. 5.3b (X85) represent another pair of photomicrographs of matched cleavage faces etched under identical conditions of etching except for the increase of the electric field by 5 volts. In addition to the above mentioned characteristics, Fig. 5.3a shows a marked change in shape of a few etch pits along with the pentagon etch pits. The plane geometrical figure of etch pit is a rectangle. It is produced by the removal of the tip of the elongated pentagon pits.

Further increase in electric field by 5 volts between electrodes produced a visible change in eccentricity along with a change in etch pit shape and size. Fig. 5.4a and Fig. 5.4b (X100) exhibit the oppositely matched cleavage faces etched by the same etchant for the same period and at the same temperature when the electric field between electrodes is 15 volts.

The figures represent microstructures on calcite cleavage faces kept under anode and cathode respectively.

The unusual characteristic features of these photomicrographs are as follows:-

(i) The pair of point-bottomed terraced pits having opposite eccentricity like A,B,C,D (Fig. 5.4a) have correspondence with the pairs A',B',C',D' (Fig. 5.4b).

(ii) The pair E (Fig.5.4a) consists of a point-bottomed terraced eccentric pit and a flat-bottomed pit. While the pair E' (Fig.5.4b) consists of point-bottomed terraced pits of opposite eccentricity.

(iii) There is a fairly good - almost complete - one to one correspondence of pits on both the photomicrographs.

(iv) The plane-geometrical figure of point-bottomed pits no. 1 to 7 (Fig.5.4a) have rectangular shape while the corresponding pit no. 1 to 7 (Fig.5.4b) have pentagon shapes.

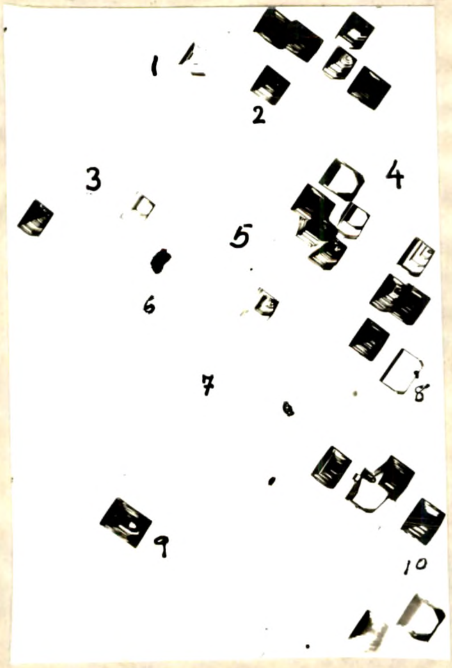


FIG.5·5a X100

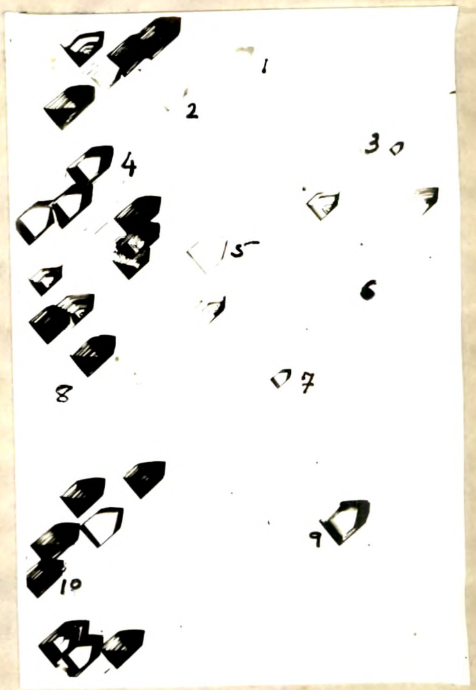


FIG.5·5b X100

Fig.5.5a and Fig.5.5b (X100) represent typical microstructures on oppositely matched cleavage faces of calcite kept respectively under anode and cathode between which is maintained an electric field of 20 volts. The close examination of these photomicrographs reveals the following characteristics:

(i) The flat-bottomed pits on either figures with the places numbered 3,4,5,6,7,8 do not show any correspondence. As a matter of fact the places corresponding to pits shown on the counterpart are blank without any visible etching effect.

(ii) There is a correspondence between point-bottomed terraced pits (such as 1,2,9 on Fig.5.5a) with flat-bottomed pits (such as 1,2,9 on Fig.5.5b).

(iii) A point-bottomed terraced pit no.10 on Fig.5.5b is not matched by a pit on Fig.5.5a at the corresponding place.

(iv) Many pits on the cleavage surface kept under anode are pyramidal with a rectangular plane figure on the plane of observation. The tips of normal elongated pentagonal pits are cut during etching in the presence of electric field.

## 5.4 DISCUSSION:

The controlled etching of cleavage surface of calcite in the presence of steady d.c. electric field has shown the following characteristics of etch patterns:

(i) The portions of a cleavage surface which are in the close vicinity of electric field exhibit assorted sizes of pits whereas this effect is not found near the edges of cleavage faces.

(ii) Those pits which are affected by the electric field are highly unsymmetrical so far as the internal structure and plane geometrical shape of etch pits are concerned.

(iii) There are finite differences between the etch patterns shown on the surfaces in close proximity of electrodes viz. anode and cathode.

(iv) The percentage of pits showing the terraced structure has comparatively increased.

(v) The plane geometrical shapes of etch pits on a cleavage surface of calcite near anode shows a change from the normal shape observed due to its normal etching. By normal etching is meant the etching of cleavage surface of calcite in the absence of any physical obstacle (except the layers of etchant above crystal surface) and of d.c. electric field. In what follows the normal etching will carry this meaning.

The above characteristics will now be discussed in detail. The existence of the assorted sizes of etch pits is associated with the evaluation of $CO_2$ gas from the surface involved in the chemical reaction with an etchant. The distance between an electrode and a crystal surface is of the order of 100 $\mu$ ; hence the evolved $CO_2$ gas will not have easy escape from the surface to the atmosphere. The electrode plate acts as an obstacle to the evolved gas. Since the $CO_2$ gas is trapped between the electrode and the crystal surface, it temporarily forms a protective layer at preferential points on the surface and the further etching is momentarily stopped. Only the lateral motion of $CO_2$ gas is possible. However this motion is not as rapid as the motion of $CO_2$ gas during the normal etching i.e. in the absence of any obstacle like electrode plate. As a result of this slow etching action the sizes of these pits are comparatively smaller than those formed near the edges. This inference is supported from the general observation that when the reaction is fast i.e. when the evolved $CO_2$ gas moves rapidly towards the free surface without any obstacle the surface exhibits pits of bigger sizes.

It was conclusively established in this laboratory (Mehta, 1972) that a change in concentration of an etchant affects the eccentricity of etch pits. However in the present case this change in eccentricity of etch pits is different from the one observed under normal etching. This can be explained by considering the combined effect of momentary dilution of etchant on the surface, the slow lateral motion of evolved $CO_2$ gas and the effect of electric field on the ions responsible for the formation of etch pit shape. Since the $CO_2$ gas evolved at various points on the surface is momentarily sandwitched between the electrode and the cleavage surface, its slow lateral movement produces impacts at various points where there is temporary dilution of etchant and where the ions are momentarily locked. These three factors influence the internal structure and the geometrical outline of etch pits. As the eccentricity of pits are different from those observed under normal etching, The remaining two factors only will be responsible for the observed change of eccentricity of pits. Out of these two factors the strength of electric field which affects the locked ions plays an important role. At low voltages, there is no noticeable change in eccentricity of pits which are of assorted sizes. Hence in this case the lateral movement of $CO_2$ bubbles is a dominant factor in affecting the sizes of etch pits. As the voltage increases, these two factors interchange their roles i.e. the electric field strength participates more actively in affecting the uneven sizes and eccentricity of pits. Since the pits are bigger and of uniform sizes the lateral movement of bubbles of $CO_2$ gas is faster at higher electric fields applied to the electrodes. This indicates increased activity of chemical reaction applied to the electrodes. This appears to act in a strange way, not yet precisely known to produce highly asymmetrical pits.

During normal etching pits produced by etchant 'C' (60% glacial acetic acid) on a cleavage surface of calcite have elongated pentagon outlines on it. The presence of electric field markedly affects the shape. It is clear from the photomicrographs that this action is quite selective.

The cleavage surfaces under anode and cathode do not exhibit pits of identical shapes. The etch pits observed on a cleavage surface under cathode do not show any noticeable change, whereas the cleavage surface under anode exhibits pits without elongation points i.e. removal of vertex of pentagon pit (Fig.5.3a). The pits have more or less rectangular outlines. This effect becomes more prominent at higher voltages applied to the electrodes. Further the matching of oppositely matched cleavage counterparts kept under cathode and anode is of poor quality so far as the internal structure of pits and their outlines on cleavage surfaces are concerned. The change in the geometrical outline of etch pits on a cleavage surface kept under anode is therefore connected with the type and possibly concentration of ions in the neighbourhood of anode. At this electrode anion will have very easy access. The nature of the ions can be inferred from a study of the electrolysis of the electrolyte, viz. diluted acetic acid. The cations and anions at the cathode and anode are $H^+$, $Ca^{++}$ and $CH_3COO^-$, $O^-$ respectively. Along with these anions there could be a formation of some negative type of complex ions formed with $H^+$. The latter unknown complex negative ion is associated with small amounts of impurities present in any chemical after a number of purification processes. It is the anions $CH_3COO^-$, $O^-$ and $HX^-$ which individually or jointly act on the highly sensitive portion of the etch pits at preferential locations. This action of the anion is responsible for the removal of the elongation points or vertices of the elongated pentagon pits and consequent creation of pits with rectangular.outlines.

It should be noted that at low voltages there are very few terraced pits on oppositely matched cleavage faces whereas at high voltages the density of pits with terraced structured is fairly high on both the cleavage counterparts. Further the matching of terraced pits on the matched faces kept under electrodes is fairly good. There are basically three factors which must be influencing the formation of terraced structure, viz. (i) high lateral velocity of bubbles of $CO_2$ gas (ii) impurities made more active in the presence of electric field and (iii) the electric field strength. It is rather difficult to determine the role of each factor in promoting terraced structure of etch pits.

## 5.5 CONCLUSIONS:

(1) The d.c. electric field is acting as a catalytic agent for the normal etching of cleavage faces of calcite.

(2) The eccentricity of pits becomes greater under the d.c. electric field than those formed under normal etching.

(3) Contrary to uniform sizes of etch pits under normal etching, the etch pits are of assorted sizes when etching was carried out in the presence of electric field.

(4) The (plane geometrical) shapes of etch pits produced by etching in the presence of comparatively high electric field are different from those produced by normal etching.

(5) For relatively high electric field the etch patterns under anode and cathode are significantly different. This is due to anions acting individually or jointly at preferred locations (nuclei of etch pits) on a cleavage surface.

(6) The number of pits with terraced structure increases with the electric field.

# CHAPTER VI

# REACTIVITY OF CALCITE CRYSTALS

# CHAPTER VI

# REACTIVITY OF CALCITE CRYSTALS

## 6.1 INTRODUCTION:

It is known that the thermally activated process has a definite value of activation energy. It is also observed that the shape of an etch pit is dependent on temperature (Chapter IV). Hence in the present investigation etch pit widening rate along a definite direction and the rate of surface dissolution as a function of temperature were determined in order to see whether any relation between the activation energy and the shape of etch pits exists.

## 6.2 EXPERIMENTAL:

The etching was carried out as mentioned earlier (Chapter IV). The measurements of width of etch pits on a crystal surface kept on the microscope stage and observed through the Vickers Projection Microscope were carried out by using filar micrometer (L.C. = 0.01 mm) eyepiece (X200). An accuracy of ±0.5 $\mu$ can be achieved with this method. The surface dissolution rate was measured by the 'step-plate' technique (Ives and Plews, 1965) and/or weight loss method by using semi-microbalance. In a 'step-plate' method a portion of the crystal surface was preserved; the difference in height of the etched and unetched portions of the crystal was determined by using the calibrated focusing adjustment.

## 6.3 OBSERVATIONS, RESULTS AND DISCUSSION:

Most of the etchants dissolves crystal surface independently of the line defects producing the etch pits. This surface dissolution has been attributed by Gilman (1960), Ives and Plews (1965) to the presence of other short lived dissolution centres such as lattice impurities. The surface dissolution plays an important role in the etching process. Hence the determination of the activation

| Sr. No. | Temp. in °K | log $V_t$ (cm/sec) |  |  | log $V_s$ (cm/sec) |  |
|---|---|---|---|---|---|---|
|  |  | Etchant A (1% HCl) | EtchantB (0.45% HĀC) | Etchant C (60% HĀC) | Etchant A (1% HCl) | Etchant C (60% HĀC) |
| 1. | 275 | $\bar{4}.3011$ | - | - | - | - |
| 2. | 278 | $\bar{4}.3980$ | - | $\bar{6}.6209$ | - | - |
| 3. | 283 | $\bar{4}.4843$ | - | - | - | - |
| 4. | 288 | $\bar{4}.5441$ | - | - | - | - |
| 5. | 293 | $\bar{4}.5911$ | - | $\bar{6}.9566$ | - | - |
| 6. | 298 | $\bar{4}.6284$ | $\bar{5}.9208$ | - | - | - |
| 7. | 303 | $\bar{4}.6532$ | $\bar{4}.1027$ | $\bar{5}.1897$ | - | - |
| 8. | 308 | $\bar{4}.6990$ | $\bar{4}.2773$ | $\bar{5}.3310$ | $\bar{5}.2246$ | - |
| 9. | 323 | $\bar{4}.7959$ | $\bar{4}.4150$ | $\bar{5}.7192$ | $\bar{5}.3038$ | $\bar{6}.1659$ |
| 10. | 333 | $\bar{4}.8196$ | $\bar{4}.5229$ | $\bar{4}.0000$ | $\bar{5}.3617$ | $\bar{6}.3202$ |
| 11. | 343 | $\bar{4}.8196$ | - | - | $\bar{5}.4160$ | - |
| 12. | 348 | - | $\bar{4}.6368$ | $\bar{4}.1011$ | - | $\bar{6}.5000$ |
| 13. | 353 | $\bar{4}.8196$ | - | - | $\bar{5}.4473$ | - |
| 14. | 358 | - | $\bar{4}.7270$ | $\bar{4}.1477$ | - | $\bar{6}.6531$ |
| 15. | 363 | $\bar{4}.8389$ | $\bar{4}.8239$ | $\bar{4}.1897$ | $\bar{5}.7617$ | - |

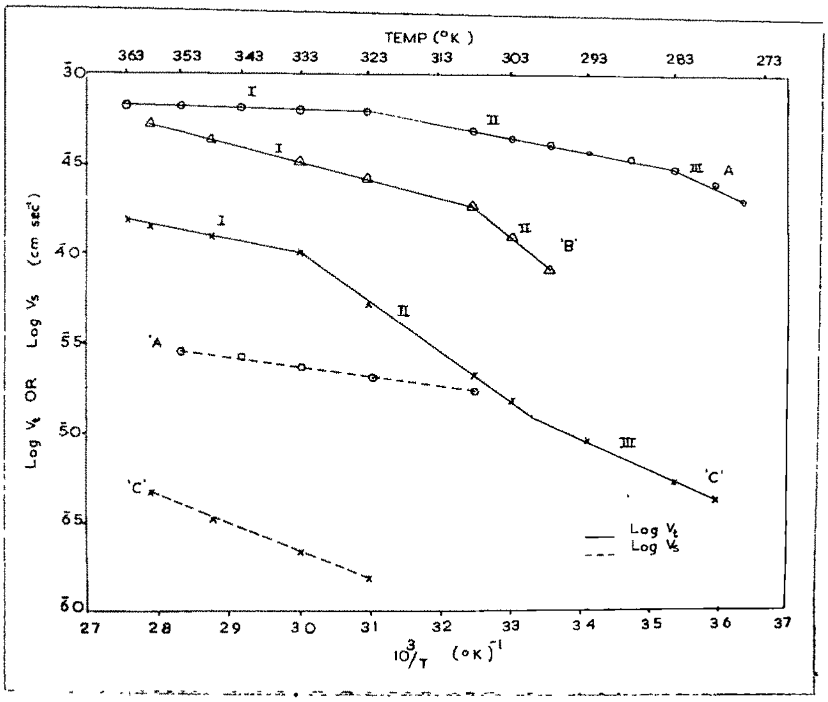

TEMP (°K)
363
353
343
333
323
313
303
293
283
273
3̄0
4̄5
4̄0
5̄5
5̄0
6̄5
6̄0
Log V_t OR Log V_s (cm sec⁻¹)
I
II
III
A
I
II
'B'
I
II
III
'C'
'A
'C'
Log V_t
Log V_s
27
28
29
30
31
32
33
34
35
36
37
10³/T (°K)⁻¹

FIG.6·1

energies for the dissolution of the surface $E_s$ and for the tangential movement of steps away from the source $E_t$ is likely to enhance the understanding of etch process.

It is known that in general all pits started growing at the same time, their lateral dimensions were equal for same concentration, period of etching, temperature and other conditions such as static or dynamic motion of etchant etc. In order to calculate the activation energy $E_t$ for tangential movement of steps away from the dislocation the etch pit widening rate ($V_t$) along [110] direction as a function of temperature has been determined. The activation energy for the surface dissolution $E_s$ was determined by measuring the rate of surface ($V_s$) dissolved at different temperatures. The observations are presented in Table 6.1

The graphs of log of etch pit widening rate ($V_t$) against the reciprocal of temperature (T°K) for various etchants are shown in Fig.6.1. This figure also shows the graphs of log of surface dissolution rate ($V_s$) against the reciprocal of temperature (T°K). According to

TABLE 6.2

| Sr.No. | Shape of etch pit | Etchant | $E_t$ (ev) | $E_s$ (ev) |
|---|---|---|---|---|
| 1. | Elongated pentagon | 60% $H\bar{A}C$ | 0.54 | 0.31 |
| 2. | Nearly regular pentagon | 1% HCl | 0.15 | 0.12 |
| 3. | Rhombic | 0.45% $H\bar{A}C$ | 0.68 | – |
| 4. | Rhombic | 1% HCl | 0.02 | 0.12 |
| 5. | Hexagon | 0.45% $H\bar{A}C$ | 0.22 | – |
| 6. | Curvilinear quadrilateral | 1% HCl | 0.38 | 0.12 |
| 7. | Rectangular | 60% $H\bar{A}C$ | 0.38 | 0.31 |
| 8. | Javelian | 60% $H\bar{A}C$ | 0.16 | 0.31 |

Arrhenius equation $V = A.\exp(-E/KT)$ , the slope of the graph of $\log V_t$ (or $\log V_s$) vs 1/T represents the value of E/K where E is the activation energy of the reacting species and K is the Boltzmann constant. The straight line graphs in some cases split into two or more portions and hence the activation energy for each linear portion of the graph is calculated. The energies thus calculated for different linear portions of the graphs and for different etchants are shown in Table 6.2. It is clear from the table that the activation energies calculated from a graph of $\log V_s$ vs 1/T are independent of temperature range whereas the energies determined from the graphs of $\log V_t$ vs 1/T depend on the range of temperature chosen for etching a crystal surface. The temperature of etching affects the plane shape of etch pits. For temperatures within a given range of temperature, the plane figure of etch pit is almost invariant. Hence in this range the activation energy is constant. Thus as the range of temperature of etching changes in a gradual and systematic manner the activation energy also changes. However this change does not appear to take place in a regular manner.

It is thus clear that for a study of the change in the plane geometrical shape of an etch pit on a crystal surface produced by an etchant due to change of temperature alone the $\log V_t$ vs $1/T$ graph is more useful i.e. the activation energy in this case will be a deciding factor. The converse of this statement is true and is conclusively established in this laboratory by Mehta (1972), who has shown that for a constant temperature of etching the plane geometrical shape of etch pits on a cleavage surface of calcite changes with concentration of an etchant (say hydrochloric acid or glacial acetic acid). Further the activation energy depends upon concentration of an etchant. However, no attempt is made to determine the activation energy of the reactive species in this case. The above observation may be generalized by applying it to etchants of different characteristics, viz., for a constant temperature of etching of a crystal surface subjected to etchants of different characteristics producing different geometrical outlines, the activation energies will be different. It should be remarked here that for a given range of concentration, the plane geometrical outline of etch pits remains unchanged; however eccentricity of etch pits changes with concentration in a given range of concentration of an etchant (Mehta, 1972).

It is also possible to predict about the quality and symmetry of etch pits on calcite cleavage surfaces produced by an etchant due to change of temperature alone. For understanding these deductions it is also necessary to observe the texture or quality of the etched surface critically. A simple glance on the table 6.2 will indicate that higher is the activation energy, better is the quality of etch pits. Further for obtaining more symmetrical etch pits the activation energy must be of a larger value. For example, the etchant A (1% HCl) produces pyramidal pits with (i) curvilinear quadrilateral outlines (ii) nearly regular pentagon outlines (iii) irregular hexagon outlines and (iv) rhombic outlines. An examination of the crystal surfaces showing these etch figures discloses better quality of pits with quadrilateral and pentagon outlines whereas the pits with irregular hexagon and rhombic outlines are of poor quality. It should be remarked here that the pits with rhombic outlines exhibit better symmetry than those of different outlines.

However quality of these pits is indeed very poor. This fact can be understood by studying the activation energy which has value 0.024 ev. This is indeed very low; the microtopographical study of the etched surface showing pits with rhombic outlines clearly indicates the tendency towards the polishing of the surface. This is supported by the fact that light profile study of the surface shows pits to be very shallow.

The above deduction can now be tested by examining the quality and symmetry of etch pits produced by a different etchant when temperature of etching is changed from one range of temperature to another. Etchant B (0.45% glacial acetic acid) produces pyramidal pits with (i) rhombic outlines and (ii) nearly regular hexagonal outlines on cleavage surfaces of calcite by suitably changing the temperature of etching. The pyramidal etch pits with rhombic outlines are of superior quality and of better symmetry (Fig.4.4a). Again this can be ~~seen to be~~ due to the fact that the activation energy in this case has a much larger value.

The rhombic pits can be produced by etchants A and B by adjusting the temperature of etching. However the etch pits produced by etchant B are of better quality than those produced by etchant A. The symmetry of pits in both the cases is the same. Therefore it can be conjectured that activation energy due to widening rate of etch pits alone cannot be a decisive factor in predicting the quality and symmetry of etch pits. It is necessary in this case to take the help of activation energy due to surface dissolution rate. The ratio $E_t/E_s$ will be helpful in giving a clear and correct indication of the quality and symmetry of etch pits. When this ratio is greater than one, the pits will be of better quality and symmetry; higher is the ratio, better are the pits in quality and symmetry.

It is also apparent from the values of activation energies that pyramidal etch pits with regular outline having more sides will have lower activation energies. However, this conclusion cannot be emphasized for want of adequate number of observations about pyramidal etch pits with regular geometrical outlines having more sides and produced by different etchants.

## 6.4 CONCLUSIONS:

(i) For a given concentration of an etchant producing etch pits with definite eccentricity and plane geometrical outline, the activitation energy is constant.

(ii) For a given geometrical outline of etch pits produced by etchants of different characteristics the activation energy is not constant.

(iii) For better quality and symmetry of etch pits the activation energy should have a higher value and that the ratio $E_t/E_s$ should be greater than one.

(iv) Polishing action sets in when the activation energy is very low and the ratio of $E_t/E_s$ is very very small ($<<1$).