

Interoffice Memorandum

To: Mr. Jerry Lawson

From: D. C. Kay

Subject: Effect of Physical and Chemical
Properties of Substrates on Substrate Performance
(A Non-Experimental Approach)

Date: March 11, 1985

I. INTRODUCTION

An investigation of the influence of various chemical and physical substrate properties on the performance of substrates in a TGA device has been carried out. This investigation involved searching the literature to learn what is known about the properties of glycerol, the interactions of a liquid such as glycerol with a solid surface and about various substrate materials which we are considering using in a TGA model. This knowledge was then applied to the TGA system to predict what characteristics would be desirable to enable a substrate to meet the requirements of a substrate needed for a TGA device. The requirements of a substrate for a TGA device have been defined. They are:

1. to hold a humectant which forms an aerosol when heated gas is passed over the adsorbed or absorbed humectant.
2. to hold the humectant tightly at conventional storage warehouse temperatures so that the humectant does not migrate over time to other parts of the TGA device such as the fuel source and paper wrappings.
3. to be able to release enough humectant at the temperatures in the capsule so that a quantity of aerosol, similar to that of conventional cigarettes, is produced.
4. not to catalyze breakdown of the humectant, ^{which} to produce^s offtasting aerosol.

In recent years, much information has been reported in the literature concerning materials which we are considering as candidates for a TGA substrate, i.e. graphites, activated carbons, and metal oxides (alumina, silica and clays). The impetus for gaining this knowledge is the wide use of these materials as catalysts, catalyst supports and as adsorbents in purification systems.

Although these ^{substrate} materials are used in ~~the~~ similar applications, there are many differences in the structure of these materials and the interactions which can occur between an adsorbing solid substrate (adsorbent) and the humectant which will interact with the solid surface (adsorbate). For a particular system, one type of adsorbent will react with the humectant, differently than another type of adsorbent. Also, within a particular class of adsorbents, i.e. activated carbons, graphites and metal oxides, wide differences in adsorption and desorption performance can be seen.

Currently at RJR, we are using B-3 (glycerol) as a humectant, so we will assume that the humectant is glycerol. In this report, the chemical and

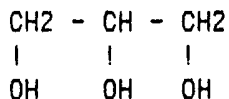
physical properties of glycerol will be considered first, so that later in the report, we can relate the properties of glycerol alone to the properties of glycerol adsorbed on a substrate surface. After the properties of glycerol are considered, adsorption phenomenon common to these substrates will be reviewed and then finally, the influence of the chemical and physical properties of these substrates, sectioned into the following classes will be considered. The four classes are:

1. Graphites
2. Activated Carbons
3. Metal Oxides (In particular, alumina)
4. Clays (in particular, vermiculite)

These classes were selected because of the differences in physical and chemical properties between the classes and because of the possibility of using these type of materials in the final TGA product.

II. Glycerol

In the simplest form, the structure of glycerol can be written:



Glycerol has been selected as a humectant for the TGA system because glycerol is inexpensive and because much is known about glycerol and the formation of aerosols from glycerol. Glycerol forms an aerosol which is almost odorless, and which visually resembles the aerosol released when a conventional cigarette burns. When considering glycerol as a humectant, the structure, physical and chemical properties of the humectant must be considered. These properties are outlined below.

A. Structure of Glycerol

It is important to consider the detailed chemical structure of glycerol when considering its adsorption or absorption by porous substrates. Structural information is needed to estimate the smallest pores into which glycerol could penetrate.

The bond angles and bond distances for glycerol have been determined by Sundaralingam et al. (1965) and are given below.

Bond	Distance	Bond	Angle
C-C	1.51 A	C-C-C	112
C-O	1.41 A	C-C-O	108

The actual size of glycerol cannot be determined simply by looking at bond angles and bond distances, because a molecule such as glycerol could preferentially be in many conformations, i.e. various arrangements in three

dimensional space arrived at by rotation about single bonds. The energy of the conformations would be influenced by intramolecular and intermolecular hydrogen bonding. A diagram showing some of the potential conformations for 1,2 propanediol are shown in Figure 1. Van Koningsveld (1968) determined the structure of glycerol by using x-ray diffraction and determined that the preferred conformation (lowest energy) was the structure shown in Figure 2. Van Koningsveld (1968) also determined the crystal structure of glycerol. From the crystal structure, the dimensions of the glycerol molecule can be obtained. The cell dimensions are:

$$\begin{aligned} a &= 7.00 \text{ +/- } 4\text{A} \\ b &= 9.96 \text{ +/- } 5\text{A} \\ c &= 6.29 \text{ +/- } 4\text{A} \end{aligned}$$

The large error in the dimensions is due to the various conformations which exist. Assuming four molecules per unit cell, the dimension of a molecule would be 3.5 x 4.98 x 3.13. Based on these dimensions, the minimum pore opening for a glycerol molecule to penetrate would be about 3.13 A.

B. Physical Properties of Glycerol

The three hydroxy groups of glycerol greatly effect its physical properties. The possibility of intermolecular hydrogen bonding between glycerol molecules via the three hydroxy groups gives physical properties to glycerol which are very different from the more simple three carbon- containing compounds, propanol and propane. These physical properties are compared below:

	M.P. (C)	B.P. (C)	Density (g/cc)
Glycerol	18	290	1.29
Propanol	-126	97	.804
Propane	-187	-162	(gas)

The boiling point of a molecule is important when looking at adsorption and desorption characteristics. For non-specific adsorption (adsorption due only to van der Waals attractions) the tendency for a molecule to adsorb or desorb is related to its boiling point. Compounds with higher boiling points tend to adsorb at lower temperature and desorb at higher temperatures than analogous compounds with lower boiling points.

C. Chemical Reactivity of Glycerol

One of the major problems with the substrates used in the TGA devices is that the substrates (and the high temperatures experienced in the aluminum capsules when the device is smoked) tend to cause oxidation, dehydration (pyrolysis), or other reactions which give an offtaste to the mainstream aerosol. Initial results from analyzing the aerosol from substrates which give an offtaste to the aerosol indicate that the offtaste detected is due to acrolein or other carbonyl containing breakdown products of glycerol. No analysis has been

carried out to detect the presence of non-carbonyl containing products. In order to prevent the off-taste which is observed, understanding and identification of the various possible off-taste products are desired.

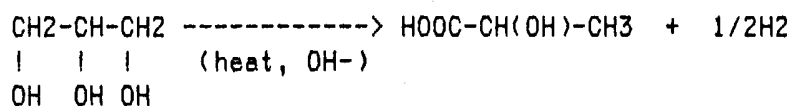
1. Oxidation of Glycerol

Glycerol is stable to atmospheric oxidation under normal conditions, but could be oxidized in the TGA system. When glycerol is exposed to hot air passing over the heated substrate surfaces (a possible catalyst), it is possible that these more severe conditions could result in oxidation of the glycerol. If glycerol is oxidized, eleven oxidation products are possible. These eleven oxidation products, given below, have been suggested by both Lawrie(1928) and Segur(1953). This oxidation products represent increasing oxidation of the hydroxyl groups.

Oxidation Products of Glycerol

Glyceraldehyde	$\text{CHOCH(OH)CH}_2\text{(OH)}$
Glyceric Acid	$\text{HOOC-CH(OH)-CH}_2\text{(OH)}$
Dihydroxy Acetone	$\text{(HO)CH}_2\text{-CO-CH}_2\text{(OH)}$
Hydroxy-pyruvic Aldehyde	(HO)CH-CO-CHO
Hydroxy-pyroracemic acid	$\text{(HO)CH}_2\text{-CO-COOH}$
Tartronic semi-aldehyde	CHO-CH(OH)-COOH
Tartronic Acid	HOOC-C(OH)-COOH
Tartronic Dialdehyde	CHO-C(OH)-CHO
Mesoxalic Dialdehyde	CHO-CO-CHO
Mesoxalic Semialdehyde	CHO-CO-COOH
Mesoxalic Acid	$\text{HOOC-C(OH)}_2\text{-COOH}$

Unlike pyrolysis which is most likely at lower pH values, oxidation increases with increasing alkalinity. According to Segur(1953) Lactic acid is most often observed when glycerol is oxidized. Lactic acid is not included in the above table because it results from reduction of the one of the primary alcohol groups (to form a methyl group) as well as oxidation of the other primary alcohol functional group (to a carboxylic acid). The net reaction is shown below. A possible mechanism for the formation of lactic acid from glycerol is given in Appendix A.



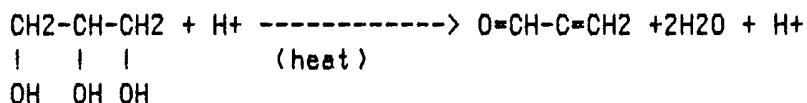
2. Pyrolysis of Glycerol

In this report, pyrolysis is considered to be different from oxidation in that oxidation is base catalyzed, whereas pyrolysis is generally acid catalyzed. Pyrolysis of glycerol occurs when glycerol is heated. The primary pyrolysis product according to Segur (1953) is acrolein. Other pyrolysis products include formaldehyde, acetaldehyde hydroxy acetone and acetone. The chemical reactions for the formation of acrolein, formaldehyde and

acetaldehyde are discussed below.

a. Formation of Acrolein

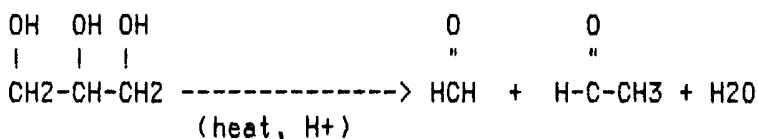
The pyrolysis of glycerol to form acrolein, shown below, is a well known reaction.



A possible mechanism for the above reaction is given in Appendix A. The formation of acrolein from glycerol results in a disagreeable choking odor and is not desired in the TGA aerosol. Since this reaction occurs at elevated temperatures (to drive off H₂O), lower temperatures in the TGA capsule would lower the amount of acrolein side products. The above reaction is acid catalyzed which suggests that increasing amounts of acrolein would be produced with increasing acidity or on more acidic substrate surfaces.

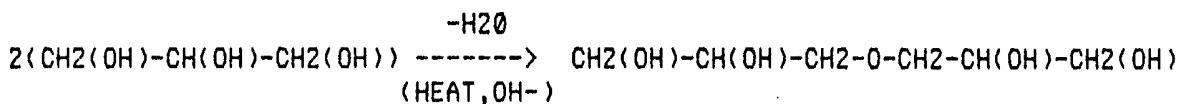
b. Formation of Formaldehyde and Acetaldehyde

Formaldehyde and acetaldehyde are usually detected in the mainstream of the aerosol from a substrate-containing TGA device. Formaldehyde gives rise to a strong pungent odor and acetaldehyde gives rise to a pungent, fruity odor in the TGA aerosol. Like the formation of acrolein, the formation of formaldehyde and acetaldehyde are acid catalyzed and occur most readily at elevated temperatures. The net reaction is given below and a possible reaction mechanism for the formation of these two species is given in Appendix A.



3. Formation of Polyglycerols

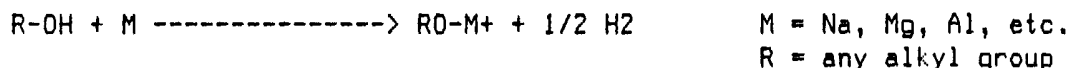
Dimers (or higher analogs) of glycerol are also possible products of glycerol which can be catalyzed by a substrate surface. According to Segur (1953), polyglycerols are formed commercially by heating glycerol over an alkaline catalyst between 200 and 275 C at either normal or reduced pressures. Passing a stream of hot gas over the catalyst enhances the probability of the reaction. The reaction is given below.



Polyglycerols are also formed in the presence of strong acid (Segur, 1953).

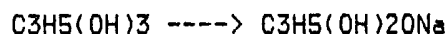
4. Formation of Metal Glyceroxide Compounds

The reaction of glycerol with metals is important to the TGA project, because we are concerned about corrosion of the aluminum capsule in the TGA device. Morrison and Boyd (1959) report that alcohols react with active metal (which includes aluminum) as shown below:



(order of alcohol reactivity- primary > secondary > tertiary)

According to Lawrie (1928), glycerol is a weak acid and dissolves the alkalis, the alkali earth and many metallic oxides, forming alcoholates or addition products in the nature of double salts. Lawrie reports that the formation of sodium salts of glycerol have been observed when glycerol reacts with NaOH, i.e..



II. Solid Substrates - Adsorption Phenomenon

A. Adsorption Phenomenon

1. Specific and Non-specific Interactions

Many of the chemical and physical properties which influence the TGA substrate's ability to adsorb and desorb glycerol are dependent on adsorption phenomenon and properties which are common to many or all of the substrates. One of the common characteristics of these materials include the ability of the substrates to interact with the glycerol by both non-specific interactions (physical adsorption or physisorption) and specific interactions (chemical adsorption or chemisorption). Non-specific interactions depend on the van der Waals attractions between the substrate and the glycerol and are generally reversible. For our TGA system, this reversibility means that the glycerol held to a surface by only van der Waals forces would be released as glycerol and not as oxidized^{decomposition} or decomposition products of glycerol. Specific adsorption is due to chemical interactions other than van der Waals interactions. These specific interactions include hydrogen, ionic and covalent bonding. Many substrate surfaces are able to catalyze various chemical reactions by bonding via specific interactions with one or more of the reactants involved in the reaction being catalyzed. If specific interactions are present, the adsorbed glycerol could be desorbed as another compound that was formed due to a reaction which was catalyzed by the surface.

One of the fundamental difficulties in identifying a TGA substrate is the problem that in order to obtain aerosol, the substrate must be able to adsorb glycerol and then to release adsorbed glycerol at the temperatures experienced during smoking, without catalyzing breakdown of the glycerol. This implies that weak non-specific adsorption forces or relatively weak specific forces are desired. However, it is also necessary to prevent migration of the glycerol throughout the TGA device. This requirement to prevent migration requires that the attraction forces to the surface of the substrate must be stronger than the attractive forces to the surface of the fuel source or other adsorptive materials found in the TGA device, in other words, that strong

specific adsorption interactions should be present.

Because of the need to find a material which can best balance these requirements, it is necessary to understand how different physical and chemical substrate characteristics influence the strength of the forces desired for a TGA substrate.

2. Van der Waals Forces

Van der Waals interactions are defined by Hawley (1981) as the weak attractive forces acting between molecules. These forces are due to a balance of the attractive and repulsive forces between molecules due to the negative electrons and positive nuclei, to permanent dipoles in the molecule and due to distortion of the charge distribution that occurs when molecules interact. Van der Waals forces are somewhat weaker than hydrogen bonding. These van der Waals forces result in "wetting" of the solid surface by the glycerol and filling of pores due to capillarity.

3. Surface Tension and Surface Free Energy

It is a commonly known fact that liquids such as water, exhibit a force at their surface known as surface tension. Surface tension is the result of an imbalance of the intermolecular forces at the interface between a gas and liquid. A molecule within the body of the liquid is attracted on all sides by adjacent molecules, and the forces of attraction (van der Waals forces) decrease rapidly as the distance between the molecules increases. Thus only the interactions between the first shell or two of neighboring molecules are important and the molecule will experience essentially symmetrical forces when it is only a few molecular layers inward from the surface. However, at the surface of the liquid, the forces are only acting sideways and inward from the interface, tending to pull a molecule into the interior of the liquid. Put in another way, since the molecules in the interfacial region are subjected to net forces which are balanced out in the interior, work must be done in order to bring molecules from the bulk of the phase to the interface with a net increase in the area of the interface. Vold and Vold (1964) define surface tension as the tension per unit length tending to contract the interface and surface free energy as the work per unit area required to create new surface.

This phenomenon of surface tension is not unique to the liquid/gas interface. Surface tension is also important in the solid/gas and solid/liquid interfaces. In the case of solids the crystal lattice structure of the solid state prevents ready changes in the surface of the solid to reduce the surface exposed to the interface. The extent of the imbalance of forces at a solid surface depends on the solid material. According to Heimenz (1977), a surface free energy in the neighborhood of 100 ergs/cm² is generally considered the cutoff value between "high energy" and "low energy" surfaces. Metals, metal oxides, metal sulfides, silica and glass are examples of high energy surfaces and most solid organic materials such as organic polymers are examples of low energy surfaces. Zettlemyer (1973) reports that Graphon, a form of graphite, has a surface free energy between that for some organic polymers and metal oxide.

4. Work of Adhesion, Work of Cohesion, Wetting and Capillarity

a. Work of Adhesion and Work of Cohesion

Although no method has yet been found to determine the surface tension of solids against liquids or gases, the work of adhesion of a solid to a liquid, W_{sl} , can be measured. This work of adhesion, a measure of the attraction between two different phases, is the work necessary to separate the liquid from the solid by separating them perpendicularly from each other against the adhesive forces between them. The work for separating the two phases is equal to the difference between the final surface free energies and the free energy of the surface before the phases were separated i.e.

$$\Delta G = W_{sl} = \gamma_{\text{final}} - \gamma_{\text{initial}} - \gamma_{sv} + \gamma_{lv} - \gamma_{sl}$$

Where ΔG = Surface free energy

W_{sl} = Work of adhesion between a solid and liquid

γ_{final} = final surface tension

γ_{initial} = initial surface tension

γ_{sv} = surface tension at solid-vapor interface

γ_{lv} = surface tension at liquid-vapor interface

When considering the interaction between two phases, it is also important to understand the affinity of a phase for itself, or the work of cohesion. The work of cohesion is the work necessary to pull a column of liquid or solid apart and produce two new interfaces i.e.

$$\Delta G = W_{ss} = 2\gamma_{ss} \quad \text{for solids}$$

or

$$\Delta G = W_{ll} = 2\gamma_{ll} \quad \text{for liquids}$$

Where:

W_{ll} = work of cohesion for the liquid

W_{ss} = work of cohesion for the solid

γ_{ss} = surface tension at solid-solid interface

γ_{ll} = surface tension at liquid-liquid interface

The difference between the work of adhesion and the work of cohesion for a liquid is known as the spreading coefficient of the liquid on the solid i.e.:

$$S_{l/s} = W_{ls} - W_{ll}$$

If $W_{ls} > W_{ll}$, the liquid-solid interaction is sufficiently strong to promote the spreading or the "wetting" of the solid by the liquid. Conversely, no

wetting occurs if $W_{11} > W_{1s}$ since the work needed to overcome the attraction between two B molecules is not compensated by the attraction between A and B. Thus a negative spreading coefficient means that the liquid will not wet the solid.

b. The Importance of Surface Free Energy and Wetting to the TGA System

The phenomenon of wetting and surface free energies is very important in selecting a substrate material. In order for a substrate to hold glycerol, it is necessary for the surface free energy of the substrate to be greater than the surface free energy of the glycerol. This is expressed by the Young Equation.

$$\text{Young Equation } \gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

The contact angle, θ , is the angle (measured in the liquid) that is formed at the junction of three phases, for example, solid liquid gas junction. Although the contact angle is a measure of the interaction between two phases, its measurement requires that three phases be present. A diagram showing how a contact angle is measured is given in Figure 3.

Liquids which wet a solid surface give a contact angle which is less than 90 degrees and liquids which do not wet a solid surface give a contact angle which is greater than 90 degrees. An example of a liquid "wetting a solid surface" is the interaction between a clean glass surface and water; an example of a liquid not wetting a solid surface is the interaction between water and waxed paper.

For the TGA system, glycerol will wet any substrate which has a higher surface free energy than glycerol. Segur (1953) reports that the surface tension of glycerol is less than water but greater than that of the majority of organic liquids. It diminishes with increasing temperature. At 18C, the surface tension of glycerol is 62.47 dynes/cm and at 130C is 54.1 dynes/cm. Because all of the substrates which we are currently using for TGA substrates hold at least 10% B-3 (dry weight basis) it is a good assumption, that glycerol wets the surfaces of all the substrates which we are considering.

However what is particularly important is that glycerol is able to wet any surface in the TGA device which has a surface free energy greater than that of glycerol. For example, the fuel source contains small carbon particles which can be wetted by the glycerol in the same way that the substrate can be wetted by glycerol. To prevent migration of the glycerol into the fuel source, it is necessary that the materials in the fuel source have a lower surface free energy than the surface free energy of glycerol. This can be achieved by using a material in the fuel source which has a lower surface free energy than glycerol, by coating the carbon in the fuel source with a material to lower the surface free energy or by putting up a physical barrier to prevent the migration.

c. Capillarity

Most of the materials which we are considering for use as substrates are porous solids. The wetting of the walls of the pores is governed by the surface free energy of the solid substrate, but the filling of these pores is governed by capillary forces. The filling of a pore by a liquid is similar to the rise of a liquid from a supply of liquid into a tube that is situated perpendicular to the supply of liquid and with an open end in the liquid supply. A well known observation is that some liquids like water, rise in glass capillary tube and the height of some liquids, such as mercury are depressed in a capillary tube. Liquids that rise in a capillary tube have a greater work of adhesion than work of cohesion and wet the walls of the capillary. Liquids that exhibit a depressed liquid level in the capillary tube have a greater work of cohesion than work of adhesion and do not wet the capillary walls. The height of liquid that will rise above the liquid supply into the tube is related to the contact angle, the radius of the tube and the weight of the liquid column. The relationship between the radius of the tube, contact angle, density of the liquid and the height of the capillary rise is approximated by the following equation.

$$\gamma = 1/2gh(d-d_0)r/\cos\theta$$

γ = surface tension of the liquid

g = gravitational constant

h = height of rise

$(d-d_0)$ = the difference in densities between the liquid and gas phases

r = radius of tube

θ = contact angle

Based on the above relationship, it can be seen that glycerol will first fill the pores which have the smallest radii and then progressively fill the larger pores. Also, liquid will not enter the small pores of the solid unless the liquid is able to wet the surface of the solid (has a contact angle of less than 90 degrees).

d. Vapor Pressure Of a Curved Liquid Surface

Simply put, the vapor pressure of a liquid over a convex surface is greater than the vapor pressure over a flat liquid surface which is greater still than greater than the vapor pressure of a liquid over a concave surface. Also, the vapor pressure over a convex liquid surface increases as the radius of curvature of the liquid surface decreases. The vapor pressure over a liquid changes as the curvature of the liquid changes because if a molecule were to condense onto the liquid surface, the surface area of the liquid would change (except in the case of the planar surface). For a convex surface, adsorption of a vapor molecule increases the surface area whereas for a concave surface, adsorption of a vapor molecule decreases the surface area. For any curved liquid interface, there is a concave and a convex side. For the interface to

be at equilibrium, there is a difference in pressure, across the interface. This is expressed by the equation of Young and LaPlace, given below:

$$P'' - P' = 2\gamma/r$$

P'' = The pressure on the concave side of the liquid surface
 P' = The pressure on the convex side of the liquid surface
 γ = The surface tension of the liquid
 r = The radius of curvature

From the equation of Young and Laplace, it is seen that the higher pressure is on the concave side on the interface and that the difference in pressure required, increases as the radius of curvature decreases.

This relationship between vapor pressure and curvature on an adsorbed liquid film is used to explain the hysteresis between adsorption and desorption isotherms which occurs when small pores are present in an adsorbing solid substrate. An example of an isotherm exhibiting hysteresis is shown in Figure 4. On desorption, the small pores empty again only at a lower pressure than when they were filled. At present, the popular viewpoint seems to be that the liquid in the smaller capillaries is made up of a multilayer adsorbed on the walls of the pore, plus "ordinary liquid" whose walls are formed by the external part of the adsorbed liquid. When a capillary is being filled, its effective radius is larger, so that a higher pressure is needed to fill it than when it is being emptied.

A second possible cause of hysteresis is also related to the equation of Young and LaPlace. In the second hypothesis, it is suggested that the cause of hysteresis is due to narrow-necked pores which are commonly referred to as ink bottle pores. An example of an ink bottle pore is shown in Figure 5. For these pores, the ability of a molecule to adsorb is dependent on the larger radius away from the pore entrance however, desorption is dependent of the radius of the neck of the pore.

III. Solid Substrates - General Physical Properties

A. General Physical Properties of Substrates

Now that background has been given on many of the physical interactions that can take place between a liquid and the solid substrates which we are considering using for the TGA device, we can look at the effects of some of the general physical characteristics of the substrate on the adsorption of glycerol (in particular the holding capacity), on the desorption of glycerol, (in particular the amount of aerosol and the tendency for migration), and on the stability of the glycerol (in particular the amount of offtaste detected). The physical characteristics which are believed to be important are the surface area, and the pore size.

1. The Effect of Surface Area

Surface area of the substrates includes not only the outer external area of

the substrate, but the surface area of the sides of the pores. The surface areas of the substrates which we are considering for use in the TGA device cover a wide range. PG-60, a graphite carbon has a surface area of less than 1 m²/g and many of the activated carbons have surface areas of over 1000 m²/g. Although many of the performance characteristics which we have observed depend on the particular substrate, there are some generalizations which can be said about the effect of surface area. In the discussion which follows, which discusses the effect of surface area on TGA performance, it is assumed that all other factors influencing the behavior of the substrate are being held constant.

First of all, it is predicted that the amount of surface which a substrate has will most significantly affect the ability of a substrate to hold glycerol. Assuming that the effects of capillary condensation are small, the more area which the glycerol can wet, the more glycerol which can be held by the substrates. More glycerol on the substrate surface generally means that more aerosol can be released from the substrate.

It is also predicted that increasing the surface area will increase the amount of breakdown products in the mainstream aerosol. According to Boehm (1966), not until the surface area exceeds 50 to 100 m²/gm do surface functional groups or heteroatoms become significant. As the surface area is increased above this limit, the surface functional groups become more important and the potential for surface catalyzed decomposition products become greater. Thus, as more surface sites are exposed which can catalyze the breakdown of the glycerol ~~and~~, more offtaste will be perceived.

If two substrates are the same (including the same loading of B-3), except that one has a larger surface area than the other it is predicted that less migration of the glycerol will be seen for the substrate which has the greater surface area. This last prognostication is based on the assumption that the glycerol forms a monolayer over the substrate surface before collecting in the pores of the substrate via capillary forces and arises from the knowledge that if the materials had the same loading of glycerol, and the surface is increased, then there is either more surface holding the glycerol to the substrate and ^{there is} less glycerol in the form of loosely held glycerol in the capillaries of the substrate.

2. The Effect of Pores

The primary characteristic of pores that must be considered when thinking about the effect of pores on the performances of substrates is pore size. Small pores have a greater tendency to adsorb due to capillary action and the strong van der Waals forces. The strong van der Waals forces are caused by the overlap of the energy fields (due to surface free energy) at the surface of the walls of the pores. For this discussion of the affect of pore size on the substrate performance, it is convenient to group pores into the following classification according to their pore size.

Micropores

20 A

Mesopores
Macropores

20 to 500 A
> 500 A

These classifications are the classifications approved by IUPAC (International Union of Pure and Applied Chemistry). The basis of the classification is that each of the size ranges correspond to characteristic adsorption effects as manifested in the adsorption isotherm. In micropores, the interaction potential is significantly higher than in the wider pores owing to the proximity of the walls, and the amount adsorbed (at a given relative pressure) is correspondingly enhanced. In mesopores, capillary condensation with its hysteresis loop takes place. In the macropores, it is almost impossible to map out the isotherm in detail, because the relative pressures are so close to unity. A diagram of the micropores of an activated carbon is shown in Figure 6.

Spencer(1967) considered the influence of pore size on the adsorption of molecules by envisualizing a pore which becomes progressively more narrow. At the entrance of this ever-narrowing, funnel-shaped pore, the surface of the entrance of the pore may be regarded effectively as a plane surface. As the pore becomes narrower, the point is eventually reached where the pore is effectively sealed. In essence, when the pore diameter becomes progressively narrower than a certain critical value, the vapor adsorption isotherm in the initial region expressed on a unit-surface-area basis becomes progressively steeper toward the adsorption action. This is due to the additivity of the van der Waals forces arising from the "opposite surfaces" of the pores. This additivity enhances the amount of non-specific adsorption.

For the porous substrates which are considering using in the TGA system, there is no problem with adsorbing liquid onto the TGA substrate. All of the substrate materials which are candidates for use in the device adsorb more glycerol than we need for aerosol delivery. Our problem with the porous substrates involves desorption. Desorption is related to the problem of migration, aerosol delivery and offtaste. For migration, desorption of the glycerol occurs too readily. For aerosol delivery desorption does not occur as readily as desired and for offtaste, some of the desorbed material is the result of decomposition of the glycerol.

Assuming that adsorption is occurring from the vapor phase, when adsorption occurs, a monolayer of adsorbate first covers the substrate surface. As the pressure is increased more and more adsorbent adsorbs on the substrate surface. For porous substrates, after a monolayer of adsorbate is adsorbed, multilayer adsorption begins. This multilayer of adsorbed liquid begins to act like a normal liquid and can flow and fill pores. Because of the possibility of capillary condensation and the stronger van der Waals interactions, the small pores will fill up first followed by pores which are larger and so forth until all the pore volume is filled.

Desorption of an adsorbed material can only occur if the adsorbed material is in contact with the vapor phase. Because of this obvious restriction to desorption, desorption occurs first from the larger pores and from the outer surfaces which are in contact with the vapor. For porous materials such as activated carbons, the general belief is that the larger pores act as avenues

for the smaller pores. If this is indeed the case, it is reasonable that when glycerol desorbs from a substrate, the larger pores empty first, followed by pores of the next size and so forth. Exceptions to this order which is the reverse to the adsorption order are the proposed causes of mesopore hysteresis which were discussed above, i.e. pores with necks which have smaller radii than the base of the pores and the hysteresis effects due to the differences in pore radii between adsorption and desorption.

A systematic study which was carried out by Kiselev and coworkers (1959, 1961a,b, 1966a,b, 1968) found that the effect of pore narrowing:

1. Had the greatest influence on the adsorption of large molecules such as the longer chain n-alkanes ; the effect becomes apparent for such hydrocarbons as n-, iso, and cyclopentane, n-butane, and benzene when the pore neck diameter decreases to less than 60-40 A.
2. Is much less pronounced with the small molecules of nitrogen, whose adsorption due to dispersion forces is supplemented by interaction between their pi electrons and the strongly protonized hydrogens of the silanol groups.
3. Is also much less pronounced with methanol whose adsorption is due partly to hydrogen bonding, which is not sensitive to pore narrowing: in fact, the effect with nitrogen and methanol becomes appreciable only when the pore neck diameter is below 30A.
4. Is least with water, which is sorbed mainly through hydrogen bonding.

Based on the studies by Kiselev and coworkers, it is unreasonable to believe that the non-specific interactions of the smaller pores have much effect on the offtaste that is detected when smoking a TGA device. Glycerol would interact with the surface of the substrate through specific interactions, i.e. hydrogen bonding. (The sites for hydrogen bonding on the individual classes of substrates are given in the later sections of this report where each class of substrate is discussed individually). The van der Waals force contributions to the adsorption in the small pores would not be very significant. Also because we do not desorb all of the glycerol from the TGA substrate when the device is used, it is likely that most of the ultramicropores are not ~~even~~ being emptied.

The effect of pores on the performance of a TGA substrate is probably more related to surface area. For materials with constant pore volume, but different surface areas, the material with the greater surface area will have smaller pores. Thus, the fact that the material has smaller pores means that more adsorbate can interact with the surface of the material. If indeed the surface of the material is catalyzing the breakdown of glycerol more offtaste products will be detected in the aerosol. Also, glycerol will not migrate as readily from the materials which has the small pores, and thus the larger surface area. As mentioned above in the section describing the influence on surface area on migration, the more that the glycerol interacts with the

substrate surface, the less there is the tendency for the glycerol to migrate.

The fact that PG-60 a material with little surface area (<1 m²/g) gives no offtaste and an activated carbon with a surface area of 1000 m²/g gives a fair amount of offtaste, supports this above proposal. Also the glycerol migrates from the PG-60, but the tendency for the material to migrate from an activated carbon is much less.

Thus, to summarize, there are many physical substrate properties that contribute to offtaste. The amount of surface area and thus surface active sites which can interact with the glycerol, seems to be very important. The effect of the potential in the small pores seems to be small, however the fact that when the pores are smaller, more adsorbate can interact with the substrate surface (assuming constant pore volume) seems to be a more reasonable explanation for the effect of pore size.

IV. Solid Substrates - General Chemical Properties

A. The effect of pH

One of the chemical properties which the substrates have in common, is that their surfaces can either be acidic or basic. The pH of a substrate is the pH of a water extract obtained under prescribed conditions. The effect of the pH of the substrate on the adsorbed glycerol is essentially the effect of the extractable hydrogen or hydroxy ions. If these ions are readily extractable, they may catalyze breakdown of the glycerol in the same way the acids and bases were shown to catalyze reactions of glycerol in the first section of the report.

pH may be also giving a measure of the surface oxide density. If the surface sites are acidic, a more acid extract would indicate that there are a greater number of oxide surface sites. This would indicate a greater number of sites for the adsorption of glycerol.

V. Graphite

A. General

Graphites, in particular PG-60 (from Union Carbide), have been found to give no perceivable offtaste to the glycerol aerosol when the substrate-containing TGA device is smoked. However, laboratory analysis of the substrate have demonstrated that the substrate does not hold enough glycerol to give enough aerosol to satisfy the consumer and ^{the} graphite does not hold the glycerol tightly enough to avoid migration of the glycerol to other parts of the TGA device. Some of these properties are due to the physical and chemical properties of graphite as well as the method used to prepare the graphite.

B. Structure of Graphite

Many of the performance properties of graphites versus other materials used as TGA substrates are related to the general structure of graphites. Graphite has the layered structure shown in Figure 7. According to Davidson et al. (1968), in perfect graphite, the carbon atoms are arranged in regular hexagons of side length 1.41 angstroms and the layers are 3.35 angstroms apart. Alternate layers repeat exactly, while adjacent layers are offset in such a way that half the carbon atoms lie above the centers of adjacent hexagons. In all graphites, the sides of the hexagons remain close to 1.52 angstroms, since this bond is very strong, but the mean spacing between the layers increases as the graphite becomes less perfect and the stacking of adjacent layers becomes more random. This randomness arises from lack of parallelism between the hexagon edges in adjacent planes.

C. Preparation of Graphite

All of the graphite which we have used for TGA substrates have been artificial graphites. Many of the properties of the artificial graphite materials depend on the raw materials which were used to make the graphite and the conditions used to make the graphite. Mantell (1979) reports that artificial graphites are made by heating amorphous carbon to around 2000 C. Typical amorphous carbon sources for graphite are petroleum coke, coal pitch coke, gas retort carbon, carbon black and polymeric materials such as polyvinyl chloride.

When graphitizing the carbonaceous materials, it has been observed, that between 1500 and 2000 C, a volume expansion of 0.2 to 0.6% occurs for most baked carbons made from petroleum coke and pitch. Crystalline growth commences towards the top of this temperature range. Above 2000 C, ash volatilization of the metallic impurities becomes significant. Graphitization occurs at approximately 2200C; however the potential crystallite growth and ordering are latent within the baked carbon structure. The more crystalline alignment in the starting material, the more alignment in the product. The graphitization mechanism involves movement and rearrangement of the microcrystallites in relation to one another. Thus, this process is both time and temperature dependent. The higher the temperature and the longer the time for graphitization, the more ordered the crystals in the final structure.

D. Physical Properties of Graphite

1. General Physical Properties

A wide range of physical properties for artificial graphites can be achieved, by altering manufacturing conditions. This wide difference in physical properties is demonstrated by the surface areas reported by Zettlemyer (1969) for Graphon and P-33 type graphites, which are given below:

Graphon	120 m ² /g
P-33	10 m ² /g

Typical physical properties for graphites have been given by Davidson et al.

(1968) and are reproduced below:

Theoretical crystal density	2.26 g/cm ³
Bulk Density	1.5-1.8 g/cm ³
Total Porosity (fraction of total volume which is empty)	15-30%
Fraction of pore volume which is open to liquid or gas penetration	20 - 60%
Mean Pore Diameter	5 to 300 A

2. Pores

In addition to the microstructure of graphite, there is a macrostructure of grains and voids. The grain size is that of the powder which was bonded to for the unfired block. The void structure is that of the pore system lying between and within these grains. The typical diameter of the pores will be of the order of one quarter of the average grain size; 500 angstroms would be a reasonable diameter for a coarse graphite (Davidson, 1968). A fine textured graphite might be made from particles ranging from 500 angstroms downward. In both grain types, the total accessible voidage might amount to 15 percent of the bulk; a further 10 to 20 percent of closed porosity must be assumed to account for densities which are commonly measured.

The pores of graphite within the grains, are probably composed of crystallites of graphite randomly stacked to give a porous network. Because the crystallites of graphite are larger and more ordered than the microcrystallite of activated carbon, the pores in graphite tend to be larger than the pores in activated carbon.

Cameron and Stacy (1960) studied the pores of an artificial graphite using both a low-pressure and a high pressure porosimeter. In their investigation, it was found that the mercury penetrated the pores at virtually one and the same pressure. This is unusual and differs from most of the substrates which we are considering which have a pressure range over which the mercury penetrates. The interpretation of this data was that the pores were slit shaped and that the measured radius of penetration, was related to the distance between the parallel slits forming the pores.

E. Graphite - Surface Functional Groups

It is generally assumed (Boehm, 1966) that the surface groups on graphite are generally the same as those on activated carbon. Very little work has been carried out on characterizing the functional groups present on the graphite surface, because the surface area and the concentration of these functional groups is very low. The most detailed investigation of surface oxides on graphite, were carried out by Kiselev and collaborators (1959, 1961a,b, 1966a,b, 1968, 1969). A chemical analysis of the surface functional groups of a natural graphite, indicated that the following functional groups were present at the indicated levels:

Group	Content (meq/m ²)
-COOH	.48
-C-OH (tertiary)	.16
-COOH	.04
-C=O	.07

Carboxyl groups were determined by Na₂CO₃ neutralization, tertiary hydroxyl groups from the difference between NaOH and Na₂CO₃ neutralization. Hydroperoxides were determined iodometrically in aqueous isopropanol. The carbonyl content was estimated from the reaction with p-bromophenylmagnesium bromide. The groups in the above table account for only 29% of the oxygen of the graphite. From the difference in the oxygen balance, it was concluded that neutral or basic hydroxyl groups, radical, and interstitial bridges might have also been present.

F. Graphites as TGA Substrate Materials

Graphites, such as PG-60 have a large pore volume and a low surface area. The large pore volume and the relatively low surface areas suggests that the glycerol being held by the PG-60 is mostly in the form of capillary liquid which is not interacting with the graphite surface as well as adsorbed glycerol. The glycerol that would be desorbed first upon smoking a TGA device containing PG-60 would be the glycerol held by the capillary interactions. The glycerol interacting with the pores walls would not be readily desorbed. This lack of interaction with the surface for the glycerol which is desorbed, prevents catalytic breakdown of the glycerol but prevents the stronger specific adsorption interactions with the glycerol which would prevents migration.

VI. Activated Carbons

A. General

There are many similarities between activated carbons and graphite. Like graphite, activated carbons are prepared synthetically and like graphite, the properties of the final activated carbon depends on the raw material used and the manufacturing conditions. The following sections are given to describe the structure, manufacturing conditions, physical properties and surface chemistry of activated carbons.

B. Structure

X-ray examinations have shown activated carbons to be microcrystalline, build up like graphite in layers of six-membered carbon rings with disorganization

between the packets. This x-ray diffraction data and comparable data for graphite, have been given by Scheffler (1968) and are reproduced below. The packets are considered as graphitic crystallites with hexagonal lattice constants "a" in the plane of the layer and "c" perpendicular to the layer. The size of the microcrystallites in the layer of the plane is denoted as "A" and the size of the microcrystallite in the "c" direction is denoted as "C". A diagram showing an activated carbon microcrystallite and pointing out the cell constants for a activated carbon crystal is given in Figure 8.

Sample	a (A)	c (A)	A (A)	C (A)
Darco S-51	2.45	7.20	27	9.6
Darco G-60	2.45	7.50	38	9.5
Darco K	2.45	7.30	27	10.7
Graphite	2.456	6.708	>1000	>1000

What is significant about the X-ray diffraction data is that although the size of the hexagonal lattice constants parallel to the plane of the microcrystallite remains relatively constant for the various forms of carbon for which data is presented, there is a difference in the hexagonal lattice constant perpendicular to the plane. The "c" parameter for the activated carbons is significantly greater than the "c" parameter for graphite. This larger "c" parameter indicates a disordering of the layers. If the layers were organized, the "c" parameter would remain the same as the "c" parameter for graphite. Also the X-ray data shows that there is a large difference in the crystal sizes between activated carbon and graphite.

Possible causes for the lack of organization of the microcrystalline layers are heterocyclic and functional groups at the edges of the layers. The ringed structures at the edges of the planes making up the microcrystallite are often heterocyclic owing to the nature of the starting material or the preparation process. Functional groups terminating the microcrystalline planes prevent orientation of the microcrystallite planes with respect to each other due to steric factors and thus are also responsible for the lack of order in the stacking of the microcrystalline platelets. The nature of the functional groups is discussed later under the section of the surface chemistry of activated carbons. Heterocyclic groups and functional groups tend to affect both the distance of separation of adjacent planes and the sorptive properties of the carbon.

C. Manufacturing

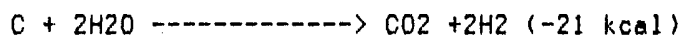
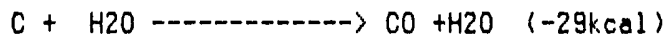
This section on the preparation of activated carbons is included in this report to distinguish activated carbons from graphite and to give background in how changing the manufacturing conditions can change the properties of the carbon.

Activated carbons can be prepared from a wide variety of materials. Materials from which activated carbons have been prepared include: coconut shell, lignite, bituminous coal, bones, carbohydrates, lignin, petroleum acid sludge, peat, pecan shells sawdust and wood. These materials are carbonized in the range of 500 -800 C. During the carbonization of the raw material, the graphite-like microcrystallites are formed. The temperatures which are used are too low to allow formation of the graphite crystal. During the formation of the microcrystallites, impurities are expelled from the interior of the carbonaceous material. Some of the impurities which are expelled are the "free carbon material" which is the benzene insoluble material.

After the material is carbonized, it is activated. Scheffler (1968) reports that precise control of both reaction temperature and reaction time is very important to impart the desired properties when activating carbons by any method. Two general methods are used to activate carbons. These are:

1. High temperature oxidation of a previously charred carbonaceous substance (i.e. coke, char and charcoal)
2. Low temperature chemical dehydration and/or chemical reaction of a carbonaceous material.

For the high temperature activation, steam or CO₂ are generally used. Temperatures usually range upwards from 800 C. The high temperature activation involves a material loss of 30 to 70% due to the following proposed reactions for steam activation.



A low yield upon activating carbon generally results in a very active material, and a high yield results in a less active material.

Dubin (1966) noticed two stages of oxidation in the activation of sucrose. First macropores were formed by burnout of the most reactive material, consisting principally of radicals attached to the edge carbons of the microcrystalline plane. Second, micropores were formed by the burnout of the microcrystalline planes. Snow et al. (1959) reported that higher ash content causes faster pore development during activation. Inorganic matter appears to cause stress locations on the surface of the microcrystallite at which points oxidation is initiated much more easily. Various inorganic additives may be added to catalyze the oxidation process (Hassler, 1963). Once a microcrystalline plane is attacked by an oxidizing gas, oxidation continues on that plane in preference to another area until a stable structure is developed (Wolff, 1959). The temperature at which the oxidation takes place is particularly important relative to the type of surface which results. It is also possible as R. L. Johnson et al. (1964) points out for carbonization and activation to take place in one step.

To make activated carbons directly from cellulosic materials primarily wood, chemical activation involving somewhat lower temperatures are employed. The

activating agents are many, but all are strongly dehydrating substances. The three most commonly used are phosphoric acid, zinc chloride, and sulfuric acid. Each has its limitations. Sulfuric acid-wood mixtures cannot be heated above 200C, and the product after leaching has adsorptive properties only when wet. Activation by phosphoric acid requires temperatures in the range of 375 to 500C. The reagent is recovered by leaching with water. Problems with the phosphoric acid treatment generally are associated with the corrosion of the equipment. Zinc chloride activation occurs in the range of 550 to 650. The reagent is recovered by leaching with dilute hydrochloric acid and water. Problems may arise from traces of zinc salts remaining in the product. The last two types of carbon can be dried with little or no loss in adsorptive capacity.

The bulk of current production in the United States is made by the high-temperature steam process. Some chemically activated carbon is produced. However, in Europe, more emphasis is placed on chemical activation.

D. Physical Properties

1. Surface Area

Activated carbon is truly a rigid sponge as a result of the manufacturing procedure. During the charring of any carbonaceous substance, considerable volatile matter is given off (Scheffler, 1972). In the course of the evolution of this volatile matter, a large number of internal spaces are formed, referred to as pores. Pores can mean cracks and crevices as well as the conventional connotation of cylinders or cones. These crack and crevices result in incredibly high surface areas for activated carbon. Typical surface areas for activated carbons range from 450 to 1800 m²/g. Chemically activated materials have surface areas in the 1600 to 1800 range and the steam activated materials have lower surface areas.

2. Pore Distribution

Activated carbon is a highly adsorptive substrate due to its complex network of pores of various shapes and sizes. The shapes include cylinder, rectangular cross sections as well as many irregular shapes and constrictions. An electron microscope photograph of an activated carbon which shows the different shaped pores is given in Figure 9. The size can range from less than 10 A to over 100,000 A (Hassler, 1967). The assortment of pore sizes depends on the source material used and the extent of activation.

An interesting result of the irregular shape of the activated carbon pores and molecular motion is that fine pores are not blocked by large molecules but are still free for entry by the small molecules (Calgon).

Because a major contribution to the surface area of activated carbons is located in pores of molecular dimensions, the size of the pores in an activated carbon are very important to adsorption. Some of the surface area of a substrate may be inaccessible to an adsorbate, because the adsorbate is too

large to penetrate the pores. Glycerol is able to penetrate almost all the pores of an activated carbon, but is not able to penetrate pores which are smaller than the smallest dimension of glycerol (estimated from x-ray data to be around 3A).

Some typical curves for the pore distributions of a so-called gas adsorbing carbon (Columbia G) and a typical decolorizing carbon (granular Darco) are given in Figure 10.

E. Chemical Properties

1. Location of Active Sites

Activated carbons are by no means chemically inert materials. They exhibit acid-base properties and can undergo halogenation, hydrogenation, oxidation, etc. When considering the chemistry of activated carbons it is useful to know where the active sites are located. Hennig (1962) used electron microscopy to answer this question. Alterations in the positions of the edges of the cleavage planes were shown to result from preferential attack of molecular oxygen on the crystals at the edges of the layer planes. He estimated that the reactivity of the edge atoms was at least 20 times that of the atoms within the basal planes.

2. Chemistry of Active Sites

Nearly every type of functional group known in organic chemistry has been suggested as being present on the surface of activated carbon (Snoeyink et al., 1972). The functional groups often suggested are carboxyl groups, phenolic hydroxyl groups and quinone carbonyl groups. Slightly less often are the suggestions of ether, peroxide, and ester groups in the forms of normal and fluorescent-like lactones, carboxylic acid anhydrides and cyclic peroxide. These groups are given in Figure 11.

F. Activated Carbons as TGA Substrate Materials

Activated carbons can adsorb and hold a large amount of glycerol, due to its large surface area and small pores. Because the pores in activated carbon have a small diameter, the glycerol is probably in contact with the walls of the pores and breakdown of glycerol occurs. If the active sites are on the edges of the activated carbon as has been suggested in the literature, then further graphitizing the active carbon could reduce the number of active sites. This graphitizing would reduce the breakdown of glycerol but would also reduce the substrates holding capacity.

Blocking the pores would probably not prevent catalysis of the glycerol pyrolysis because of the irregular shape of the activated carbon pores.

Chemically reacting the active sites to render the sites inactive (perhaps react the activated carbon with an alcohol?) could prevent breakdown of the glycerol on an activated carbon surface.

According to Hassler (1963) the pH of the surface is important to the catalytic activity of an activated carbon. Thus adjusting the pH to an optimum level could also better the substrate properties of an activated carbon.

VII. Alumina

A. General

Alumina is a member of a group of substrates commonly referred to as metal oxides. Alumina was selected for this discussion because laboratory data suggests that some forms of alumina give little or no off-taste when used as a substrate and then smoked in a TGA device. Alumina finds use as a support material in very many catalytic processes: Pt-Al₂O₃ (reforming) and CoO/MoO₃/Al₂O₃ (Hydrodesulfurization) are just two examples of the use of alumina as a catalyst component in high tonnage processes. There is ample evidence that alumina is far from a passive support in these catalyst applications. A great deal of research effort has been channeled into gaining understanding of the catalytic role of alumina and it has emerged that pure alumina can exhibit extremely diverse behavior depending on the mode of preparation.

B. Preparation

Although alumina, Al₂O₃ has only one chemical formula (i.e. Al₂O₃), alumina can occur in many crystalline forms and can occur with varying degrees of hydration. Only two crystalline forms of alumina are recognized. These forms are α -alumina and γ -alumina. These two polymorphs are derived from hydrated forms of alumina as shown in Figure 12. The importance of these polymorphs is that the surface chemistry of the various polymorphs are different and therefore the interaction with the glycerol is different for the various polymorphs.

C. Physical Properties

The physical properties of alumina depend on both the crystalline form and the thermal treatment to which the sample has been subjected. Generally the higher the pre-treatment temperature for a particular alumina, the lower the surface area and the larger the pores.

Mikhail and coworkers (1979) characterized the pore structure and surface areas of various aluminas in order to determine the influence of the physical nature of the materials on the catalytic behavior. To obtain alumina samples with different surface areas and pore sizes, three samples of alumina were heated to either 500 or 800 C. Their data for various aluminas are given below:

Sample	Temperature	Starting Material	Surface area	Most Probable
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	of Thermal Treatment (C)		m ² /g (BET)	pore size (A)
Al-I	600	boehmite	178.3	42
Al-II	600	gibbsite	227.5	20
Al-III	600	η -Al ₂ O ₃	117.1	(non-porous)
Al-I	800	boehmite	142.7	60
Al-II	800	gibbsite	135.7	30
Al-III	800	η -Al ₂ O ₃	118	(non-porous)

The effect of pretreatment temperature on a sample of Al₂O₃ was reported by Kittaka (1974). X-ray diffraction data indicated that the samples which were treated at temperatures at or above 800 C were α -Al₂O₃ and the crystal structure of the Al₂O₃ treated at temperatures below 800 C was γ -Al₂O₃. This data is presented below:

Temperature	Crystal Type	Surface Area
600	γ -Al ₂ O ₃	92.4
800	α -Al ₂ O ₃	54.9
1000	α -Al ₂ O ₃	44.7
1200	α -Al ₂ O ₃	4.62
1400	α -Al ₂ O ₃	2.61

D. Surface Chemical Properties

Surface hydroxyl groups are often found on the surface of metal oxide. The surface hydroxyl groups have a large influence on the surface properties of the metal oxide and on the catalytic activity. The dissociative behavior of surface hydroxyl groups varies with such bulk chemical properties as the valency and radius of the metal involved, the crystal structure and degree of hydration. The surface chemistry of alumina is complicated inasmuch as there exist many crystalline forms as well as amorphous alumina. Furthermore there are various forms of hydroxides and oxyhydroxides, i.e. hydrargillite, bayerite, and boehmite.

Most of the studies carried out to identify the functional groups on the alumina surface have utilized infrared spectroscopy. Under normal conditions, hydroxyl groups are present on the alumina surface. On γ -Al₂O₃ there are at least three kinds of isolated hydroxyl groups (Peri and Hannon, 1960). These groups have been described as hydroxyls as

1. hydroxyl groups bridging vacancies between octahedral and tetrahedral ions.
2. tetrahedral hydroxyl groups
3. octahedral hydroxyl groups

Infrared spectroscopy has determined that α -Al₂O₃ has only one type of hydroxyl group, absorbing at about 3733 cm⁻¹; H-bonded polymers of the same OH unit show up in the spectra at intermediate stages of dehydration (Morterra et al., 1976). These hydroxyl groups are of the octahedral type similar to what is observed for γ -Al₂O₃. The other forms of hydroxyl groups are not observed on α -Al₂O₃.

The number and type of hydroxyl groups present could influence the catalytic activity of the alumina. It is possible that only certain types of hydroxyl groups will interact with various adsorbates and catalyze various reactions.

E. Reactivity of Alumina with Alcohols

Many studies have been carried out to investigate the reactivity of alumina with alcohols. Alumina reacts with alcohols by removing water. Alumina can ~~hydrate~~ easily be hydrated, thus this reaction is thermodynamically favorable. These dehydration reactions could be occurring between glycerol and the alumina surface in our TGA system. A knowledge of the reaction mechanisms and the surface sites responsible for the dehydration of alumina can shed light as to why some aluminas are good substrate candidates and some aluminas give too much off-taste to be considered as a potential substrate.

Aluminas which have more surface active groups that would react with alcohols would catalyze the dehydration reaction more readily than a group which has fewer reactive sites. A γ -Al₂O₃ would probably react more readily with an alcohol than an α -Al₂O₃, because the γ -Al₂O₃ has more hydroxy sites. Also a γ -Al₂O₃ probably would have more surface area than an α -Al₂O₃ and thus would have a greater amount of area to react with the alumina.

The mechanism for ether formation from alcohols over alumina catalysts has been reported by Padmanabhan and Eastburn (1972). In this study, it was concluded that an ether was formed by a nucleophilic displacement reaction. This reaction takes place between an alcohol adsorbed on an acidic site and an alcohol adsorbed on a basic site. Chemisorption (specific adsorption) of an alcohol on a basic site, represented as hydrogen bonding to the surface, increases the nucleophilicity of the oxygen resulting in an incipient alkoxide ion. The proposed reaction mechanism is given in Figure 13.

Knozinger et al. (1972) reported the reaction mechanism for the dehydration of alcohols to form olefins over an alumina surface. In their proposed reaction mechanism, two sites were needed to catalyze dehydration. One site being an oxygen atom on the surface and the other site a hydroxy group. A transition step was proposed in which the bond between the carbon and the alcohol hydroxy group weakens and the bond between the alcohol hydroxy group and the hydrogen atom of the surface hydroxy group strengthens. This transitional species and the reaction mechanism is shown in Figure 14.

A similar reaction which is also shown in Figure 14 was proposed to take place on two oxide groups.

F. Alumina as a TGA substrate.

Alumina can be treated at various temperatures to form various alumina polymorphs which have different surface properties. Heating alumina can result in a decreased surface area, but larger pores. Heating alumina

can also result in varied surface chemistry. Only one type of hydroxy group results on the surface of alumina which has been treated above 1470 K (α -Al₂O₃) whereas three types of hydroxy groups are present on the surface of alumina prepared from boehmite at 720 K (γ -Al₂O₃). The different species present on the different polymorphs as well as the different surface areas could be responsible for the different oftaste properties which we see with different aluminas.

VIII. Vermiculite

A. Structure

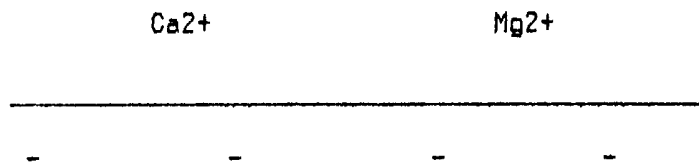
Vermiculite is a phyllosilicate or a mineral made of layers of alumina and silica. A diagram showing the silica and alumina layers of vermiculite is shown in Figure 15. The surface of the silica layers are negatively charged, due to substitutions of Al³⁺ for Si⁴⁺ in the silica tetrahedral layers. These substitutions may be partially balance by other substitution within the lattice, but there is always a net charge deficiency of 1 to 1.4 per unit cell.

The structure of vermiculite also contains water between the layers which hydrates the interlayer cations. In Figure 16 is shown the silica layers of vermiculite and the interlayer water.

B. Physical Characteristics

Unlike the other substrates which we are considering as substrate candidates, vermiculite does not possess pores to achieve its highly adsorptive properties. Vermiculite has a high ability to adsorb glycerol, because glycerol not only adsorbs on the outer surface of the vermiculite but adsorbs in the interlayers as well.

The external surfaces parallel to the silica and alumina layers and the interlayer surfaces of the vermiculite can be thought of as a plane possessing a net negative charge balanced by cations as shown:



C. Chemistry

1. General Chemistry

A general chemical formula for natural vermiculite is:

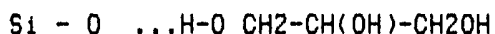


with $x = 1$ to 1.4
 $y = \text{about } 8$

The Mg^{2+} and Ca^{2+} ions serve to balance the charge deficiency due to lattice substitutions and are largely exchangeable ions.

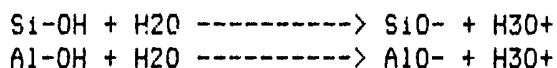
2. Surface Chemistry

Because the sites giving rise to the negative charge are due to substitutions within the lattice and not to broken bonds, the interaction between glycerol and the surface oxygen groups can be due to hydrogen bonding.



Because of the three glycerol hydroxy groups and the possibility to interact strongly with the glycerol surface. It is likely that the glycerol is adsorbed on each face of the interlayers.

The charged planar surface sites of vermiculite which account for about 80% of the adsorption properties of vermiculite are not pH dependent. However, pH dependent sites can be found on the edge of the vermiculite crystals. These sites are pH dependent as follows:



D. Interaction with Glycerol

van Olphen (1977) reports that many organic compounds with a dipole character (which includes glycerol) are adsorbed on the layer surfaces and probably also on the edge surfaces of a clay in analogy with the behavior of a clay with water. As is the case with the adsorption of water on clays, it is not known to what extent the polar groups of the organic molecule associate with the counterions of the clay and to what extent they are hydrogen-bonded to the oxygen surfaces. According to van Olphen infrared data indicates that the hydrogen-bonding interaction is the significant interaction.

Eltantawy (1977) studied the adsorption of glycerol on vermiculite. In this study, it was found that the adsorption of glycerol was dependent on the counterion in the interlayer and that only one layer of glycerol adsorbed in the interlayer. No explanation of the types of interactions which take place between glycerol and vermiculite was given.

E. Vermiculite as a TGA Substrate

Vermiculite is a suitable candidate for a TGA substrate. The physical and chemical nature of this material are much different than the other materials

which we are considering for use as TGA substrates. Vermiculite does not possess pores in the same sense as activated carbon or alumina, but adsorbs adsorbates such as glycerol in the interlayers of the clay structure. Glycerol can probably desorb more readily from the interlayers than glycerol can from pores. There should be a statistical advantage to the desorption of glycerol from vermiculite, because glycerol can desorb for the four sides of the interlayers, whereas for activated carbon pores, glycerol can only desorb from the pore opening. In the interlayers, there is also little steric hindrance to desorption of the glycerol because other glycerol molecules in the interlayers act as pillars to allow the easy desorption of glycerol.

Although the exact nature of the bonding of the glycerol in the interlayers is not known, the interaction can only occur between oxides and not hydroxyl groups, because there are no hydroxyl groups in the interlayers.

VIII. Summary

Much has been learned about the reactivity of glycerol, adsorption of glycerol on solid surfaces, the chemistry of the substrate surfaces and the interaction of glycerol with the various substrates.

Generally, it has been found that there are two main substrate properties that dictate how the substrate will interact with the glycerol. These two are the ease in glycerol reaching and being released from the active surface sites, which is related to pore size and surface area, and the chemistry of the substrate surface. To obtain a suitable TGA substrate we need to balance the tendency of the substrate to catalyze reactions involving glycerol with the tendency of the substrate to adsorb the glycerol via physical interaction in order to prevent migration of the glycerol in the TGA device.

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FIGURE 1

CONFORMATIONS OF PROPANEDIOL-1,2

(STAGGERED ONLY)

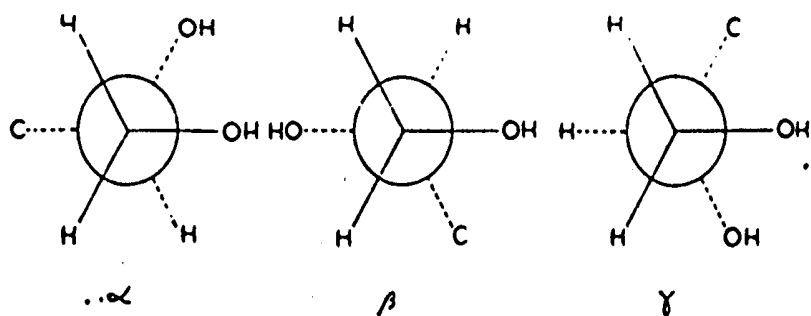


Fig. 5. Conformations of propanediol-1,2

CONFORMATIONS OF GLYCEROL RELATED TO PROPANEDIOL-1,2

Table VI
Energies of the (staggered) conformations of glycerol
in kcal per mol relative to the *uu*-conformation

<i>uu</i> -	0
<i>u₁'</i> -	0.6
<i>u₂'</i> -	1.4
<i>βu</i> -	4.3
<i>β'₁</i> -	4.9
<i>β'₂</i> -	8.6

(FROM H. VAN KONINGSVELD, 1968)

FIGURE 2

STRUCTURE OF GLYCEROL

(DETERMINED BY XRD)

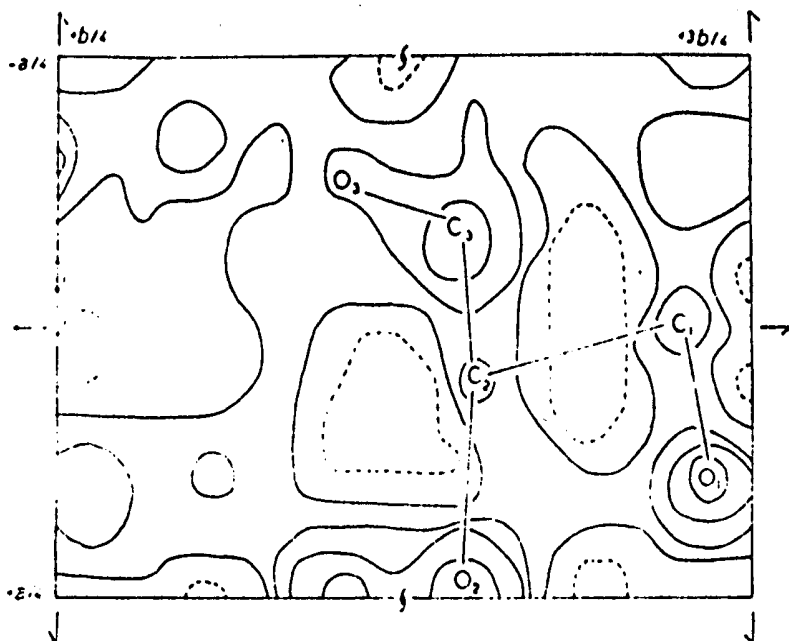
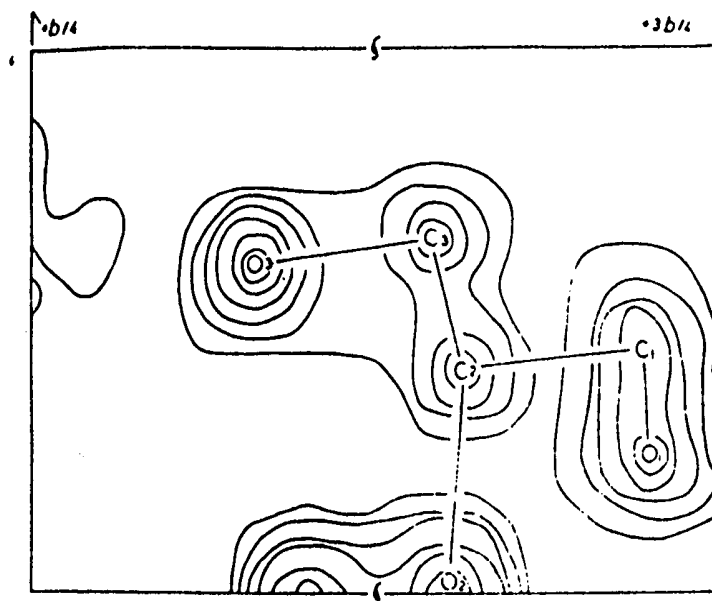


Fig. 3. Electron density projection on (001) with the structure factors listed in Table IV. Dashed line is zero-line.



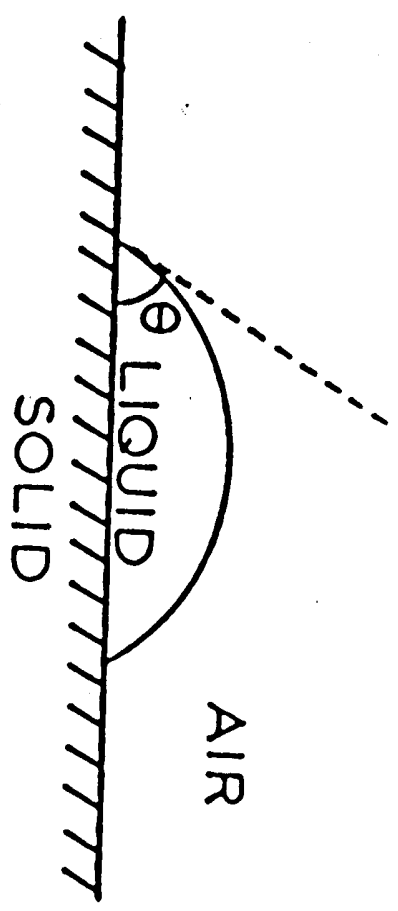
4°. Final electron density projection on (001) with 78 structure factors. Contours are drawn with intervals of $2eA^{-3}$ from $2eA^{-3}$.

Some intermolecular contacts ($< 3.5 \text{ \AA}$)

O1 O2 (I):	2.75 \AA
O1 O3 (I):	3.21
O2 O2 (I):	3.29
O2 O3 (I):	2.73
O1 O3 (II):	2.73

(FROM H. VAN KONINGSVELD, 1968)

FIGURE 3

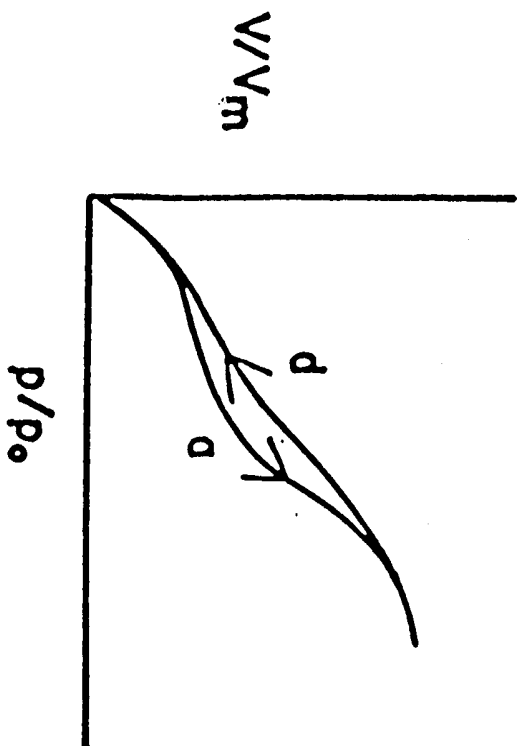


Cross-section of a liquid drop resting on a solid surface
with angle of contact θ .

CONTACT ANGLE

(FROM PARFITT, 1966)

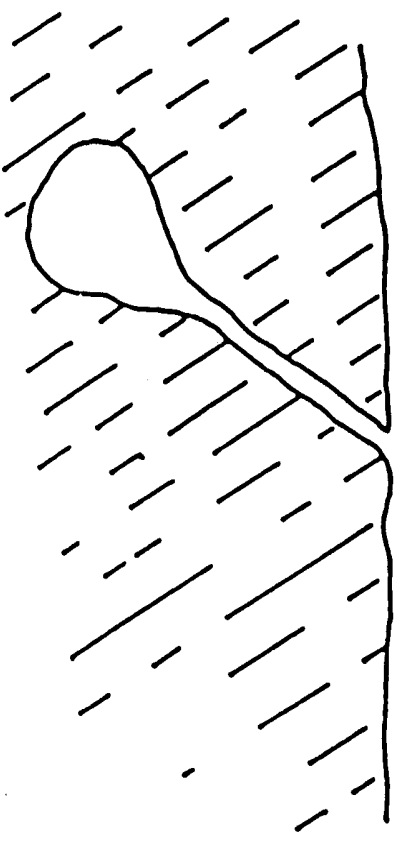
FIGURE 4



A schematic illustration of hysteresis between the adsorption (a) and desorption (d) branches of an experimental isotherm.

(FROM HEMENZ, 1977)

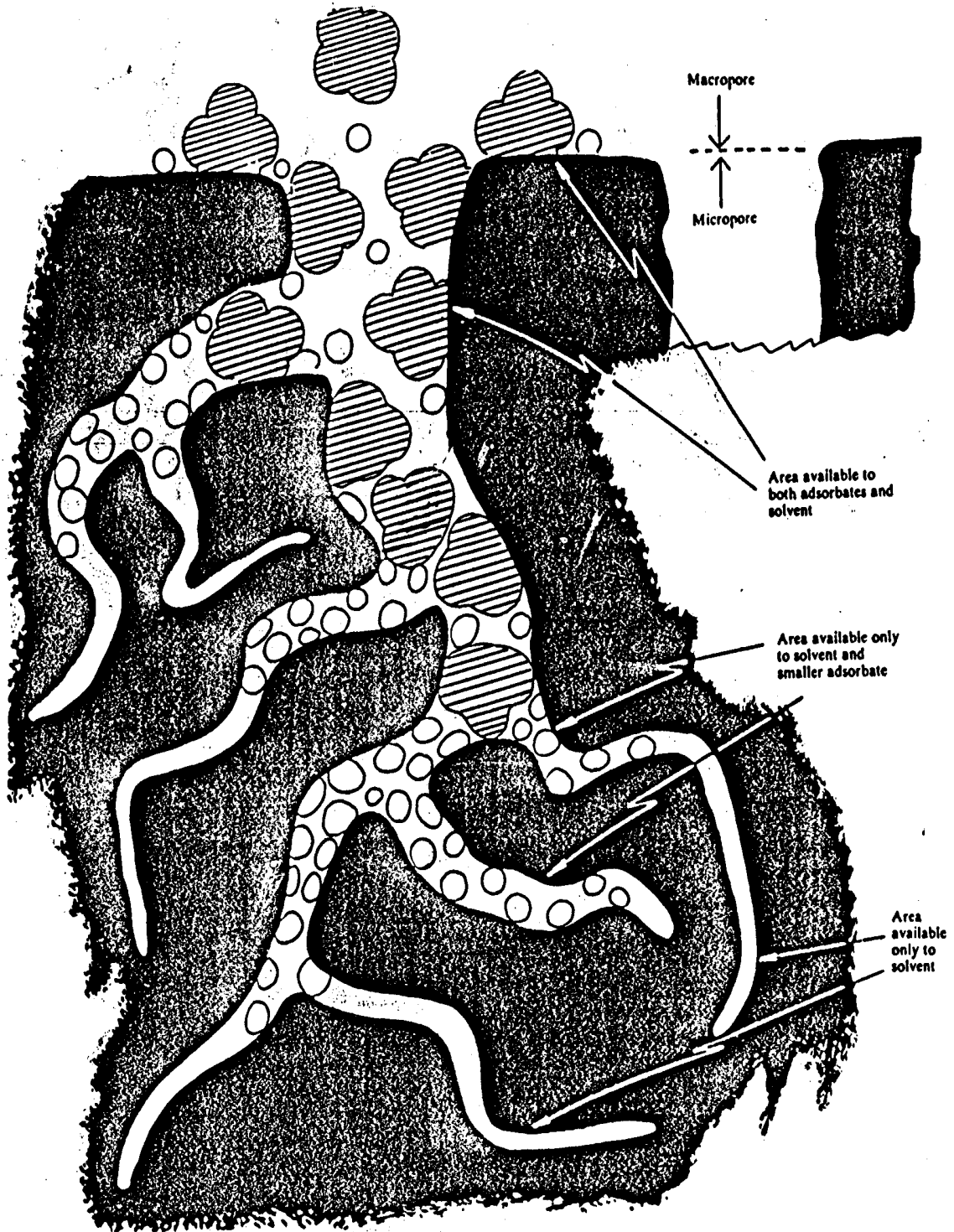
FIGURE 5



An "ink bottle" pore.

(FROM ADAMSON, 1976)

FIGURE 6

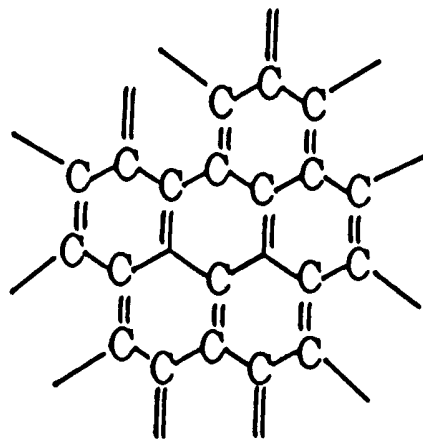
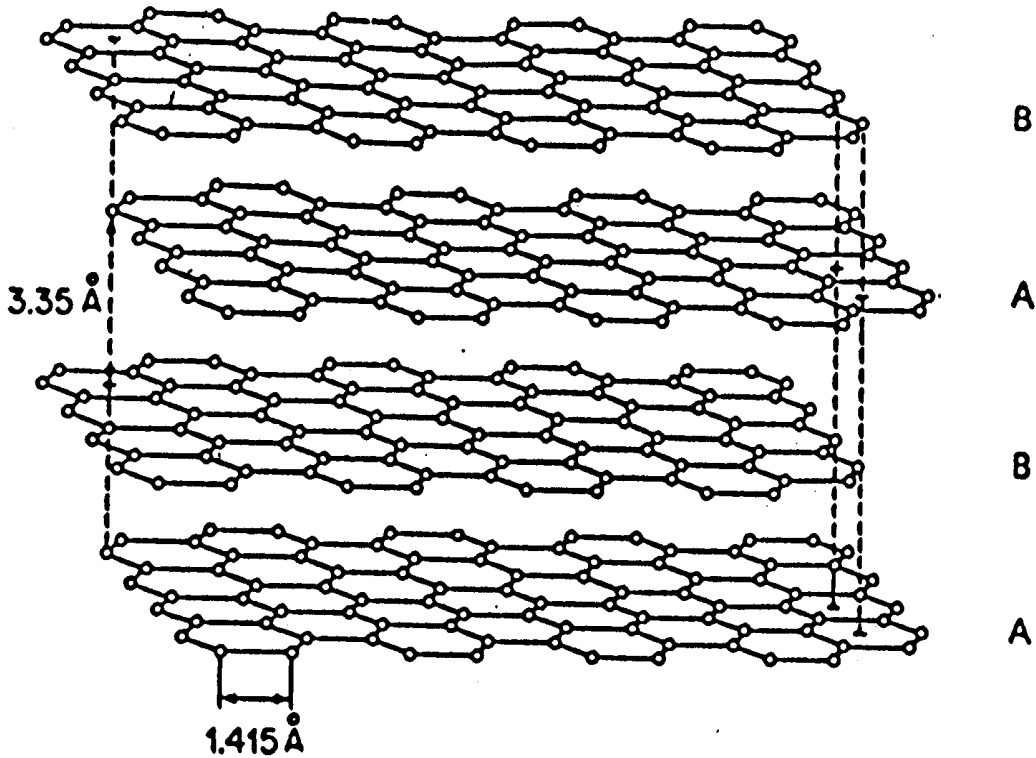


**MICROPORE
(IN ACTIVATED CARBON)**

(FROM CALGON CORPORATION LITERATURE)

50587 7010

FIGURE 7



(11·IX)

STRUCTURE OF GRAPHITE

(FROM COTTON AND WILKINSON, 1980)

CRYSTALLITE
SHOWING DIMENSIONS

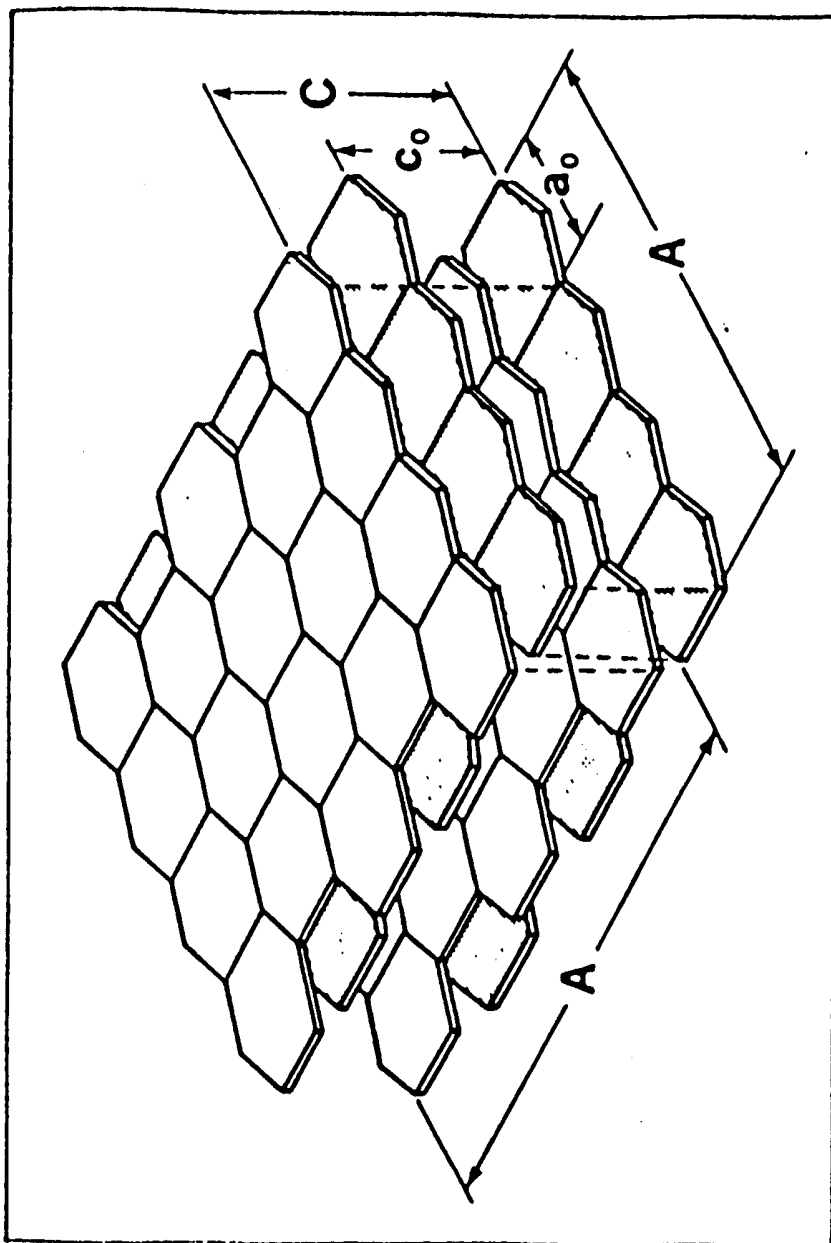


FIGURE 8

FIGURE 9

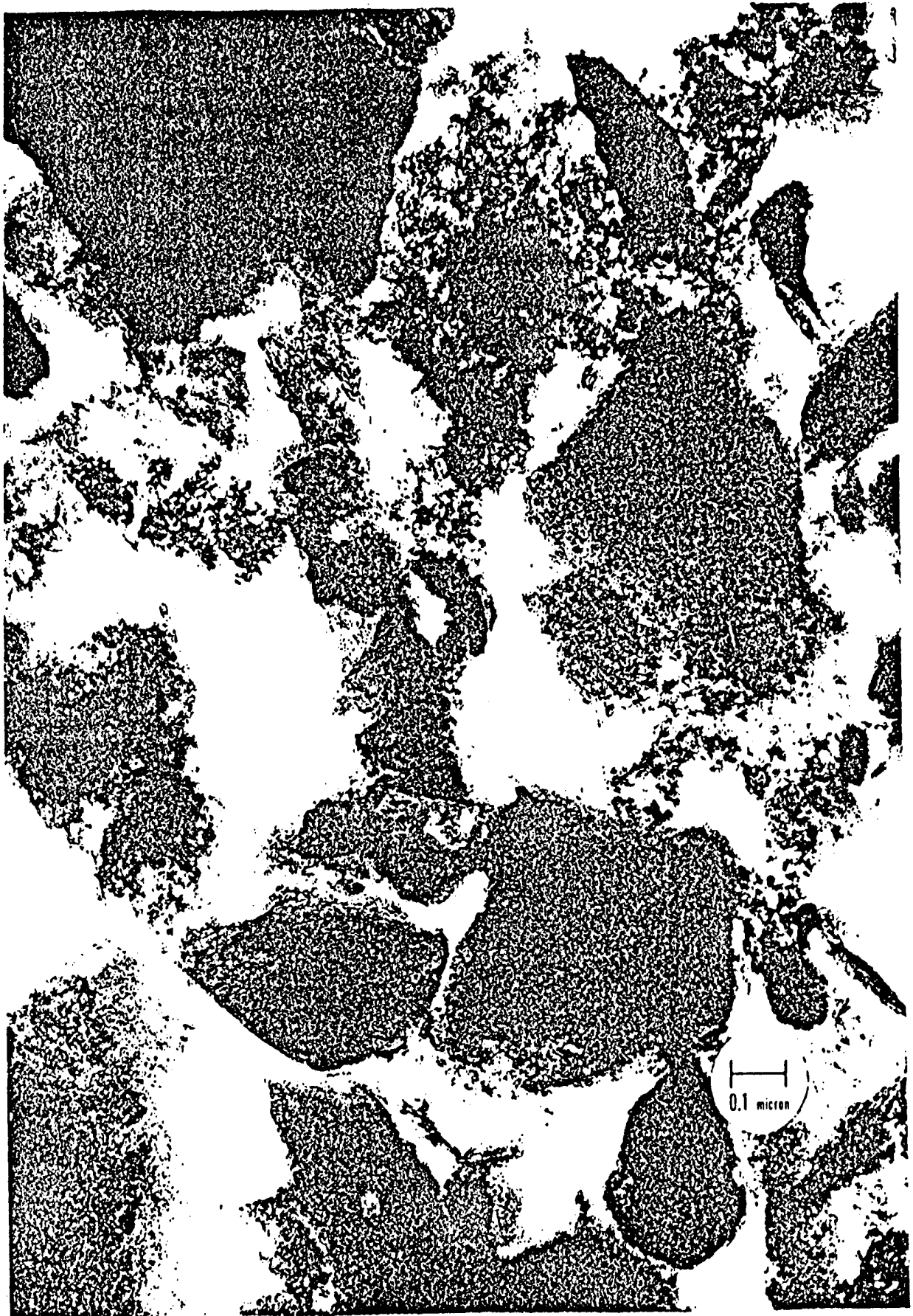


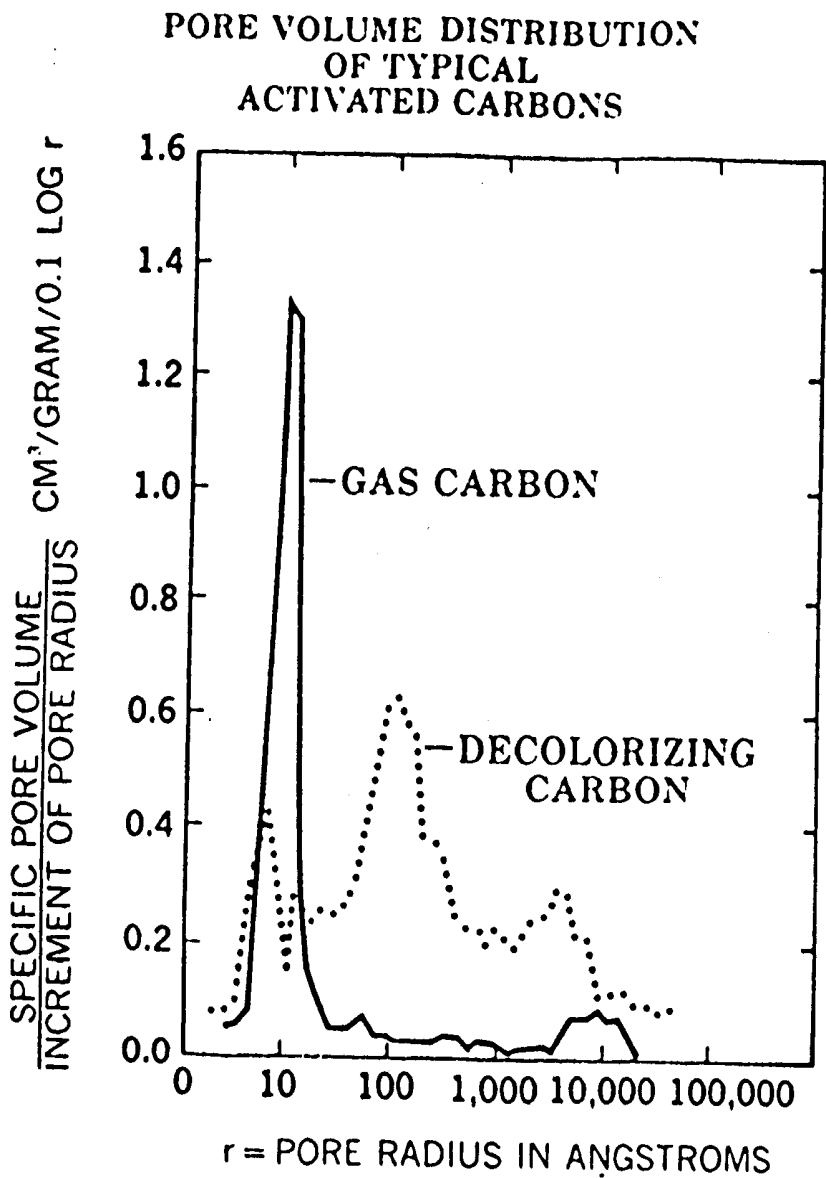
Figure 10A

ELECTRON MICROSCOPE PHOTOGRAPH OF A PITTSBURGH ACTIVATED CARBON

While the artist's conception on the preceding page shows a cross sectional view, the above illustration is an actual photograph. Light areas are pore openings. Dark areas represent the carbon skeletal structure.

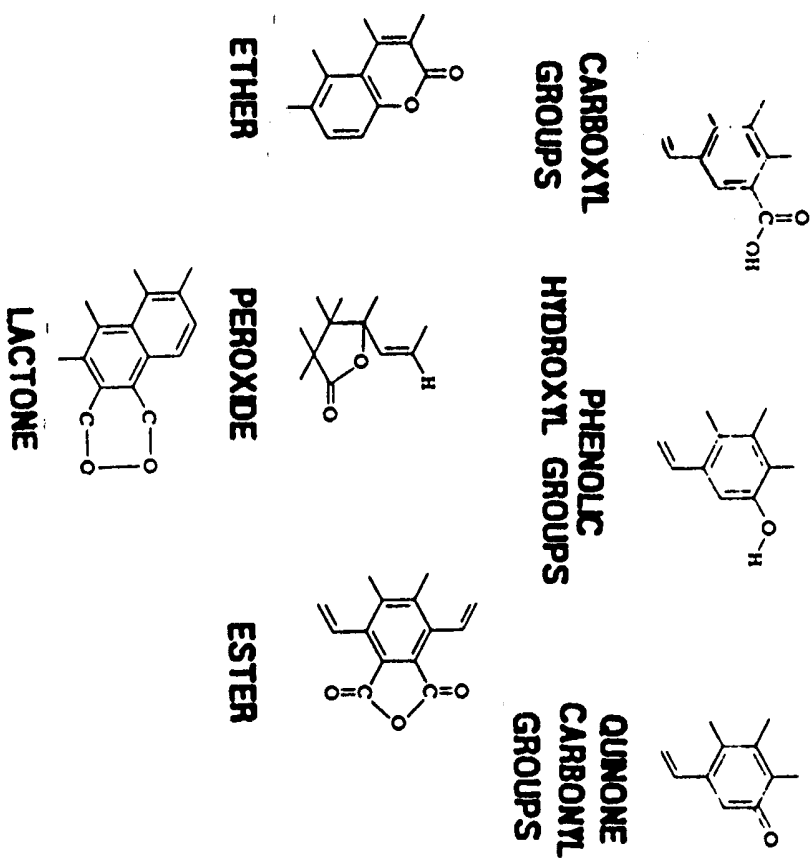
(FROM CALGON CORPORATION LITERATURE)

FIGURE 10

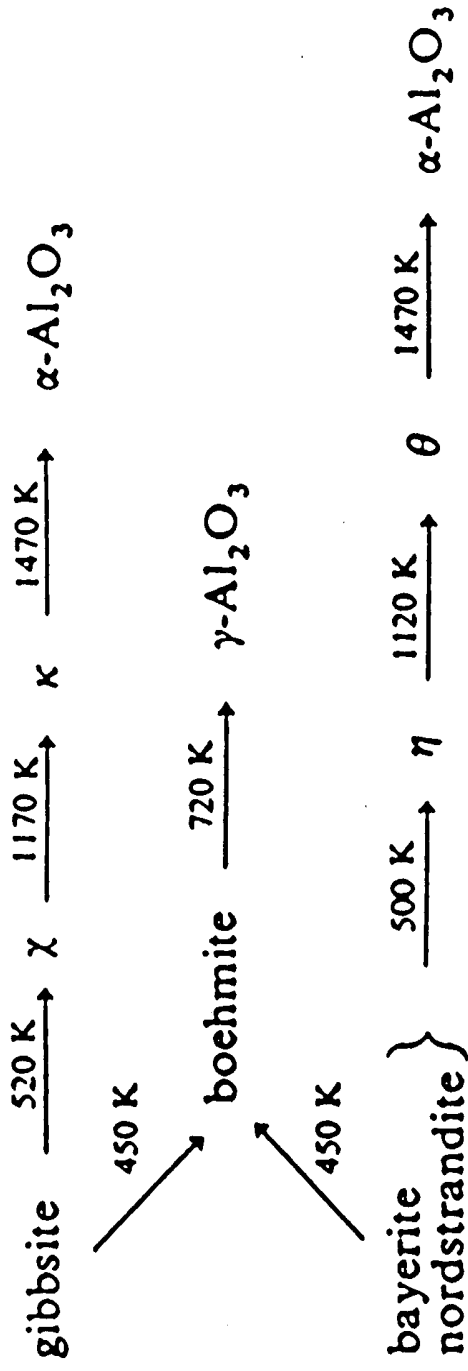


(FROM ICI AMERICAS LITERATURE)

FIGURE 11



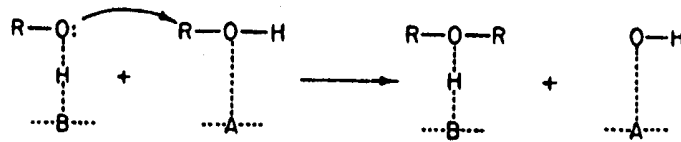
SURFACE FUNCTIONAL GROUPS OF ACTIVATED CARBON



The dehydration sequences of the aluminium trihydroxides in air
 (Adapted from 'Physical and Chemical Aspects of Adsorbents and Catalysts',
 ed. B. G. Linsen, Academic Press, New York, 1970, p. 171)

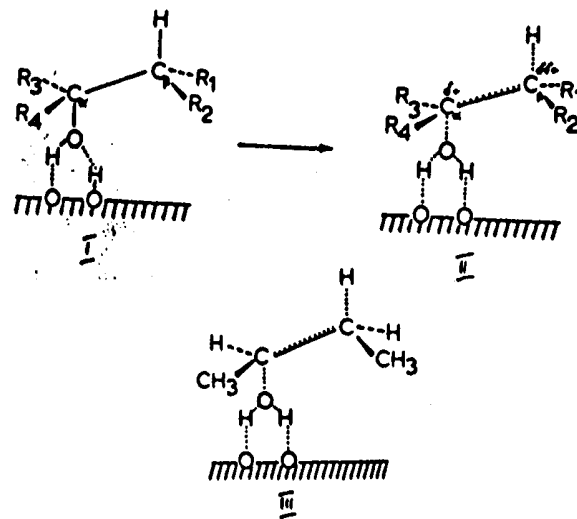
FIGURE 12

ETHER FORMATION FROM ALCOHOLS OVER ALUMINA



ETHER FORMATION
ON ALUMINA

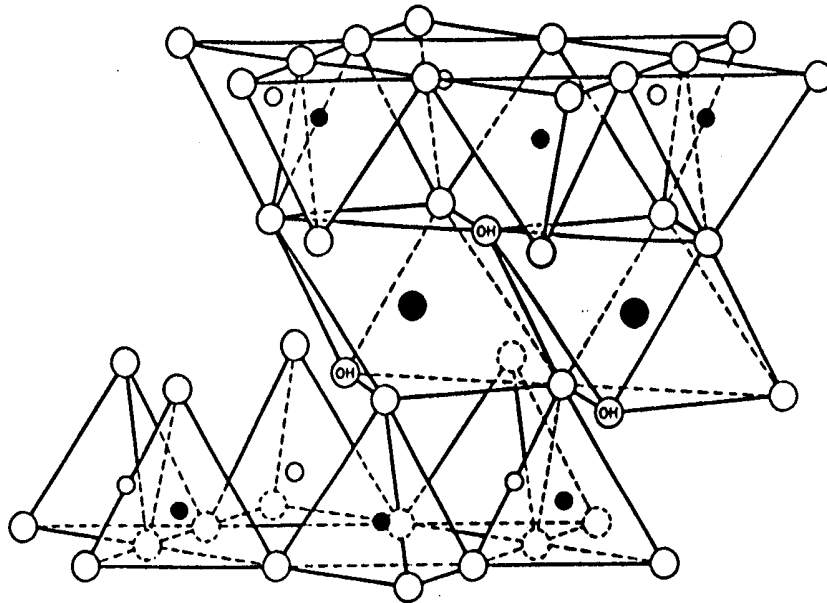
FIGURE 13



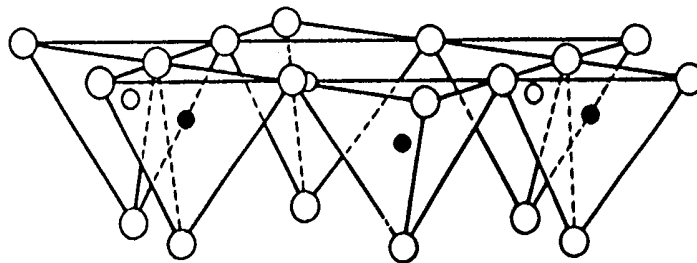
MECHANISM FOR OLEFIN FORMATION
ON ALUMINA

FIGURE 14

FIGURE 15



Exchangeable cations
 nH_2O



- Oxygens (OH) Hydroxyls ● Aluminum, iron, magnesium
- and ● Silicon, occasionally aluminum

STRUCTURE OF VERMICULITE

FIGURE 16

INTERLAYER WATER OF VERMICULITE

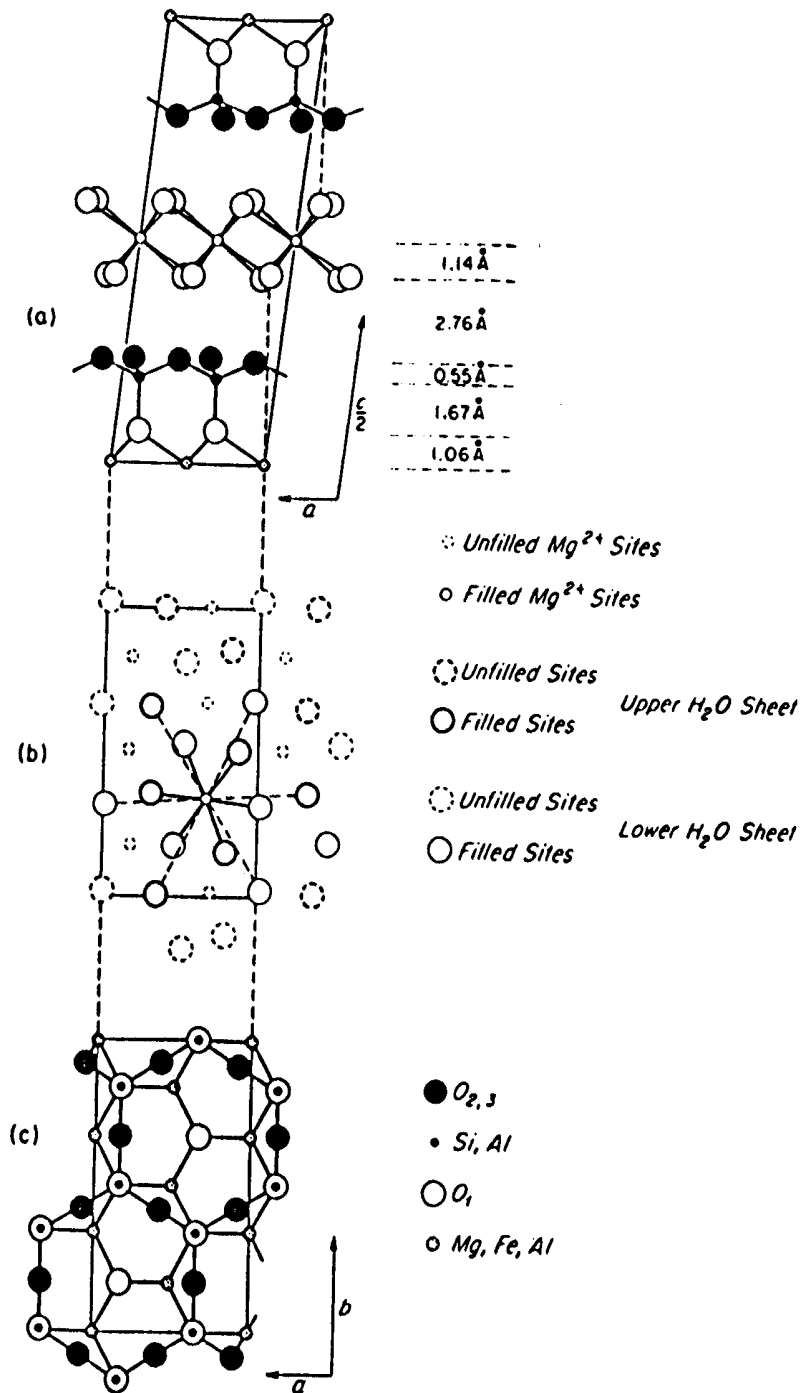
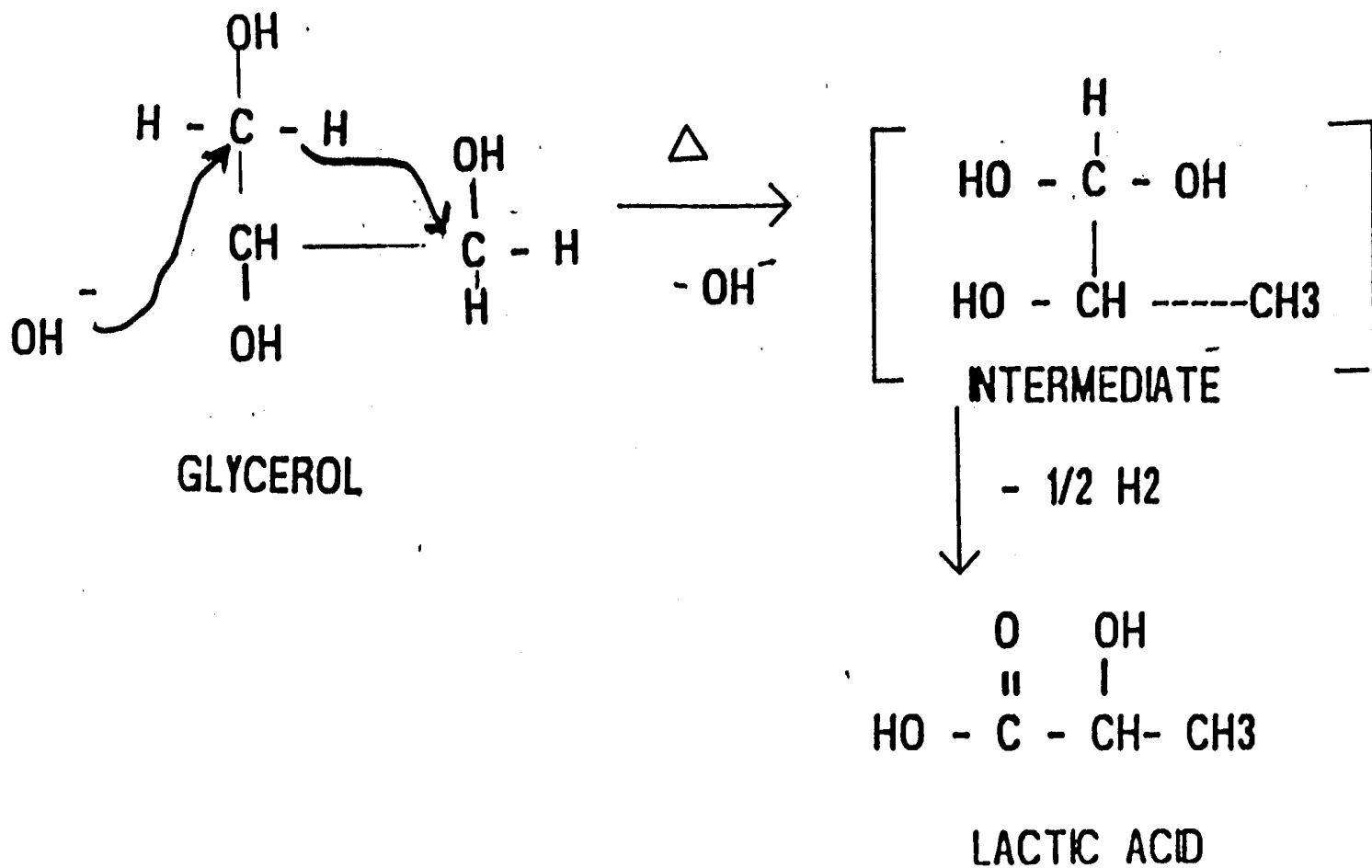


Fig. 4-20. The crystal structure of Mg vermiculite: (a) projection normal to the ac plane, (b) projection normal to the ab plane, showing the inter-layer region; (c) projection normal to the ab plane showing one-half of a silicate layer ($z = 0$ to $c/8$). (After Mathieson and Walker.¹⁰¹)

APPENDIX A

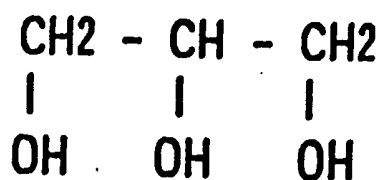
REACTION MECHANISMS

1. FORMATION OF LACTIC ACID FROM GLYCEROL

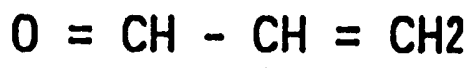
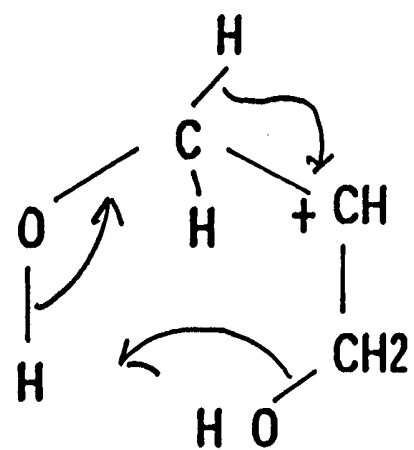
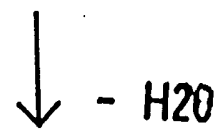
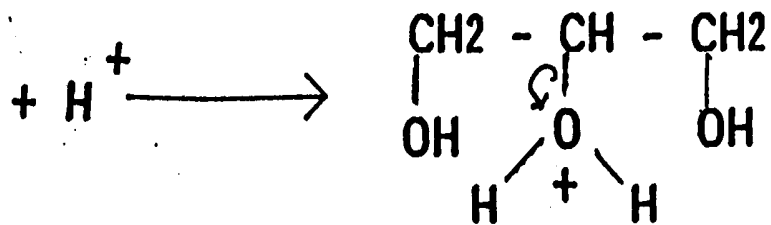


APPENDIX A (CON'T)

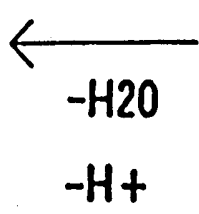
2. FORMATION OF ACROLEIN FROM GLYCEROL



GLYCEROL



ACROLEIN



APPENDIX A (CONT)

3. FORMATION OF FORMALDEHYDE AND ACETALDEHYDE FROM GLYCEROL

