A STUDY OF THE EFFECTS OF SURFACE ACTIVE MATERIALS ON OXYGEN TRANSFER

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SCOPE AND CONTENTS:

The effect of surface active agents on the rate of gas absorption into water was investigated. Pure oxygen was absorbed into quiescent degasified distilled water through adsorbed monomolecular films of alkylbenzene sulphonate (ABS) or sodium lauryl sulphate (NaLS).

The rate of absorption was characterized by effective diffusivity as measured in detergent solutions up to 20 mg/1 and temperatures between 10 and 30°C.

Gas transfer mechanistic models plus physical and chemical properties of surface films were reviewed in order to understand the fundamental processes of interfacial interference which would account for anomolies in results reported in the literature.

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CHAPTER 1

INTRODUCTION

The absorption of oxygen through the surface of lakes, ponds, reservoirs, and streams is a very critical natural process. Without continual oxygen renewal many bodies of water would quickly become anaerobic, unable to support higher forms of aquatic life. Pungent and obnoxious odours could result from extreme cases of complete oxygen utilization in a stream. The reduction in oxygen concentration by biological oxidation of only several parts per million can create conditions where desirable game and commercial fish will not survive.

The waste assimilation capacity of a stream is critically dependent on the rate of reaeration occurring in the stream. Of the two rates governing the oxygen concentration in a body of water, the biological oxidation rate and the reaeration rate, the latter has been found to be the most difficult to estimate. The point of minimum dissolved oxygen in a stream is very sensitive to the reaeration rate.

The rate of reaeration has been shown to be dependent on several factors. Much has been written on the influence of temperature, however, recent investigations, Metzger (1968) have shown that temperature is not an independent variable but interacts with the degree of turbulence. Surface turbulence can greatly increase the rate of oxygen transfer through an interface. Many authors have indicated that wastes containing surface active agents in a bubble system can cause a decrease in oxygen uptake, Eckenfelder & Barnhart (1961), Hammerton & Garner (1954) while others have reported that they may increase the rate of mass transfer, Baars (1955), Zieminski et al. (1960).

Contamination by surface active material is not only important in natural bodies of water, but it is also a factor to be considered in waste treatment as extra aeration capacity may be required to overcome the reduced rate of oxygen transfer due to surfactants. Sources of surface active agents are household detergents and industrial wastes such as sulphonated lignins from the pulp and paper industry.

A fundamental approach to the problem of gas transfer through a surface active material film was deemed necessary due to the lack of interpretation of the mechanism of surfactant interference as applied to recent models of mass transfer of a gas into solution.

Recently Mancy & Barlage (1966) have proposed two effects of SAA (surface active agents) on the properties of surface water. The first, called "effects of the first kind", are related to the physical resistance to gas transfer as offered by the adsorbed interfacial film and the second, called "effects of the second kind", which are related to the increase in viscosity and depression of the hydrodynamic activity of the surface. The relative importance of these effects has not been determined; however, they are thought to depend on the structure and the physicochemical characteristics of the SAA molecules. If one of these effects is predominant in retarding gas transfer, then suitable parameters relating surface properties to gas transfer resistance can be proposed.

The aim of this study, therefore, is:

- to determine what characteristics of a system will influence the effects SAA have on it. If the effect will be that of a physical resistance, a change in the hydrodynamic properties of the surface, or both, and
- to rationalize conflicting views in the literature with respect to the role of surfactants in gas transfer, and
- to relate mechanisms by which surface active agents influence gas transfer, to the problems of water pollution. The absorption of oxygen under quiescent conditions was considered to be ideal, a base case to compare natural occurring aeration in a pond or reservoir.

CHAPTER 2

LITERATURE REVIEW

MECHANISTIC MODELS OF GAS ABSORPTION INTO LIQUIDS

Mechanistic models to describe gas absorption have developed over the years to account for gas transfer under varying circumstances. Lewis & Whitman (1924) applied Fick's Law governing the diffusion process to describe a steady-state mass transfer condition:

Fick's Law is stated as

$$\frac{dm}{dt} = -DA\frac{dc}{dx} \qquad (1)$$

where: $\frac{dm}{dt}$ is the rate of mass transfer,

A is the area normal to the direction of mass transfer,

$\frac{dc}{dx}$ is the concentration gradient, and

D is the diffusivity.

It was their hypothesis that gas transport into a turbulent liquid occurred by molecular diffusion through a thin film of gas and a film of quiescent liquid. This is known as the two-film model. With a gas of low solubility in water such as oxygen, the gas film offers little resistance to the transfer, hence, the liquid film at the interface was considered to govern the transfer rate. It was assumed that:

1. the liquid surface was saturated by the gas ,
2. the entire resistance was due to the liquid film ,and

3. the bulk of liquid beneath the film has a uniform concentration due to the higher diffusivity accomplished by eddy turbulence.

Giving the liquid film a thickness L the steady-state transfer rate across the film can be written from equation (1).

$$\frac{dm}{dt} = DA\frac{C_s - C_L}{L} = K_L A \ (C_s - C_L) \qquad (2)$$

where: C_s is the saturation concentration,

C_L is the bulk liquid concentration, and

K_L is the absorption coefficient.

In terms of the rate of change of concentration

$$\frac{dC_L}{dt} = K_L \frac{A}{V} \ (C_s - C_L)$$

where V is the total volume of the liquid from equation (2) it can be seen that the absorption coefficient can be written

$$K_L = \frac{D}{L}$$

It is important to note here that K_L varies directly as the Diffusivity. This is a relationship which characterizes the type of mass transfer and in particular the degree of surface turbulence. This steady-state assumption requiring a uniform concentration gradient across the film can only be valid after a time during which unsteady-state gas absorption occurs If the age of the surface is short compared to that required for absorption to come to equilibrium conditions, serious deviations from the film model of Lewis & Whitman can result.

This period of transient absorption conditions was considered by Higbie (1935) who proposed the "Penetration model ". Higbie arrived at a value for the mass transfer coefficient (K_L) by considering diffusion into an infinitely deep liquid. In the case where the concentration gradient is changing with depth, X, the Diffusion into an infinite half-space can be described as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \qquad (3)$$

Solving for the initial condition:

$$C = C_o \quad \text{at} \quad X > 0 \qquad (3a)$$

where C_o is the initial concentration.

The boundary conditions are:

$$C = C_s \quad \text{at} \quad X = 0 \ \& \ t > 0 \qquad (3b)$$

and $$C = C_o \quad \text{at} \quad X = \infty \ \& \ t > 0 \qquad (3c)$$

The solution of equation (3) for the Diffusion through a stagnant liquid is:

$$C = C_o + (C_s - C) \ \text{erfc} \left[\frac{X}{2\sqrt{tD}} \right] \qquad (4)$$

where: erfc = 1-erf (erf is the error function)

The rate of gas transfer is given by:

$$\frac{1}{A} \frac{dm}{dt} = (C_s - C_o) \sqrt{\frac{D}{\pi t}} \qquad (5)$$

and the total mass absorbed after a time t during which the surface has been exposed is:

$$m = 2A\,(C_s - C_o)\sqrt{\frac{Dt}{\pi}} \qquad (6)$$

From this analysis the mass transfer coefficient is as derived from equation (5) to be:

$$K_L = \sqrt{\frac{D}{\pi t}} \qquad (7)$$

Higbie concluded from this that the mass transfer coefficient varies as the square root of the Diffusivity :

$$K_L \propto \sqrt{D}$$

This relationship suggests that at unsteady-state conditions the transfer can be described by an index of 0.5 on the Diffusivity.

Danckwerts (1951) found fault with each of the previous hypothyses. He felt that,

> " the conditions required to maintain a stagnant film at the free surface of an agitated liquid appeared to be lacking, and it is probable that the turbulence extends to the surface of the liquid."

The conditions for diffusion through a stagnant surface layer of infinite depth are difficult to maintain due to surface instability arising from convection currents. These considerations led Danckwerts to propose the "Surface Renewal" model . This model, he suggested, pictures eddies as continually exposing fresh surfaces to the gas while at the same time removing parts of the surface exposed for varying lengths of time. During the period of exposure the gas is absorbed as predicted by the penetration model; this he justifies by suggesting that the period of exposure is so short that the depth of penetration is less than the depth at which the velocity of the eddy is appreciably different from its velocity at the surface. This implies that the scale of the turbulence is much greater than the depth of penetrations hence the velocity profile of the liquid beneath the interface can be ignored.

The mean rate of absorption per unit area of turbulent surface is:

$$\frac{dm}{A\,dt} = (C_s - C_o)\sqrt{DS} \tag{8}$$

$$\frac{dc}{dt} = \frac{A}{V}(C_s - C_o)\sqrt{DS} \tag{8a}$$

where :S is the rate of surface renewal

It is obvious from this equation that $\sqrt{DS}$ can be identified with the mass transfer coefficient K_L.

Dobbins (1956) was not as quick as Danckwerts in disposing of the idea of a liquid film. He felt that the film maintained its existence in a statistical sense. A film was always present, however, the liquid in the film could be exchanged at any time after its creation for liquid in the bulk of the system. Dobbins, therefore, considered the case of absorption into a thin liquid film when the film is being continuously replaced by turbulence from below. Dobbins showed the mass transfer rate to be:

$$\frac{dm}{dt} = A(C_s - C_L)\sqrt{DS}\ \coth\sqrt{\frac{SL^2}{D}} \tag{9}$$

where the mass transfer coefficient is expressed as:

$$K_L = \sqrt{DS} \quad \coth \sqrt{\frac{SL^2}{D}} \qquad (10)$$

This model is called the film-penetration model. At its extremes it describes the Lewis&Whitman Two Film Model and the Danckwerts Model. At low turbulence when S approach zero the value of K_L approaches D/L. This is the same as for the steady-state absorption through an unbroken film. At the other extreme (values of $\sqrt{\frac{SL^2}{D}}$ greater than 3.0) K_L is equal to $\sqrt{DS}$ or the result predicted by the Penetration-Surface Renewal Theory. The particular significance of this result is that a single model can describe different mechanisms due to different levels of surface turbulence and also account for intermediate values of the absorption coefficient.

King (1966) has proposed a model which combines concepts of molecular diffusion, small scale eddy diffusion, and large scale surface renewal. For convenience, he defined a zone of primary resistance to mass transfer as the distance over which most of the change in concentration between the interface and the mixed bulk liquid occurs. Eddies causing surface renewal must obviously be large in comparison to the thickness of this zone, while eddies associated with an eddy diffusivity must be smaller than this distance.

He defined the eddy diffusivity as:

$$E = ay^n \qquad (11)$$

where:E is the eddy diffusivity,

a is a constant,

y is depth normal to the surface and

n is a characteristic of the eddy diffusivity profile.

The differential equation for unsteady state diffusion, including both molecular and eddy diffusivities may be written:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y}\left[(D_m + ay^n)\frac{\partial c}{\partial y}\right] \tag{12}$$

Applying the same initial conditions and boundary conditions used in the solution of the unsteady-state absorption at an infinite depth, the result is a mass transfer coefficient as a function of surface age and the exponent n.

Like the film-penetration model it is a continuous function which describes both the surface renewal mechanism and the steady-state film model.

For low values of a or short exposure times the depth of penetration is small and hence the eddy diffusion term is small giving eqn(7):

$$K_L = \sqrt{\frac{D}{\pi t}}$$

as predicted by the penetration model. If a depth x is defined such that $D = ax^n$ then as n approaches infinity in the limit, at values of $y < x$ the eddy diffusivity is small compared to Dm and when $y > x$ the eddy diffusivity is much larger than Dm. This is the model of molecular diffusion in a region of thickness x followed by instantaneous diffusion in the bulk phase. This situation is the basis of the film-penetration model of Dobbins.

CHAPTER 3

PROPERTIIES OF THE LIQUID SURFACE

The solution of a gas into a liquid requires a physical transport through the interface, the physical and chemical properties of which can be very important in controlling the rate of mass transfer between phases. This is particularly true where the interfacial resistance to mass transfer is comparable to the resistance of the gas and/or liquid phase. Since the interface can take many forms: a bubble rising in a tank, a water droplet, the surface of a lake or stream, it is essential to consider the surface under both static and dynamic conditions.

This chapter summarizes some of the concepts of surface chemistry that apply to gas transfer through a surface as they may relate to problems involving water pollution.

3.1 PROPERTIES OF THE WATER INTERFACE

The interface between two homogeneous phases is not a discrete plane, but it is rather like a lamina or film with a characteristic thickness and properties very much different than those of the homogeneous phases. The interface of interest in this study is that between gas and water phases. The surface has its own density, viscosity, and energies.

3.1.1 SURFACE TENSION

The properties can be explained in terms of the water molecule orientation in the bulk phase and the surface. In the bulk phase the molecules are subjected to equal forces of attraction in all directions; whereas, the molecules at the surface have unbalanced forces of attraction which result in a net inward pull. The spontaneous contraction of the surface is due, therefore, to these forces which cause molecules to leave the surface. This is known as the phenomena of surface tension.

The surface tension can be described as the force at the surface causing contraction. Defined by Davies and Rideal as the force in dynes acting at right angles to any line of 1 cm length in the liquid surface having units of dynes/cm. The symbol generally given to surface tension is γ_o.

3.1.2 HELMHOLTZ FREE ENERGY

Thermodynamically the energy relationship of a system can be written as:

$$dF = -SdT - PdV + \gamma_o dA + \mu dn \qquad (13)$$

where :S is entropy,

T is temperature,

P is pressure,

V is volume,

A is area,

μ is chemical potential,

n is number of moles in the system, and

F is Helmholtz free energy.

For constant temperature, volume, and number of molecules in the system

$$dF = \gamma_o dA \qquad (14)$$

or $$\gamma_o = \left[\frac{F}{A}\right]_{T,V,n} \tag{15}$$

If F^s is the Helmholtz free energy of the surface, then

$$dF = d(AF^s) \tag{16}$$

Thus, $$\gamma_o = F^s + A\left[\frac{\partial F^s}{\partial A}\right]_{T,V,n} \tag{17}$$

However, in a one-component liquid, F^s depends only on the configuration of the molecules in the surface, and not the areas, so that: $\partial F^s = 0$ and $\gamma_o = F^s$

The surface free energy of a liquid is defined as the work in ergs required to increase the area of the liquid surface 1 cm^2. The units of $ergs/cm^2$ are dimensionally equivalent to those of surface tension. Surface tension and surface free energy are numerically equivalent provided the viscosity is not too great.

3.2 EFFECT OF SURFACTANT ON SURFACE

It has been found that the tendency of the surface area to decrease spontaneously can be altered by adding a second component. Surface active agents (SAA) are materials which can alter the physico-chemical properties of the water surface. Surfactants can be defined as those materials which in solution are preferentially adsorbed at the interface resulting in an excess surface concentration over that of the bulk. Materials such as fatty and resin acids, alcohols and detergents adsorb at the surface in the form of an oriented monomolecular layer. Surfactants are characterized by their tendency to diffuse to the surface where their hydrophilic groups are immersed in the liquid surface and the hydrophobic or water insoluble parts, such as paraffin tails, protrude into the gas phase.

This tendency for surface active molecules to pack into an interface, favours an expansion of the surface which must be balanced against the tendency for the surface to contract under normal surface tension forces. If π is the expanding pressure (or surface pressure) of an absorbed layer of surfactant, then the surface tension will be lowered to the value:

$$\gamma = \gamma_0 - \pi \qquad (18)$$

This is also called the interfacial tension. The absorption process is governed by diffusion of surfactants to the surface and desorption away from the interface. The great affinity of the soluble part of the molecule (i.e. carboxyl, sulphate, hydroxyl, sulfonate, etc. groups) for water and the insolubility of the hydrocarbon chain in water creates a high energy barrier to desorption. This results in a situation of higher surface concentrations of bulk concentrations of the solute.

3.2.1 TYPES OF MONOLAYERS

There are two types of monomolecular films which are discussed in the literature. As far as gas absorption studies are concerned, there is no difference between the nature of the films. The distinction lies in the manner in which the monolayer is formed, and the nature of the accessible experimental data.

Monolayers which are formed by absorption from the liquid phase are called Gibbs Monolayers. These are fairly soluble materials which present problems in the determination of the surface excess. The surface excess can be estimated using Gibbs adsorption equation and bulk concentration vs surface tension data.

Spread monolayers are formed by materials of low solubility in water solutions. These are usually spread from above on the water surface, often dissolved in organic solvents which quickly evaporate from the surface. Since the amount applied is measurable, the surface excess is known directly.

3 2.2 GIBBS MONOLAYERS

Gibbs monolayers are of most interest to those concerned with waste treatment. Surfactants found in waste water are generally of this type.

The surface excess of the Gibbs monolayer is given by the Gibbs adsorption isotherm. For dilute solutions, it is written as:

$$\Gamma = - \frac{1}{RT} \frac{d\gamma}{d \ln c} \qquad (19)$$

where: Γ -surface excess moles/cm^2;

γ -interfacial tension,

R- gas constant,and

T -absolute temperature, and

c -bulk concentration.

3.2.2.1 SURFACTANTS FORMING GIBBS MONOLAYERS

The hydrophilic part of the most effective surfactants (e.g. soaps, synthetic detergents and dyestuffs) is usually an ionic group, (Shaw 1966). These ions have a strong affinity for water due to their electrostatic attraction to the water dipoles which enables them to keep fairly long hydrocarbon chains in solution. Surfactants are classified as anionic, cationic or non-ionic according to the charge carried by the surface active part of the molecule.

For example:

ANIONIC - sodium dodecyl benzene sulphonate

$$CH_3(CH_2)_{11}C_6H_4\ SO_3Na^+$$

CATIONIC - laurylamine hydrochloride

$$CH_3(CH_2)_{11}NH_3^+Cl^-$$

Nonionic surfactants are not electrolytes, but they do possess the general polar- nonpolar character typical of surfactants (Adamson 1960).

Nonionic detergents compare favourably with soaps and synthetic anionic detergents and are common in many household products.

3.2.3 SPREAD MONOLAYERS

Much of the literature dealing with gas absorption has to do with spread monolayers. These are films produced by materials insoluble in water, a fact which makes the Gibbs equation impossible to employ. However, surface concentrations are known from the amount applied and surface pressure π can be determined very accurately by use of a Langmuir Trough (Davies and Rideal 1961).

3.3 ORIENTATION OF SURFACE FILMS

Besides knowing the surface concentration of an adsorbed or spread monolayer, it is suggested in the literature (Metzger and Dobbins 1967) that the orientation and the compressibility of the surface is an important factor in governing gas transfer under dynamic conditions. For each surfactant a force-area curve can be drawn from which the compressibility of the monolayer can be calculated. The surface pressure is plotted against the area per molecule of the surfactant at the surface. A typical force-area curve is shown in Figure 1. The two-dimensional compressibility is defined by:

$$c_s = -\frac{1}{A}\left(\frac{\partial A}{\partial \pi}\right)_T \tag{20}$$

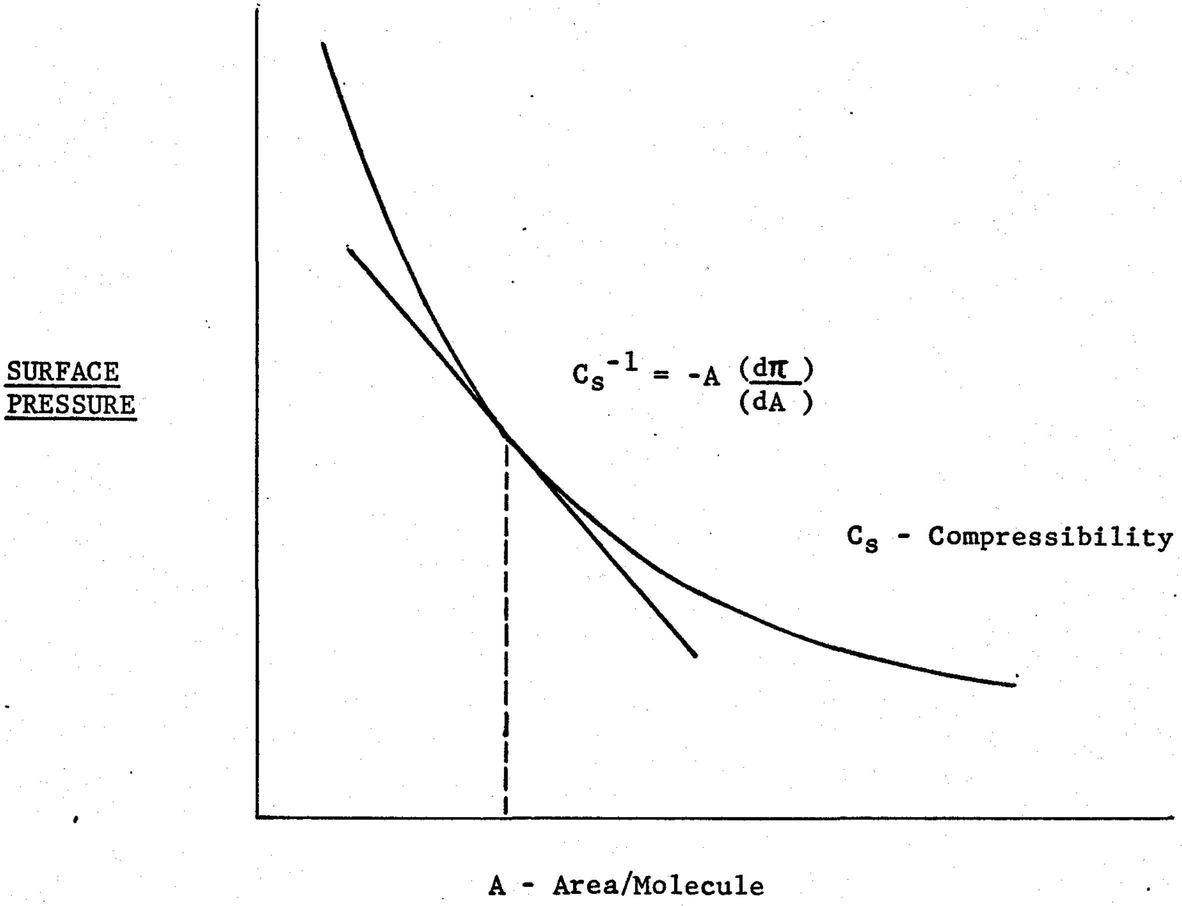


FIGURE 1

Compressibility of Surface Films

It is often more convenient to consider the reciprocal of C_s in discussing surface films. This is called the surface compressional modulus C_s^{-1} (Davis and Rideal 1961) and M_s (Metzger and Dobbins 1967).

$$C_s^{-1} = -A \left(\frac{\partial \pi}{\partial A}\right)_T \tag{21}$$

This is shown on Figure 1 to be the absolute slope of the π -A diagram times the area per molecule at which the slope is measured.

3.3.1 CONDENSED FILMS

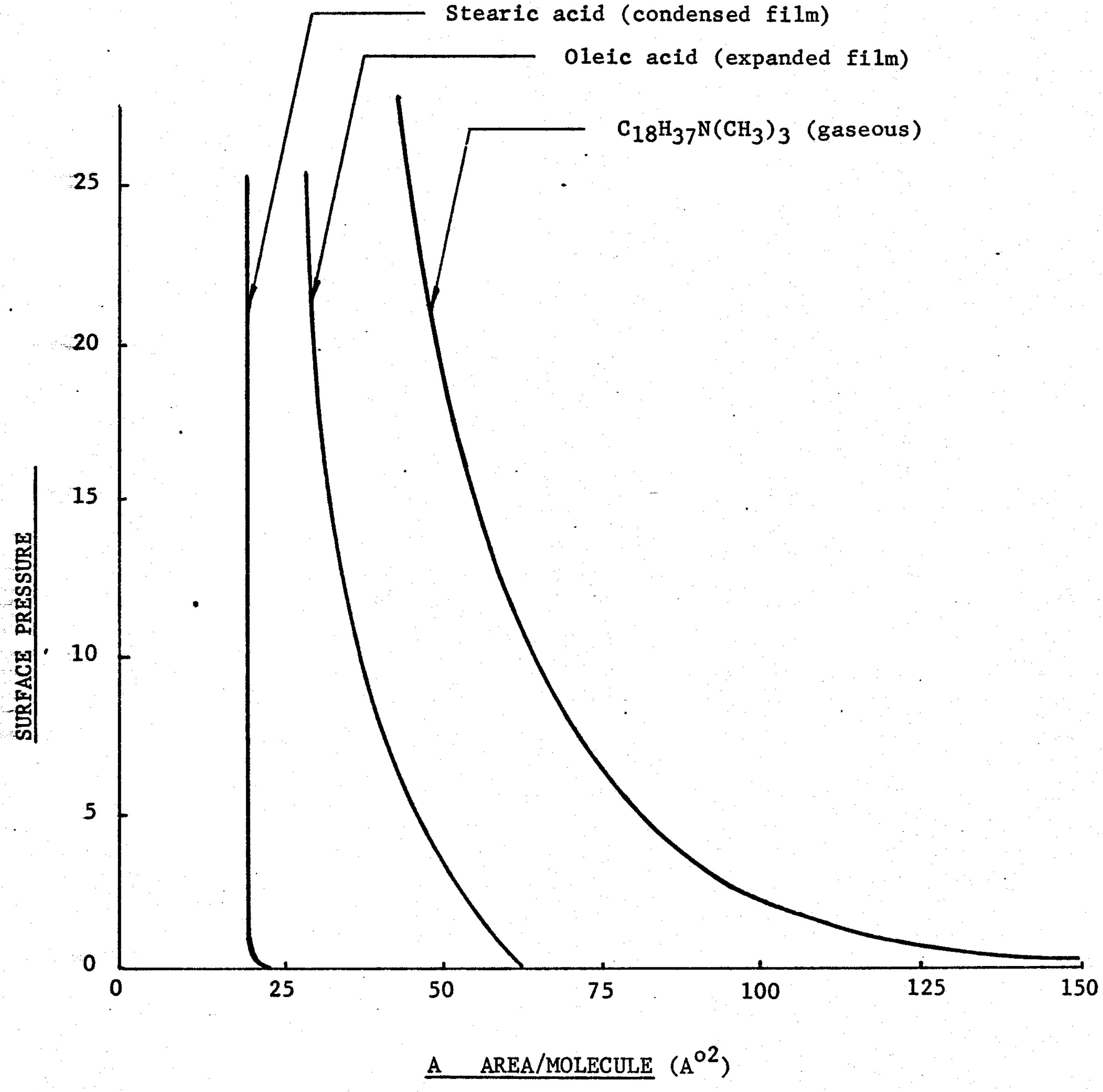
There are three main types of films, condensed, expanded and gaseous as shown in Figure 2. Condensed films exhibit a very small surface pressure up over a broad range of areas until the molecules come very close to the "limiting area" Ao. At this point when the area is reduced a little further a sudden rise in the surface pressure occurs. This limiting area is usually about 20 A^{o2}. It is thought that at areas greater than this the film consists of large islands held together by the van der Waals forces of cohesion between the hydrocarbon chains. When closely packed these films have a high modulus of compression.

3.3.2 EXPANDED FILMS

Many surfactants with a double bond in the chain will have a different shape π -A curve. Expanded films have a less distinct sudden increase in surface pressure due to greatly reduced forces of cohesion. At low areas the molecules are compressed and resemble that of a condensed film. At higher areas the film is called expanded. The molecules are bent and the hydrocarbon chain will lie on the surface giving greater surface pressures than condensed films.

FIGURE 2

Types of Films as Represented by Force-Area Curves



3.3.3 GASEOUS FILMS

Charged films exert a greater pressure than un-ionized monolayers due to the internal repulsion within the interface. Films such as these are called "gaseous films". They exhibit a more gradual increase in surface pressure as the area is decreased. The compressional modulus of gaseous films is very often the same magnitude as the surface pressure. Adsorbed films at low concentrations tend to be gaseous in nature.

CHAPTER 4

LITERATURE REVIEW - The Effects of Surfactants on Gas Transfer.

4.1 INTRODUCTION

Over the years conflicting reports on the effects of surfactants on oxygen transfer have caused confusion as to the actual role these materials play in gas absorption. Some investigators have shown that SAA decrease the transfer rate. Downing et al. (1957) found that anionic surface active materials reduced the mass transfer coefficient 56%. Holyrod and Parker (1952) found SAA interfered greatly with oxygen transfer in bubble systems but hardly at all under stagnant conditions. In aeration systems where mechanical aeration systems were used, Barrs (1955) showed SAA to cause a 100% increase in efficiency. Linton and Sutherland (1958) were able to show a decrease in oxygen transfer through a spread monolayer of hexadecanal found effective in reducing evaporation only when the surface was disturbed by a wind across the interface. Stirring alone was not effective in reducing the exchange coefficient.

Recently Mancy and Okun (1965) and Mancy and Barlage (1968) have suggested that there are two effects of SAA. "Effects of the first kind" are related to the adsorbed film and the material resistance it exerts on gas transfer by means of physical blocking of absorption sites and distortion of intermolecular forces between the water surface and the approaching gas molecules. "Effects of the second kind" are related to the increase in viscosity and the depression of the hydrodynamic activity of the interface caused by the SAA molecules. These authors however, were unable to suggest the relative importance of these two effects and the mechanistic models to which each would apply, other than to say that,

> "whether the resistance to gas transfer is that of the first kind or the second kind will depend on the structure and physicochemical characteristics of the SAA molecule"

In the literature there are many reported valves for gas absorption through monolayers under quiescent and turbulent conditions.

4.2 GAS ABSORPTION UNDER QUIESCENT CONDITIONS

Gas absorption under quiescent conditions will occur by the mechanism of molecular diffusion. If a surfactant is present the oriented molecules will cause a surface resistance to gas transfer which can be attributed to "effects of the first kind".

Plevan and Quinn (1966) studied the effects of monomolecular films on the rate of gas absorption into a quiescent liquid. They measured directly by means of a pressure transducer, the difference in gas absorption between cells, one containing a surfactant and the other having a clean surface. Using insoluble and Gibbs monolayers they were able to measure the surface resistance of a condensed layer of hexadecanol at a maximum of 200 sec/cm while expanded and gaseous films had an indeterminable small value. Thus only condensed films gave appreciable values for gas transfer interference. The gas used in these experiments was sulphur dioxide because of its high solubility in water.

Plevan and Quinn also presented values for surface resistance for condensed films of octadecanol 80 sec/cm, and stearic acid 35 sec/cm.

Sada and Himmelblau (1967) reported results for desorption through condensed monomolecular layers of long-chain hydrocarbons, namely hexadecanol and octadecanol. The surface resistance of these compounds to desorption of carbon dioxide were 95 sec/cm and 690 sec/cm respectively. The greatest reduction in the mass transfer flux occurred for the condensed monolayers in the range of 20 A^{o2} /molecule to 25 A^{o2} /molecule. Above 25 A^{o2} /molecule there was no measurable surface pressure although there is some indication that the "islands of molecules" offer some mass transfer resistance.

Hawke and Alexander (1962) and Hawke and Parts (1964) applied radiotracer techniques to measure the desorption rate of carbon dioxide and hydrogen sulphide from water. For expanded films they were unable to detect any resistance to gas transfer while condensed films gave measurable surface resistances. Increasing chain length of long chain alcohols gave higher values of surface resistances. For example, the surface resistance for desorption of carbon dioxide as computed from the transmission coefficient (1/R) was not determinate for hexadecanol (C16), 720sec/cm for octadecanol (C18),1490 for docosyl alcohol (C22) and 3000 sec/cm for hexacosyl (C26). These results appear to be less precise than other reported valves using different techniques.

Blank (1962) presented results for absorption of gases into réactive solutions. Blank used carbon dioxide and oxygen as the absorbing gases through condensed monolayers of hexadecanol and octadecanol. The two gases gave very similar results. Hexadecanol had a resistance of 80 sec/cm to carbon dioxide and 64.5 to oxygen while octadecanol had a surface resistance of 227 sec/cm and 312 sec/cm for carbon dioxide and oxygen respectively.

More sophisticated techniques were required to determine the surface resistance of Gibbs monolayers. Princen et al. (1967) and Princen and Mason (1965) were able to measure the surface resistance by measuring the rate of shrinkage of a bubble due to outward diffusion of gas through a monolayer. For a 4% solution of hexadecyltrimethylammonium bromide (HDTAB) and 1% HaBr the resistance of the monolayer was 1.56 sec/cm. This is several orders of magnitude less than for insoluble films. The reason for this can be found in the large area/molecule, 50 A^{o2} compared to 20 A^{o2} for insoluble spread monolayers.

Harvey and Smith (1959) used an interferometric technique to measure absorption of carbon dioxide into quiescent water. For Lissapol-N and Teepol the interfacial resistance was calculated to be approximately 35 sec/cm at high concentrations. It was suggested by Mancy and Barlage (1968) that an SAA such as Teepol, a blend of alkyl sulphonates may give misleading results due to preferential adsorption at the surface.

Mancy and Barlage (1968) present data for the interfacial resistance to carbon dioxide absorption in a laminar jet. For dodecyltrimethylammonium chloride the instantaneous resistance to the adsorbed SAA layer was determined to be 3-5 sec/cm and 6-8 sec/cm for hexadecyltrimethylammonium chloride. These compare favourably with the results of Princen and Mason. Sodium Lauryl Sulphate was found to have a resistance of approximately 4 sec/cm to absorption of CO_2.

4.3 GAS ABSORPTION UNDER TURBULENT CONDITIONS

The preceding section presented some of the reported valves for gas transfer through a surface monolayer under quiescent conditions; however, it is unlikely that quiescent conditions occur in natural systems, in fact it was found in this study that completely stagnant conditions were difficult to obtain in the laboratory. What is more important is the steady-state gas transfer under turbulent conditions.

Downing et al. (1957) studied the effect of contaminants on the rate of aeration of water. The experiments were performed in glass or earthenware absorption vessels in which the water was agitated by stirring with an impeller. The effect of mixed household detergents on the rate of aeration was determined in a rectangular vessel. At a concentration of 1.0 mg/l. as Manoxol O.T. the percent reduction of the transfer coefficient is a function of the transfer coefficient as determined in clean water.

TABLE 1

PERCENT REDUCTION OF K_L WITH MIXED DETERGENTS
(Downing et al 1957)
(1 mg/l. SAA in rectangular vessel)

K_L (cm/hr)	% Reduction K_L
3.4	26%
6.4	55%
22.4	57%
92.1	23%

In experiments with sodium dodecylbenzenesulphonate increasing from 0.07 to 0.73 ppm the transfer coefficient was progressively reduced from the initial valve of 18.6 cm/hr to 11.1 cm/hr a drop of 40.3%.

Linton and Sutherland (1958) studied the solution of oxygen through a monolayer with a surface resistance under quiescent conditions of around 200 sec/cm. The laboratory tests were performed in stirred cylindrical absorption cells. It was reported that little or no reduction in oxygen transfer coefficient occurred in the range 0.3 to 7 cm/hr. When a jet of air was blown on the surface of the water surface the hexadecanol monolayer reduced the oxygen transfer coefficient from 6.7 cm/hr to 4.1 cm/hr a reduction of 38.8 percent.

Davies, Kilmer and Ratcliff (1964) studied the rates of absorption of various gases into turbulently stirred water. The absorption cells were cylindrical glass with two concentrically mounted stirrers rotated in opposite directions with a baffle to eliminate the formation of a vortex. The surface-active agent chosen was the protein crystallized bovine plasma albumin. For carbon dioxide gas with a protein concentration of 2 mg/m^2 and stirrer speeds of 437 RPM and 137 RPM the following reductions in mass transfer were obtained.

TABLE 2

PERCENT REDUCTION IN K_L WITH PROTEIN MONOLAYER
(Davies et al 1964)

K_L initial (cm/hr)	K_L with protein (cm/hr)	% Reduction
7.0	3.8	45 %
3.3	2.9	12.1%

Additional work was performed in stirred cells by Mancy and Okun (1965). The SAA used was sodium dioctyl sulfosuccinate and the oxygen was measured by a Galvanic Cell. Results were presented in the form of R_T vs the mixing Reynolds no. R_T is the total resistance and is the inverse of K_L the overall gas transfer coefficient. The percent reduction in oxygen transfer coefficient as a function of the transfer coefficient at an aerosol O.T. concentration of 0.5 mg/l. as reported by Mancy and Okun is presented in the following table.

TABLE 3

PERCENT REDUCTION IN K_L WITH AEROSOL O.T.

(Mancy and Okun 1965)

K_L initial	K_L with SAA	% Reduction
1.72	1.72	0.0
3.5	2.7	20.0
4.29	3.00	30.0
5.25	3.15	40.0
7.24	3.43	52.5
10.1	4.14	59.0

Mancy and Okun concluded that

> "at laminar flow mixing conditions, the bulk resistance is very high and masks any change in surface resistance caused by SAA. At turbulent flow mixing conditions oxygen transfer is dependent mainly on surface renewal. Under these conditions, there is no apparent effect of the SAA on oxygen transfer. It is only within a certain range of mixing conditions which is between the laminar and turbulent flow regions, that the effect of SAA can be detected."

CHAPTER 5

INTERPRETATION OF REPORTED GAS TRANSFER WITH SURFACE RESISTANCE

5.1 GAS ABSORPTION UNDER QUIESCENT CONDITIONS

In a stagnant or quiescent body of water gas absorption will occur by molecular diffusion only and interference by surfactants should be caused solely by "Effects of the first kind". The following analysis is performed in an attempt to understand the relative importance of the mechanism of resistance to gas transfer.

The mass transfer of a gas into a liquid can be described in an analogous manner to heat radiation and conduction problems if the following conditions are true

1) only molecular diffusion occurs, and
2) the liquid layer is considered a semi-infinite body.

The diffusion into the liquid can be described by Fick's Second Law, eqn(3):

$$\frac{\partial c}{\partial \theta} = \frac{D \partial^2 c}{\partial X^2} \qquad (22)$$

where: θ is time, and

X is the distance perpendicular to the surface.

For the case where there is a surface resistance the following initial and boundary conditions can be written. These are:

initial conditions

$$C = C_o \qquad X>0 \qquad \theta=0 \qquad (23)$$

boundary conditions

$$-D \frac{\partial C}{\partial X} = K(C_s - C) \qquad X=0 \qquad \theta>0 \qquad (24)$$

and $$C = C_o \qquad X=\infty \qquad \theta>0 \qquad (25)$$

From an anology with the heat conduction problem (Carslaw and Jaegar 1959, p71)

$$\frac{C - C_s}{C - C_o} = \operatorname{erf}\left(\frac{X}{2\sqrt{D\theta}}\right) + e^{\left[\frac{K}{D}X + \left(\frac{K}{D}\right)^2 D\theta\right]} \operatorname{erfc}\left(\frac{X}{2\sqrt{D\theta}} + \frac{K}{D}\sqrt{D\theta}\right) \qquad (26)$$

The concentration at the surface C_* can be written by setting $X = 0$.

$$\frac{C_s - C_*}{C_s - C_o} = e^{\left(\frac{K}{D}\right)^2 D\theta} \operatorname{erfc}\left(\frac{K}{D}\sqrt{D\theta}\right) \qquad (27)$$

$$\frac{C_s - C_*}{C_s - C_o} = e^{\frac{K^2\theta}{D}} \operatorname{erfc}\left(K\sqrt{\frac{\theta}{D}}\right) \qquad (28)$$

The flux through the surface can be written as

$$\psi(\theta) = -D\frac{\partial C}{\partial X} = K(C^s - C_*) \qquad (29)$$

$$= K(C_s - C_o)e^{\frac{K^2\theta}{D}} \operatorname{erfc}\left(K\sqrt{\frac{\theta}{D}}\right) \qquad (30)$$

The importance of this analysis is that the resistance R or (1/K) is due entirely to "Effects of the first kind". The magnitude of R; in relation to the total resistance of the liquid phase will determine the magnitude that "Effects of the first kind" will have on gas absorption.

The mass transferred per unit area over a period t will be:

$$m = \int_0^t \left[\psi(\theta)\right] d\theta \qquad (31)$$

$$m(\theta) = \int_0^t K(C_s - C_o)e^{\frac{K^2\theta}{D}} \operatorname{erfc}\left(K\sqrt{\frac{\theta}{D}}\right) d\theta \qquad (32)$$

$$= K(C_s - C_o)\int_0^t e^{\frac{K^2\theta}{D}} \operatorname{erfc}\left(K\sqrt{\frac{\theta}{D}}\right) d\theta \qquad (33)$$

Developing these equations beyond Harvey and Smith(1959) and Plevan and Quinn (1966) a transformation can simplify the evaluation of the integral.

Let:

$$\beta^2 = \frac{K^2\theta}{D} \qquad (34)$$

Where β is now dimensionless:

$$m(\beta) = 2(C_s-C_o)\frac{D}{K}\int_o^t \beta e^{\beta^2} \operatorname{erfc}\beta d\beta \tag{35}$$

$$\text{since}\; d\theta = \frac{D}{K^2} 2\beta d\beta \tag{36}$$

In Chapter 2 it was shown that the Higbie equation without a surface resistance gave the total mass transferred per unit area to be

$$m(\theta) = 2(C_s-C_o)\sqrt{\frac{D\theta}{\pi}} \tag{37}$$

or written in terms of the transformation

$$m(\beta) = 2(C_s-C_o)\frac{D}{K\sqrt{\pi}} \beta \tag{38}$$

The difference in total mass transferred can be written as

$$M(\beta) = \frac{m(\beta)R=0 - m(\beta)R>0}{m(\beta)_{R=0}} \times 100 \tag{39}$$

where $M(\beta)$ is the percentage difference in gas transferred per unit area between conditions of surface resistance due to surfactants and no surface resistance for clean surfaces

$$M(\beta) = \frac{2(C_s-C_o)\frac{D}{K\sqrt{\pi}}\beta - 2(C_s-C_o)\frac{D}{K}\int_o^t \beta e^{\beta^2}\operatorname{erfc}\beta d\beta}{2(C_s-C_o)\frac{D}{K\sqrt{\pi}}\beta} \times 100 \tag{40}$$

simplifying this becomes

$$M(\beta) = \left[1 - \frac{\sqrt{\pi}}{\beta}\int_o^t \beta e^{\beta^2} \operatorname{erfc}\beta d\beta\right] \times 100 \tag{41}$$

This result shows the total mass transferred to be a function of β alone where β has been shown to be a dimensionless parameter containing a surface mass transfer coefficient K, diffusivity of the liquid, and time θ. Fig. 3 and Fig. 4 shows $M(\beta)$ as a function of β. These particular curves can be of assistance in evaluating the importance of surface resistance in reducing gas transfer. At very short times the effect of surfactants can be of great significance.

FIGURE 3

Percent Reduction In Gas Transfer as a Function of Time, Resistance and Diffusivity

Short Exposure Time

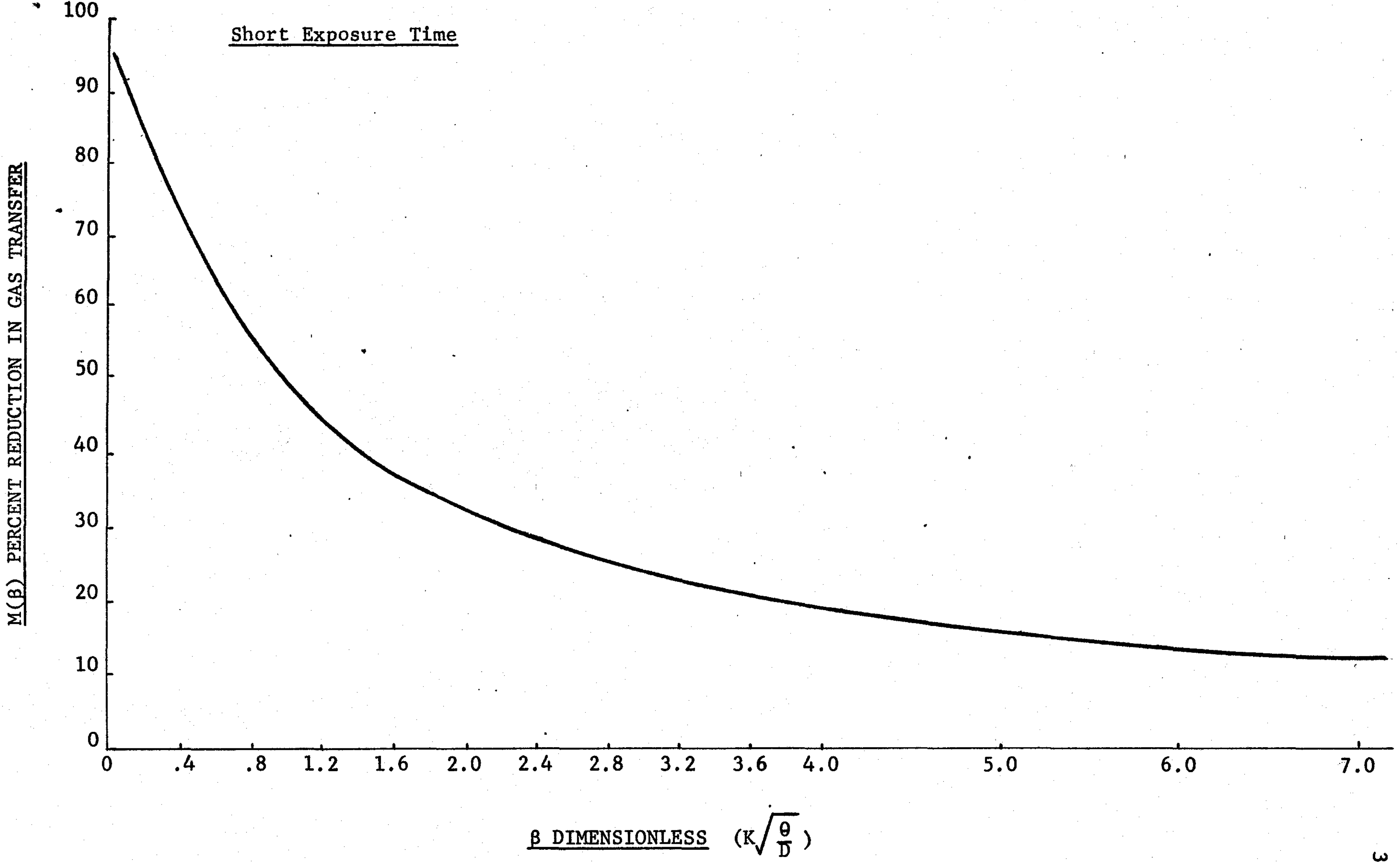
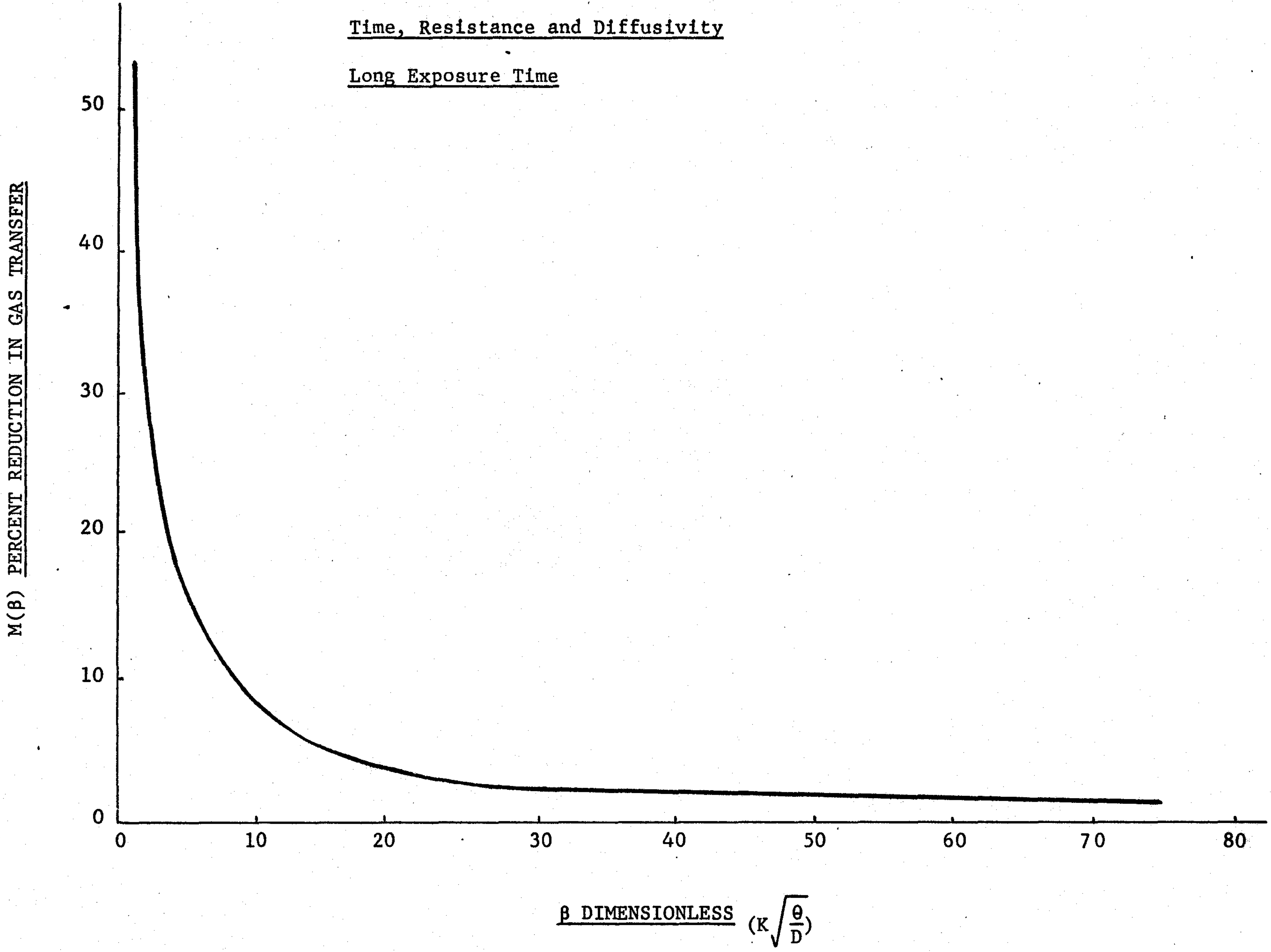


FIGURE 4

Percent Reduction in Gas Transfer as a Function of Time, Resistance and Diffusivity

Long Exposure Time



Knowing the surface resistance of a surface active material the percent reduction in gas transfer can be calculated using Figures 3 and 4. Table 4 below shows the effect of oxygen absorption at 20°C through an insoluble spread monolayer with a surface resistance of 200 sec/cm and an adsorbed monolayer densely packed with a resistance of 8 sec/cm.

TABLE 4

EFFECT OF SURFACE RESISTANCE ON OXYGEN TRANSFER

R_s sec/cm	θ sec	β	M(β) %
200	1.0	1.17	46
	2.0	1.66	37
	5.0	2.62	27
	10.0	3.70	21
	30.0	6.40	13
	60.0	9.06	9
8	0.1	7.2	11.5
	0.2	28.8	2.8
	0.3	64.3	1.6

The following conclusions can be drawn from this review of the literature.

1) Soluble monolayers have an interfacial resistance from one to two orders of magnitude less than insoluble spread monolayers.
2) The effect on gas transfer under quiescent conditions is much greater for insoluble spread monolayers than for absorbed monolayers for the same exposure time.

3) For exposure times greater than 0.1 secs the effect of soluble monolayers will be small.

4) For exposure times greater than 1 min. the effect of spread monolayers on the rate of gas transfer will be small.

5.2 GAS ABSORPTION UNDER TURBULENT CONDITIONS

The "Effects of the second kind" or changes in the hydrodynamic properties of the surface are most easily measured in stirred absorption vessels. Absorption of various gases with different surfactants were made in three independent studies of note. An evaluation of the percent reduction of gas transfer on the surface renewal rate in the agitated cells employed was made in order to understand the effects of surfactant characteristics and hydrodynamic activity on the transfer coefficient.

The surface renewal rate was assumed to be related to the gas transfer coefficient according to the film penetration model of Dobbins:

$$K_L = \sqrt{Dr} \quad \coth\sqrt{\frac{rL^2}{D}} \tag{42}$$

where: D is the molecular diffusivity,

r is the surface renewal rate, and

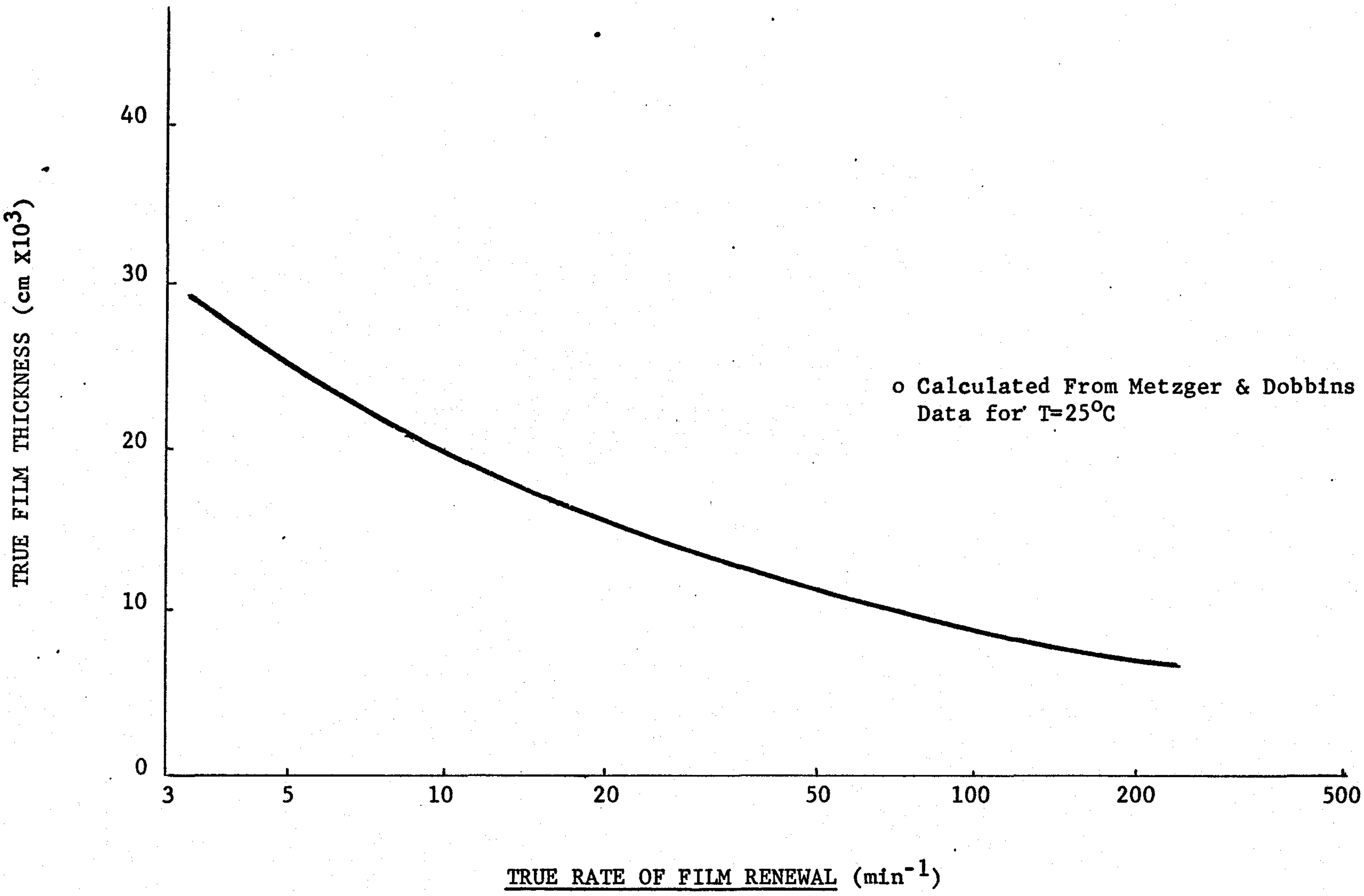
L is the film thickness.

Use was made of the relationship of the true film thickness and the surface renewal frequencies as calculated by Metzger and Dobbins (1967) from absorption data with helium and nitrogen and presented here in Figure 5. Figure 5 cand be used to standardize results at different temperatures and absorbing gases.

As a basis of comparison, the surface renewal rate was calculated from the reported transfer coefficient K_L ,the temperature, and the absorbing gas used by simultaneously solving equation (42) with Figure 5. The percent reduction in the transfer coefficient was calculated between the condition of no surfactant interface and that with an absorbed or spread monolayer at the same mixing speed.

FIGURE 5

Relationship Between Film Thickness and Surface Renewal Rate (Metzger & Dobbins)



Downing et al (1957) performed absorption studies in a rectangular vessel using a mixture of seven proprietary household detergents at a concentration of 1.0 ppm as manoxal O.T. Mancy and Okun (1965) used the surfactant aerosol O.T. in various quantities; however, as little as 0.5 mg/1 of the surfactant caused up to 90% of the ultimate reduction in gas transfer. Davies,Kilmer and Ratcliffe (19640 employed the surface active agent bovine plasma albumin which was spread by means of a micro-syringe. No further reductions in the transfer rate occurred above protein concentrations of 1 mg/cm^2.

The results of this analysis are presented in Table % and shown graphically in Figure 6.

TABLE 5

PERCENT REDUCTION IN GAS TRANSFER AS A FUNCTION OF SURFACE RENEWAL RATE

SURFACE RENEWAL RATE (min^{-1})	PERCENT REDUCTION IN K_L		
	HOUSEHOLD DETERGENTS	AEROSOL O.T.	PROTEIN-BOVINE PLASMA ALBUMIN
0.3	10.0	0.0	-
2.0	-	16.0	-
2.3	-	-	12.5
5.0	46	40	-
10.0	55	52.5	45
20.0	55	59	-
100.0	55	-	-
	DOWNING	MANCY&OKUN	DAVIES et al.

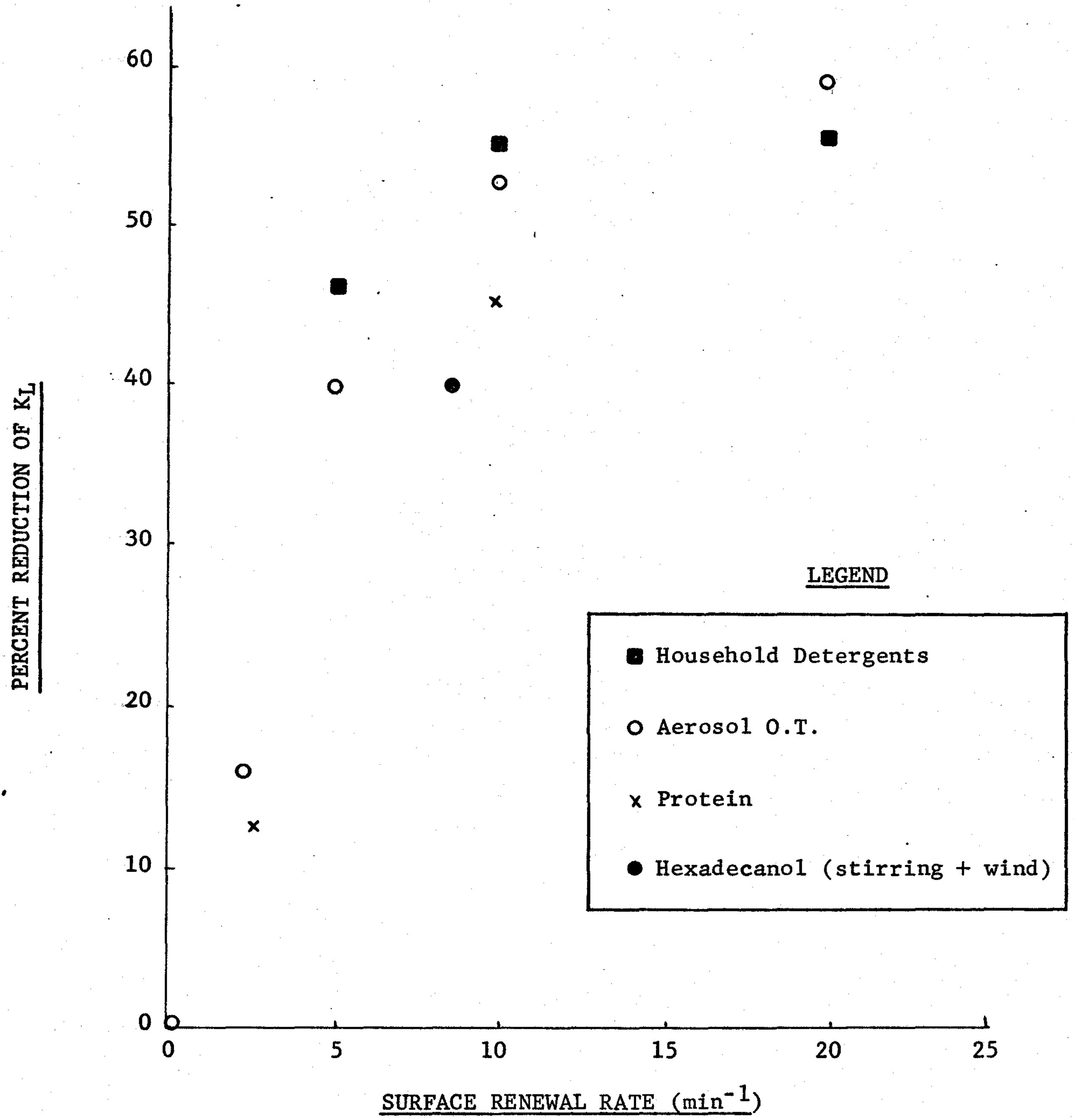


FIGURE 6

Percent Reduction of Transfer Coefficient

With Various Surfactants

The following implications can be derived as to the role of surfactants in reducing gas transfer.

1. Figure 6 shows that totally different types of surfactants although having widely different physical resistances, behave similarily in reducing gas transfer under a broad range of turbulent conditions.
2. Bulk concentrations of SAA as low as 0.5 mg/l produce significant reductions in K_L at specific surface renewal rates.
3. Rates of surface renewal greater than 5 renewals/minute can result in reductions of greater than 40% for most surfactants.
4. Downing et al.(1957) reported a decrease in the percent reduction in the transfer coefficient at higher levels of turbulence. It is expected that for renewal rates greater than 50 per minute the effect of the surfactant is reduced below 40%.

CHAPTER 6

EXPERIMENTATIONS

6.1 EXPERIMENTAL OPERATION

The experimental part of this study was to determine the effects of surfactants on gas transfer under quiescent conditions. The rate of absorption of oxygen into degasified distilled water was measured as a pressure change in an absorption cell as a function of time. The parameters which were varied in the experimental design were temperature (10-30°C) and concentration of surfactant. The surfactants used were alkylbenzene-sulphonate (ABS) and sodium lauryl sulphate (NaLS).

6.2 SYSTEM DEFINITION

6.2.1 ABSORPTION CELLS

The rate of gas absorption through a quiescent interface was measured in glass absorption cells. These were four liter glass reagent bottles with rounded bottoms. One vessel contained the absorbing water with surfactants, the other was a dummy cell employed to negate the atmospheric pressure changes during the run. The purpose of the rounded vessel bottoms was to permit stirring by means of a teflon coated air-driven magnetic stirrer during the degasification procedure. The absorption vessel was filled with three liters of distilled water. This was found to produce the best ratio of air volume to water volume, hence better sensitivity for the pressure change measurements.

6.2.2 TEMPERATURE CONTROL

The absorption cells were placed in a large water bath controlled by a mercury thermostat sensitive to ± .005°F.

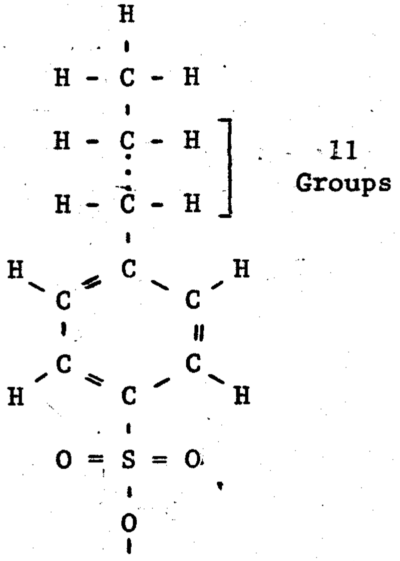
Two laboratory mixers were placed in the water bath to assume uniform and constant temperature distribution. For temperature runs above the ambient room temperature, heat was added by means of a 800 watt heater element coiled between the absorption vessels and near a mixer. Cold tap water was used as a cold source except for low temperature runs when water was recirculated through the refrigeration unit of the Warburg respirometer apparatus.

6.2.3 PRESSURE MEASUREMENT

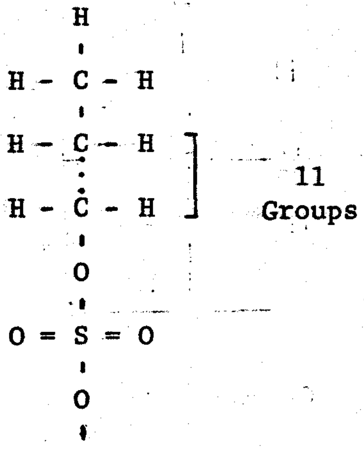
The pressure change in the absorption cell was measured as a pressure differential between the absorption cell and the dummy vessel. This pressure difference was measured by a differential micromanometer (2" total head change, accurate to 0.0005"). Coloured mineral oil was used as the manometer fluid. The dummy cell contained a small quantity of water so that both vessels were in vapour pressure equilibrium when the dry-oxygen was added to the vessels. During the absorption run the vessels were connected only through the manometer. The equipment was connected as illustrated in the schematic drawing Figure 7.

6.2.4 SURFACE ACTIVE AGENTS

The surfactants used in the experiment were alkylbenzene sulphonate (ABS) and sodium lauryl sulphate. Both of these surfactants behave as Gibbs monolayers and are anionic (i.e. the chain structure is negatively charged.) The structure of these materials is illustrated below



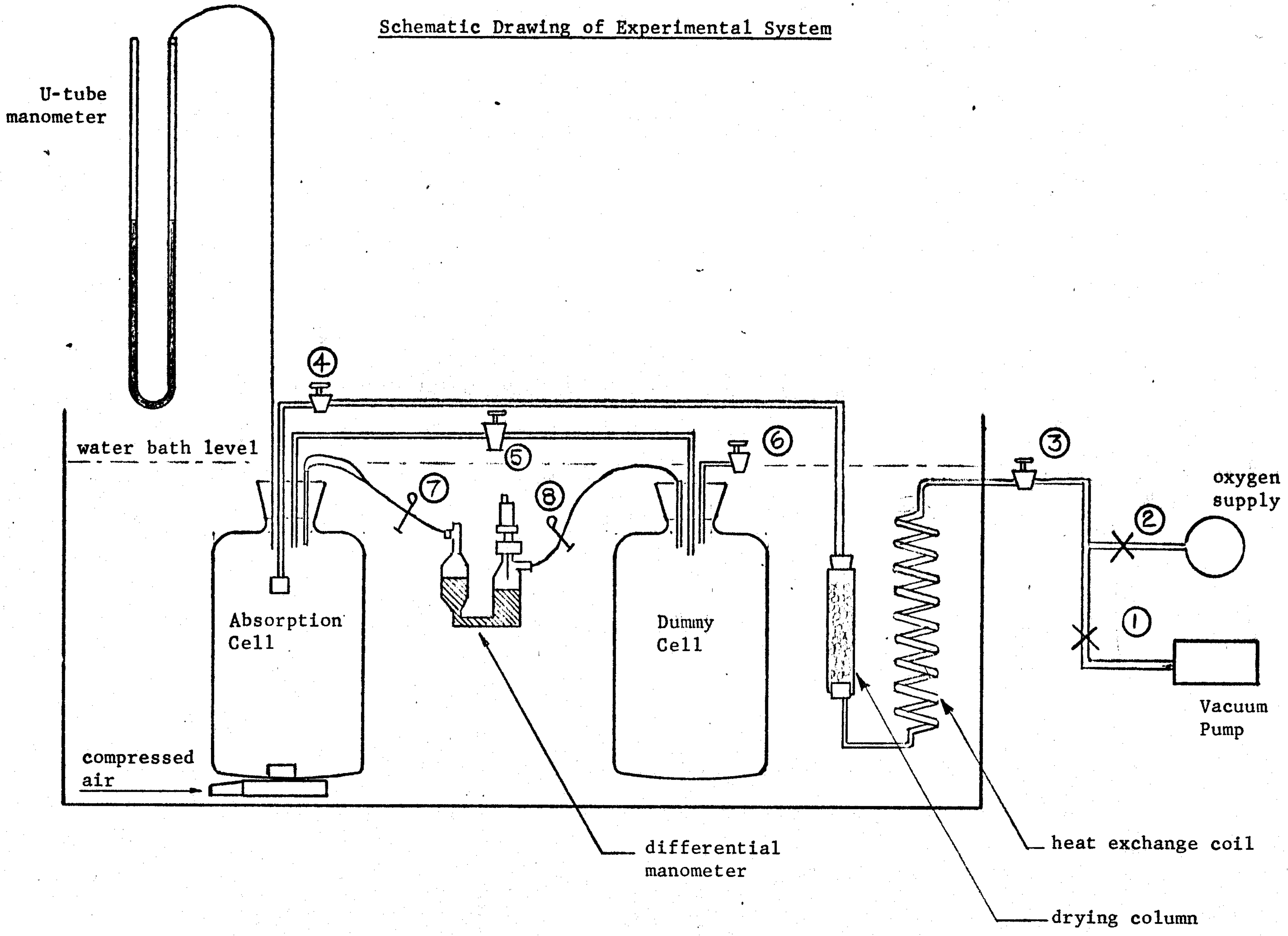
ALKYLBENZENE SULPHONATE



SODIUM LAURYL SULPHATE

FIGURE 7

Schematic Drawing of Experimental System



The surfactants were added to distilled water such that a 5 ml quantity corresponded to 5 mg/l in a 3 liter volume of oxygen absorbing solution.

6.3 EXPERIMENTAL TECHNIQUE

6.3.1 RUN PREPARATION

The absorption cell was removed from the water bath and thoroughly washed followed by the exposure of all interior surfaces to warm chromic acid. The absorption cell was then rinsed with hot tap water then distilled water. The distilled water for the next run was added to the vessel plus the amount of surfactant required according to the statistical design. All glassware used was chromic acid cleaned. Before placing the absorption cell in the water bath a teflon stirrer was added to the vessel.

6.3.2 DEAERATION

When the absorption cell was placed in position as shown in Fig. 7 , the pressure in the two cells was equalized. The level in the differential micromanometer was left equal after the previous run and the small volume in the manometer trapped by clamps 7 and 8 contained pure oxygen. With valve 6 closed and 5 open the cells were evacuated by starting the vacuum pump and opening valves 1, 3 and 4. Compressed air was passed through the magnetic stirrer under the absorption cell to drive the teflon stirrer. The stirring action increased the rate of deaeration and also brought the absorbing liquid to a uniform and consistent temperature more readily.

When the pressure in the absorption cells reached a steady-state condition valves 4 and 3 were closed and the vacuum pump shut off. This condition existed over-night with the stirrer going to ensure equilibrium with the small partial pressure remaining in the cell and constant temperature. The effect of thermal convection currents were minimized in this manner. The stirrer was stopped a period of 3 hours before the absorption run to eliminate bulk motion imparted by the stirrer. The system was thus prepared for the oxygen transfer experimental trial.

6.3.3 ABSORPTION OF OXYGEN

Pure oxygen at atmospheric pressures was bled into the absorption cell by closing valves 1 and 6 and opening valves 2, 3 and 4 in series. The gas entered the absorption cells at the water temperature by passing it through a coil in the water bath. It was then passed through a drying column of calcium chloride in order that the vapour pressure would not be upset in the closed system. It should be noted at this point that oxygen was fed through glass and copper tubing joined where necessary by polyethylene tubing. The need for an excellent air-tight seal dictated the use of rubber stoppers. To reduce surface contamination the stoppers were sealed with lubriseal lubricant found to cause no reduction of water surface tension on exposure. The oxygen entered the absorption cell through a porous glass diffuser so as to prevent disturbance of the quiescent water surface.

When the pressure in the vessels reached atmospheric pressure the oxygen fed valves were closed and the experiment timer started. Valve 6 was opened briefly to allow the pressure to return to atmospheric pressure. Clamps 7 and 8 were removed and at 1.9 minutes after the clock was started valve 5 was closed so that oxygen absorption occurring in the absorption cell would be indicated by the differential manometer. The height of the manometer fluid was recorded at frequent time intervals up to 81 minutes. The barometric pressure was recorded at the commencement of the run.

6.3.4 SURFACE TENSION MEASUREMENTS

At the conclusion of each absorption run a sample was pipeted from the absorption vessel for surface tension measurement. The DuNuoy ring tensiometer was the instrument used for the determination of the surface tension. The sample was put in a small glass petrie dish for the determination. The dish was washed in methyl ethyl ketone, benzene, hot chromic acid and then rinsed in distilled water to reduce contamination. The ring was rinsed in the organic solvents listed and then flamed to eliminate organic contamination. Determinations were performed in replicate until a reproduceable result was achieved. The instrument was calibrated and the ring correction factor applied.

6.4 ANALYTIC TECHNIQUES

6.4.1 DIFFUSIVITY DETERMINATION

Assuming the normal diffusion law is obeyed in the liquid, then the total mass of gas absorbed in time θ is :

$$\Delta m = 2A\ (C^{*}-C)\sqrt{\frac{D}{\pi}}\ \theta^{1/2} \tag{43}$$

where : A is the surface area (cm^2) ,

C^{*} saturation concentration at temperature T and pressure D ,

C_o initial uniform dissolved oxygen concentration ,

D effective diffusivity to be determined ,and

θ time (sec.) ,

The change in mass is determined experimentally by a change in pressure :

$$\Delta m = f\Delta L \tag{44}$$

where f relates the change in manometer height to the mass of oxygen absorbed. f is a function of the absorption cell geometry, manometer fluid, gas used and temperature.

The absorption cells interconnected by the differential manometer is shown schematically in Fig. 7 . The value of f is determined by the following analysis.

Initially: $$P_G = P_D \qquad (45)$$

where: P is the pressure, and
the subscripts $_G$ and $_D$ refer to the
absorption and dummy cells respectively.

At any time t:

$$V_{D_t} = V_D + \Delta hAm \text{ and } V_{G_t} = V_G - \Delta hAm \qquad (46a\&b)$$

$$P_{D_t} = P_D + \Delta P_D \qquad (47)$$

where: V is gas volume,
Am the cross-sectional area of the manometer, and
Δh the change in manometer fluid level.

According to the ideal gas law for a closed system, such as the dummy cell, where m is constant:

$$P_D V_D = P_{D_t} V_{D_t} = (V_D + \Delta hAm)(P_D + \Delta P_D) \qquad (48)$$

simplifying and neglecting second order terms ΔP_D is very small compared to P_D

$$\Delta P_D = \frac{-\Delta hAmP_D}{V_D} \qquad (49)$$

The pressure change can be determined for the side containing the liquid and gas phase by considering:

$$P_{G_t} + 2\gamma\Delta h = P_{D_t} \qquad (50)$$

where: γ relates the units and accounts for the specific gravity of the manometer fluid.

Writing this in terms of a change in pressure:

$$\Delta P_{G_t} = P_{G_t} - P_G \qquad (51)$$
$$= P_{D_t} - 2\gamma \Delta h - P_G$$

Since $P_G = P_D$ at time =0:

$$\Delta P_{G_t} = P_{D_t} - P_D - 2\gamma \Delta h \qquad (52)$$
$$= \Delta P_D - 2\gamma \Delta h$$

Since there is mass transfer through the liquid surface, the change in mass of gas above the liquid can be determined from:

$$\Delta m = m_t - m_o \qquad (53)$$

Thus, using the ideal gas law:

$$\Delta m = \frac{PV}{RT}_t - \frac{PV}{RT}_o \qquad (54)$$

or:

$$\Delta m RT = (P_G V_G)_t - (P_G V_G)_o \qquad (54b)$$

where the temperature is constant. Substituting the derived equations (52) and(46b)

$$P_{G_t} = P_G + (\Delta P_D - 2\gamma \Delta h)$$

and $$V_{G_t} = V_G - Am\Delta h$$

gives

$$\Delta m RT = \left[P_G + (\Delta P_D - 2\gamma\Delta h)\right]\left[V_G - \Delta m \Delta h\right] - P_G V_G \qquad (55)$$

This equation can be further simplified by cancelling and neglecting the second order terms $(2\gamma Am\Delta h \Delta h)$:

$$\Delta m RT = P_G(-Am\Delta h) + (\Delta P_D - 2\ \Delta h)V_G \qquad (56)$$

substituting for ΔP_D:

$$\Delta m RT = \left[-P_G Am - \frac{Am P_G V_G}{V_D} - 2\gamma V_G\right] \Delta h \qquad (57)$$

further simplification gives:

$$\Delta m = \frac{-V_G}{RT}\left[2\gamma + P_G Am \frac{(V_D + V_G)}{V_G V_D}\right] \Delta h \qquad (58)$$

Thus the change in mass is a linear function of the change in manometer height.

The change in mass can be expressed as μg if the following units are used

V_G	cm^3
V_D	cm^3
P_G	atm.
Am	cm^2
Δh	cm
γ	atm/cm
R	$2.56 \times 10^{-3} \frac{atm \quad cm^3}{mg \quad {}^oK}$

For a given temperature, cell geometry and volume of absorbing water

$$\Delta m = f \Delta h$$

$$\text{where } f = \frac{-V_G}{RT} \left[2\gamma + P_G \, Am \; \frac{(V_D + V_G)}{V_D V_G} \right] \frac{mg}{cm \text{ oil}} \qquad (59)$$

6.5. EXPERIMENTAL DESIGN

The experimental investigation into the effects of temperature and bulk concentrations of surfactants on the rate of oxygen absorption into water was performed following a randomized statistical design. The design permitted the determination of the following information about the physical process.

(1) The main effects of every factor to be estimated independently of each other.

(2) The dependence of the effect of every factor upon the levels of the others.

(3) An estimate of the experimental error for the purpose of significance tests.

In this study two quantitative factors were varied from trial to trial. These were temperature and the bulk concentration of surfactants. The type of surfactant was a qualitative factor which did not vary.

The central composite design was employed in this study over the two level factorial experiments and the three level factorial experimental designs to provide:

(1) information on the linear and quadratic components of the effects.

(2) the greatest efficiency with respect to the number of experimental trials, and

(3) an estimate of the experimental error in the region of the center of the factor levels.

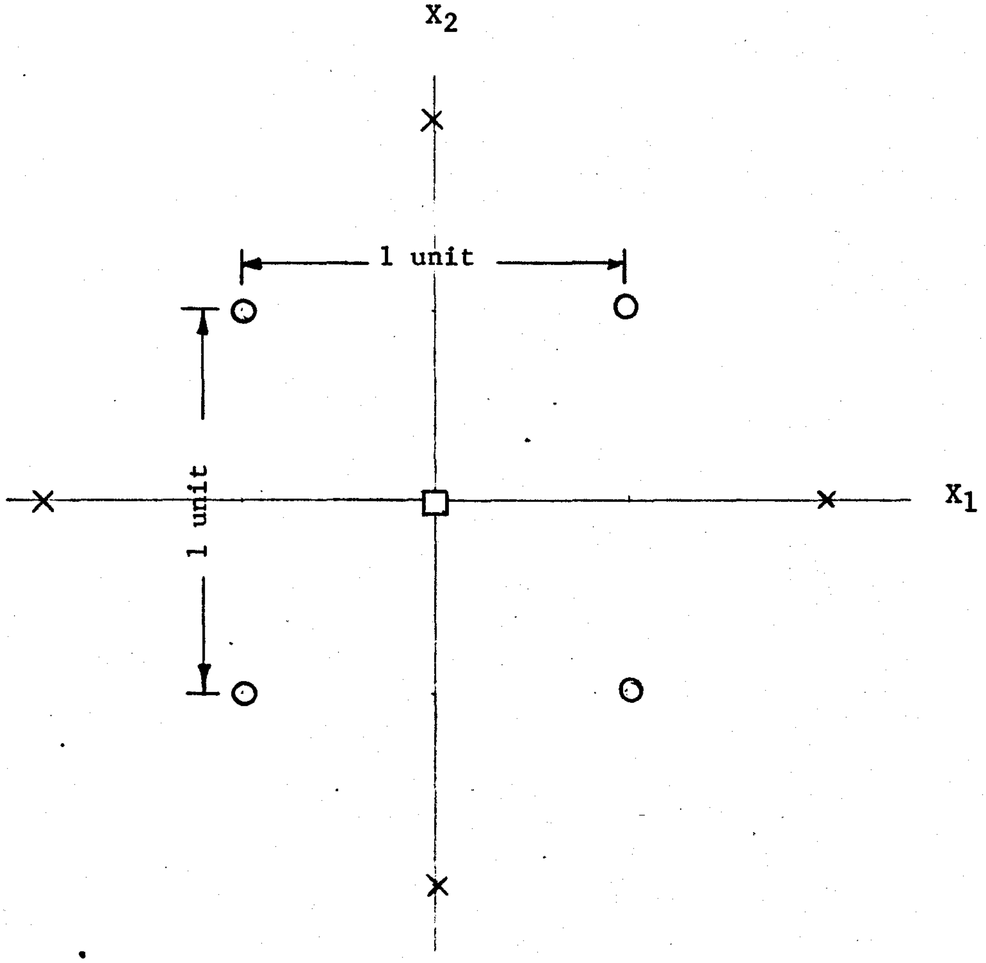
The composite design is built up from two-level factorial experiments. The composite design for a two factor experiment is constructed by adding five supplementary trials to the two level factorial design.

- one at the center point of the 2^2 design.
- the remaining four in pairs along the co-ordinate axis at distances of ± 1 unit.

Three additional trials were performed at the center point to obtain a better estimate of the experimental error.

The design is illustrated geometrically in Figure 8 . The center point of the design was taken at a temperature of 20°C. which is the temperature at which oxygen transfer and biological uptake rate are expressed and 10 mg/l of ABS in distilled water solution. This is a higher concentration than normally found in surface waters; however, if the effect of surfactants were to be determined with statistical significance a wide range of surfactant concentration was felt necessary.

The randomized experimental design is described at the following factor levels. The response of a given treatment was the diffusivity.



o basic two level factorial design

x supplementary experimental trials

□ four trials at center of composite design for experimental error.

FIGURE 8

Geometric Description of Experimental Design

TABLE 6

FACTOR LEVELS OF ABS SERIES

RUN NO.	TEMP. (°C.)	ABS CONCENTRATION (mg/l)
C1B	20.0	20.0
C2	20.0	10.0
C3	15.0	5.0
C4	25.0	15.0
C5B	10.0	10.0
C6	20.0	10.0
C7	20.0	0.0
C8	20.0	10.0
C9	20.0	10.0
C10	30.0	10.0
C11	25.0	5.0
C12B	15.0	15.0

Another series of runs was performed using sodium lauryl sulphate as a surfactant. The only quantitative factor for this set of trials was the bulk concentration of the surfactant. The temperature was held constant at 20°C. for all four trials in this experiment.

The treatment was randomized initially to give three levels with replication. Unfortunately, the last two trials in the sequence were eliminated due to experimental equipment failure. The test series is tabulated below.

TABLE 7

FACTOR LEVELS OF NaLS SERIES

TRIAL NO.	NaLS CONC. (mg/l)
D1	12.45
D2	4.15
D3	4.15
D4	8.30

CHAPTER 7

RESULTS AND INTERPRETATION

7.1 PRIMARY DATA

7.1.1 ABSORPTION INTO ABS SOLUTION

The response of the experimental design was the effective diffusivity of oxygen in water under near quiescent conditions. The diffusivity is calculated from the uptake of oxygen in the absorbing solution assuming the normal diffusion law is obeyed in the liquid

$$\text{ie} \quad \Delta m = 2A(C^* - C)\sqrt{\frac{D}{\pi}}\,\theta^{1/2} \qquad (43)$$

$$\text{or} \quad D = \left[\frac{f\ \Delta h/\theta^{1/2}}{2A(C^* - C_o)}\right]^2$$

The primary data is presented in Appendix 1 as Δh (change in manometer height) vs $\theta^{1/2}$ (the square root of the exposure time). The driving force $(C^* - C_o)$ and f were calculated for each test. From the pressure change data the slope $\Delta h/\theta^{1/2}$ was calculated.

It was found that the diffusion law was obeyed up to 50 minutes after exposure to the gas. A straight line was fitted to the data points in this region. Usually steady-state did not appear to occur until after 15 minutes of exposure time. This could be due to the vapour pressure and gas temperature coming to complete equilibrium. The calculated effective diffusivity is indicated on each graph.

7.1.2 ABSORPTION THROUGH SODIUM LAURYL SULPHATE

The primary data for the D series of trials with Sodium Lauryl Sulphate solution is presented as the manometer response to the decrease in gas pressure. These results are presented in Appendix 2 for the trial D1 - D2 inclusive.

From the fitted straight line the effective diffusivity was calculated from the slope of the pressure response.

7.1.3 SURFACE PRESSURE OF ABSORBING SOLUTIONS

The surface pressure of the absorbing solutions was determined at the end of each run in the manner described in section 6.3.4. Since the surface tension could not be measured in situ in the absorption vessel a portion was removed by pipet.

The surface pressure was calculated by subtracting the measured surface tension from the surface tension of distilled water at the temperature of the absorption run.

The surface pressures for both the C and D series are presented in Table 8. The surface tension measurements were used only as a means of confirming that the surfactant employed was in fact adsorbing on the interface.

TABLE 8

SURFACE PRESSURE OF ABS ABSORBING SOLUTIONS

TRIAL	TEMP. (°C.)	SAA CONC. (mg/1)	SURFACE PRESSURE (dyne-cm)	MEAN SURFACE PRESSURE (dyne-cm)
C7	20	0	1.0	1.0
C4	15	5	2.3	1.7
C11	25	5	1.1	
C5B	10	10	2.9	2.2
C2	20	10	-	
C6	20	10	2.6	
C8	20	10	2.0	
C9	20	10	1.9	
C10	30	10	1.8	
C12B	15	15	3.5	2.9
C4	25	15	2.3	
C1B	20	20	2.2	2.2

SURFACE PRESSURE OF NaLS ABSORBING SOLUTIONS

D2	20	4.15	0.2	0.3
D3	20	4.15	0.4	
D4	20	8.30	0.7	0.7
D1	20	12.45	1.0	1.0

7.2 EFFECTIVE DIFFUSIVITY OF OXYGEN ABSORBING SOLUTION

The effective diffusivity of pure oxygen in water was calculated from the rate of pressure change in the absorbing solution using equation 43.

$$D = \left[\frac{f\Delta h/\theta^{1/2}}{2A(C^{*}-C_{o})}\right]^{2}$$

The value of f is based on the physical properties of the absorption cells as indicated in equation 2 of Section 6.4.1. These properties are:

1. volume of gas in absorption cell,
2. volume of gas in dummy cell
3. specific gravity of manometer fluid
4. area of manometer
5. initial gas pressure
6. temperature of trial.

The rate of absorption is determined as indicated from the slope of the pressure response of the system to the absorption of the oxygen gas. The area of the exposed surface was determined from the volume and the depth of the cylindrical vessel to be 200 cm^2.

Finally the driving force was calculated from the oxygen saturation value at one atmosphere of pure oxygen less the residual based on the vacuum pressure maintained in the absorption vessel during the twelve hour stirred desorption period.

The effective diffusivity calculations are presented in Table 10, and shown in Table 11 geometrically for the experimental design of the ABS absorption test series.

TABLE 9

CALCULATED EFFECTIVE DIFFUSIVITIES

SERIES C - ABS

TRIAL	$\Delta h/\theta^{1/2}$	$\frac{f\Delta h/0^{1/2}}{2A(C^*-C_o)}$	D
	"oil/sec$^{1/2}$	cm/sec$^{1/2}$	cm^2/sec
C1B	0.00522	5.20×10^{-3}	8.49×10^{-5}
C2	0.00558	5.60 "	9.85 "
C3	0.00664	6.06 "	11.54 "
C4	0.00629	6.73 "	14.23 "
C5B	0.00755	6.20 "	12.08 "
C6	0.00690	6.95 "	15.17 "
C7	0.00597	6.07 "	11.58 "
C8	0.00722	7.23 "	16.42 "
C9	0.00586	5.87 "	10.82 "
C10	0.00645	7.56 "	17.92 "
C11	0.00793	8.57 "	23.07 "
C12B	0.00600	5.56 "	9.71 "

SERIES D - NaLS

D1	0.00581	5.71×10^{-3}	10.2×10^{-5}
D2	0.00558	5.49 "	9.46 "
D3	0.00536	5.27 "	8.71 "
D4	0.00615	6.04 "	11.45 "

7.3 STATISTICAL INTERPRETATION

The effective diffusivity response to the two level control statistical design was studied using the method of analysis of variance. The experimental design matrix with the diffusivity response is presented in Table 10 and the response is shown geometrically in the statistical design in Table 11 for the C series of trials with ABS surfactant.

The analysis of variance (Table 12) using data perpendicular to the centre point (i.e. 8 trials neglecting those with interactions) indicated that the lack of fit was not significant at the 95% level relative to experimental error. None of the first order effects were significant based on the error estimate based on the centre point of design; however, the first order temperature variable was significant at the 95% level based on the residual mean square. This model accounted for 97.06% of the total sum of squares being removed.

Employing the entire twelve experimental design data with a first order plus interaction model (Table 13) the analysis of variance again showed temperature effects to be significant at the 95% level, while surfactant concentration and interaction effects were insignificant.

Although the model contained more degrees of freedom and four extra trials there was a decrease in the total sum of squares removed to 96.08%.

The model was expanded to include second order terms of the temperature and surfactant concentration. Again only the mean and temperature first order effect was significant. The model, however, resulted in a slightly higher percentage of the total sum of squares removed to 98.27%. The lack of fit was not significant at the 95% level.

TABLE 10

EXPERIMENTAL DESIGN MATRIX

TRIAL	FACTORS						RESPONSE
	X_o	X_1	X_2	X_1X_2	X_1^2	X_2^2	D eff $\times 10^5$
1	1	1	1	1	1	1	14.23
2	1	1	-1	-1	1	1	23.07
3	1	-1	1	-1	1	1	9.71
4	1	-1	-1	1	1	1	11.54
5	1	2	0	0	4	0	17.94
6	1	-2	0	0	4	0	12.08
7	1	0	2	0	0	4	8.49
8	1	0	-2	0	0	4	11.58
9	1	0	0	0	0	0	9.85
10	1	0	0	0	0	0	15.17
11	1	0	0	0	0	0	16.42
12	1	0	0	0	0	0	10.82

TABLE 11

GEOMETRIC DISPLAY OF DIFFUSIVITY RESPONSE TO TWO FACTOR COMPOSITE DESIGN

FACTORS	TEMP. °C	10.	15.	20.	25.	30.
ABS CONC.	X_1 X_2	-2	-1	0	+1	+2
0.	-2			11.58		
5.	-1		11.54		23.07	
10.	0	12.08		9.85 15.17 16.42 10.82		17.96
15.	+1		9.71		14.23	
20	+2			8.49		

TABLE 12

FIRST ORDER EFFECTS
with ABS

MODEL ESTIMATE

$$Y = a_o + a_1X_1 + a_2X_2$$

COEFFICIENT	ESTIMATE	VARIANCE
a_o	13.85125	1.321
a_1	4.0125	2.641
a_2	-2.6675	2.641

ANALYSIS OF VARIANCE

SOURCE	SUM OF SQUARES	DEGREE OF FREEDOM	MEAN SQUARE	F TEST ERROR	F TEST RESIDUAL
a_o	1534.8570	1	1534.8570	145.3	158.9
a_1	64.4006	1	64.4006	6.10	6.67
a_2	28.4622	1	28.4622	2.70	2.95
Error	31.6961	3	10.5654	1.00	1.096
Lack of fit	16.59772	2	8.2989	0.785	0.858
Residual	48.2938	5	9.6588	0.915	1.00
Total	1676.0137	-	97.06% Sum of Squares Removed		

Confidence Level	Value of F Error	Value of F Residual
.95	10.13	6.61
.975	17.44	10.01
.99	34.12	16.26

TABLE 13

FIRST ORDER + INTERACTION EFFECTS with ABS

MODEL ESTIMATE

$$Y = a_o + a_1X_1 + a_2X_2 + a_3X_1X_2$$

COEFFICIENT	ESTIMATE	VARIANCE
a_o	13.4083	.88045
a_1	2.31416	.88045
a_2	-1.40416	.88045
a_3	-1.7525	2.64135

ANALYSIS OF VARIANCE

SOURCE	SUM OF SQUARES	DEGREE OF FREEDOM	MEAN SQUARE	F TEST ERROR	F TEST RESIDUAL
a_o	2157.4008	1	2157.4008	204.	187.
a_1	64.2644	1	64.2644	6.08	5.57
a_2	23.6602	1	23.6602	2.24	2.05
a_3	12.2850	1	12.2850	1.16	1.06
Error	31.6961	3	10.5654	1.00	0.92
Lack of fit	60.6537	5	12.1307	1.15	1.05
Residual	92.3498	8	11.5437	1.09	1.00
Total	2349.9602	96.08 % Sum of Squares Removed			

Confidence Level	Value of F Error	Value of F Residual
.95	10.13	5.32
.975	17.44	7.57
.99	34.12	11.26

The temperature was significant at the 97.5% level where based on the residual mean square. The coefficient of this term was 2.3142 indicating an increase of effective diffusivity of 2.3142 cm^2/sec for every five degrees centigrade of temperature increase. This would result in a 17% increase at the center point of the experimental design with a 5°C temperature rise. This compares to 12.5% and 25.8% increase for temperature correction constants of 1.024 and 1.047 respectively. These are used to extrapolate first-order absorption rate constants to temperatures less than or greater than 20°C.

A very simple first-order model was devised to describe the one factor statistical design with the surfactant sodium lauryl sulphate as the qualitative factor. A linear equation was used to determine the effect of surfactant concentration on the diffusivity. The constant term was highly significant while the surfactant concentration was not significant at the 95% level.

It is concluded that temperature has a significant quantitative effect on diffusivity rates; however, low concentrations of adsorbed monolayers at small surface pressures do not significantly affect the transfer rate of oxygen into quiescent water.

TABLE 14

SECOND ORDER EFFECTS with ABS

MODEL ESTIMATE

$$Y = a_o + a_1X_1 + a_2X_2 + a_3X_1X_2 + a_4X_1^2 + a_5X_5^2$$

COEFFICIENT	ESTIMATE	VARIANCE
a_o	13.6195	2.2011
a_1	2.3142	0.88045
a_2	-1.4042	0.88045
a_3	-1.7525	2.64135
a_4	-0.4863	0.4953
a_5	+0.7575	0.4953

ANALYSIS OF VARIANCE

SOURCE	SUM OF SQUARES	DEGREE OF FREEDOM	MEAN SQUARE	F TEST	
				ERROR	RESIDUAL
a_o	2190.8904	1	2190.8904	208.	331.
a_1	64.1033	1	64.1033	6.08	9.68
a_2	23.6608	1	23.6608	2.24	3.58
a_3	12.2850	1	12.2850	1.16	1.85
a_4 a_5	18.2959	2	9.1479	0.87	1.38
Error	31.6961	3	10.5654	1.00	1.59
Lack of fit	9.0287	3	3.0096	0.29	0.45
Residual	40.7248	6	6.6208	0.63	1.00
Total	2349.9602	98.27% Sum of Squares Removed			

Confidence Level	Value of F	
	Error	Residual
.95	10.13	5.99
.975	17.44	8.81
.99	34.12	13.75

TABLE 15

FIRST ORDER EFFECTS
with NaLS

MODEL ESTIMATE

$$Y = a_o + a_1X_1$$

COEFFICIENT	ESTIMATE
a_o	9.328
a_1	.358

ANALYSIS OF VARIANCE

SOURCE	SUM OF SQUARES	DF	MEAN SQUARE	F TEST
a_o	371.4410	1	371.4410	214.
a_1	25.2999	1	25.2999	14.65
Residual	3.4573	2	1.7286	1.00
Total	400.4982	4		

Confidence Level	Value of F Residual
.95	18.51
.975	38.51

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

A study of the literature and a limited number of experimental trials has led to the conclusion that:

1. The results of the absorption studies confirm the conclusions made in Chapter 5 that "effects of the first kind" a physical blockage of available absorption sites are negligible in reducing gas transfer rates under quiescent conditions.
2. Experiments with two different surfactants adsorbed at the surface revealed that surfactant concentrations to a maximum of 20 mg/l of ABS did not significantly affect the rate of oxygen absorption at low surface pressures and turbulence.
3. It is expected that surface renewal rates in natural systems would result in conditions whereby depression of the hydrodynamic activity of the surface by the presence of a surface film could reduce gas transfer rates.

8.2 RECOMMENDATIONS

It is recommended that:

1. Additional studies be performed to determine the effect of surfactants on gas transfer at higher levels of surface turbulence. The apparatus described here is ideally suited to this purpose.
2. The method of inducing surface renewal is considered to be a critical factor. Rates of gas absorption through surface monolayers should be studied bubble aeration and surface agitation.

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APPENDIX 1

PRIMARY DATA ABS SERIES

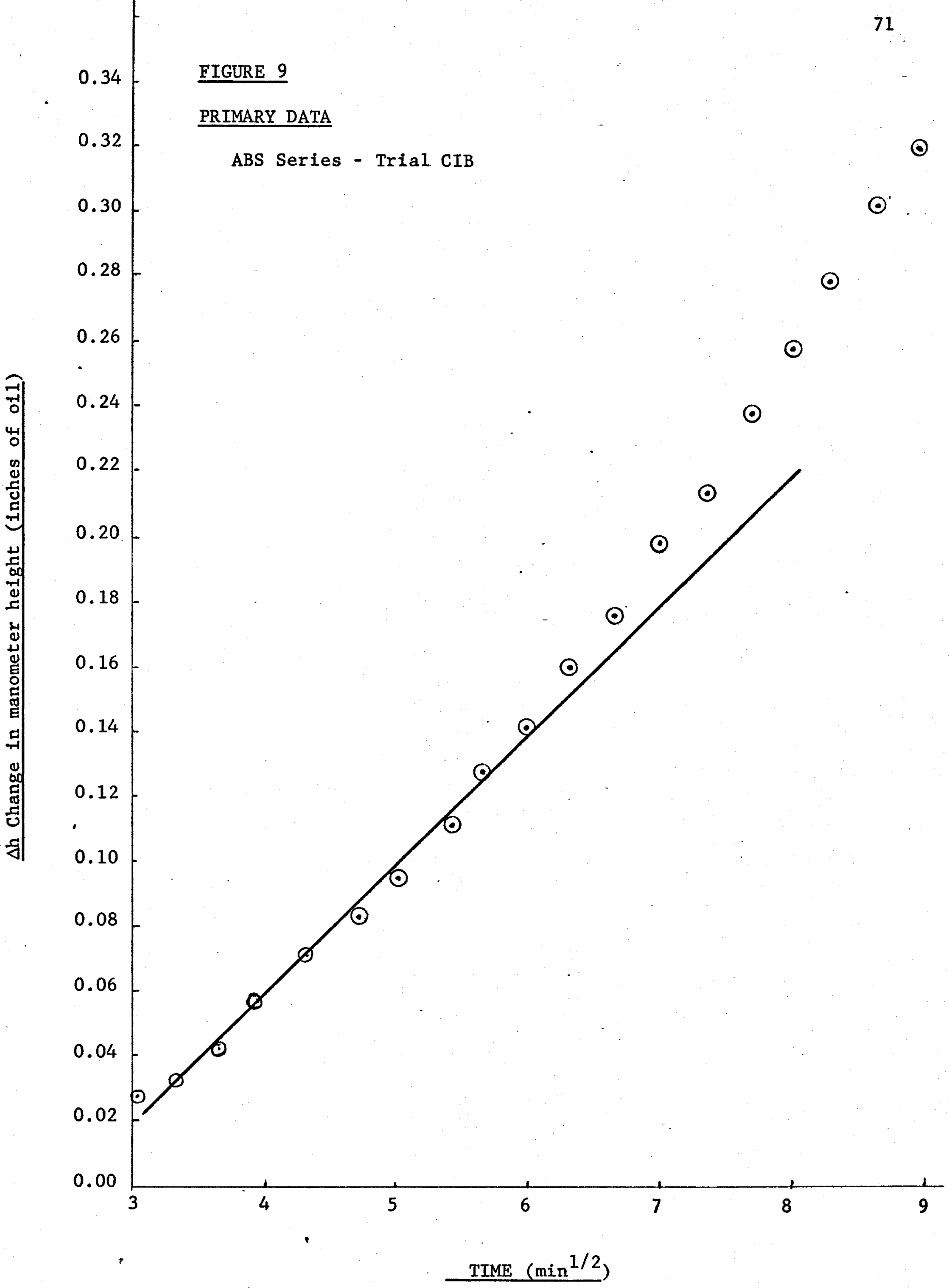


FIGURE 9

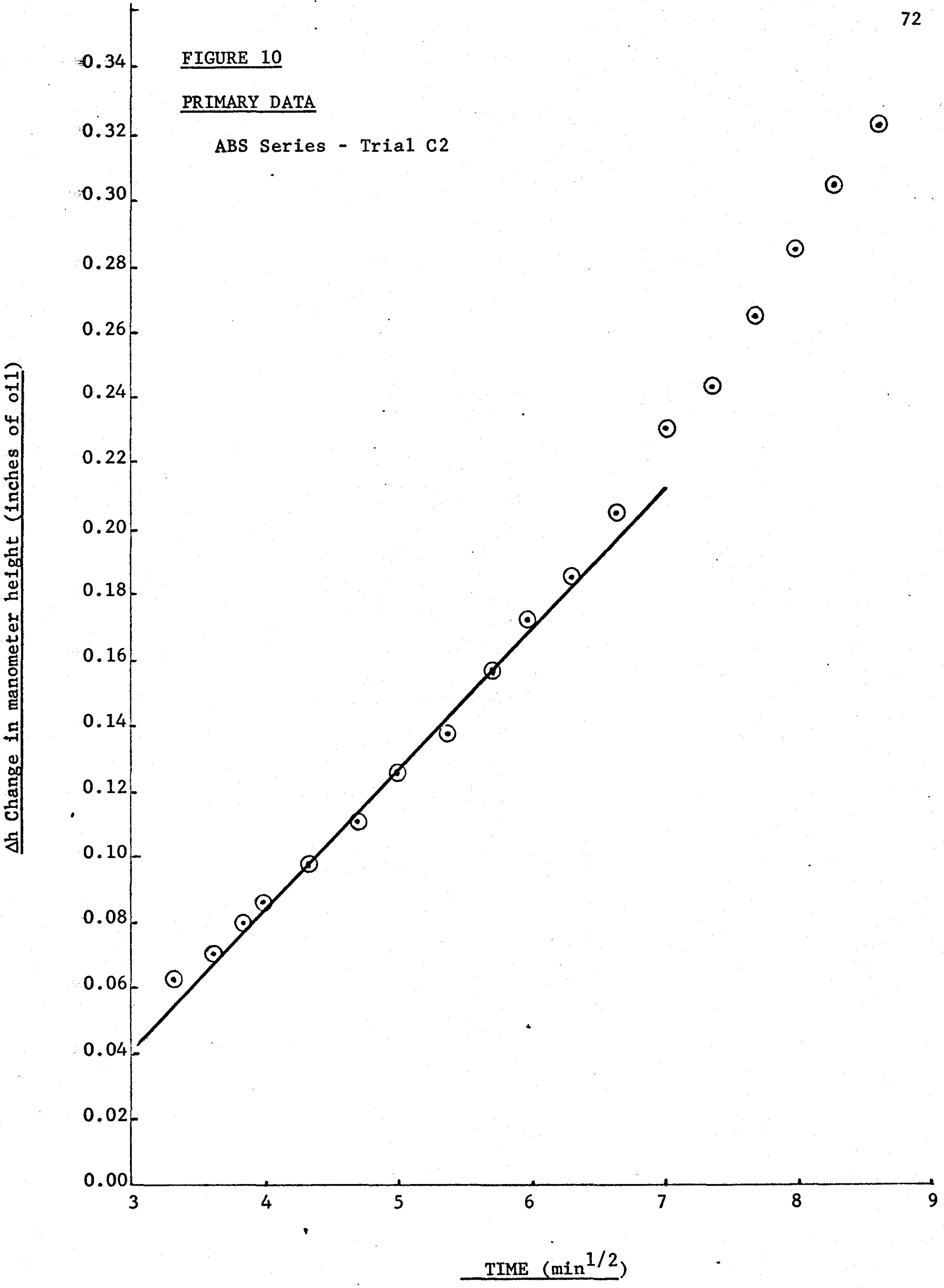
PRIMARY DATA

ABS Series - Trial CIB

FIGURE 10

PRIMARY DATA

ABS Series - Trial C2



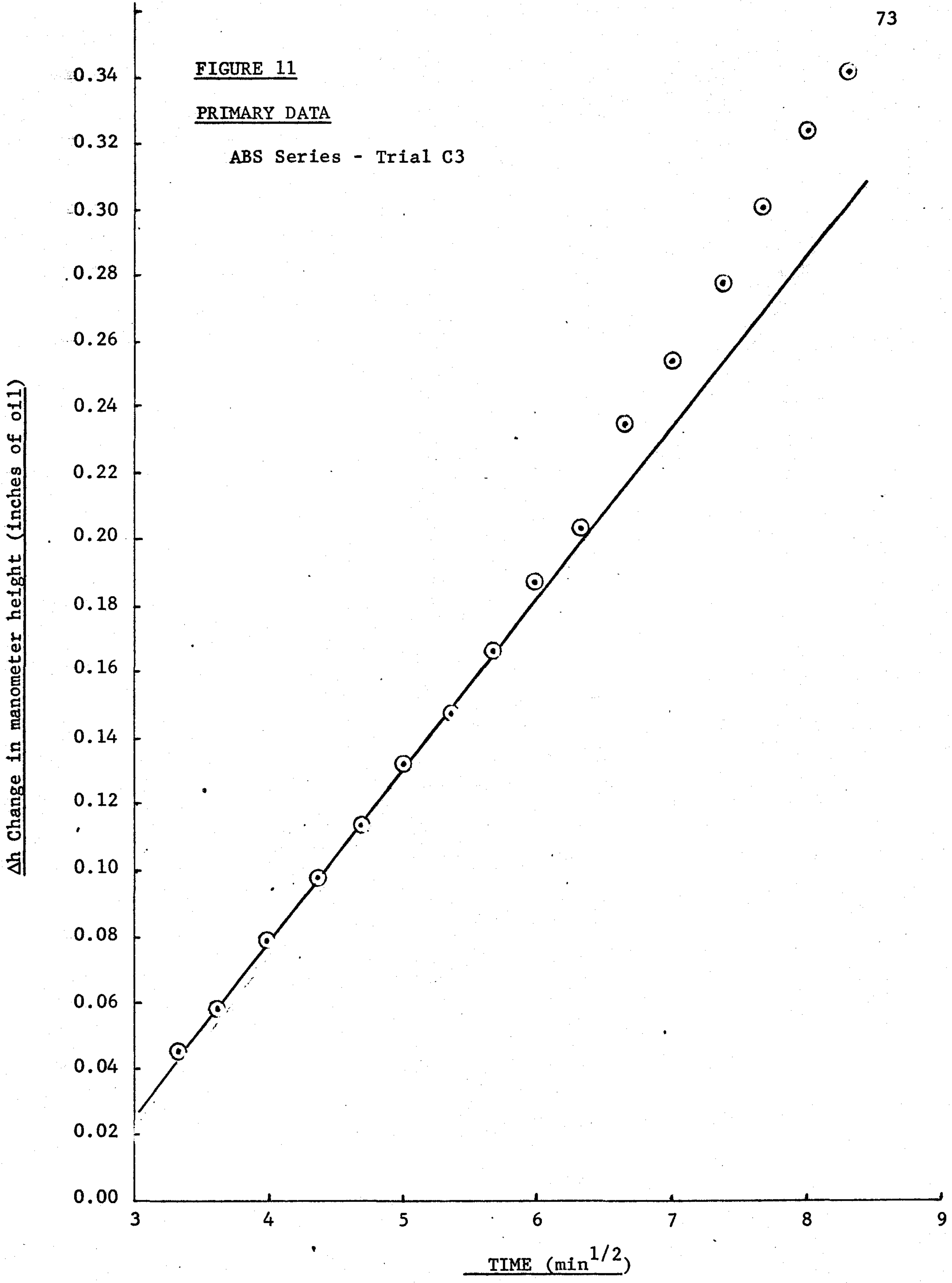


FIGURE 11

PRIMARY DATA

ABS Series - Trial C3

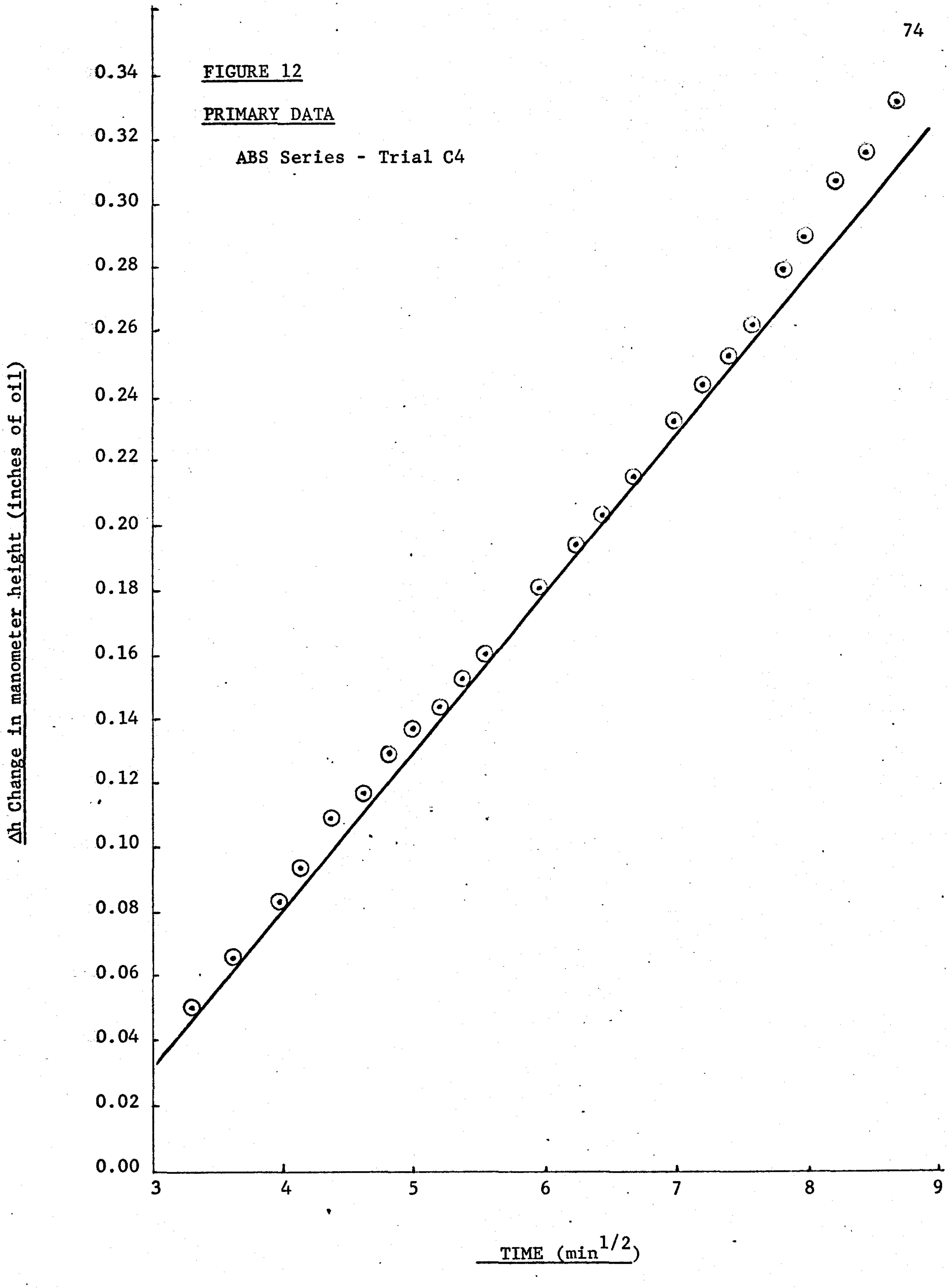


FIGURE 12

PRIMARY DATA

ABS Series - Trial C4

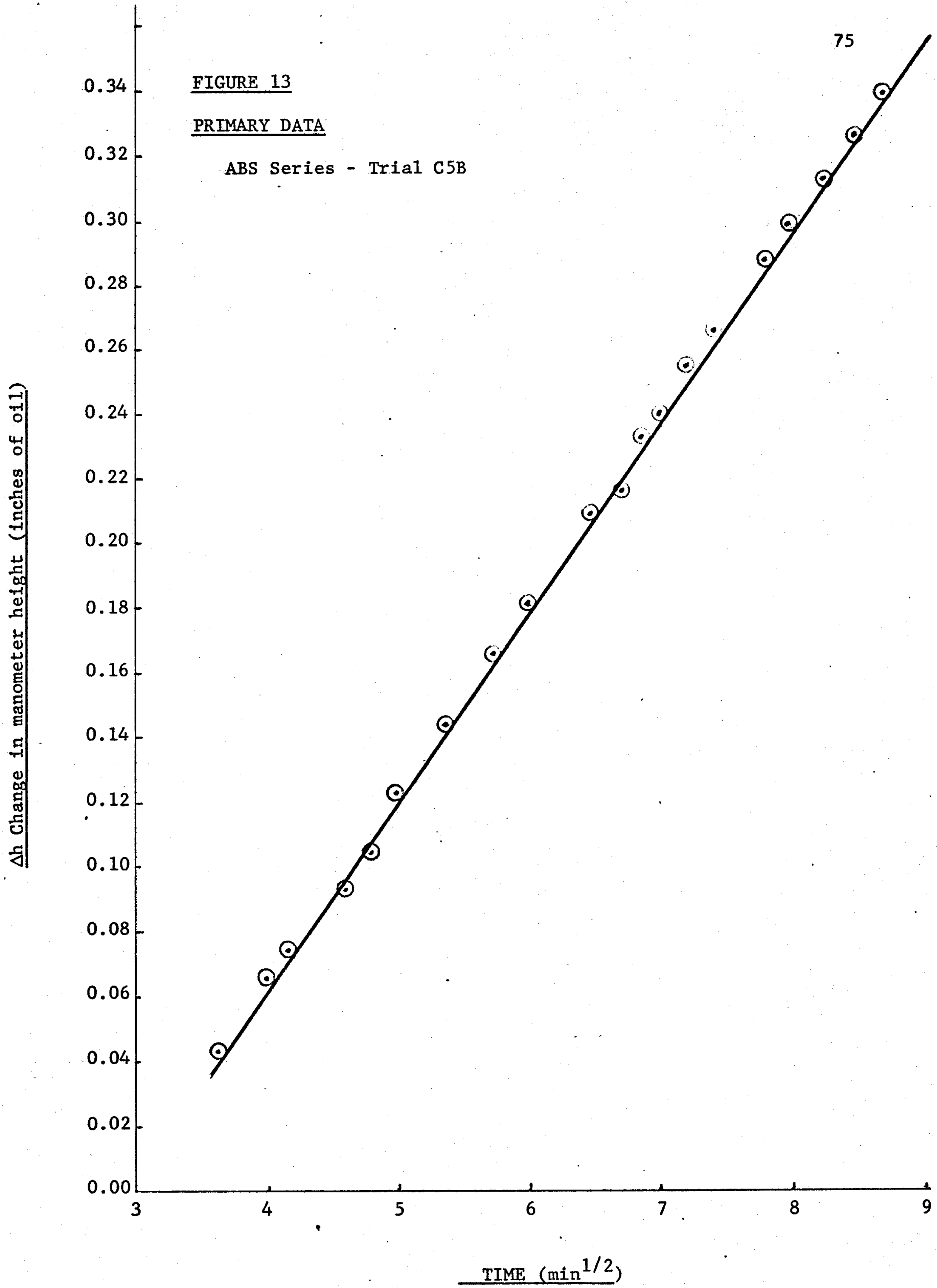


FIGURE 13

PRIMARY DATA

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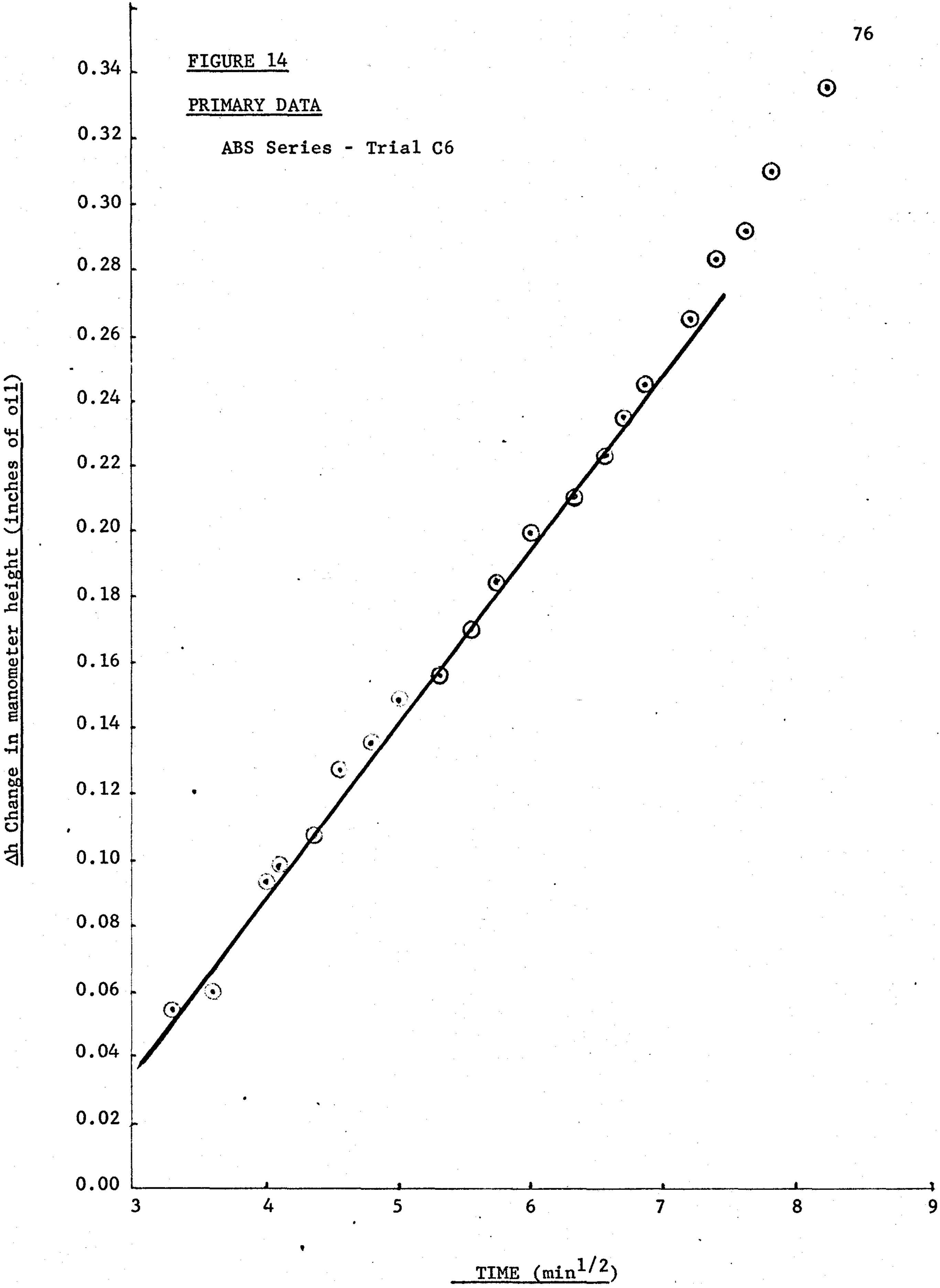


FIGURE 14

PRIMARY DATA

ABS Series - Trial C6

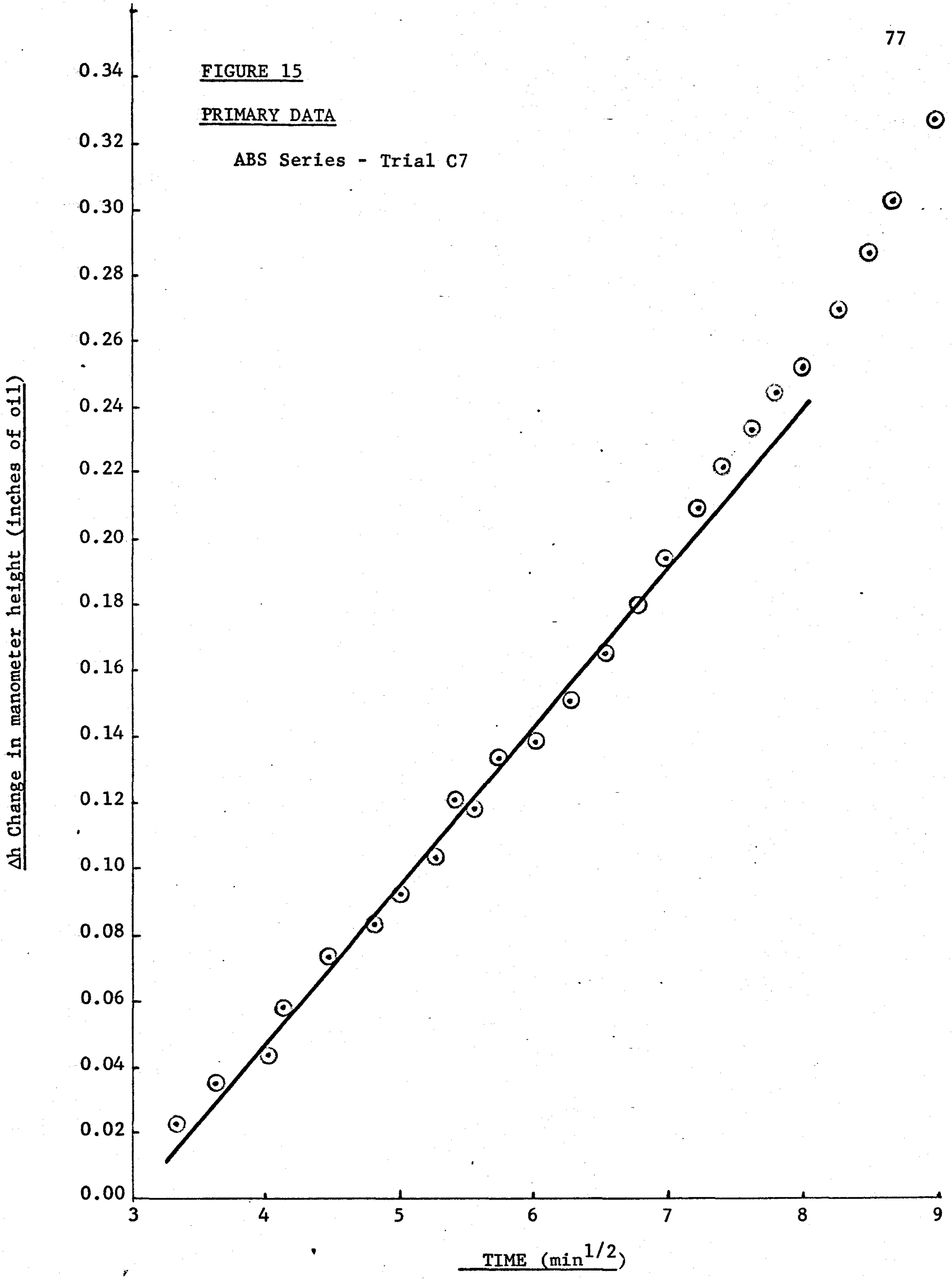


FIGURE 15

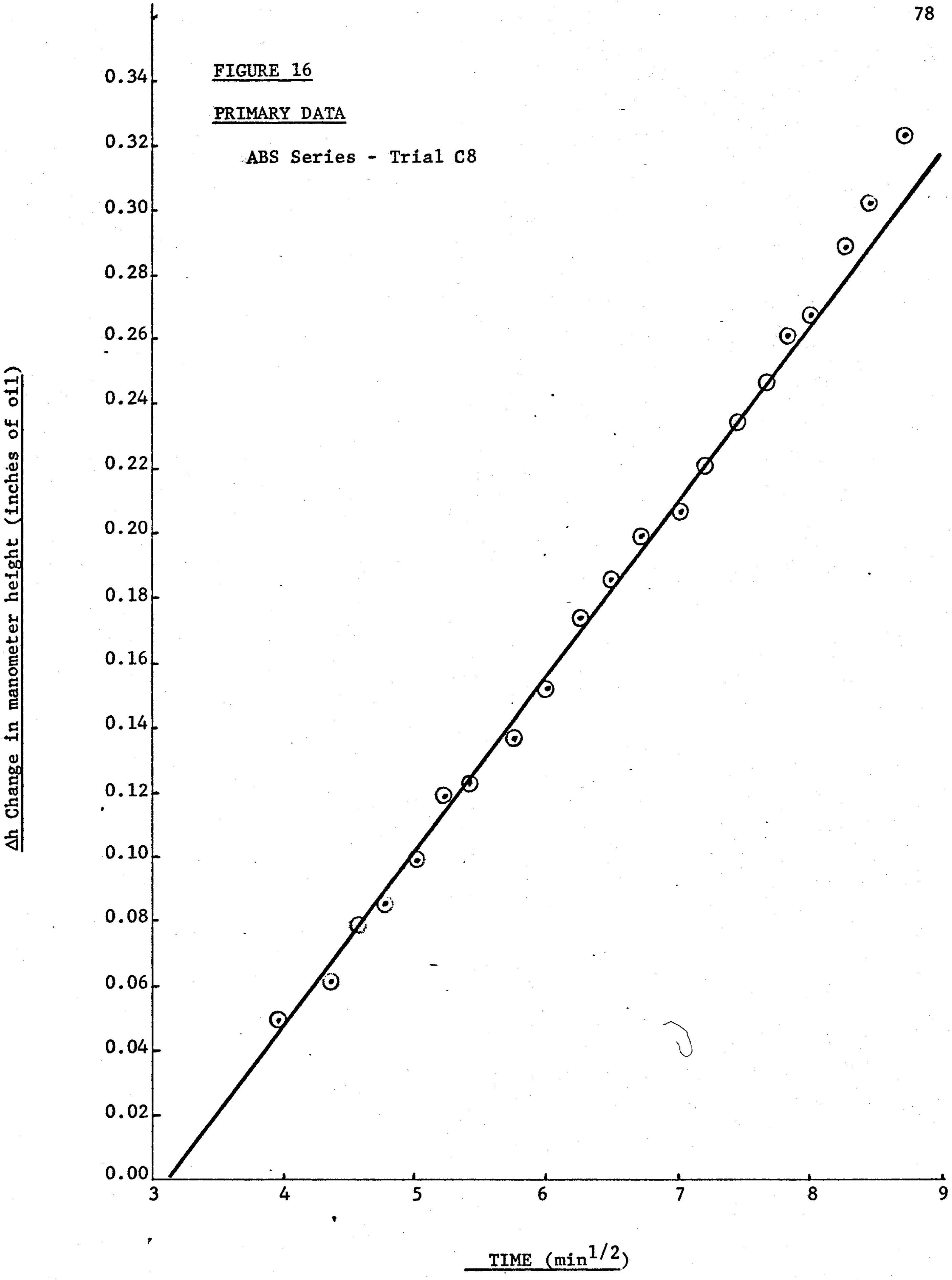
PRIMARY DATA

ABS Series - Trial C7

FIGURE 16

PRIMARY DATA

ABS Series - Trial C8



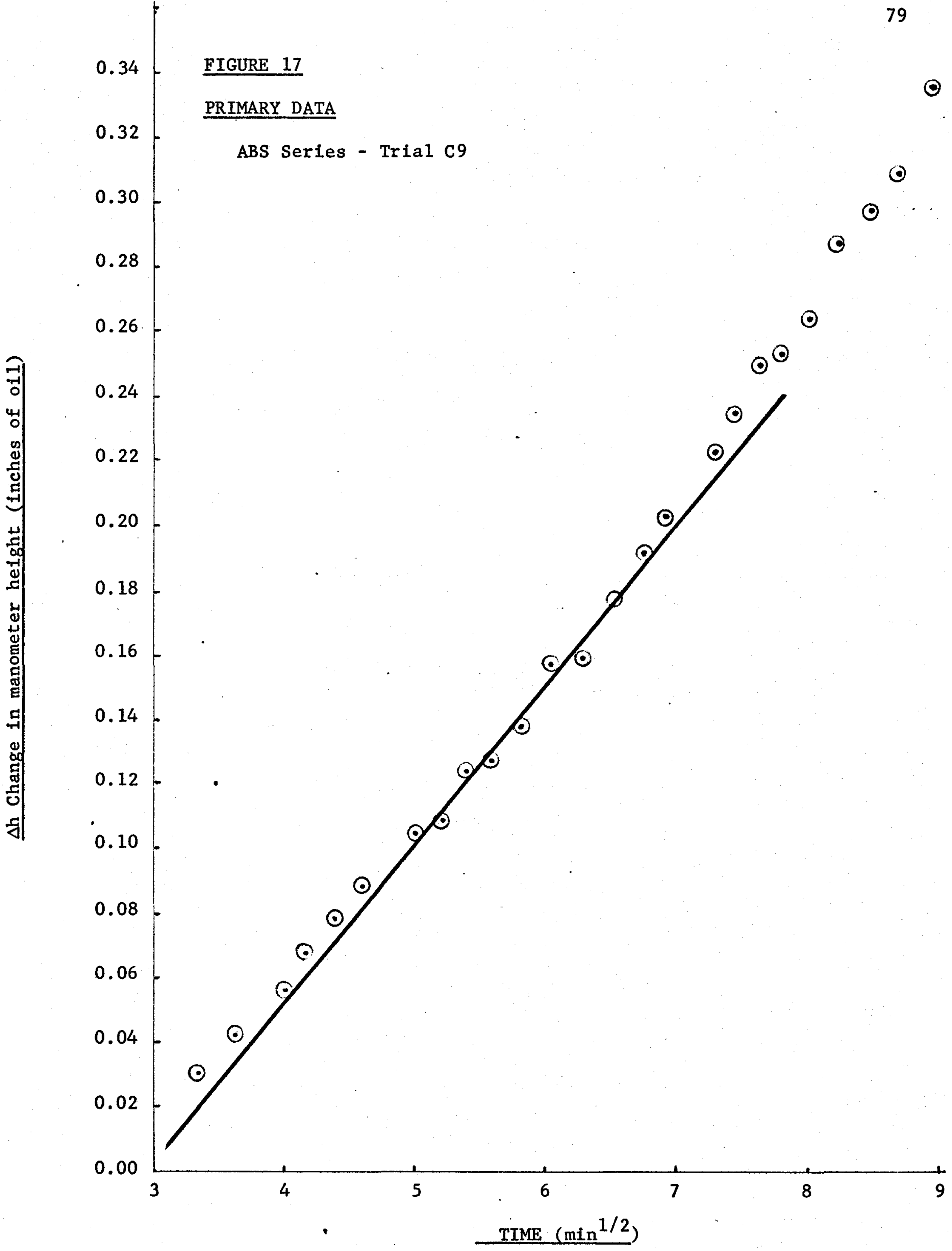


FIGURE 17

PRIMARY DATA

ABS Series - Trial C9

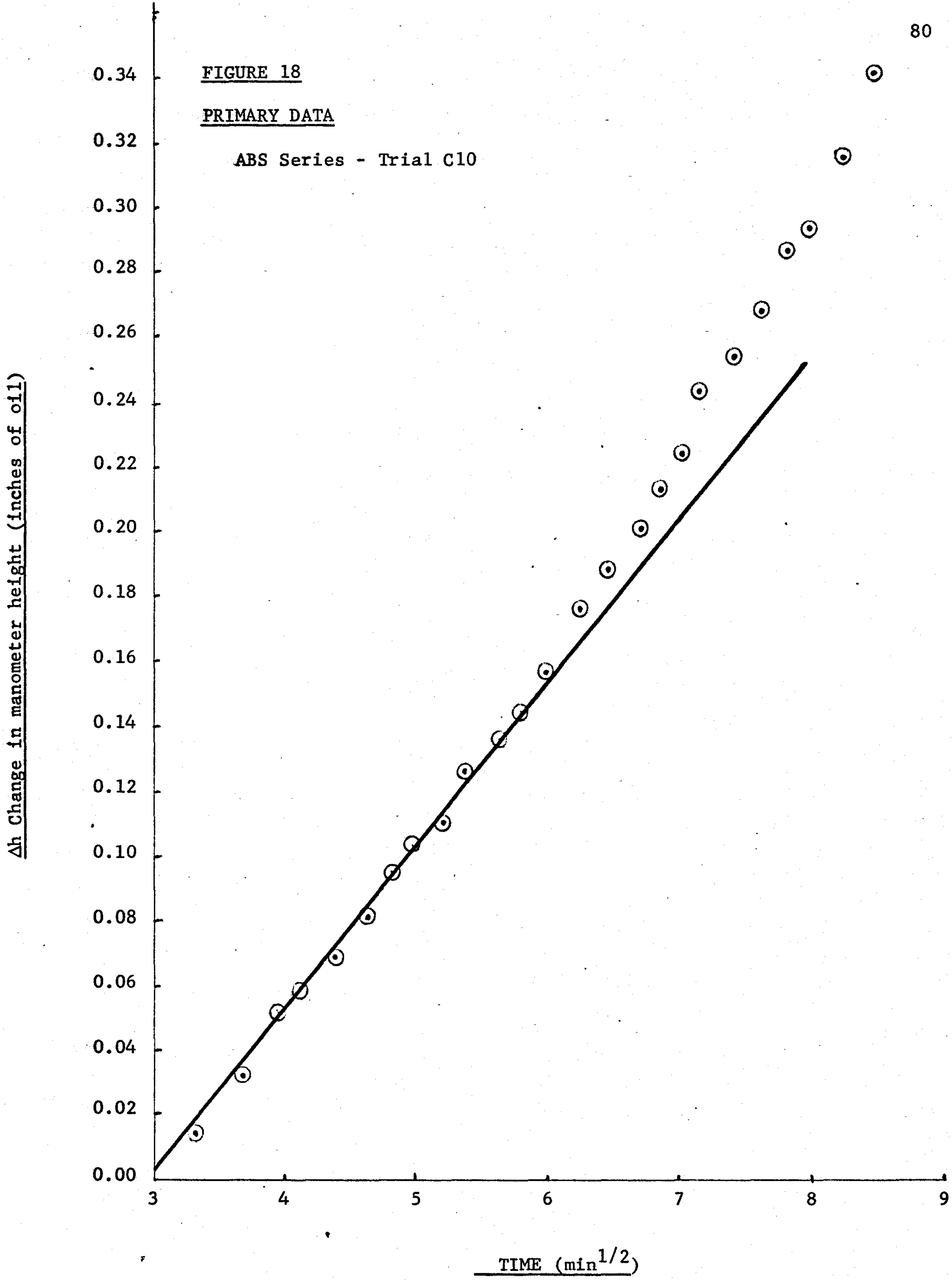


FIGURE 18

PRIMARY DATA

ABS Series - Trial C10

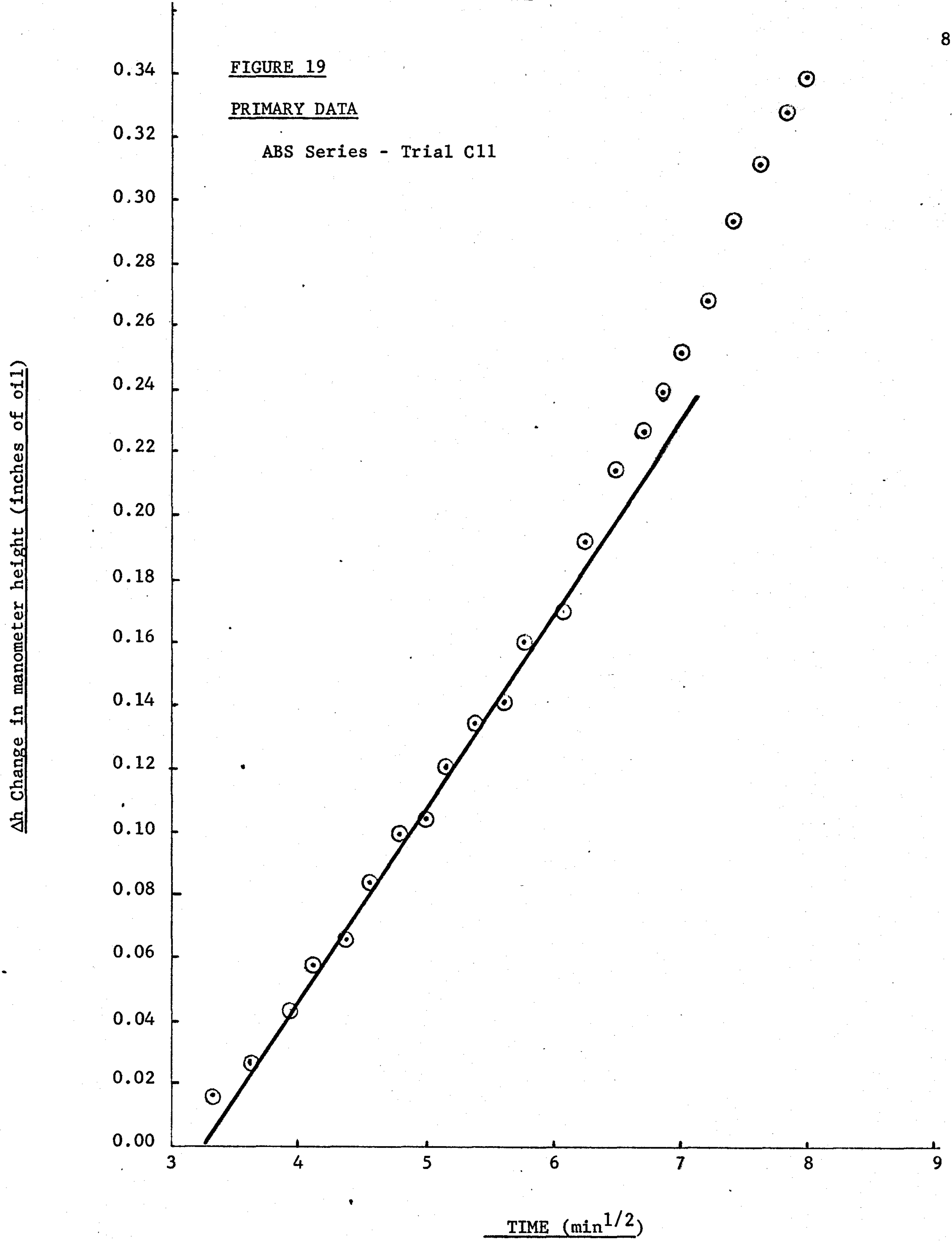


FIGURE 19

PRIMARY DATA

ABS Series - Trial C11

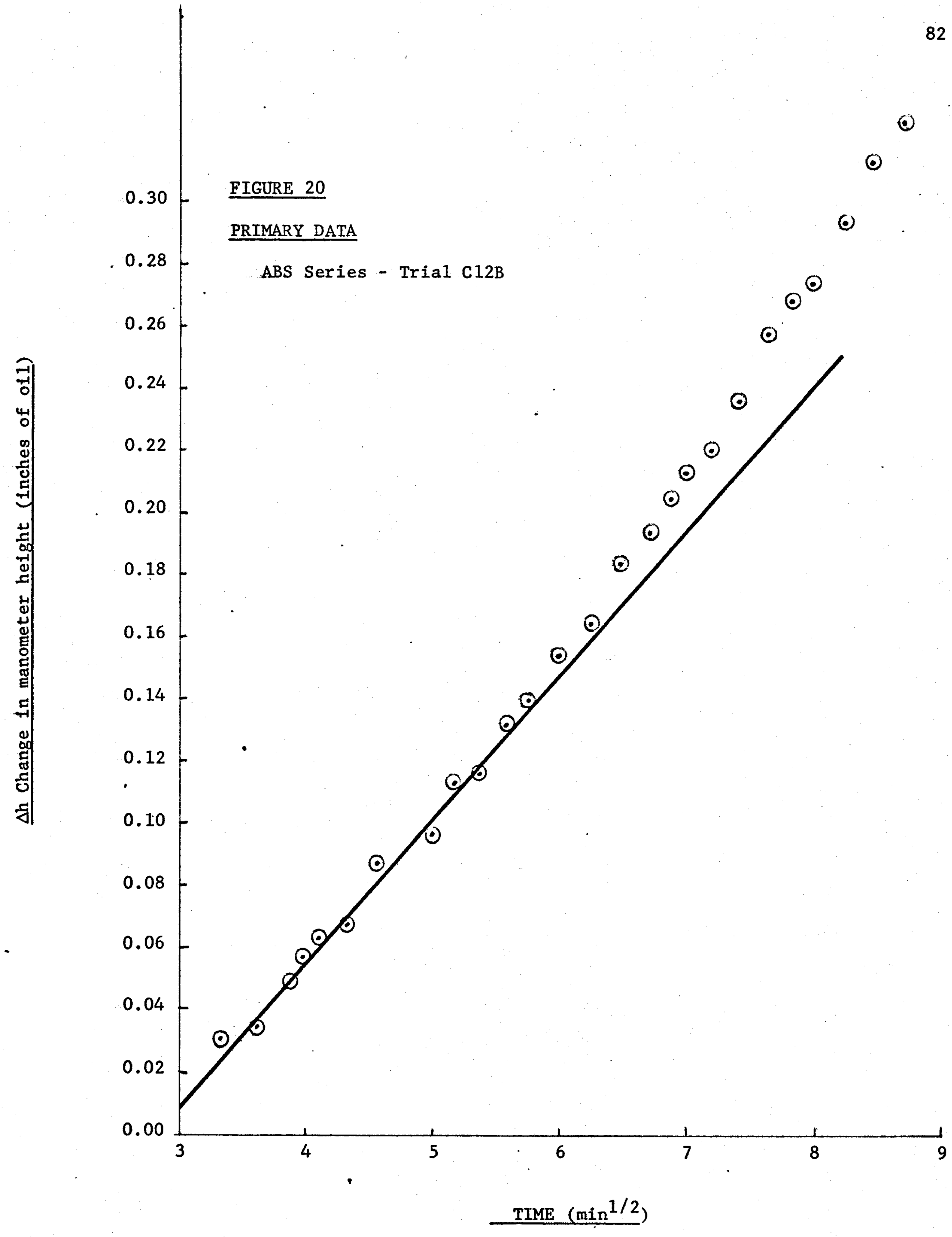


FIGURE 20

PRIMARY DATA

ABS Series - Trial C12B

APPENDIX 2

PRIMARY DATA NaLS SERIES

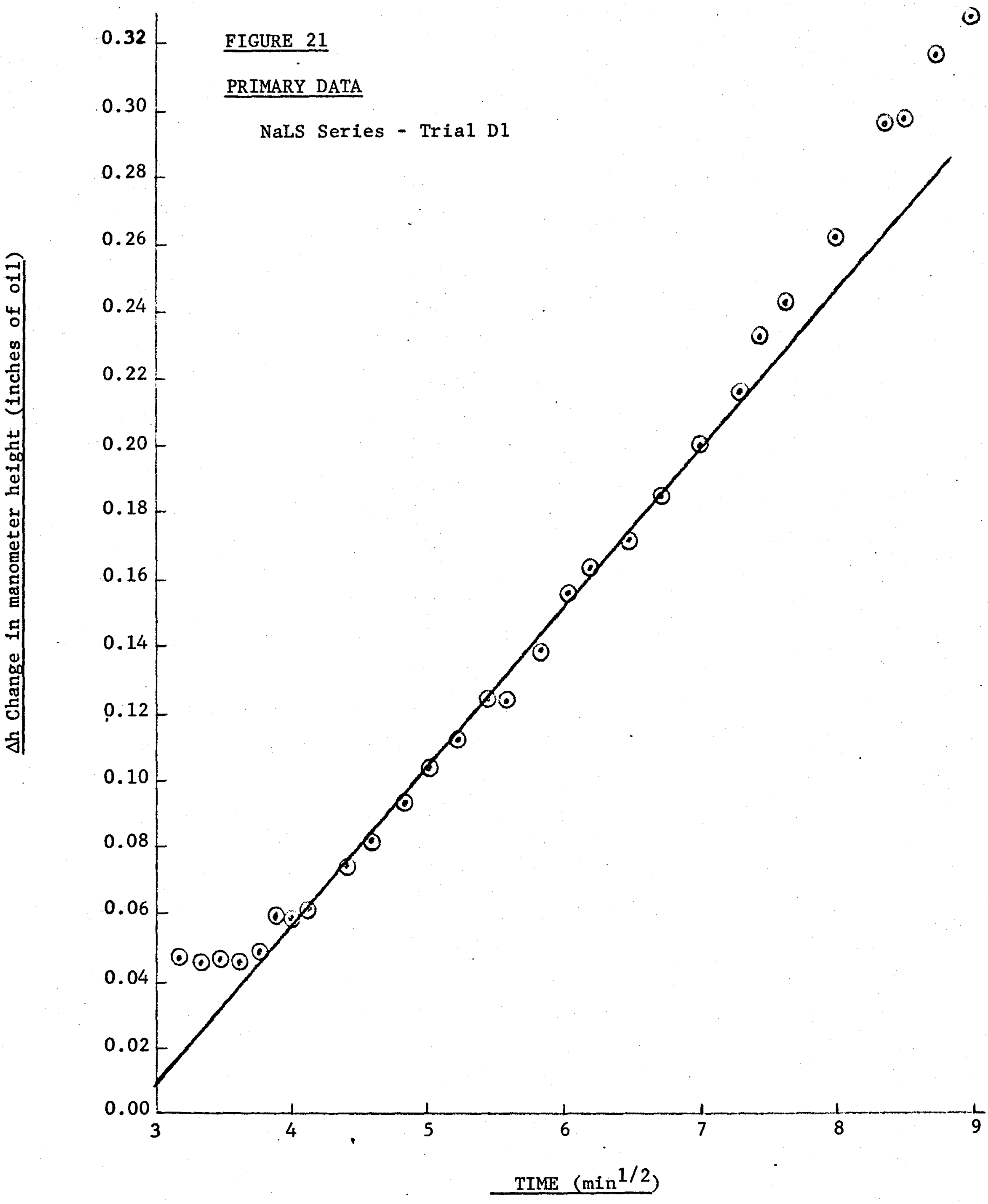


FIGURE 21

PRIMARY DATA

NaLS Series - Trial D1

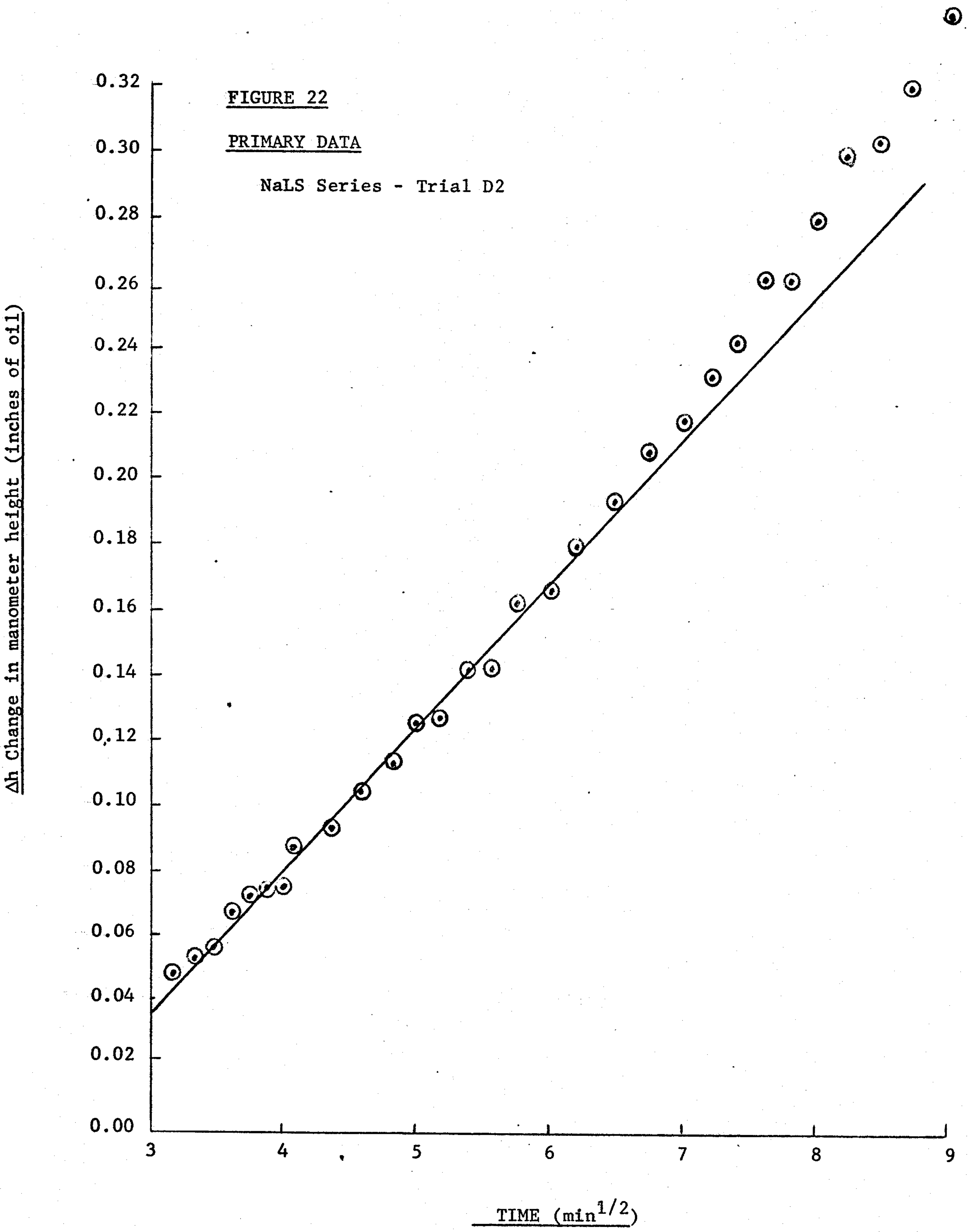


FIGURE 22

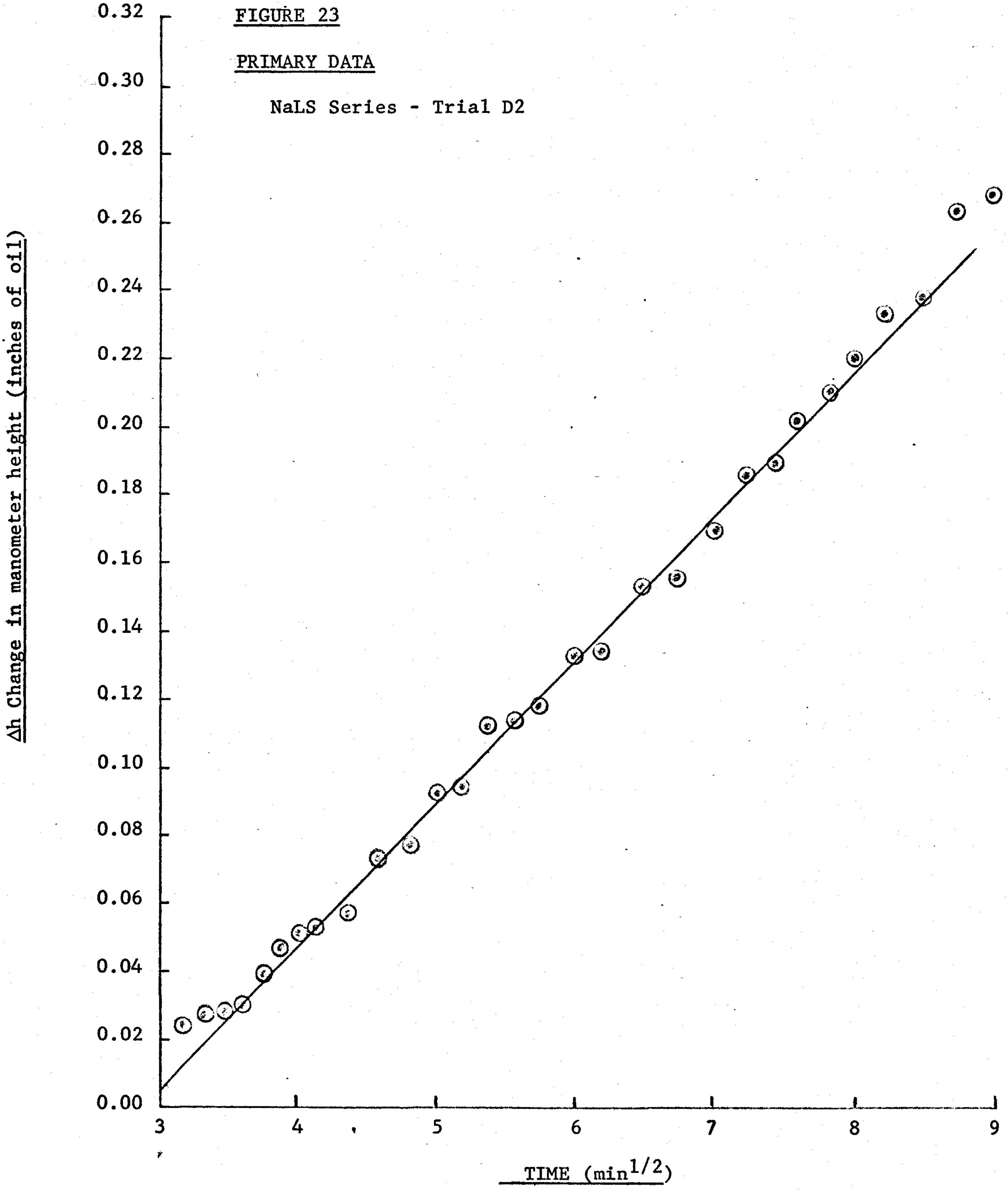
PRIMARY DATA

NaLS Series - Trial D2

FIGURE 23

PRIMARY DATA

NaLS Series - Trial D2



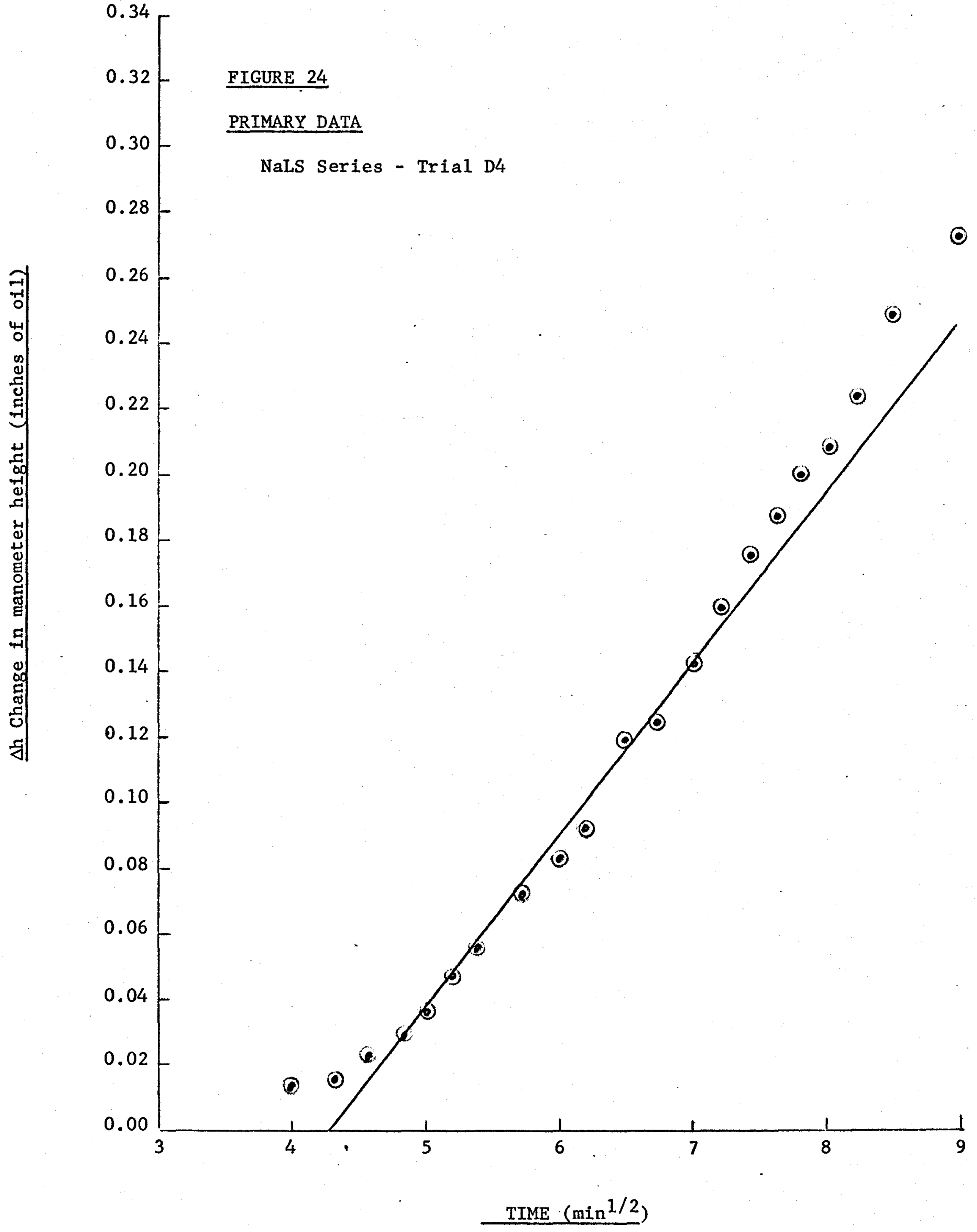


FIGURE 24

PRIMARY DATA

NaLS Series - Trial D4