DIFFUSION OF DYES

THROUGH CELLULOSE

A THESIS SUBMITTED

TO

THE VICTORIA UNIVERSITY OF MANCHESTER

BY

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FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY

OCTOBER 1955

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Ann Arbor, MI 48106 – 1346

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Introduction

Since the realisation of the fundamental concepts of the diffusion processes by Parrot [1], Graham[2] and the first most significant theoretical contribution by Fick [3,4], an enormous amount of experimental work has been done on the diffusion of matter in liquids and in and through solids. New fields of promising scope are being explored and the number of such fields is by no means limited. Modern trends in both science and technology are demanding precise information about numerous processes in which diffusion plays a major role.

One of the domains where diffusion processes have attracted much attention during the past 25 yers is the dyeing of textile fibres. Though dyeing processes have been carried out for a long time, it is only recently that a quantitative picture has become available, which explains the mode of penetration of the dye molecules, their affinity and attachment to the substrate, and various other factors influencing the actual processes.

Dyeing of cellulosic materials with direct dyes is now frequently regarded as a process of diffusion with simultaneous absorption. So one convenient way of assessing the compatibility of a dye is to observe its rate of diffusion inside the fibre under a set of fixed conditions. Obviously, dyes diffusing rapidly into the interior of fibres are most likely to diffuse out quickly, when

the conditions are reversed. In a similar way, bulky or sluggish dye molecules will take long to penetrate far into fibres, but once they have done so, offer great resistance to removal.

An important consideration about diffusion processes in solids is the "affinity" of the diffusing molecules for the substrate. This "affinity" may become synonymous with "solubility" under certain circumstances, especially when gases or vapours diffuse through membranes of organic materials[5]. Then the diffusion is governed both by Henry's law and the concentration of the gas. This affinity controls the interstitial flow of matter, as for example, that of water through certain zeolites and silicates, which offer active sites or "holes" to the diffusing substance [6]. This is particularly borne out when the diffusing substance has no affinity for the substrate or the substrate itself has no holes big enough to allow the passage of the diffusible substance.

Of the numerous available methods for the experimental determination of diffusion co-efficients, the simplest is to bring the solid substrate in contact with the gas, vapour or the solution of the penetrant and measure the rate of uptake as a function of time, which is compared with the equilibrium value, theoretically attained after infinite time. This technique was developed by Hill [7] and has been extended to the study of direct dyes on cotton [8].

Though this method enjoys the merit of extreme simplicity and does not require any elaborate apparatus, yet it is limited to

short times. During the initial stages, any change in the duration of the experiment would result in a corresponding, noticeable change in the uptake. However, it would take too long to measure a detectable change in the values of uptake, when it approaches equilibrium. Another important consideration is that diffusion should not be too rapid; its rate should be comparable to the time factor, which necessarily limits this method to substance diffusing with moderate speed.

Determination of the diffusion co-efficient through a material obtainable in the form of a sheet is fairly easy, for example, Garvie and Neale's [8] steady state method for direct dyes through a film of cellulose. It has got the disadvantage of requiring a long time, before steady state is attained and also the double manipulation of emptying and refilling the apparatus with fresh solutions in the middle of the experiment after the steady state conditions have been reached. Furthermore, all the measurements of the required quantities cannot be made in a single experiment; the equilibrium concentration of the dye on the film must be determined by a separate experiment.

Films can be compressed together to constitute one single "multiple" film and the distribution of the dye studied at different stages inside the compound film, when one or both faces are exposed to the dye solution. This method has yielded valuable information in the hands of Garvie and Neale (loc.cit.), but it is very

laborious and involves a double graphical differentiation before one knows the value of the concentration gradient and the flux of the dyestuff across a particular plane, which makes the results rather inaccurate.

The diffusion of gases and vapours through films of polymeric materials has been studied extensively, both from technological as well as academic points of view in order to assess the permeability of the material to the penetrants. Daynes [9] seems to have been the first to use a method in which both the steady and the non-steady states of flow are analysed in a single experiment. He developed the mathematical treatment and showed that the diffusion co-efficient D was related to the thickness l of the film and a factor called the 'time lag', L, in the following manner:-

$$D = \frac{l^2}{6\,L}$$

Here L denotes the time, which elaspes after the diffusible substance makes contact with the film, before flow in the non-steady state changes into one of steady state, the concentration at the outgoing side being assumed zero.

The method seems to be very simple at the outset and the essential requirements are: two reservoirs, in which to start with, the concentration of the diffusing substance is different and which are partitioned by means of a film of the material through which

diffusion is taking place. Transfer of matter across the film occurs from the regions of higher concentration to the one of low or even zero concentration at the start of the experiment. Increase in concentration is measured from time to time by analysis and a plot of the amount of the substance diffusing against time shows the two states of diffusion ---- the non-steady and the steady; the former being indicated by the curved portion of the plot which merges into a straight line at a time when it switches over to the latter. Extrapolation of the straight line to the time-axis gives an estimate of the "time lag", L.

Barrer [10,11,12] later on, developed the technique and studied the diffusion of gases through metallic sheets and gathered valuable information about the underlying diffusion mechanism. The fundamental technique, however, remained the same, though refinements in individual cases were introduced.

It is surprising that inspite of its simplicity, this method has not received any attention so far as the experimental determination of diffusion co-efficients of dyes in textile fibres is concerned. It was thought that it would yield valuable results concerning the diffusion of dyes together with their absorption on the substrate.

Suitable cellulosic materials availabe in sheet form are of regenerated cellulose (Cellophane) and of cellulose acetate.

It was the purpose of this work to investigate and correlate the different factors involved in the diffusion of dyes through these films according to the technique of Daynes' and Barrer's (loc.cit.). To this end, dyes from 3 main classes (viz., direct, acid and basic) were used for the determination of the diffusion co-efficients in a specially designed diffusion cell, to be described fully at a later stage.

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Chapter I

General Kinetics of Diffusion Processes.

The diffusion or spontaneous transfer of matter, from one part of the system to another has been the subject of extensive study over the past hundred years, covering problems of great diversity in nature and with wide implications. The fundamental observation was that there was diffusion of a solute from a solution of higher concentration to one of a lower concentration. It was Fick [1,2] in the year 1855 who made a "reasonable assumption" that the flow of matter in diffusion follows an analogous course to the conduction of heat through solids, i.e., the rate of diffusion or the amount of the substance crossing a given area in an infinitesimally small interval of time ought to be proportional to the cross-sectional area and to the concentration gradient, i.e.,

$$\frac{dS}{dt} = - D.A.\left(\frac{dC}{dx}\right)_t \qquad 1.1$$

where dS is the amount of the substance which passes in time dt from a region of high concentration to one of low, A is the effective area of cross-section and dC/dx is the concentration gradient, the diffusion taking place in a direction perpendicular to the plane A. D is the constant of proportionality.

Fick realized that D tends to increase somewhat with

temperature and also increases to a limiting value as the solution is diluted. The latter trend is specially characteristic of electrolytes and because of these variations, it is preferable to refer to D as the diffusion co-efficient rather than the diffusion "constant".

The dimensions of equation 1.1 are those of area/time and therefore in the C.G.S. system D is expressed as $cm^2\ sec^{-1}$.

Diffusion processes are related to chemical kinetics on the one hand and to sorption and solution equilibria on the other. It is apparent that the study of diffusion touches upon numerous aspects of physico-chemical research. There are two states of flow by diffusion --- the so-called stationary and the non-stationary states. From the former, one derives the permeability constant, P, the quantity transferred per unit time per unit area of unit thickness under a standard concentration gradient. The two quantities, the permeability constant P and the diffusion co-efficient D, are related by

$$P = - D.\frac{dC}{dx} \qquad 1.2$$

which is a modified form of equation 1.1. The problem is, therefore, also concerned with the solubility of the diffusing substance in the solvent/or the medium and the permeability of the latter to the former.

Fick's Second Law of Diffusion.

The second form of Fick's law refers to the non-stationary state of flow by diffusion and deals with the accumulation of

matter at a given point in the medium as a function of time. It can be derived from equation 1.2, by considering the diffusion in the +x direction of a cylinder of unit area of cross-section. Then in an element of volume δx, bounded by the two parallel planes 1 and 2, which are also δx apart and normal to the axis of the cylinder, the concentration will be changing in time dt from C to $(C+dC/dx.\delta x)$. The amount which accumulates within the volume δx can be estimated as follows:

The rate of accumulation is given by the difference between the two rates of permeation, P_1 and P_2 at the two planes 1 and 2 respectively.

$$\therefore P_1 - P_2 = -D \frac{dC}{dx} - -D \frac{d}{dx}\left(C+\frac{dC}{dx}\delta x\right)$$

$$= D \frac{d}{dx}\left(\frac{dC}{dx}\right)\delta x \qquad 1.3$$

But the rate of accumulation in the volume element bounded by the planes 1 and 2 is $dC/dt.\delta x$. Equating this quantity to that in equation 1.3, we have:

$$\frac{dC}{dt}\delta x = D \frac{d}{dx}\left(\frac{dC}{dx}\right)\delta x \qquad 1.4$$

or

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \qquad 1.5$$

which is the second form of Fick's law.

In two dimensions, the above equation becomes

$$\frac{dC}{dt} = D\left(\frac{d^2C}{dx^2} + \frac{d^2C}{dy^2}\right) \qquad 1.6$$

and in three dimensions,

$$\frac{dC}{dt} = D\left(\frac{d^2C}{dx^2} + \frac{d^2C}{dy^2} + \frac{d^2C}{dz^2}\right) \qquad 1.7$$

or more generally,

$$\frac{dC}{dt} = D\nabla^2 C \qquad 1.8$$

All these equations, 1.6, 1.7, and 1.8, assume an isotropic medium for the diffusion to take place; if this is not the case, one may simply write:

$$\frac{dC}{dt} = D_x\frac{d^2C}{dx^2} + D_y\frac{d^2C}{dy^2} + D_z\frac{d^2C}{dz^2} \qquad 1.9$$

In many cases, the diffusion co-efficient, D, depends upon the concentration of the substance in the medium [3-23,26], and often the medium swells during the processes of diffusion, as for example, when the passage of organic vapours and liquids takes place through high polymers [3,4,5,15,23], or when diffusion proceeds through simultaneous absorption of the penetrant on the medium [8,14,29,39,40,42-5]. Under these circumstances, it is therefore, necessary to solve an equation of the type

$$\frac{dC}{dt} = \frac{d}{dx}\left(D\frac{dC}{dx}\right) + \frac{d}{dy}\left(D\frac{dC}{dy}\right) + \frac{d}{dz}\left(D\frac{dC}{dz}\right) \qquad 1.10$$

in which D has the characteristics of concentration dependence.

Not many problems in diffusion can be solved completely in terms of mathematics and no exact solution of the diffusion equation in the form 1.10 exists[26] for any boundary conditions, though approximate solutions have been evolved for determining D as a function of C from the equation:[3,27,28]

$$\frac{dC}{dt} = \frac{d}{dx}\left(D\frac{dC}{dx}\right) \qquad 1.10a$$

We are confined to certain limited cases, for example, the infinite plane of sheet of finite thickness, the semi-finite solid, the cylinder and the hollow sphere, and even in these cases, a solution is generally available under certain particular conditions.

In dealing with kinetics of diffusion processes, consideration of the dimensions alone will often provide valuable information. The diffusion co-efficient D being of dimensions L^2T^{-1}, we may expect an equation of the type [24,25]

$$x \,/\!\_\, \sqrt{Dt} = \text{a dimensionless constant}$$

to hold for certain specific conditions, where x is a space variable and t time.

The quantity Q of the substance which diffuses in or out in time t per sq.cm. of the surface (ML^{-2}) must bear to C, the concentration (ML^{-3}) which determines it, a ratio, which must be of the dimension L and therefore proportional to $\_/\sqrt{Dt}$; we must therefore be able to write in any specified condition,

$$Q \propto C/\sqrt{Dt}$$

provided that t is not too great.

Diffusion during a Steady State.

The rate of diffusion as mentioned previously is $-D.dC/dx$. If $-D.dC/dx$ is constant, i.e., the concentration gradient is uniform, there is no accumulation of matter at any point. Hence if $-dC/dx$ diminishes as x increases, more substance reaches a region than passes on from it and the matter tends to accumulate in that region. The measure of rate of accumulation is given by the equation

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \qquad 1.6$$

The tendency to accumulate is met either by an increase in comcentration or by the utilisation of the diffusing substance by the medium such as that of oxygen by muscular tissues [24], or of iodine when diffusing into a gel containing sodium thiosulphate[25] or diffusion of dyes into textile fibres with the simultaneous absorption of the former by the latter [8,13,14,39,40]. Expressed mathematically equation 1.6 takes the form

$$\frac{dC}{dt} + A = D \frac{d^2C}{dx^2} \qquad 1.11$$

Since we are dealing with a steady state of flow of matter in which case $dC/dt = 0$, we have:-

$$A = D \frac{d^2C}{dx^2} \qquad 1.12$$

The solution of this equation is given as [24],

$$C = \frac{Ax^2}{2D} + Bx + C_0 \qquad 1.13$$

where B is a constant to be determined under the condition

$$x = 0, \quad C = C_0$$

at which it should happen.

Now, if A is positive, C must diminish as we pass inward from the boundary along the direction in which diffusion occurs and a point must be reached where C = 0. Since the concentration can never be negative, the diffusion process must come to an end at this point and therefore the concentration gradient becomes zero. Fig.1.

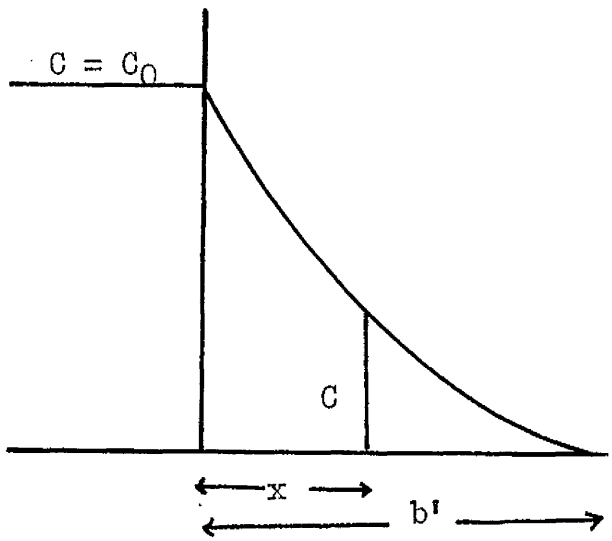

Fig.1

Thus if $x = b'$, the distance from the surface at which concentration vanishes, we must have,

$$C = 0 = Ab'^2 / 2D + Bb' + C_0 \qquad 1.14$$

and $$\frac{dC}{dx} = \frac{A\,b'}{D} + B = 0 \qquad 1.15$$

$\therefore$ $$B = - Ab'/D \text{ and } \quad C_0 = Ab'^2 / 2D \qquad 1.16$$

and $$b' = \sqrt{2DC_0 / A} \text{ and } B = - \sqrt{2AC_0 / D} \qquad 1.17$$

Hence the solution required is:

$$C = \frac{Ax^2}{2D} - x\sqrt{2AC_0 / D} + C_0 \qquad 1.18$$

and the greatest distance to which the diffusing substance penetrates is given by

$$b' = \sqrt{2DC_0 / A} \qquad 1.19$$

The amount Q' of the penetrant dissolved in the medium per sq.cm. of its surface during the steady state is

$$\int_0^{b'} C.dx$$

which on integerating equation 1.18 becomes,

$$Q' = 1/3\ C_0 \sqrt{2DC_0/A}$$

$$= C_0\ b'/3 \qquad 1.20$$

This is one-third of the full amount of the solute which should be dissolved in the absence of its consumption by a lamina of thickness b' of the medium.

However, if the membrane is limited by its contact with an impermeable wall at x = b or if it is of thickness 2b and exposed to the diffusing substance on either side, then two cases arise, according to whether b>b' or b<b'. When b>b', the above solution

holds (see Fig.1); if $b<b'$, C does not attain the zero value at any point of the membrane and the condition determining B is that there is no diffusion across the plane at $x = b$ and therefore $dC/dx = 0$ at $x = b$ (Fig.2). This gives

$$dC/dx = 0 = Ab/D + B \text{ and } \therefore \quad B = - Ab/D \qquad 1.21$$

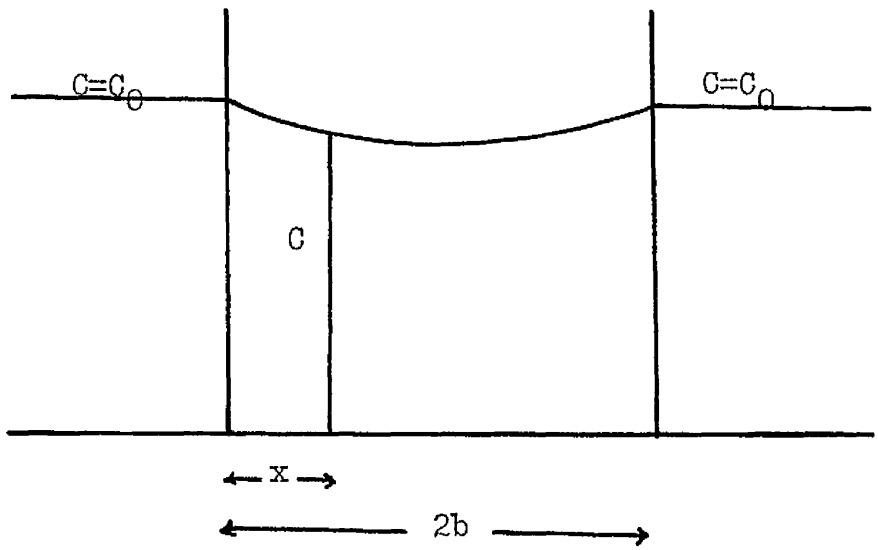

Fig.2

Hence the required solution is:-

$$C = \frac{Ax^2}{2D} - \frac{Abx}{D} + C_0 \qquad 1.22$$

and the total amount of the solute dissolved from $x = 0$ to $x = b$ per sq.cm. of the surface during the steady state flow is:-

$$Q = C_0 b - \frac{Ab^3}{3D} \qquad 1.23$$

The full amount which the membrane would dissolve while there is no consumption is $C_0 b$. Hence the fraction of the full saturation value

actually dissolved is:-

$$f = \frac{Q}{C_0 b}$$

$$= \frac{C_0 b - Ab^3/3D}{C_0 b}$$

$$= 1 - \frac{A b^2}{3 D C_0} \qquad 1.24$$

which may be written as

$$f = 1 - 2/3\ b^2/b'^2 \qquad 1.25$$

where b' is the greatest thickness of the medium which can be supplied with solute as defined previously in equation 1.19.

Application of the Diffusion Equation.

Before the equation $dC/dt = D\ d^2C / dx^2$ can be successfully used, it must be solved. Such an equation has many solutions [30] and one which is to be applied in any particular case must be determined by the boundary characteristics of the experiment. The simplest case is the diffusion of a solute in a vessel of uniform cross-section, from an infinitely long column of solution into a similar column of the solvent. In Fig.3, the abscissae represent the distances from the initial boundary; the ordinates represent concentrations. At zero time, the value of C lies on the broken line ABFG; after a long time, C is constant throughout the system as shown by the horizontal line KEL. At any intermediate time, the values of C at

different distances fall on a curve of the type HEJ or H'E J'.

Stefan [31] provided a solution of the diffusion equation, which was given by Svedberg [46] in the form

$$C = \frac{C_0}{2}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}.dy\right) \qquad 1.26$$

where

$$y = \frac{x}{2\sqrt{Dt}},$$

C_0 = the initial concentration in the lower column,

C = the concentration at time t,

x = the distance from the initial boundary.

Equation 1.26 applies to experiments with finite or small columns, if the time is short enough, so that there is practically no change due to diffusion at the bottom or top of the lower column from which diffusion takes place in the upward direction. The function $\int_0^y e^{-y^2}.dy$ is a probability integral, whose values can be found from mathematical tables [32,33,34]. The value of this integral lies between zero and one, passing from 0 to 0.9953 as y varies from 0 -2.0.

In using equation 1.26, a value of the integral is obtained by substituting the numerical value of C and C_0 and the table is worked backward to evaluate y and finally D from measured values of x and t . The nature of variations of C with x as given by equation 1.26 is shown in Fig.3. At the level of the initial boundary (x=0), the equation indicates that C will have the value $C_0/2$ at all times after the diffusion has started; if the initial volumes of the

solution and the solvent columns are equal, $C_0/2$ will also be the final concentration at any point.

In a somewhat different type of experiment, the concentration of the initial layer is maintained constant at the value C_0 throughout the experiment. For this case, the solution of the equation $dC/dt = D.d^2C/dx^2$ is

$$C = C_0 - \left(1 - \frac{2}{\pi}\int_0^y e^{-y^2} .dy \right) \qquad 1.27$$

with the same notations as in equation 1.26.

Equation 1.27 was found to apply to diffusion from a solution kept saturated by the presence of the solid salt, to diffusion from a large volume of the solution, not necessarily saturated, into a tube full of jelly containing the solvent and diffusion of salts into columns of jelly containing the appropriate reagent, so that the diffusing substance is eliminated during the process [25], as for example sodium thiosulphate - iodine, copper sulphate - sodium sulphide and lead acetate-sodium sulphide systems. In such cases, the final concentration in the solvent layer will be C_0 and the relation of C to x will be as shown in Fig.4, which is in fact the lower half of Fig. 3.

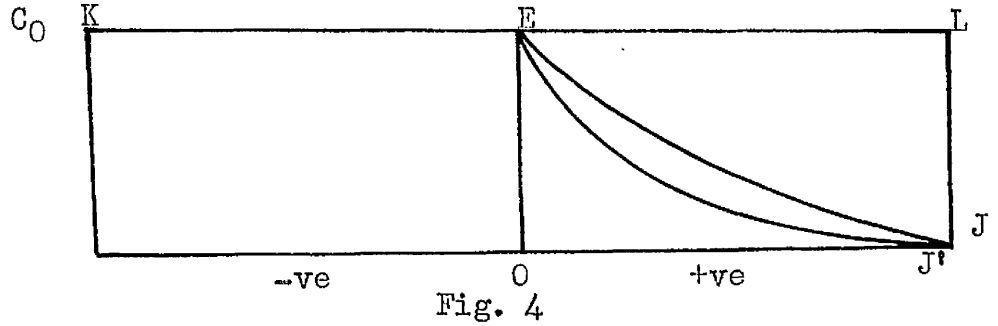

Fig. 4

Equations 1.26 and 1.27 yield an important and simple relation which is characteristic of diffusion processes. If C is kept constant, y must also be constant and the definition of y indicates that under such conditions, the distance through which the initial boundary has shifted is proportional to $\sqrt{t}$. This relationship has often been verified, the experimental technique being particularly simple, when the diffusion takes place in a jelly containing an indicator [25,37,38].

A very interesting case of diffusion has been studied and its kinetics developed by Hill [24]. It finds wide applications where sorption is used for the evaluation of the diffusion co-efficients --- of dyes into textile fibres. Hill's treatment of the problem applies to the diffusion and simultaneous consumption of oxygen, into muscular tissue. Consider a plane sheet, b cm. thick, exposed on one side to the solution or the gas and in contact with an impermeable wall on the other. In fact, the sheet is such that the area of the plane surface is much larger than the area of the edges, so that diffusion through the latter towards the centre is neglible. The problem remains the same as that of a plane sheet with 2b cm. thickness and exposed to the penetrant on both sides.

Let C be the concentration of the solute at x cm., at t time and D, the diffusion co-efficient. We will neglect the consumption of the diffusing substance by the medium. As usual, the

equation governing the flow is

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \qquad 1.6$$

If we assume that the sheet is initially free of solute and exposed suddenly at t = 0 and kept exposed thereafter to a constant concentration $C = C_0$ at x = 0 to x = 2b, the solution of equation 1.6 under these boundary conditions is :-

$$\frac{C}{C_0} = 1 - \frac{4}{\pi}\left[e^{-\theta}.\sin\frac{\pi x}{2b} + \frac{1}{3}e^{-9\theta}.\sin\frac{3\pi x}{2b} + \frac{1}{5}e^{-25\theta}.\sin\frac{5\pi x}{2b} + \text{.....}\right] \qquad 1.28$$

where $\theta = \dfrac{D\pi^2 t}{4b^2}$.

Equation 1.28, involving an infinite series might appear difficult to handle; fortunately it is very rapidly convergent. When, for example, $e^{-\theta}$ i.e., $e^{-D\pi^2 t / 4b^2} = 0.70$, the next term $e^{-9D\pi^2 t/4b^2}$ is only 0.040; when the former is 0.60, the latter is 0.010, so that when the term $e^{-D\pi^2 t / 4b^2}$ is smaller than 0.60, we can safely neglect all terms except the first one and write :-

$$\frac{C}{C_0} = 1 - \frac{4}{\pi}.e^{-D\pi^2 t / 4b^2}.\sin\frac{\pi x}{2b} \qquad 1.29$$

Equation 1.29 may be used to calculate the degree of saturation, C / C_0, at any point and at any time. A series of curves may be

drawn relating C / C_0 , the degree of saturation to x / b, the relative depth for a series of values of $t / 100\ b^2$. Fortunately, one need not calculate all these values, because of the existence of such tables [14,24,40,41], from which one may easily find the required figures and construct the curves showing the variations of C / C_0 against $t / 100\ b^2$. However, to attain anything like complete saturation, it takes a very long time, theoretically an infinite time.

Equation 1.28 was derived under the condition when only one face of the sheet was exposed to the solute and a thickness of 2b cm. comes into play. If it is exposed on both sides, this thickness becomes one half and the total amount of the solute inside the membrane at a time t from the start, bears to the full saturation value, a ratio given by equation 1.30.

$$\frac{\int_0^b C.dx}{C_0 b} = 1 - \frac{8}{\pi}\left[e^{-\theta} + \frac{1}{9} e^{-9\theta} + \frac{1}{25} e^{-25\theta} + \ldots\ldots \right] \qquad 1.30$$

where, as before,

$$\theta = \frac{D \pi^2 t}{4 b^2} .$$

Again, this series is rapidly converging when t is large, but it is convenient to use it for quite short times, so that all the necessary terms are included to make the calculations correct upto 3 places of decimals.

These calculations apply equally well to whether the

the penetrant is diffusing in or out and indeed to any sudden changes in the concentration of the external solution. If C_0 be suddenly altered to C_1, the concentration proceeds to change and the value of $\frac{C - C_0}{C_1 - C_0}$ as a function of x and t can be obtained from the curves constructed from the tables [14,24,40,41].

Equations 1.28 and 1.30 are of fundamental importance and have been used to make measurements of D of liquids and organic vapours from sorption data for slabs of high polymers, such as, rubber [42], bakelite[43], cellulose derivatives [44], and leather [45] and the diffusion of dyestuffs into textile fibres [14,29,39,40]. The basic assumption underlying these latter measurements is that the dimensions of the sheet do not change appreciably due to swelling during the course of sorption [17].

Measurement of Diffusion Co-efficients.

An extremely simple, though laborious method for the determination of diffusion co-efficient, based on the principles of equations 1.26 and 1.27, is to allow the solute to diffuse upwards from a layer of the solution at the bottom of a uniform cylindrical vessel into a large one containing the pure solvent. The bulk of the pure solvent is several times that of the initial solution. At the end of the experiment, the mixture is separated with as little disturbance as possible into several equal layers and the concentration in each layer is determined by appropriate physical or chemical means. Detailed references to the various forms of the apparatus used according to this technique and the means to assess the concentration are given in the reviews by Caddy and Williams [9], Harned [47], and Holmes [48]. In all these cases, the origin from which the space co-ordinate is measured, is the base of the containing vessel, provided that there is no overall change of volume of the system.

This technique had been widely used by Oholm [49,50], whose results occupy prominent place in the tables of diffusion co-efficiemts. The method was greatly improved by Cohen and Bruis [51] which yielded results accurate upto 0.3 °/°. Alternately, the boundary may be followed with the help of a microscope for a coloured solution or with an elaborate refractometer [52]. The latter method gives the refractive index - distance or some more complicated

relation from which diffusion co-efficient can be calculated if the relation between the concentration and the refractive index is known.

In some cases, following Wiener [53] and Thovert [54], observation are made of the interference bands produced by light passing through different layers of the diffusion cell or of the deviations of a narrow beam of light falling on the boundary, while in others [46,55], the blurring of an initially sharp boundary between two solutions in contact is observed. A recent developement in optical methods has been reported by Coulson and co-workers [56] in which a monochromatic light from a horizontal slit is focussed after passing through a cell where diffusion is occurring. The pattern , a set of horizontal band contracts towards the optical axis as diffusion proceeds, at a rate from which the diffusion co-efficient can be calculated. However, whichever way the concentration is determined or the boundary followed, in all these cases, the condition of zero volume change is considered to hold or can be assumed to do so to a sufficiently good approximation, and the measurements are with reference to an initial boundary or fringe, on both sides of which the volume remains constant.

Of great experimental simplicity and convenience is the porous plate method, devised by Northrop and Anson [57]. The principle of the method is that two uniform solutions of different concentrations are brought into contact , usually with a plane, horizontal interface in a cell of known dimensions. The diffusion

is allowed to occur and the resulting changes in concentration are observed at intervals. It has the characteristic feature that the two solutions are separated by a porous plate which allows free diffusion, but prevents conventional currents between the two solutions. In each separate solution, however, convection occurs freely and since the denser solution is the uppermost, gravitation is considered to promote mixing adequately to keep each solution homogeneous during loss or gain of solute by diffusion, with the result that the underside of the membrane or plate always remains in contact with practically pure solvent, while likewise, the upperside remains in contact with a solution of virtually original concentration, provided that the diffusion is not too rapid. A concentration gradient, therefore, exists only in the liquid confined in the pores of the plate and this greatly simplifies the mathematical theory of the method. Conditions of the flow follow those of a steady state, which assists the interpretation of the results [58].

The attainment of a steady state is checked by removing and analysing the lower (external) solution at intervals and immediately replacing it with the same volume of the fresh solvent. From the point of view of calculations, it is immaterial to withdraw solution before or after the addition of the solvent, but in order that the plate may be kept immersed in solution throughout, it is preferrable [59] to add the solvent first, mix thoroughly and then withdraw the same volume of the solution. When equal amounts

of the solute are found to pass through the membrane in the same interval, this constant rate of diffusion may be used for the calculation of the diffusion co-efficient. However, owing to the lack of knowledge of the effective dimensions of the porous plate, the method is essentially one of comparison [60] and does not yield absolute value of the diffusion co-efficient. The plate has, therefore, to be calibrated by means of an experiment, with a solute of known diffusion co-efficient, yielding a calibration constant which embodies the unknown dimensions of the plate. An aqueous solution, N/2, of KCl [60] whose diffusion co-efficient at 25 °C is 17.7×10^{-6} or 2N HCl [57], whose diffusion co-efficient does not vary appreciably with concentration are the usual standardising substances employed.

While the porous plate technique was primarily developed for the appropriate studies of biological materials of high molecular weight, it was found by McBain and Liu [10] that it could be made to yield values reproducible within a few tenths of 1 °/° for diffusion co-efficients of substances of smaller particle size, such as sugar or simple electrolytes.

Apart from its experimental simplicity and great convenience, the porous plate method is suitable over a wide range of diffusion co-efficients [59]. It is moreover the only convenient method for use at elevated temperatures [61]. Other additional advantages are :-

1. The rate of diffusion, particularly of dyes in presence of a uniform concentration of a foreigh electrolyte can be measured [59]. In the well-known method of Furth[62] such observations are sometimes vitiated by streaming [63,64].

2. The concentration of the aliquot portions can be measured with leisure after the diffusion experiment has been completed.

The method is characterised not only by its simplicity, but also by the ease with which diffusion co-efficients are calculated. If the amount of the substance which has diffused is so small that the initial concentration may be considered to be unchanged and the constant concentration gradient is simply -C / x, where x is the unknown length of the path of diffusion in the pores of the plate and C is the concentration in the upper (internal) solution. Analysis of the lower (external) solution at different intervals gives dS / dt and hence employing the first form of Fick's law, diffusion co-efficient may be calculated from the relation:

$$\frac{dS}{dt} = - D.A.\frac{C}{x}$$

or

$$D = x.\frac{dS}{dt}.\frac{1}{A}.\frac{1}{C} \qquad 1.31$$

where A is the effective, but unknown area of cross-section of the membrane. The ratio x / A or the "cell constant" [65] for the apparatus is obtained from the calibration data.

Northrop and Anson [57] considered the above simple calculation to be adequate, if the amount of the substance which has diffused through the membrane during an experiment was not more than a few per cent of the total amount present.

The membrane or the diaphragm method is not limited to those diffusion experiments in which the initial concentration changes but little. McBain and Liu [10] replaced the external solution by fresh solvent after the diffusin gradient was set up by a preliminary flow of a few hours and started the experiment proper with the upper solution at an unknown initial concentration C_0. The value of C_0 could be assessed from the volumes of the two compartments and the analysis of both the solution at the end of the experiment. Under such conditions, equation 1.31 assumes the form:-

$$\frac{dS}{dt} = - D \cdot \frac{C_2 - C_1}{x / A} \qquad 1.32$$

where C_2 and C_1 are the concentrations of the internal and the external solutions respectively at the time t.

When the two compartments have the same volume, v, and diffusion is started with pure solvent in the external chamber, equation 1.32 may be integerated and solved for D. D is then given by

$$D = \frac{v.\ x/A}{2t} \cdot \ln \frac{C_0}{C_0 - 2C_2} \qquad 1.33$$

However, if the two volumes are not equal, but v_1 and v_2 , the

corresponding relation is:

$$D = \frac{v_1 \cdot v_2 \cdot x/A}{(v_1 + v_2) \cdot t} \ln \frac{C_0}{C_0 - C_2(1+v_2/v_1)} \qquad 1.34$$

The above equation has been used by Northrop and Anson [57(1)] and Mehl and Schmidt [65] for the calculation of diffusion co-efficients of both ionised and non-ionised solutes, and was considered to be adequate for the purpose irrespective of the characteristics of the solutes. The diffusion co-efficients of non-ionised solutes can, however, be calculated from Stoke's equation

$$D = R.T.B \qquad 1.35$$

where R = the gas constant (in ergs per degree C per mole),

T = the absolute temperature,

and B = the absolute mobility, the velocity of the solution under a force of one dyne per mole.

If the molecules are spherical of radius r, r being larger than the radius of the solvent molecules, D is related to the radius by Stoke-Einstein eqation,

$$D = \frac{RT}{6\pi\eta Nr} \qquad 1.36$$

where N = Avagadro's number,

r = the radius of the diffusing particle,

η = the viscosity of the medium.

Hence from a knowledge of D, the paricle size can be calculated.

The problem however is not so simple for electrolytes, for a number of complicating factors come into play, the most important being the electrical charge on the particles, while the Stoke-Einstein equation is applicable to uncharged particles only. The ionisable groups are dissociated to a certain extent and each ion is surrounded by an atomphere of oppositely charged ions. In the early days of the ionic theory, Nernst[66,67] pointed out that, although the two ions of an electrolyte may have different mobilities, they are prevented by electrostatic forces from becoming appreciably separated during free diffusion. In other words, the diffusion of an electrolyte may be described by a single diffusion co-efficient. At the junction between two unequally concentrated solutions of the same electrolyte there will be a tendency for hthe more mobile ion to get ahead, thereby setting up a potential gradient. This potential gradient will not be established rapidly and will not increase as the diffusion proceeds, since the electrostatic forces prevent any appreciable separation of oppositely charged ions and electro-neutrality must prevail in any tangible portion of the solution. However, the effect of the above potential gradient would be to accelerate the diffusion of the sluggish ion and to retard that of the more mobile. This is particularly interesting in case of free diffusion of dyes, where the inorganic ions pass ahead of the large dye ions and consequently give rise to a higher observed rate of diffusion from a solution into water [59,61,68,69 - 72].

Under such conditions, Nernst's [66] equation for the free diffusion of a uni-uni-valent electrolyte finds its application:

$$D = \frac{RT}{F} \cdot \frac{u.v}{u + v} \qquad 1.37$$

where u = mobility of the cation,

v = " " " anion,

and F = the Faraday, 96,500 coulombs.

When the ions of the electrolyte have a valence higher than one, another form of Nernst's equation, one modified by Noyes (as reported by Haskell [35]) is used. A further modification is to make use of the limiting equivalent conductances of the ions in place of their mobilities u and v. The equation - Nernst - Haskell equation is:

$$D = \frac{RT}{F^2} \cdot 10^{-7} \cdot \frac{\lambda c \cdot \lambda a}{\lambda c + \lambda a} \cdot \left(\frac{1}{z_c} + \frac{1}{z_a} \right) \qquad 1.38$$

where z_c and z_a are the valences of the cations and the anions and λc and λa their respective equivalent conductances. This general equation has been used widely for the determination of D for dyes diffusing into water by various workers [59,61,68 - 72], with suitable regard to the electrical effects.

In spite of the fact that an enormous amount of work has been done in the field of diffusion in liquid systems over the past hundred years [47], the experimental study of diffusion is still in a rudimentary stage and is illustrated by the fact that very

substantial differences exist between the results of different workers for the diffusion co-efficient of such a simple system as KCl - H_2O [8,73] . The numerical difficulties inherent in the compilation of diffusion co-efficient from the rate measurements, the elimination of turbulent flow, the very accurate control of temperature and the analytical accuracy required, are all contributing obstacles to the attainment of perfect agreement.

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Chapter II

Diffusion of Dyes into Cellulose.

Introduction .

The kinetics of diffusion become much more complicated when it proceeds within solids and many factors absent in free diffusion, come into play. While in liquid systems, the rate determining quantities are the gradient of concentration [1,2], size and nature of both the solute and solvent[3,4,5], the situation is not so well-defined when the transfer of matter occurs through solids. The structure of the solid and its compactness [6,10], distribution of various phases in the material [7], compatibility of the dimensions of the pores in the solid with those of the diffusing molecules [8, 9,10,13], presence of polar or non-polar groups [11,27], the affinity of the penetrant for the substrate [12-15,21], and consequently the sorption and solution phenomena [13-17,25,26], make the situation greatly obscure. The boundary conditions remain vague and poorly defined unless the exact nature of the process is known - whether diffusion is accompanied by swelling [18,19] or it proceeds through compound formation [20,22], or utilisation [23,24] of the substance thereby eliminating a part of the penetrant or it is one of simultaneous absortion and solution which tends to accumulate the diffusing substance within the medium, as for example, diffusion of direct dyes into cellulose.

Again, in liquids, the essential feature is that the

homogeneity of the system is preserved throughout the course of diffusion. On the other hand, the flow of matter through solids is frequently composite in nature [28], the various modes of transport being dependent on the micro-heterogeneity of the substrate as is the case when migration depends on the existance of molecular or ionic holes [6] or specific sites as is frequently pictured in the case of the absorption of direct dyes by cellulose [7]. Various phenomena of a physico-chemical nature, such as,

1. the alteration of space variables, when the solid and the penetrant form a solution or a swollen compound due to imbition or absorption [13,14,16,18,25,26,29,30] and hence a treatment of absorption isotherms,
2. the disruption of van der Wall forces between the molecules of the substrate, which involves surmounting energy barriers by the diffusing molecules and therefore acquiring energies of activation [6,26,31] (before transfer can take place), which may differ considerably from those involved in diffusion in homogeneous systems - all present complicating factors. A situation equivalent to a Donnan membrane equilibrium is found in the diffusion of direct dyes into cellulose [26,32 - 38].

From the above general discussion, it follows that a complete picture of the structure of the substrate is essential, to understand the mechanism of diffusion. The crystal structure, the nature of the forces which bind together the molecules of the substrate,

the intera-molecular chain distances, and the presence of capillaries, all contribute towards determining rates of diffusion.

Factors Controlling the Dyeing Process with Direct Dyes.

The kinetics of dyeing of textile fibres have been the subject of extensive study during the past two decades from different angles and though there are still a great many obstacles to overcome, yet the investigations and developements made by numerous workers in the field have placed the subject on a more or less quantitative basis. Discrepancies exist between the experimental data and the theoretical treatment [39,40], which need elaborate explainations, because dyeing is not an instantaneous process. It is heterogeneous in nature, and proceeds with a measurable rate, which is itself dependent on many factors such as concentration of the dye and the added electrolyte [10,13,16,17,25,27,32,34-38,41-45,53], characteristics of the substrate [10,27,35,38,46-53], affinity of the dye for the fibre [35,38] and consequently the rate of absorption and desorption and penetration of the dye into the fibre. The last named factor i.e., the penetration is borne out by the compatibility [54,55,63,66] of the size of the dye molecules with the dimensions of the pores in the mass of the fibre and thus giving an idea of the migration or levelling when dyeing is carried out from a mixture of dyes [44,53,56].

Different Stages of Diffusion of Dyes into Fibres.

When cellulose in the form of fibre or sheet is immersed in a solution of a direct dye, absorption takes place immediately. In the initial stages, the dye is entirely located on the surface of the material and a 'near-equilibrium' between the dye on the surface and that in solution in its immediate vicinity is assumed to take place instantaneously [57,58,59], as compared to the inward transport of the dye. It was early noticed that dyeing is essentially a diffusion process [16] and soon after the surface of the fibre comes into contact with the dye solution, the dye penetrates into the fibre from its surface, at a rate depending on the concentration of the dye and hence more dye should become available to the surface from the bulk of the solution.

During the early stages of the process, the concentration on the surface differs very slightly from the concentration which would have been in equilibrium with the external solution, due to a constant drainage of the dye into the interior of the individual fibres. This difference will become narrower with the elapse of time and eventually vanish when a 'true equilibrium' is established [10,13], theoretically after an infinite time. The attainment of this stage means that no more dye is carried inside the fibres and Neale [13] very truly argued that the diffusion (and hence the diffusion co-efficient) of dyes into the fibres " should indicate the

relative permeability and levelling power of different dyes and their compatibility for mixing in compound shades".

For the sake of convenience, the dyeing process can be split into three distinct steps [60] as follows :-

1. Absorption of the dye on the surface which is regarded as instantaneous,
2. Diffusion of the dye absorbed, into the interiors of the fibre,
3. Diffusion of dye in solution to become availabe at the surface of the fibre.

Out of the two diffusion processes, the diffusion inside the fibre is far slower than the free diffusion because of the mechanical obstructions offered by the net-work of the molecular chains and also because of the physico-chemical attraction between the dye and the fibre which with-holds a certain amount of the dye due to absorption from playing its part actively and has a retarding influence on the speed of diffusion [10,13,23,26,58,60 - 67].

It is this rate determining process, which has direct bearing on the kinetics of dyeing and in the recent years, apart from technological studies, much scientific effort has been expended in this direction to elucidate the problem in order to have a better insight picture of the dyeing processes.

Non-equilibrium Dyeing and the Conc.Gradient inside the Fibre.

The rate of diffusion of a particular direct dye for a given substrate, under a given set of conditions, is dependent upon

the concentration of the dye in the solution [10,13,16,17,25,27,32, 34 - 38,41 - 45]. Since in the early stages, there exists a "near equilibrium" between the concentration of dye on the surface of the fibre and the bulk of the solution (There is a change in concentration of the solution in the immediate vicinity of the fibre surface, but it is assumed that this deficiency is made up with extreme rapidity due to mechanical and thermal agitation of the solution.), the concentration of the absorbed dye decreases towards the centre of the fibre. Schematically, the early distribution of the dye within the fibre as a function of distance is shown in Fig. 5, in which the concentration is high at the surface and decreases towards the centre.

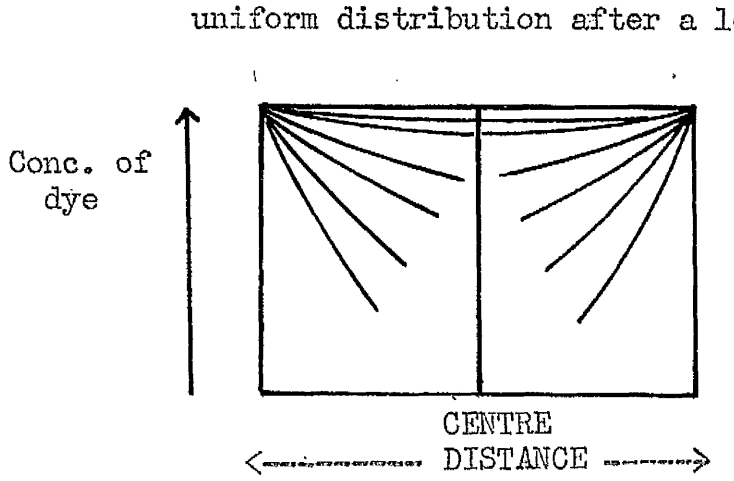


Fig. 5, showing the distribution of dye in the fibre as a function of distance and time.

This simply means that there exists a gradient of concentration at any two points within the fibre, long before it is in true equilibrium with the dye solution, and that the rate of

diffusion can be determined by Fick's law [1,2,10,14,16,26,54] :-

$$dS / dt = - D.A. dC / dx$$

where dS is the amount of the dye transferred across any plane of area A in time dt, dC / dx is the concentration gradient, the concentration being that of the dye within the substrate and not that in the solution. Further, this quantity must be expressed in appropriate units i.e., mass per unit volume of the substrate, the units of mass being the same as those of dS / dt. Then D is the diffusion co-efficient of the dye within the fibre.

When dC / dx = 1 = A, D = dS / dt, so that numerically D is the amount of the dye passing at any point in the fibre across unit area in unit time, when there exists a unit concentration gradient. Its dimensions are area / time, i.e., $L^2 T^{-1}$.

The definition of D and hence its determination, therefore, indicates a very useful relationship between the dye and the fibre and gives information regarding the permeability of the latter to the former.

Cellulose - Requirements for Dyeing.

Cellulosic fibres (See Ott [68,69], Hermans [70], Marsh and Wood [71], Preston [72]) on X-ray examination have shown a certain amount of crystallinity and the general picture at the moment is that cellulose consists of a continuous net-work of chains which are tightly packed in certain places, called the "crystallites" or

"micelles" embeded in a matrix of chemically identical, but non-crystalline material.

From the point of view of dyeing, the most significient aspect of the picture is the compatibility of the distances between the "micelles" and the dimensions of the dye molecules which can penetrate the fibre. It has been shown by McBain and Kistler [9] that dry "Cellophane" is practically impermeable even to compounds with small molecules such as ethyl and amyl alcohols and aniline, but when "Cellophane" is soaked in water, it becomes permeable to these and other solvents. They, therefore, concluded that the "pores" are non-existent in dry "Cellophane". Boulton and coworkers [10] hold the same view and according to them, in water-swollen cellulose, the osmotic forces push the chains apart in the less orderly regions and increase the inter-micellar distances to allow the entry of bigger molecules such as the direct dyes.

Affinity of the Dyes for the Fibre.

From the above general picture, it at once follows that an idea of the numerical magnitude of D will throw light on different aspects, such as probable shape and the dimensions of the diffusing dye molecules and their relation with the existing "holes" in the substrate and the affinity of the dye for cellulose. As a general observation [12], the greater the affinity of the diffusing substance for the medium, the less readily does the interstitial flow occur,

i.e., the increase in the rate of flow due to higher affinity for the medium is more than offset by decrease in intrinsic mobility. Thus a small value of D in direct dyes indicates, apart from the larger molecular size, larger aggregation and a greater affinity for the fibre and suggests the sluggish behaviour of the dye in diffusing through it and once such dyes are fixed, it would be difficult to reverse the process through desorption, which can be regarded as diffusion in the opposite direction, i.e., from the interior of the fibre to its exterior. Such dyes will, therefore, offer great difficulty in migrating and levelling out [15,73,74]. The converse is true for rapidly diffusing dyes which show good migration and better penetration.

Free Diffusion of Direct Dyes.

Diffusion of dyes into cellulose offers a unique picture as compared to that of free diffusion in solution. The direct dyes are strong electrolytes and their dissociation into cations and the dye anions occurs freely when dissolved in pure water. Under such circumstances, if the diffusion is allowed to take place, the more mobile cations (usually Na^+) will proceed ahead of the much larger dye ions and will set up a potential gradient along the direction of the diffusion. However, since the maintenance of electrical neutrality requires no appreciable separation between the two species of ions in any tangible part of the system, the fast moving

Na^+ would drag the dye ion alongwith it, with the result that diffusion is accelerated. In the presence of an excess of a foreign electrolyte, such as NaCl, this potential gradient is reduced to zero, because of the diffusion of Na^+ of the dye in a uniform atmosphere of Na^+ from the electrolyte and the two ions of the dye diffuse together at a much reduced rate [75 - 85]. This pronounced effect of salts on free diffusion of dyes has been attributed to the aggregation of the dye molecules [81-83,86,87].

Negative Charge on Cellulose in Water.

The behaviour of the direct dyes when diffusing through cellulose however becomes different from the above. Cellulose, when immersed in water, acquires a negative charge, which has been estimated by electro-kinetic measurements of the streaming potential or streaming current when the electrolyte is forced through a porous plug of the fibre [25,26,88 - 91]. Its magnitude is quite large (20 mv for cotton in water [89]); though its origin is uncertain[25,26], Alexander [92] associates the charge with the Helmholtz double layer and is the one determined by electro-kinetic measurements. This charge is in no way peculiar to cellulose [92] ; every material, even the most inert, will exihibit it. Its origin, according to Alexander (loc.cit.) lies in the attraction of matter for matter. Thus any powder placed in water, will attract both the hydrogen and the hydro-

hydroxyl ions and at neutrality, when their numbers are equal, will attract more hydroxyl than hydrogen ions, because the former are heavier and therefore the material will obtain a negative charge.

Now the direct dyes anions which carry a negative charge (depending upon the number of $-COO^{1}$ or $-SO_3^{1}$ groups) experience a force of electrical repulsion from the surface of the fibre, when the latter is placed in an aqueous solution of the former. The dye molecules thus have to surmount this electrical barrier before they can be effectively absorbed by the fibre. The magnitude of this charge falls rapidly when pure water is replaced by a solution of an electrolyte and its value in 10^{-3} M NaCl is - 18 mv, but only - 1 mv in a decimolar solution of NaCl [25]. That explains why more dye is transferred to the fibre in presence of an electrolyte. Since the diffusion of a dye inside the fibre is controlled by its concentration in the surface in equilibrium with the external solution, the presence of a salt, therefore, gives an increased rate of diffusion as compared with water alone [10,13,15,16,25,32,35,36,58,65,66,93,94].

However, there is another opposing factor which comes into play during the absorption of dye by cellulose. With an increasing amount of dye on it, cellulose again acquires a negative potential and therefore the approaching dye molecules will experience a force of repulsion due to the previously absorbed molecules [13] and the latter will reduce the rate of diffusion.

Variations in Diffusion Co-efficient with Salt Concentration.

The diffusion co-efficient varies from dye to dye, but for a particular dye, will depend on the concentration of the foreign electrolyte in the solution. Generally speaking, the effect of increasing the concentration of salt is to raise the diffusion co-efficient, pass through a maximum and either fall or remain unaffected with further increase in salt concentration. The nature of variation with salt has been attributed to the aggregation of the dye particles [80,95], to endomosis [96], and as stated above, to the repulsion of diffusing ions by those previously deposited in cellulose [13].

These suggestions are, however, purely qualitative and Crank [26] has treated the subject from a quantitative point of view, where diffusion of a dye into a sheet of cellulose is considered to be a process of activated diffusion with absorption. The activation energy is that required by a dye ion to surmount an electrical potential barrier at the outer surface of the fibre. This electrical barrier is due to the combined surface charge of cellulose[25,26, 88,91] and due to dye ions instantaneously absorbed on the outer surface of cellulose [13].

High Absorption and Retardation of Diffusion of Dyes.

The water-swollen cellulose is frequently pictured as possessing a number of capillaries [9,10] along which the dye ions

diffuse and are simultaneously deposited on the walls of the capillaries [16,26,35,38,61,62,64,65,97,98]. It is reasonable to assume that the concentration of the dye absorbed on the outer surface of cellulose in equilibrium with the external dye solution is the same as the internal surface concentration of the dye, when the final equilibrium state is reached throughout the fibre or the sheet. This assumption has been utilised by Hanson and coworkers [38] and Crank [26] in their consideration of the variations of the "apparent" diffusion co-efficient with the concentration of salt and forms the basis of the existing theories of equilibrium dye absorption. According to this view, the decrease in the value of "apparent" diffusion co-efficient after passing through a maximum may be regarded as a necessary consequence of the increased dye absorption when the concentration of the salt is increased[58]. Higher absorption whether due to the addition of salt, change of dyestuff, or falling temperature, results in reduced diffusion rate. The inverse relation between absorption and diffusion, which breaks down at low salt concentration, is readily understood if the process is regarded as one of diffusion of the dye molecules through inter-micellar water channels and of their absorption on the micellar surface.

It may be remarked here that whether diffusion proceeds unhindered in water along the pores, which are large enough as compared with the dye molecules, or whether it is better to consider diffusion through a viscous water - cellulose solution, the

mathematics remains the same[99], though the physical significance of some parameters involved may differ. The essential postulate is that the dye molecules can be in two states, viz.,

1. Free to diffuse 2. Attached to the cellulose chains.

Certainly if the published data about the pore size are meaningful[8,26,68-72,97,100], the figure of 20 ~ 30 Å quoted for their diameter is hardly in keeping with the free diffusion in water, of a dye molecule measuring 30 x 10 x 3 $Å^3$. (cf. Dimension of Chlorazol Sky Blue FF and Chrysophenine G are 30 x 9 x 3 and 34 x 7 x 3 $Å^3$, respectively[8]).

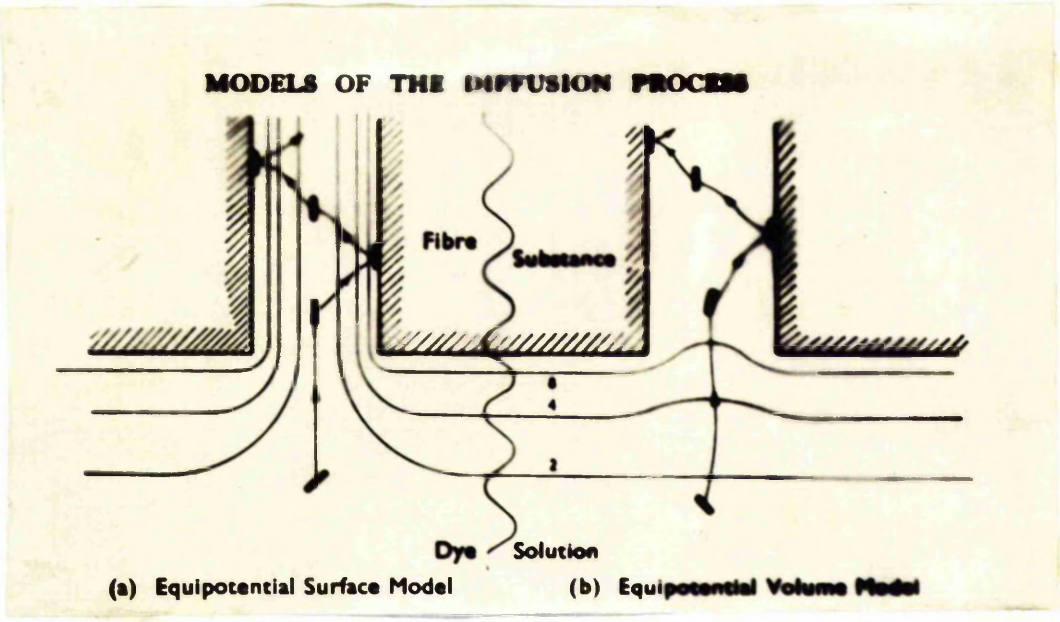
Considerations of the Electrical Forces in the Fibre-Dye solution System.

Diffusion with simultaneous absorption will have the effect of partially blocking the minute capillaries in cellulose, reducing their effective cross-sectional area and thus restrict the diffusion[62,101]. Diffusion on such a model has been treated by Standing and Coworkers[61,102], who have shown that the experimental data are best fitted by assuming that the dye molecules diffuse only in the aqueous solution in the pores and that surface diffusion of the absorbed dye along the walls of the capillaries either does not occur or is negligible in comparison with the aqueous diffusion. Obviously, if the surface diffusion is considered to be predomimant, high absorption of the dye along the capillary walls as a consequence

of increased salt concentration, should be expected to enhance the rate of diffusion, because of the establishment of a higher local concentration gradient on the surface of the fibre during the early stages. This is contrary to the observations that diffusion coefficient only attains a limiting value or passes through a maximum and falls with the increasing concentration of salt.

Two different treatments of diffusion with regard to the electrical effects have been described by Standing and coworkers [61] and Crank [26] respectively. According to the former, the fibre is to be regarded as an equipotential surface model, with potential variations across the diameter of the pore, but the centre of the pore is at the same electrical potential as the external solution, so that every time a dye molecule undergoes absorption on or desorption from the walls of the pores, it has to pass up or down a potential gradient. This is schematically illustrated as below [101], though the model is purely conjectural. Fig 6A.

The potential gradient is the one determined by the combined effects of various ions present in the dye-bath and the surface charge phenomenon of the fibre [25,26,88,91]. Standing and coworkers (loc.cit.) therefore put forward the view that the equilibrium between the absorbed dye and the free dye in the centre of the pore (which is assumed to govern the diffusion) is related to the equilibrium betwwen the entire mass of the fibre and the external



Equipotential Surface Model of Standing et.al.

Equipotential Volume Model of Crank.

Fig. 6 (A),(B), showing a single pore of the fibre and the diffusion of a dye molecule through successive layers of the electrical potential.

solution by the same absorption isotherm and derived the expression

$$D_A = D_0 \cdot \frac{V.C_p}{S} \qquad 2.1$$

where C_p is the concentration of the dye in moles per litre in the aqueous solution inthe pores,

V is the fractional volume of the pores in litres per Kg of the fibre,

S is the amount of the dye per Kg of the fibre and

D_0 is the true diffusion co-efficient of the dye in solution and is supposed to be constant. D_A is the observed "apparent" diffusion co-efficient.

In a bath of constant dye concentration or in which the

concentration can be assumed to remain constant, the concentration of free dye within the pores would not differ from that in the external solution when the equilibrium condition is reached. It is therefore reasonable to replace C_p by C_B , the actual concentration of the dye in solution and the above relationship is modified to

$$D_A = D_0 \frac{C_B}{S} \qquad 2.2$$

Thus in a bath of known, but constant composition, the equilibrium absorption can be determined experimentally and if we know, either D_A or D_0 , we can calculate the other quantity. It should be noted that due regard should be paid to employing consistent units in this expression. The concentration of the dye solution is in moles per litre, while that of the absorbed dye in g . per kg . Then the dimensions of D_A and D_0 are L^2T^{-1} i.e., cm^2/sec.

It is also evident from the above relationship that since the value of the equilibrium absorption appears in the denominator, an increased figure acquired by it at a high salt concentration or low temperature would make the right hand side smaller and hence D_0 being constant, there would be a decrease in the "apparent" diffusion co-efficient D_A .

The most significant assumption underlying the theoretical treatment of Standing and coworkers [61] is that the concentration of the free dye within the pores is equal to that in the external solution. But Crank [26,39,99] points out that this assumption of

equality of the two concentrations is incompatible with the requirements of Böltzman's distribution of ions in an electric field or Donnan equation for membrane equilibria [26,32 - 38]. The ratio of the two concentrations is calculable from either of these two phenomena. Thus dye ions which have sufficient energy to surmount the potential barrier due to the surface charge of cellulose and the previously absorbed ions, can take part in the subsequent diffusion into the substrate and the effective concentration of the dyebath is reduced from C_B to $f.C_B$, where f is the fraction of molecules having sufficient energy to cross the boundary. Since diffusion takes place with absorption i.e., accompanying a concentration C of ions free to diffuse is a concentration S of ions bound to the cellulose, it is assumed that

$$S = R.C \qquad 2.3$$

where R is a constant, independent of dye concentrations C_B and C, but dependent on the salt concentration, the dye attached to the cellulose being assumed not to diffuse. R is determined by the final equilibrium condition, viz.,

$$\begin{aligned} S &= (R + 1)\, C \\ &= (R + 1)\, f.C_B \end{aligned} \qquad 2.4$$

where C is the equilibrium concentration of free dye within the substrate, S is the equilibrium absorption value, associated with C_B. Making allowance for absorption in the diffusion equation

$$\frac{dC}{dt} = D_0 \frac{d^2C}{dx^2},$$

the modified form is

$$\frac{dC}{dt} = D_0 \frac{d^2C}{dx^2} - R \frac{dC}{dt}$$

$$= \frac{D_0}{R + 1} \cdot \frac{d^2C}{dx^2} \qquad 2.5$$

where D_0 is the true diffusion co-efficient in aqueous solution.

In actual practice the value of R is very large and it is immaterial whether it is determined by equation 2.3 or 2.4. Substituting for (R + 1) in equation 2.5 from equation 2.4, we have:-

$$\frac{dC}{dt} = D_0 \frac{f\ C_B}{S} \cdot \frac{d^2C}{dx^2} \qquad 2.6$$

This is the final form of the diffusion equation, representing diffusion with linear absorption when a potential barrier exists.

The "apparent" diffusion co-efficient is given by

$$D_A = D_0 \frac{f.C_B}{S} \qquad 2.7$$

S is expressed in g per 100 g cellulose and C_B in g per litre of the solution. It is necessary to take into consideration the quantity W of water imbibed by 100 g of cellulose, so that the amount of free dye per 100 g of cellulose is $W.C_B$. Thus finally we get the expression

$$D_A = D_0 \cdot f.W.C_B / S \qquad 2.8$$

It should be noted that the quantity f.W.C_B, instead of C_B, the actual dye-bath concentration, makes this treatment different from that of Standing and coworkers [61,102].

Neale [67] has criticised Crank's assumption and pointed out that diffusion is governed by the overall concentration S of the dye within the cellulose sheet, i.e.,

$$\frac{dS}{dt} = D_A \frac{d^2S}{dx^2}$$

where D_A, as before is the apparent diffusion co-efficient. This difference can be easily removed if the two equations

$$\frac{dC}{dt} = D_O \frac{f.C_B}{S} \cdot \frac{d^2C}{dx^2} \qquad 2.6$$

and $$\frac{D_O.f.C_B}{S} = D_A \qquad 2.8$$

are combined together. The result is :-

$$\frac{dC}{dt} = D_A \frac{d^2C}{dx^2} \qquad 2.9$$

Now the assumption made by Crank [26] is

$$S = (R + 1).C \text{ , so that}$$

$$C = S / (R + 1) \qquad 2.10$$

Substituting the value of C from 2.10 in 2.9 ,

$$\frac{dS}{dt} = D_A \frac{d^2S}{dx^2} \qquad 2.11$$

in which the apparent diffusion co-efficient has the same

significance as used by Neale and coworkers [38].

Variations in the Apparent Diff.Coeff. with Salt Concentration.

The increase in the apparent diffusion co-efficient D_A with the increased concentration of salt can be satisfactorily explained on the basis of the foregoing condiderations due to Standing and coworkers, Neale and coworkers and Crank (loc.cit.), but the initial effect of electrolyte in increasing the value of D_A has not been accounted for and a quantitative treatment has not been offered so far. Vickerstaff [101] has given a possible explanation by considering the potential variations through the cross-section of a pore. At low concentrations of the electrolyte, when the potential is large, the Helmholtz double electrical layer [92] of the charge extends over a considerable distance from the surface of the pore. Consequently, the distribution of the potential in the central zone of the pore (where diffusion occurs) and the bulk of the external solution is the same and under these conditions, the diameter of the pore will be very small. On the addition of the electrolyte, the size of the central zone will increase and will approach a limiting value of the full geometrical cross-section of the pore. From this point of view regarding the diffusion of dyes, the bigger pore size would therefore be more compatible with the increased diffusion when the concentration of the electrolyte is raised in the initial stages.

The equipotential surface model of Standing and coworkers [61,102] (Refer to Fig. 6 (A),(B)) has been criticised by Crank [39,99] on the basis of Boltzman's distribution of ions between the solution near the charged surface of the fibre and the bulk of the external solution (cf. p.55). The assumption made is that the fibre constitutes an equipotential region, which implies that an approaching dye molecule will have to surmount an electrical barrier before it can enter a pore and that subsequent absorption and desorption are not affected by these factors. His theory is based on the argument that the concentration of the dye solution within the pores is less than that in the external solution and that the partition between the absorbed and free dye within the cellulose is independent of the dye concentration. The concentration - independence of the partition factor means that in the equation

$$D_A = D_0 \frac{V.C_p}{S} \qquad 2.1$$

the factor C_p / S remains constant, which is however not borne out by experimental evidence and is equally incompatible with the equilibrium theories. In his own statement [99,103], Crank says that the absorption of a direct dye is one of Langmuir type and since only the dye ions are considered to have an affinity for the fibre, the equilibrium absorption is dependent on the concentration of the dye ions in the pores and not on the electrolyte concentration or on the interaction between the diffusing molecules and those already

absorbed or " it may be that the equilibrium theories need revision "[99].

Variations in D_A with the Dye Concentration.

The variations in D_A with the concentration of the dye were early reported by Garvie and Neale [93] during the measurements of rates of diffusion of Sky Blue FF, through a single and multiple membrane and also by determining the apparent diffusion co-efficient by dyeing single pieces of "Cellophane" for different times in solutions containing different amounts of the dyestuff. The results of all these experiments and those by Boulton and Morton [46], Garvie, Griffith and Neale [31] and Hanson and Neale [36], all confirm substantial variations in the observed diffusion co-efficient with concentration of direct dyes on "Cellophane" substrate, the latter group of workers having made their observations by measuring the overall absorption of the dye on the film or fibre as a function of time. On the basis of their results, Garvie and Neale (loc.cit.) arrived at the conclusion that the measured diffusion co-efficient D_C is directly proportional to the square root of the dye concentration in the substrate, i.e.,

$$D_C = D_O \cdot C^{0.5} \qquad 2.12$$

where D_O is a constant, the true diffusion co-efficient. Later on, a refined analysis of the same data , by Crank [39] suggested the diffusion co-efficient to be more or less directly proportional to

the concentration, i.e.,

$$D_C = 4.8 \ (1 + 0.24 \ C) \qquad 2.13$$

This expression gives a reasonably good fit in the range of $0 \leqslant C \leqslant 20.0$, C being expressed in mgm per c.c in the original paper of Garvie and Neale.

Garvie and Neale used the expression

$$dS / dt = - D_C . \ dC / dx \qquad 2.14$$

to calculate their results from the experimental data, where dS/dt is the amount of the dye which has passed across the plane at x, dC/dx is the concentration gradient, determined from the analysis of absorption - distance curves (in case of the " multiple"membrane) by drawing tangents at the curved portions. It has been pointed out by these workers that for each value of time t they used, D_C showed a steady increase with rising concentration. In the regions of low concentration, the values of the concentration gradient were regarded rather inaccurate and so were the corresponding values of the rate of diffusion, dS/dt, when t was the highest, since the gradients of the curves of S against t became very small. They therefore suggested that the diffusion of a dye in "Cellophane" might be represented better by an expression of the type :-

$$\frac{dS}{dt} = - A . \frac{dC}{dx} F(C) \qquad 2.15$$

where A is a constant and F(C) a function of the concentration.

The observed diffusion co-efficient of Chlorazol Sky Blue FF through a single piece of "Cellophane" was calculated from the equation

$$D_C = \frac{1}{A} \cdot \frac{dS}{dt} \cdot \frac{x}{\Delta C} \qquad 2.16$$

where A = the area of the membrane,

x = its thickness,

ΔC = the mean concentration difference,

and D_C = the observed diffusion co-efficient. dS / dt represents the amount of the dye which has passed to the other side of the membrane, during an interval of dt.

Average Diffusion Co-efficient in a Range of Concentration.

Since in the determination of the rate of absorption, concentration of the dye at any point in the substrate can vary from zero to the equilibrium value of the dye on it, Standing and coworkers [61,102] pointed out that the apparent diffusion co-efficient D_A so determined must be a mean of the values, which the 'real' diffusion coefficient would take in this range of the concentration. Thus assuming the dependence of the diffusion co-efficient on the concentration C, the flux dS/dt and the equilibrium absorption value E of the dye on the fibre, they showed that

$$D_C = \left[\frac{dS / dt}{dC / dx} \right]_C \qquad 2.17$$

Further, it was suggested that D_C calculated from equation 2.17, may be regarded as approximately equal to the integral diffusion co-efficient $\bar{D}$, given by the relation :

$$\bar{D} = \frac{1}{E} \int_0^E D_C \, dC \qquad 2.18$$

More recently, the apparent diffusion co-efficient has been shown to differ from the suggested integerated value by about 20 °/° by Crank and Henry [104], who have examined theoretically a number of diffusion co-efficients, varying in different ways with the concentration of the diffusing substance. In all the cases they considered, they found that when the diffusion co-efficient varies uniformly with increasing concentration, absorption is quicker than desorption, but when the diffusion co-efficient decreases with increasing concentration, the reverse is true. In the case, when the diffusion co-efficient first increases, passes through a maximum value and finally decreases as the concentration increases, the absorption - and desorption - time curves may cross each other. They have shown that the agreement between the integerated value of D_C and the observed value of $\bar{D}$ is better (within 5 °/°), when the apparent diffusion co-efficient D_C is taken as the mean of the values of $\bar{D}$, estimated from absorption and desorption data. A series of values of $\bar{D}$ can be determined from absorption-time curves

for several values of the surface concentration C_0 and by assuming as a first approximation that

$$\bar{D} = \frac{1}{C_0} \int_0^{C_0} D_C \, dC \qquad 2.19$$

a graph showing the integral as a function of C_0 can be plotted. Further differentiation of this graph gives a first approximation to the diffusion co-efficient and by repeating the same process, the error involved can be estimated. A similar method of successive approximation has been proposed by Fujita and Kishimoto [105], Fujita [106] and Prager [107]. However, the practical difficulties for the determination of diffusion co-efficient from desorption make the use of these methods impracticable.

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Chapter III

Experimental Methods for the Determination of Diffusion Co-efficients of Dyes in Cellulose.

The distribution of a dye between the fibre and the dye-bath is of fundamental importance and considering that dyeing is a heterogeneous process, the attainment of a true equilibrium need not be over-emphasised when measurements pertaining to equilibrium conditions are made. In the case of non-equilibrium conditions, the interpretation and application of the experimental data becomes doubtful and consequently of little value towards the understanding of the dyeing behaviour.

Steady State of Flow.

As has been outlined in Chapter I (Pages 9 - 13), there are two distinct types of flow of matter in diffusion processes. They are :-

(a) Diffusion in a steady state,

(b) Diffusion in a non-steady state.

In the following pages, methods available for the determination of diffusion co-efficients of the dyes, when diffusing in the steady state, will be described first and those for the non-steady state will be discussed at a later stage.

Theoretical Background of the Steady State Methods.

The diffusion equation

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \qquad 3.1$$

takes a particularly simple form in this case and since there is no accumulation of matter at any point in the medium,

$$\frac{dC}{dt} = 0 = D \frac{d^2C}{dx^2} \qquad 3.2$$

Considering the diffusion to take place through a plate of thickness l , under the following boundary conditions,

$$\begin{aligned} C &= C_1 \text{ at } x = 0 \text{ for all } t \\ C &= C_2 \text{ at } x = l \text{ for all } t \end{aligned} \qquad 3.3$$

Barrer [1] has given the solution of the diffusion equation 3.1 in the form

$$C = Ax + B \qquad 3.4$$

This equation may further be elucidated by putting $x = 0$ and $x = l$, and eliminating the constants A and B. Thus when $x = 0$ and $x = l$, equation 3.4 becomes respectively :

$$C_1 = B \qquad 3.4a$$

and

$$C_2 = Al + B \qquad 3.4b$$

From these two equations, 3.4a and 3.4b, we have,

$$C_2 = Al + C_1$$

or

$$A = C_2 - C_1 / l \qquad 3.4c$$

Substituting the values of A and B in equation 3.4, we have :

$$C = \frac{C_2 - C_1}{l} \cdot x + C_1$$

or

$$\frac{C - C_1}{C_2 - C_1} = \frac{x}{l} \qquad 3.5$$

where C denotes the steady state concentration of the diffusing substance at a point, distant x from the ingoing boundary.

The flow through unit area of the plate is given by

$$V \cdot \frac{dC_d}{dt} = -D \left(\frac{dC}{dx} \right)_{x = l}$$

$$= D \frac{C_1 - C_2}{l} \qquad 3.6$$

where C_d represents the concentration of the dye which has diffused through the plate into a volume V in time dt. The condition $C = C_2$ at $x = l$ for all t naturally makes it necessary that $C_d \ll C_2$. Then the total amount of the dye which has diffused in time t is

$$V.C_d = D \frac{C_1 - C_2}{l}.t \qquad 3.7$$

Equation 3.7 thus offers a very convenient method of determining D by measuring the amount diffused in a given time through the membrane. All the other quantities can be found experimentally. This equation assumes a still simpler form if the concentration of the dye at the outgoing face is very small as compared to the one at the ingoing face, which may be neglected. This assumption still

finds weight, when the amount diffusing is within a few per cent of the original concentration C_1. Under these conditions, we have

$$V.C_d = D.\frac{C_1}{l}.t \qquad 3.7a$$

Diffusion according to the above treatment is assumed to proceed "unhindered" through the net-work of the substrate and no consideration is given to any interaction between the diffusing substance and the medium.

Garvie and Neale's Technique.

Garvie and Neale [2] have used this technique in their investigations of the diffusion co-efficient of Chlorazol Sky Blue FF through "Cellophane", by interposing a film of the latter between the dye solution and the blank solution. The establishment of a steady state in the membrane was confirmed by removing and analysing suitable portions from the external solution till equal amounts of the dyestuff were passing through the membrane in equal intervals of time. The rate at which the dye is transferred from the internal to the external solution can be conveniently determined, provided that the conditions of the experiment are so arranged that no appreciable change takes place in the concentration of the dye on either side of the membrane.

However, since the diffusion of direct dyes into cellulose occurs with simultaneous absorption, the concentration of the dye

within the membrane is bound to differ from that on the ingoing face. Equation 3.7 does not suggest the variation in concentration and assumes that when the steady state conditions are reached, the concentration within the film is that of the more concentrated solution. This view is certainly upheld when diffusion of a non-substantive dye takes place, which has no or very little affinity for the substrate.

The effect of absorption during the course of diffusion is to accumulate the dye within the membrane before the establishment of a steady state, in which case, as much dye is being transferred across a fixed plane as it receives and conditions approach approximately those of true equilibrium between the dye within and on the membrane, and the solution. It is thus evident that the equilibrium absorption value of the dye under these conditions governs the diffusion and further, this quantity is to be expressed as mass per unit volume of the membrane. Garvie and Neale (loc.cit.) employed ΔC, the mean concentration difference on the two sides of the film in their single-membrane experiments, this value being determined separately from equilibrium absorption isotherms.

The Time Lag Method.

The separate determination of the solubility factor or the equilibrium absorption value may be avoided by following the technique originally employed by Daynes[3] and later developed by Barrer [4,5]

during the course of their investigations on the permeation, solubility and diffusion co-efficients of vapours and liquids through membranes of organic materials. This technique , hitherto, has not been applied to the diffusion of dyes and will be discussed in detail in Chapter IV under "Experimental".

The essentiad outline of this method is to observe both the non-steady and steady states of flow of the dye through a membrane. The amount of the dye diffusing is plotted against time. According to the original workers,(loc.cit) in the initial stages, the plot takes the form of a curve and changes into a straight line at a point B (Fig.7) where the non-steady state of flow becomes that of the steady state.

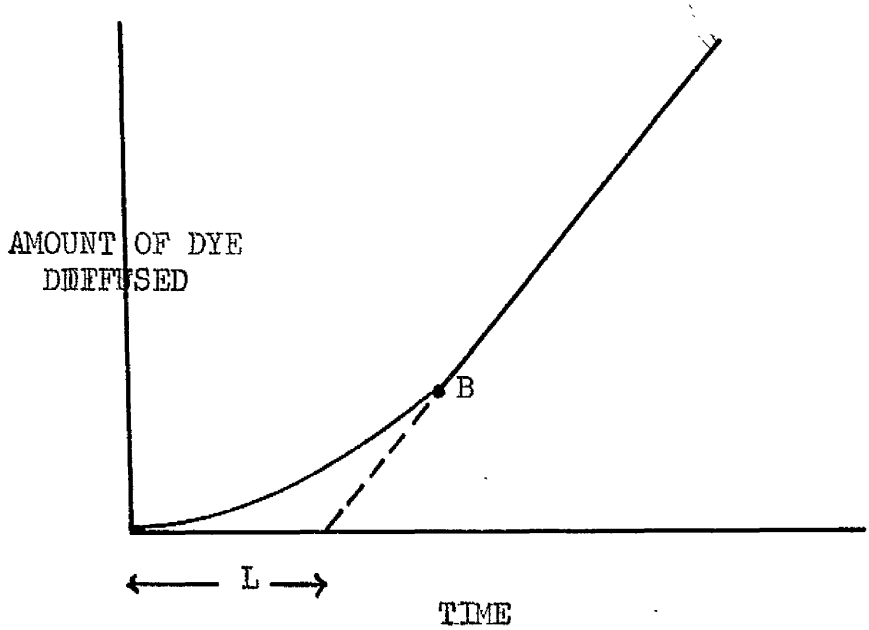

Fig.7

When the straight line passing through the transition point B is

extrapolated to the time-axis, it yields an intercept, conveniently called the time-lag, L, which means that a certain time interval passes before the steady state is reached, when the film is brought into contact with the two solutions. This intercept on the t-axis can be readily determined, provided that the diffusion is not rapid and the concentration of the dye is fixed before hand by preliminary experiments. The time-lag, L is related to the diffusion co-efficient D by the following expression:

$$D = \frac{l^2}{6L} \qquad 3.8$$

where l = the thickness of the membrane.

Diffusion in the Non-steady State.

From the Overall Rate of Absorption.

It is now an established fact that in many systems, diffusion processes do not obey Fick's law; particularly, in systems where one of the components is a high polymer, the deviations from the classical law are considerable [10]. The deviation which arises frequently is the one in which the diffusion co-efficient varies with the concentration of the diffusing substance.

The essential feature of a flow in a non-steady state is the tendency of the penetrant to accumulate within the medium. The rate of accumulation of a dye in an absorbing medium can be calculated from Fick's first law of diffusion. Consider the diffusion of a dye through a fibre (Fig. 8) and imagine two parallel planes 1 and 2 within the bulk of the fibre, separated from each

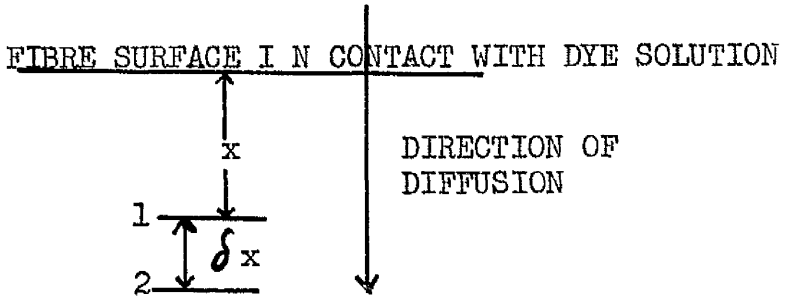

Fig.8

other by a very small distance δx and let x be the distance of

plane 1 from the fibre surface, which is exposed to the dye solution at a concentration C.

$$\therefore \text{ the concentration gradient at plane 1} = \frac{dC}{dt}$$

If the area of each of the two planes 1 and 2 is A, then the flux of the dye across plane 1 is

$$\frac{dS_1}{dt} = - D.A.\frac{dC}{dx} \qquad 3.9$$

Since accumulation of matter takes place within the volume bounded by planes 1 and 2, and the distance δx, the concentration gradient at plane 2 is C + dC/dx.δ x and hence the flux across it is given by

$$\frac{dS_2}{dt} = - D.A.\frac{d}{dx}\left(C + \frac{dC}{dx}.\delta x \right) \qquad 3.10$$

$\therefore$ the rate of accumulation within the volume A.δx is (equation 3.9 minus equation 3.10)

$$= D.A.\frac{d}{dx}\left(\frac{dC}{dx}.\delta x \right) \qquad 3.11$$

and in unit volume

$$= D.\frac{d}{dx}\left(\frac{dC}{dx} \right)$$

$$= D\frac{d^2C}{dx^2} \qquad 3.12$$

But this quantity is given by dC / dt.

$$\therefore \frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad 3.13$$

When the diffusion co-efficient varies with the concentration of the dye, the general form of equation 3.13 is

$$\frac{dC}{dt} = \frac{d}{dx}\left(D \frac{dC}{dx} \right) \qquad 3.14$$

The measurement of a variable diffusion co-efficient is not an easy matter, firstly, because of considerable experimental difficulties and secondly, because the formal mathematical solution of the diffusion equation 3.13 for a non-steady state applies to a constant diffusion co-efficient. No exact solution of equation 3.14 has been found for any boundary conditions [6], although approximate solutions have been derived [7]. Variants of a graphical method have been evolved for determining D as a function of C from the above equations [7,8,9].

The two kinds of methods which have been mainly used during the non-steady state, are designed to avoid the necessity of solving the diffusion equation in the subsequent evaluation of the diffusion co-efficient. Since it is obvious that the total amount of dye on the fibre is a factor controlled by diffusion, there must be a relationship between the diffusion co-efficient and the amount of the dye entering the fibre, in turn itself depending upon the time and the space variable. Two methods of approach to this problem in a non-steady state are :-

(i) Concentration - distance Curves.

(ii) Concentration - time Curves.

(i) Concentration - distance Curves.

This technique was followed by Garvie and Neale [2] for the determination of diffusion co-efficient for Chlorazol Sky Blue FF in wad of 14 "Cellophane" sheets, by analysing a number of concentration - distance curves for various values of the time variable. Suppose, for example, a thick slab of cellulose is exposed to a dye solution on one side for a certain period of time. The concentration of the dye within the slab will fall as shown in Fig. 9.

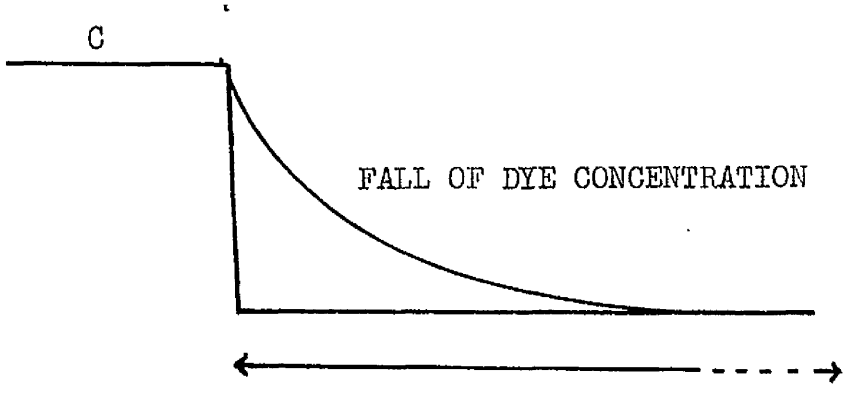

Fig. 9.

If after the conclusion of the experiment, the slab is chopped into uniform sections, it is possible to study the variations of the concentration gradient with the distance, the time being kept constant.

In the "multiple membrane" experiment of Garvie and Neale [2] 14 sheets of "Cellophane" were rolled out together to remove the crinkles and clamped into the diffusion cell. Pre-heated dye solution was brought into contact with the membrane on both sides, so

that diffusion of dye proceeded from both sides towards the centre of the wad. The experiment was stopped after a definite time and the "multiple membrane" separated into individual pieces. The amount of dye on each sheet was estimated for a complete record of the changes of distribution of dye across the membrane and from this record, instantaneous values of the dye concentration at any point within the membrane could be deduced by a graphical method shown in Fig. 10.

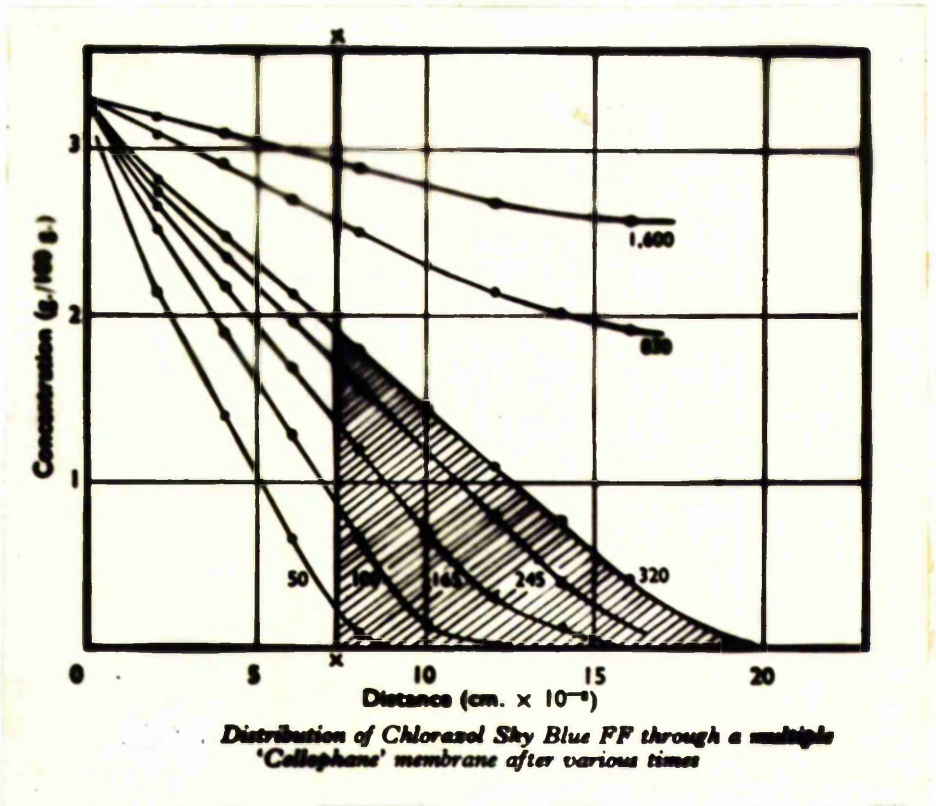

Fig.10. Distribution of dye in the "multiplemembrane" after various times.

Values of the concentration gradient in mg of dye per 100 mg of cellulose per cm were obtained directly from the slopes

of the curves at various times.

To measure S, the amount of the dye which has passed across any plane (represented by a value of x) in a given time, the area bounded by the curve, x-axis and the vertical line representing this value of x was estimated for each value of t. These values of S were again plotted against time t and gradients read off from the tangents against t at all experimental values of t and each value of x. By this procedure, both dC/dx and dS/dt were determined and hence D calculated from the relation

$$\frac{dS}{dt} = - D.A. \frac{dC}{dx}$$

This method gives very good information about the distribution of the dye within cellulose, but is very laborious and the accuracy involved is low because of the double graphical differentiation of the experimental data.

Montano [11] has shown for the inter-diffusion of two metals, provided that each metal is effectively semi-infinite in extent, that the diffusion co-efficient - concentration relation can be obtained by analysis of a single concentration - distance curve at a fixed time. This mathematical analysis has recently been applied to concentration - distance curves by an inferometric technique in a study of the diffusion of solvents and swellers into cellulose acetate [12]. The mathematical analysis involved in these methods is simple, but the measurements of the concentration - distance - time

data usually demand a refined micro-analytical technique and for low diffusion co-efficients, the time needed to carry out a number of successive experiments of this nature becomes prohibitively long.

(ii) Concentration - time Curves.

The equation which governs diffusion in this case is the same as before, i.e.,

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2}$$

where D is assumed to have a constant value. The technique is extremely simple. It is based on the principle of determining the total amount of the dye which has entered into the fibre as a function of time. Solving and integerating this equation over all distances in the substrate and for all values of time from t = 0 to t = t, the end of the experiment, gives the total amount of dye absorbed in a specified time.

Hill [13] provided the solution of the diffusion equation under the above boundary conditions and applied it to the diffusion of oxygen through muscular tissue. The solution for a slab of thickness 2b cm has been given earlier on page 21 and is based on the assumption that D does not show any variations with concentration and that concentration of diffusing substance remains constant throughout the experiment. A near approach to an "infinite dyebath"

is achieved by dyeing small pieces of the sheet from a large volume of the solution, so that there is no appreciable change in the concentration. Another important assumption made is that the entire diffusion is confined in a direction perpendicular to the plane of the sheet and that no diffusion takes place through the edges of film or if any does occur, that it is negligbly small compared with the main diffusion. Further, the sheet is regarded as of infinite thickness, so long as the concentration of the dye at its centre is not appreciable.

The implication of this solution, both when the sheet is exposed on one side to the solute or on both sides, have been discussed in Chapter I (Refer to equations 1.28,1.29 and 1.30 on pages 21 and 22). It has been shown that when the quantity $e^{-D\pi^2 t/4b^2}$, where 2b is the thickness of the sheet and t is time, is greater than 0.60, the series can well be approximated to include only the first term in e. Moreover, when Q_t / Q_∞ is greater than 0.40, the series need not be expanded beyond the first term in e and in that case, plot of $\ln(1-Q_t/Q_\infty)$ against t would yield a linear relationship. Further, when Q_t / Q_∞ is less than 0.60, the full equation can well be approximated to [14]

$$\frac{Q_t}{Q_\infty} = \sqrt{\frac{16\ D\ t}{\pi 4b^2}} \qquad 3.15$$

How to Use These Equations.

Equations 1.28 and 1.30 incluse 3 variables and at first sight it would appear rather difficult to evaluate D from the experimental data. However, the task is much simplified if theoretical curves are constructed. Thus assigning any arbitary value to the quantity $D\pi^2t / 4b^2$, the corresponding value of Q_t / Q_∞ can readily be calculated and a curve can be plotted, showing variations in Q_t / Q_∞ against the assumed values of $D\pi^2t / 4b^2$.

The experimental technique is very simple. A small piece of the sheet of known weight (or dimensions and density) is dyed to an equilibrium condition from a large dye-bath and the amount of the dye absorbed by the sheet estimated in the usual way. The experiment is repeated for a definite length of time t, taking due care that the results are reproducible. The quantity Q_t / Q_∞ is thus known and from the curves, the corresponding value of $D\pi^2t/4b^2$ can be read off. A series of values of $D\pi^2t/4b^2$ are obtained for different ratios of Q_t to Q_∞.

In general, these values of $D\pi^2t/4b^2$ will not be exactly equal, particularly as Q_t approaches Q_∞, small change in its value would correspond to a relatively large change in t, so that higher values of Q_t may lead to uncertain results. In deciding what values to give to the latter, more emphasis has been given to shotter times [15], i.e., those for which Q_t / Q_∞ is less than 0.75. Thus having decided the best representative value for $D\pi^2t/4b^2$, the

diffusion co-efficient is calculated from a knowledge of the thickness of the membrane and the time t for which it was dyed.

Neale and Sringfellow [15] applied these equationsto the calculation of diffusion co-efficient of direct dyes in cellulose. Their observations are:-

1. The shape of the observed absorption - time curves is in close agreement with the theoretical curves.
2. When cellulose sheets of various thicknesses are dyed, the time required for the absorption to reach any given fraction of its equilibrium value is inversely proportional to the square of the thickness [15,16].
3. The distribution of the dyestuff across a sheet dyed for a long time is approximately uniform [15].

Determination of D in Cylindrical Fibres.

The above work was limited to the materials which are obtainable in sheet form. But most of the textile materials are in the fibrous form, approximately more or less of a cylindrical shape.

The equation derived by Hill [13] for an infinite cylinder of radius r, under the conditions similar to those of the slab, is:

$$\frac{Q_t}{Q_\infty} = 1 - 0.692 \left(e^{5.785\, D.t / r^2} + 0.190\, e^{-30.5\, D.t / r^2} + 0.0775\, e^{-74.9\, D.t / r^2} + \ldots \right) \qquad 3.16$$

Since this series is not a rapidly converging one, the number of terms involved is comparatively large.

The calculation of D from equations 1.28, 1.30 and 3.16 has been much simplified, because the theoretical values for different quantities involved have been published for the most interesting cases. From these tables [13,15,17,18,19], it is easy to draw graphs showing the variations of Q_t/Q_∞ against $D\pi^2t/4b^2$ or $D.t/r^2$.

Although, these equations have become very convenient to handle, their use is limited to materials which have regular, geometrical dimensions. However, in the case of fibrous materials, the variations in the cross-section of individual fibres restrict the application of equation 3.16 and the results are therefore only approximate. In the case of man-made fibres, where various factors can be controlled and the cross-section is near-cylindrical, the experimental results fit satisfactorily with those derived from the theoretical treatment [20], such as dyeing of nylon with dispersed dyes from large dye-baths. Since $D.t/r^2$ can be found from the graphs of Hill's equation, dividing this by t, gives D/r^2. Since the average radius of this fibre is constant, this figure will be proportional to the diffusion co-efficient and hence D/r^2 should remain constant. The experimental values for D/r^2 and those calculated from Hill's equation, lie very close to each other.

Similar observations were made by Boulton [21,22,23], while determining the diffusion co-efficient of Chlorazol Sky Blue FF in

a specially regenerated viscose cylinder and found the value of D to vary at 90 °C from 1.1 to 4.0 x 10^{-10} cm^2 per sec from a bath containing 0.005 g. dye per 100 cc and according to the concentration of the added electrolyte. Boulton [24] has also quoted two values of D for Chlorazol Sky Blue FF in viscose yarn and sheet.

Viscose rayon yarn at 90 °C (according to salt conc.)

D = 1.4 to 4.0 x 10^{-10} $cm^2 sec^{-1}$ (Boulton [24])

Viscose sheet at 101 °C (according to salt conc.)

D = 1.3 to 2.5 x 10^{-9} cm^2 sec^{-1}. (Neale [24])

Application of Hill's Equation to Irregular Fibres.

The application of Hill's equation for cylinders (cf. 3.16) has been extended to animal fibres by Speakman and Smith[25], where there is a great possibility of variations in the cross-section of the individual hair. In their technique of dyeing wool, the colorimetric readings of the dye solution were taken at intervals during the process of dyeing, so that during the passage of time, the concentration of the dye-bath fell and that on the fibre increased. On plotting these readings against $\sqrt{t}$, a linear relationship was obtained.

According to Hill [13], when a semi-infinite solid is brought into contact with a large volume of the solution of the diffusible substance at a concentration C_0, the total amount which diffuses

across unit area of the boundary in time t, is given by

$$C_t = 2C_0 \sqrt{D.t/\pi} \qquad 3.17$$

Since this view is equally applicable to dyeing, it is obvious that under the conditions required by this equation, the amount of the dye which has diffused from a bath of constant composition, is directly proportional to the square root of the time for which the dyeing has been carried out and a straight line should result when C_t is plotted against $\sqrt{t}$, whose slope is proportional to the diffusion co-efficient D.

Though this technique seems very simple, yet it has not been widely employed. One essential requirement of this equation is that the concentration should not be too high, which makes it easy to follow C_t with time. In a concentrated bath, C_t will approach the equilibrium value in a much shorter time and deviation from the linear plot are bound to occur.

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Chapter IV

Present Work

Theoretical.

It was as early as 1879 that Wroblewski [1] observed that the movement of a gas or vapour through a material follows Fick's linear diffusion law, i.e., the net rate of flow of the gas in a given direction varies as the gradient of the concentration of the gas in that direction. He, therefore, expressed the permeability of a rubber membrane to a gas or vapour by the simple formula:

$$Q = \frac{D.\alpha.(p_1 - p_2)}{l} \qquad 4.1$$

where Q = the amount passing through the membrane per sec.,

α = the absorption co-efficient (solubility) of the gas,

l = the thickness of the film,

and p_1 and p_2 are the partial pressures of the permeating gas on the two faces of the membrane, $p_1 > p_2$; either being unity, when the gas or the vapour is at normal pressure. D is the diffusion co-efficient of the gas in the material of the membrane.

It might be expected that each set of conditions would hold over an extreme ranges of very thick and very thin films respectively and that there should be an intermediate range of thickness where a formula, such as,

$$Q = \frac{p_1 - p_2}{R + 1/D\alpha} = \frac{D.\alpha\ (\ p_1 - p_2\ )}{R.D.\alpha + 1} \qquad 4.2$$

would hold. Here R may or may not be a constant for different values of l. However, if it were a constant, the quantity RDα might be called the "equivalent extra thickness" of the film.

Another observation of fundamental importance made by Wroblewski (loc.cit.) was that when one side of the membrane is exposed to a gas and the other to air, the concentration of the gas in the membrane at a very short distance from the gas surface is the same as if whole of the membrane was immersed in it, and that at a very short distance from the air surface, the concentration of the gas is negligble.

From the results of absorption experiments within membranes and fabrics by Wroblewski [1], Draper and Mitchelle [3], Barr and Shakespeare [5], it has been concluded [2] that these results are consistent with the following assumptions:-

1. that Fick's law holds inside the material,
2. that absorption of the gas is proportional to the partial pressure, independently of the presence of any other gas,
3. that there is no appreciable resistance at the surface to the passage of the gas, and finally,
4. that different gases present, do not appreciably impede one another in passing through rubber membranes.

If one of these conditions did not hold, the others would have to be adjusted in some complicated manner to account for the experimental results.

If these conditions do hold, we can speak of a definite concentration of the gas at a given point in the membrane and the problem of permeation in the film becomes calculable according to the same laws as those governing the diffusion of gases through one another.

It is possible to arrange the air-permeability of organic membranes in a permeability spectrum [6], covering a 10^{12}-fold range. In this spectrum, rubbers, resins, lacquers, and paints form the least permeable group and papers, leathers, and finally textile fabrics occur at the high permeability end.

The assumptions outlined above concerning the passage of gases through membranes, suggested the desirability of finding out the time taken to set up steady state conditions and to use it in differentiating the parts played by diffusion and by absorption during the process taken as a whole.

Daynes [2] calculated the time required to set up a sready state of diffusion of a gas through a membrane and on the basis of the evidence given above (cf. the assumptions), treated the problem in the same way as that of diffusion through a similar space, filled with the gas itself.

We start from the differential equation of diffusion

$$Q = - D. \frac{dC}{dx} \qquad 4.3$$

where Q = the flux of the gas in the x-direction, in cc/sec.,

D = the diffusion co-efficient of the gas in the material of the film,

C = the concentration of the gas at the point x, in cc of the gas at N.T.P. per cc of the material.

Now the solubility of a gas is given by Henry's law, i.e.,

$$C = \alpha . p \qquad 4.4$$

where α is the absorption co-efficient of the gas in the film, viz., the saturation value of C for the gas at normal pressure, and p is the partial pressure of the gas.

From the permeability experiments alone, it is not possible to gain any idea of the separate values of D and α. For example, in the case of a sheet of uniform thickness l, the volume of the gas passing through it per second in the steady state is given by:-

$$Q = D.\alpha.p / l \qquad 4.5$$

Thus measurements of the permeability only determine the product $D.\alpha$ and the estimation of the time taken to set up a steady state might give some information concerning the absolute values of D and α.

Calculation of the Time Necessary to Attain a Steady State.

Consider a film of uniform thickness l, initially free from the gas and both the faces being exposed to air. At a given time, one face is brought into contact with the gas. It is required to

find out the rate at which the gas effuses from the other face at any given time.

The boundary conditions for this case are :

$$C = C_1 \text{ for } x = 0 \text{ for all } t$$

$$C = C_2 \text{ for } x = l \text{ for all } t \qquad 4.6$$

$$C = f(x) \text{ at } t = 0 \text{ for } 0<x<l$$

The general solution of the diffusion equation for such conditions is given [7] as follows:

$$C = C_1 + (C_2 - C_1) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{n=\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{l} \exp$$

$$\left[- \frac{D n^2 \pi^2 t}{l^2} \right] + \frac{2}{l} \sum_{n=1}^{n=\infty} \sin \frac{n\pi x}{l} \exp \left[- \frac{D n^2 \pi^2 t}{l^2} \right] .$$

$$\int_0^l f(x') . \sin \frac{n \pi x'}{l} . dx' \qquad 4.7$$

In this particular case,

$$f(x') = 0 , \; C_1 = 0 \text{ and } C_2 = \alpha . p \qquad 4.8$$

where α is the absorption co-efficient for the gas and p is the partial pressure of the gas.

Under these conditions, we therefore have,

$$C = \alpha.p.\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty} \alpha.p.\frac{(-1)^n}{n}.\sin\frac{n\pi x}{l}\exp\left[-\frac{D\,n^2\pi^2 t}{l^2}\right] \qquad 4.9$$

Hence from equation 4.9, we have,

$$\frac{dC}{dx} = \frac{\alpha.p}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty}\alpha.p.\frac{(-1)^n}{n}.\frac{n\pi}{l}.\cos\frac{n\pi x}{l}.\exp\left[-\frac{D\,n^2\pi^2 t}{l^2}\right] \qquad 4.10$$

At the face x = 0,

$$\underset{x\to 0}{Lt}\left(\frac{dC}{dx}\right) = \alpha.p/l + \frac{2}{\pi}\sum_{n=1}^{n=\infty}\alpha.p.\frac{(-1)^n}{n}.\frac{n\pi}{l}.\exp\left[-\frac{D\,n^2\pi^2 t}{l^2}\right] \qquad 4.11$$

The volume of the gas emitted per second from this face

$$= D\ \underset{x\to 0}{Lt}\left(\frac{dC}{dx}\right)$$

$$= \frac{D.\alpha.p}{l}\left\{1 + 2\sum_{n=1}^{n=\infty}(-1)^n.\exp\left[-\frac{D\,n^2\pi^2 t}{l^2}\right]\right\} \qquad 4.12$$

If the gas from a given area of the film be collected into a space such that,

$$\frac{\text{the volume of the space}}{\text{area of the film}} = V \text{ cm}, \qquad 4.13$$

i.e., the "effective depth" of the space is V cm. If there is no leakage from this space and if initially it does not contain any gas, the concentration Z of the gas in it will begin to increase steadily and we shall have,

$$\frac{V.dZ}{dt} = \frac{D.\alpha.p}{l}\left\{1 + 2\sum_{n=1}^{n=\infty}(-1)^n . \exp\left[-\frac{D\,n^2\,\pi^2 t}{l^2}\right]\right\}$$

4.14

Integerating 4.14 and putting in the condition that Z = 0 at t = 0 , we have,

$$Z = \frac{D.\alpha.p}{V.l}\left\{t + 2\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}.\frac{l^2}{D\pi^2}\left(1 - \left[\exp - \frac{D\,n^2\,\pi^2 t}{l^2}\right]\right)\right\}$$

4.15

As t increases indefinitely, the graph of C approximates to the line,

$$Z = \frac{D.\alpha.p}{V.l}\left\{t + 2\frac{l^2}{D\pi^2}\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n^2}\right\} \qquad 4.16$$

But the summation factor in the second term of the above equation is $-\pi^2/12$.

$\therefore$ the final line is $Z = D.\alpha.p/V.l\left[t - l^2/6D\right]$ 4.17

Had there been no non-steady state of flow, the quantity Z would have been given by

$$Z = \frac{D.a.p}{V.l}.t \qquad 4.18$$

Thus $l^2/6D$ gives the estimate of the time required to establish the steady state conditions across the film.

When the amount of the diffused substance is plotted against time, the curve approaches asymptotically a straight line, which when extrapolated, gives an intercept on the t-axis, whose magnitude, as defined above, is

$$L = \frac{l^2}{6D} \qquad 4.19$$

Here L is called the "time-lag".

It is thus possible by this technique to analyse the non-steady and steady states of diffusion. In Fig. 7 on page 75, the point B indicates the time when the non-steady state of flow changes into a steady state.

The quantity emitted per second, per unit area of the film, under the conditions of steady state flow is called the permeability. Different units have been employed by different workers to express permeability, without mentioning the thickness of the sheet. It can be very conveniently estimated from the slope of the line in Fig. 7.

Now, the quantity diffusing through the film depends upon the concentration gradient in the film and the diffusion co-efficient. If we assume that the concentration at the outgoing side is zero, or negligible and C_1 is the concentration within the film which is in equilibrium with C, the concentration with which we started, C_1 / l gives the concentration gradient. Hence the permeability P is related to the diffusion co-efficient D as follows:

$$P = - D.A.\frac{C_1}{l} = \frac{dS}{dt}$$

$$= \text{the slope of the line in Fig. 7} \qquad 4.20$$

where dS/dt is the rate of increase in the concentration on the outgoing side and A is the area of the film. Thus in a single experiment, one can find D and C_1, making a separate determination of C_1 unnecessary.

Solids in which no surface reactions are involved during the diffusion process, have a similar solution of the diffusion equation as above [9], such as for diffusion in and through a plate of thickness l.

$$P = D\frac{C_1 - C_2}{l} \qquad 4.21$$

where C_1 and C_2 are the concentrations at $x = 0$ and $x = l$, respectively.

Thus from equations 4.19, 4.20, 4.21, one may measure D by observing the rate of passage of the diffusing substance through a slab of the material.

The time-lag method was first introduced by Daynes [2] and was developed by Barrer [8,9,10] for the flow of different gases through membranes of both organic and inorganic materials, including metals.

Though the technique, is very simple and the mathematical requirements already achieved, it had not been applied to a study of diffusion of dyes in the fibre forming substances, which can be obtained in sheet form. It had been speculated that the method might yield notable results and the present investigations were undertaken to test the suitability of this technique in this comparatively new, but rich field, which offers immense scope for such a work, both from technological as well as academic point of view.

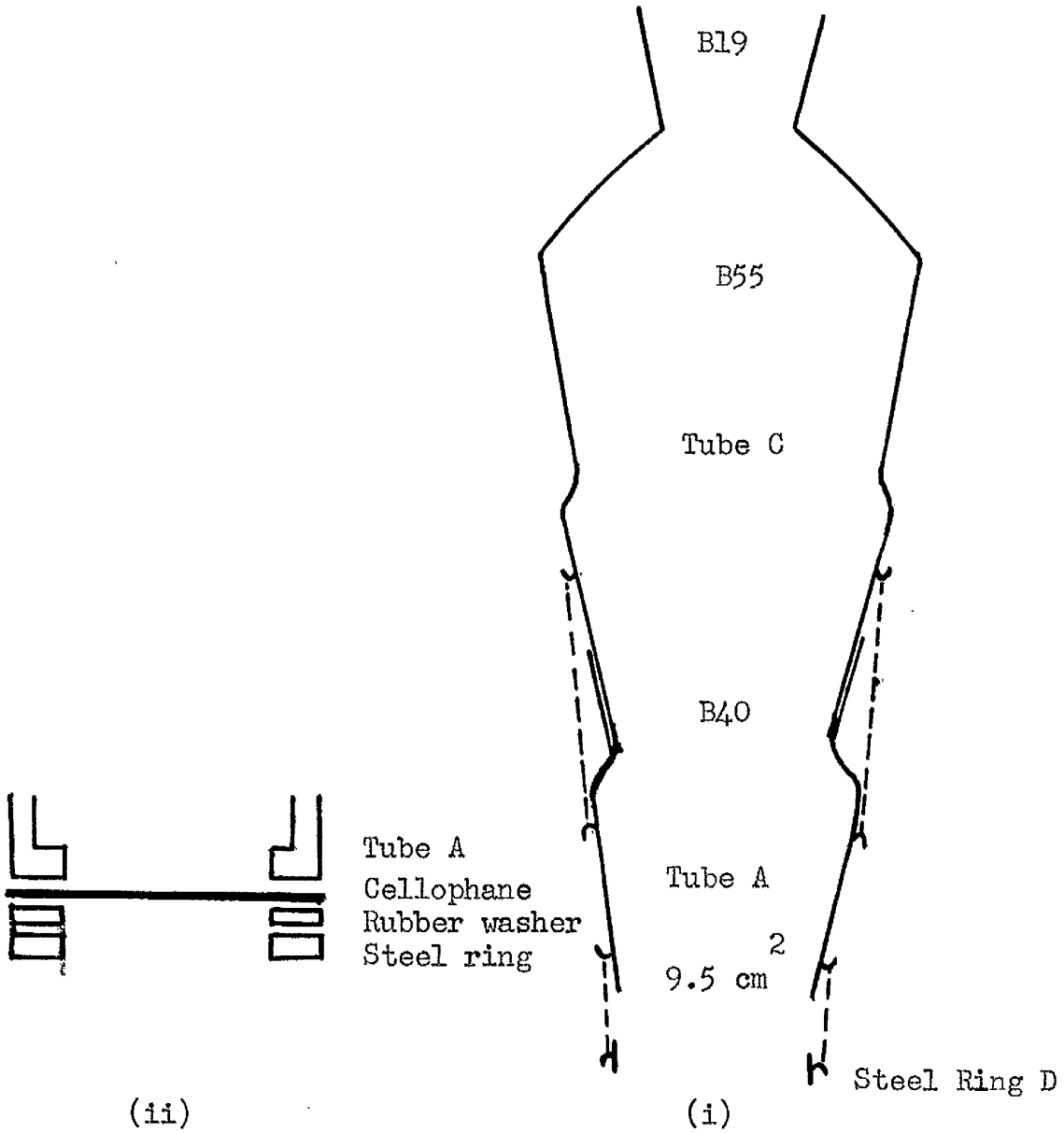


Fig. 11 (i) showing the different parts of the Diffusion Cell

(ii) showing the fastening of the Cellophane

Experimental

Description of the Apparatus

The specially designed apparatus made of Pyrex glass is shown in Fig. 11 and consists of the following parts:-

1. A 1-litre capacity, 3-mouthed round bottom flask, whose contents constitute the external solution. The dimensions of the three necks are:- Central neck B55, Outer necks B19. One of the B19 necks carried a condenser and the other was used for withdrawals and replacements of the external solution by fresh solution.
2. The diffusion cell. The cell from which actual diffusion took place through "Cellophane" into the flask, had the following detachable parts:-
   (a) A vertical tube A, with a polished edge and an opening of 9.5 cm^2 had fused to it at the top, a B40 joint.
   (b) A second cylindrical tube C which had three different glass joints:- Top B19 to hold a condenser, Middle B55 to fit in the central mouth of the flask and the Bottom B40 for the corresponding B40 of tube A.
   (c) A stainless steel ring D which made good contact with the polished edge of A, and carried two hooks on it.
   (d) A soft rubber washer E, whose internal circumference was slightly smaller and the external a little larger than the corresponding ones of the polished edge of A. This washer served the purpose of keeping the "Cellophane" sheet in

close contact with the polished edge of A, by applying pressure with the help of rubber bands, running round the hooks on A and D.

Another refinement in the apparatus was introduced by drilling two small holes in the steel ring. The idea was to free the lower part of the assembly from the entrapped air by tilting the flask slightly, which would otherwise give imperfect contact between the outgoing face of the film and the external solution and thus lead to erroneous observations.

Purity of the Materials Used

1. Sodium chloride and urea used in these experiments were A.R. quality.
2. "Cellophane" Grade PT 600 was obtained from Messrs."Cellophane", Cellulose Film Manufacturers, Manchester. It was specially cut from the central portion of the roll by the Firm so that variations in orientation during the process of stretching were minimised and there was a uniformity in texture. It had glycerol as softening agent.

Circular pieces corresponding to the external circumference of the rubber washer were punched put and thoroughly washed in running water for over 48 hours at room temperature. The water-swollen discs so obtained were used for the diffusion experiments in the cell described above.

40 small rectangular pieces of "Cellophane" were prepared as described above and their total thickness was measured with a micrometer screwgauge, having a pressure safety device. A mean of 10 readings from different parts was taken to obtain the water-swollen thickness of the whole wad and hence of one sheet. This was also checked with a microscope by viewing a sharply cut edge of the film.

3. Rubber washer and Bands:- Washers were cut from a soft and easily compressible sheet of rubber , of approximately 0.3 cm thickness. The rubber bands gave a good tension when strung between the hooks.

The washers and the bands were thoroughly scrubbed in hot water to remove any adhering impurities and were given a pre-treatment in water at a temperature higher than that at which the experiment was to be conducted. This was considered to be necessary, because the bands did lose their elasticity during the experiment especially at higher temperatures.

4. Purification of the Dyes:-

All the dyes used in these experiments were purified according to a method due to Robinson and Mills [11], by making a fairly concentrated (ca 20 °/°) solution of the dye in the batch form in hot water, filtering it hot to remove insoluble impurities and precipitating the dye with a highly concentrated solution of A.R. sodium acetate. In the first precipitation, not all the dye

in solution was thrown down completely to avoid the entrapping of the impurities within the dye aggregates.

The precipitated dye was well stirred while still hot and after allowing to cool, it was filtered on a sintered glass funnel at about 40 - 45 °C. It was collected, redissolved and re-precipitated as before. The process of precipitation and dissolution was repeated till the filtrate showed the absence of carbonate, sulphate and chloride. About 6-8 repetitions were found to suffice.

The removal of sodium acetate was affected by extraction with hot 95 °/° alcohol, in which both the salt and the dye dissolve but the solubility of the former is much greater than that of the latter. After filtering the dye and washing it twice with hot alcohol on the funnel, it was again extracted. The process was repeated, till a portion of the alcoholic filtrate after being evaporated, gave a negative cacodyl test [11]. The check was always done by comparison with two pilot tests --- one with sodium acetate and arsenic oxide and the other with sodium acetate, arsenic oxide and the dyestuff.

Though the dyes, especially the direct class of dyes, are very hygroscopic in nature and still retain about 1 °/° moisture when dried at 105 °C for 12 hours,[12] we considered the drying at 110 °C for 7-8 hours in an air-oven adequate for our purpose. The stock solutions of the dyes were stored in the dark for short periods until used. The solution of the acid dye, Carbolan

Brilliant Green was prepared afresh every week, since it showed a tendency to deposit tarry matter if stored over 3 weeks, even in the dark.

In the case of Naphthalene Scarlet, a different technique was developed for its purification. It was found that the dye could be easily precipitated in a fairly granular and filterable form from a hot concentrated solution, simply by adding 95 °/° alcohol to bring down the proportion of water to alcohol to about 45 - 50 °/°. The necessity of adding sodium acetate and its subsequent extraction was thus avoided, as the dye could be filtered while still hot and the loss of the dye was well compensated both by the avoidance of double extraction in the sodium acetate-alcohol method and the rapidity of the present procedure.

The salting out and extraction of the dyes removed undesired coloured impurities from the dyes. In the case of Chlorazol Sky Blue FF, it has been reported [13] that a red coloured dye solution is left in the dye-bath when it has been exhausted. This impurity is preferrably removed during the extraction of the dye with hot alcohol.

Similarly the direct dye, Chlorazol Pink Y contains a fluorescent impurity Primuline in appreciable amounts and its removal was successfully done during the salting out stage. Aqueous solutions of Primuline show a strong fluorescence in ultra-violet light and even a minute trace could be detected in the filtrate by this technique.

No other special tests were carried out for the rest of the dyes, other than those mentioned previously.

The two basic dyes, New Victoria Blue B and Malachite Green were purified by crystallisation from water for four times, followed by washing on the funnel.

Stability of the Dyes Solutions.

100 cc of the solutions of the dyes were kept at the desired temperatures for a period longer than the duration of the experiment. The optical densities of these solutions were compared with those of the untreated portions of the solutions, all the measurements being made under identical conditions. Though the results set in Table I refer to single measurements, yet there is enough indication that the dyes do not show any appreciable decomposition when the actual experiment is carried out.

Table I

Opt.Density ---->	Non-treated		Treated		Temp.	Time
Dye	Water	20°/° urea	Water	Urea	°C	Hours
Sky Blue FF	0.86	0.85	0.86	0.84	90	6
Chlorazol Pink Y	0.82	0.82	0.82	0.79	90	5
Chrysophenine G	0.83	0.84	0.82	0.84	90	5
Naphthalene Scarlet	0.72	0.67	0.72	0.67	80	4
Carbolan Brilliant Green	0.68	0.70	0.66	0.66	80	4

Experimental Technique.

A circular piece of "Cellophane" punched and prepared as described previously, was well shaken by hand to remove the water adhering to it and placed on the polished edge of tubeA, which was clamped vertically in an inverted position. Due care was taken that there appeared no folds in the sheet and that the portion extending over the glass rim was well-spaced on all sides. Next the rubber washer was placed on it which was followed by the steel ring with the hooks in the appropriate positions.

The accurate assembly of these parts is very essential and requires some practice in order to judge that the position of the different parts is not disturbed and that there are no folds produced in the sheet while stringing the rubber bands between the hooks on different parts.

Though very little surface of the film, other than that desired, was exposed to the external solution, yet the uncovered portion extending in the external solution was trimmed as far as possible to avoid any absorption of the dye taking place on it from the external solution. This was found particularly necessary when the concentration of the added electrolyte was high and hence absorption enhanced. If this precaution is not taken, it might result in an appreciable error, since the concentration of the diffused dye is very small and a small amount removed through absorption would tend to make the concentration of the external solution lower than it should have been. For example, in the case of Chlorazol Sky

Blue FF, the following data from such an experiment is given to illustrate this effect, when 1.0 °/° dye diffuses at 90 °C in presence of 1.0 °/° NaCl, the duration of the experiment being 5 hours.

Total amount of the dye diffused	= 2.22 mg.
Dye estimated on the film	= 1.76 "
" " " " edge, untrimmed and extending beyond the washer	= 0.03 "

The magnitude of the error involved would become larger if the experiment is conducted for a longer period.

After these essential steps, the diffusion cell is lowered into the flask, the external solution added and the flask slightly tilted and gently given a swirling motion to remove the air entrapped between the outgoing face of the film and the external solution. The volume of the external solution to be used was assessed beforehand, so that the film was well within the solution even when the samples were withdrawn for analysis.

The flask and its contents were brought to the desired temperature in a thermostat and pre-heated dye solution added to the diffusion cell. Water-jacketed condensers were fitted in the flask and the cell to avoid loss of water by evaporation.

No stirring arrangement was considered necessary either for the external or for the internal solution. Since diffusion takes place in a vertical direction, the more concentrated solution being above the one of low concentration (zero, to start with)

gravitation was regarded as adequate inkeeping the two solutions uniform in composition at all points through loss or gain of the dyestuff as the case may be. Further, since this work was carried out at elevated temperatures, the invetable convectional currents present in both the chambers promote the homogeneity of the solutions. Thus it is reasonable to assume that since the amount of the dye diffused was negligible as compared to the initial amount, the ingoing face was always in contact with a solution of almost constant concentration.

Any leakage, whether due to poor fitting of the sheet or uneven pressure soon becomes apparent after the two solutions are brought into contact. Moreover, after the conclusion of the experiment, the presence of a clear, untinted portion of the sheet where it was sandwiched between the rubber washer and the glass tube shows that there was a satifactory seal.

An essential requirement of this technique is that the diffusion should not be too rapid and the concentration of the dye solution should be so adjusted that the rate of diffusion is neither very fast nor immeasurably small, particularly at rather lower temperatures.

When two solutions with different concentrations of the dyestuff are brought together with a permeable membrane such as "Cellophane", between them, there are two opposing forces acting in the system.

1. Osmotic forces, acting in both the solutions, in either direction.
2. Hydraulic pressure of the upper solution, which might tend to influence the diffusion.

As far as osmosis is concerned, we made no precise study of its magnitude or its effect on the diffusion process through the film. But, nevertheless, the effect was there because a slight increase in the volume of the internal solution was observed, when the concentration of the dye solution was high and the experiment was conducted for a long time (7 - 8 hours). The exact increase in the volume of the internal solution after the experiment could not be determined accurately because the geometry of the cell did not permit it being measured in situ and the solution could not be wholly collected for separate measurement. However, in the case of Chlorazol Sky Blue FF, the only dye where a concentration as high as 1.0 °/° was used and where the duration of the experiment was as long as 8 hours, the increase in the volume of the internal solution was about 5 °/°. The concentration of the other chemicals was always constant.

To investigate the effect of the pressure head on the diffusion due to the internal solution, 10,20,30,40 and 50 cc of the solution were introduced into the cell and the rate of diffusion measured as usual. No change could be detected and it was decided to use 30 cc of the dye solution, so that the conditions approached those of an infinite dye-bath.

Temperature Control.

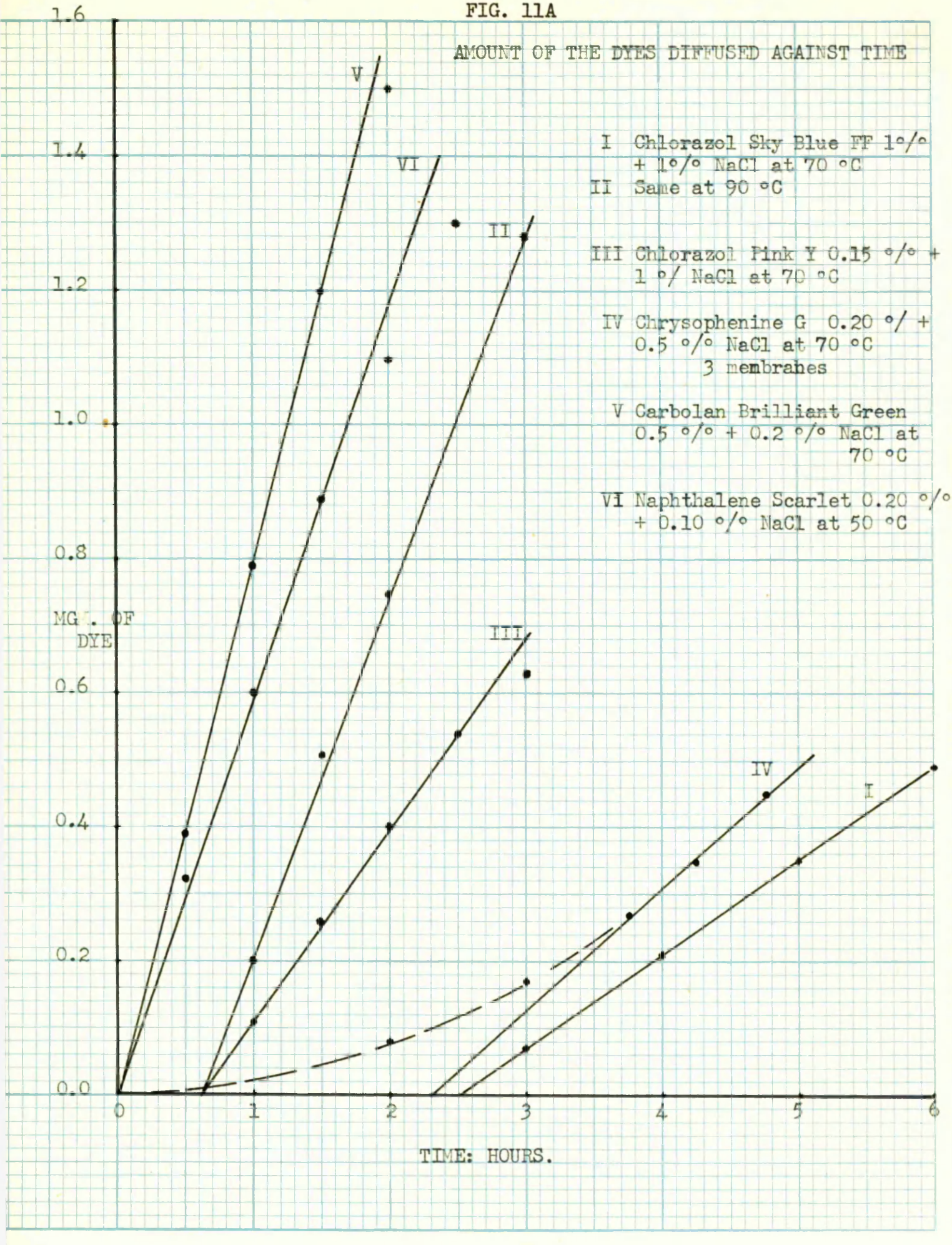
The variations of temperature in the external solution were well within ± 0.5 °C at 50,60 and 70 °C, but within ± 1 °C at 80 and 90 °C. The temperature of the internal solution was 1 to 1.5 °C lower than the desired one. This was due to the fact about half of the solution was above the level of the external solution and could not be heated effectively by the rising water-vapour from the surface. However it is not un-reasonable to assume that the internal solution in the immediate vicinity of the film was at the desired temperature.

The existance of a thermal gradient in a system is known to offset the diffusion and is often employed in the separation of isotopes, gases and metals [14]. But the temperature differences which can bring about such separations are very great, for example, for CO_2 and H_2, the thermal gradient is of the order of 600 °C [14]. It is, therefore, believed that a temperature difference of 1.5 °C between the top and bottom of the internal solution would produce hardly any effect on the diffusion of the dyes through "Cellophane"

Analysis of the External Solution.

The appearance of the dye in the external solution was watched from time to time in the initial stages of the experiment, till it was observed to give a reading on the Hilger's Spekker, using a 4-cm cell for faintly coloured samples and replacing it

FIG. 11A


AMOUNT OF THE DYES DIFFUSED AGAINST TIME
I Chlorazol Sky Blue FF 1°/° + 1°/° NaCl at 70 °C
II Same at 90 °C
III Chlorazol Pink Y 0.15 °/° + 1 °/ NaCl at 70 °C
IV Chrysophenine G 0.20 °/ + 0.5 °/° NaCl at 70 °C 3 membranes
V Carbolan Brilliant Green 0.5 °/° + 0.2 °/° NaCl at 70 °C
VI Naphthalene Scarlet 0.20 °/° + 0.10 °/° NaCl at 50 °C
MGM. OF DYE
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
TIME: HOURS.

with 1 cm cell when the solution became denser. 25 cc of the solution were withdrawn at noted intervals and the deficiency made up immediately with the same volume of the blank solution of a similar composition at that temperature. The estimation of the dye in the test portions was carried out under conditions identical with those of calibration, requiring a separate calibration graph for each concentration of urea, salt or both, used in the actual experiment. At first, about 10 - 12 observations were made at different intervals of time, but later, it was found that 5 - 6 readings were enough for the purpose.

Estimation of the Time - lag.

The amount of the dye diffused through the film and calculated in the above manner, was plotted against time and in each case, a perfect line was obtained right from the beginning of the experiment(with the exception of Chrysophenine G, when diffusing through 3 membranes), unlike the observations of Daynes [2] and Barrer [8,9,10] on the diffusion of gases and vapours through organic and inorganic membtanes. Fig. ~~12~~ II A shows some of these lines, representative of each dye studied during the course of the present work.

The disappearance of the curved portion in the graph strongly indicates that the diffusion is one of steady state conditions from the start of the experiment and once the sheet has attained " near - equilibrium "absorption value (in the case of

direct dyes) or the concentration of the dye within the sheet and the internal solution (in case of acid dyes) is same, the diffusion proceeds in a steady fashion.

A very detailed examination of the plot of the amount diffused against time revealed that when the experiment was carried out for longer times, the straight line took a slight curvature, which was more noticeable with direct dyes. This is according to the expectations, because, when the concentration of the dye has become appreciable in the external solution, the condition that the concentration at the outgoing face is zero, no longer exists, with the result that the rate of diffusion is retarded. Thus in the case of acid dyes, the readings were confined to the first few hours only and were adequate to give a good line.

Reproducibility and the Co-efficient of Variation.

From an examination of the results of duplicate experiments on diffusion, the co-efficient of variation has been calculated in the following manner, which expresses the spread of the observations from the most probable values of the variable.

For the linearly related cases, with one variable only liable to error, the measure of the dispersion of the observed y-values (x is time in this case) about the least-square line is

given by [15]

$$S_y = \sqrt{\frac{\Sigma(y - y_c)^2}{n}}$$

where S_y is the "Standard Error of Estimate".

Keeping the x-variable (time) fixed, the most probable values of y, the amount of the dye diffused at a particular time was calculated from the above relation. It was found that the co-efficient of variation was well within $\pm$ 1.6 °/°, though the deviations were slightly greater during the early stages of diffusion, when the diffusion was very small and the optical density of the solution, determined with the Hilger's Spekker, becomes particularly liable to error as this instrument works best between the range of 0.5 to 0.9.

Calculation of the Diff.Co-eff. from the Equilibrium Absorption.

At the end of the experiment, the apparatus was quickly dismantled, the film removed and rinsed well in chilled water. After pressing it between folds of filter paper, the slightly tinted edge exposed to the external solution was cut off and the amount of the dye on the film estimated by stripping with aqueous 25 °/° pyridine and expressed in g/cc of the water-swollen "Cellophane".

Since in these experiments, diffusion is in the steady state right from the beginning, it is assumed that the equilibrium absorption within the disc takes place comparatively rapidly.

Further, it is assumed that because of the constant concentration of the internal solution, this equilibrium value remains unchanged during the course of the diffusion and that the amount of the dye which leaves the outgoing face is constantly being made up. It should, therefore, be possible to calculate this value from a measurement of the rate of permeation. Assuming the concentration at the outgoing face negligible, the latter quantity is defined by the following expression :

$$P = \frac{D.A.C_e}{l}$$

where A is the area of cross-section of the membrane and l is its thickness. C_e is the concentration of the dye on and within the film which is in equilibrium with the internal solution.

It has been found that there is a good agreement between the two equilibrium values obtained from a knowledge of the permeability on the one hand and the total amount of the dye absorbed on the other hand. This agreement is not so good when diffusion of direct dyes takes place in presence of uniform concentration of urea, when the desorbing action of urea comes into play. This departure is further increased when swelling produced by urea solutions is taken into consideration. The increased dimensions of the capillaries greatly modify the pattern of diffusion, which occurs in a less restricted manner and consequently there are fewer chances of the dye being deposited on the capillary walls. (See Part II)

The diffusion processes are greatly influenced by the boundary conditions. In the steady state flow of matter, as much diffusible substance is being transferred across a particular plane as is being received from regions of higher concentration. This implies that once the steady state is reached, the diffusion is controlled by the amount of the dye held within the membrane, mechanically or through a physico-chemical process. Assuming this amount C_e to be uniformly distributed over the sheet, the existing gradient of concentration between the internal and the external solutions is C_e / l, where l is the thickness of the film. Thus if we determine the amount C_e after the experiment is over, we can calculate the diffusion co-efficient D from the relation :

$$d\$ / dt = - D.A.C_e / l$$

where every factor is known except D.

The values of D calculated from the above relation have been compared with those obtained from

$$D = l^2 / 6L$$

where L is the time-lag. The two sets of values agree fairly well. This agreement is particularly good when diffusion proceeds in the presence of uniform concentration of electrolyte.

Calculation of the Diff.Co-eff. of Acid Dyes.

It may be remarked here that the foregoing only holds good when diffusion takes place with simultaneous absorption on

the medium, such as that of direct, substantive dyes through cellulose. In the case of non-substantive acid dyes when diffusing through "Cellophane", it has been found that the time-lag method no longer yields any fruitful results. When the amount diffused is plotted against time, there appears no intercept on the t-axis and the straight line so obtained, passes through the origin. We have thus to find some other means of calculating the diffusion co-efficient from a measure of the permeability of the "Cellophane" to acid dyes.

Since the acid dyes are not absorbed by cellulose, the only resistance which the dye molecules experience while diffusing through "Cellophane" is due to the net-work of cellulose chains and the molecules diffuse in solution in a random manner through the capillaries. The model thus becomes analogous to that of diffusion through a porous plate of sintered glass. Assuming that the average length of each capillary is given by the thickness of the water-swollen "Cellophane" and that the concentration on the outgoing face is negligible, the concentration gradient is simply C / l where C is the concentration of the dye, g./l. in the internal solution. The diffusion co-efficient was calculated from the following expression

$$dS / dt = - D.A.C / l$$

where each term has the usual significance.

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Chapter V

Results and Discussion

The numerical values of the diffusion co-efficients for the three direct dyes calculated from the relation

$$D = l^2 / 6L$$

and for the two acid dyes, calculated from the equation

$$D = dS/dt. \; 1/C. \; 1/A$$

are set in the following tables. The values for the direct dyes are also compared with those calculated from a knowledge of the equilibrium concentration of the dye in the film and the rate of permeation through it.

Units and Symbols Employed.

The units and symbols employed throughout these tables are as given below :-

1. The equilibrium concentration of the dye in the film is expressed as g. per cc of the material in the water-swollen form.
2. The thickness of the film is 0.0086 cm in the wet state at room temperature.
3. The time-lag is given in seconds.
4. The dimensions of the diffusion co-efficient are cm^2 sec^{-1}
5. Permeability:- The numerical measure of permeability constant P is dependent upon the units in which it is expressed. The literature shows a lack of uniformity with respect to units and

it is especially important to mention the thickness of the membrane.

The definition of the permeability constant P, as given by Barrer [1], for the permeation of a gas through materials, such as, rubbers, leathers, balloon fabrics, packing materials and celluloid, has the dimensions $L^3\ T\ M^{-1}$ and "denotes the number of cc of the gas at one atmosphere pressure and a standard temperature (273 °K) passing per second, through a membrane 1 cm^2 in area, 1 mm or 1 cm thick, when the pressure difference is 1 cm of Hg or 1 atmosphere".

Since this definition would not serve our purpose, the permeability constant is defined by the equation

$$dS / dt = D.A.C_e / l = P$$

where each term has the usual significance.

The permeability constant P is thus defined as the number of g. of the dye diffusing in unit time per unit area of the membrane, the dimensions of the membrane being taken as under the conditions of the experiment.

The following symbols are used for the notation of different quantities in these tables.

L = the time-lag.

D_L is the diffusion co-efficient calculated from L.

C_L is the equilibrium value of the dye concentration in the film, calculated from L.

P is the permeability constant.

C_E is the equilibrium value of the concentration of the direct dyes in the film, found experimentally at the end of the experiment. D_E is the diffusion co-efficient, calculated from C_E and P.

The ratio of the internal to external solution was always 30 to 250.

Table II

Effect of the concentration of Chlorazol Sky Blue FF, X °/° dye, diffusing through "Cellophane" at 90 °C in 1.0 °/° NaCl.

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.2	4200	29.35×10^{-10}	24.83×10^{-3}	8.41×10^{-9}	32.31×10^{-10}	22.66×10^{-3}
0.4	3900	31.56	35.38	12.91	37.13	30.03
0.6	3540	35.83	39.67	15.96	35.14	39.35
0.8	2880	42.80	36.67	18.22	44.61	35.12
1.0	2220	55.52	22.91	15.50	61.43	21.69

It will be seen from this Table as well as those which follow, that there is generally a good agreement between the values of the diffusion co-efficients by the time-lag method and from a knowledge of the absorption of the dye by the film. Furthermore, the theoretical value C_L of the equilibrium concentration of the dye in the film is very close to that of C_E found experimentally at the end of the experiment.

FIG. 12

EFFECT OF CONCENTRATION OF THE DYE ON THE DIFFUSION OF CHLORAZOL SKY BLUE FF AT 90 °C IN PRESENCE OF 1.0 °/° NaCl.

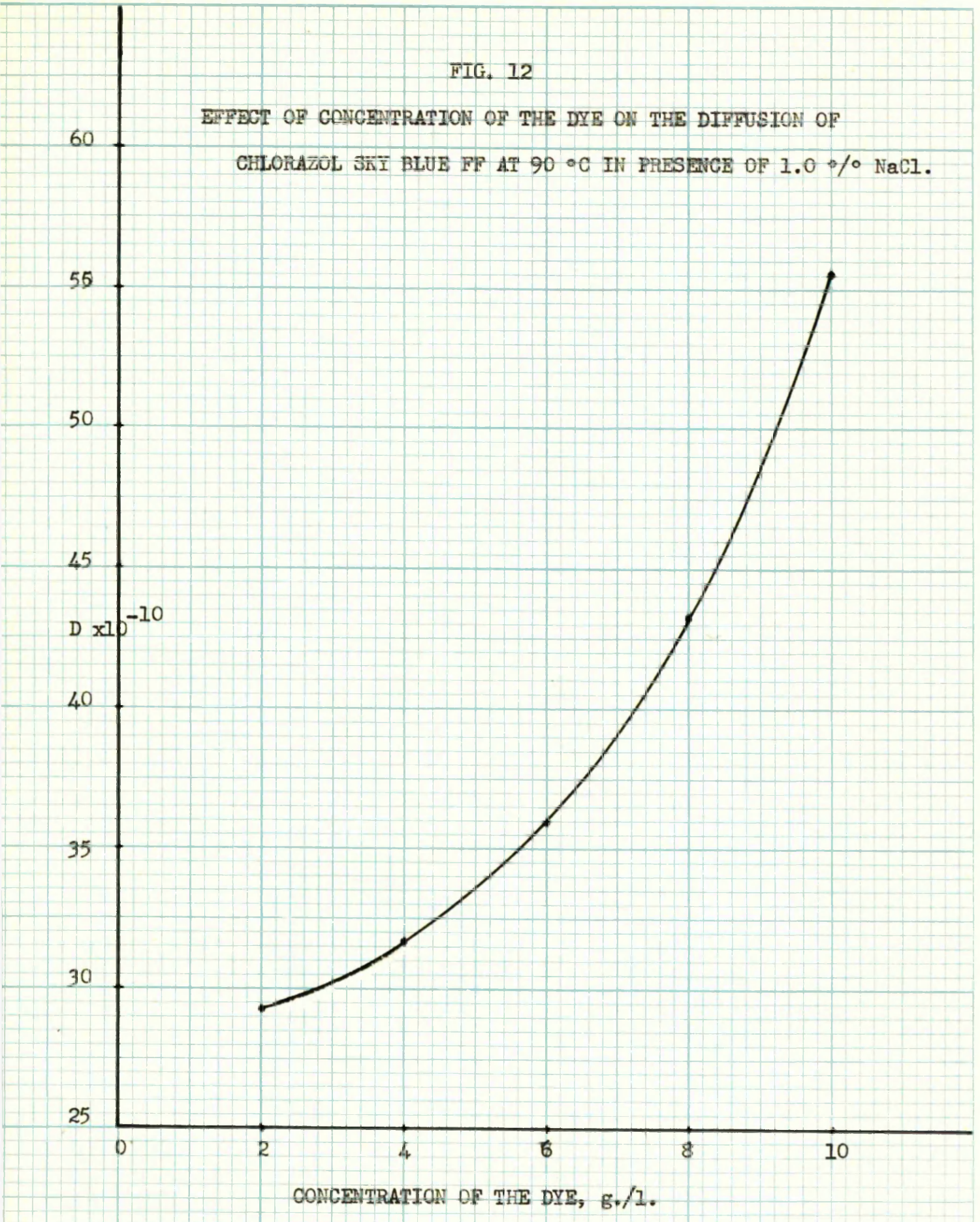


FIG. 13

DIFFUSION OF CHLORAZOL SKY BLUE FF AT 90 °C

THROUGH "CELLOPHANE".

LOG P AGAINST LOG C.

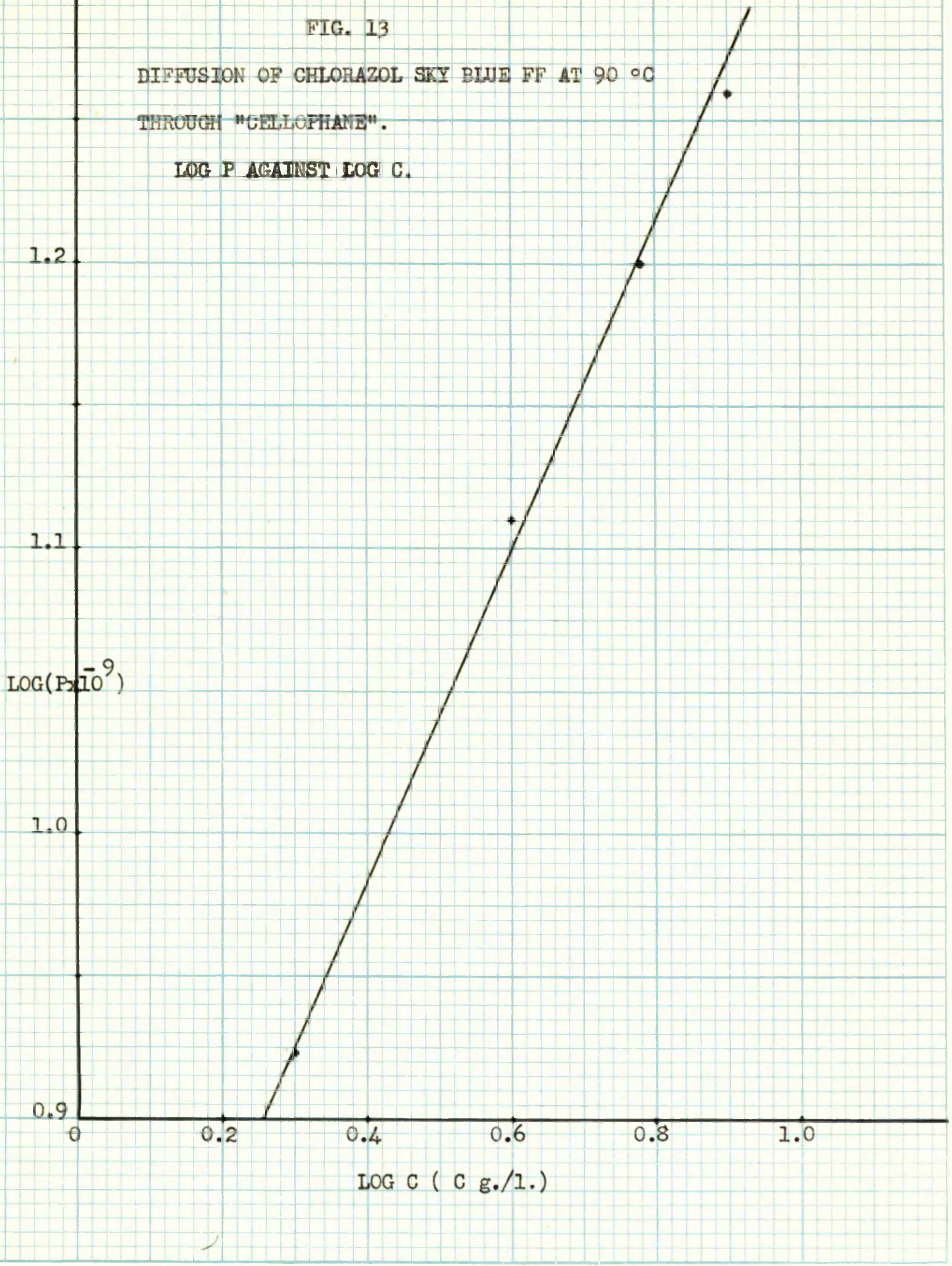
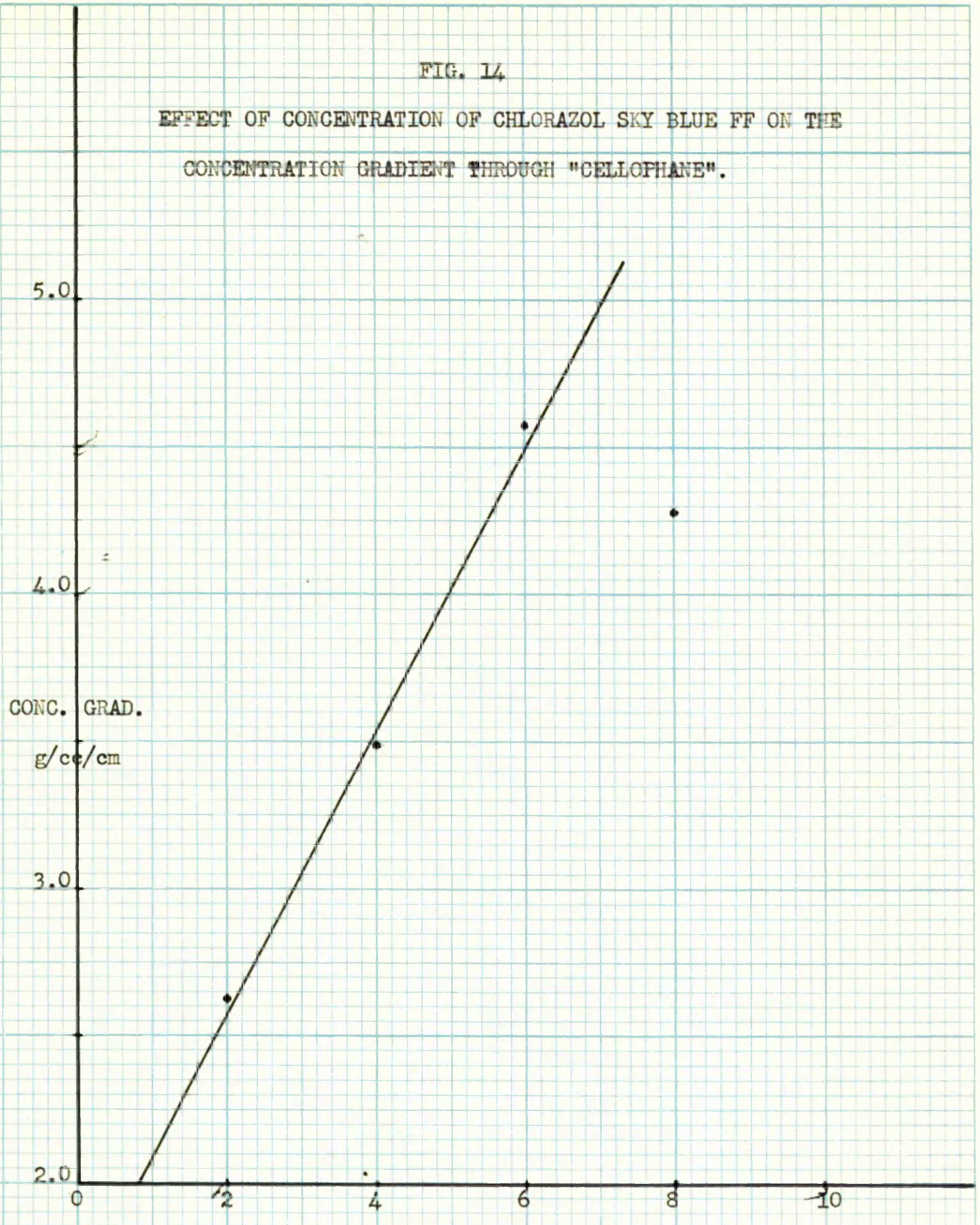


FIG. 14

EFFECT OF CONCENTRATION OF CHLORAZOL SKY BLUE FF ON THE CONCENTRATION GRADIENT THROUGH "CELLOPHANE".



These data are represented graphically in Fig.12. It will noticed that the diffusion co-efficient does not vary, in a linear manner, with the concentration of the dye. The variation in D are appreciable and the influence of the concentration on D is established as follows.

Starting with the equation

$$dS / dt = - D.A. dC / dx$$

having the usual notations, a plot of $\log_{10}$ dS/dt against $\log_{10}$ C (C in g. per litre) lies on a straight line (Fig. 13), whose gradient is 0.483, from which it becomes apparent that dS /dt varies with the concentration as $C^{0.483}$. Now D in fact is given by dS / dt which includes a constant term A, the area of the film, and dC / dx, the concentration gradient. The values of the concentration gradient dC / dx calculated from C_E / 1 from Table II for different concentrations used are :-

Conc., g./l.	C_E , g./cc	dC / dx, g./cc/cm.
2.0	22.66 $\times 10^{-3}$	2.64
4.0	30.03	3.50
6.0	39.35	4.58
8.0	35.12	4.26

A plot of the concentration gradient against concentration falls on a straight line (Fig. 14), though with higher concentration, there is a fall in the value of the former. Hence it can be safely concluded that dC / dx following C linearly, D varies

with C as $C^{0.483}$ i.e., $D_A = D_0 C^{0.483}$, where D_A is the apparent observed diffusion co-efficient and D_0 is a constant, the true diffusion co-efficient.

In another series of experiments, concentration of the dye was kept constant, while that of the electrolyte was varied. These results are set below.

Table III

Diffusion of Chlorazol Sky Blue FF, 1.0 °/° dye + X °/° NaCl, at 90 °C.

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.00	2880	42.81 x10^{-10}	16.00 x10^{-3}	7.98 x10^{-9}	78.44 x10^{-10}	8.75 x10^{-3}
0.10	2100	58.68	14.13	9.70	64.42	12.86
0.20	2400	51.36	17.51	10.41	56.44	15.52
0.40	2760	44.66	26.08	13.36	56.60	20.44
0.60	2340	52.68	21.61	13.19	43.33	26.11
0.80	2340	52.68	31.22	17.19	48.12	32.39
1.00	2220	55.52	22.91	15.50	61.43	21.69

The effect of the electrolyte does not follow any regular pattren. As will be seen from Table III, the diffusion co-efficient is raised abruptly during the first additions of the electrolyte, it then drops and rises steadily with the increased concentration of the salt. It may be added here that a direct dye, such as this, is itself a strong electrolyte and shows an anamolous salt effect [2].

Tables IV and V give the data regarding the diffusion of Chlorazol Sky Blue FF at diffrent temperatures in the presence of a uniform concentration of the electrolyte, as well as in its absence.

Table IV

Diffusion of Chlorazol Sky Blue FF, 1.0 °/° dye + 1.0 °/° NaCl

Temp. °C	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
70	9000	13.70×10^{-10}	25.85×10^{-3}	4.09×10^{-9}	12.70×10^{-10}	27.71×10^{-3}
80	5400	22.83	36.20	9.50	---	---
90	2220	55.52	22.91	15.50	61.43	21.69

Table V

Diffusion of Chlorazol Sky Blue FF, 1.0 °/° dye into Water

70	10080	12.22	12.62	1.78	15.57	9.85
80	4140	29.77	10.90	4.01	---	---
90	2880	42.81	16.00	7.98	78.44	8.75

The effect of temperature on the rate of diffusion may be expressed quantitatively by determining the energy of activation of the process. The diffusion of a solute through a solid differs from that through liquids in being generally much slower and in having a much higher temperature co-efficient. The average velocity of a molecule whether it is in a gas, liquid or solid, is of the same order, but in solids, it spends most of its time in vibrating

to and fro, occasionally breaking loose and moving on. According to the theory of activated diffusion (See Laidler, Eyring and Glasstone [4]), the higher temperature co-efficient of diffusion through solids can be explained by supposing that the diffusing molecules remain vibrating about an equilibrium position, until by random exchange with the neighbouring molecules, they acquire a certain critical energy. They are then in an activated state and are able to surmount the restraint of their surroundings and diffuse further.

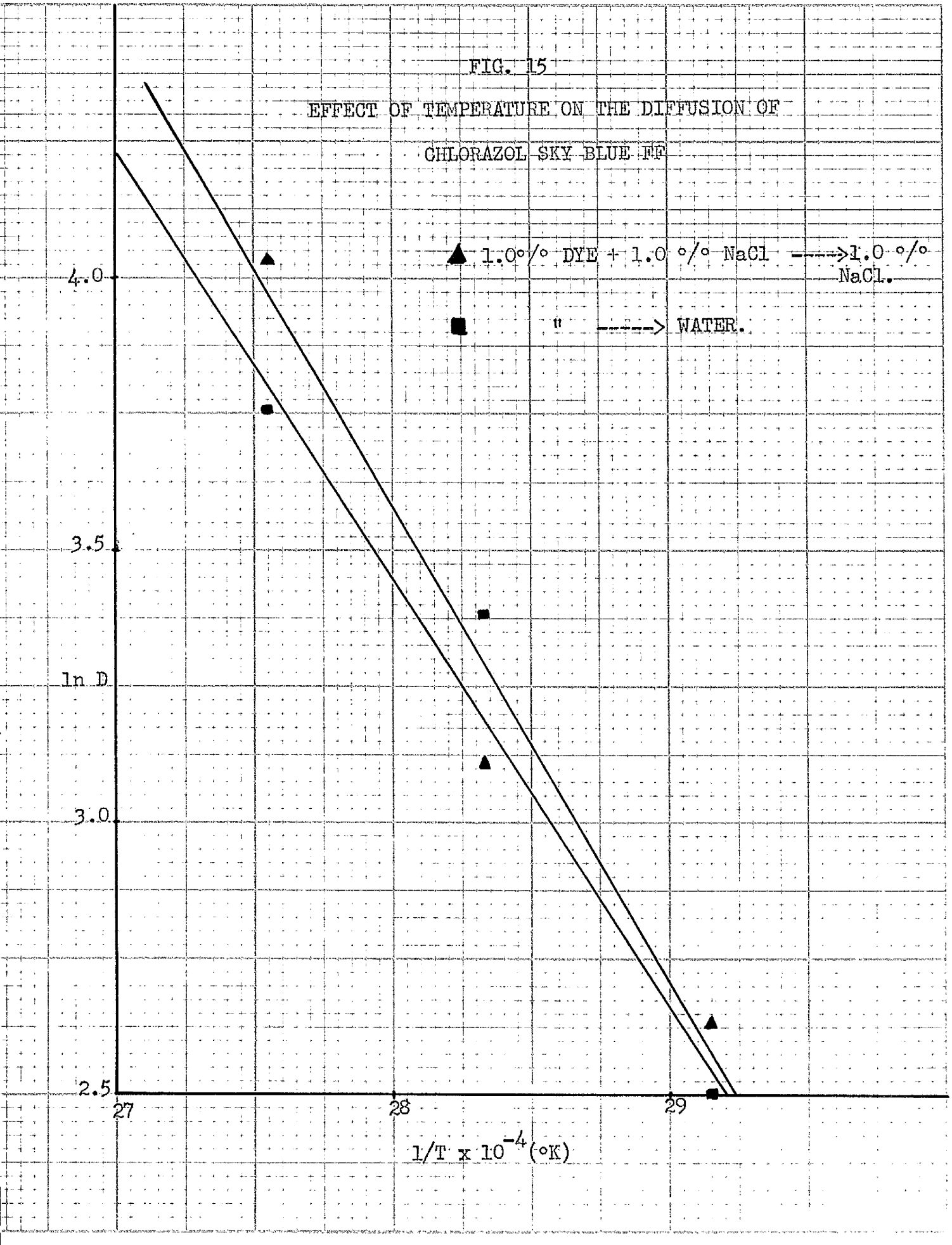
Now the number of such activated molecules at any moment is proportional to the concentration of the solute and to the exponential term $e^{-E / RT}$, where E is the amount by which the energy of activated molecule exceeds the average energy of the solute molecules. On this account, Fick's law applies only to the activated molecules, whose concentration cannot be measured, but since this concentration is proportional to $C.e^{-E / RT}$, where C is the total concentration of the diffusing substance, Fick's law can be applied to the observed concentration gradient, if the exponential term is included in the diffusion co-efficient:

$$D_T = D_0 e^{-E / RT}$$

where D_T is the observed diffusion co-efficient at a temperature T, and D_0 is a constant.

FIG. 15

EFFECT OF TEMPERATURE ON THE DIFFUSION OF CHLORAZOL SKY BLUE FF



Taking logarithms, we have:

$$\ln D_T = \ln D_0 - E / RT$$

so that a plot of $\ln D_T$, at different temperatures against the reciprocal of the absolute temperature should fall on a straight line, the slope of which is E / R, from which the energy of activation of diffusion may be calculated.

In an attempt to calculate the energy of activation of diffusion according to the above relation and making use of the data in Tables IV and V, $\ln D_T$ has been plotted against 1/T. Though the points (Fig. 15) do not give a perfect linear relation, yet a straight line can be drawn through the mean positions by making use of least-square method (Here values on the Y-axis are kept constant), which shows this effect reasonably well.

The slope when the dye diffused in presence of a uniform concentration of the electrolyte is $- 86.90 \times 10^2$ and equating it to E/R (R = 1.987 cal./ degree/mole), the value of E is -17,189 cal./degree/mole. Similarly, when there is no electrolyte, the slope is -78.41×10^2 and hence E = - 15,509 cal./degree/mole.

The effect of changing the volume of the external solution has been observed and it is found that, according to expectations the time-lag is not affected and so is the diffusion co-efficient. However, the rate of permeation shows a slight, but definite variations when the external volume is changed, as is shown in Table VI.

Table VI

Effect of the Volume of External Solution X cc on the Diffusion of Chlorazol Sky Blue FF, 0.10 °/° dye + 0.50 °/° NaCl at 90 °C.

X cc	L s	D_L $cm^2/s, 10^{-10}$	C_L $g/cc, 10^{-3}$	P $g/cm^2/s, 10^{-9}$	D_E $cm^2/s, 10^{-10}$	C_E $g/cc, 10^{-3}$
150	3600	34.24	9.88	3.59	19.77	15.65
250	"	"	10.44	4.15	28.80	12.37
500	"	"	12.32	4.85	32.14	13.89

The reason why the rate of permeation is influenced is plain enough. The diffusion of direct dyes takes place with absorption and so long the substrate is surrounded by a solution of constant composition, no backward reaction takes place. However, when the dye has penetrated upto a stage, where it comes into contact with the blank solution, the conditions are reversed and desorption of the dye from the film occurs, which is obviously dependent upon, if other factors are fixed, on the volume of the liquor and hence more dye will pass when the volume is increased.

Incidentally, the concentrations of the components of the internal solution used for the determination of the diffusion co-efficients shown in Table VI are those used by Garvie and Neale [3] for the same dye at 90 °C. The average value of the diffusion co-efficient found by these workers from steady state conditions through a single membrane of "Cellophane" is 346 x 10^{-8} cm^2/min. or 576.66 x 10^{-10} cm^2 /s.

In another experiment by dyeing a single piece of "Cellophane" in a dye-bath of similar composition and by making use of Hill's [5] equation, they found a value of 16.4×10^{-8} cm^2/min. or 27.33×10^{-10} cm^2/s. The latter figure is fairly in good agreement with the values of D shown in Table VI. The reason why there exists a discrepancy between the former value of 576.66×10^{-10} cm^2/s and those in Table VI is that Garvie and Neale, while calculating the diffusion co-efficient from the rate of permeation throgh the film, employed a different unit to express the concentration gradient. They used the actual concentration of the internal solution (g./l.), whereas it should have been the concentration of the dye in the film (g./cc) under those conditions, which gives the real concentration gradient.

For the sake of discussion, the following data are reproduced from the original paper.

Thickness of the film (x) = 2.93×10^{-3} cm.

Area " " = 8 cm^2

dS / dt =10.2 g./ min.

Conc. C = 0.968 g./l.

The value of D calculated from

$$D = 1/A. \; dS/dt. \; x \; / \Delta C$$

is 576.6×10^{-10} cm^2/s.

The thickness of the film used in the present work is 0.0086cm i.e., approximately 3 times thicker. For the sake of

argument let us assume that the concentration of the dye in the film (because they are of the same material) under the same conditions was the same as in the present work. Taking an average of the values shown in the last column of Table VI i.e., 13.97×10^{-3} g. /cc and keeping all the other quantities same as in the original paper but replacing ΔC by 13.97×10^{-3} g/cc,

$$D = 267.49 \times 10^{-8} cm^2/s$$

or $$= 44.58 \times 10^{-10} cm^2/s$$

which is not so far away from the values given in Table VI as the original value $576.6 \times 10^{-10} cm^2/s$.

The results of the Tables II, III and VI are reproduced in a different style in Tables VII, VIII and IX respectively. According to the treatment of the kinetics of dyeing and theory of diffusion of direct dyes into cellulose given by Standing and Coworkers [6], the apparent, observed diffusion co-efficient D_A is a function of the concentration of the dye in the solution C_B, the equilibrium absorption value S of the dye in the substrate and is related to these quantities as follows.

$$D_A = D_0 . C_B / S$$

where D_0 is a constant, the diffusion co-efficient of the dye in the aqueous solution. C_B is expressed as moles per litre and S in g/kg of the substrate. Hence by khowing D_A , S and C_B, it should be possible to calculate D_0 from the above relation.

In the following Tables, the values of D_0, which have been calculated by making use of the data of the time-lag method are given, employing the same units as mentioned on the previous page.

Table VII

Diffusion of Chlorazol Sky Blue FF, X °/° dye + 1.0 °/° NaCl at 90 °C

Weight of one disc of "Cellophane" used = 0.046 g.

Concentration of Dye		D_A (D_L)	S	$D_0 = D_A.S / C_B$
Per cent	Molar C_B	cm^2/s	g/kg.	cm^2/s
0.20	0.002016	29.35×10^{-10}	40.00	58.23×10^{-6}
0.40	x 2	31.56	53.04	41.51
0.60	x 3	35.83	69.56	41.20
0.80	x 4	42.80	61.95	32.88
1.00	x 5	55.52	38.26	21.07

Table VIII

Diffusion of Chlorazol Sky BlueFF, 1.0 °/° dye + X °/° NaCl at 90°C

X	C_B, Molar Dye	Same notations and Symbols as above		
0.10	0.01008	58.68	22.69	13.21
0.20	"	51.36	27.39	13.96
0.40	"	44.66	36.08	15.98
0.60	"	52.68	46.08	24.08
0.80	"	52.68	57.17	29.88
1.06	"	55.52	38.28	21.07

Table IX

Diffusion of Chlorazol Sky Blue FF, 0.10 °/° dye + 0.50 °/° NaCl at 90 °C, in X cc of the External Solution.

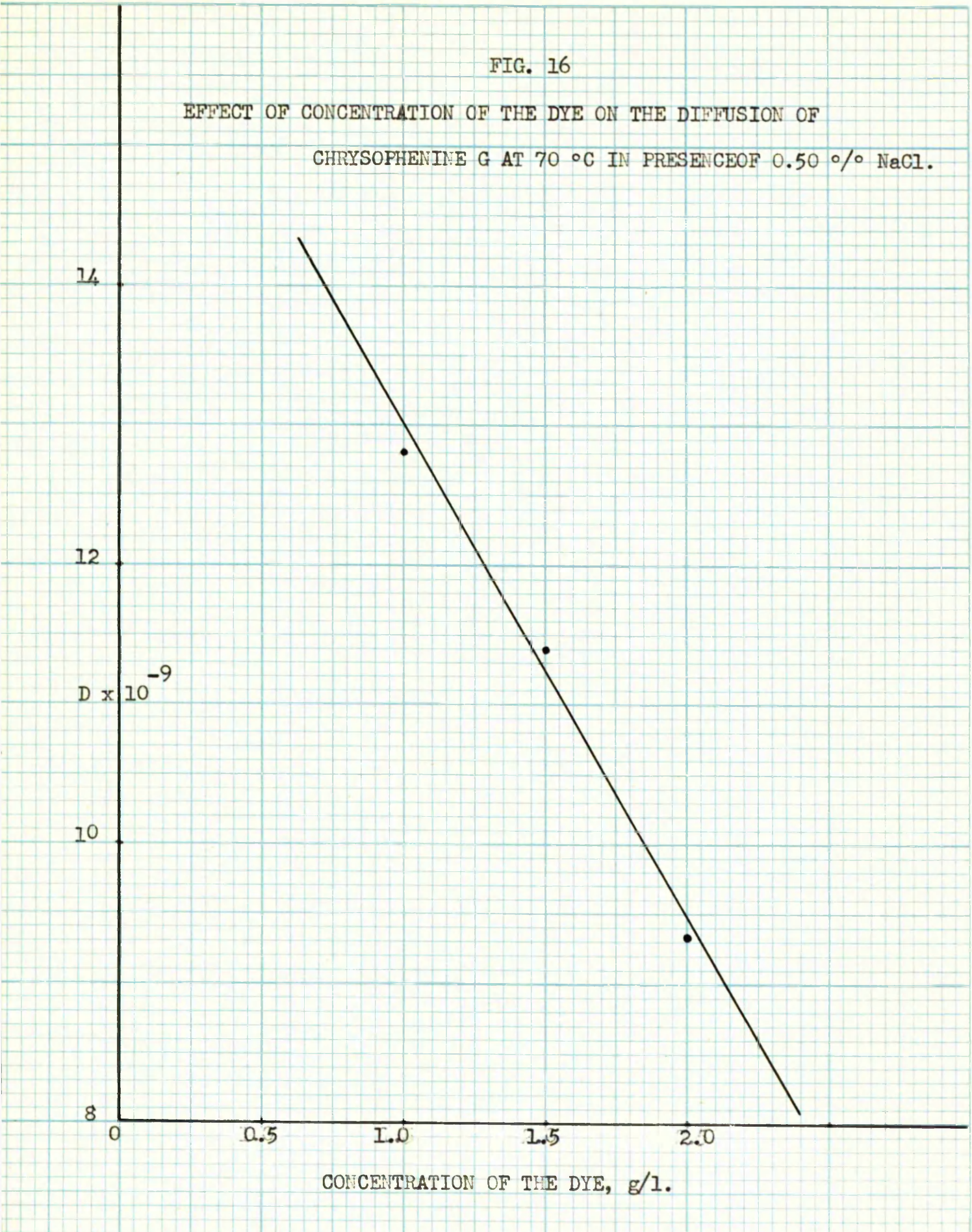
X	C_B, Molar Dye	D_A (D_L) cm^2/s	S , g/kg	$D_O = D_A \cdot S / C_B$ cm^2/s
150	0.001008	34.24×10^{-10}	27.60	93.75×10^{-6}
250	"	"	21.82	74.11
500	"	"	24.52	83.33

The values of D_O in the last columns of these Tables, especially in Table IX were compared with the diffusion co-efficient of Chlorazol Sky Blue FF, diffusing in aqueous solutions under similar concentrations of the dye and the electrolyte. Valko[7] records a value of the diffusion co-efficient at 25 °C as 11.8×10^{-7} cm^2/s, the concentration of the dye and the electrolyte being 2.0 and 29.25 g/l. The highest value he has given, is 72.45×10^{-7} cm^2/s, when the dye, 1.0 g/l, diffuses in pure water, which is still approximately 10 -13 times smaller compared with the values in the last column of Table IX.

In a later paper [8], Valko determined a value of 35.07×10^{-7} cm^2/s for this dye, the concentration of the dye and NaCl being 0.20 and 2.925 g./l. respectively. The aggregation number at the temperature of the experiment (90 °C) is 1.4 and allowing

FIG. 16

EFFECT OF CONCENTRATION OF THE DYE ON THE DIFFUSION OF CHRYSOPHENINE G AT 70 °C IN PRESENCEOF 0.50 °/° NaCl.



for the effect of the concentration of the dye and NaCl used in the present work, it is reasonable to assume that the diffusion co-efficient determined under these conditions will be comparable to the values recorded in the last column of Table IX.

Diffusion of Chrysophenine G through "Cellophane".

In the following Tables, giving the values of the diffusion co-efficients of Chrysophenine and Chlorazol Pink Y, the same notations and symbols are used as in the case of Chlorazol Sky Blue FF, and a similar theoretical treatment is applied to these dyes, as well.

Table X

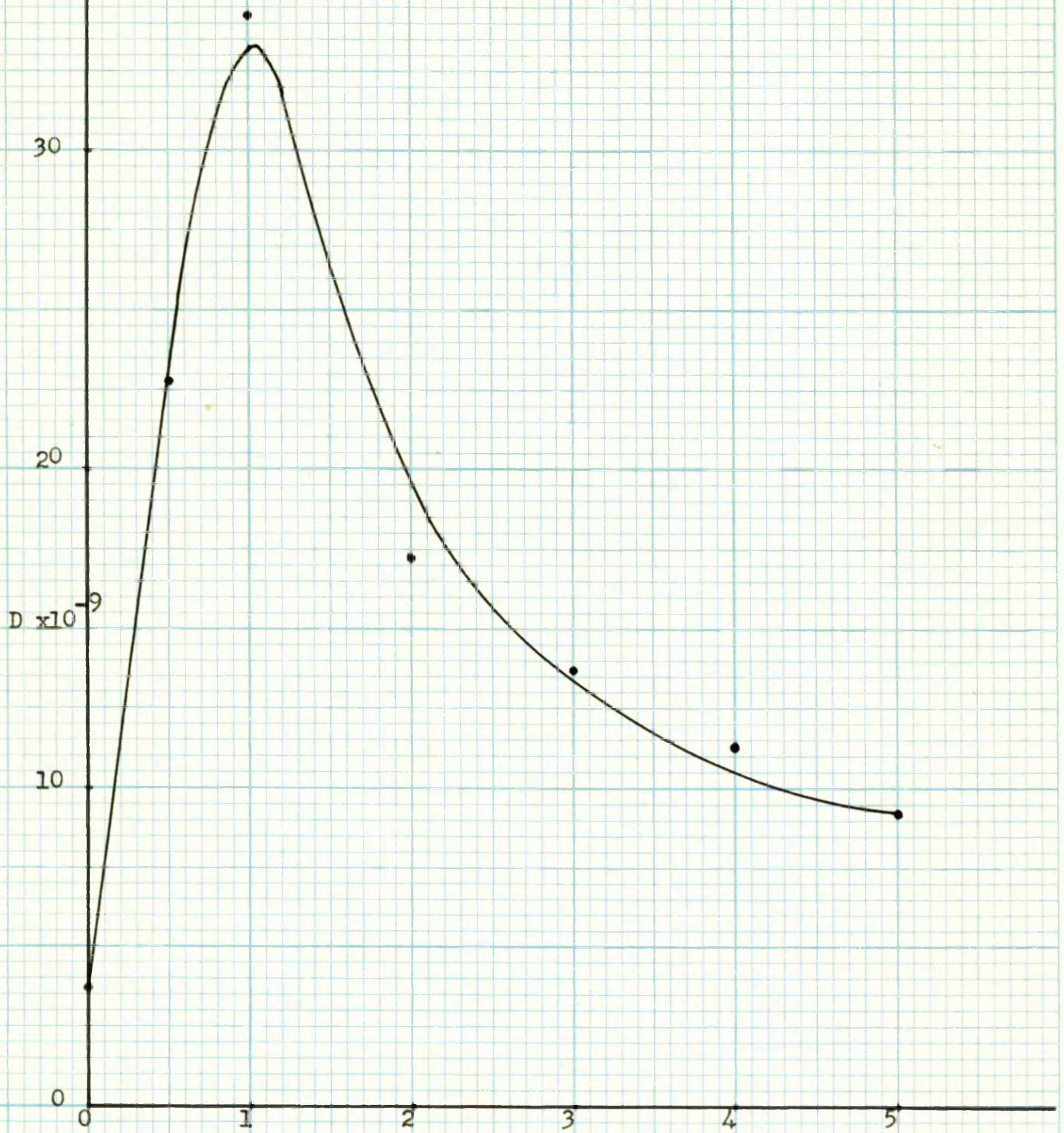
Diffusion of Chrysophenine G , X °/° dye + 0.50 °/° NaCl at 70 °C

X	L s	D_L cm^2/s	C_I g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.10	960	12.84×10^{-9}	7.15×10^{-3}	10.64×10^{-9}	8.12×10^{-9}	11.23×10^{-3}
0.15	1080	11.41	16.68	14.09	8.94	13.56
0.20	1320	9.33	15.98	17.25	11.20	13.30
0.25	1140	10.81	12.98	15.82	8.50	16.00

Fig. 16 shows that an inverse rectilinear relationship is found when the values of the diffusion co-efficient are plotted

FIG. 17

EFFECT OF THE CONCENTRATION OF SODIUM CHLORIDE ON THE DIFFUSION OF CHRYSOPHENINE G AT 70 °C.



against the concentration of the dye.

Table XI

Effect of X °/° NaCl on the Diffusion of Chrysophenine G, 0.20 °/° dye, at 70 °C

X	L s	D_L cm^2 /s	C_L g/cc	P g/cm^2 /s	D_E cm^2 /s	C_E g/cc
0.0	3240	3.80 $x10^{-9}$	7.31 $x10^{-3}$	3.19 $x10^{-9}$	11.87 $x10^{-9}$	2.31 $x10^{-3}$
0.05	540	22.83	2.05	5.41	12.74	3.66
0.10	360	34.24	2.22	8.77	14.33	5.25
0.20	720	17.13	4.07	10.94	12.17	9.63
0.30	900	13.70	11.08	17.54	13.43	11.23
0.40	1080	11.40	12.85	16.96	10.64	11.82
0.50	1320	9.33	15.96	17.25	11.20	13.30

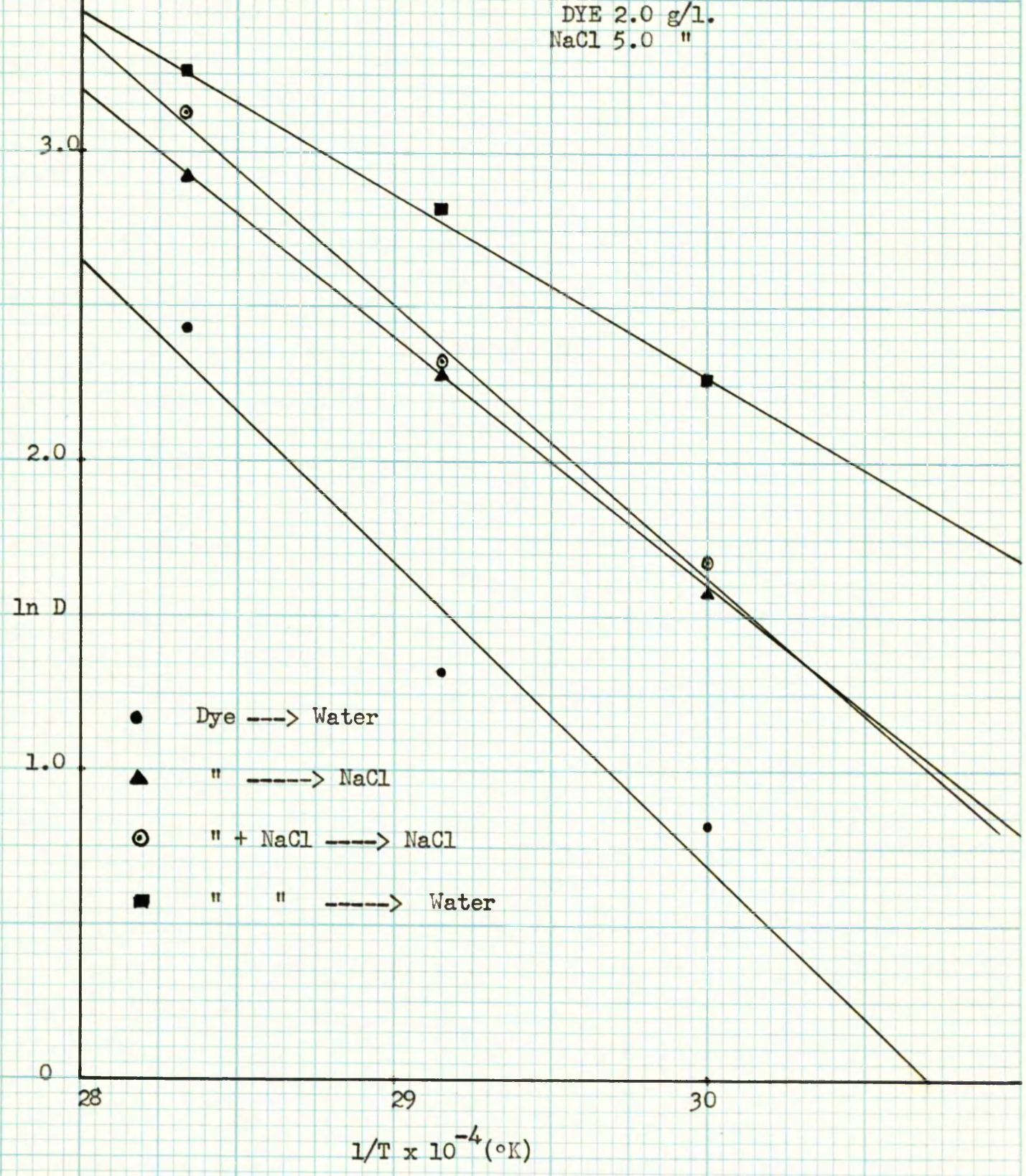
It will be seen from Fig. 17 that the diffusion co-efficient rises rapidly as the concentration of the electrolyte is increased and then falls gradually.

Table XII shows the effect of temperature when the dye diffuses in solutions with the composition listed below. As in the case of Chlorazol Sky Blue FF, a value of energy of activation of diffusion has been calculated in each case and the plots of ln D_L against the reciprocal of absolute temperature are shown together in Fig. 18, from which the slopes of the lines give the factor E/R.

FIG. 18

EFFECT OF TEMPERATURE ON THE DIFFUSION OF CHRYSOPHENINE G

DYE 2.0 g/l.
NaCl 5.0 "



The composition of the solutions is given below.

Expt. 1. 0.20 °/° dye + 0.50 °/° NaCl, diffusing into 0.50 °/° NaCl.

" 2. " " " " Water.

" 3. " diffusing into Water.

" 4. " " " 0.50 °/° NaCl.

Table XII

Temp °C	L s	D_L cm^2 /s	C_L g/cc	P g/cm^2 /s	D_E cm^2 /s	C_E g/cc
			Expt. 1			
60	2340	5.27 $\times 10^{-9}$	18.46 $\times 10^{-3}$	11.23 $\times 10^{-9}$	6.13 $\times 10^{-9}$	15.76 $\times 10^{-3}$
70	1320	9.33	15.98	17.25	11.20	13.30
80	540	22.83	8.42	19.30	8.42	10.34
			Expt. 2			
60	1260	9.78	8.86	9.91	8.66	10.20
70	720	17.12	8.03	15.88	15.40	8.87
80	480	25.68	8.20	24.68	27.62	7.68
			Expt. 3			
60	5400	2.28	6.65	1.75	5.92	2.55
70	3240	3.80	7.31	3.19	11.86	2.31
80	1080	11.40	3.54	4.68	20.94	1.92

Table XII continued.

Expt. 4

60	2520	4.90	12.26	6.93	6.11	9.75
70	1320	9.33	10.62	11.46	10.37	9.46
80	720	17.07	5.83	11.52	14.60	6.90

The slopes of these lines and hence the energies of activation of diffusion are set out below.

Expt.	Slope, E/R, x 10^2	E, Cal./degree/mole.
1	- 87.95	-17,396
2	- 60.00	-11,868
3	- 98.15	-19,414
4	- 89.52	-17,707

Membranes in Series.

Two membranes of "Cellophane" were compressed together with a rubber roller on a flat surface to make good contact with each other and the experiment was carried out as usual at 70 °C, using 0.20 °/° and 0.50 °/° of the dye and NaCl respectively. The experiment was repeated with three membranes and the results are set out in Table XIII on the next page.

Table XIII

Diffusion of Chrysophenine G, throgh "Membranes In Series " at 70 °C

Membranes	L s	D_L cm^2 /s	C_L g/cc	P g/cm^2 /s	D_E cm^2 /s	C_E g/cc
1	1320	9.33×10^{-9}	15.98×10^{-3}	17.25×10^{-9}	11.20×10^{-9}	13.30×10^{-3}
2	3960	12.62	11.22	8.70	8.92	15.34
3	7380	15.03	9.19	5.32	11.63	11.80

These values are calculated on the basis of 1 to 3 layers of the film and C_E denotes the mean of the amount of the dye in one film. However, the analysis of the compound films is as follows :-

Two membranes	Inner	18.84×10^{-3} g / cc
	Outer	11.84 "
Three membranes	Innermost	17.65 "
	Middle	11.70 "
	Outermost	6.05 "

From the absorption values of the dye concentration in the 3 - membrane experiment, the corresponding concentration gradients can be calculated. They are given below as function of the distance from the boundary, x = 0.

x (0.0086 cm)	Conc. gradient, g/cc/cm.
1	2.05
2	1.36
3	0.70

A plot of the concentration gradient against distance falls on

FIG. 19

CONCENRATION GRADIENT OF CHRYSOPHENINE G AGAINST DISTANCE.

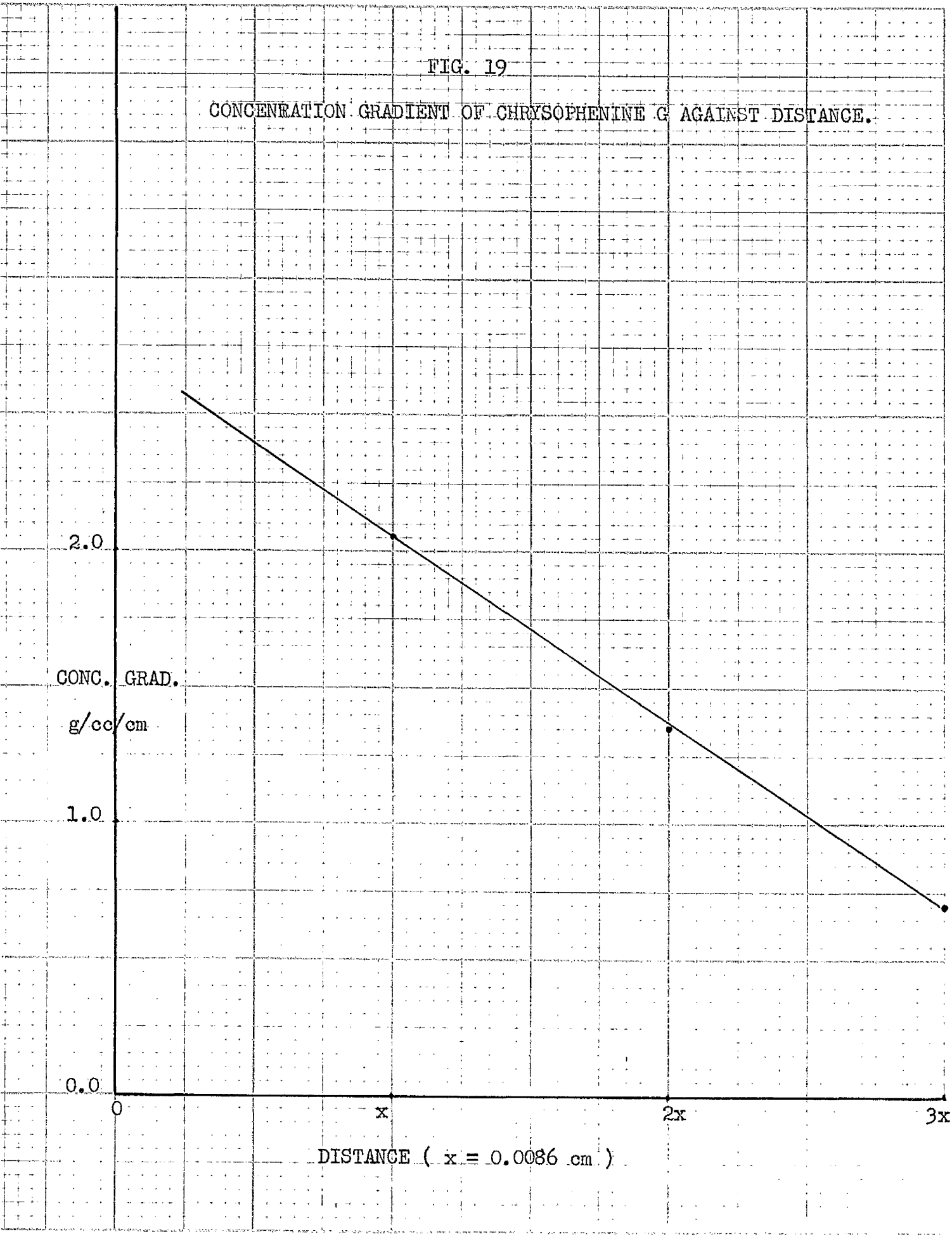
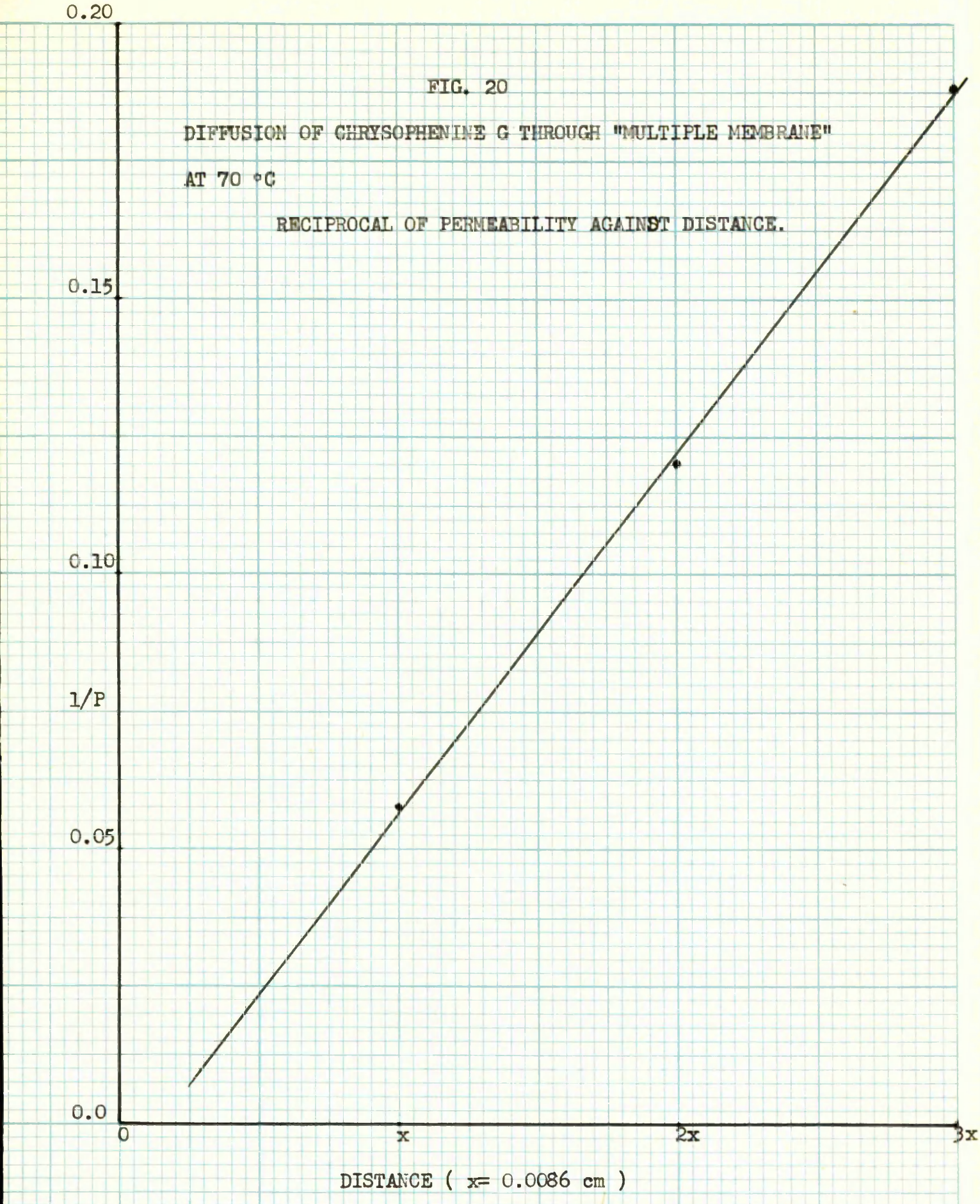


FIG. 20

DIFFUSION OF CHRYSOPHENINE G THROUGH "MULTIPLE MEMBRANE"

AT 70 °C

RECIPROCAL OF PERMEABILITY AGAINST DISTANCE.



a straight line as is shown in Fig. 19.

Similarly, the concentration gradient in 2 - membrane experiment is as follows:-

x (0.0086 cm)	2.19 g/cc/cm
2x	1.38 "

Referring back to Table XIII, it will be seen that the permeabilities P_3 , P_2 , P_1, of the 3, 2, and 1 thicknesses of the film are 5.32, 8.70 and 17.25 (10^{-9} g/cm^2/s) and that the first and the second values are respectively, 1/3 and 1/2 of the third value. These values can be expressed by the relation

$$\frac{1}{P} = \frac{1}{P_1} + \frac{1}{P_2} + \frac{1}{P_3} + \ldots\ldots$$

Since in the present case, the same material is used in the experiments, $P_1 = P_2 = P_3$ and therefore, the permeability P of the compound film, consisting of n pieces together can be obtainedd from $1/P = 1/ n P_1$, where P_1 is the permeability when one thickness is used. The reciprocals of the permeablities in Table XIII fall on a straight line when plotted against distance. Fig. 20.

Tables X and XI are reproduced below in a different manner and the treatment of Standing and Coworkers [6] is applied to these data as was done in the case of Chlorazol Sky Blue FF (Refer to Tables VII, VIII and IX). The values of D_0, the free diffusion co-efficient have been calculated from D_L and the equilibrium

absorption value S of the dye.

Table XIV

Diffusion of Chrysophenine G, X °/° dye + 0.50 °/° NaCl at 70 °C

Weight of one disc of "Cellophane" used = 0.046 g.

Concentration of Dye		D_A (D_L)	S, g/kg.	$D_0 = D_A \cdot S/C_B$
X °/°	C_B, Molar	cm /s, 10^{-9}		cm^2 /s, 10^{-6}
0.10	0.00158	12.84	19.98	61.13
0.15	0.00237	11.41	23.50	113.10
0.20	0.00316	9.33	21.73	64.20
0.25	0.00395	10.81	28.26	77.34

Table XV

Diffusion of Chrysophenine G, 0.20 °/° dye + X °/° NaCl at 70 °C.

X	C_B, Molar Conc. of Dye	Same notations as above.		
0.00	0.00316	3.80	4.30	5.17
0.05	"	22.83	9.46	46.68
0.10	"	34.24	9.26	100.35
0.20	"	17.13	17.00	92.16
0.30	"	13.70	19.82	85.93
0.40	"	11.40	20.87	75.29
0.50	"	9.33	21.73	64.15

The values in the last column have been compared with those in literature [9] for the diffusion co-efficient of this dye in aqueous solutions. At 60 and 90 °C, when the dye (0.50 g/l.)

diffuses in pure water, the values recorded are 15.0 and 22.2 x 10^{-6} cm^2 /s, respectively, and the corresponding values for diffusion in the presence of NaCl at 60 and 90 °C are as below:-

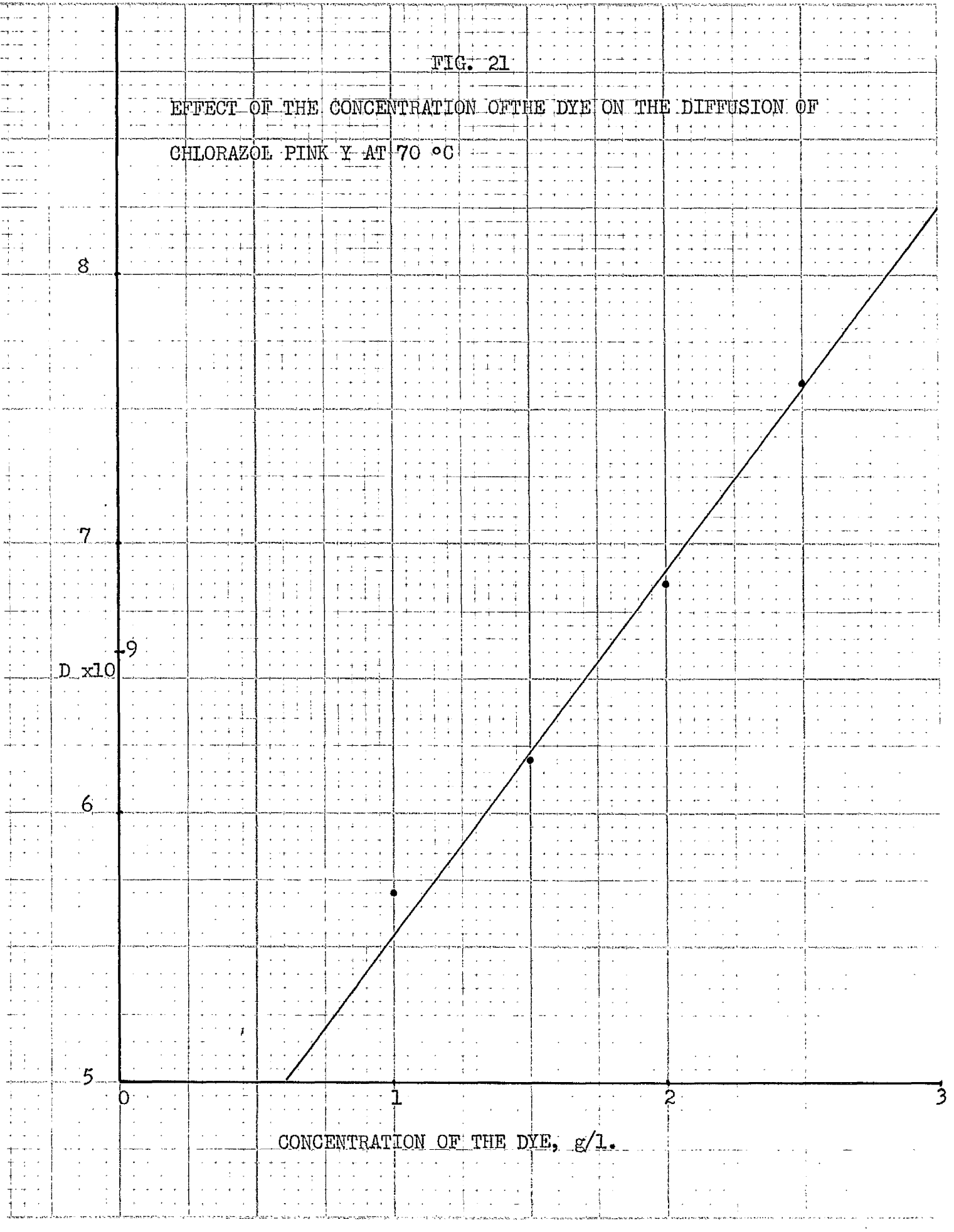
0.50 g/l. dye +	2.0 g/l.	NaCl at	90 °C	11.7 x 10^{-6} cm^2 /s.
"	1.0	"	60	6.89 "

Again, it will be seen that these figures are approximately 10 - 15 times smaller than those in the last columns of Tables XIV and XV, with the exception of the value 5.17 x 10^{-6} cm^2 /s when there is no electrolyte present.

However, if the equilibrium absorption value S of the dye is expressed as g per 100 g of the substrate, instead of g/kg as used in the treatment of Standing and Coworkers [6], the values of D_0 calculated from the time-lag data, fall very close to those found in literature, both for Chlorazol Sky Blue FF and Chrysophenine G.

FIG. 21

EFFECT OF THE CONCENTRATION OFTHE DYE ON THE DIFFUSION OF CHLORAZOL PINK Y AT 70 °C



Diffusion of Chlorazol Pink Y through "Cellophane"

Table XVI

Diffusion of Chlorazol Pink Y, X °/° dye + 1.0 °/° NaCl at 70 °C

X	L s	D_L cm^2 /s	C_L g/cc	P g/cm^2 /s	D_E cm^2 /s	C_E g/cc
0.10	2160	5.71 $\times 10^{-9}$	9.75 $\times 10^{-3}$	6.43 $\times 10^{-9}$	6.37 $\times 10^{-9}$	8.74 $\times 10^{-3}$
0.15	1980	6.22	12.00	8.60	6.76	10.94
0.20	1800	6.85	14.04	11.11	9.35	10.22
0.25	1620	7.60	13.60	12.00	8.40	12.25

The plot of the diffusion co-efficient against the concentration of the dye yields a linear relationship, as seen in Fig. 21.

Table XVII

Diffusion of Chlorazol Pink Y, 0.20 °/° dye + X °/° NaCl at 70 °C.

X			Same notations as above			
0.00	4680	2.64	2.87	0.88	7.54	1.00
0.05	1800	6.85	3.26	2.58	10.73	2.07
0.10	1080	11.41	3.55	4.68	12.44	3.22
0.20	1260	9.92	5.60	6.32	10.40	5.23
0.40	1260	9.92	6.83	7.72	8.72	7.61
0.60	1620	7.60	10.87	9.56	9.42	8.92
0.80	1620	7.60	11.11	9.67	9.25	9.80
1.00	1800	6.85	14.04	11.11	9.35	10.22

FIG. 22

EFFECT OF THE CONCENTRATION OF SODIUM CHLORIDE ON THE DIFFUSION OF CHLORAZOL PINK Y AT 70 °C

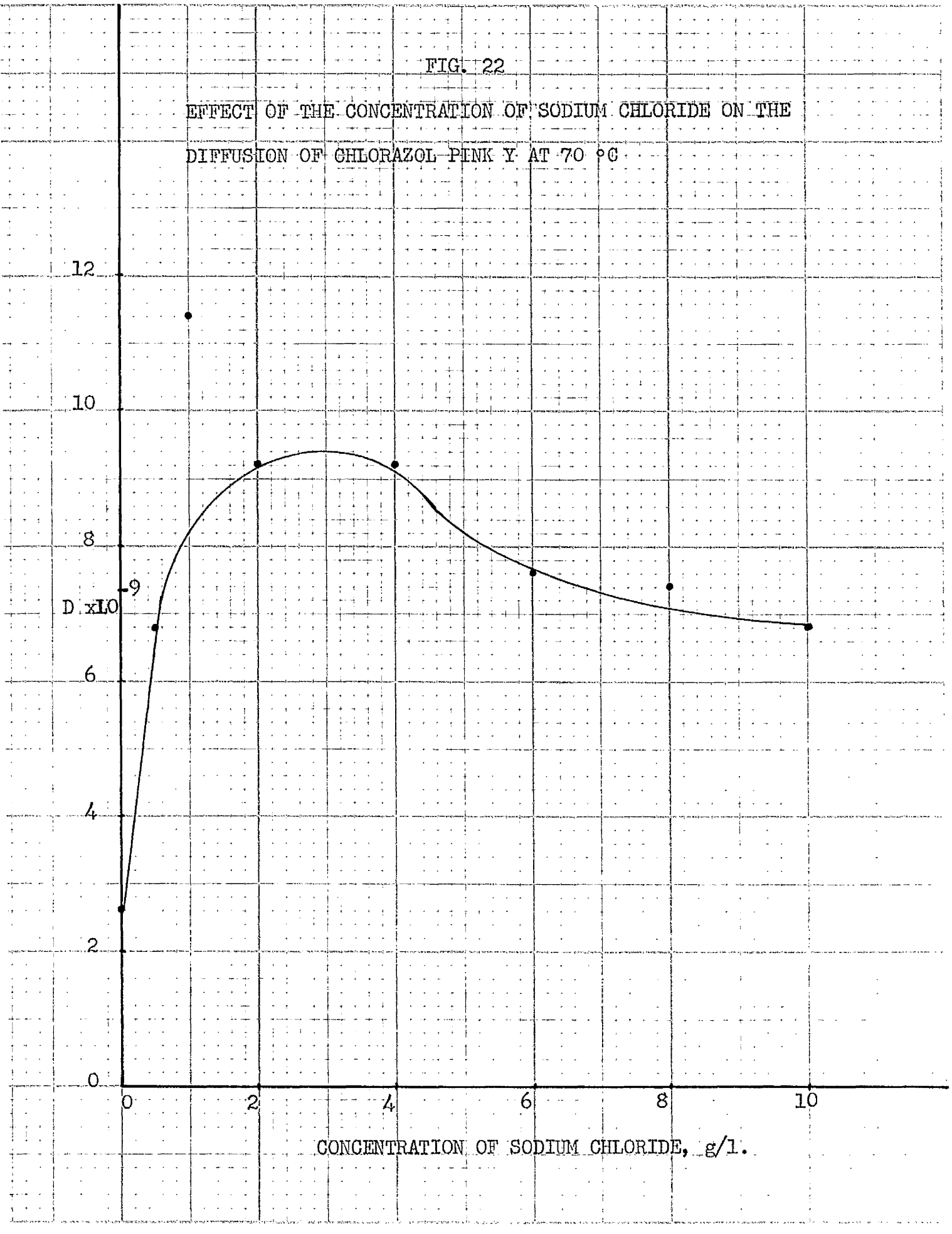


Fig. 22 shows graphically how the diffusion co-efficient is affected by the concentration of the electrolyte. The rise in the value of the diffusion co-efficient during the early additions of salt is sharp, but beyond the maximum, the fall is comparatively gradual and will probably reach a limiting value at a concentration of about 1.5 °/° NaCl.

Table XVIII

Effect of temperature on the diffusion of Chlorazol Pink Y

Expt. 1 0.20 °/° dye + 1.0 °/° NaCl diffusing into 1.0 °/° NaCl.

Expt. 2 " diffusing into Water.

Temp. °C	L s	D_L cm^2 /s	C_L g/cc	P g/cm^2 /s	D_E cm^2 /s	C_E g/cc
Expt. 1						
60	4680	2.64 x10^{-9}	14142 x10^{-3}	4.39 x10^{-9}	4.06 x10^{-9}	9.29 x10^{-3}
70	1800	6.85	14.04	11.11	9.35	10.22
80	900	13.70	6.54	10.35	12.90	6.90
Expt. 2						
70	4680	2.64	2.87	0.88	7.54	1.00
80	2880	4.28	2.94	1.47	12.65	1.00
90	1620	7.60	3.00	2.63	19.10	1.17

These data are shown in Fig. 23 and an energy of activation of diffusion has been calculated, which is - 19,483 and - 12,520 cal./degree/mole for the two sets of experiments 1 and 2 respectively.

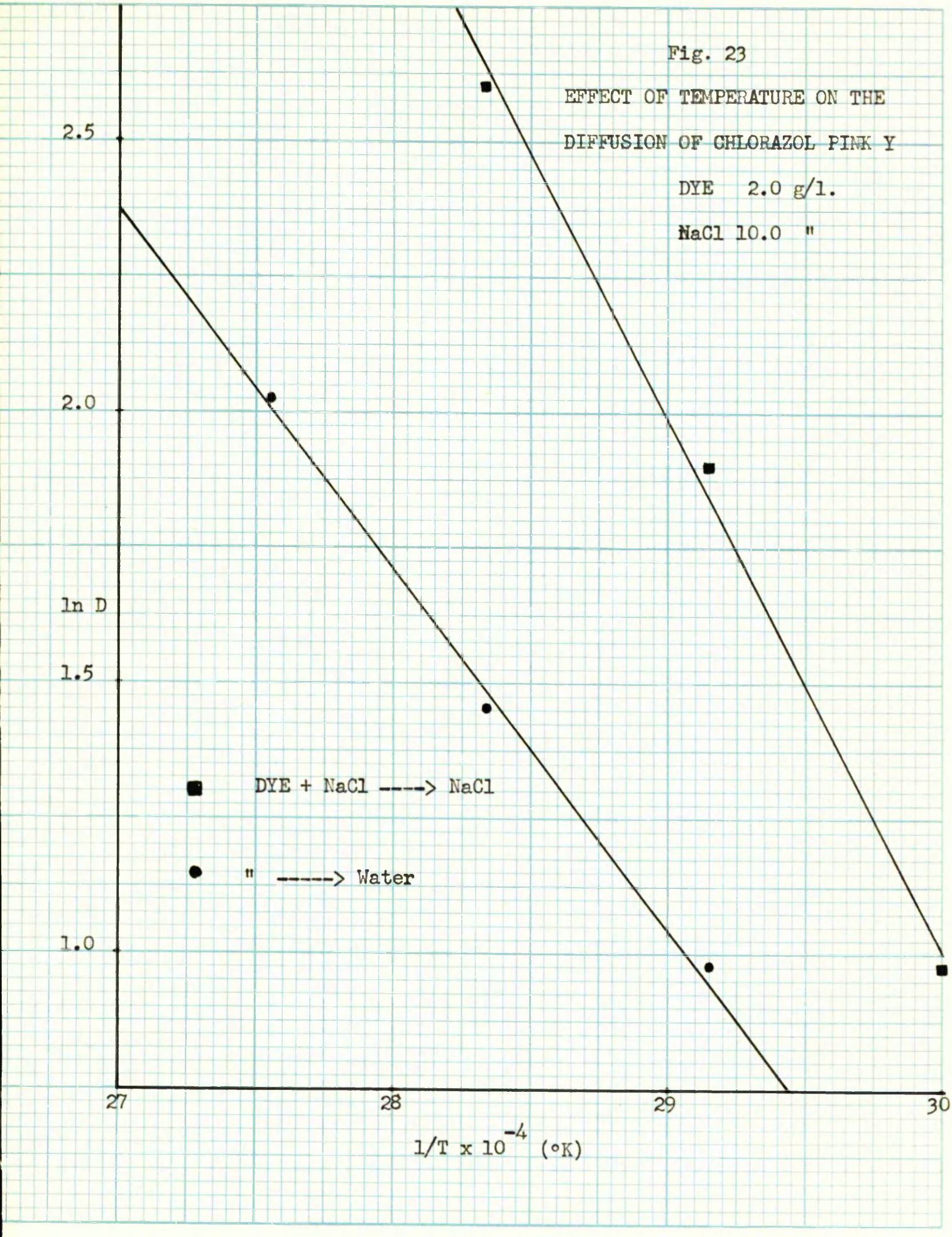


Fig. 23
EFFECT OF TEMPERATURE ON THE
DIFFUSION OF CHLORAZOL PINK Y
DYE 2.0 g/l.
NaCl 10.0 "
2.5
2.0
ln D
1.5
1.0
DYE + NaCl ----> NaCl
" -----> Water
27
28
29
30
1/T x 10^-4 (°K)

On comparing these values with the corresponding values for Chlorazol Sky Blue FF and Chrysophenine G, it is found that Chlorazol Sky Blue FF and Chlorazol Pink Y show a similar, but different behaviour from that of Chrysophenine G. The energies of activation of diffusion for the three dyes are set out below.

Dye	E (cal./degree/mole), when diffusing	
	in presence of NaCl	in absence of NaCl
Chlorazol Sky Blue FF	- 17,189	- 15,509
" Pink Y	- 19,483	- 12,520
Chrysophenine G	- 11,868	- 19,414

Further, referring back to Tables II (p.122) and X (p.133) and XVI (p.141) for these dyes, it is found that while the diffusion co-efficient of Chlorazol Sky Blue FF and Chlorazol Pink Y increases with the concentration of the dye, that for Chrysophenine G shows a decrease when the concentration of the dye is increased. Crank and Henry [10] (cf.p63) have examined a number of theoretical diffusion co-efficients varying in different ways with the concentration, and have arrived at the conclusion that if the diffusion co-efficient increases uniformly with the concentration, absorption is quicker than desorption; but if the diffusion co-efficient decreases uniformly with the concentration, the converse is true. This statement agrees well with the behaviour of these three dyes, for there is experimental evidence that Chrysophenine G comes off readily from the film, while the other two dyes offer considerable

resistance to their removal and in fact, the last traces are difficult to remove even on repeated extraction experiments. Diffusion, as described in these experiments, consists of absorption of the dye on one face of the film and desorption on the other. It therefore follows that in the case of Chlorazol Sky Blue FF and Chlorazol Pink Y, the presence of salt would enhance the absorption many fold, while the corresponding change in desorption would not be so effective, with the result that diffusion would be comparatively retarded and the dye molecules would have to acquire higher energies of activation than when the absorption is less, as in the absence of salt. However, in the case of Chrysophenine G, the converse argument applies and that explains why the activation energies stand in the opposite order.

Membranes in Series.

Two thicknesses of the film were used in the experiment, the results of which are given below. The results, both from the time-lag method and the equilibrium absorption value are consistent with each other.

The dye, 0.20 °/° + 1.0 °/° NaCl, diffuses at 70 °C.

Thick-ness	L	D_L	C_L	P	D_E	C_E
	s	cm^2 /s	g/cc	g/cm^2 /s	cm^2 /s	g/cc
1	1800	6.85×10^{-9}	14.04×10^{-3}	11.11×10^{-9}	9.35×10^{-9}	10.22×10^{-3}
2	5040	9.92	9.20	5.21	9.26	9.70

These values are calculated on the basis of two thicknesses of "Cellophane" and it will be seen that the permeability of two films is approximately 1/2 of that of one film. The analysis of C_E is as follows:

Inner layer 13.67 x 10^{-3} g/cc

Outer " 5.73 "

Diffusion of Acid Dyes through "Cellophane"

In the following Tables, results pertaining to the diffusion of two acid dyes, viz., Naphthalene Scarlet and Carbolan Brilliant Green are given. As was stated in Chapter IV under "Experimental" (p. 118), the linear plot of the amount of the dye diffused against time, passes through the origin and does not yield any intercept on the t - axis. Consequently, the time-lag method is no longer applicable. Furthermore, since there is no absorption of the dye taking place on the film, the measurements of the equilibrium concentration of the dye are of no avail either.

Since the acid dyes leave the "Cellophane" practically untinted (the slight tint is due to the dye held mechanically and disappears immediately when the film is put in cold water), it is apparent that the diffusion proceeds in a random manner through the water-filled channels in the film, like the free diffusion of the dye in water. It is assumed that the average length of these channels is given by the thickness of the film in the water-swollen state. Moreover, since the dye present only in the pores controls the diffusion, it is assumed that the concentration of this is that of the internal solution. The diffusion co-efficient is then given by

$$dS / dt = - D.A. dC / dx$$

$$= - D.A. C / l$$

where C is the concentration of the internal solution (g./l.)

FIG. 24

EFFECT OF THE CONCENTRATION OF THE DYE ON THEPERMEABILITY CONSTANT OF NAPHTHALENE SCARLET AT 50 °C

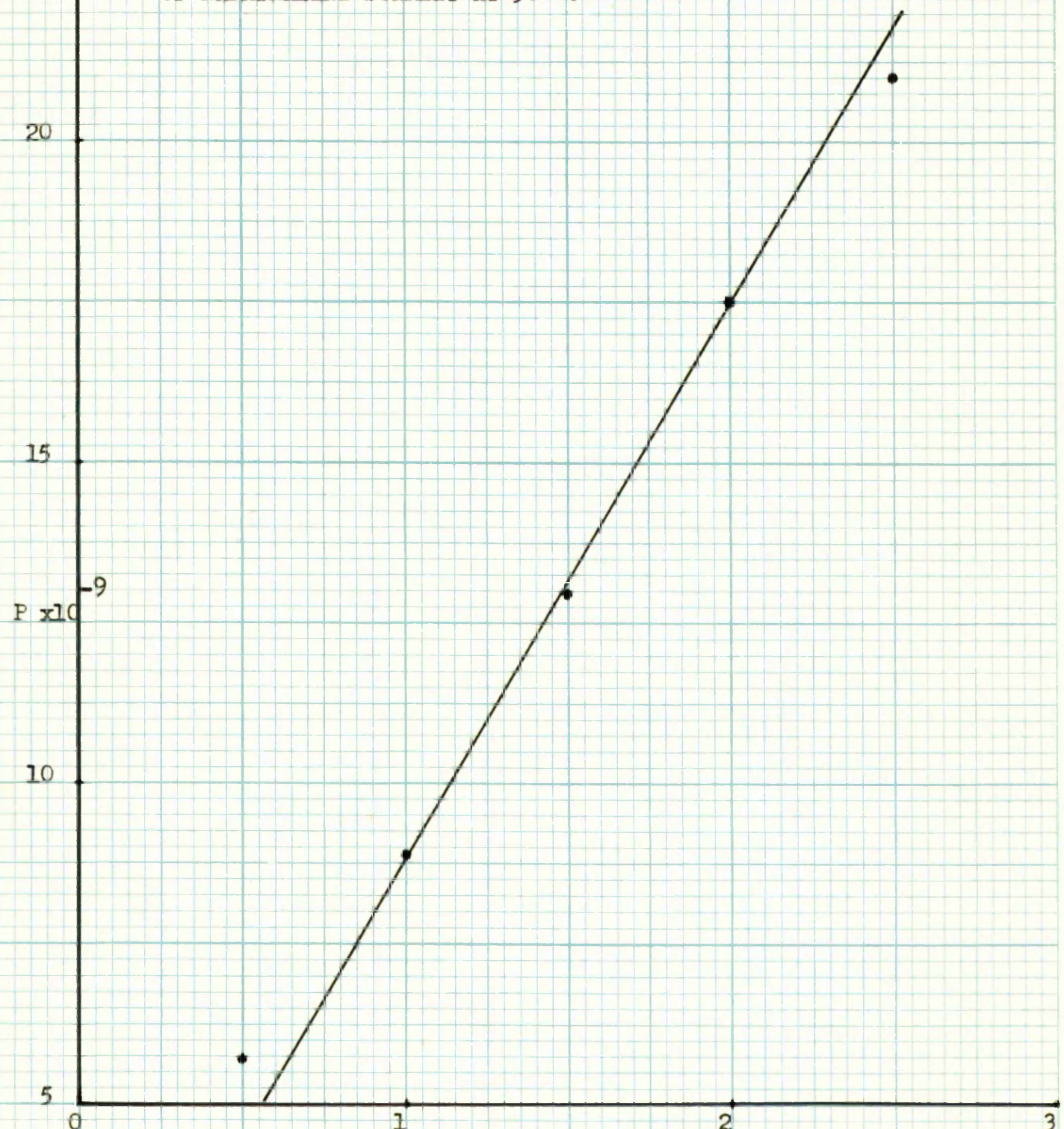
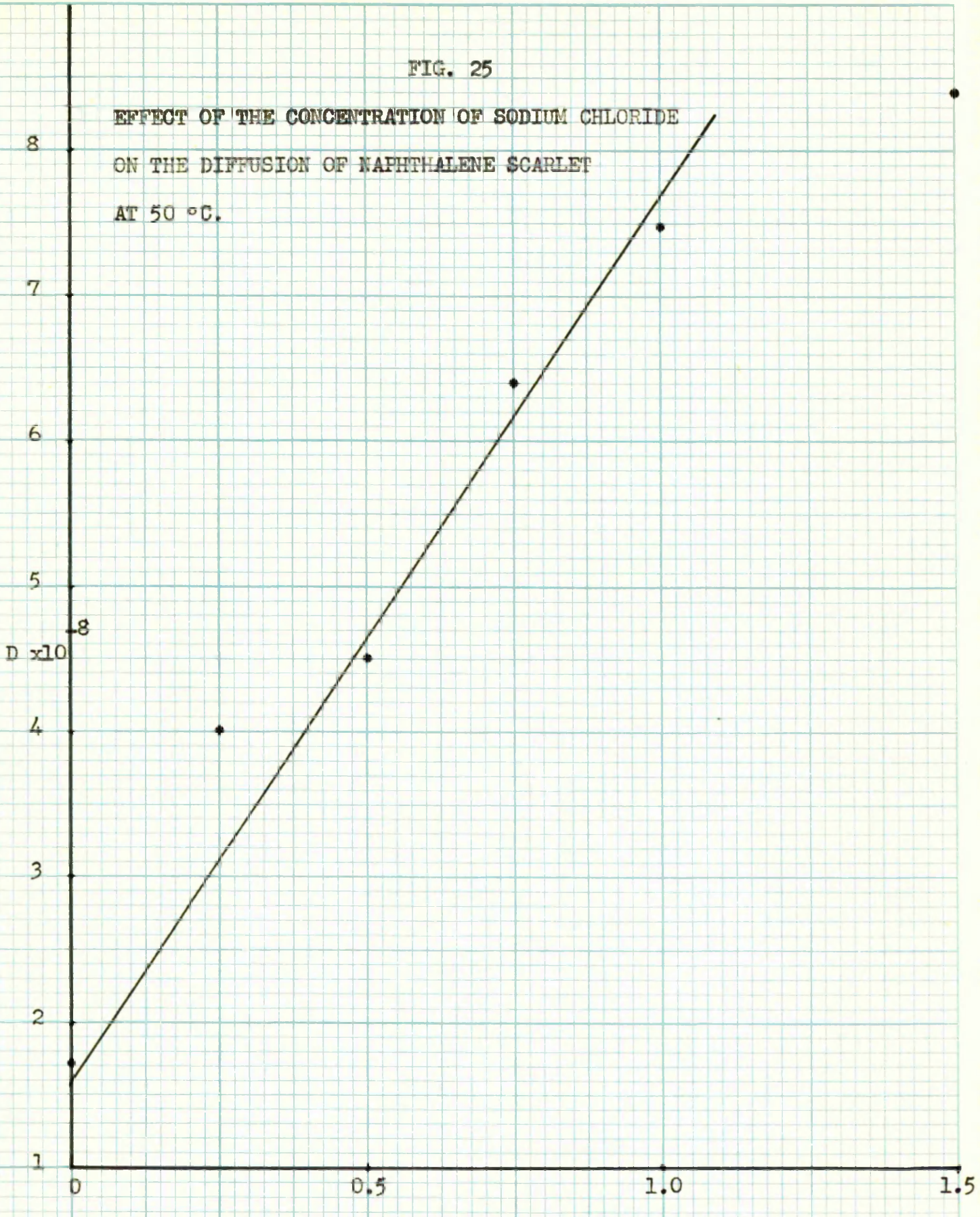


FIG. 25

EFFECT OF THE CONCENTRATION OF SODIUM CHLORIDE ON THE DIFFUSION OF NAPHTHALENE SCARLET AT 50 °C.



and l is the thickness of the film. Other factors have the usual significance.

Table XIX

Diffusion of Naphthalene Scarlet, X g/l. dye + 10 .0 g/L. NaCl at 50 °C

X	dS/dt = P, g/cm^2 /s	D, cm^2 /s
0.5	5.7×10^{-9}	9.81×10^{-8}
1.0	8.77	7.54
1.5	12.87	7.38
2.0	17.54	7.54
2.5	21.05	7.48

It will be seen that while the permeability P increases continuously with the concentration in a linear manner (Fig. 24) the diffusion co-efficient , with the exception of one value, remains constant at about $7.5 \times 10^{-8} cm^2$ /s , which is more or less characteristic of free diffusion in water.

Table XX shows the effect of the concentration of the electrolyte on the diffusion of the dye at 50 °C, when the concentration of the dye is kept constant. The plot of the diffusion co-efficient against the concentration of the electrolyte, as shown in Fig. 25, falls on a straight line, which takes a slight curvature at higher concentration of salt, showing thereby a tendency to achieve a maximum value when the concenttation of salt is raised

further. Since the concentration of the dye is kept constant, the corresponding plot of permeability against the concentration of NaCl will yield a similar result because of the fact that the diffusion co-efficient is obtained by dividing the permeability by a constant factor, i.e., A.C / l.

Table XX

Effect of the Concentration of NaCl, X g/l. on the diffusion of Naphthalene Scarlet , 2.0 g/l. dye, at 50 °C.

X	P, g/cm^2 /s	D, cm^2 /s
0.00	3.95×10^{-9}	1.70×10^{-8}
0.25	9.33	4.02
0.50	10.38	4.46
0.75	14.62	6.43
1.00	17.54	7.54
1.50	19.60	8.42

Effect of Temperature.

Diffusion of the dye was observed at different temperatures with the following composition of the internal and external solutions.

Expt. 1 2.0 g/l. dye + 10.0 g/l. NaCl into 100 g/l NaCl.

Expt. 2 " 1.0 " " 1.0 "

Expt. 3 " " " " Water

Expt. 4 " into 1.0 g/l. NaCl

Expt. 5 2.0 g/l. dye into Water.

Table XXI

Temperature °C	P, g/ cm^2 /s	D, cm^2 /s
Expt. 1		
50	32.54×10^{-9}	13.96×10^{-8}
60	40.64	17.48
70	51.40	22.25
Expt. 2		
50	17.54	7.54
60	24.47	10.56
70	32.46	15.42
Expt. 3		
50	10.00	4.30
60	14.97	6.42
70	29.24	12.60
Expt. 4		
50	10.15	4.36
60	14.62	6.29
70	19.00	8.15
Expt. 5		
50	3.95	1.70
60	7.31	3.00
70	15.50	5.05

FIG. 26

EFFECT OF TEMPERATURE ON THE DIFFUSION OF NAPHTHALENE SCARLET

DYE 2.0 g/l
NaCl 1.0 "

● Dye ----> Water

■ " + NaCl ----->Water

▲ " -----> NaCl

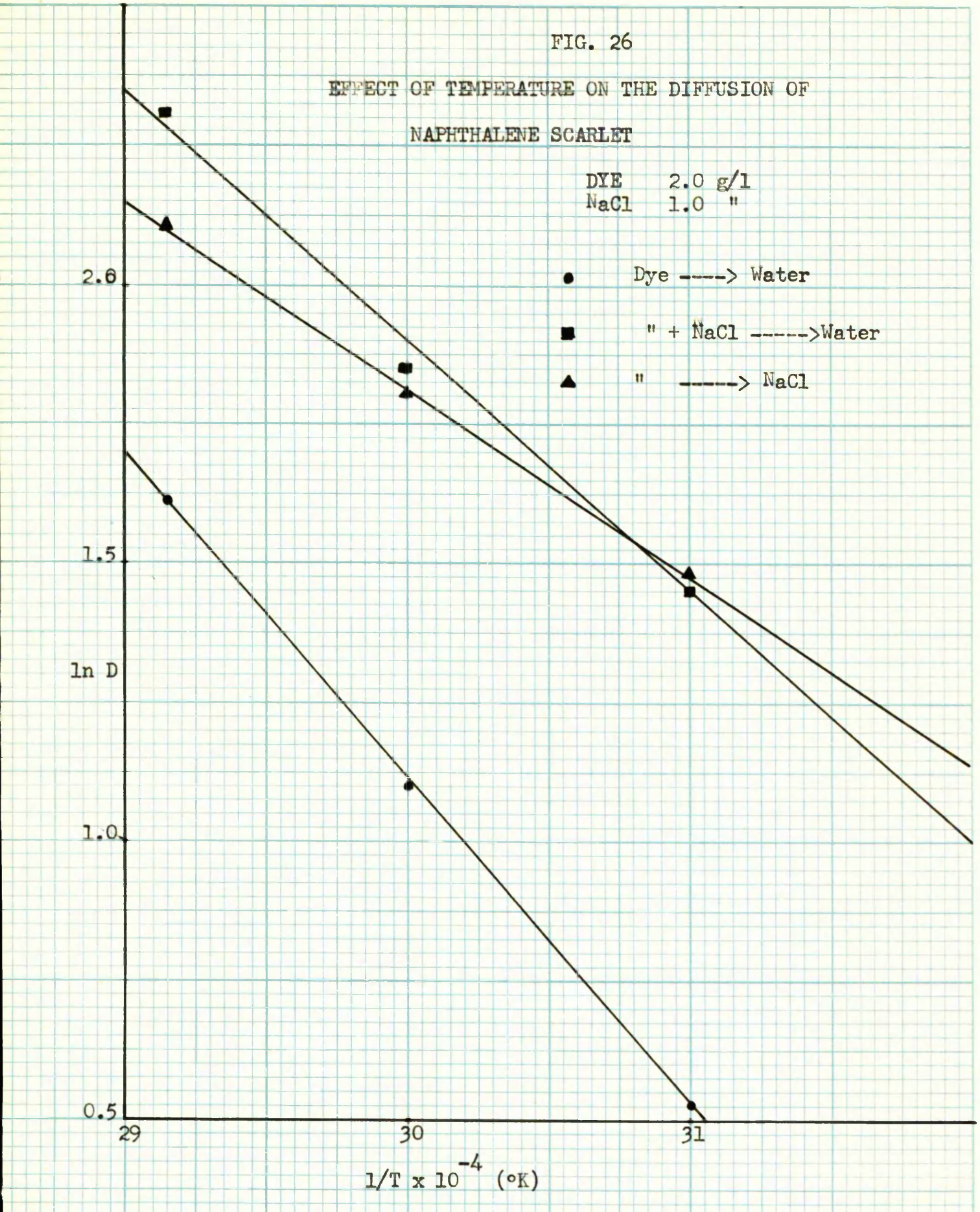
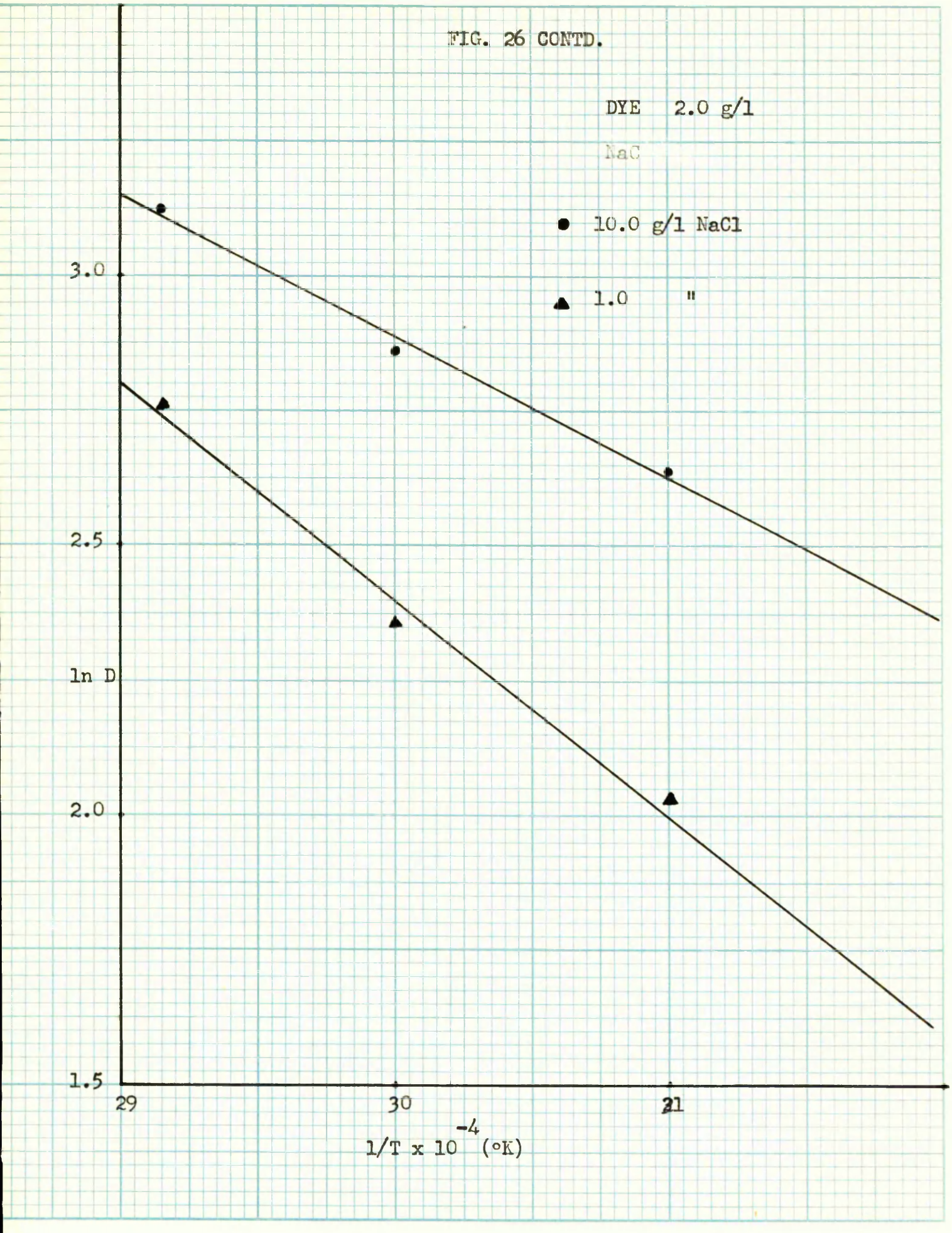


FIG. 26 CONTD.



The plots of ln D against the reciprocal of absolute temperature are shown in Fig. 26 from which the slopes of the lines have been determined and hence the energies of activation of diffusion, which are set out below.

Experiment	Slope, E/R	E, cal./degree/mole
1	$- 26.24 \times 10^{2}$	- 5,190
2	- 40.63	- 8,037
3	- 45.71	- 9,041
4	- 33.82	- 7,690
5	- 58.53	- 11,576

Diffusion of Carbolan Brilliant Green through "Cellophane".

Table XXII

Diffusion of Carbolan Brilliant Green, X g/l. dye + 2.0 g/l. NaCl at 70 °C

X	P, $g/cm^2/s$	D, cm^2/s
1.0	7.11×10^{-9}	6.11×10^{-8}
2.0	9.74	4.19
3.0	17.54	5.03
4.0	30.26	6.58
5.0	30.70	5.29

FIG. 27

EFFECT OF THE CONCENTRATION OF THE DYE ON THE PERMEABILITY CONSTANT OF CARBOLAN BRILLIANT GREEN AT 70 °C.

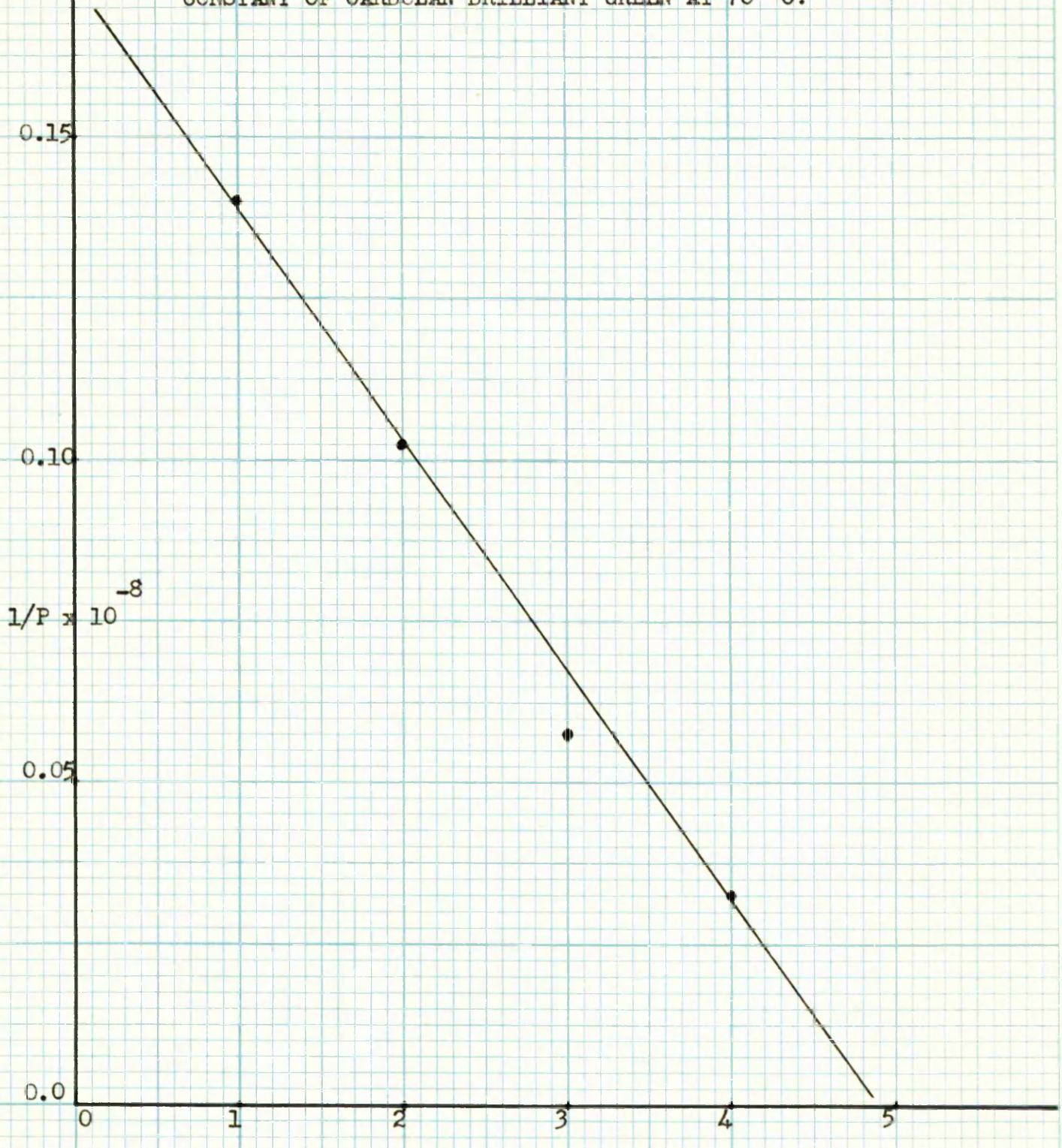
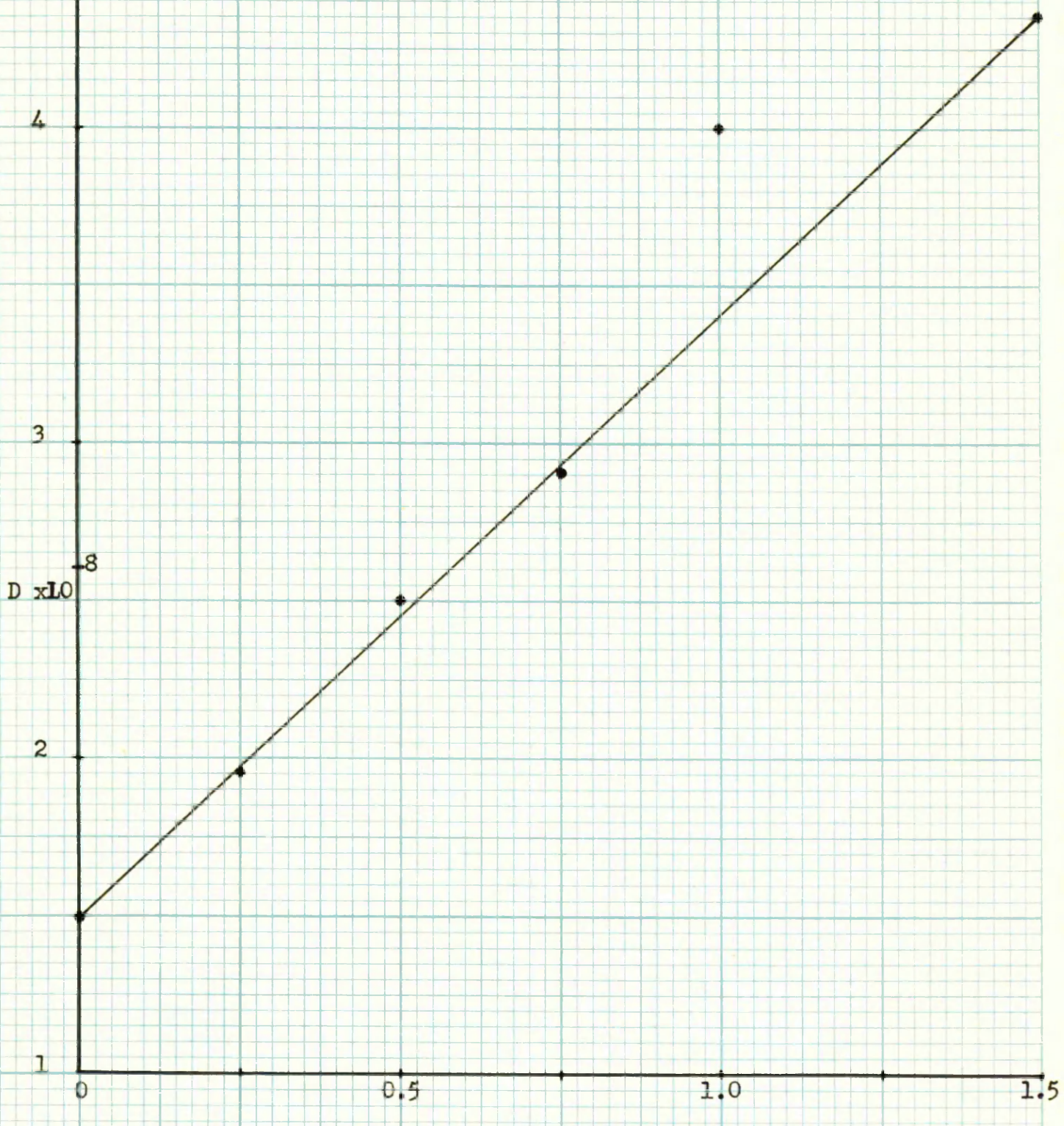


FIG. 28

EFFECT OF THE CONCENTRATION OF SODIUM CHLORIDE ON THE DIFFUSION OF CARBOLAN BRILLIANT GREEN AT 70 °C



The diffusion co-efficient does not show uniform variations with the concentration of the dye, but when the reciprocal of P is plotted against the dye concentration, the points fall on a straight line, as shown in Fig. 27

Table XXIII

Effect of X g/l. NaCl on the Diffusion of Carbolan Brilliant Green, 5.0 g/l. dye, at 70 °C

X	P, g/cm^2 / s	D, cm^2 /s
0.00	8.63×10^{-9}	1.51×10^{-8}
0.25	11.26	1.94
0.50	14.36	2.47
0.75	16.70	2.87
1.00	23.39	4.02
1.50	27.19	4.68

Fig. 28 shows graphically the recti-linear variations in the value of the diffusion co-efficient with the concentration of the electrolyte. The corresponding plot of P against the electrolyte concentration would also fall on a straight line because of the fact that P is a sub-multiple of D, the common factor being A.C/l.

Table XXIV shows the results of using more than one thickness of the film, the concentration of the dye and electrolyte being kept constant.

FIG. 29

PERMEABILITY CONSTANT OF CARBOLAN BRILLIANTGREEN AGAINST THETHICKNESS OF THE FILM AT 70 °C

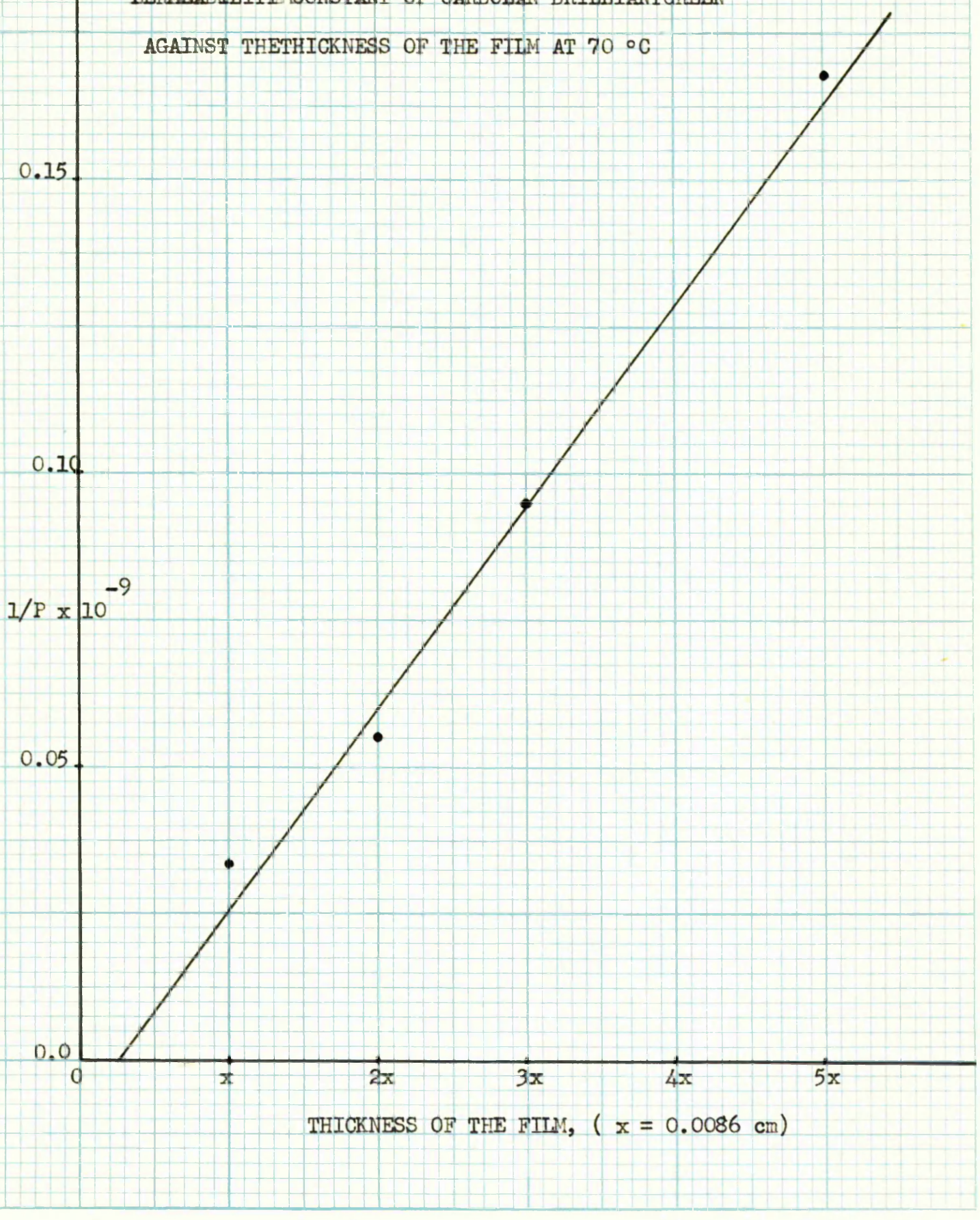


Table XXIV

Diffusion of Carbolan Brilliant Green, 5.0 g/l. dye + 2.0 g/l. NaCl, through "Multiple"Membrane at 70 °C.

No. of Thicknesses	P, $g/cm^2/s$	D, cm^2/s
1	30.70×10^{-9}	5.29×10^{-8}
2	16.81	5.53
3	10.53	5.43
5	5.99	5.16

It is clear from the above table that the diffusion coefficient remains fairly constant, while the permeability varies according to the relation

$$1/P = 1/ n P_1$$

where P_1 is the permeability of one thickness and P that of n thicknesses. The plot of the reciprocal of P against distance falls on a straight line, as shown in Fig. 29.

Effect of Temperature on the Diffusion of Carbolan Brilliant Green.

The results of the following set of experiments are given in Table XXV.

Expt. 1 5.0 g/l. dye + 2.0 g/l NaCl diffusing into 2.0 g/l NaCl.

Expt. 2 " " " " Water

Expt. 3 " diffusing into Water.

Expt. 4 " " " 2.0 g/l NaCl.

Table XXV

Temperature °C	P, $g/cm^2/s$	D, cm^2/s
Expt. 1		
60	22.22×10^{-9}	3.82×10^{-8}
70	30.70	5.29
80	43.86	7.54
Expt. 2		
60	14.62	2.51
70	26.32	4.53
80	29.53	5.08
Expt. 3		
60	6.64	1.14
70	8.63	1.51
80	13.60	2.34
Expt. 4		
60	12.98	2.33
70	16.52	2.84
80	18.71	3.22

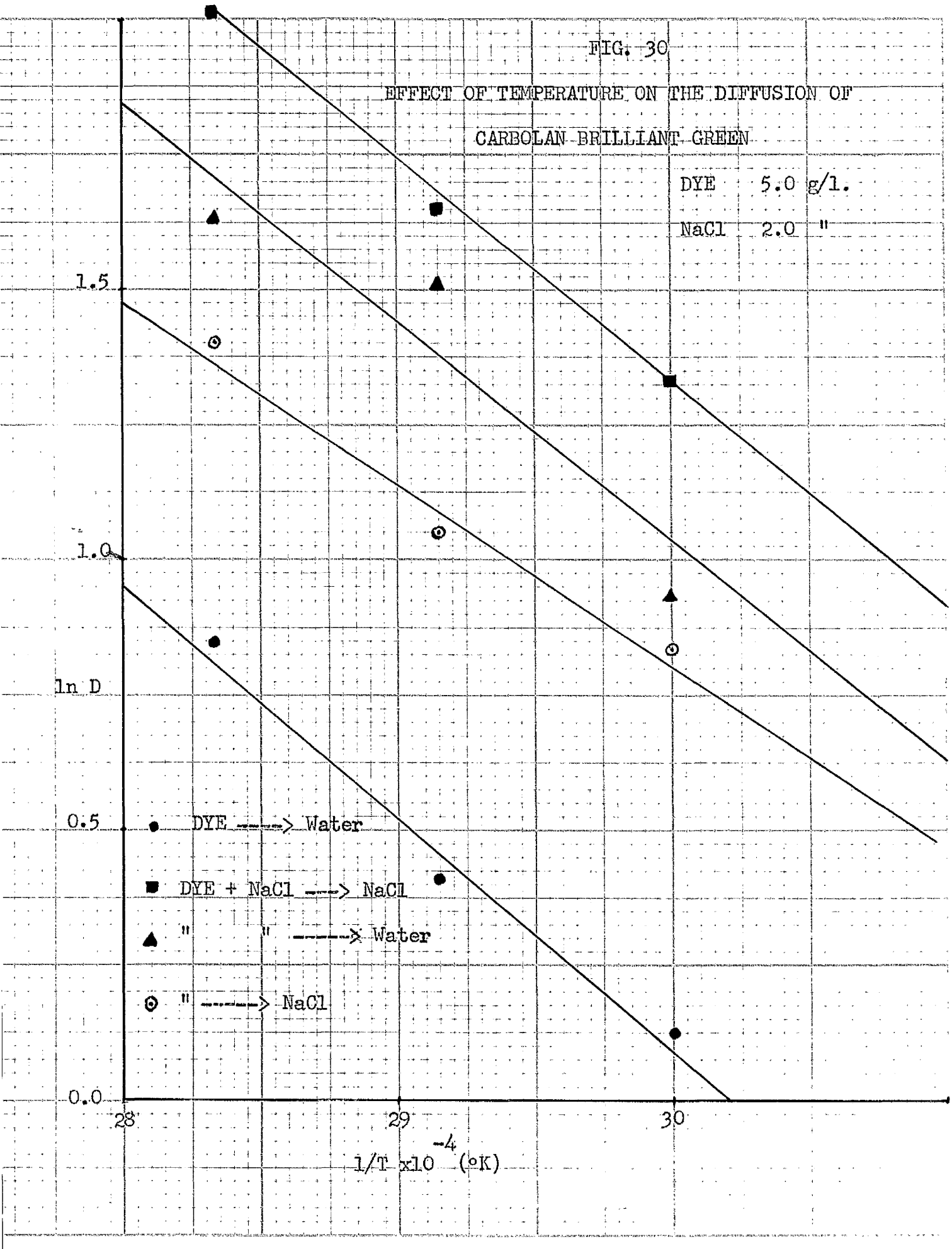
These data are graphically represented by Fig. 30, where ln D is plotted against the reciprocal of the absolute temperature. The slopes of the lines and the corresponding

FIG. 30

EFFECT OF TEMPERATURE ON THE DIFFUSION OF CARBOLAN BRILLIANT GREEN

DYE 5.0 g/l.

NaCl 2.0 "



energies of activation of diffusion are given below :-

Experiment	Slope, E/R	E, cal./degree/mole.
1	-40.71×10^{2}	- 8,052
2	- 40.18	- 7,948
3	- 43.18	- 8,541
4	- 33.62	- 6,650

Once again, as was the case with Naphthalene Scarlet, the energy of activation of diffusion is the highest when the dye diffuses in the absence of the electrolyte.

Diffusion of Dyes through Cellulose Acetate.

Introduction

A number of ester and ether derivatives of cellulose are known [11], but the only derivative which is used to any great extent for textile purposes is the acetate. The commercially produced cellulose acetate is not completely acetylated because of the reason that the tri-acetate is soluble only in expensive solvents, such as, chloroform, whereas the so-called " secondary cellulose acetate " with a lower degree of acetylation, corresponding roughly to 2.5 acetyl groups per glucose unit of cellulose [12] is readily soluble in acetone.

An outstanding property of cellulose acetate is that its dyeing behaviour is completely different from that of the cellulose from which it is derived. Direct dyes, almost without exception, leave the fibre completely uncoloured, as do most acid dyes [13]. The origin of this great change lies in the highly hydrophobic nature of cellulose acetate, as shown by low moisture regain of the fibre. Further, very little swelling of the fibre takes place in aqueous dye-baths, so that the intermicellar cannals are narrow and the entry of the dye molecules is not possible. Moreover, cellulose acetate shows a greater negative surface potential in water than cellulose and this will again assist the repulsion of anionic dyes.

As mentioned on page 5, cellulose acetate is one of the textile material which can be obtained in the sheet form and to which

the time-lag technique can be applied. Because of the completely different nature of the substrate, it was thought desirable to carry out the following experiments, by using a film of this material in the diffusion cell instead of "Cellophane", as described earlier. The dyes studied include, one direct dye, one acid dye and two cationic, basic dyes.

Cellulose acetate sheet was punched into discs as described before, and the pieces were extracted with petroleum ether (b.p. 40 - 60 °C) for 8 hours to remove the plasticizers etc. This solvent was selected because it is chemically inert towards cellulose acetate and does not cause any swelling [14]. The last traces of the solvent were removed under vacuum at 50 $\pm$ 2 °C and finally the extracted pieces were thoroughly rinsed in water at 40 - 45 °C.

Experiments were carried out at 70 °C as usual with the purified cellulose acetate film, using one direct dye, Chlorazol Pink Y, 2.0 g/l. and one acid dye, Naphthalene Scarlet, 2.0 g/l., both in the presence and absence of the electrolyte. The time allowed for these experiments was 7 hours and it was found that no dye diffused through or even tinted the film.

The experiments with these dyes were repeated, using a uniform concentration, 20.0 °/° of urea, (See Part II) and even in this case, no diffusion or absorption of the dyes occurred at all.

In the case of the two basic dyes, i.e., New Victoria Blue 2B and Malachite Green, the behaviour was altogether different. A solution of 0.125 g/l. of New Victoria Blue 2B, in presence of 5.0 g/l. NaCl , was found to stain the film slightly without causing any diffusion through the film. When NaCl was replaced by 20.0 °/° urea solution, a fairly heavy shade resulted, but no diffusion took place. Incidentally, it was noticed that the solubility of 0.125 g/l. of New Victoria Blue 2B was far better in urea solution and even an amount of the dye, 10 times larger, i.e., 1.25 g/l. needed only slight warming to give a clear solution. (The system had to be warmed to about 60 °C to get a clear solution, even if there was 5.0 g/l NaCl or not,) when there was only 0.125 g/l. of the dye.)

Malachite Green, too, showed a similar behaviour towards diffusion through cellulose acetate film, though 1.25 g/l. dye + 5.0 g/l. NaCl coloured the film to a heavier shade than New Victoria Blue 2B. But in the presence of 20.0 °/° urea, it was found that almost all the dye was deposited on the film in the form of a thick layer, which could be scrapped off, leaving a heavily dyed surface underneath.

When the experiment was conducted for comparatively shorter times, using the film and the solution in a flask instead of the diffusion cell, clear dyeing was observed to take place. After the experiment was finished, the dyed pieces were treated with 20.0 °/° urea solution to see if the process was reversible or not. It was found that urea solution did remove both of the dyes, i.e., New

Victoria Blue 2B and Malachite Green from the dyed film, when it was gently warmed with urea solution.

From the above experiment it is clear that the dyeing of cellulose acetate with these two dyes is reversible, at least in the presence of urea. Considering diffusion of dyes through a film as a double process,--- absorption on the ingoing side and desorption on the outgoing side ---- it is safe to conclude that although cellulose acetate was dyed, yet the dye had not penetrated deep enough to be desorbed on the other side.

This view was checked in a different manner. Cross-sections of the film used in the diffusion cell were cut on a microtone and viewed under a microscope(magnification 40 times). It was observed that one face of the film was left absolutely untinted, while the dye had penetrated approximately to 1/3 thickness of the film from the other side, under the conditions of these experiments. It would have taken the dye, roughly 24 hours, to diffuse through the film at 70 °C and that explains why the diffusion right through the film did not occur when the experiment was conducted for 7 hours only.

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PART II

DIFFUSION OF DYES IN CELLULOSE - UREA SYSTEM.

CHAPTER VI

Part II

Diffusion of Dyes in Cellulose-Urea System.

Introduction.

Textile fibres swell when placed in water and both the swelling and extent of swelling are matters of great technical importance from the point of view of various textile processes. The way the fibres swell depends on their chemical constitution and the amorphous - crystalline order distribution, and greatly affects their behaviour during dyeing and finishing. For this reason, a knowledge of the swelling behaviour of the fibres is valuable in order to ascertain the suitability of a particular process before carrying it out.

Generally speaking, the swelling of high polymeric material in a swelling agent or its preliminary swelling prior to its dissolution in a solvent is frequently regarded as a distinct phenomenon from ordinary diffusion [1], though when solution takes place, the two phases are ultimately miscible in all proportions and under stagnant conditions, it is possible to observe a visible, although not sharp, boundary between the solid and the viscous, swollen solid and again, between the latter and the dilute solution. If swelling is treated according to this pattern, it is easy to conceive an exchange of positions between the molecules of the polymer and the penetrant, in which the liquid molecules diffuse and occupy the positions previously occupied by the macromolecules.

Taking the point of view that macromolecular substances consist essentially of a molecular net-work structure with junctions points i.e., cross links either of a chemical or physical nature, there are a number of consequences regarding the nature of structural changes upon swelling, shrinking and deformation, which have been recognised in the field of polymers [2,3,4,5,6]. Both swelling and deformation bring about a change in spatial arrangement of the junction points and the degree of crumpling or coiling the molecular chains interconnecting them. Swelling is thus essentially associated with a certain amount of "uncoiling" of the molecular chains.

This "uncoiling" of the molecular chains is of great importance in some of the textile operations, such as dyeing; indeed this is the main factor in determining the receptivity of a fibre to a dye. X - rays examination of the dyed fibres has failed to reveal any change in the crystalline pattern due to the penetration of dyes and in consequence, it is believed that the dye molecules cannot penetrate beyond the surface of the crystallites and may largely lie in the amorphous regions.

It has been shown by McBain and Kistler [7], Morton [8], and Boulton and Coworkers [9] that dry "Cellophane" is practically impermeable to compounds such as ethyl and amyl alcohols having small molecular weight, but if it is first soaked in water, these compounds and even bigger molecules, like those of direct dyes, can wriggle through the swollen structure. Boulton and Coworkers [9]

expressed the view that the amorphous regions have a capacity for the sorption of water and as a result of this sorption, osmotic forces tend to cause the cellulose chains to move apart. In doing so, the net-work expands and the "trap doors" are opened to the the entry of the dye molecules.

Swelling of cellulosic fibres beyond the water-swollen dimensions is caused by most acids, bases including the amines, aqueous solutions of strong electrolytes and certain organic compounds (See Ott [10]). Recently some work has been carried out by Preston and Coworkers [11] on the aqueous solutions of urea - cellulose system and they have demonstrated a positive sorption of urea by cellulose, when the latter is brought into contact with a solution of the former. These authors have measured the volumetric and axial swelling caused by urea solutions and have shown that there is a decrease in the tensile strength of viscose filaments when they are treated with urea solutions.

The intensifying action of urea on printing fabrics has been noticed by Haller [12], who has shown that urea does not act as an electrolyte in direct dye-baths nor does urea increase the dispersion of direct dyes. However, he has not put forward any explanation for the action of urea on printing. It has been suggested that the use of urea in printing pastes may depend upon its hygroscopic power [13] or its solvent action on dyes [14], but no experimental evidence has been forth-coming.

The object of this work has been to study the cellulose - urea solutions system in detail from the view point of the diffusion of dyes into cellulose, both according to the usual technique of dyeing as well as observing the rate of diffusion of dyes through a film of regenerated cellulose in the diffusion cell described in Part I. This study includes the determining the absorption isotherms, the levelling effect of urea solutions on Class C direct dyes and the accessibility of cellulose to urea solutions as compared with water alone, by direct measurements of the heat evolved when the former is placed in an excess of the latter. Finally, a mechanism has been offered, which explains these facts satisfactorily.

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Reactivity of Cellulose Fibres.

The properties and reactions of cellulose are greatly influenced by the proportions of the crystalline and amorphous regions and it is now well understood that the former is far less accessible than the latter to chemical attacks or physical phenomina, such as sorption and swelling.

The solubility and swelling of high polymers are complex functions of at least two principal factors [1]:

1. The flexibility of the chain molecules
2. The attractive forces between the chains.

In a crystalline region, the chain molecules are tightly packed and this arrangement provides contacts between the neighbouring chains along the whole length. That means that their attractive forces are mutually satisfied, whereas in the amorphous regions, the picture is otherwise, for the inter-molecular forces remain unsatisfied. This gives rise to higher solubility and swelling of an amorphous region than that of one of a higher order of crystallinity. It is, therefore, obvious that the ease of swelling will decrease with increasing chain order and with increasing size of the crystallite regions.

Swelling of Cellulose Fibres.

The swelling of fibrous materials differs from its counterpart, the solution of a substance with a low molecular weight, in

that the latter is characterised by complete disintegeration of the substance into individual molecules or ions, whereas in swelling, the macro-molecules separate to a limited extent. The capacity for great swelling without complete dispersion is a characteristic property of the fibrous macromolecular structures, and its origin lies in the nature and the great length of polymer chains [12]. A process wherein the individual chain molecules are separated from each other, though without shortening them, would be one degradative in nature and chemically irreversible. The phenominon of swelling is closely associated with the structural changes and the mechanism of the reactions involved.

According to Katz [2], a solid is said to swell, when it imbibes a liquid, while at the same time,

1. it does not lose its apparent homogeneity,
2. its dimensions are enlarged,
3. its cohesion is diminished, i.e., instead of hard and brittle, it becomes soft and flexible.

Since in cellulose, the regions of higher crystallinity are separated by those of lower crystallinity, the swelling behaviour is depicted by the inter-chain forces, operating in the non-crystalline regions due to the presence of polar groups. As a consequence of the change in the dimensions, the swelling agent should be able to disrupt these secondary valency bonds, which in the fibre, hold each chain molecule to its neighbour, without breaking the covalent

bond which provides the link within each chain. It, therefore, implies that it would be harder for a liquid to break the strong net-work of hydrogen bonding in a crystalline region than to disrupt a similar "loose" frame-work in less orderly regions. It is thus safe to conclude that all the swelling occurs in the amorphous regions of cellulose and that the amorphous content is responsible for its reactions.

Swelling may be divided into two distinct classes (Katz[2]) as revealed by the X-ray diagrams of the swollen fibres, viz., into intercrystalline and intracrystalline. Comparative X-ray and microscopic studies on the same material indicate that in the case of intercrystalline swelling, such as is produced by water or weak acids or alkalis, all of the swelling takes place in the amorphous regions. The pattern itself is not changed. This swelling, on taking up the liquid in the intercrystalline phase, apparently accounts for the appearance of the amorphous pattern in the X-ray diagram, which is superimposed upon the unchanged crystalline cellulose pattern [2,3].

With the intracrystalline swelling such as with ethyl-diamine [4], when there is the appearance of a new crystalline pattern corresponding to that of the swelling compound, the cellulose crystallites may be observed to increase in diameter. This increase is of the same order as the lateral increase in the unit cell dimensions calculated from X-ray diagrams [3]. Intracrystalline

swelling is also produced by strong alkali, but here it is accompanied by excessive fibre swelling and the appearance of a liquid pattern superimposed upon the crystalline pattern of the new swelling compound. In this case, the liquid pattern and most of the fibre swelling has been explained by simultaneous swelling of the intercrystalline material [5].

In a second type of swelling, such as that produced by sulphuric acid, when the crystalline pattern disappears completely, microscopic examination shows the micelle to swell first in diameter and later in all directions [6]. In this type, the swelling is progressive with further addition of the reagent until the pattern disappears. In such cases where solution occurs at elevated temperatures, the process of solution can usually be attributed to increased swelling, resulting from simultaneous degradation which is enhanced at high temperatures.

To understand the type and extent to which swelling occurs, we should have a knowledge of the following [9]:-

1. Nature of the swelling agent.
2. Its specific interaction with cellulose.
3. Distribution of amorphous and crystalline regions in the given sample of cellulose.

Intercrystalline Swelling.

Cellulose when placed in water, merely swells by imbibition

and indeed the water is able to penetrate only the amorphous or more loosely packed regions of cellulose. This system affords the best example of intercrystalline swelling. Swelling starts as soon as cellulose is brought into contact with water vapour and it increases with increased R.H., till it attains its maximum value when the fibre is submersed in water [7], and it is assumed to a first approximation that the volume increase due to swelling is additive, i.e., each water molecule contributes its normal molecular volume to the system [8]. However, the magnitude of the swelling depends upon the individual fibre as is shown by a maximum increase of 20 - 35 °/° in area of cross-section in natural fibres against the corresponding maximum increase of 50 - 70 °/° in regenerated fibres [7].

That the polarity and molecular volume of the penetrant have a marked influence on swelling is shown by the fact that organic liquids generally swell cellulose less than water, the order of the magnitude being the following in case of aliphatic alcohols[13].

Water < methanol < ethanol < propanol < n-butanol, negligible.

Benzene, too, produces negligible swelling, but its derivatives give increased swelling in the following order [10].

$-NO_2 > -Cl > -CHO > -NH_2 > -CH_3$.

This order is the same as that of decreasing dipole moments of these liquids.

Swelling with Aqueous Solutions of Organic Compounds.

Aqueous solutions of certain organic compounds cause swelling beyond the water-swollen dimensions [2]. The compounds, such as chloral hydrate, thiourea, resorcinol and benzene sulphonates, which seem rather inactive, give, in concentrated aqueous solutions, strong swelling of cellulose.

Katz [2] is of the opinion that all substances containing non-oxidised sulphur, which he has examined, with the exception of thiourea, cause strong swelling and the analogous oxygen compounds are less effective than the sulphur compounds. The phenomnon can be explained by considering a strong adsorption of the S-compounds on the surface of cellulose, the hydrophilic groups such as $-NH_2$ in thiourea bringing their influx of water, which is responsible for strong swelling. That the S-compounds work much more strongly than O-compounds, is probably due to the residual valency of oxygen in cellulose, which binds the sulphur of the organic compounds, increases its adsorption and hence a strong swelling results.

In the case of phenol and resorcinol, the phenolic groups are bound to the surface of cellulose and in the case of benzene sulphonates, the benzene nucleus is turned towards cellulose and the $-SO_3$ groups towards the liquid, so that it can act as a hydrophilic group and bring its sphere of water with it.

The swelling agent acts as a lubricant for the molecular chains to slip over each other, so that under appropriate conditions,

a transition of a meta-stable form such as amorphism to crystallinity can be effected. This is shown by the fact that "amorphous"cellulose produced by dry grinding [14,15], readily crystallises on swelling in water. A similar observation has been made by Waller and Coworkers[16] during the heating of rayon yarns at elevated temperatures in the presence of slight amount of water vapour, when crystallisation takes place. This is obviously due to the fact that swelling makes the chains slip over each other in the swollen regions and allows the re-ordering which is not possible at low temperatures. Preston and Nimkar [17], too, arrived at the same conclusion by subjecting rayon fibres to thermal treatment in closed vessels. The observed reduced swelling and consequently the reduced absorbency is attributed to a new pattern of cross-linkages or increased crystallinity of the samples. However, if the exposure to heat is made in excess of water [18], the absorbency of cellulose fibres is increased due to a momentarily freed hydrophobic group being satisfied by a water molecule. An exactly similar behaviour is expected from a penetrant which swells cellulose fibres in an an analogous, but intensified, manner to that of water.

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Chapter VII

Determination of the Absorption and Desorption Isotherms.

Preparation of the Fibres.

Viscose Yarn 30 %/° Stretch:- Hanks weighing about 25 mg were mildly scoured at 60 - 65 °C in 1 °/° ammonia for an hour, washed thoroughly with water and dried in the air. The air-dried hanks were transferred to a controlled humidity chamber and conditioned for a week. The loose ends of the hanks were trimmed and weighed on an accurate and sensitive torsion balance so that each hank was 20.0 mg. (Weight of the dry hank = 16.2 mg)

Cotton :- 30s/2, bleached cotton was employed and it was further purified in a manner as described above. The final weight of each hank was 40.0 mg. (Weight of the dry hank = 37.4 mg.)

Dyeing Technique and Estimation of the Dyes.

The dyeing experiments were carried out in Pyrex tubes, fitted with condensers to avoid evaporation at higher temperatures. The tubes were heated in a large water bath, in which the level of water was well above that of the dye solutions in the tubes.

The temperature control was within ± 1 °C.

The hanks of the yarn, prepared as above, were suspended from long silver wires, which could move freely through the condensers. When thermostatic conditions were obtained, the fibres were transferred to the dye solution and the experiment started.

The upper end of the silver wires rested, in the form of a hook, on a horizontal rod, which was moved up and down by means of an electric device. Each stroke was 3 cm long so that the fibre was always well within the dye solution. There were 60 strokes per minute. Under these conditions the reproducibility was good.

After continuing the experiment for a definite length of time, the fibres were taken out and rinsed in a small amount of chilled water and pressed between folds of filter paper. The extraction of the dye from the fibre was affected with hot 25 °/° aqueous pyridine, adding small portions at a time and collecting the dye solution. The final volume was made up according to the depth of the shade so as to get a good reading on the Spekker.

In the case of heavy shades of dye on the fibre, it was found difficult to remove the last traces of the dye, even on prolonged boiling treatment with aqueous pyridine or higher concentrations of the stripping agent. The residual colour on the fibre was compared to a similar tinted fibre from which the dye could be easily removed. It was found that the estimation of the latter was not possible on the Spekker, because its absorption of light was too small to give a reading. It was thus considered safe to neglect the residual dye on the heavily-shaded samples.

The amount of the dye taken up by the fibre (g/100 g of the dry fibre) was calculated with the help of a calibration chart of the dye in aqueous (25 °/°) pyridine.

The small weight of the fibre used in these experiments afforded easy manipulations in the experimental technique. Further, the concentration of the dye solution was purposely kept low (0.30 g/l. for Chlorazol Sky Blue FF), so that the absorption of the dye and subsequent diffusion into the mass of the fibre proceeded at a moderate speed and could be followed easily over different intervals of time and also at elevated temperatures, where equilibrium is rapidly reached. Moreover, the concentration of the dye-bath was adjusted so that no appreciable change occurred during the dyeing period and the bath was thus of "infinite" composition. The highest uptake of the dye for Chlorazol Sky Blue FF was 2.56 °/° at 80 °C in the presence of 5.0 g/l. NaCl, which corresponds to a reduction of 1.38 °/° in the concentration of the dye-bath.

In the following Tables, the uptake is expressed as g per 100 g of the dry fibre, against time and the concentrations of urea solutions.

Table XXVI

Absorption of Chlorazol Sky Blue FF(0.30 g/l. dye; 100 cc soln.)

by Viscose at 70 °C.

Uptake °/° ------>	Concentration of Urea, °/°					
Time, Hours	5	10	15	20	25	30
1/4	-	0.05	0.05	0.05	0.20	0.20
1/2	0.06	0.06	0.09	0.09	0.24	0.22
3/4	-	0.10	0.21	0.24	0.28	0.28
1	0.16	0.19	0.33	0.41	0.35	0.54
1 1/2	0.21	0.36	0.39	0.46	0.41	0.68
2	0.29	0.41	0.49	0.69	0.60	0.78
3	0.39	0.51	0.69	0.87	0.63	0.85
4	0.44	0.62	0.71	0.92	0.68	0.87
6	0.47	0.73	0.84	0.99	0.78	0.95

Table XXVII

Absorption of Chlorazol Sky Bluee FF by Viscose at 80 °C.

0.30 g/l. dye; 100 cc solution

Uptake °/° ⟶ / Time	Concentration of Urea, °/°						
	2.5	5	10	15	20	25	30
10 minutes	0.02	0.06	0.04	0.15	0.26	0.16	0.14
20 "	0.06	0.17	0.20	0.28	0.41	0.35	0.29
30 "	0.08	0.22	0.26	0.36	0.47	0.44	0.38
40 "	0.12	0.24	0.29	0.41	0.56	0.52	0.44
50 "	0.17	0.30	0.44	0.50	0.60	0.54	0.46
1 hour	—	0.35	0.38	0.52	—	0.56	0.48
1 1/2 hour	—	—	0.47	0.52	0.67	0.60	0.52
2 hours	0.21	0.43	0.60	0.65	0.70	—	0.55
3 "	0.31	0.53	0.62	0.71	0.73	0.63	0.56
4 "	0.34	0.61	0.65	0.73	0.76	0.68	0.57
6 "	0.37	0.63	0.67	0.77	0.77	0.70	—

Table XXVIII

Absorption of Chlorazol Sky Blue FF by Viscose at 90 °C

0.30 g/l. dye ; 100 cc solution

Uptake °/° ------> Time	Concentration of Urea, °/°						
	2.5	5	10	15	20	25	30
5 minutes	--	--	0.29	0.34	0.38	0.36	0.28
10 "	0.14	--	0.43	0.54	0.60	0.60	0.45
15 "	0.20	0.23	0.54	0.62	0.75	0.74	0.50
20 "	---	---	0.60	0.67	0.78	0.76	0.60
30 "	0.29	0.34	0.67	0.70	0.80	0.77	0.71
40 "	0.31	0.46 (45 min.)	0.79	0.81	0.84	0.81	0.68
50 "	0.35	---	0.88	0.89	0.86	0.83	0.70
1 hour	0.39	0.58	0.91	0.90	0.89	0.85	0.72
2 hours	0.56	0.69	0.98	1.01	0.98	0.88	0.83
4 "	0.68	0.80	1.11	1.11	1.09	1.03	0.91
6 "	0.72	0.90	1.17	1.23	1.23	1.17	1.07

Table XXIX

Absorption of Chlorazol Sky Blue FF by Viscose at 100 °C

0.30 g/l. dye ; 100 cc solution

Uptake °/° ---->	Concentration of Urea, °/°						
Time	2.5	5	10	15	20	25	30
5 minutes	--	0.09	0.33	0.35	0.38	0.36	0.37
10 "	0.14	0.18	0.46	0.49	0.51	0.46	0.43
20 "	0.17	0.26	0.49	0.51	0.53	0.51	0.48
30 "	0.19	0.31	0.52	0.55	0.54	0.52	---
40 "	0.30	0.34	0.54	0.58	0.57	0.55	0.54
50 "	0.32	0.35	0.56	----	0.59	0.56	0.56
1 hour	0.34	0.37	0.57	0.62	0.62	0.58	0.57
2 hours	0.35	0.50	0.62	0.65	0.69	0.64	0.62
4 hours	0.44	0.61	0.76	0.80	0.84	0.80	0.77
6 hours	0.48	0.69	0.88	0.95	1.00	0.96	0.91

FIG. 31

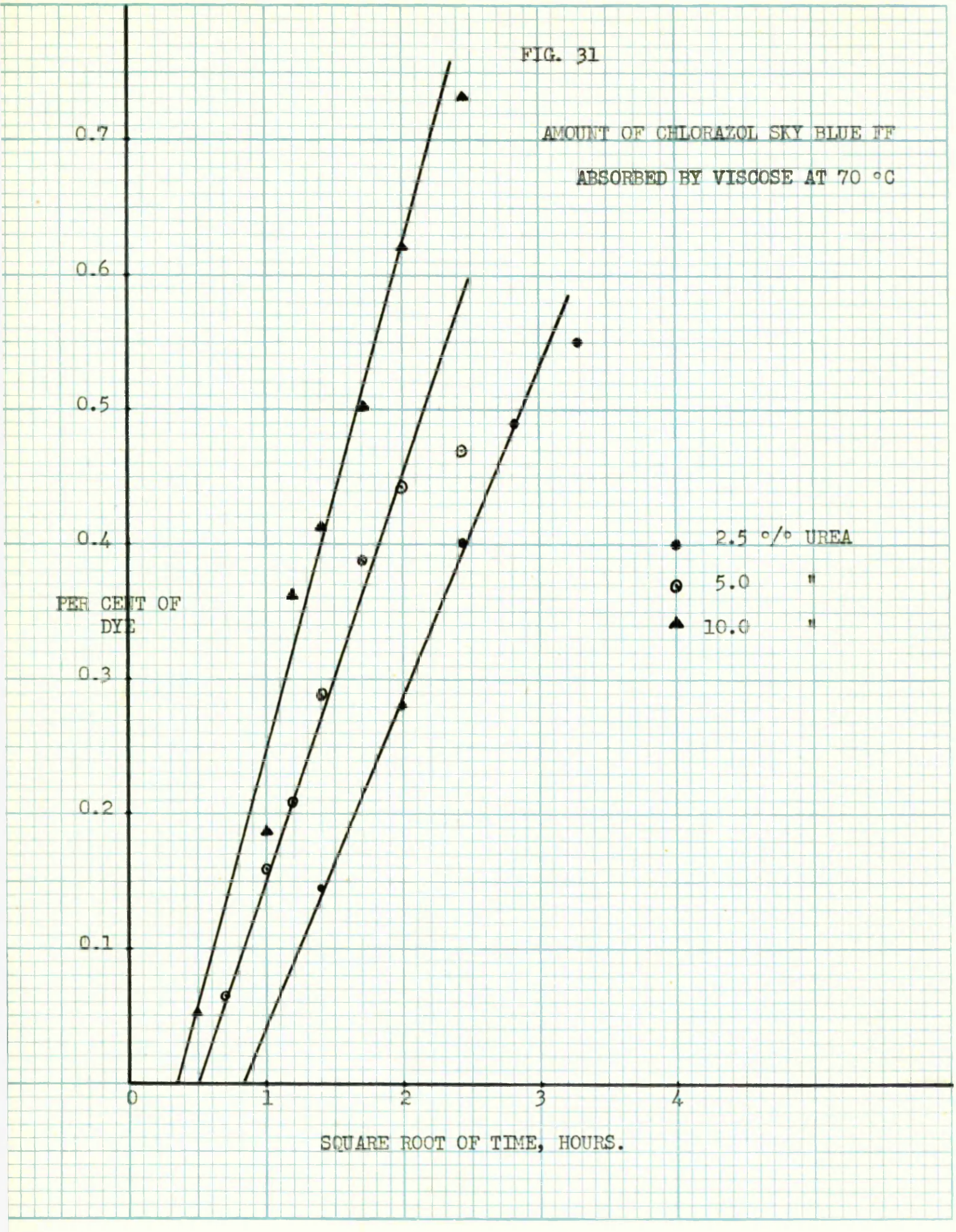

AMOUNT OF CHLORAZOL SKY BLUE FF
ABSORBED BY VISCOSE AT 70 °C
0.7
0.6
0.5
0.4
0.3
0.2
0.1
PER CENT OF DYE
2.5 °/o UREA
5.0 "
10.0 "
0
1
2
3
4
SQUARE ROOT OF TIME, HOURS.

FIG. 32

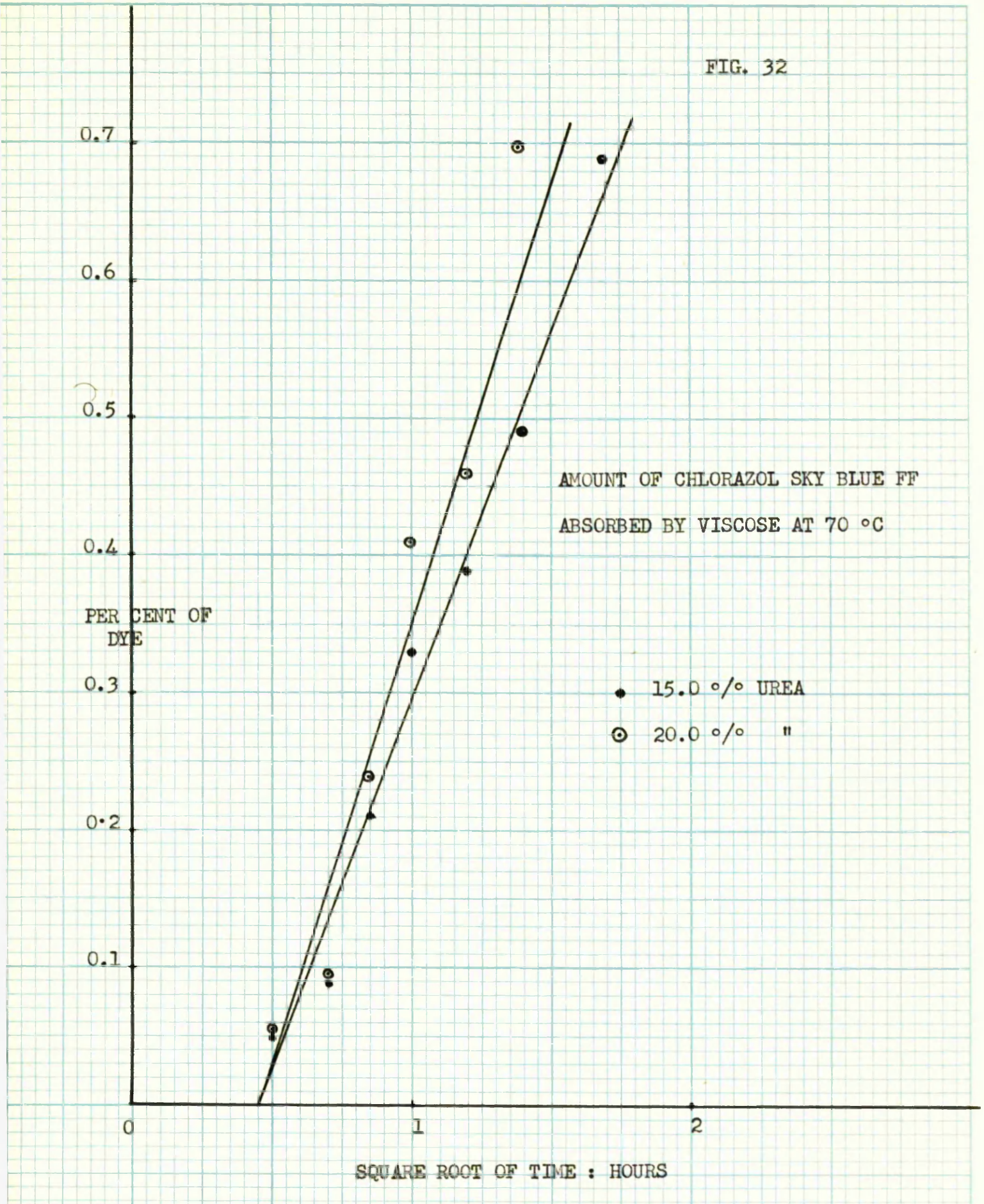

0.7
0.6
0.5
0.4
0.3
0·2
0.1
PER CENT OF DYE
AMOUNT OF CHLORAZOL SKY BLUE FF
ABSORBED BY VISCOSE AT 70 °C
15.0 °/° UREA
20.0 °/° "
0
1
2
SQUARE ROOT OF TIME : HOURS

FIG. 33

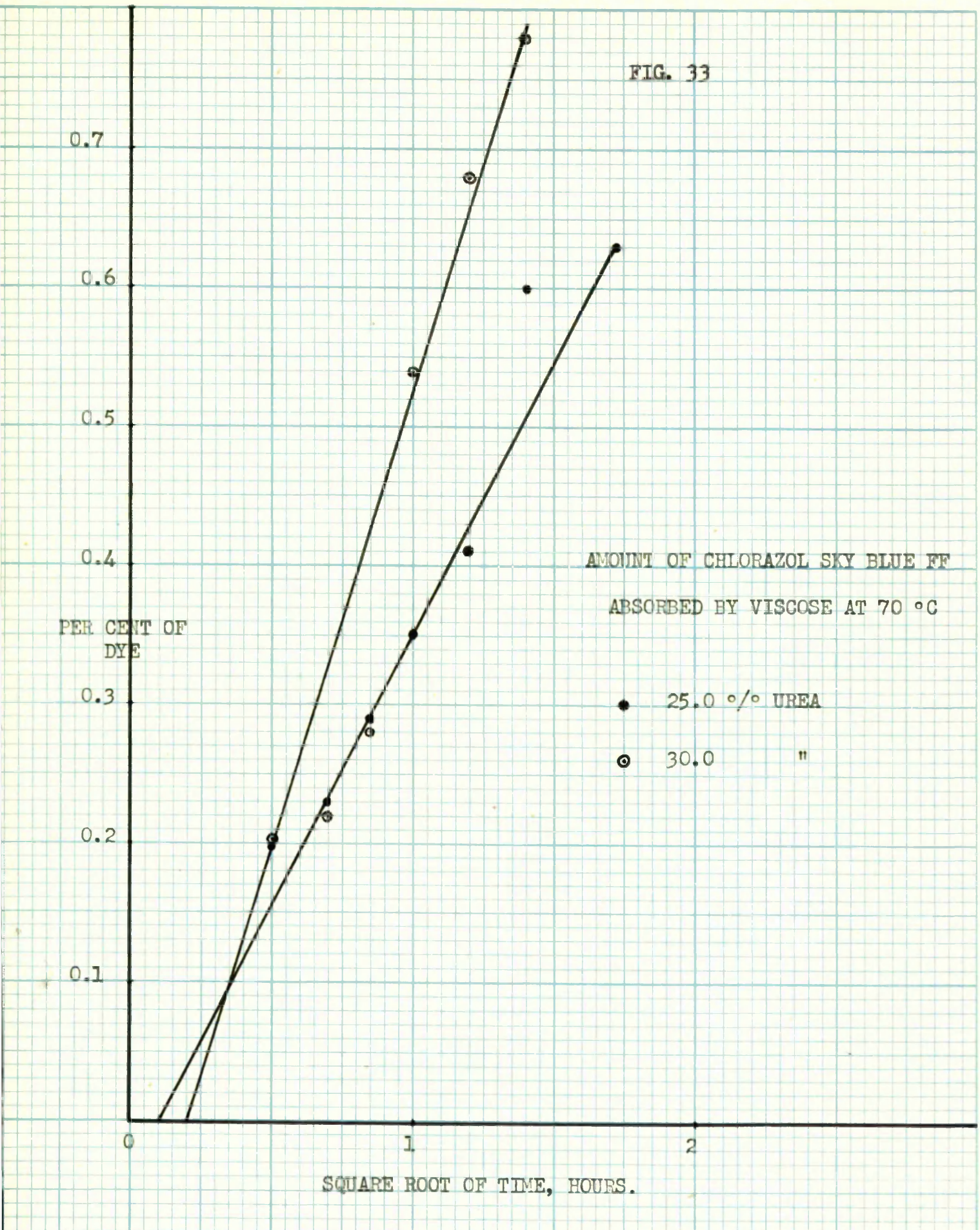

0.7
0.6
0.5
0.4
PER CENT OF DYE
0.3
0.2
0.1
0
1
2
SQUARE ROOT OF TIME, HOURS.
AMOUNT OF CHLORAZOL SKY BLUE FF
ABSORBED BY VISCOSE AT 70 °C
25.0 °/° UREA
30.0 "

FIG. 34

AMOUNT OF CHLORAZOL SKY BLUE FF ABSORBED BY VISCOSE AT 80 °C

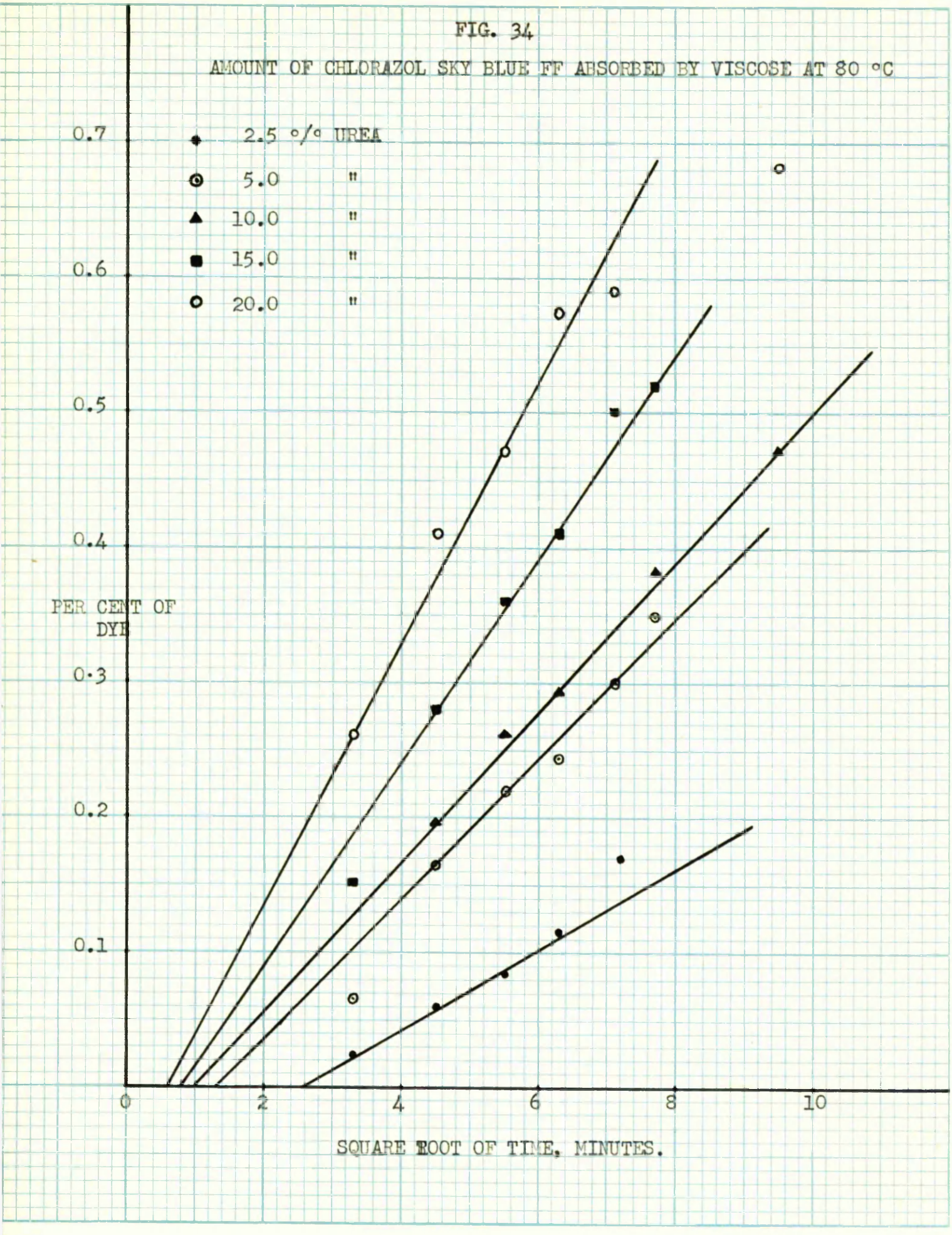


FIG. 35

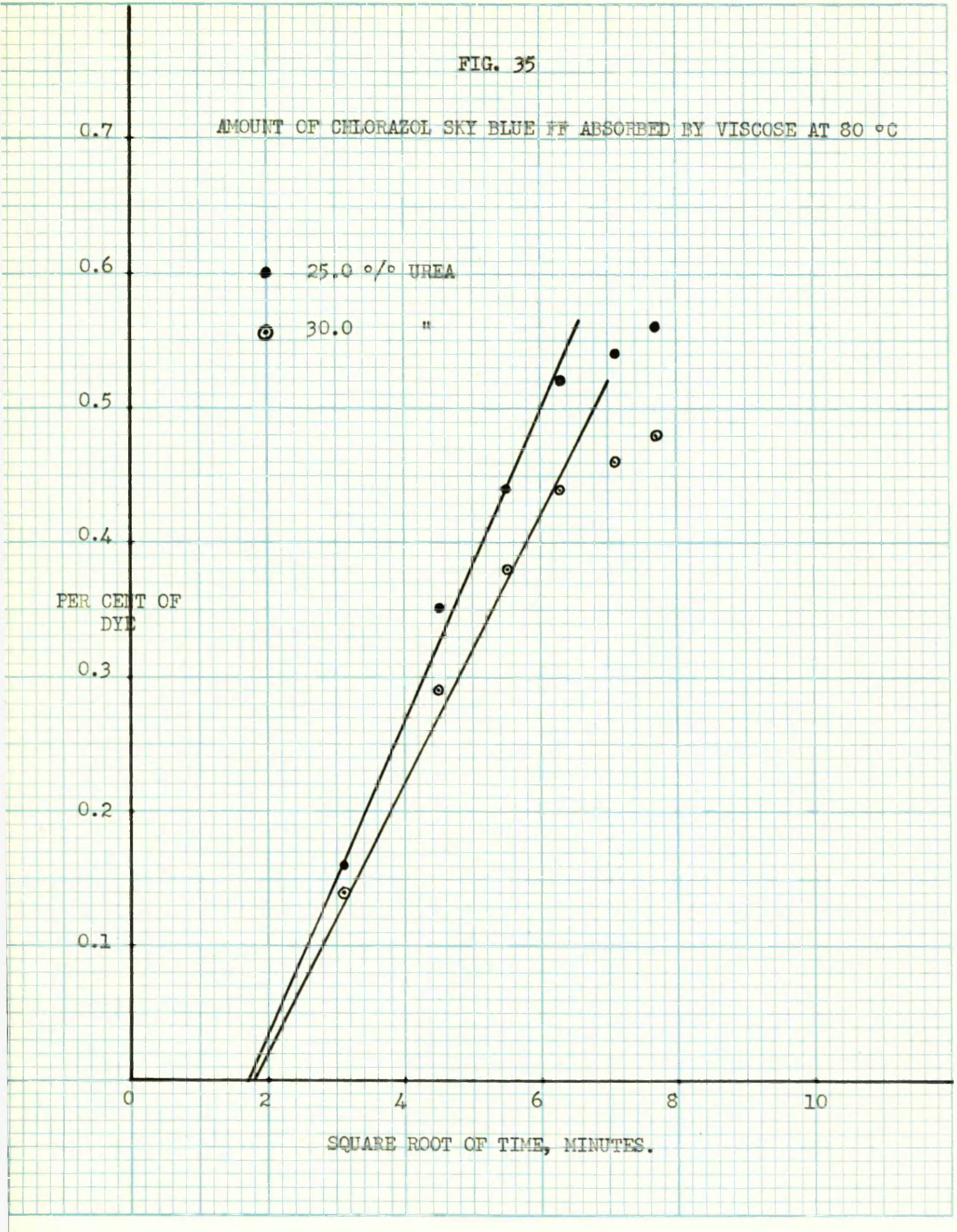

AMOUNT OF CHLORAZOL SKY BLUE FF ABSORBED BY VISCOSE AT 80 °C
25.0 °/° UREA
30.0 "
PER CENT OF DYE
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2
4
6
8
10
SQUARE ROOT OF TIME, MINUTES.

FIG. 36

AMOUNT OF CHLORAZOL SKY BLUE FF ABSORBED BY VISCOSE AT 90 °C

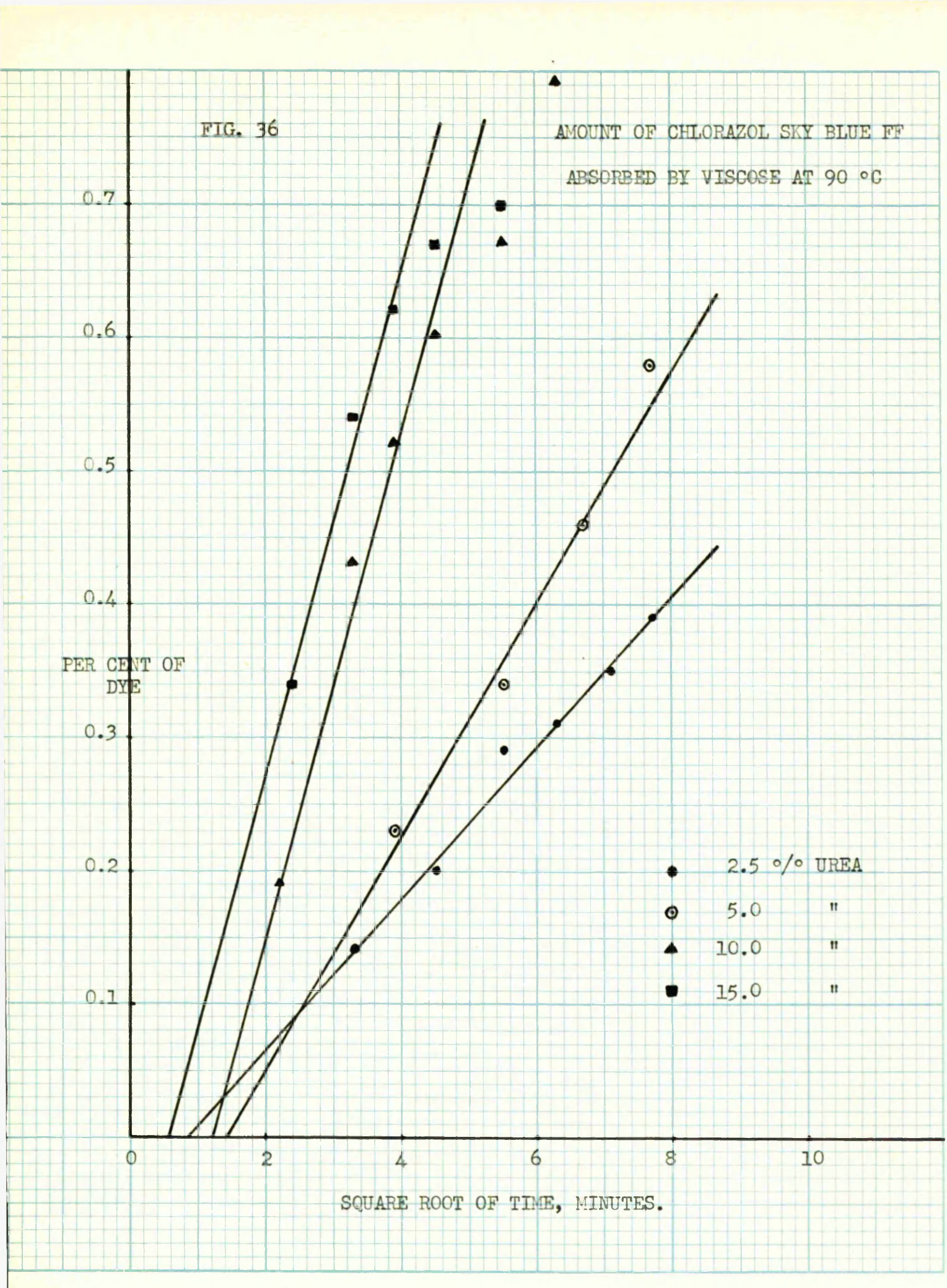
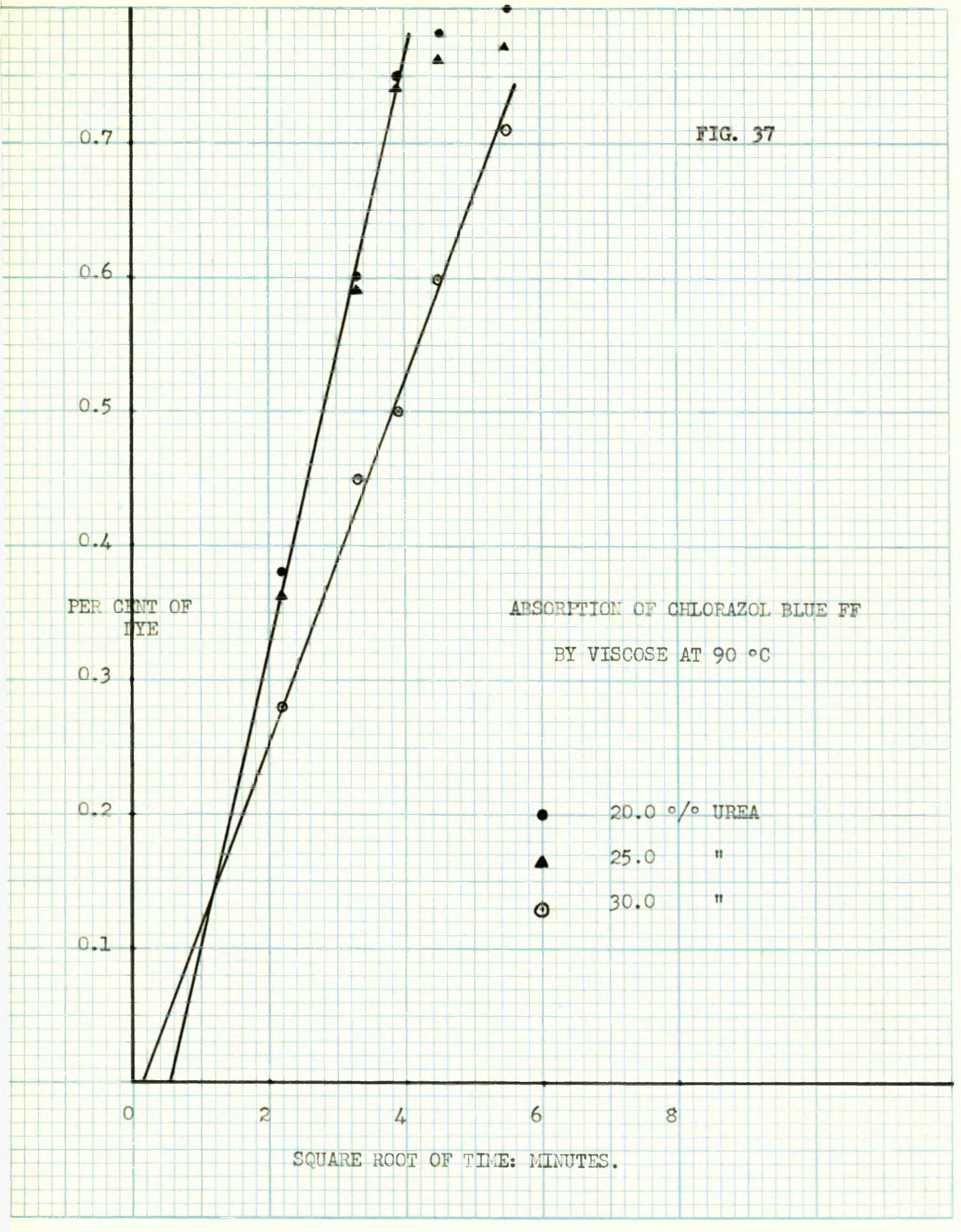


FIG. 37


0.7
0.6
0.5
0.4
0.3
0.2
0.1
PER CENT OF DYE
ABSORPTION OF CHLORAZOL BLUE FF
BY VISCOSE AT 90 °C
20.0 °/° UREA
25.0 "
30.0 "
0
2
4
6
8
SQUARE ROOT OF TIME: MINUTES.

The results of these Tables are shown graphically in Figs. 31 - 37, where plots of the dye uptake against the square root of time fall on straight lines, in accordance with Hill's equation (cf. page 89):-

$$C_t = 2\, C_0 \,/\, \overline{D.t\,/\pi}$$

where C_t = the amount of the dye absorbed by the fibre at time t,

C_0 = the concentration of the dye in the solution, which is kept constant,

and D = the diffusion coefficient of the dye, inside the fibre.

It will be noticed from these Figures that the points give a perfect linear plot for the values of the uptake at comparatively low temperatures and the deviations are more pronounced at 90 and 100 °C, when the diffusion is rapid and the equilibrium is reached quickly which makes it difficult to follow C_t with time t.

In another series of experiments, the fibres were first treated with urea solutions at 90 °C for an hour and then immediately entered into the dye-bath at the same temperature and containing the same amount of urea. The uptake of the dye was observed to be higher than before and a comparison of the two sets of values can be made from Tables XXVIII and XXX.

Table XXX

Absorption of Chlorazol Sky Blue FF by Viscose at 90 °C

1 hour's pre-treatment with Urea solutions

Uptake °/° ——>	Concentration of Urea, °/°				
Time, Minutes.	5	10	20	25	30
5	0.06	0.28	0.41	0.39	0.30
10	0.28	0.49	0.64	0.64	0.51
15	0.42	0.58	0.71	0.65	0.60
20	0.48	0.66	0.83	0.81	0.73
30	0.68	0.67	0.85	0.83	0.81
40	0.66	0.79	0.88	0.88	0.85
50	0.72	——	0.89	——	0.92
60	0.78	——	0.95	0.90	0.95

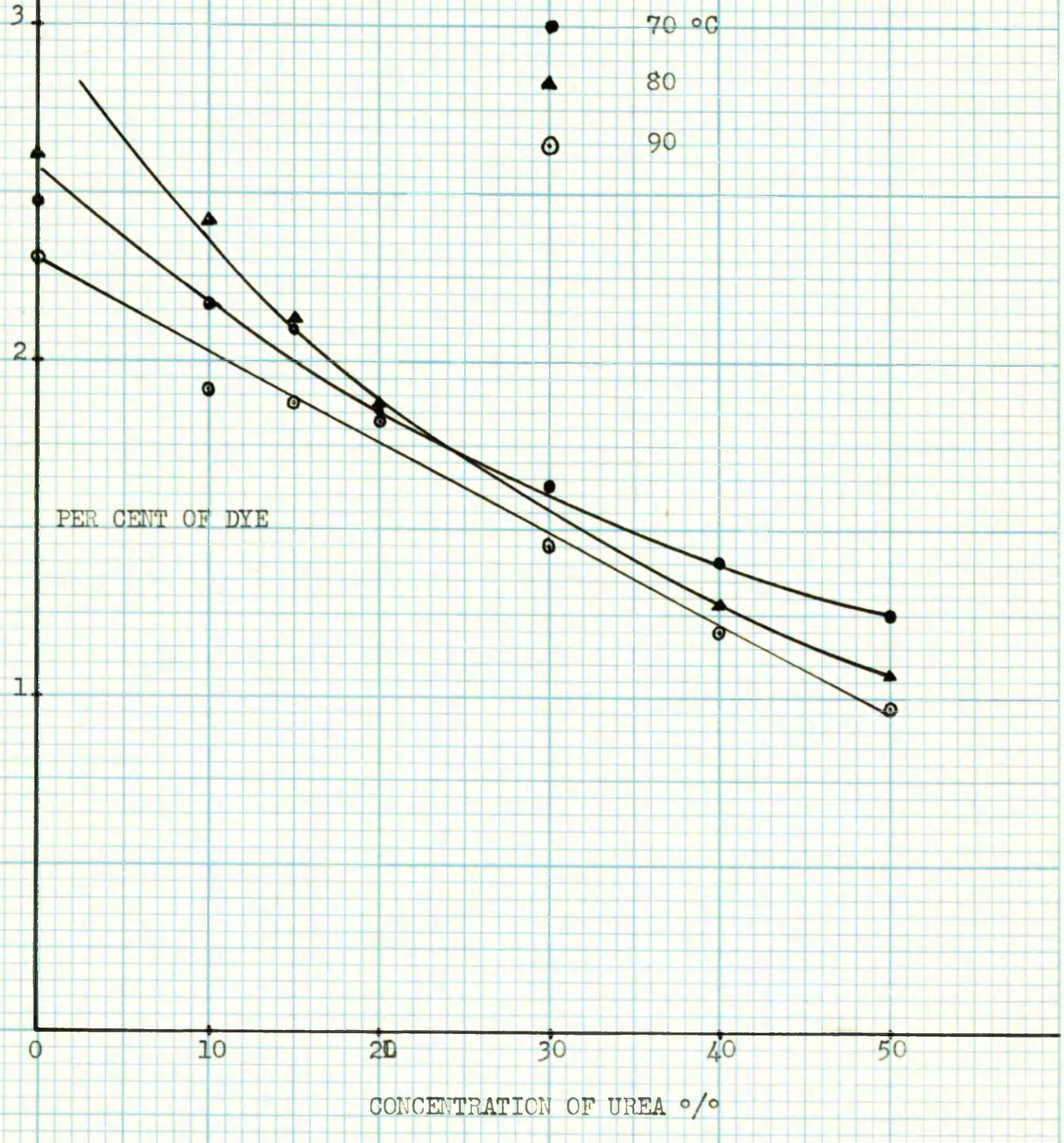
From a study of the results in Tables XXVIII and XXX, it follows that the treatment of the fibres with urea solutions prior to dyeing, opens the "trap doors" in the fibres and the absorption of the dye proceeds quicker than before. However, the absorption values for longer times nearly approach those when there was no pretreatment, in which case, urea helps enlarging the pores alongwith the dyeing.

It was thought desirable to have an idea how urea would influence the absorption of the dye in the presence of electrolyte.

FIG. 38

EFFECT OF THE CONCENTRATION OF UREA ON THE ABSORPTION OF CHLORAZOL SKY BLUE FF IN PRESENCE OF 1°/° SODIUM CHLORIDE.

VISCOSE



Consequently, dyeing was carried out from baths containing both the urea and the electrolyte. The uptake, g / 100 g of the dry fibre, is shown in Tables XXXI, XXXII and XXXIII. It will be seen from these data that increased concentrations of urea lower the absorption of the dye and at the three temperatures studied, viz., 70, 80 and 90 °C, the absorption value with 50.0 °/° urea at one hour is almost 1/2 of that without any urea. The effect of the concentration of urea is shown graphically in Fig. 38, which also depicts the effect of temperature. The curve for the values at 80 °C is steeper than the one for 70 °C and the values at 90 °C are better represented by a straight line than a curve, which is still steeper than that for 80 °C.

Table XXXI

Effect of the Concentration of Urea on the Absorption of Chlorazol Sky Blue FF by Viscose at 70 °C.

0.30 g /l. dye + 5.0 g/l NaCl.

Uptake ----> Conc. of Urea °/°	Time, Minutes. 5	10	20	30	45	60
0.00 only salt	0.70	0.99	1.36	1.75	2.17	2.47
10.0	0.62	0.87	1.25	1.59	1.97	2.17
15.0	0.65	0.89	1.27	1.62	1.98	2.12
20.0	0.57	0.81	1.17	1.44	1.62	1.85
30.0	0.47	0.65	0.95	1.28	1.57	1.63
40.0	0.41	0.57	0.82	1.05	1.26	1.39
50.0	0.36	0.48	0.70	0.91	1.05	1.23

Table XXXII

Effect of the Concetration of Urea on the Absorption of Chlorazol Sky Blue FF by Viscose at 80 °C. 0.30 g/l. dye + 5.0 g/l NaCl.

Uptake ------> Conc. of urea °/°	Time, Minutes. 5	10	2o	30	45	60
Salt only	0.89	1.25	1.72	2.11	2.44	2.56
10.0	0.76	1.02	1.57	2.07	2.28	2.36
15.0	0.85	1.13	1.65	1.85	1.97	2.11
20.0	0.68	0.94	1.26	1.62	1.76	1.85
30.0	0.64	0.92	1.22	1.50	1.48	---
40.0	0.49	0.77	1.01	1.18	1.23	1.28
50.0	0.42	0.59	0.83	0.92	0.99	1.07

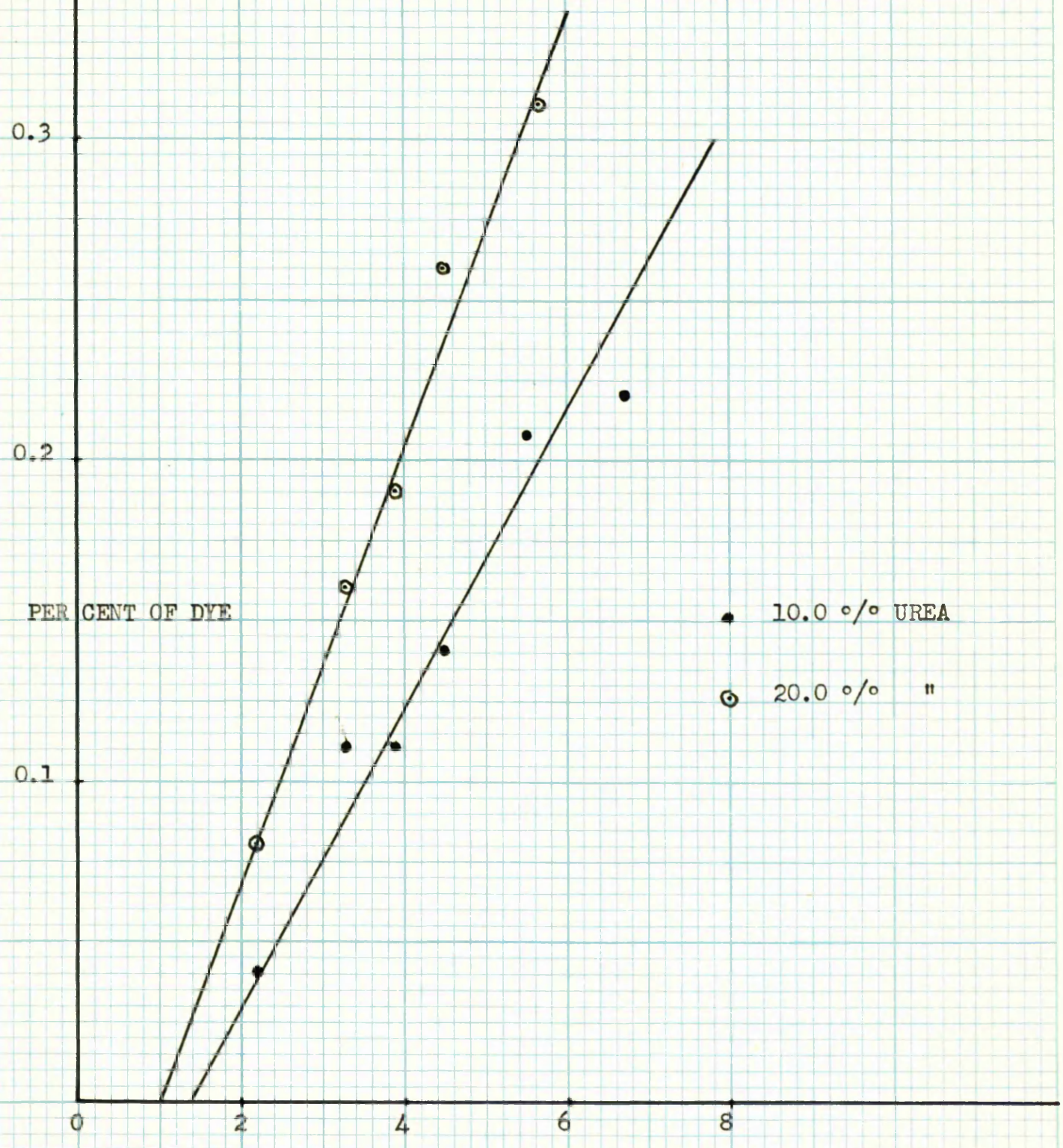
Table XXXIII

Same at 90 °C.

Salt only	1.29	1.55	1.89	2.15	2.24	2.29
10.0	0.99	1.43	1.79	1.87	1.92	1.92
15.0	0.94	1.33	1.57	1.79	1.82	1.87
20.0	0.87	1.31	1.47	1.73	1.79	1.85
30.0	0.87	1.11	1.23	1.41	1.44	1.44
40.0	0.69	0.97	1.07	1.17	1.19	1.19
50.0	0.53	0.73	0.70	0.86	0.94	0.97

FIG. 39

ABSORPTION OF CHLORAZOL SKY BLUE FF BY COTTON AT 80 °C



The corresponding experiments with cotton were not carried out in such a detail as with viscose, because the effect of urea was anticipated to be identical. Table XXXIV shows some of the results of these experiments, conducted under similar conditions to those of viscose.

Table XXXIV

Absorption of Chlorazol Sky Blue FF by Cotton at 80 °C.

Wt. of each hank, dry = 37.4 mg.

Vol. of the solution = 100 cc (0.30 g/l. dye)

Uptake ------> / Conc. of Urea °/°	Time, Minutes. 5	10	15	20	30	45	60
10.0	0.04	0.11	0.11	0.14	0.21	0.22	0.24
20.0	0.08	0.16	0.19	0.26	0.31	---	0.31
One hour's pre-treatment with 20.0 °/° Urea							
	0.20	0.24	0.27	0.25	0.28	0.29	---

The data of this Table are represented in Fig.39, where the plot of the uptakes against the square roots of time falls on a straight line.

In a slightly different style, the pre-treated fibres were entered ~~t~~ into a dye-bath containing the electrolyte instead of urea. The amount of the dye absorbed is compared with that when the fibres are dyed as such for the same length of time at 80 °C.

Uptake of Chlorazol Sky Blue FF (for 1/2 hour)

0.30 g/l. dye, 100 cc of dye solution

Fibre	Untreated	Treated with 20.0 °/° urea for 1 hour.
Viscose	2.17 °/°	2.52 °/°
Cotton	0.82	0.90

Since there is no urea in the dye-bath, the equilibrium value of the dye absorbed in the two cases will necessarily be the same and the difference due to the pre-treatment with urea will vanish. However, it is quite easy to visualise that when the time of dyeing is in the neighbourhood of 5 - 10 minutes, this difference would be very substantial.

Desorption and Levelling of Dyes with Urea.

It is clear from the results of the foregoing experiments that when the fibres are given a treatment with urea, the absorption of the dye is much quicker and higher in the initial stages of the dyeing and that when urea is a component of the dye-bath alongwith salt, absorption is lower than that in the absence of urea. It therefore, follows that

1. treatment with urea opens the "trap doors", thus liberating the active sites quicker, which accounts for the initially higher uptake.

2. there is a competition between the urea molecules and the dye molecules to occupy these sites, and this competition is always in favour of urea as the concentration of the former increases in the dye-bath.

Preliminary experiments on desorption and levelling of Class C direct dyes on the Obermaier dyeing machine showed that when equal amounts of the dyed and the undyed viscose stapple were mixed together and a 20.0 °/° urea solution was circulated through the mass near the boil, the tintorial value of the liqour first increased, reached a maximum at about 10 minutes and then decreased gradually. Almost complete exhaustion was effected by adding small amounts of salt at intervals (5 °/° on the weight of the material).

Though complete levelling was not possible in these experiments due to the defective circulatory system of the machine, yet the results were better and less patchy in shade as compared to those when levelling was attempted with a solution of salt. (5 °/° on the weight of the material; initial volume of the liquor 6 litres)

These results provided an incentive to investigate the desorbing and levelling effect of urea, on a still smaller scale and to work out the conditions under which complete levelling of Class C dyes could be effectively done. For this purpose, dyed and the same amount of the undyed samples of viscose and cotton were treated in 20.0 °/° urea solution, 0.5 °/° NaCl, 20.0 °/° + 0.5 °/° NaCl solution and water alone. The amounts of the dye

present in the three components, viz., residual dye on the original sample, dye on the undyed sample, and dye left in the liquor, were estimated colorimeterically. The results for Chlorazol Sky Blue FF are quantitative, while for the other dyes are semi-quantitative, the units of reference being the amounts of the dyes on the originally dyed samples. All these experiments were carried out in tubes, fitted with water-cooled condensers as described earlier.

In the following Tables, the desorbing action of water, salt, urea and urea + salt are compared with each other. It will be noted that urea shows the greatest desorption and most of the dye originally present on the dyed sample becomes available in the solution form.

Table XXXV

Desorption of Chlorazol Sky Blue FF from Viscose at 80 °C.

Wt. of each sample = 81.1 mg. Vol. of the soln. = 100 cc

	Amount of the dye present in liquor, mg.			
Time, Minutes	Water	0.5 °/° NaCl	20.0 °/° Urea	Urea+Salt
1	---	---	0.34	---
2 1/2	---	---	0.46	---
5	0.64	0.26	0.79	0.46
10	0.87	0.45	1.08	0.71
15	1.11	0.56	1.33	0.88
30	1.36	0.74	1.67	1.18
45	1.50	0.80	1.96	1.24
60	1.80	0.82	2.02	1.33

Table XXXVI

	Residual amount of the dye on the original fibre, mg.			
1	---	---	1.72	---
2 1/2	---	---	1.53	---
5	1.72	2.00	1.38	1.72
10	1.51	1.85	0.83	1.33
15	1.27	1.70	0.67	1.21
30	1.00	1.32	0.44	0.76
45	0.63	1.23	0.31	0.70
60	0.52	1.08	0.24	0.65

Table XXXVII

	Amountof the Dye transferred to the undyed fibre, mg.			
5	---	0.05	---	0.05
10	-----	0.09	---	0.06
15	---	0.13	0.01	0.09
30	---	0.26	0.02	0.24
45	---	0.34	0.04	0.24
60	---	0.39	0.05	0.28

The data for Chlorazol Brown MS and Direct Fast Orange SE 180 are relative in the sense that the commercial dyes were used for these experiments and the readings on the Spekker at a particular wave length were converted to a suitable scale, for example, in the case of Chlorazol Brown MS, the optical densities of the dye liquor using a Wratten Filter No. 602 (Blue) and a 4 cm cell with reference to 100 cc of the dye liquor are compared. The original samples were dyed in 100 cc of the solution, containing 0.60 g/l. of the commercial dye + 1.0 g/l. NaCl at 80 °C.

Incidentally, it may be remarked here that the optical density of a solution, containing the same amount of the dye, in the presence of salt, urea and urea + salt was determined, using the above Filter. The values are:- 0.67 for water, 0.67, 0.68 and 0.67 for the solutions containing salt, urea and urea + salt respectively, with 1 cm cell, so that the comparison of the Spekker readings ~~in~~ *of* different solutions is quite justified.

Table XXXVIII

Desorption of Chlorazol Brown MS from Viscose at 80 °C

Wt. of each sample = 81.1 mg.

Vol. of the liquor = 100 cc. 4 cm cell

Relative amounts of the dye in solutions

Time, Minutes	Water	0.50 °/° NaCl	20.0 °/° Urea	Urea + Salt
5	0.67	0.14	0.90	0.39
10	0.82	0.18	1.00	0.51
15	1.15	0.21	1.15	0.50
30	1.20	0.28	1.26	0.51
45	1.30	0.27	1.22	0.57
60	1.37	0.26	1.20	0.63

Table XXXIX

Relative amounts of Residual Dye on the Fibres.

Volume of dye soln. in pyridine = 50 cc 1 cm cell

5 minutes	0.58	0.84	0.71	0.86
10	0.49	0.79	0.46	0.76
15	0.42	0.70	0.45	0.62
30	0.30	0.70	0.33	0.59
45	0.25	0.68	0.33	0.54
60	0.23	0.66	0.30	0.48

Table XL

Relative amounts of Chlorazol Brown MS, transferred to the undyed Fibre. Reference of Vol. = 25 cc with 1cm cell.

Time	Water	0.50 °/° NaCl	20.0 °/° Urea	Urea + Salt
5 minutes	---	0.06	0.02	0.06
10	---	0.07	0.06	0.14
15	---	0.18	0.11	0.18
30	---	0.36	0.18	0.29
45	---	0.42	0.25	0.36
60	---	0.42	0.31	0.40

The results obtained with Direct Fast Orange SE 180, using 0.30 g/l of the commercial dye + 5.0 g/l NaCl (100 cc solution) for dyeing the original samples are set out in the following Tables. The filter used for this dye was Wratten No. 602 (Blue).

Table XLI

Relative amounts of the dye in solutions desorbed from Viscose at 80 °C. Vol. of the solns. = 100 cc, each; cell 4 cm.

Time, minutes	Water	0.50 °/° NaCl	20.0 °/° Urea	Urea + Salt.
5	0.92	0.40	1.24	0.82
10	1.20	0.57	1.74	0.96
15	1.32	0.72	1.92	1.12
30	1.80	0.65	2.44	1.36
45	2.00	0.68	2.64	1.68
60	2.08	0.69	2.64	1.60

Table XLII

Relative amounts of the residual dye on Viscose at 80 °C.

Scale of Reference 50 cc of dye soln. in pyridine with 1 cm cell.

Time, minutes	Water	0.50 °/° NaCl	20.0 °/° Urea	Urea + Salt
5	1.18	1.30	0.96	1.04
10	0.94	1.26	0.79	0.95
15	0.91	1.12	0.63	0.92
30	0.62	1.08	0.35	0.66
45	0.56	0.90	0.28	0.62
60	0.47	0.86	0.27	0.57

Table XLIII

Relative amounts of Direct Fast Orange SE transferred to the undyed Fibre(Viscose) at 80 °C.

Reference 25 cc of the dye soln in pyridine with 1 cm cell.

Time, minutes.				
5	---	---	----	----
10	----	0.12	----	0.16
15	----	0.24	0.04	0.17
30	----	0.40	0.12	0.29
45	----	0.51	0.18	0.42
60	----	0.65	0.20	0.44

The experiments with Cotton were carried out with Chlorazol Sky Blue FF only, using 0.30 g/l dye+ 5.0 g/l. NaCl (100 cc), at 80 °C, for the obvious reason that its behaviour is similar to that of Viscose. The values of the dye desorbed, the residual dye and the dye transferred are given in the following Tables.

Table XLIV

Amounts of Chlorazol Sky Blue FF in solutions, desorbed from Cotton at 80 °C.

Wt. of each sample = 74.8 mg. Vol. of the solns. = 100 cc each.

Time, minutes	Dye in solution, mg.			
	Water	0.50 °/° NaCl	20.0 °/° Urea	Urea + Salt
5	0.28	0.21	0.48	0.28
10	0.34	0.23	0.54	0.36
15	0.40	0.23	0.55	0.38
30	0.49	0.29	0.53	0.44
45	0.51	0.27	0.51	0.41
60	0.55	0.25	0.51	0.38

Table XLV

Residual amounts of Chlorazol Sky Blue FF, mg., on Cotton at 80 °C

5	0.36	0.47	0.17	0.32
10	0.30	0.38	0.13	0.24
15	0.24	0.34	0.10	0.23
30	0.15	0.26	0.08	0.16
45	0.13	0.25	0.07	0.14
60	0.09	0.23	0.07	0.13

FIG. 40

DESORPTION OF CHLORAZOL SKY BLUE FF FROM VISCOSE AT 80 °C

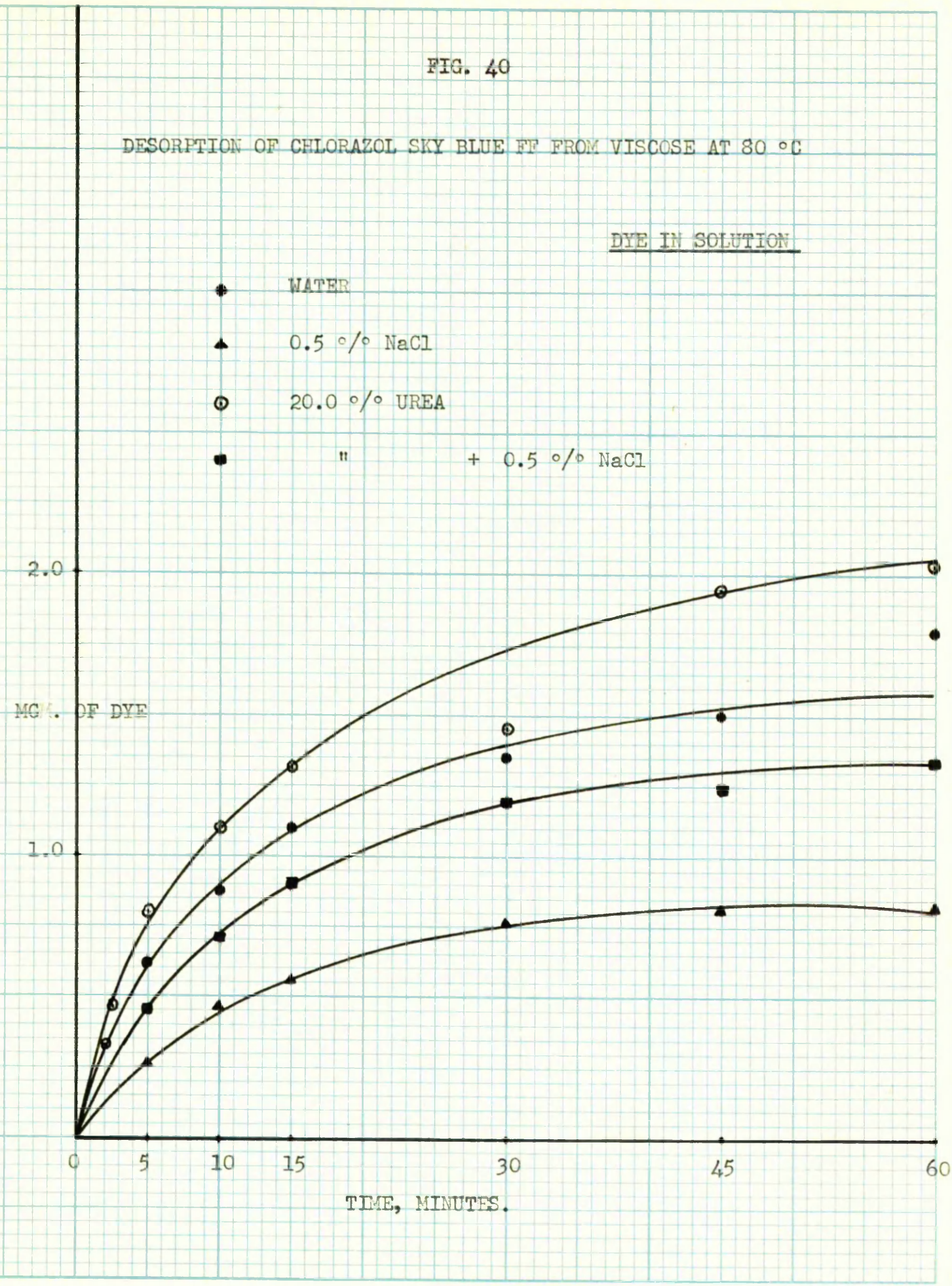


FIG. 41

DESORPTION OF CHLORAZOL SKY BLUE FF FROM VISCOSE AT 80 °C .

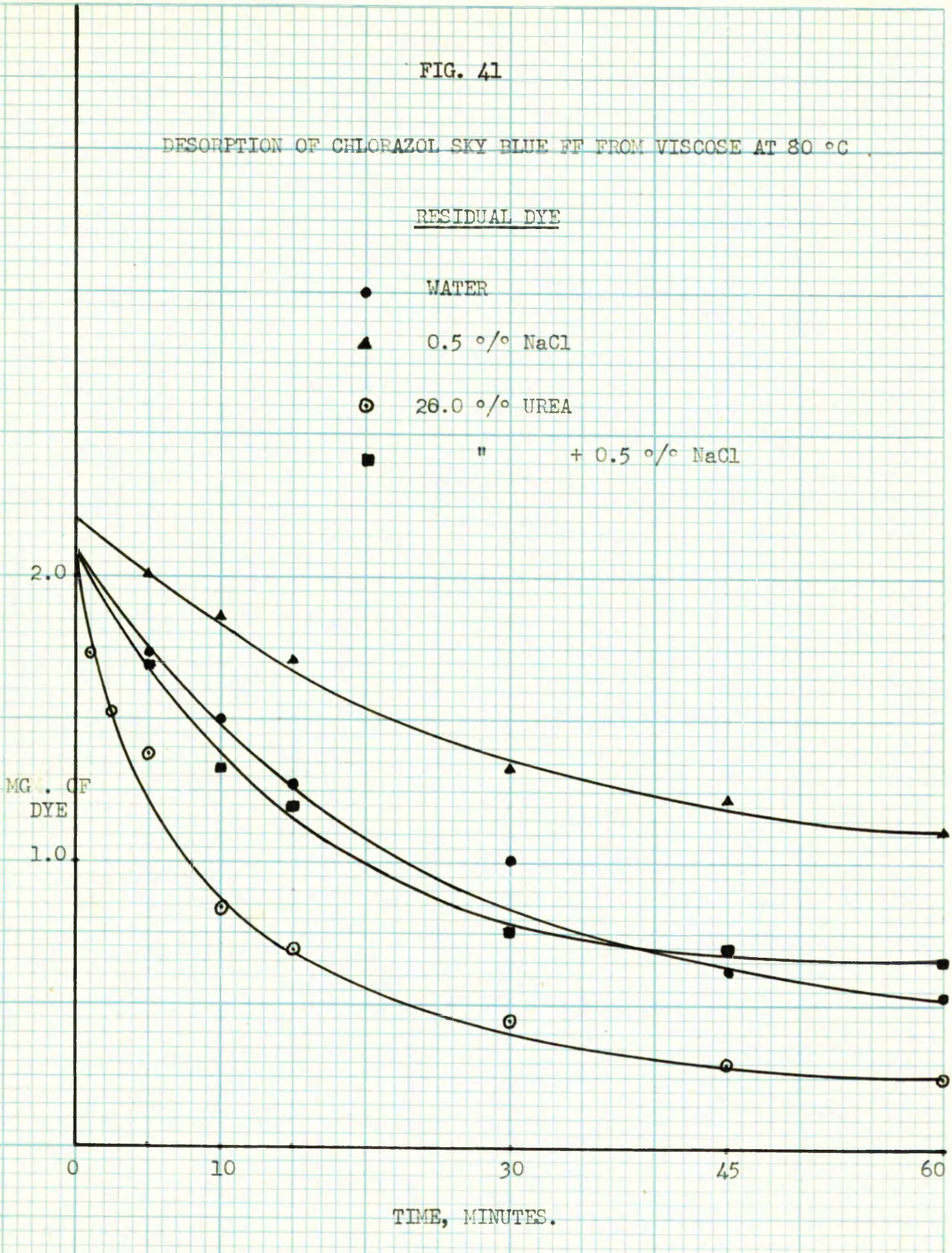


FIG. 42

DESORPTION OF CHLORAZOL SKY BLUE FF FROM VISCOSE AT 80 °C

DYE TRANSFERRED TO THE UNDYED FIBRE

▲ 0.5 °/° NaCl

⊕ 20.0 °/° UREA

■ " + 0.5 °/° NaCl

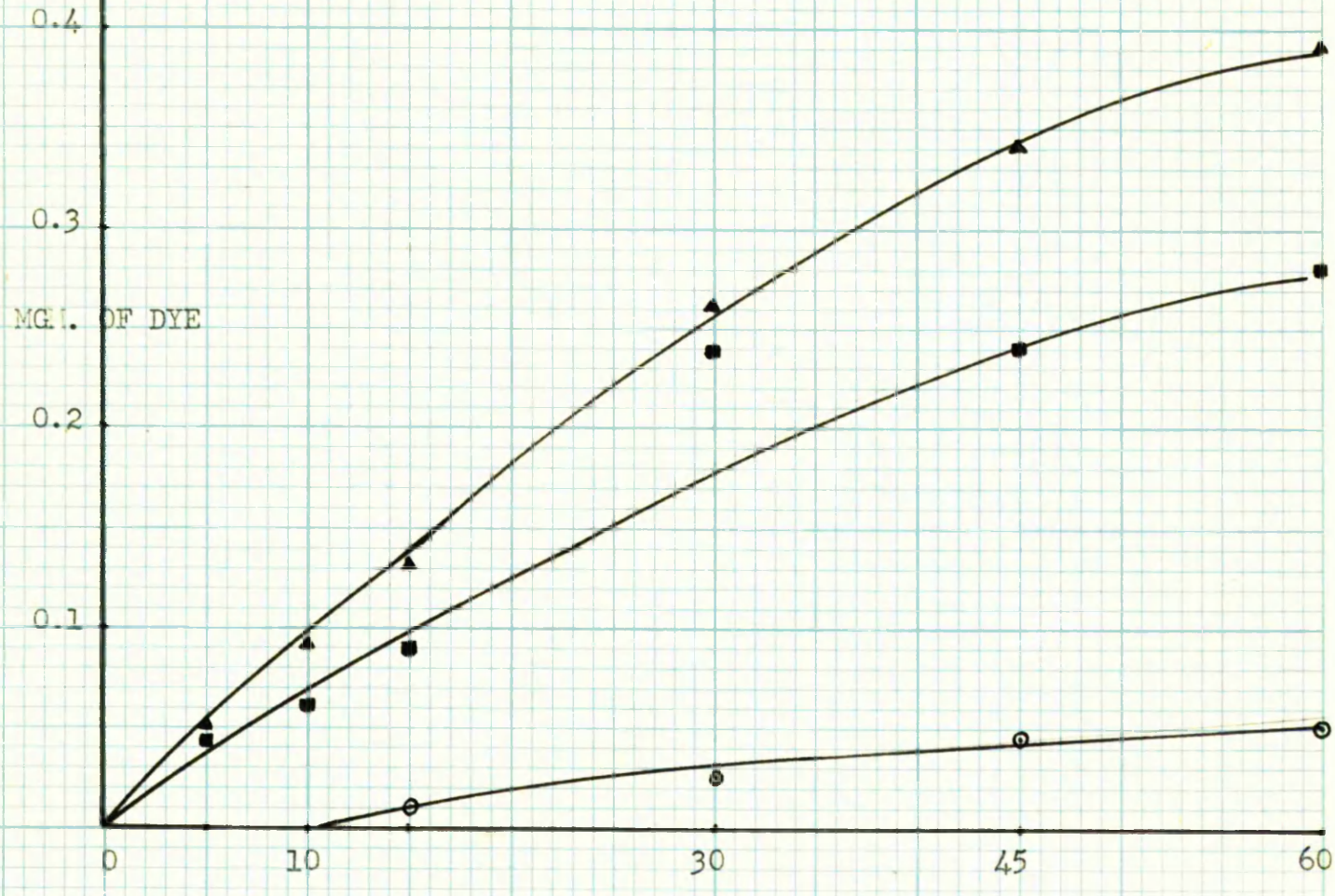


FIG. 43

DESORPTION OF CHLORAZOL BROWN MS FROM VISCOSE AT 80°C

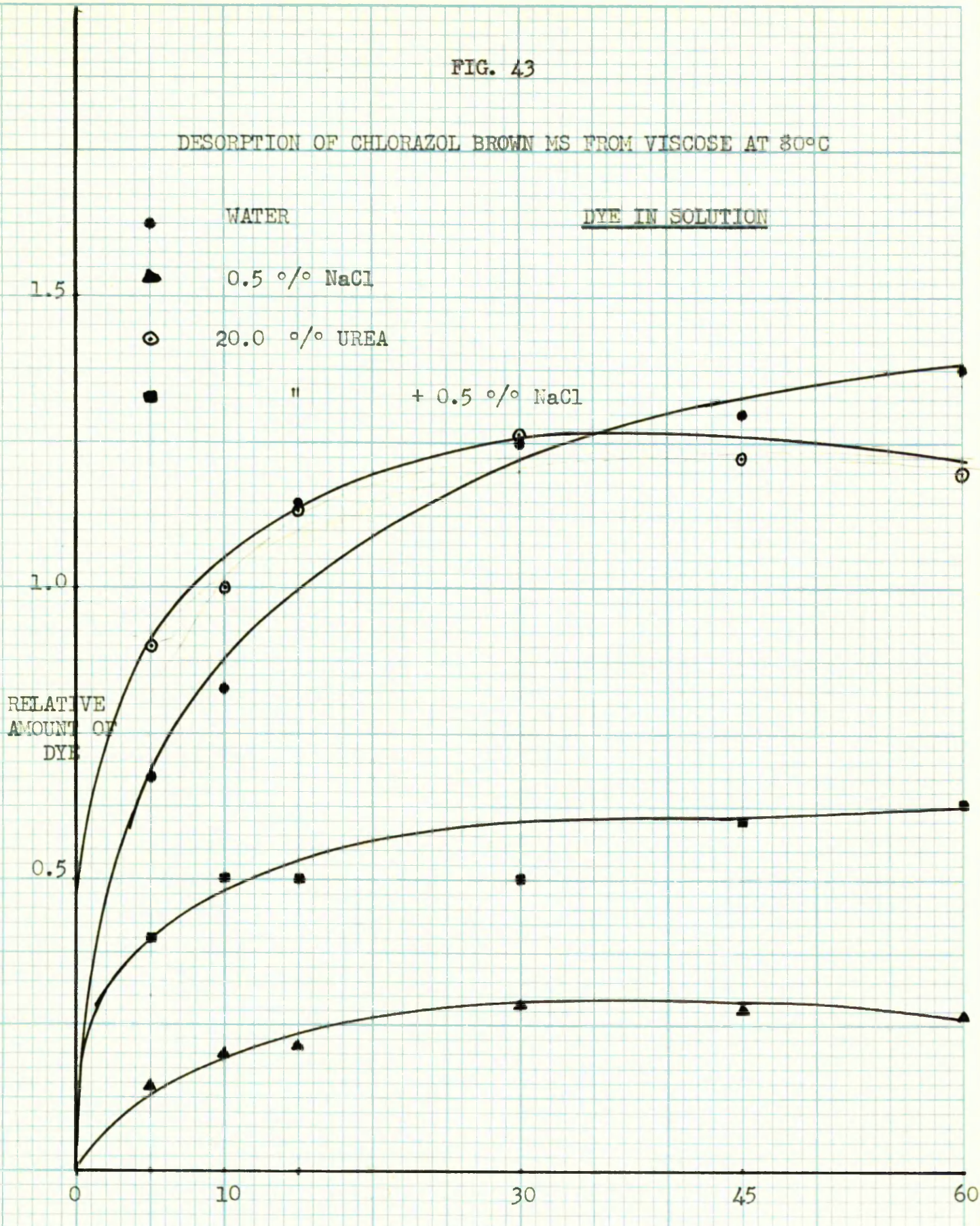


FIG. 44

DESORPTION OF CHLORAZOL BROWN MS FROM VISCOSE AT 80°C

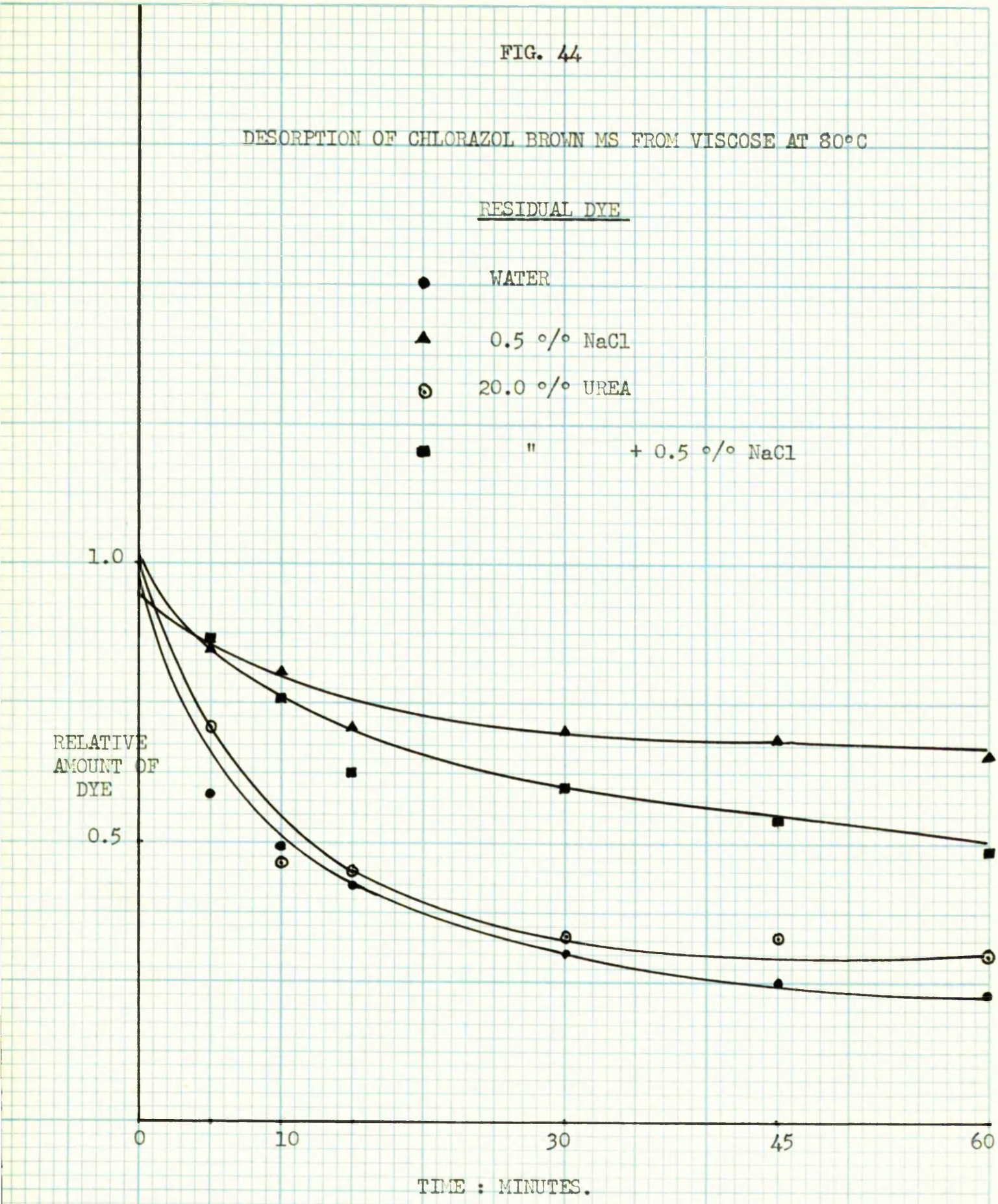


FIG. 45

DESORPTION OF CHLORAZOL BROWN MS FROM VISCOSE AT 80 °C

DYE TRANSFERRED TO THE UNDYED FIBRE

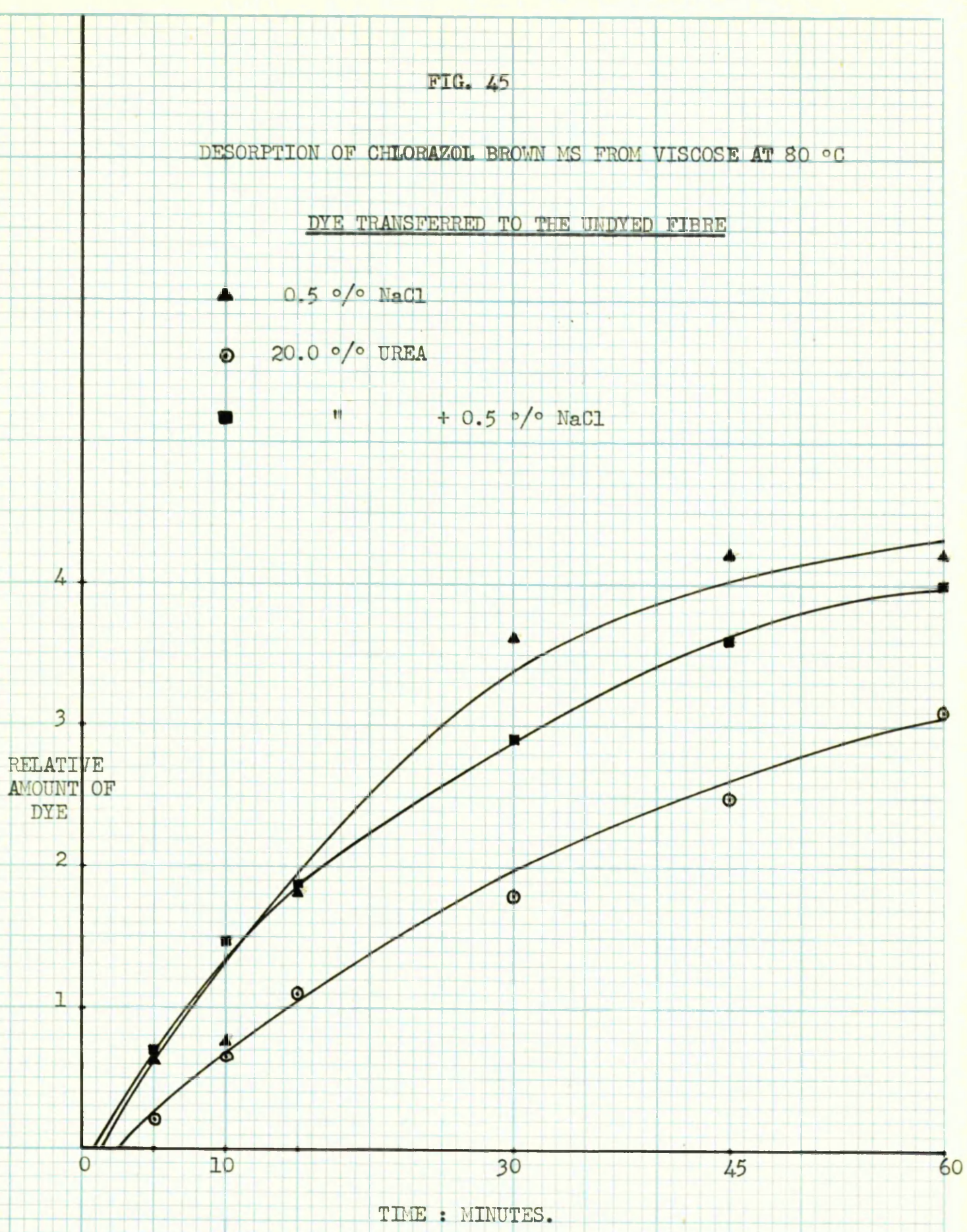


FIG. 46

DESORPTION OF DIRECT FAST ORANGE SE FROM VISCOSE AT 80 °C

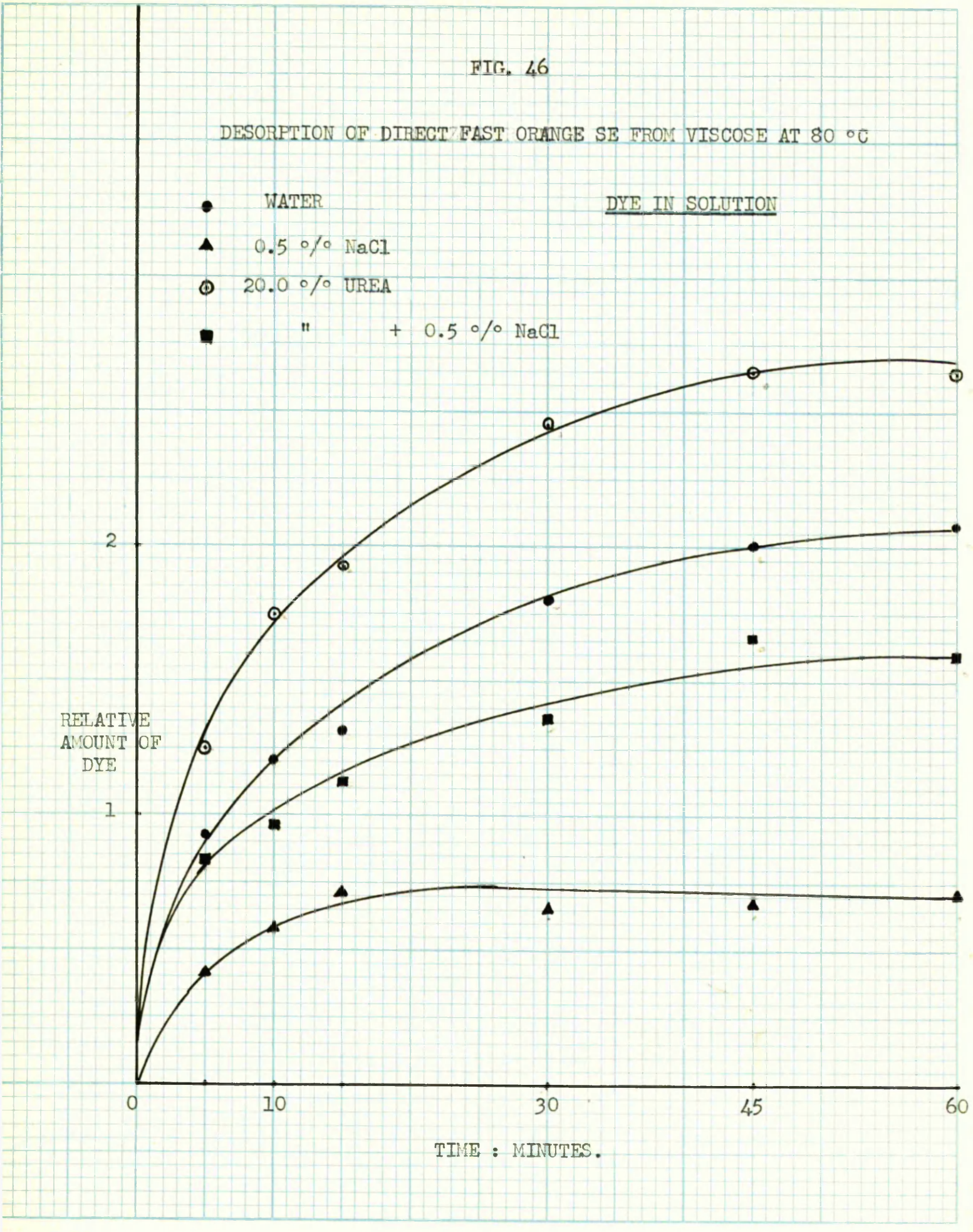


FIG. 47

DESORPTION OF DIRECT FAST ORANGE SE FROM VISCOSE AT 80 °C

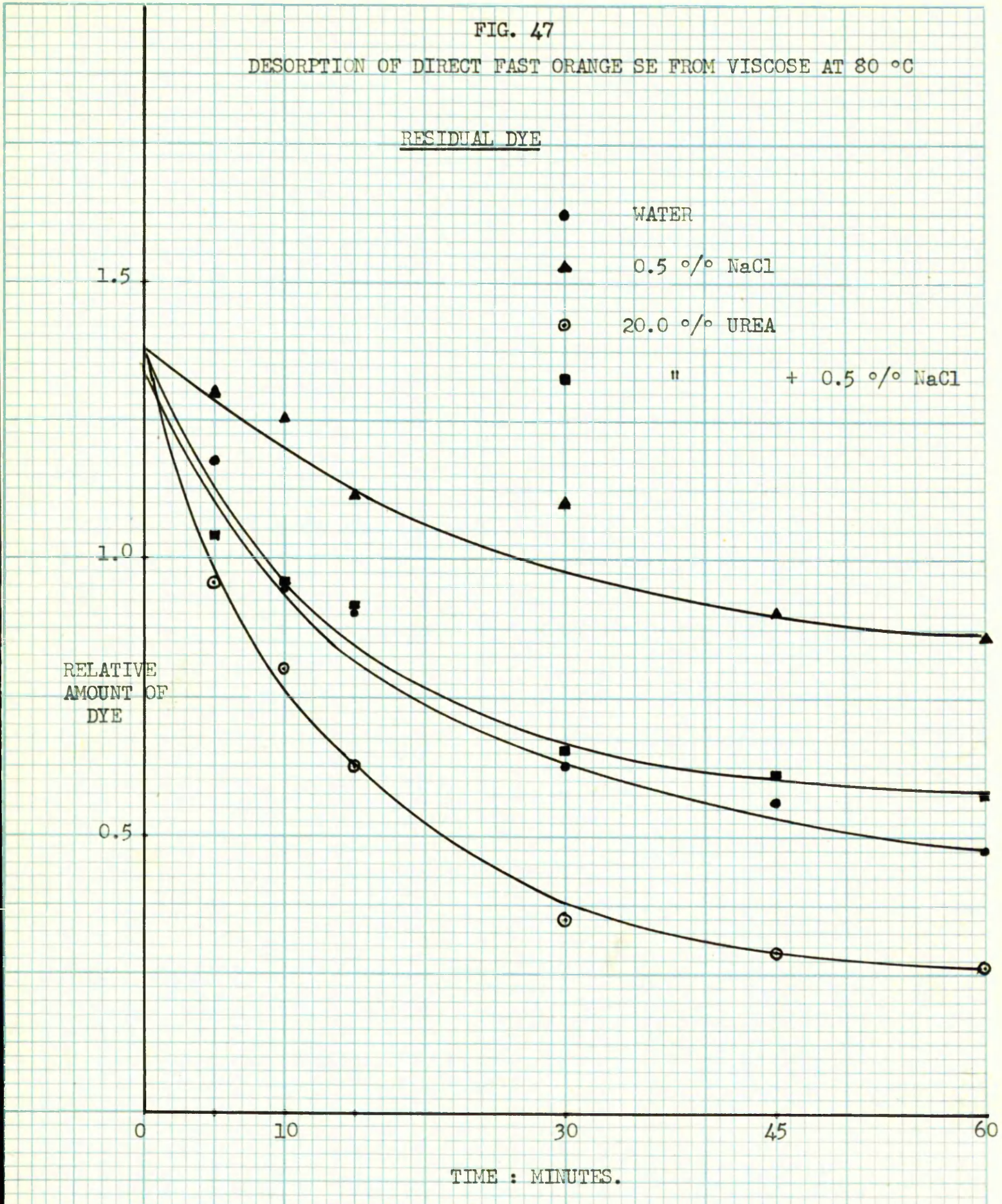


FIG. 48

DESORPTION OF DIRECT FAST ORANGE SE FROM VISCOSE AT 80 °C

DYE TRANSFERRED TO THE UNDYED FIBRE

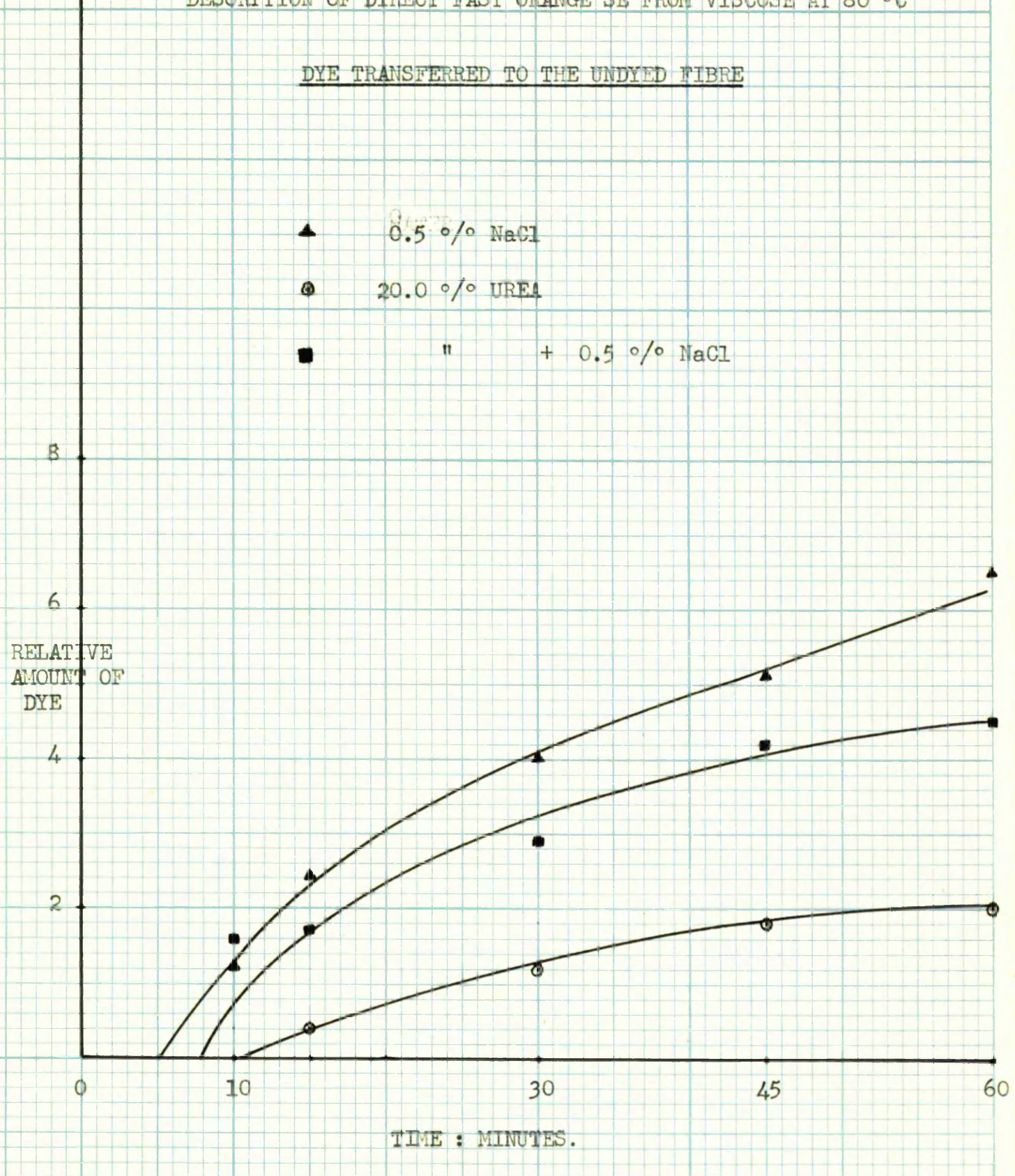


FIG. 49

DESORPTION OF CHLORAZOL SKY BLUE FF FROM COTTON AT 80 °C

DYE IN SOLUTION

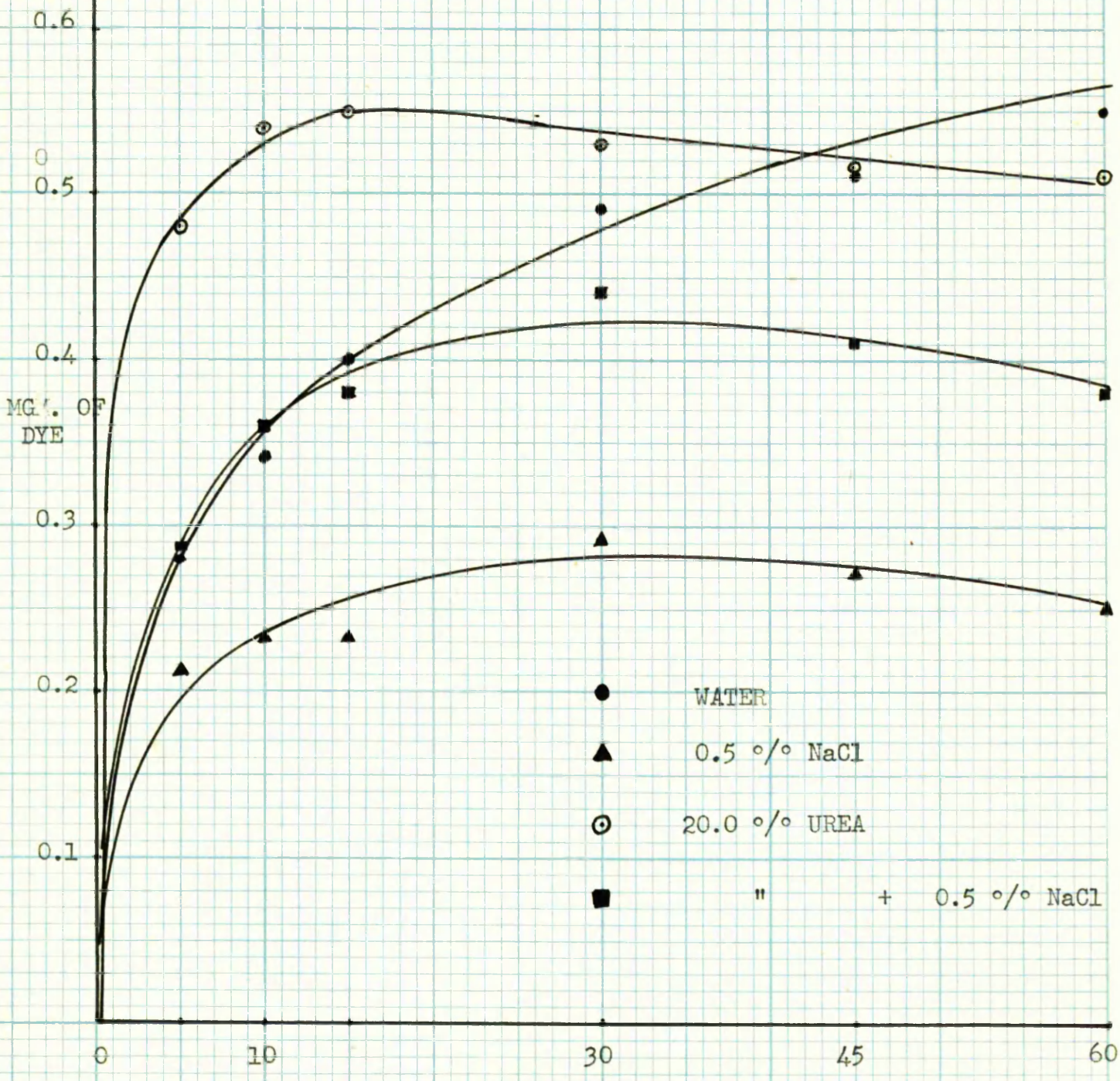


FIG. 50

DESORPTION OF CHLORAZOL SKY BLUE FF FROM COTTON AT 80 °C

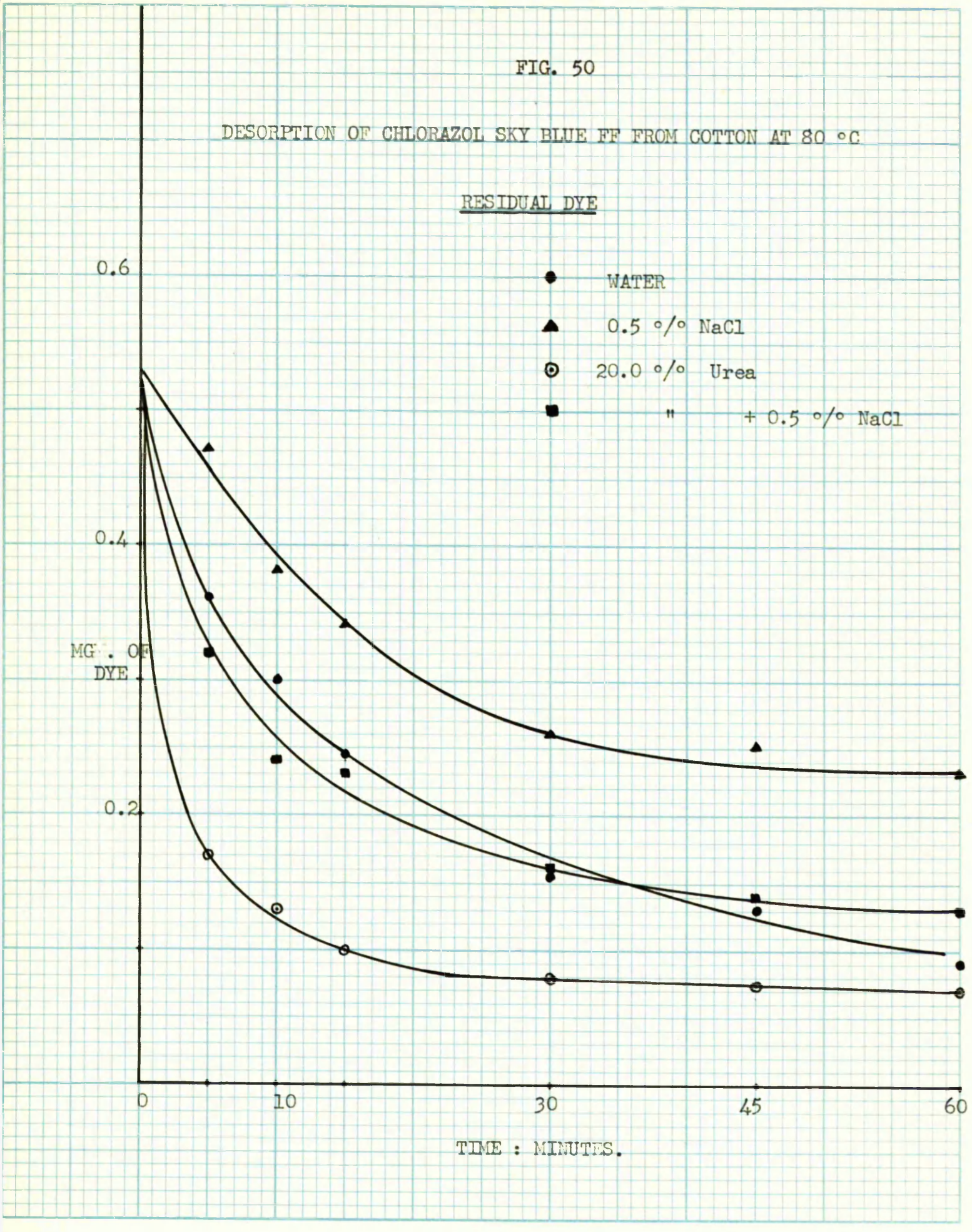


FIG. 51

DESORPTION OF CHLORAZOL SKY BLUE FF FROM COTTON AT 80 °C

DYE TRANSFERRED TO THE UNDYED FIBRE

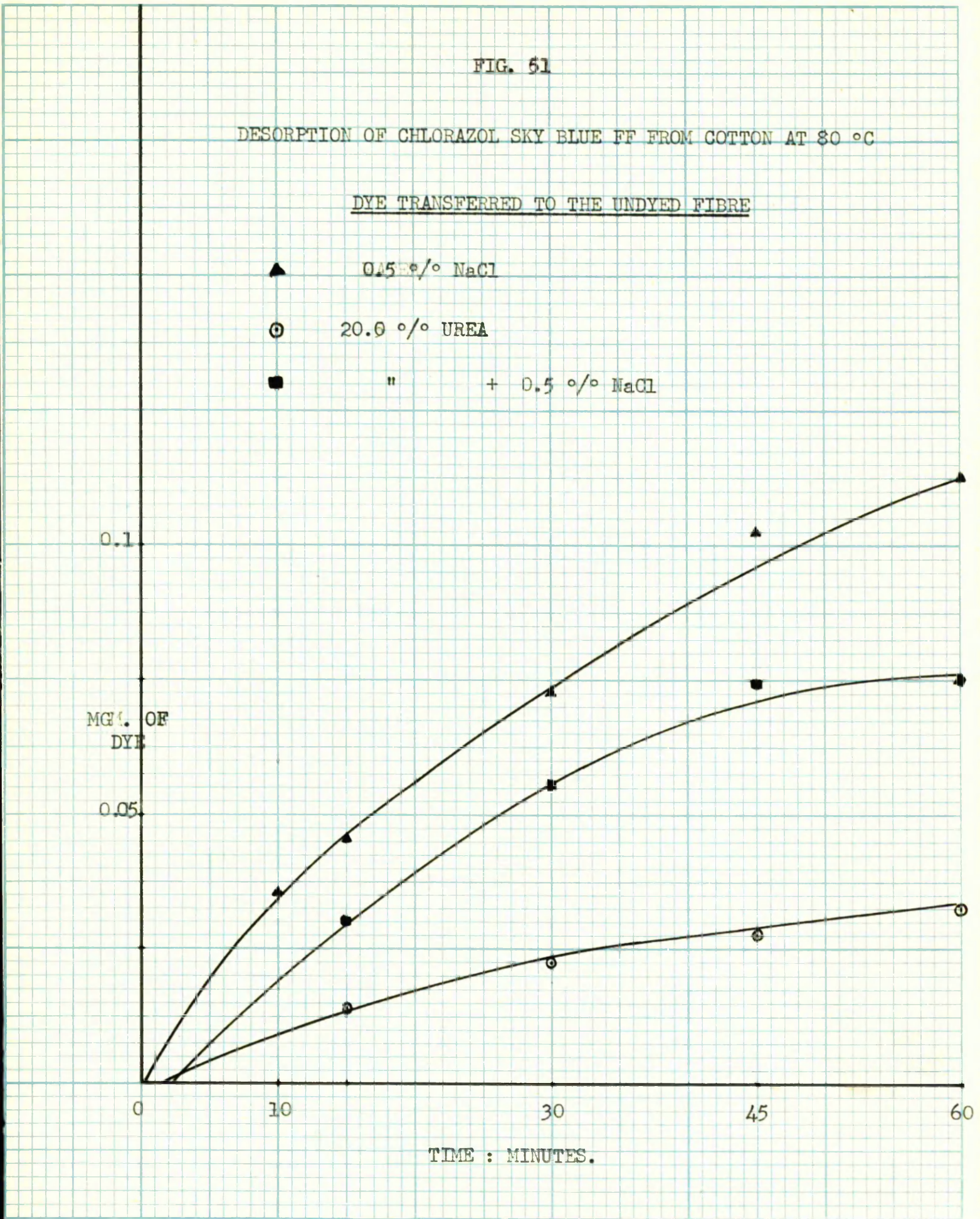


Table XLVI

Amount of Chloeazol Sky Blue FF, transferred to the undyed Fibre (Cotton) at 80 °C.

	Dye, mg.		
Time, minutes	0.50 °/° NaCl	20.0 °/° Urea	Urea + Salt
10	0.04	---	----
15	0.05	0.01	0.02
30	0.07	0.02	0.06
45	0.10	0.03	0.07
60	0.11	0.03	0.08

The results of all these Tables --- XXXV to XLVI, are shown in Figures 40 to 51. Further, it is quite evident from these experiments that when a dyed sample is treated with urea solution, almost all the dye becomes available in the solution. Since the ratio of the liquor to fibre is very large, the desorbed dye remains necessarily in solution on account of its low and unfavourable concentration as compared to that of the ura solution. In the following experiments, the dyed and the undyed samples were first given a treatment in 10 cc of 20.0 °/° urea solution for one hour at 80 °C and the desorbed dye put back on the two samples by the addition of 0.5 cc of 10.0 °/° NaCl (2.5 cc in all) at 5 intervals, each of 10 minutes, so that the final volume was 12.5 cc. The

results of these experiments are given below:-

VISCOSE. Ratio of the dye on the two samples

Chlorazol Sky Blue FF 0.92

Dye left in the soln. = 8.9 °/° of the total amount

Chlorazol Brown MS 0.88

Liquor colourless

Direct Fast Orange SE 0.77

Dye left in soln = 4.1 °/° of the total amount

(Approximately)

Cotton.

Chlorazol Sky Blue FF 0.90

Dye left in soln = 3.8 °/° of the total amount.

Chlorazol Brown MS 0.80

Liquor colourless.

Chapter VIII

Diffusion of Dyes through "Cellophane" in the Presence of Urea.

The ease with which the Class C direct dyes are stripped from the fibre and also the initial higher absorption of Chlorazol Sky Blue FF gave enough indication of the increased rate of diffusion of the dyes in the presence of urea. Investigations were, therefore, thought desirable to be made on the rate of diffusion through a sheet of regenerated cellulose in the diffusion apparatus described in Part I and to calculate the diffusion co-efficients for the dyes studied.

In using the diffusion data, the thickness of the membrane has been taken as that of water-swollen conditions at room temperature (18-20 °C), though there is an increase in the thickness of the film, when it is transferred from water to 20.0 °/° urea solution and viewd under the microscope. A very simple piece of apparatus was devised for this purpose which is shown in Fig. 52.

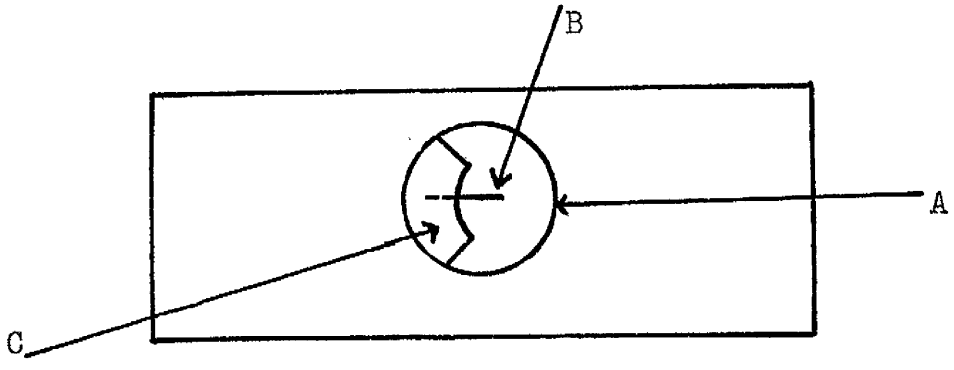


Fig. 52

A piece of glass tube A approximately 1 cm long and 1 cm in diameter was fused on a microscopic slide to hold the solution. A small strip of "Cellophane" B, with a sharply cut edge, was fixed in a slit made vertically on the inside wall of a semi-circular piece of rubber tubing C, which could be slid down the glass tube. By this arrangement, the "Cellophane" strip could be viewed vertically under the microscope.

The increase in thickness observed when water was replaced with 20.0 °/° urea solution, corresponded to 5.3 °/° on the basis of water-swollen thickness.

Though this change is quite significant, yet due to the uncertainty of this value at higher temperatures which could not be established because of the experimental difficulties, the thickness of the water - swollen membrane has been used in these calculations.

The corresponding check on the length and breadth of the sheet used, was made with the help of a cathetometer. Strips about 15 cm long and 11 cm broad (maximum breadth) were first soaked in water at 20 °C and their lengths measured between two marks, the film being held between two glass compressed strips. The same pieces were then transferred to 20.0 °/° urea solution at the same temperature, without the glass strips, and the lengths measured in solution after allowing sufficient time for the equilibrium. Under these

conditions, no change could be detected. In fact, the "Cellophane" used in the diffusion experiments was very highly orientated and would not show great variations in length and breadth.

In the following Tables, the same notations are retained as those in Part I.

Table XLVII

Diffusion of Chlorazol Sky Blue FF through "Cellophane",

10.0 g/l. dye + X °/° Urea

X °/°	L s	D_L cm^2 /s	C_L g/cc	P $g/cm^2/s$	D_E cm^2 /s	C_E g/cc
0.0			At 90 °C			
0.0	2880	42.81 x10^{-10}	16.00 x10^{-3}	7.98 x10^{-9}	78.44 x10^{-10}	8.75 x10^{-3}
5.0	1980	61.57	16.26	11.70	83.05	12.10
10.0	1980	61.57	19.51	14.04	104.77	11.51
15.0	1800	68.48	24.60	19.47	138.26	12.11
20.0	1380	89.32	16.10	17.54	133.00	11.36
30.0	1200	102.73	16.53	19.62	184.35	9.77
			At 80 °C			
0.0	4140	29.77	10.90	4.00	--	--
5.0	3960	31.55	13.57	4.88	--	--
10.0	3600	34.24	18.17	7.19	--	--
15.0	2520	49.91	14.60	8.30	63.98	11.16
20.0	1932	63.84	11.35	8.42	--	--
30.0	1440	85.61	11.84	11.78	76.70	13.21

FIG. 53

EFFECT OF TEMPERATURE AND CONCENTRATION OF UREA ON THE DIFFUSION OF CHLORAZOL SKY BLUE FF THROUGH "CELLOPHANE".

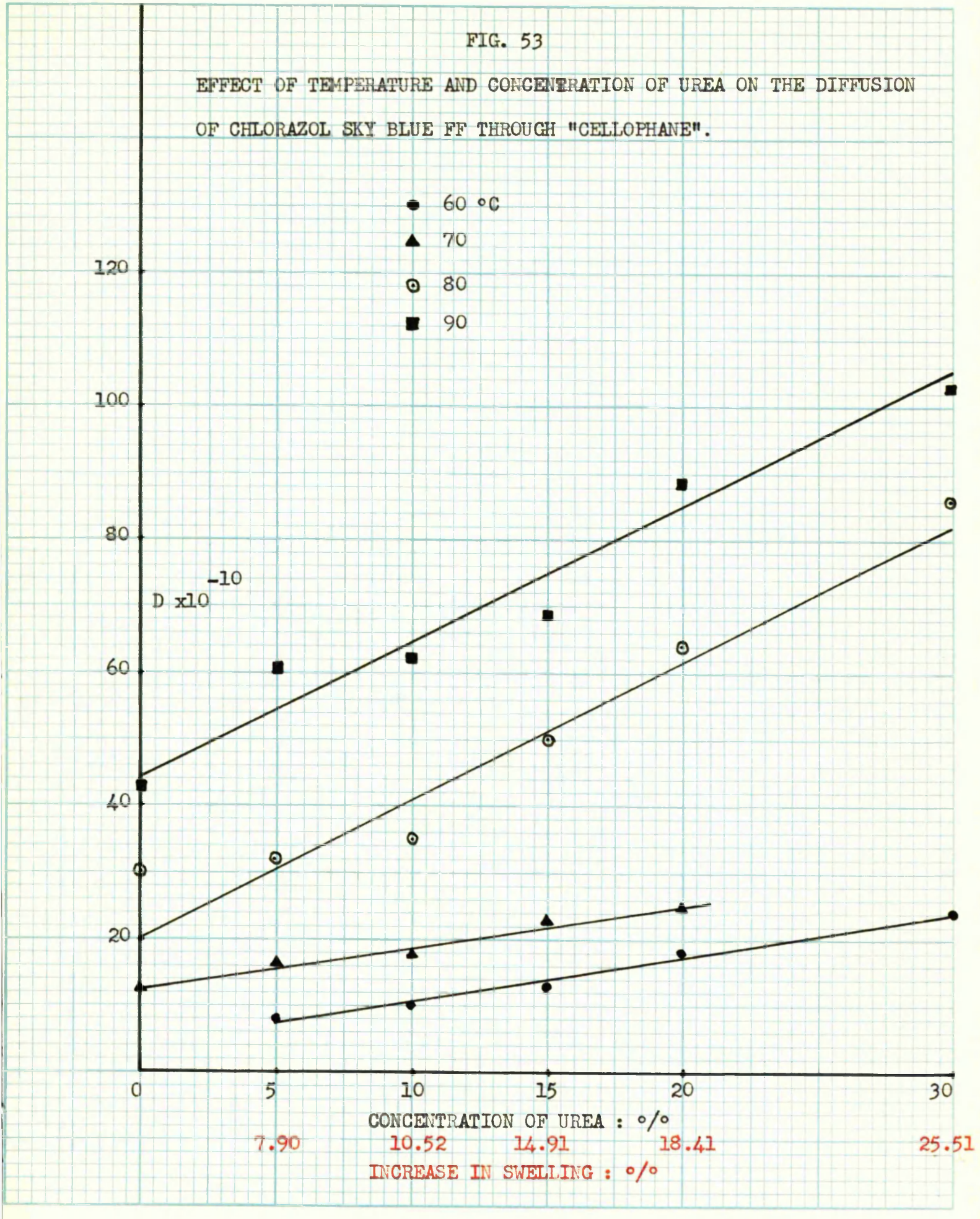


FIG: 54

EFFECT OF TEMPERATURE ON THE DIFFUSION OF CHLORAZOL SKY BLUE FF THROUGH "CELLOPHANE"

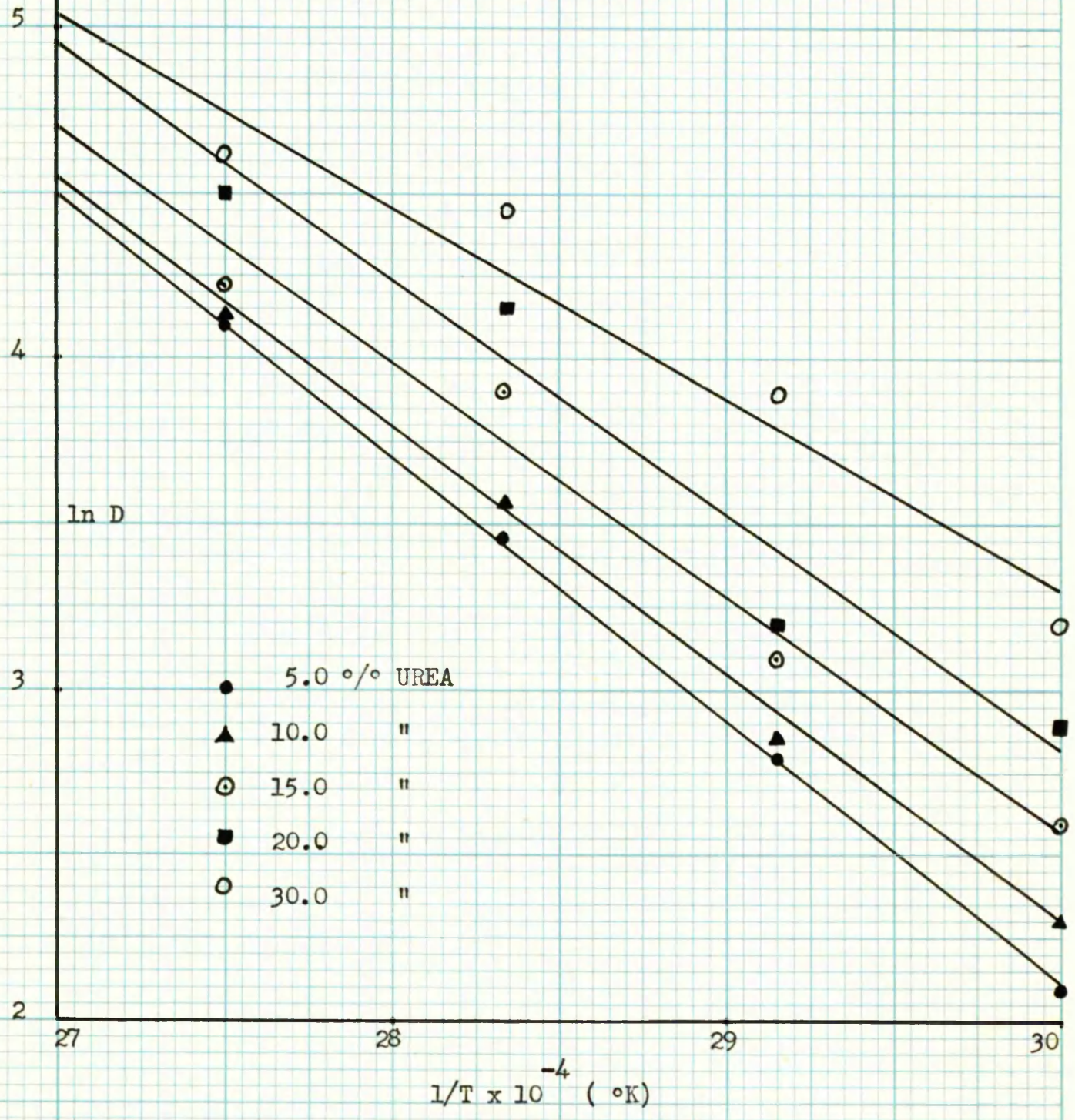


Table XLVII contd.

At 70

0.00	10080	12.22	12.62	1.78	15.57	9.85
5.0	7560	16.31	12.69	2.37	—	—
10.0	7200	17.12	16.70	3.40	—	—
15.0	5400	22.83	16.74	4.44	32.53	11.75
20.0	5040	24.46	17.48	4.89	—	—
30.0	2520	48.90	10.57	6.02	42.36	12.24

At 60 °C

5.0	15120	8.15	10.11	0.96	6.40	12.80
10.0	12000	10.02	11.23	1.40	10.06	12.00
15	9360	13.17	10.64	1.61	13.00	10.49
20.0	6840	18.02	10.02	2.09	15.35	11.70
30.0	5040	24.46	14.50	4.09	31.67	11.16

The effect of the concentration of urea and temperature on the diffusion is shown in Fig. 53 and Fig. 54. From Fig. 53, it is clear that the diffusion co-efficient increases uniformly with the concentration of urea and that this relationship is better represented by a straight line. Moreover, the slopes of the lines fall as the temperature decreases. The figures in red along the X-axis in Fig.53 indicate the °/° increase in swelling of viscose. These values have

been taken from a paper by Preston and Coworkers (J.Text. Inst., 1954, 45(7), T504) and it is assumed that the order of swelling of viscose and "Cellophane" is similar.

Quantitatively, the effect of temperature is shown in Fig. 54, in which ln D is plotted against the reciprocal of absolute temperature. The lines have been drawn by applying the principle of least square distance, keeping Y constant, for the points which show some scatter. The slopes of the lines at different concentrations of urea and hence the energies of activation of diffusion are given below:-

Table XLVIII

Concentration of Urea	Slope, E/R	E, cal./degree/mole.
5.0 °/°	- 80.00 x 10^2	- 15,824
10.0	- 76.11	- 15,055
15.0	- 72.13	- 14,267
20.0	- 71.22	- 14,087
30.0	- 64.28	- 12,715

The decreasing order of the value of E with increased comcentration of urea explains clearly the ease with which diffusion occurs as compared to that in the presence of electrolyte for which the corresponding value of E is - 17,189 cal./degree/mole.

FIG. 55

EFFECT OF THE CONCENTRATION OF CHLORAZOL SKY BLUE FF ON THE DIFFUSION CO-EFFICIENT THROUGH "CELLOPHANE" AT 30°C IN PRESENCE OF 20.0 °/° UREA.

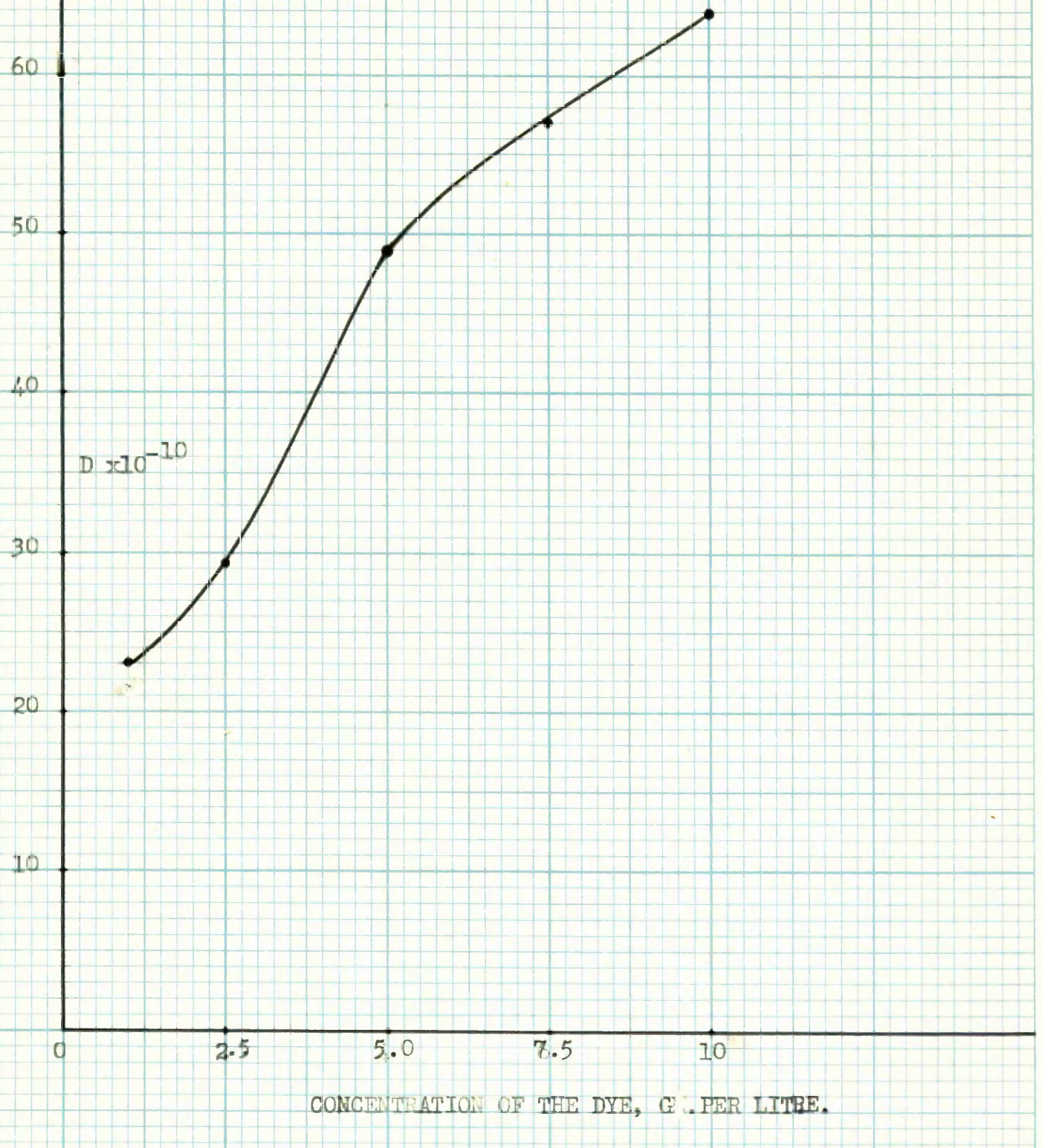


Table XLIX

Effect of the Concentration of Chlorazol Sky Blue FF, X °/° dye, Diffusing through "Cellophane" at 80 °C in the presence of 20.0 °/° Urea.

X	L	D_L	C_L	P	D_E	C_E
	s	cm^2/s	g/cc	$g/cm^2/s$	cm^2/s	g/cc
0.10	5400	22.83×10^{-10}	8.64×10^{-3}	2.28×10^{-9}	--- $\times 10^{-10}$	--- $\times 10^{-3}$
0.25	4200	29.35	11.48	3,89	47.17	7.09
0.50	2520	48.91	10.55	5.96	55.77	9.20
0.75	2160	57.07	11.08	7.31	53.74	11.70
1.00	1932	63.84	13.08	8.40	---	---

These results are shown in Fig. 55 and it will be seen that the diffusion co-efficient rises rapidly with the concentration of the dye and afterwards, the rise is gradual.

Table L gives the data, when 1.0 °/° of the dye diffuses in the presence of urea as well as 1.0 °/° NaCl. As was anticipated, the effect of NaCl on the diffusion is opposite to that of urea. The results in the last row are for a film that was treated for 1 hour in 20.0 °/° urea solution before the addition of the dye. There is practically no change in the time-lag but the rate of permeation is definitely increased.

Table L

Diffusion of Chlorazol Sky Blue FF at 80 °C.

Composition of the Int. Soln. 1.0 °/° dye + 1.0 °/° NaCl + X °/° Urea.

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_{E_2} cm^2/s	C_E g/cc
Salt	5400	22.83 x10^{-10}	36.20 x10^{-3}	9.50 x10^{-9}	-- x10^{-10}	-- x10^{-3}
5.0	4860	25.36	35.50	10.41	--	--
10.0	3600	34.24	29.55	11.70	--	--
20.0	2520	49.91	27.77	15.70	---	---
One hour's pre-treatment; diffusion in 20.0 °/° Urea only.						
	1920	63.08	13.08	9.80	61.04	13.80

A similar behaviour is observed when the dye diffuses in the presence of both urea and the electrolyte, at 70 °C. Table LI shows the data of these experiments.

Table LI

Diffusion of Chlorazol Sky Blue FF at 70 °C , with similar concentrations as in Table L.

5.0	8680	14.27	24.11	3.98	9.25	36.96
10.0	7200	17.12	30.55	6.61	15.00	34.88
20.0	5220	23.64	33.00	9.06	26.07	29.90
One hour's pre-treatment ; diffusion in 20.0 °/° Urea only.						
	5040	24.46	18.62	5.26	39.20	11.55

The time-lag, as before remains unaffected, but the permeation rate is increased from 4.89 x10^{-9} to 5.26 x10^{-9} $g/cm^2/s$ due to the pretreatment.

Diffusion of Chrysophenine G through "Cellophane"
in the Presence of Urea.

In the following Tables, results of the diffusion of Chrysophenine G in the presence of uniform concentrations of urea are given. The symbols used retain the original significane as in Part I. It may be remarked here that when a mixture of this dye and urea is heated for some time at or above 60 °C, and then allowed to cool, a small amount of the dye is thrown down as a fine precipitate, which re-dissolves on heating, although nothing happens to the mixture in the cold and the solution remains clear. It has already established (cf. page 107) that heating of the dyestuff in the presence of 20.0 °/° urea solution at 80 °C for5 hours does not produce any loss in the tinctorial value of the dye, when the readings on the Spekker are compared to those for a similar , but untreated dye solution. It may be due to a loose addition compound formed between urea and the dye, which breaks on warming or dilution since it was found that the amount of this precipitate increased stoichiometrically with the concentration of the dye and urea.

Table LII gives the results of the diffusion of Chrysophenine G, 0.20 °/° dye , diffusing in X °/° Urea, at different temperatures.

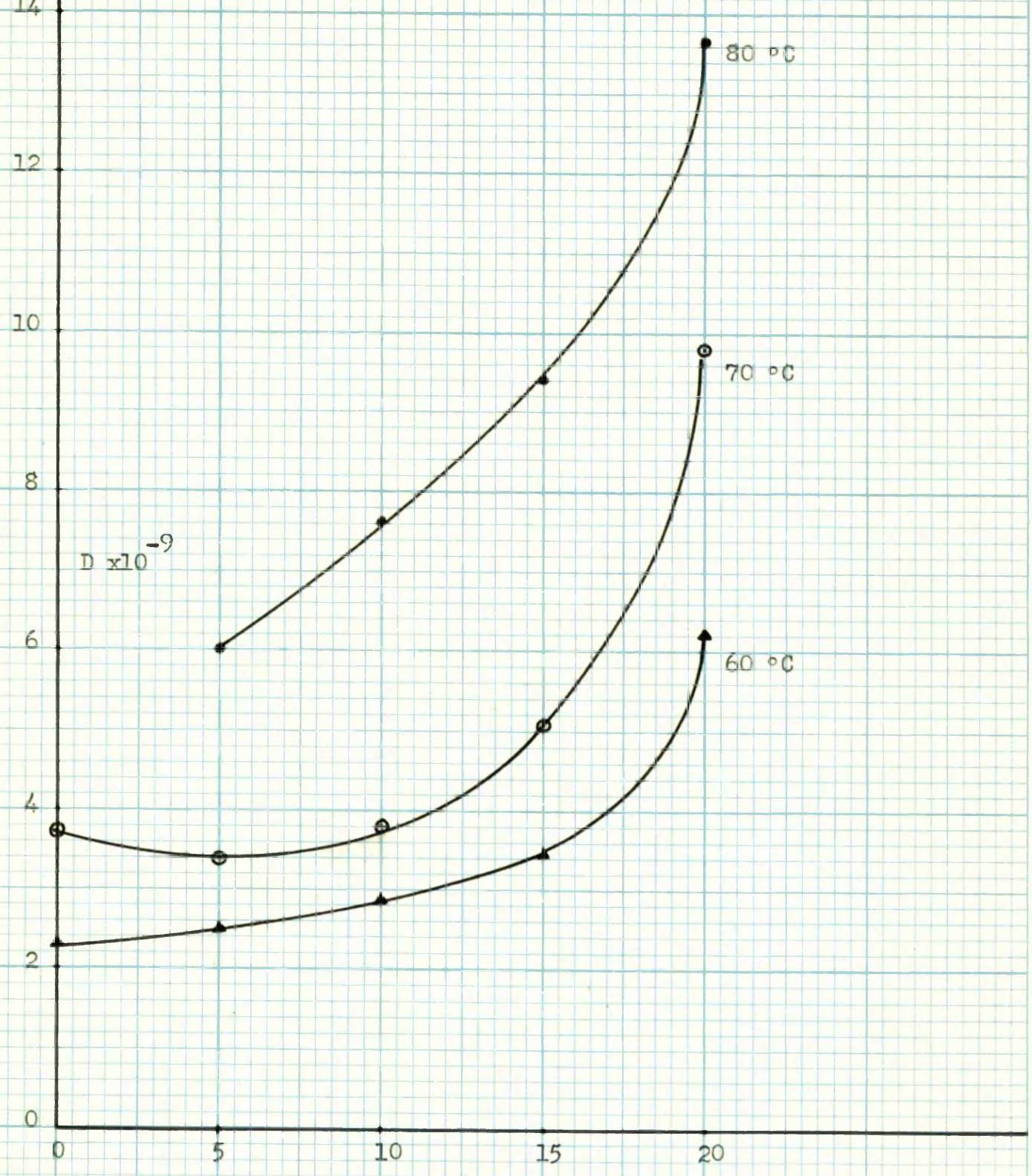
Table LII

Diffusion of Chrysophenine G, 0.20 °/° dye + X °/° Urea

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
			At 80 °C			
0.0	1080	11.41 $\times 10^{-9}$	3.54 $\times 10^{-3}$	4.68 $\times 10^{-9}$	20.94 $\times 10^{-9}$	1.92 $\times 10^{-3}$
5.0	2040	6.04	11.28	7.89	18.66	3.64
10.0	1620	7.60	12.48	10.96	27.39	3.44
15.0	1320	9.34	10.56	11.40	24.94	3.94
20.0	900	13.70	7.56	11.99	33.12	3.20
			At 70 °C			
0.0	3240	3.80	7.31	3.19	11.87	2.31
5.0	3600	3.42	11.08	4.39	9.92	3.01
10.0	3240	3.80	10.60	4.68	17.00	2.49
15.0	2400	5.13	8.42	5.00	15.94	2.68
20.0	1260	9.78	5.17	5.85	20.00	2.49
			At 60 °C			
0.0	5400	2.28	6.65	1.75	5.92	2.55
5.00	4860	2.54	6.08	1.78	7.31	2.09
10.0	4320	2.85	5.81	1.92	7.16	2.30
15.0	3600	3.43	4.62	1.83	6.64	2.42
20.0	1980	6.22	3.98	2.87	11.47	2.12

FIG. 56

EFFECT OF THE CONCENTRATION OF UREA ON THE DIFFUSION CO-EFFICIENT OF CHRYSOPHENINE G THROUGH "CELLOPHANE".



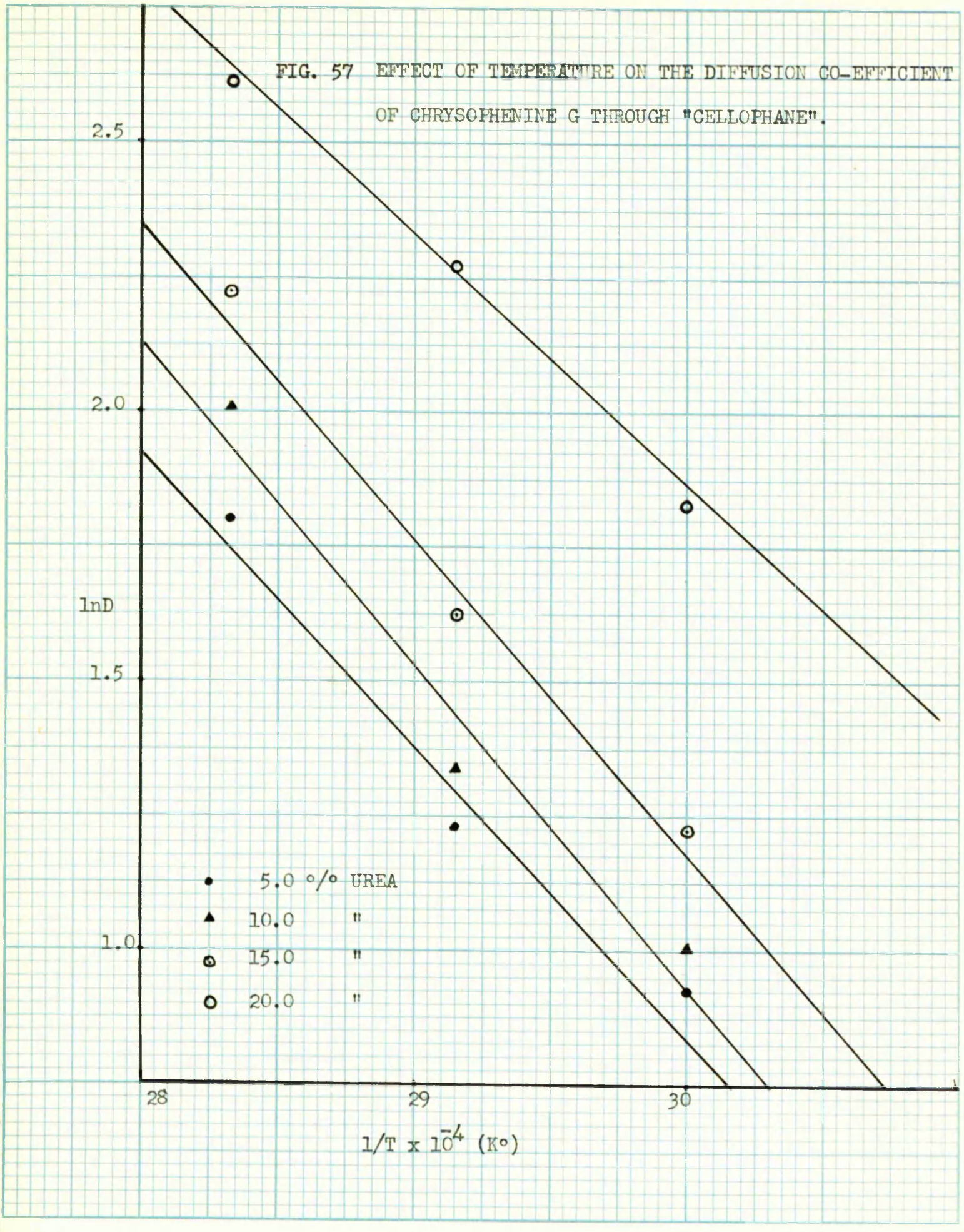
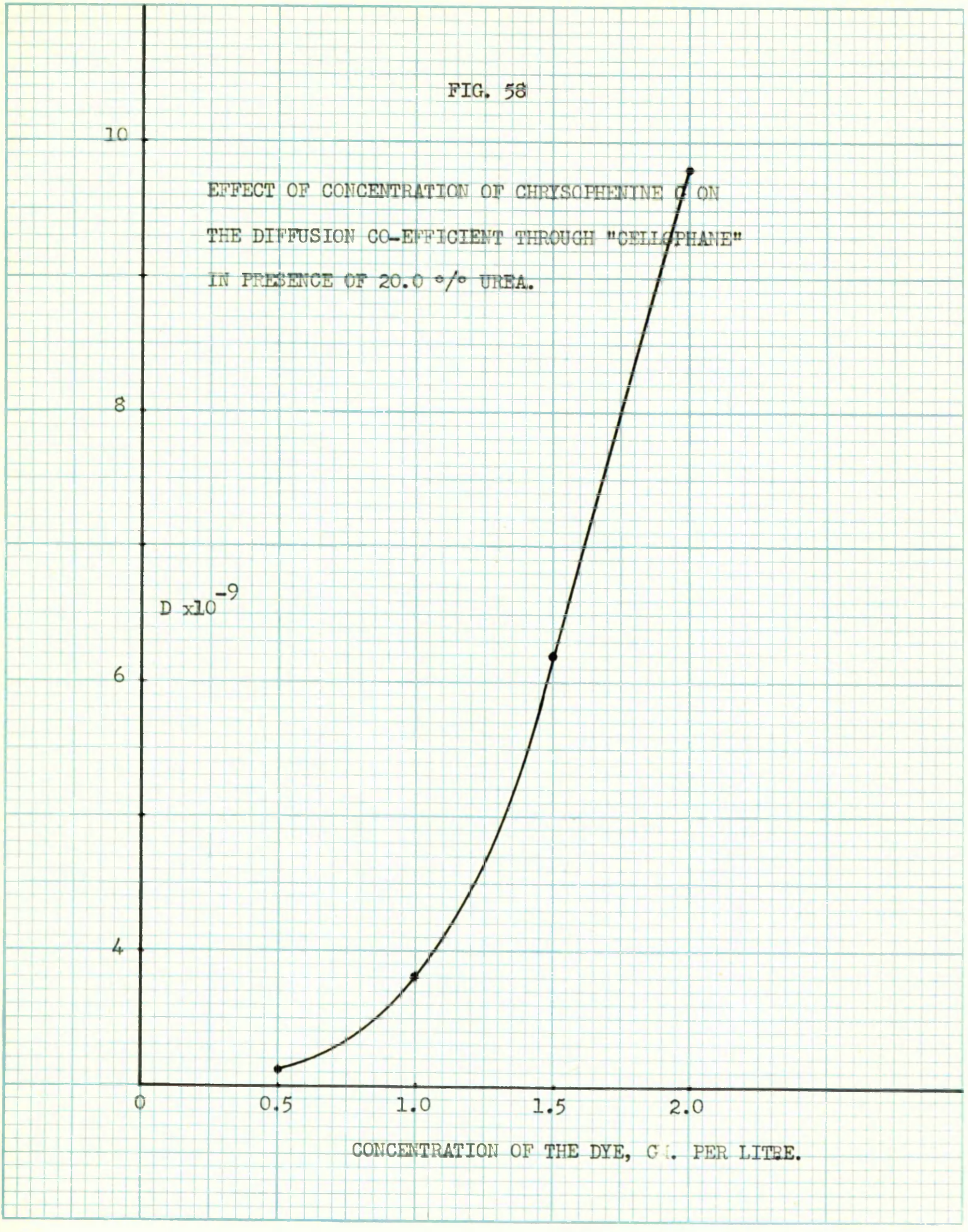


FIG. 57 EFFECT OF TEMPERATURE ON THE DIFFUSION CO-EFFICIENT OF CHRYSOPHENINE G THROUGH "CELLOPHANE".

FIG. 58


EFFECT OF CONCENTRATION OF CHRYSOPHENINE G ON
THE DIFFUSION CO-EFFICIENT THROUGH "CELLOPHANE"
IN PRESENCE OF 20.0 °/° UREA.
10
8
6
4
D x10^-9
0
0.5
1.0
1.5
2.0
CONCENTRATION OF THE DYE, G.M. PER LITRE.

The results of Table LII are shown graphically in Figs. 56 and 57. In Fig. 56, the curves for the plot of diffusion co-efficient against the concentration of urea become steeper with a rise in temperature and the same effect is determined quantitatively in Fig. 57. The values derived from the lines are set out below.

Table LIII

Energies of Activation of Diffusion for Chrysophenine G.

Conc. of Urea, °/°	Slope, E/R	E, cal./degree/mole
0.0	-98.15×10^{2}	- 19.414
5.0	- 53.77	- 10636
10.0	- 60.18	- 11,904
15.0	- 58.71	- 11,613
20.0	- 47.12	- 9,320

It will be seen that in the case of 20.0 °/° urea, the value of E is reduced by more than 1/2 of that for water alone.

Table LIV

Effect of the Concentration of the Dye, X °/° on the Diffusion of Chrysophenine G in 20.0 °/° Urea at 70 °C.

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.05	3960	3.11×10^{-9}	5.28×10^{-3}	1.90×10^{-9}	10.90×10^{-9}	1.50×10^{-3}
0.10	3240	3.80	7.05	3.10	12.35	2.18
0.15	1980	6.22	4.79	3.45	10.23	2.89
0.20	1260	9.78	5.17	5.85	20.00	2.49

These results are shown graphically in Fig. 58.

Table LV

Effect of the Concentration of Urea, X °/° on the Diffusion of Chrysophenine G, 0.20 °/° dye + 0.50 °/° NaCl, at 70 °C.

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.0	1320	9.33×10^{-9}	15.98×10^{-3}	17.25×10^{-9}	11.20×10^{-9}	13.30×10^{-3}
5.0	720	17.14	8.47	16.75	18.47	7.76
10.0	660	18.65	6191	14.91	12.82	10.01
15.0	780	15.80	9.29	16.99	19.95	7.29
20.0	840	14.67	10.01	16.99	22.34	6.54

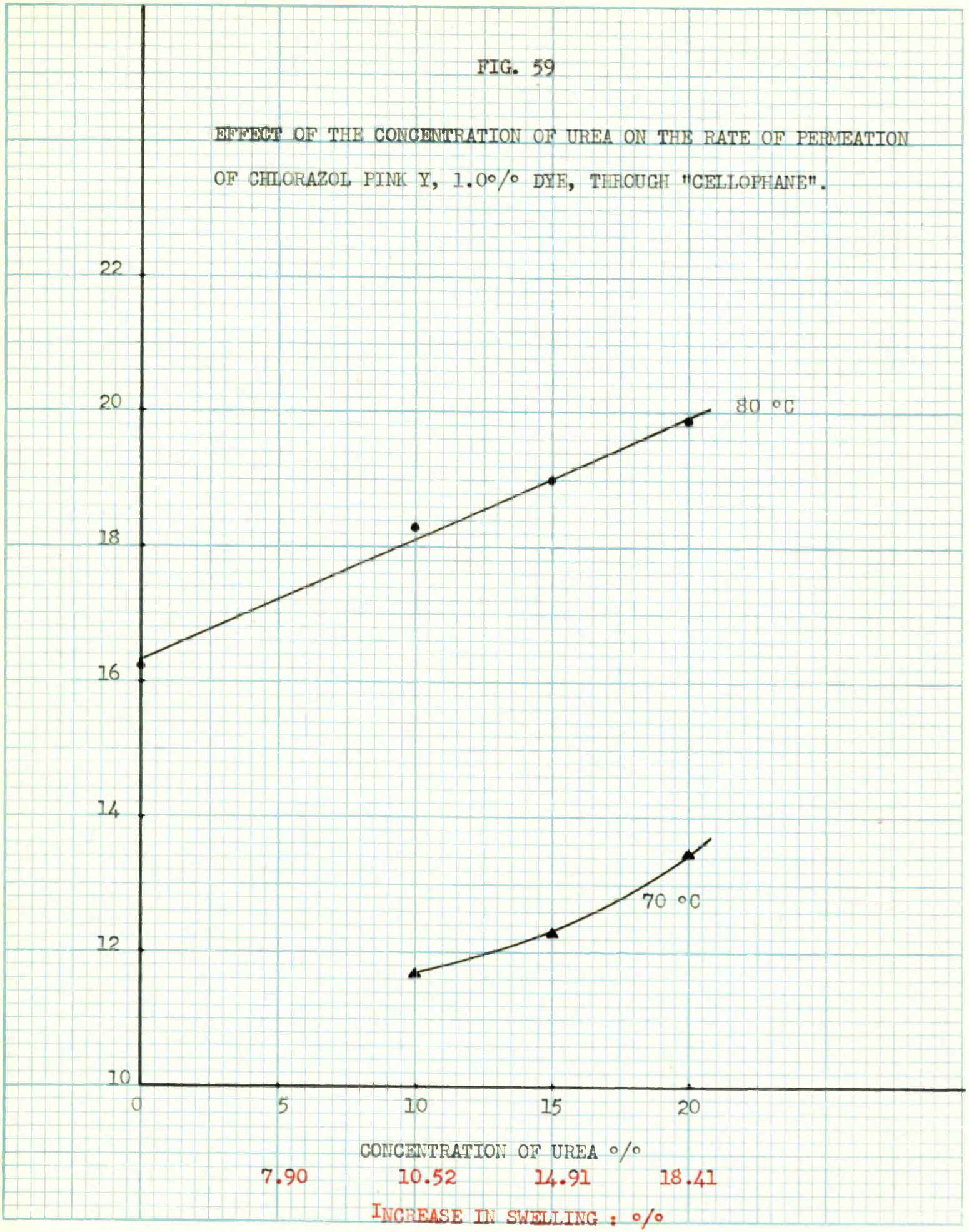
On comparing the values of D_L with those for urea or NaCl alone, it will be found that the combined effect of urea and salt enhances the rate of permeation of the dye for two reasons :

1. The effect of the electrolyte is to increase the absorption of the dye within the film.

2. The effect of urea is to desorb the dye, but this effect is offset by the electrolyte on the ingoing side of the film, while it remains undisturbed on the outgoing side of the film, where urea and the electrolyte function as usual and consequently, due to higher absorption, the desorption is also proportional to it.

FIG. 59

EFFECT OF THE CONCENTRATION OF UREA ON THE RATE OF PERMEATION OF CHLORAZOL PINK Y, 1.0°/° DYE, THROUGH "CELLOPHANE".



Diffusion of Chlorazol Pink Y through "Cellophane" in the Presence of Urea.

Table LVI

Diffusion of Chlorazol Pink Y, 1.0 °/° dye + X °/° Urea.

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
			At 80 °C			
0.0	360	34.24×10^{-9}	4.10×10^{-3}	16.23×10^{-9}	28.54×10^{-9}	4.92×10^{-3}
10.0	"	"	4.62	18.28	22.41	6.98
15.0	"	"	4.80	19.00	20.00	8.14
20.0	"	"	5.02	19.88	26.43	6.53
			At 70 °C			
10.0	1080	11.41	8.86	11.70	17.55	5.72
15.0	"	"	9.33	12.31	18.10	5.85
20.0	"	"	10.26	13.48	22.53	5.23

These results show how careful adjustment of the concentration of the dye is essential for the measurements of the diffusion co-efficients by this technique. The time-lag is hardly affected, while there is an increase in the rate of permeation with the increased concentration of urea. The plot of P against the concentration of urea at 80 is linear, while the one for 70 °C is nearly linear, as shown in Fig. 59.

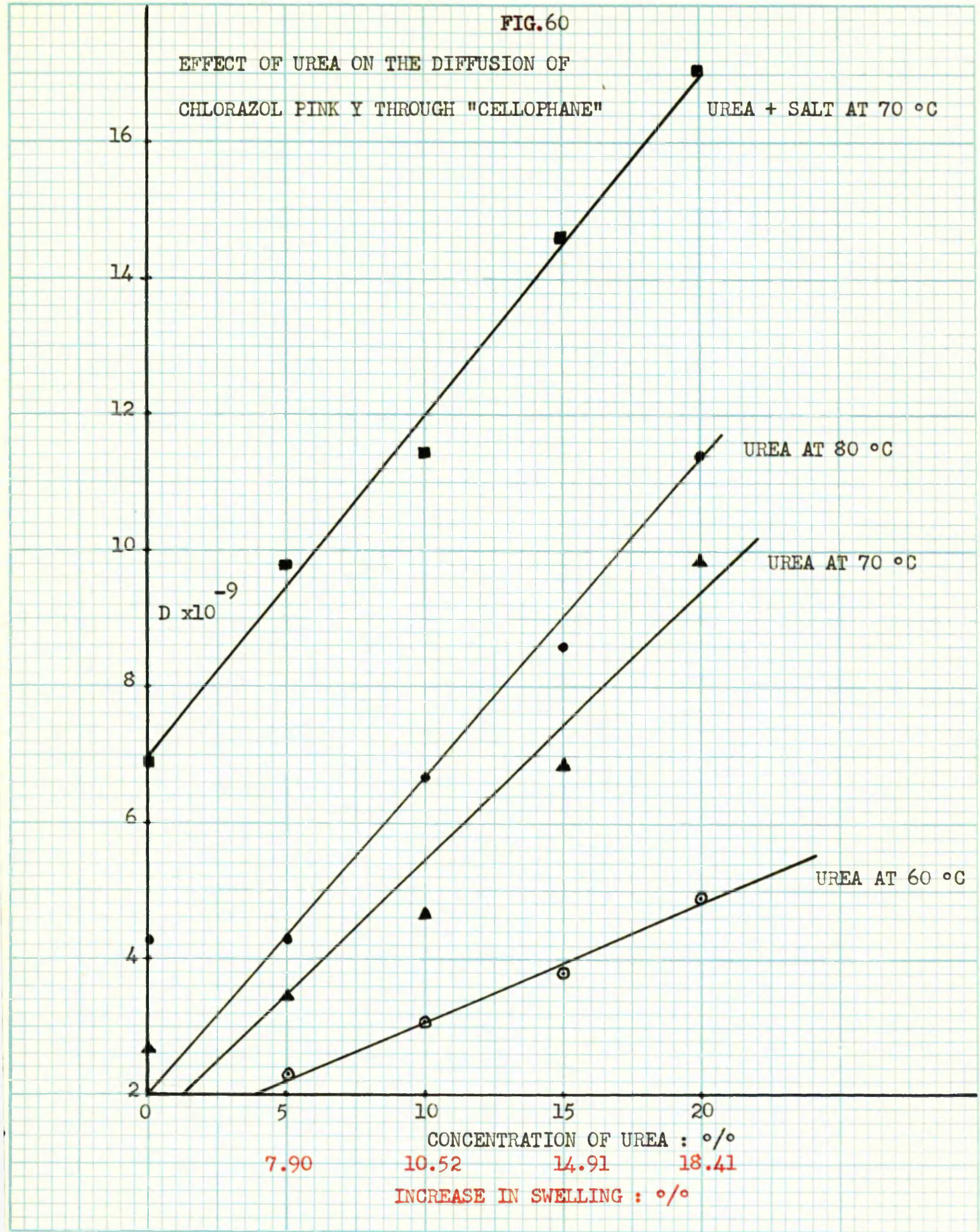
Table LVII

Diffusion of Chlorazol Pink Y, 0.20 °/° dye + X °/° Urea

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
			At 80 °C			
0.0	2880	4.28×10^{-9}	2.94×10^{-3}	1.47×10^{-9}	12.65×10^{-9}	1.00×10^{-3}
5.0	2880	4.28	10.70	5.29	14.17	2.84
10.0	1800	6.85	8.50	6.73	16.52	3.50
15.0	1440	8.56	7.86	7.78	21.72	3.08
20.0	1080	11.41	5.98	7.89	19.40	3.50
			At 70 °C			
0.0	4680	2.64	2.87	0.88	7.54	1.00
5.00	3600	3.42	5.91	2.33	9.72	2.07
10.0	2700	4.56	6.31	3.33	10.90	2.63
15.0	1800	6.85	4.62	3.65	15.72	2.00
20.0	1260	9.80	3.70	4.18	12.00	2.95
			At 60 °C			
5.0	4500	2.34	3.53	1.08	7.95	1.14
10.0	3960	3.11	3.66	1.32	7.75	1.46
15.0	3240	3.80	4.19	1.84	11.08	1.43
20.0	2520	4.90	4.14	2.34	15.71	1.28

FIG.60

EFFECT OF UREA ON THE DIFFUSION OF CHLORAZOL PINK Y THROUGH "CELLOPHANE"



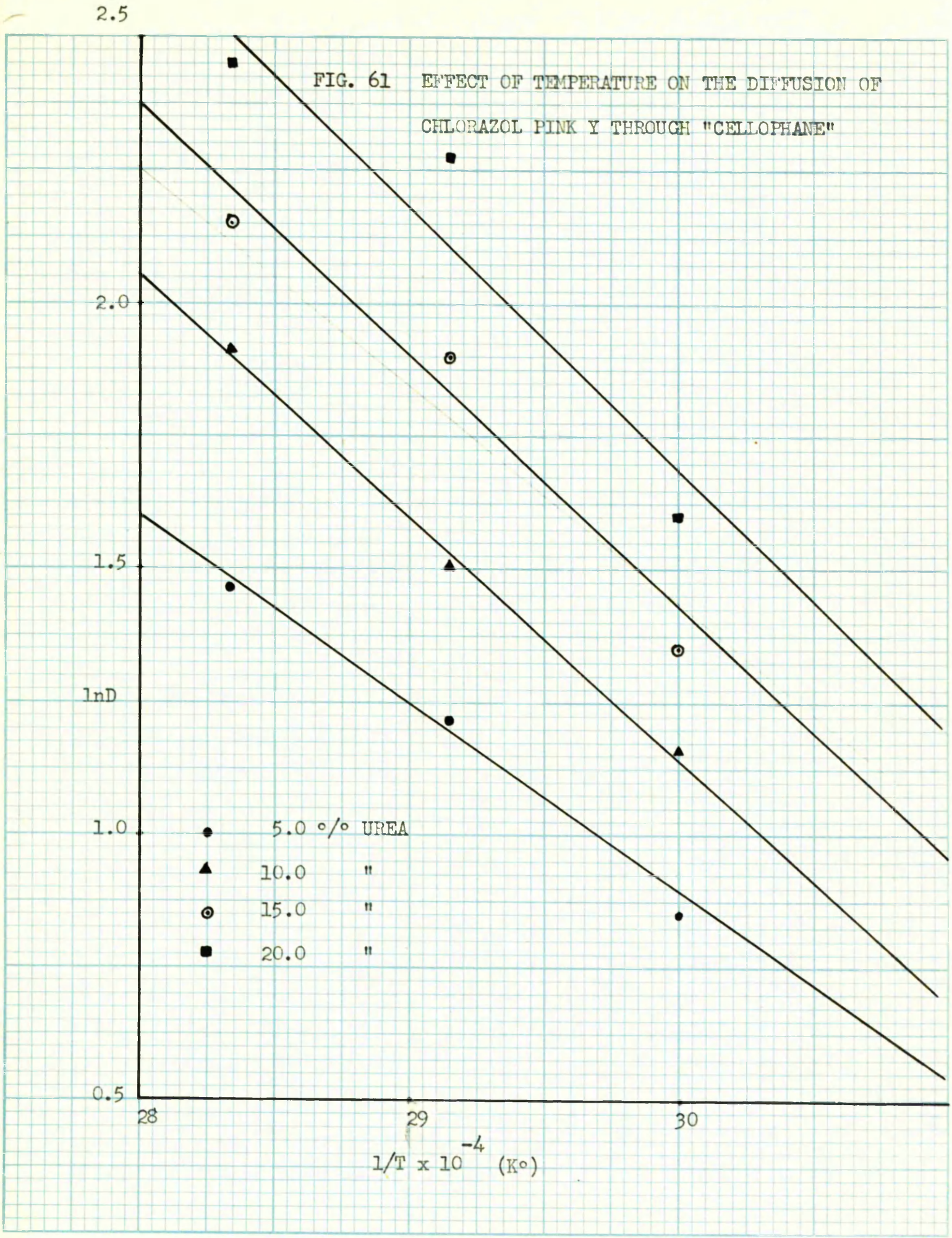


FIG. 61 EFFECT OF TEMPERATURE ON THE DIFFUSION OF CHLORAZOL PINK Y THROUGH "CELLOPHANE"

The results shown in Table LVII are graphically represented in Figs. 60 and 61. In Fig. 60, the plot of the diffusion coefficient against the concentration of urea is linear for all the temperatures. Quantitatively, the effect of temperature from these data is derived from Fig. 61. Table LVIII shows the values calculated from Fig. 61.

Table LVIII

Concentration of Urea, °/°	Slope, E/R	E, cal/degree/mole.
0.0	-63.80×10^2	- 12,520
5.0	- 34.48	- 6,820
10.0	- 45.59	- 9,018
15.0	- 47.41	- 9,378
20.0	- 49.27	- 9,746

When the values for different concentrations of urea are compared with those for water alone or electrolyte, (E = - 19,483 cal./degree/mole), E shows a big decrease , though there is an apparent paradox between these values themselves. This is most probably due to the higher absorption of the dye on the film with the increased concentration of urea, as is indicated by the last column in Table LVII, i.e., the absorption superceeds the desorption, the dye molecules become passive and have to acquire a greater energy of activation of diffusion.

FIG. 62

EFFECT OF THE CONCENTRATION OF THE DYE ON THE DIFFUSION OF CHLORAZOL PINK Y THROUGH "CELLOPHANE" AT 80 °C IN THE PRESENCE OF 20.0 °/° UREA.

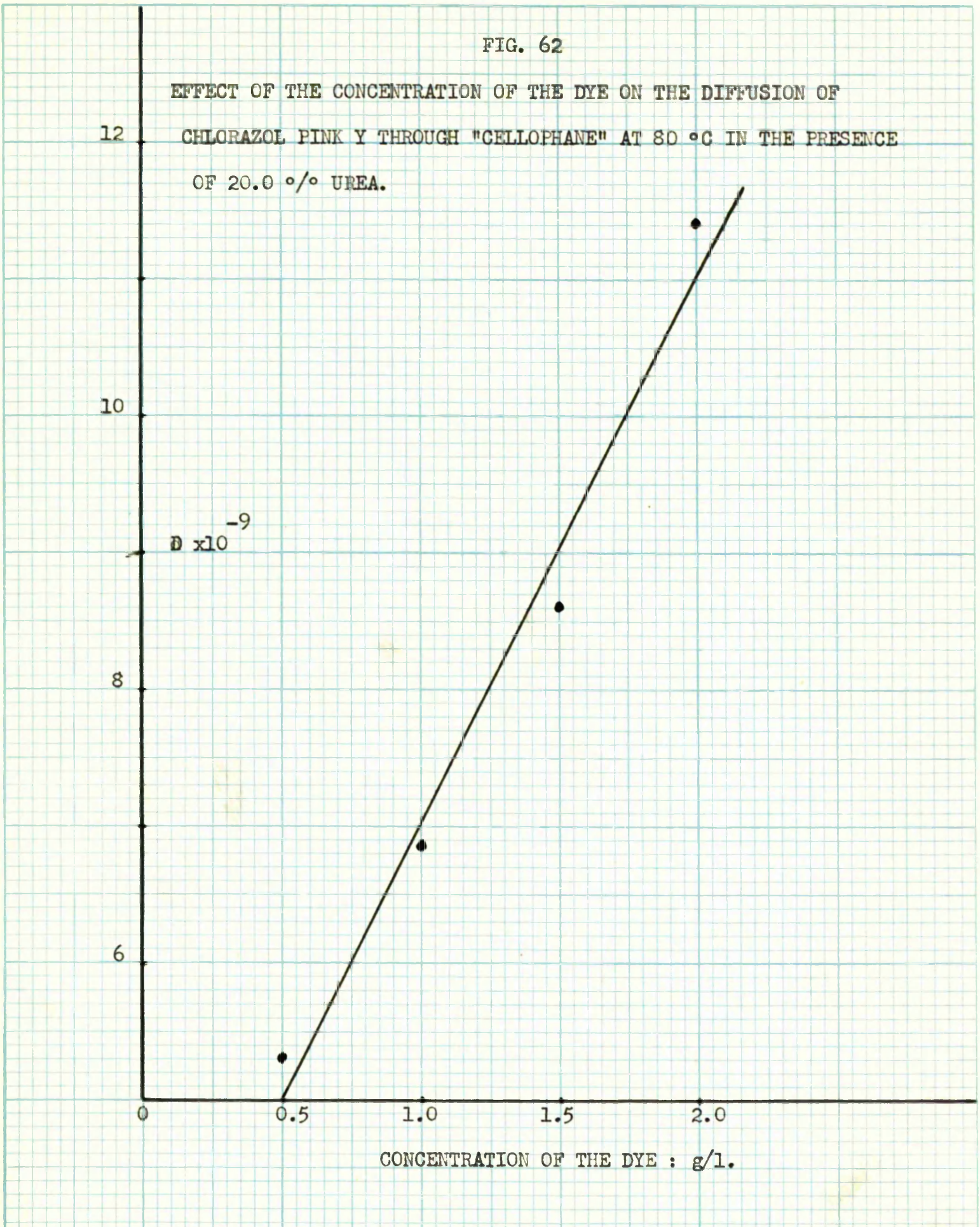


Table LIX

Effect of the Concentration of Chlorazol Pink Y, X °/° dye + 20.0 °/° Urea, at 80 °C

X	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.05	2340	5.30×10^{-9}	7.20×10^{-3}	4.39×10^{-9}	18.00×10^{-9}	2.10×10^{-3}
0.10	1800	6.85	8.84	7.02	28.86	2.10
0.15	1440	8.56	6.62	6.55	17.07	3.30
0.20	1080	11.41	5.98	7.89	19.40	3.50

Fig. 62 shows the plot of the diffusion co-efficient against the concentration of the dye, which falls on a straight line.

Table LX

Effect of the Concentration of Urea on the Diffusion of Chlorazol Pink Y, 0.20 °/° dye + 1.0 °/° NaCl at 70 °C.

Urea °/°	L s	D_L cm^2/s	C_L g/cc	P $g/cm^2/s$	D_E cm^2/s	C_E g/cc
0.0	1980	6.85×10^{-9}	12.70×10^{-3}	9.24×10^{-9}	7.78×10^{-9}	10.22×10^{-3}
5.0	1260	9.80	7.65	8.77	8.60	8.80
10.0	1080	11.41	7.49	9.88	10.90	7.79
15.0	840	14.70	5.90	10.00	12.12	4.10
20.0	720	17.12	6.22	12.31	15.60	6.80

These results are shown in Fig. 60, alongwith those for urea.

Diffusion of Naphthalene Scarlet through "Cellophane" in the Presence of Urea.

Table LXI

Diffusion of Naphthalene Scarlet, 2.0 g/l. dye + X °/° Urea

X	P, $g/cm^2/s$	D, cm^2/s
	At 70 °C	
0.0	15.50×10^{-9}	5.05×10^{-8}
5.0	16.17	6.96
10.0	18.33	7.91
15.0	19.59	8.37
20.0	26.90	11.58
	At 60 °C	
0.0	7.31	3.00
5.0	8.36	3.60
10.0	10.29	4.43
15.0	12.00	5.16
20.0	14.33	6.16
	At 50 °C	
0.0	3.95	1.70
5.0	4.97	2.12
10.0	6.73	2.89
15.0	7.25	3.14
20.0	8.04	3.46

FIG. 63

EFFECT OF UREA ON THE DIFFUSION OF NAPHTHALENE SCARLET THROUGH "CELLOPHANE".

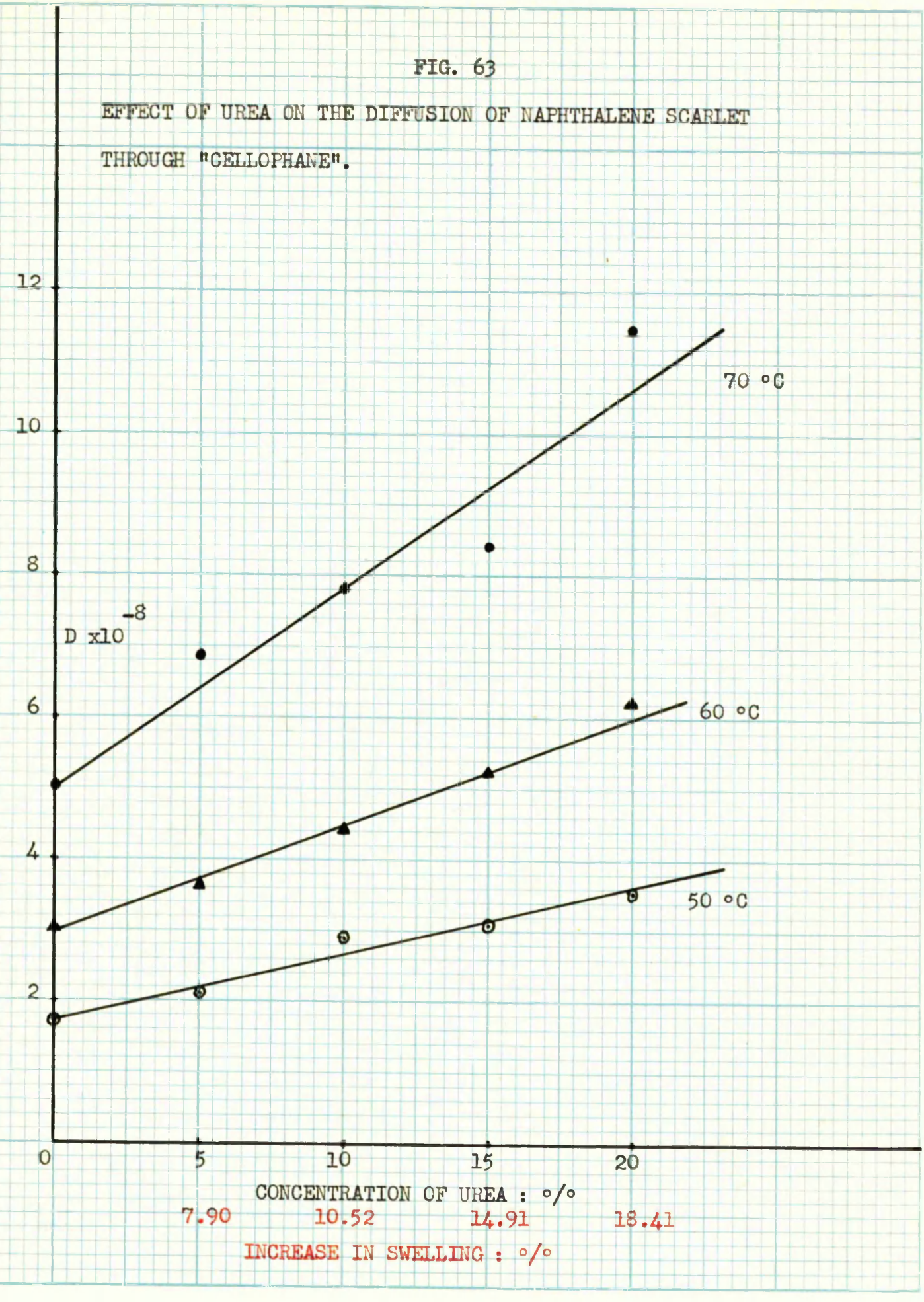
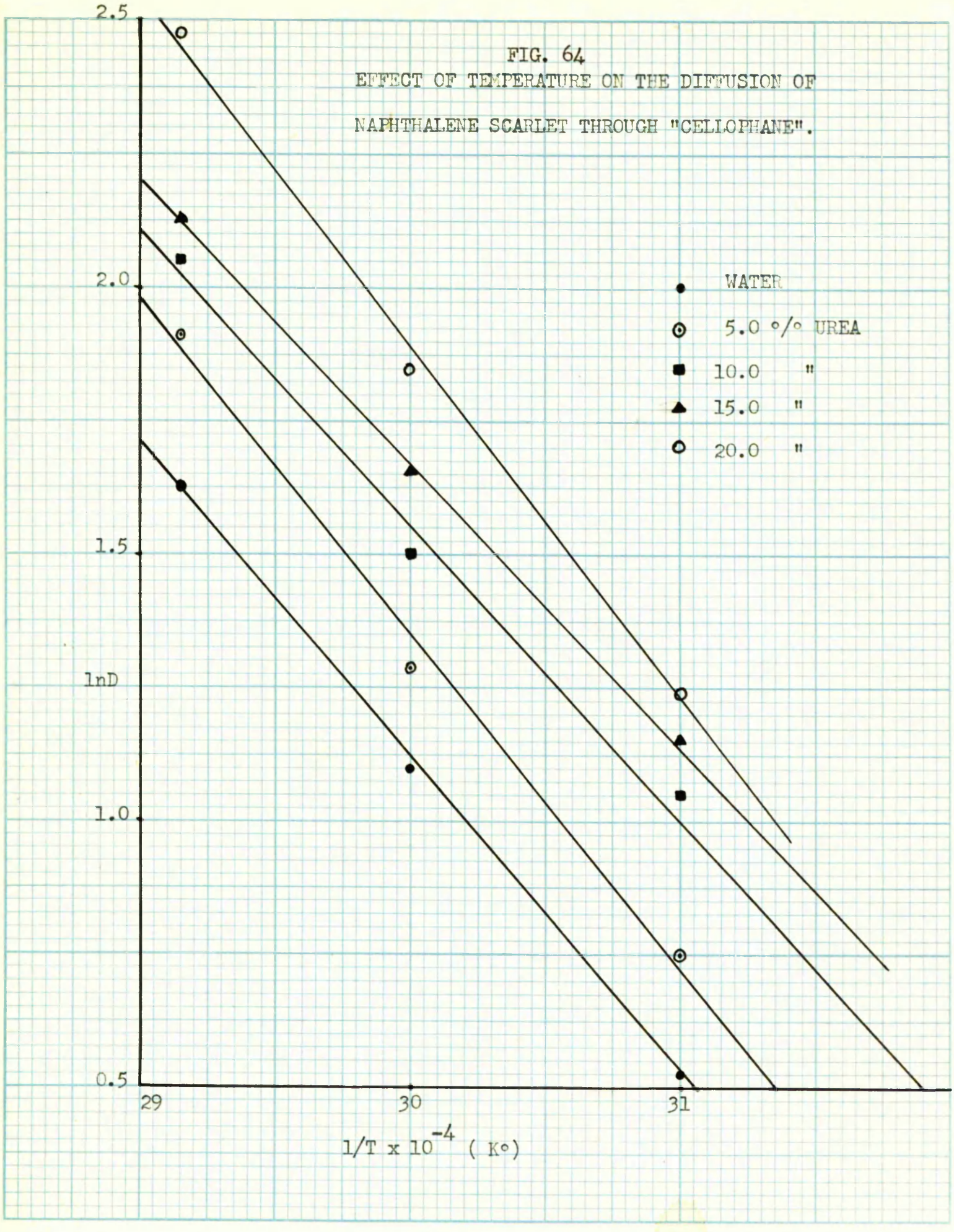


FIG. 64

EFFECT OF TEMPERATURE ON THE DIFFUSION OF NAPHTHALENE SCARLET THROUGH "CELLOPHANE".



These results are shown in Figs. 63 and 64 and the energies of activation of diffusion are calculated from Fig.64, which are set out below.

Table LXII

Energies of Activation of Diffusion for Naphthalene Searlet

Conc. of Urea, °/°	Slope, E/R	E, cal./degree/mole
0.0	$- 58.53 \times 10^2$	- 11,576
5.0	- 63.00	- 12,461
10.0	- 55.51	- 10,980
15.0	- 53.13	- 10,509
20.0	- 66.13	- 13,080

The corresponding values of E, when the dye is diffusing in 1.0 and 0.10 °/° NaCl are respectively, -5190 and - 8037 cal./degree/mole and a comparison of these values shows that the diffusion proceeds much according to the free diffusion of dyes through a porous plate, where the dyes do not undergo any interaction with the medium. The effect of urea is not so particularly pronounced as in the case of the direct dyes.

Table LXIII shows the values of the diffusion coefficient when a varying amount of the dye diffuses in the presence of 20.0 °/° urea. It will be seen that, with the exception of one, all the values fall pretty close to each other. However, the

permeabilities increase progressively with the concentration of the dye.

Table LXIII

Effect of the Concentration of Naphthalene Scarlet on the Diffusion, in 20.0 °/° Urea at 60 °C

Conc. of the dye, g/l.	P, $g/cm^2/s$	D, cm^2/s
0.5	3.89×10^{-9}	6.63×10^{-8}
1.0	6.61	5.98
1.5	8.77	4.86
2.0	14.33	6.16

Table LXIV

Combined Effect of 0.10 °/° NaCl + X °/° Urea on the Diffusion of Naphthalene Scarlet, 2.0 g/l. dye.

X	P, $g/cm^2/s$	D, cm^2/s
	At 60 °C	
10.0	21.93×10^{-9}	9.43×10^{-8}
20.0	"	"
	At 50 °C	
10.0	14.62	6.43
20.0	"	"

The corresponding values in the absence of urea, but in 0.10 °/° NaCl, at these temperatures are:-

50 °C	17.54	7.54
60 °C	24.47	10.56

Diffusion of Carbolan Brilliant Green through "Cellophane" in the Presence of Urea.

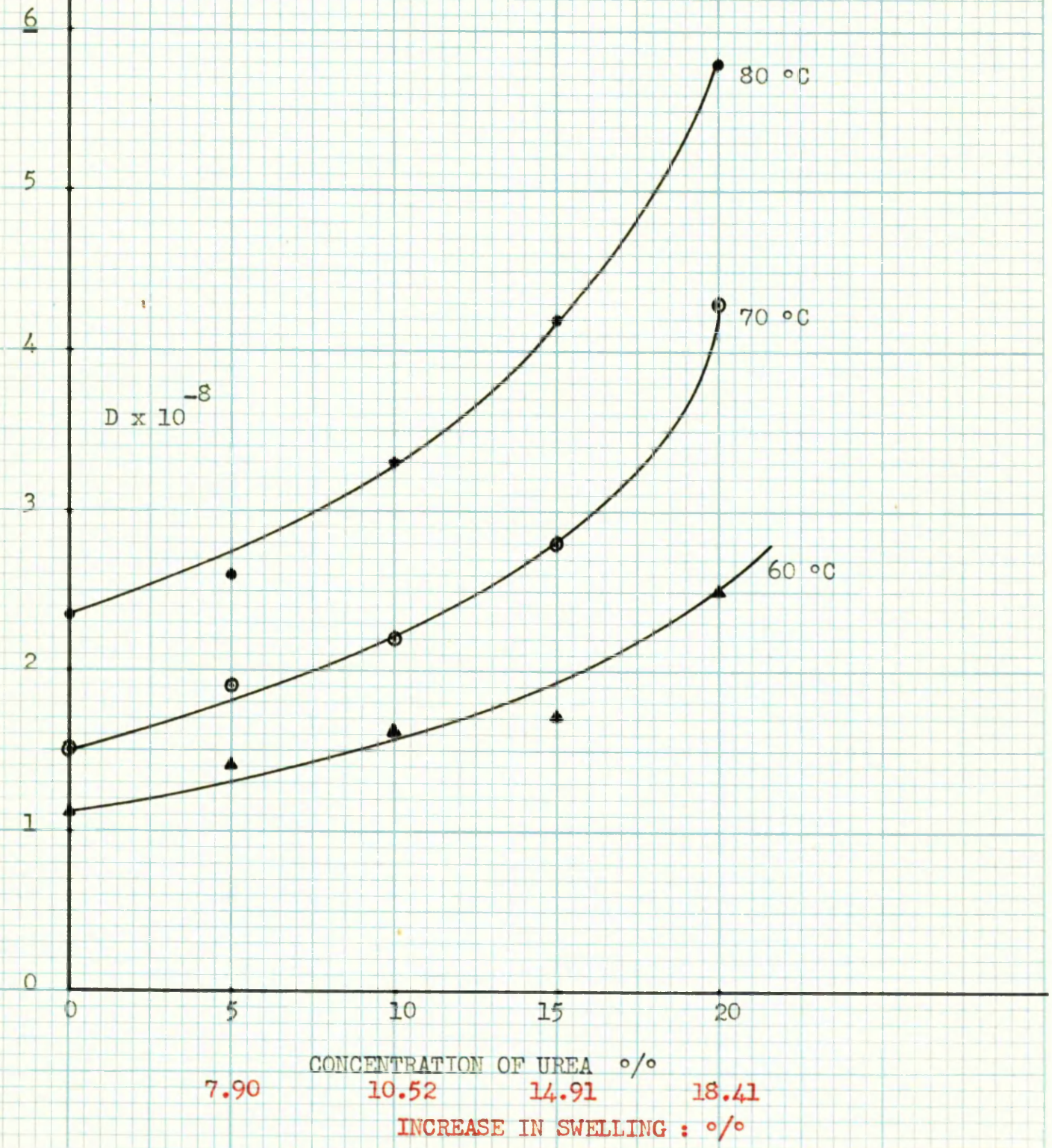
Table LXV

Diffusion of Carbolan Brilliant Green, 5.0 g/l. dye + X °/° Urea.

X	P, $g/cm^2/s$	D, cm^2/s
	At 80 °C	
0.0	13.60×10^{-9}	2.34×10^{-8}
5.0	14.62	2.57
10.0	19.09	3.26
15.0	24.62	4.24
20.0	33.04	5.67
	At 70 °C	
0.0	8.63	1.51
5.0	10.82	1.86
10.0	12.87	2.19
15.0	15.57	2.82
20.0	25.15	4.33
	At 60 °C	
0.0	6.64	1.14
5.0	8.36	1.44
10.0	9.15	1.56
15.0	9.85	1.71
20.0	14.62	2.51

FIG. 65

EFFECT OF CONCENTRATION OF UREA ON THE DIFFUSION OF CARBOLAN BRILLIANT GREEN THROUGH "CELLOPHANE".



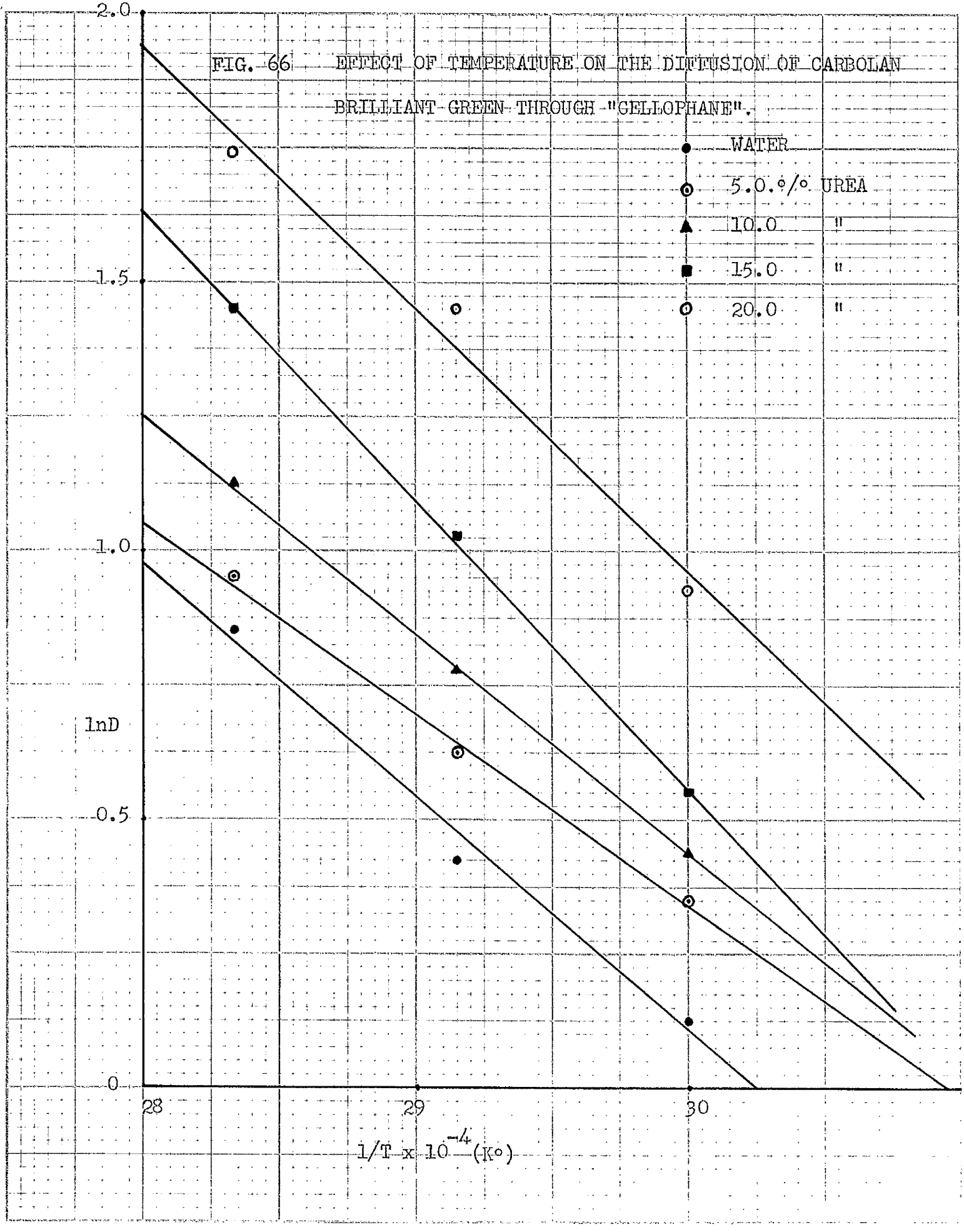


FIG. 66 EFFECT OF TEMPERATURE ON THE DIFFUSION OF CARBOLAN BRILLIANT GREEN THROUGH "GELLOPHANE".
WATER
5.0 % UREA
10.0 "
15.0 "
20.0 "
2.0
1.5
1.0
0.5
0
lnD
28
29
30
1/T x 10^-4 (K°)

Figures 65 and 66 show these data graphically. In Fig. 65 the plot of the diffusion co-efficient against the concentration of urea flattens out as the temperature falls. The same effect is determined quantitatively in Fig. 66 and the energies of activation of diffusion calculated from it, are tabulated below.

Table LXVI

Energies of Activation of Diffusion for Carbolan Brilliant Green

Conc. of Urea, °/°	Slope, E/R	E, cal./degree/mole.
0.0	$- 43.18 \times 10^2$	- 8,541
5.0	- 35.35	- 6,992
10.0	- 40.98	- 8,106
15.0	- 53.33	- 10,549
20.0	- 48.69	- 9,331

As was the case with Naphthalene Scarlet, the value of E in the case of urea are higher than that for water alone or 0.20 °/° NaCl (E = - 8,052 cal./degree/mole), with the exception of the value for 5.0 °/° Urea. The two acid dyes thus show a similar behaviour when diffusing through "Cellophane" in the presence of urea.

Table LXVII shows the effect of the concentration of the dye on the diffusion of Carbolan Brilliant Green, when diffusing in 20.0 °/° urea. It will be seen that the diffusion co-efficient

remains fairly constant within the experimental error, when the concentration of the dye is increased, which is more or less characteristic of free diffusion in solution.

Table LXVII

Effect of the concentration of the dye on the diffusion of Carbolan Brilliant Green in 20.0 °/° urea at 70 °C

Conc. of the dye, g/l.	P, $g/cm^2/s$	D, cm^2/s
2.0	7.89×10^{-9}	3.39×10^{-8}
3.0	11.99	3.44
4.0	15.38	3.31
5.0	25.15	4.33

Table LXVIII

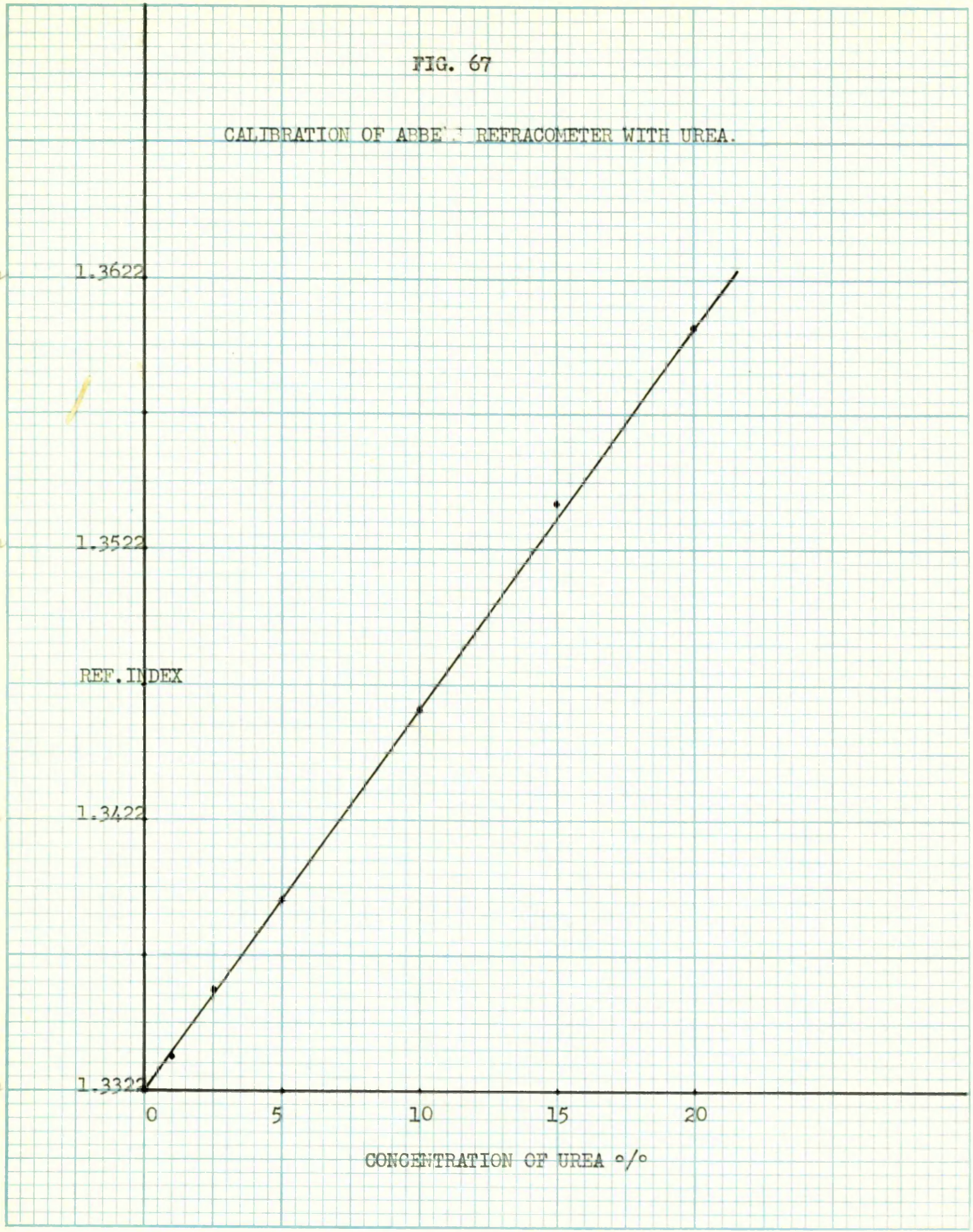
Combined Effect of Urea, X °/° + 2.0 g/l. NaCl on the Diffusion of Carbolan Brilliant Green, 5.0 g/l. of the dye

Conc. of Urea, °/°	Same Symbols as above.	
	At 70 °C	
0.0 (Salt only)	30.70	5.29
5.0	31.29	5.38
10.0	"	"
20.0	"	"
	At 60 °C	
0.0 (Salt only)	22.22	3.82
5.0	22.25	3.82
10.0	"	"
20.0	"	"

From these results, it is obvious that urea plays hardly any part, when the dye diffuses in the presence of both urea and salt.

FIG. 67

CALIBRATION OF ABBE'S REFRACOMETER WITH UREA.



Chapter IX

Absorption of Urea by Cellulose and Heat of Wetting in Urea Solutions.

Purified samples of viscose and cotton, as used in the previous experiments, were conditioned to contain a known amount of moisture and a fixed weight of the fibres was brought into contact with an excess of urea solution in stoppered flasks. The system, fibre – urea solution, was allowed to reach equilibrium at room temperature (23 ± 0.5 °C), shaking gently at intervals. The change in the concentration of the external solution was determined by means of an Abbe refractometer and the amount of urea absorbed by cellulose was calculated with the help of the chart shown in Fig.67, the original calibration chart being twice larger in scale . The relevent data for one such experiment are given below:-

Wt. of the conditioned fibre = 1.000 g.

" " dry " = 0.886 g.

∴ " " moisture = 0.114 g.

Vol. of this moisture at 23 °C = 0.115 cc

Vol. of 10.0 °/° urea soln. used = 10.0 cc

∴ Total vol. of the soln. after equilibrium = 10.115 cc

Conc. of urea determined after the expt. = 9.625 °/°

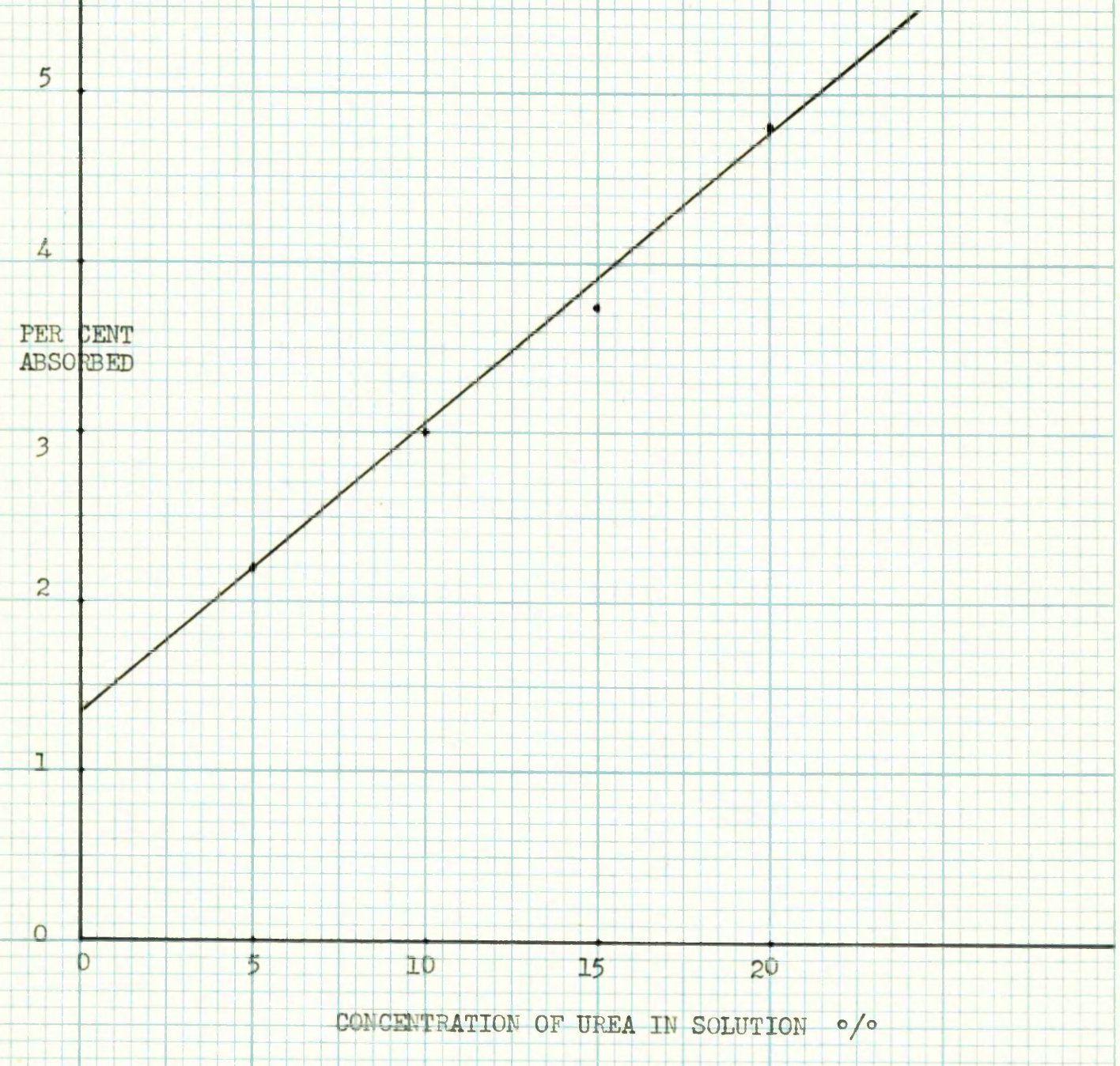
∴ Amount of urea absorbed by cellulose $= 1.0 - \frac{10.115 \times 9.625}{100}$

$= 0.026_5$ g.

Hence °/° amount of urea absorbed by cellulose = 2.99 °/°

FIG. 68

AMOUNT OF UREA ABSORBED BY VISCOSE AT 23 °C



In a similar way, the amount of urea absorbed was determined in different concentrations of urea solutions, keeping the fibre to solution ratio at 1 : 10. The results are tabulated below.

Table LXIX

Absorption of Urea by Viscose at 23 ± 0.5 °C.

Conc. of Urea soln., °/°	Conc. after the expt., °/°	°/° of Urea absorbed
5.00	4.75	2.20
10.00	9.62_5	2.99
15.00	14.50	3.75
2 20.00	19.35	4.82

In calculating these results, no consideration has been given to any volume change brought about by the moisture in the fibre or by the fibre itself. It will be seen from Fig. 68 that upto the concentration of urea solutions studied, the amount absorbed increases in a linear manner, which is a characteristic feature of simple absorption.

An attempt was made to find the temperature co-efficient of the absorption of urea by cellulose. The fibre and the solution were brought to equilibrium at elevated temperatures, ~~40~~, 60 and 90 °C in flasks with long, narrow necks, which were tightly closed with rubber bungs. Rubber - tubing with thin walls, was wrapped round the necks and cold water circulated through it, so that the neck of the flask acted as a condenser as well. Half an hour

was considered enough for the equilibrium at these temperatures and at the end of the experiment, the contents of the flask were vigorously shaken for a few seconds and the liquid immediately transferred to small flasks placed in ice. The concentration of the solution was determined after allowing it to reach room temperature.

The following values were found:-

Temp. °C	Conc. of Urea Soln.	°/° amount of Urea absorbed
60	5.00 °/°	2.20
	10.00	2.99
	20.0	4.82
90	10.00	2.99
	20.00	4.82

The amount absorbed is thus the same as that at room temperature. This is due to a small temperature co-efficient of urea-cellulose system, as established by measuring the heat of wetting of cellulose with urea solutions.

Measurement of Heat of Wetting with Urea Solutions.

Preparation of the Fibres :-

Purified viscose and cotton, as used in the previous experiments, were conditioned in a controlled R.H. room and the moisture content of the fibres determined by drying them in an air-oven at 110 °C.

2.000 g of the conditioned fibres, chopped into small pieces (dry weight : viscose = 1.721 g, cotton = 1.880 g) and pushed inside a slender Pyrex glass capsule having approximately the following dimensions :-

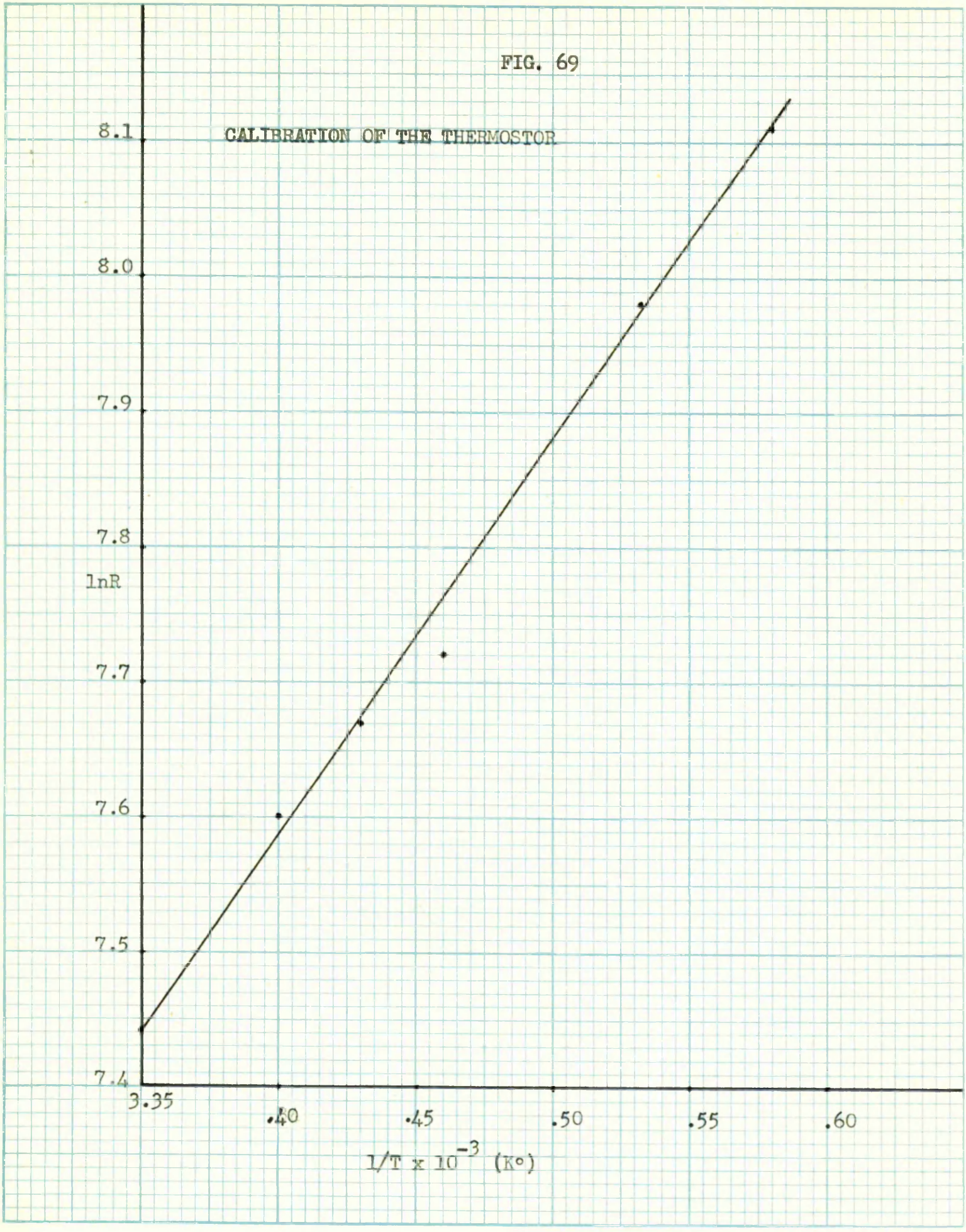
Length 5 cm, diameter 2 cm, neck 5 cm, bore of the neck 3/4 cm. The fibre was carefully pressed against the bottom and gently tapped to get tiny fibres together. The neck was then drawn into a jet in the middle to facilitate the sealing later on. The fibre sample was dried under vacuum (0.2 mm Hg) at a temperature 50 - 52 °C for over 20 hours and the capsule sealed immediately by a micro - flame. The total weight of the capsule and its contents minus that of the dry fibre, as given above, gave the weight of glass introduced in the experiment.

Calibration of the Thermostor :-

A thermostor of the type [1] F.2311 /300, was employed to detect the changes of temperature in conjuction with a Cambridge Wheatstone Bridge. Keeping the ration of the two known arms at 1:1, resistances were measured at different temperatures which were

FIG. 69

CALIBRATION OF THE THERMOSTOR



recorded with the help of a N.P.L. certified thermometer, reding directly to 0.2 °C and by estimation to 0.1 °C. The thermometer and the thermostor were kept close to each other. The relation between the observed resistance and the absolute temperature is [2]

$$R = a \cdot e^{-b/T}$$

where R is the resistance observed and T is the absolute temperature. a and b are constants. Taking $\log_e$

$$\ln R = \ln a - b / T,$$

so that ln R when plotted against the reciprocal of T, should result in a linear relation. Fig. 69 shows the calibration graph and the portion covering the range of 20 - 25 °C was enlarged and used for calculating the temperatures.

Heat Capacity of the Flask and Urea Solutions.

Though the thermal losses in a Dewar flask are supposed to be very small, yet due to the small magnitude of the temperatures involved, it was considered necessary to determine the heat losses from the flask, including the glass stirrer and the thermostor, by heating 25 cc of water electrically in the flask [3]. The difference between the electrical equivalent of heat and that actually measured, gave the losses of heat or the amount of heat retained by the apparatus.

Since the experiment proper lasted for 2 1/2 minutes, the voltage and amperage of the current used were so adjusted as to produce the required rise in temperature in 2 minutes and the extra time was allowed for the heating wire and the whole system to reach a steady state before taking the reading. In this way, it was ensured that the heat losses due to unavoidable factors were cancelled out. Further, it was assumed that the "nicron" wire did not undergo any change in its resistance

$$R_t = R_s (1 + 0.0004 (t - 20)).$$

due to small rise of temperature and that the current passing through the galvanometer (Resistance ca 500 ohms) was negligibly small as compared to that passing through the wire. (One meter of the wire had a resistance of 24 ohms and the length of the wire used as heating coil was about 15 cm).

After having determined the heat capacity of the flask, the specific heat of urea solutions was determined at different concentrations, since no value of the specific heat could be found in literature except for 10.0 °/° urea solution or lower concentrations.[4] The heat losses from the flask for different temperatures produced and the specific heats of urea solutions are given in Table LXX.

FIG. 70

HEAT CAPACITY OF THE FLASK AGAINST TEMPERATURE DIFFERENCE

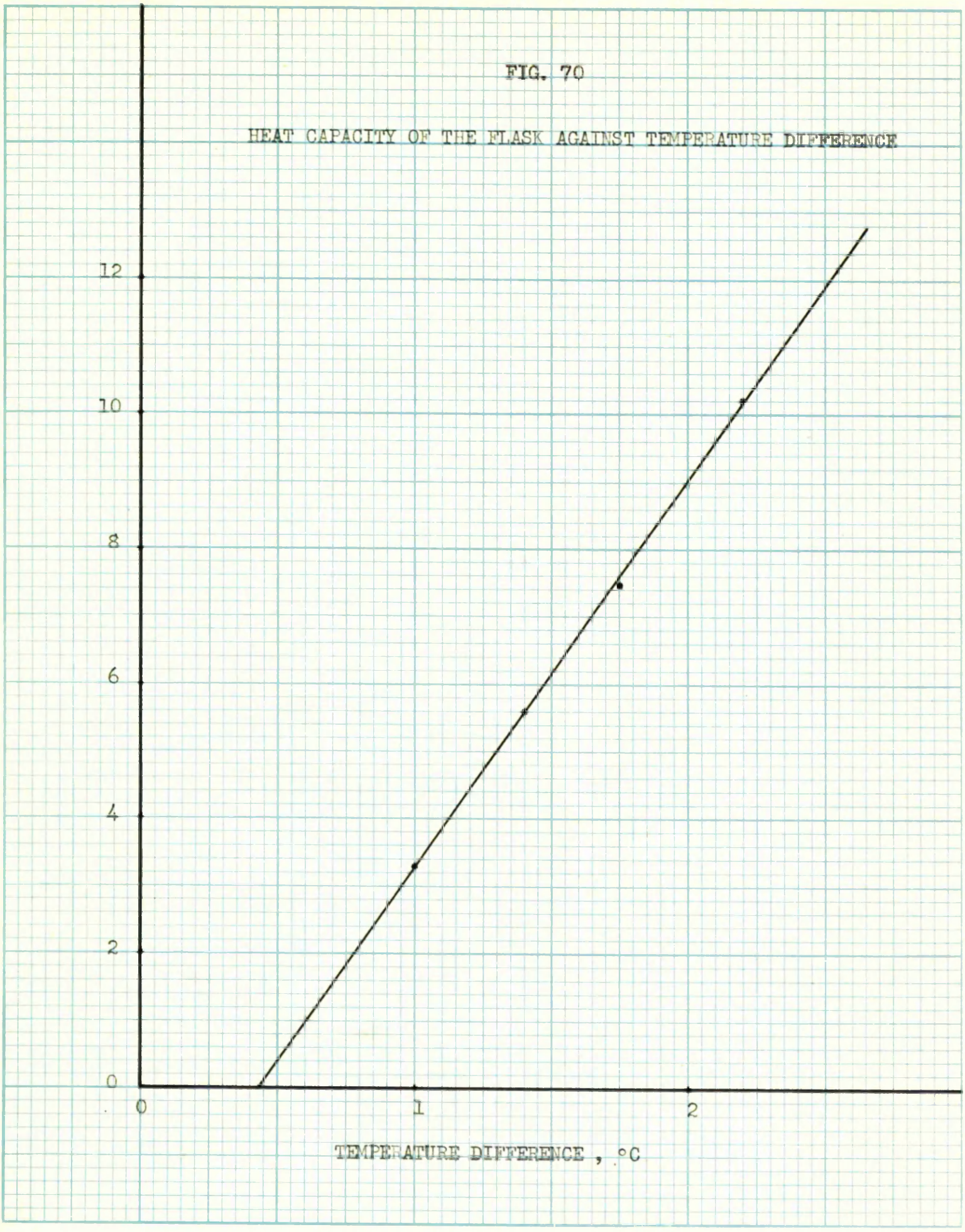


Table LXX

Loss of Heat from the Apparatus, with 25 cc of Water.

Heat, Cals.			Rise in Temp. °C
Produced electrically.	Measured actually.	Difference.	
28.34	25.02	3.30	0.997
28.09	24.79	3.28	0.998
28.09	24.81	3.32	1.006
39.89	34.10	5.79	1.371
40.31	34.57	5,74	1.390
51.26	43.53	7.73	1.752
50.76	43.38	7.38	1.744
51.51	44.03	7.48	1.771
64.33	54.30	10.03	2.184
64.33	54.11	10.22	2.176
63.50	53.16	10.34	2.138

The plot of heat lost against the rise in temperature falls on straight line and this relationship, shown in Fig. 70 was used for applying corrections in the actual experiments.

The specific heats of the urea solutions are :-

10.0 °/° Urea solution 0.9328 [4]

20.0 °/° (Mean) 0.9204 (Rise in temp. app. 1.2 °C)

40.0 °/° " 0.8085 (" " " " 1.5 °C)

Procedure :-

The weighed and sealed capsule with its contents was introduced in the Dewar flask alongwith 20 cc of water or urea solution and the flask corked. The stirrer and the thermostor passed through separate holes in the cork.

After allowing enough time, usually over 4 hours, for thermal equilibrium, the resistance of the system was determined. The thermostor was then pulled upwards and the glass capsule crushed between the stirrer and the walls of the flask. The solution, fibre and the pieces of glass were thoroughly mixed and after 2 1/2 minutes, the second resistance was noted. From a knowledge of the different quantities, the heat evolved was calculated. One such calculation is given below.

Wt. of the capsule + fibre (Viscose) = 4.975 g

" " " dry " = 1.721 g

" " glass = 3.254 g

Sp. heat of cellulose, dry (Mean) [5,6] = 0.30

" " " Pyrex glass [7] = 0.20

Wt. of 20.0 cc of 20.0 °/° urea soln. = 20.922 g

Its sp. heat = 0.9204

Resistance R_1 = 2073 $\therefore$ temp. = 292.757_1 °K

" R_2 = 1932 $\therefore$ " = 294.776_5 °K

$\therefore$ total heat evolved =

(20.922 x 0.9204 + 1.721 x 0.30 + 3.254 x 0.20) x 2.0194 plus correction for the heat lost (9 cal.) = 50.26 cals.

T The different values of heat evolved for 1.721 g of viscose and 1.880 g of cotton, both for water and urea solutions are tabulated below.

Table LXXI

Heats of Wetting of Viscose and Cotton

Solution	Viscose		Cotton	
	Rise in temp. °C	Heat evolved cal.	Temp. rise °C	Heat evolved cal.
Water	1.581	39.96	0.814	19.24
	1.578	38.37	0.822	19.43
			0.814	19.20
10.0 °/° Urea				
	1.770	44.67	0.888	20.54
	1.820	44.42	0.895	20.72
	1.783	44.32		
20.0 °/°	2.014	50.10	1.040	24.43
Urea	2.003	49.74	1.032	24.40
	2.019	50.26	1.046	24.56
40.0 °/°	2.129	50.19	1.119	25.04
Urea	2.109	49.79	1.177	25.09
			1.105	25.04

The values of heat of wetting with water for viscose and cotton as reported in literature [8] are :-

Cotton 11.0 cal per g.

Viscose:-

Durafil	20.4 cal/g	determined at 65 °/° R.H and 25 °C.
Tenasco	22.9 cal/g	

From the data of Table LXXI, the average amount of heat evolved per 162 g of cellulose is calculated.

Solution	Heat evolved, cals.	
	Viscose	Cotton
Water	3,663	1,716
10.0 °/° Urea	4,189	1,775
20.0	4,706	2,111
40.0	4,706	2,163

From the literature [9 - 15], the accepted values for the accessibility of viscose and cotton at the present moment are 70 and 35 °/° respectively. Hence converting the above data into the heat evolved per 162 g of accessible cellulose, we have the following values for the different solutions.

Solution	Viscose	Cotton
Water	5,233 cals.	4,903 cals.
10.0 °/° Urea	5,984	5,071
20.0	6,723	6,031
40.0	6,723	6,180

Taking the values of heat of wetting for 20.0°/° urea solution and comparing these with those for water alone, it is found that the accessibility of cellulose (in viscose and cotton) is increased by 28.47 and 23.00 °/° respectively. For cotton, with 40.0 °/° urea solution, this value is 26.04 °/° which is closer to the one for viscose with 40.0 °/° urea.

Conclusions.

From the study of the cellulose - urea solution system, we arrive at the following conclusions :-

1. The dielectric constant of aqueous solutions of urea is greater than that of water, as reported by Preston and Coworkers [16], increasing from 80 for water to 90 and 98 for 15.5 and 30.0 °/° urea solutions. This means that the loosely packed cellulose chains in the amorphous regions will be pushed apart to a greater extent in urea solutions than in water alone and accessibility of cellulose will become greater. Thus, while the dielectric constant is increased by 22.5 °/° from water to 30.0 °/° urea solution, the accessibility of cellulose to 20.0 °/° urea solution for viscose and cotton is increased by 28.47 and 23.00 °/°. These two properties -- the dielectric constant and the accessibility thus go hand in hand with each other.

2. The residual valency of the carbonyl group in urea will probably exert an attractive force for the cellulose surface and since the amino groups in the urea molecules are hydrophillic in nature, they will bring their atomspheres of water with them.

3. The amount of urea absorbed by cellulose from aqueous solutions, as determined by the positive sorption technique, increases in a linear way with the concentration of the external urea solution, which agrees with Langmuir's surface adsorption. The equilibrium between the fibre and the solution is reached rapidly

even at room temperatures. From this, it follows at once that the process is quickly reversible and in fact, that is the case, because urea can be readily washed off from the fibre. This view is further upheld by the fact that the heat evolved for one mole of accessible cellulose with 20.0 °/° urea is 6,723 and 6,031 cals. for viscose and cotton respectively, which is hardly in confirmity with the heat evolved, when the process is one of chemisorption in which relatively greater heat is evolved (20 to 100 K.cals per mole)[17] in view of the fact that the disruption of stronger chemical bonds is involved.

4. In an attempt to find the change in the absorption of urea at higher temperatures, it was found that the amount of urea absorbed was the same as that at room temperature for the same concentration of the solution. This is readily explained by the fact that the difference between the heats of wetting with water and urea (say for viscose with 20 .0 °/° urea) is only 6.4 cal/g of the fibre, which implies that the temperature co-efficient for cellulose - urea solution system is very small and is difficult to detect experimentally.

5. There is a very keen competition for the sites between urea and direct dyes molecules as is shown by the absorption and desorption of the dyes with urea solutions. This competition is in favour of urea when its concentration is increased, as is proved by the almost complete removal of direct dyes with urea solutions and also

by the enhanced rate of diffusion of direct dyes in the presence of urea through "Cellophane".

Once the sites are occupied by urea, in proportion to its concentration, the direct dye molecules would diffuse more freely with rather less strong forces operating between the dye molecules and the cellulose chains. In other words, urea, by reducing the absorption of the dye (as compared with salt) increases the rate of diffusion, which is in fact true, because diffusion of direct dyes through cellulose is greatly reduced by higher absorption either due to salt or low temperature [18]. Reduced absorption of the direct dye by cellulose means that less repulsive forces are exerted by the deposited dye molecules on those which are in the solution, either in the pores or in the external solution. This implies that the diffusing dye molecules have to overcome not such a strong electrical barrier as the one when the value of the absorbed dye is greater. Quantitatively, this should result in a reduction in the energy of activation of diffusion, which is, in fact found. As a corollary of this argument, urea should not affect the energy of activation of diffusion for acid dyes to the same extent, because they do not possess any affinity for cellulose, but will merely enhance the rate of diffusion by making the membrane more permeable to the dye molecules. This view is also borne out by the results of these experiments.

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Acknowledgements

The author wishes to express his most sincere thanks to J. M. Preston, Esq., D.Sc., F.R.I.C., F.T.I., for his guidance, constant advice and encouragement given throughout the course of the present work.

Grateful acknowledgements are also made to the Government of the Punjab for the award of the Scholarship and also to the Education Committee, Manchester for a grant.