FACTORS CONTROLLING MODIFIER ACTIVITY IN EMULSION POLYMERIZATIONS

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Note: The information herein reported is the property of the Office of Rubber Reserve. As such it may not be disclosed without authorization.

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Introduction

The present investigation was undertaken as a part of the Rubber Reserve Company research project on synthetic rubber at the Applied Science Research Laboratory, University of Cincinnati.

Mercaptans act as modifiers in the emulsion polymerization of butadiene and styrene. Much work has been done in both the synthetic rubber plants and the research laboratories in order to determine the exact role of mercaptans[1,2]. This has been a difficult task because of the heterogeneity of the polymerization system.

Emulsion polymerizations are carried out in soap solutions. The mutual formula for the polymerization of GR-S (styrene-butadiene copolymer) gives an idea of the system used:

S.F. Flakes	5	parts
$K_2S_2O_8$	0.3	parts
Water	180	parts
Butadiene	72	parts
Styrene	28	parts
DDM	0.5	parts

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1. Technical Report to Rubber Reserve Company No. CR-339, Modifier Studies, by Subcommittee on Modifier Action, April 1943 to February 1944.

2. W.E.Harris and I.M.Kolthoff, Technical Report to Rubber Reserve Company No. CR-626, "A Comprehensive Review of Modification, Disappearance Curves of and Activation by Mercaptans in the G.R.S. Recipe." February 1945.

SF-Flakes is a soap made up of the sodium salts of stearic, palmitic, oleic, and appreciable amounts of lauric and other short chain soaps. DDM is a commercial mixture of normal mercaptans with an average molecular weight corresponding to $C_{12}H_{25}SH$. The amount of each ingredient is given in parts per 100 parts of monomer. A great variety of soaps may be substituted for SF-Flakes, and polymerization will proceed as long as the soap is micellar. However, the polymerization will not occur in the absence of either mercaptan or persulfate.

In the above system the mercaptan is dissolved in the oil phase, and diffuses into the soap micelles, where polymerization is generally believed to be initiated. The persulfate is water soluble and acts on the mercaptan possibly either in the water phase, at the interphase of the monomer emulsion droplets, or in the soap micelle. The last is most likely.

The mechanism commonly advanced for the initiation and modification action of mercaptans is the following:

$RSH + K_2S_2O_8 \longrightarrow RS\cdot$

initiation $RS\cdot + M \longrightarrow RS\text{-}M\cdot$

$RS\text{-}M\cdot + nM \longrightarrow RS\text{-}M(M)_nM\cdot$

modification $RS\text{-}M(M)M\cdot + RSH \longrightarrow RS\text{-}M(M)_nMH + RS\cdot$

It can be seen that both the initiation function and the modifier function depend on an important property inherent to a particular mercaptan, i.e., the ease with which the mercaptan undergoes a single-electron oxidation.

In the initiator system the mercaptan undergoes a single-electron oxidation to the mercaptan radical through the oxidation by persulfate; in the chain transfer system the mercaptan is oxidized to the mercaptan radical by the polymer radical.

In addition to the inherent ease with which a mercaptan is oxidized to the free radical, the amount of mercaptan consumed depends upon its concentration at the important locus of the oxidation, i.e., in the soap micelles, or later, in the polymer-monomer particle. This concentration may depend upon the solubility of the mercaptan in the soap micelles or in the polymer-monomer particle if the diffusion rates of the mercaptan from the monomer phase into the micelles or polymer-monomer is sufficiently high to maintain solubility equilibrium. However, in general, the diffusion rates are very low and there is evidence that mercaptan solubility equilibria are not realized under the conditions of most emulsion polymerizations. Thus the rate of diffusion becomes the important factor in determining mercaptan concentration at the oxidation locus. The mercaptans can then be adequately characterized by the two inherent properties - diffusion rate and oxidation rate. The product of these two rates, expressed relative to n-DD as a standard, we shall term the Relative Diffox Product, and an attempt will be made to correlate this with mercaptan disappearance.

Historical Development

Diffusion Rate Measurements.-Diffusion rate measurements of oils into soap solutions were first carried out by J.R.Vinograd[3] by means of a microscope using oil droplets of 0.3 to 0.8 mm in diameter. He found that their diameters "decline linearly with time". This method is also being used at the University of Chicago by Harkins and Stearns[4]. They find that the "rate of decrease of the diameter of the oil drop increases with time, i.e., as the drop grows smaller". No work has been reported on the solubility rates of mercaptans in soap solutions.

Oxidation Rates.-Very little work has been accomplished concerning the ease with which the various aliphatic mercaptans can be oxidized. V. von Fisher and J.H.Day[5] measured the disappearance of n-dodecyl mercaptan in alcoholic solutions. They examined the effect that persulfate, sulfuric acid, soap, and base had on the amount of n-DD mercaptan which disappeared in a given time. The greatest loss was observed when soap, persulfate and base were used together. Kolthoff[6] investigated

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[3] Unpublished paper by Vinograd, Fong, and Sawer presented at the Sept. 11-15,1944 Meeting of the Am. Chem. Soc.

[4] J. Chem. Phys. 14, 214, (1946).

[5] Technical Report to Rubber Reserve Company No. CR-194 from Case School of Applied Science.

[6] Kolthoff and Miller, Report to Rubber Reserve Company No. CR-206 from the University of Minnesota.

the disappearance of mercaptan from soap solutions through air oxidation. He reported that O.E.I. and lorol mercaptans are oxidized to the disulfide "at a measurable rate" in soap solutions. Tertiary dodecyl mercaptan (3B) was found to have a slower oxidation rate than the primary mercaptan.

Regulating Index for Mercaptans.-A method for evaluating the modifier efficiency of a mercaptan has been developed by use of the disappearance curves of mercaptans during the actual polymerization.

Ewart, Smith, and Hulse[7] found that in the emulsion polymerization of butadiene the effectiveness of a modifier could be expressed in terms of a "regulating index":

$$r = -\frac{d\ln R}{dP}$$

where r is the regulating index, R the fraction of unreacted mercaptan at any fraction of the conversion P. They found that r is independent of the starting concentration of mercaptan, and that it has a constant value for a given mercaptan throughout a large percentage of the conversion.

Kolthoff[8] showed the same thing to hold for the GR-S recipe.

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[7] Technical Report to Rubber Reserve Company No. CR-73 from United States Rubber Company, June 16, 1943.

[8] Technical Report to Rubber Reserve Company No. CR-185 from the University of Minnesota, Oct. 15, 1943.

He proposed the following equation:

$$P = -K \log_{10} \frac{R}{R_o} - \text{const.}$$

where P equals the fraction of monomers converted to polymer

$\frac{R}{R_o}$ equals the fraction of modifier left at conversion P

K equals a constant comparable to the above regulating index.

The greater is the value of K, the smaller is the modification exerted by a modifier. The integration constant gives the amount of mercaptan used in non-modification reactions.

In the mutual formula a mixture of normal mercaptans corresponding to a formula of n-C_{12} is used. With primary mercaptans higher than C_{12} the modifier disappears so slowly that there is under-modification. With primary mercaptans lower than C_{12}, the mercaptan is used rapidly in the early stages of conversion giving overmodification; while undermodification results in the later stages since the mercaptan is almost all used up in the first stages.

With tertiary mercaptans the same is found to be true. However, there is not as great a divergence in the disappearance curves of the tertiary mercaptans as there is in those of the primary.

Scope and General Method

The purpose of this investigation was to measure the inherent ease of oxidation of mercaptans and their diffusion rates into aqueous soap solutions in order to obtain a more quantitative measurement of the modifier efficiency of a given mercaptan. Also it was desired to find the effect of various variables on the oxidation and diffusion rates.

It was at first proposed to measure the oxidation rates of the mercaptans in an homogeneous solution. Preliminary experiments along this line led to no suitable system, and were abandoned. The system finally adopted consisted of mercaptan in true solution in aqueous soap. The mercaptan was dissolved in the soap solution, and the solution allowed to stand overnight in a constant-temperature bath in order to destroy the peroxides present in the soap. Then persulfate was added, and the rate at which the mercaptan disappeared was measured by amperometric titrations for mercaptan. This system offers many advantages:

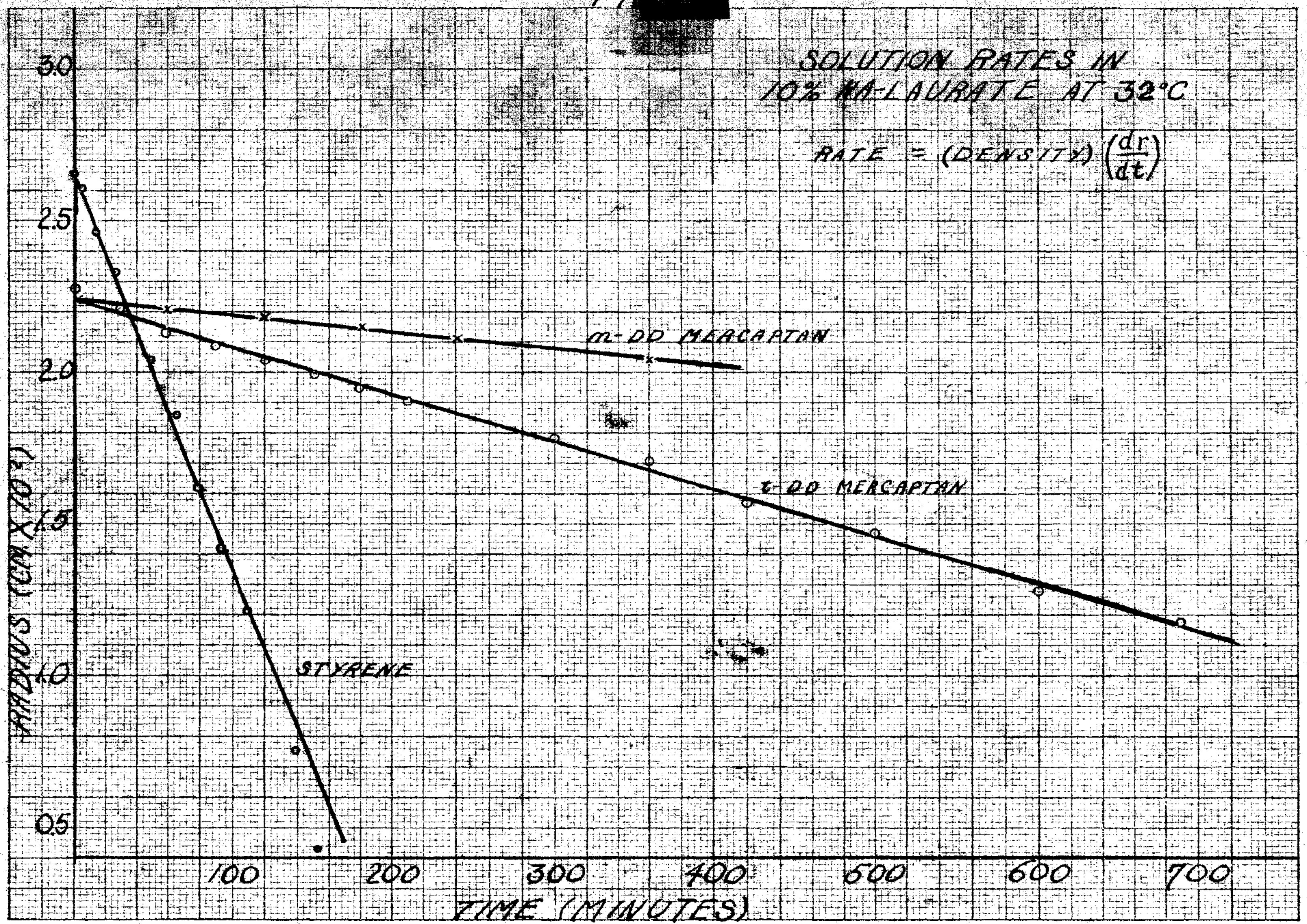
1. The oxidation can be carried out under conditions closely approximating those met in actual emulsion polymerizations.

2. Potassium persulfate can be used as the oxidizing agent.

3. Diffusion of the mercaptan from the monomer layer into the micelle is eliminated as a variable in the oxidation rates.

4. The mercaptan disappearance can be followed accu-

FI[redacted]



SOLUTION RATES IN
10% NA-LAURATE AT 32°C

RATE = (DENSITY) $\left(\frac{dr}{dt}\right)$

rately and easily by means of the Kolthoff amperometric procedure.

The diffusion rates were determined by the Vinograd microscopic method. The soap solution was held in a 5 ml pH-meter cup on a microscope. A cover glass was placed over the cell, and a drop of mercaptan was introduced under the cover glass. The rate at which the drop decreased in radius was measured with the microscope. As will be shown later, the diffusion rate is found by plotting the radius against time, the slope of this line multiplied by the density of the mercaptan gives the diffusion rate in grams-cm^{-2}-hr^{-1}. This can be converted into millimoles-cm^{-2}-hr^{-1} by dividing by the molecular weight of the mercaptan and multiplying by 1000.

Summary and Discussion of Results

Diffusion Rate Measurements.-Assuming that the rate of volume change of an oil drop in an aqueous soap solution is proportional to the surface area of the drop, then

$$-dV/dt = k' 4 \pi r^2 \qquad (1)$$

where k is the proportionality constant and depends on the nature of the oil, and V is the volume of the oil drop.

For an oil droplet suspended in an aqueous soap solution, assuming the droplet to be spherical,

$$V = 4/3 \pi r^3$$

and

$$dV/dt = 4 \pi r^2 \, dr/dt \qquad (2)$$

Thus equating (1) and (2),

$$k' = -dr/dt$$

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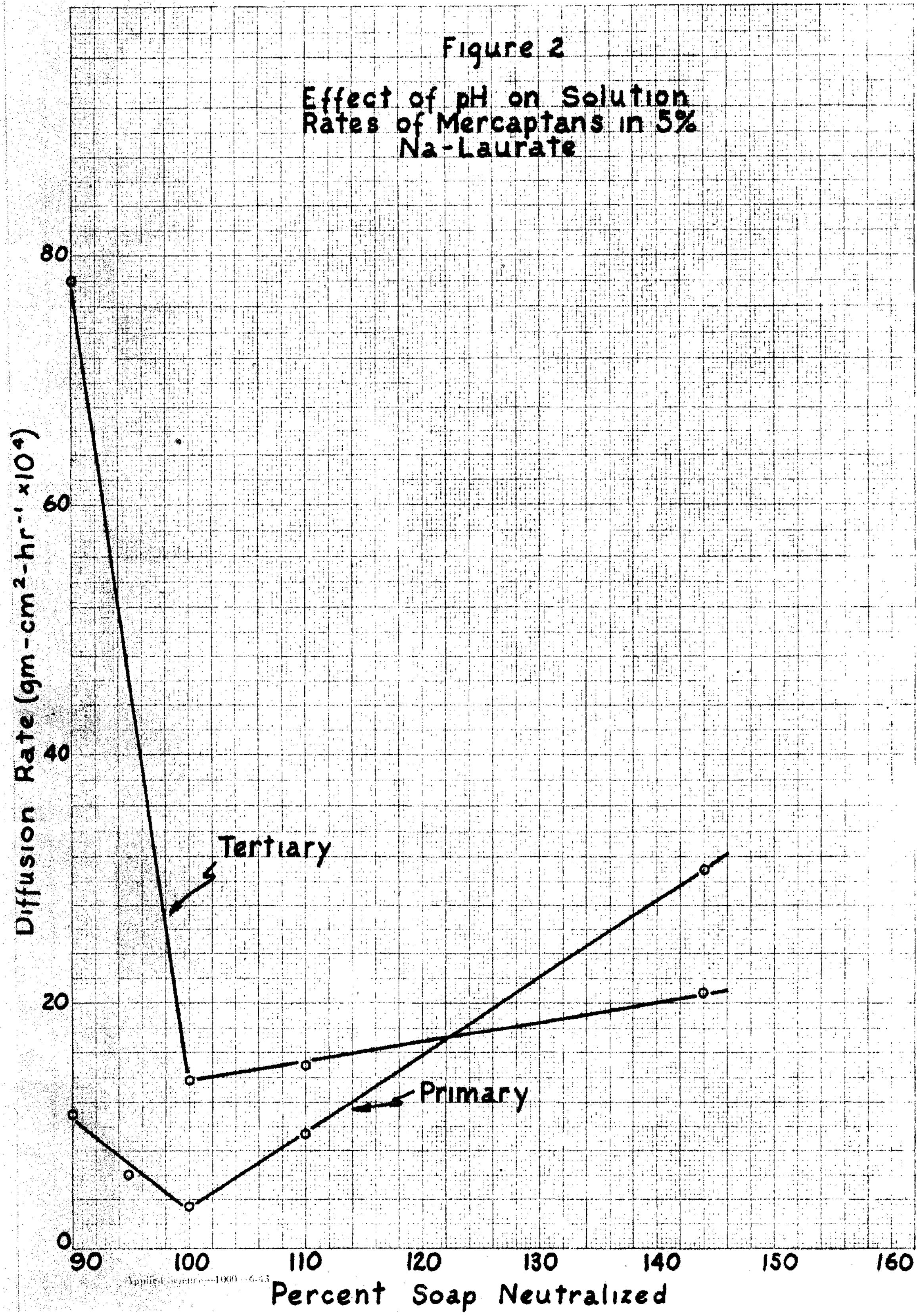

Figure 2

Effect of pH on Solution Rates of Mercaptans in 5% Na-Laurate

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Using mercaptan droplets of 0.3 to 0.8 mm in diameter, the above assumption is found to hold. A large volume of soap solution (5 ml) was used so that the concentration of mercaptan dissolved in the micelles is very low at all times during the diffusion measurements. As an illustration, when totally dissolved, a drop of 0.6 mm diameter will furnish only 0.11 mg of mercaptan, and this would saturate 5 ml of a 5% SF-Flakes only a fraction of one percent.

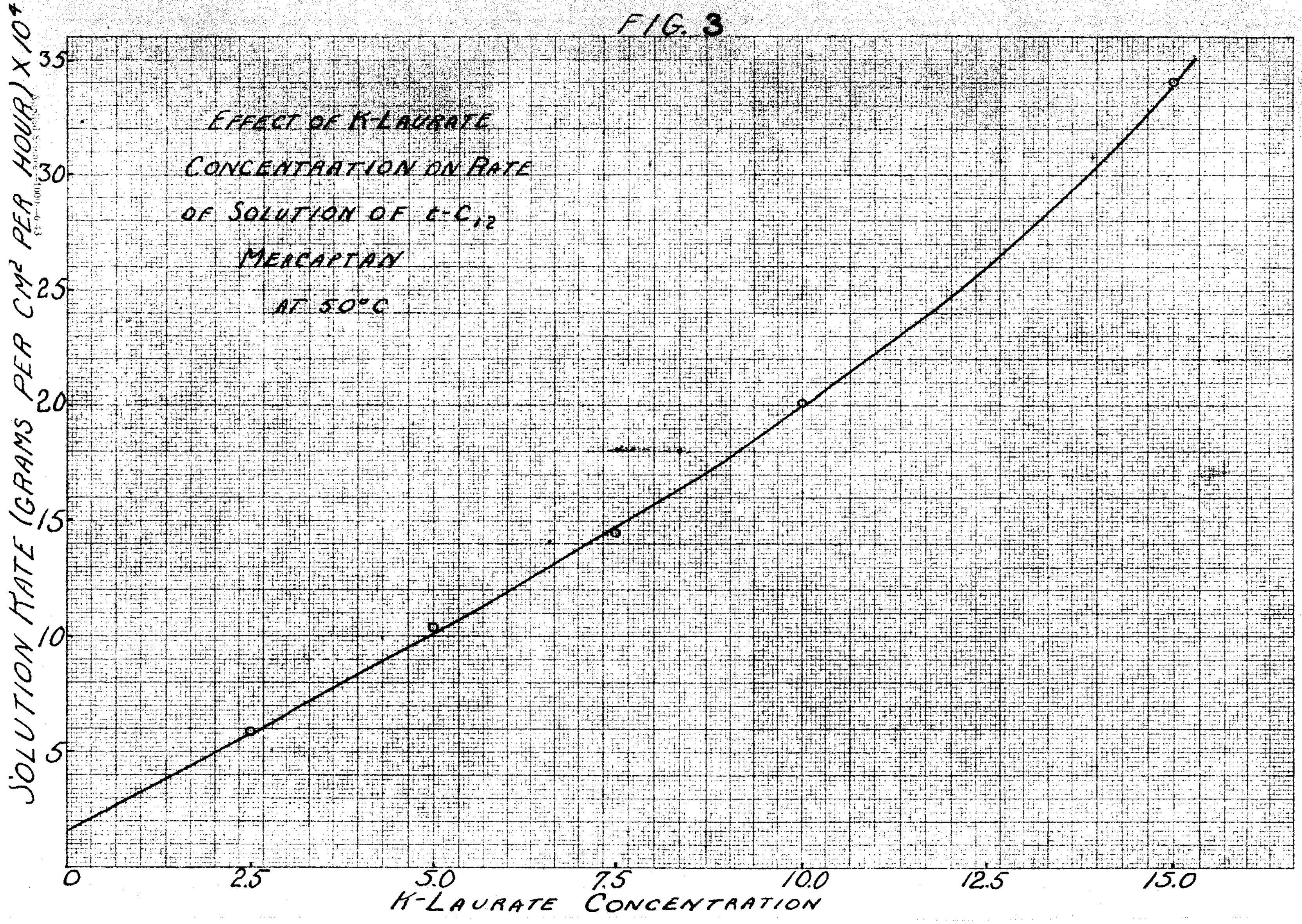
The results of some rate measurements are illustrated in Figure 1, where it may be seen that the radius plotted against time results in a straight line. The slope of this line, multiplied by the density D of the mercaptan, gives the value of k in grams-cm^{-2}-hr^{-1} when r is expressed in centimeters:

$$Dk' = D\,\frac{dV/dt}{4\pi r^2} = \frac{1}{A}\cdot\frac{dW}{dt} = k$$

Effect of pH on Solution Rates.- The values in Table I, which are plotted in Figure 2, show the effect of pH on diffusion rates of normal and tertiary dodecyl mercaptans. The pH of each of these solutions was measured at temperatures ranging from 15° to 40° C at 5 degree intervals, and the pH at 50° C was obtained by extrapolation.

These data demonstrate the surprising fact that the solution rates are at a minimum at approximately 100% fatty acid neutralization for the C_{12} mercaptans. The

FIG. 3



EFFECT OF K-LAURATE CONCENTRATION ON RATE OF SOLUTION OF t-C_{12} MERCAPTAN AT 50°C tertiary C_{12} mercaptan increases slowly in solution rate with increasing amount of free caustic while the primary mercaptan increases much more rapidly (approximately four times as rapidly). The diffusion rates of both increase greatly in the presence of unneutralized fatty acid.

Effect of Soap Concentration.-Figure 3 shows that the solubility rate for t-C_{12} mercaptan increases linearly with increasing concentration of K-Laurate solution at 50°C. At higher concentrations of soap the curve departs from linearity, the rates being abnormally high.

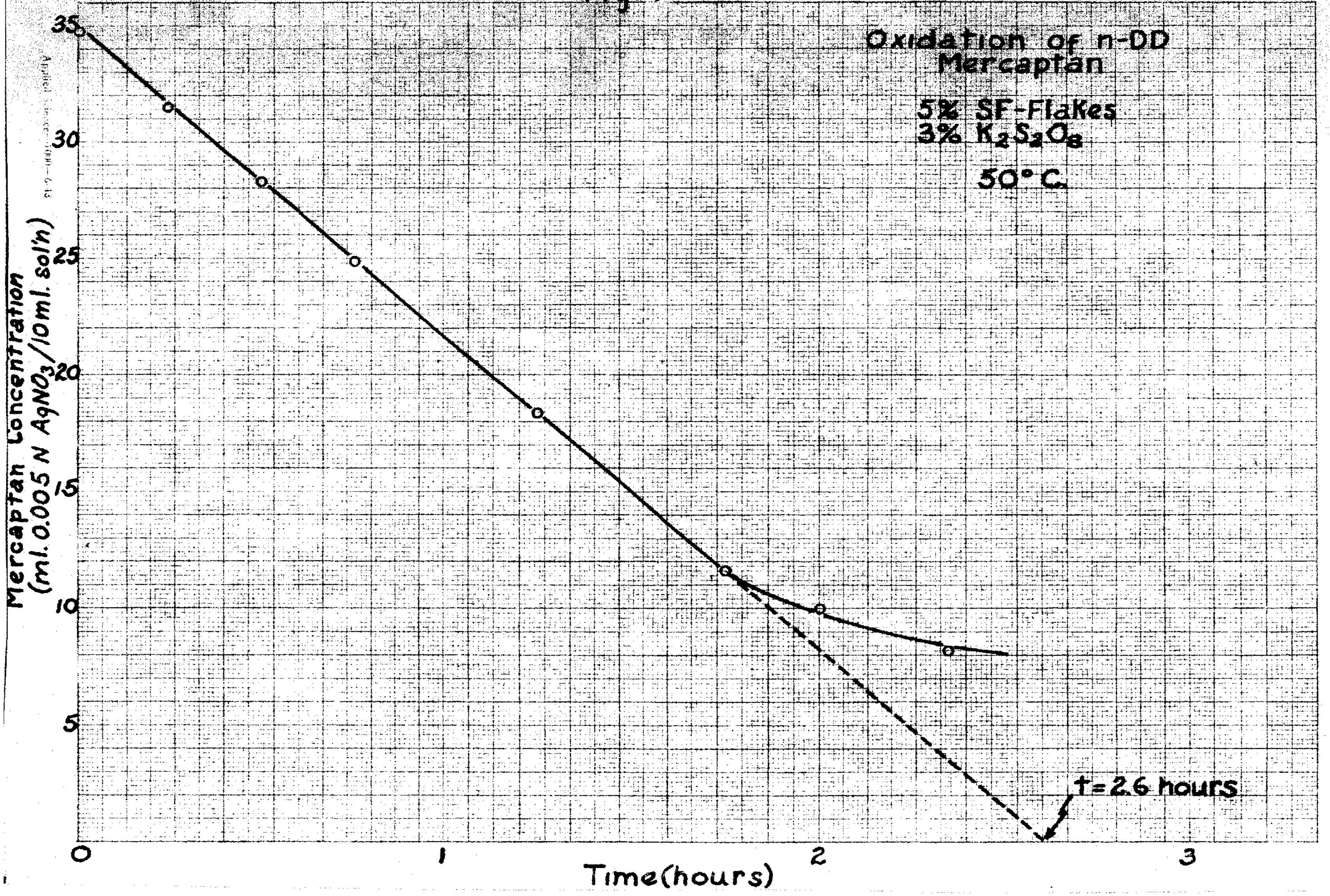
Effect of Chain-Length of Mercaptan.-Table II gives the diffusion rates of 17 mercaptans of different chain length and structure in 10% K-Laurate solution at 30°C, pH 10. The diffusion rates are listed both as grams per cm^2 per hour, and millimoles per cm^2 per hour. The third column gives the rates of the various mercaptans relative to that of n-dodecyl (Illinois). As may be seen from this table, the diffusion rates of mercaptans t-C_{12} and higher are considerably higher than those of the corresponding straight chain mercaptans. The diffusion rates appear to depend chiefly upon the amount of branching, however, and probably do not represent an inherent difference between primary and tertiary mercaptans. The dependence upon the amount of branching can be shown if the diffusion rates are compared with the longest straight chain in the molecule, including the sulfur. This relation may be brought out by Table III. This gives the chain length and diffusion rates of the University of Illinois isomeric C_{12} mercaptans. In addition to the Illinois samples, which were kindly submitted by Dr. R.L.Frank, fractionated Sharples 3B (t-C_{12}) and n-dodecyl mercaptan from O.E.I. are included.

This series of mercaptans offers striking evidence that the amount of branching is a very important factor in determining mercaptan diffusion rates at pH 10. We have already shown that mercaptan diffusion rates are at a minimum at pH 10.0, so that this comparison is made under truly comparable conditions. The length of the longest chain of the various mercaptans, including sulfur, might be taken as an approximate measure of the amount of branching. The last column lists the longest chain of each mercaptan. The correlation with diffusion rate is obvious.

This relation between amount of branching and diffusion rates does not seem to hold, however, for mercaptans C_{10} and shorter. n-Decyl mercaptan actually has a higher diffusion rate than does t-Decyl mercaptan.

Effect of Temperature on Diffusion Rates.-Comparison of diffusion rates at 30°C to rates measured at 50°C indicate that the rates at 50° are uniformly about 3 times those at 30°. Thus the rate for n-DD increases from 1.32 to 5.2; t-C_{12} from 6.25 to 20.1.

Fig. 4


Oxidation of n-DD Mercaptan
5% SF-Flakes
3% $K_2S_2O_8$
50° C.
t=2.6 hours
Mercaptan Concentration
(ml. 0.005 N $AgNO_3$/10 ml. sol'n)
35
30
25
20
15
10
5
0
1
2
3
Time (hours)

Oxidation Rate Measurements.-In order for the oxidation to proceed fairly rapidly a large excess of persulfate was used (about 10 equivalents). In such a system it was expected that the oxidation of mercaptan would be first order. Surprisingly, the rates proved to be exactly zero order until 50-70% of the mercaptan had been oxidized, after which the rates appeared to become first order. The point at which the rate departed from zero order seemed to coincide roughly with the appearance of cloudiness in the solution often accompanied by a tendency toward gelation. In order to illustrate the type of result obtained, a typical oxidation experiment is given in Figure 4. Here the concentration of n-DD mercaptan (pure) is plotted versus time at 50° C in a medium 5% in SF-Flakes and 3% in potassium persulfate. Concentration is expressed as ml of 0.005 N $AgNO_3$ required to titrate a 10 ml aliquot of the solution by the amperometric procedure. The curve is linear until 65% of the mercaptan has disappeared. The rate can be expressed in terms of millimols oxidized per liter of solution per hour by simply multiplying the slope of the straight line by the normality of the $AgNO_3$ times 100. However, as will be developed later, the rates are logically expressed in terms of the reciprocal of the time to complete mercaptan oxidation, using the time obtained by extrapolating the straight line to zero mercaptan concentration.

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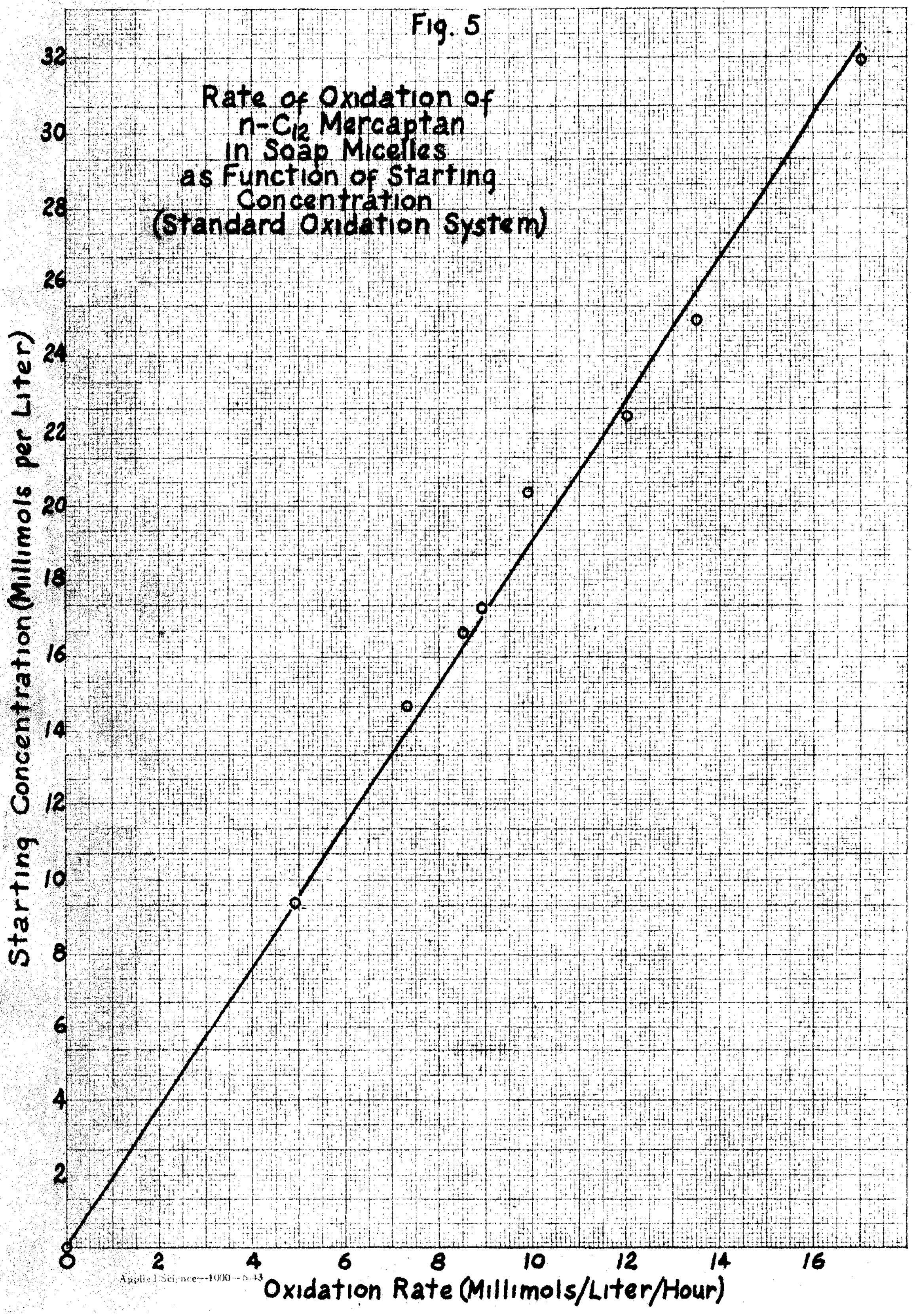


Fig. 5

Rate of Oxidation of n-C_{12} Mercaptan in Soap Micelles as Function of Starting Concentration (Standard Oxidation System)

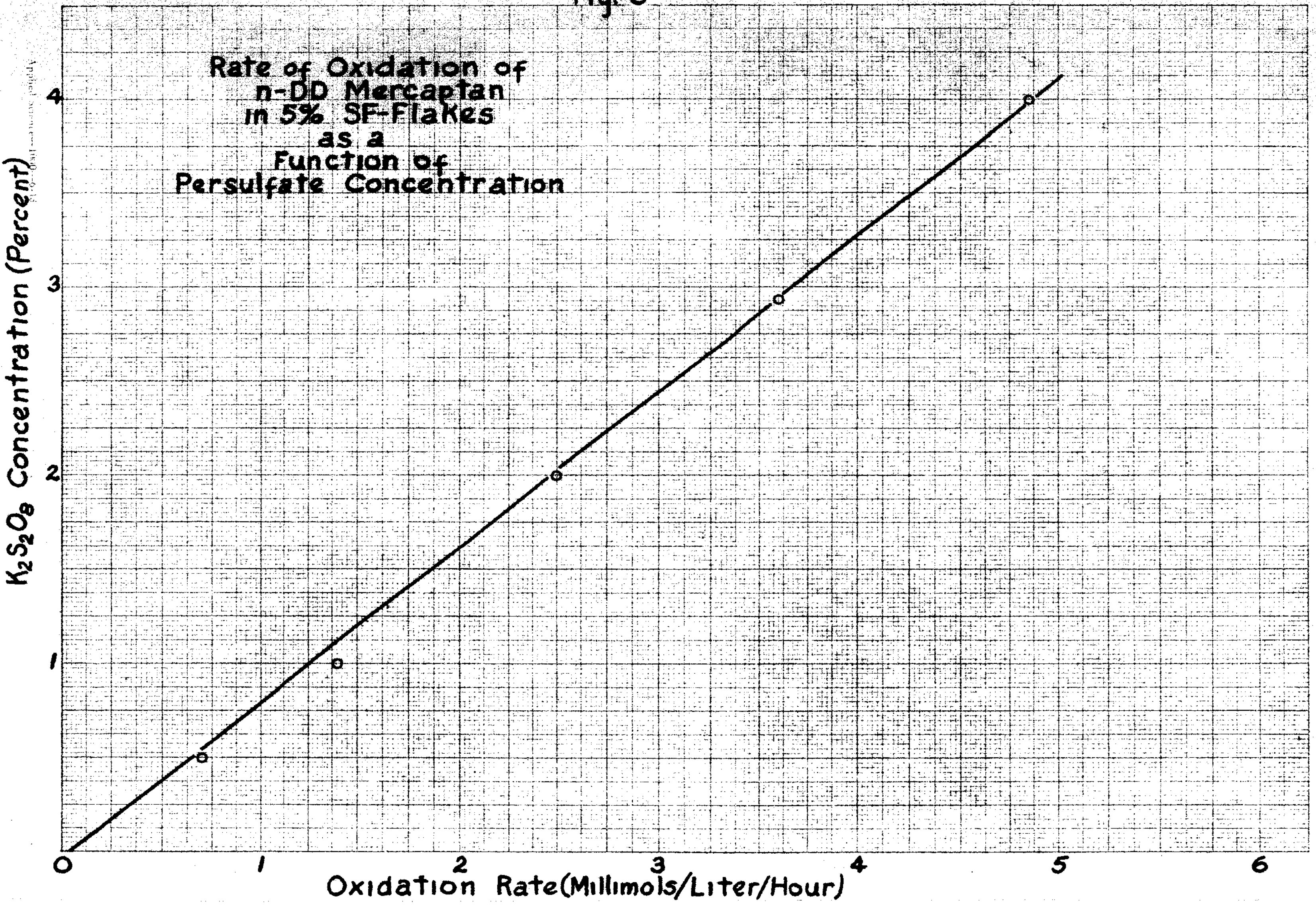
The following variables were found to affect the oxidation rates, and were evaluated;

1. initial mercaptan concentration
2. soap concentration
3. persulfate concentration
4. pH
5. temperature
6. structure of the mercaptan (mercaptan type)

The effect of initial concentration of mercaptan, structure of mercaptan, and temperature, were investigated in solutions buffered to a pH of 10.0. The effect of soap and persulfate concentrationswas evaluated in unbuffered solution. SF-Flakes was used in the investigation of the effect of soap concentration, persulfate concentration, and pH; while Standard RR Soap was used for the evaluation of the effect of structure of mercaptans, initial mercaptan concentration, and temperature effect.

Effect of Initial Mercaptan Concentration.-Judging from the result shown in Figure 4, it might be predicted that the oxidation rate would be independent of the starting concentration of the mercaptan. The complex nature of the reaction is indicated by the fact, however, that, although pseudo zero-order rates are obtained, the rates are exactly proportional to the starting concentration of the mercaptan. Thus, when the amount of mercaptan

Fig. 6



Rate of Oxidation of
n-DD Mercaptan
in 5% SF-Flakes
as a
Function of
Persulfate Concentration

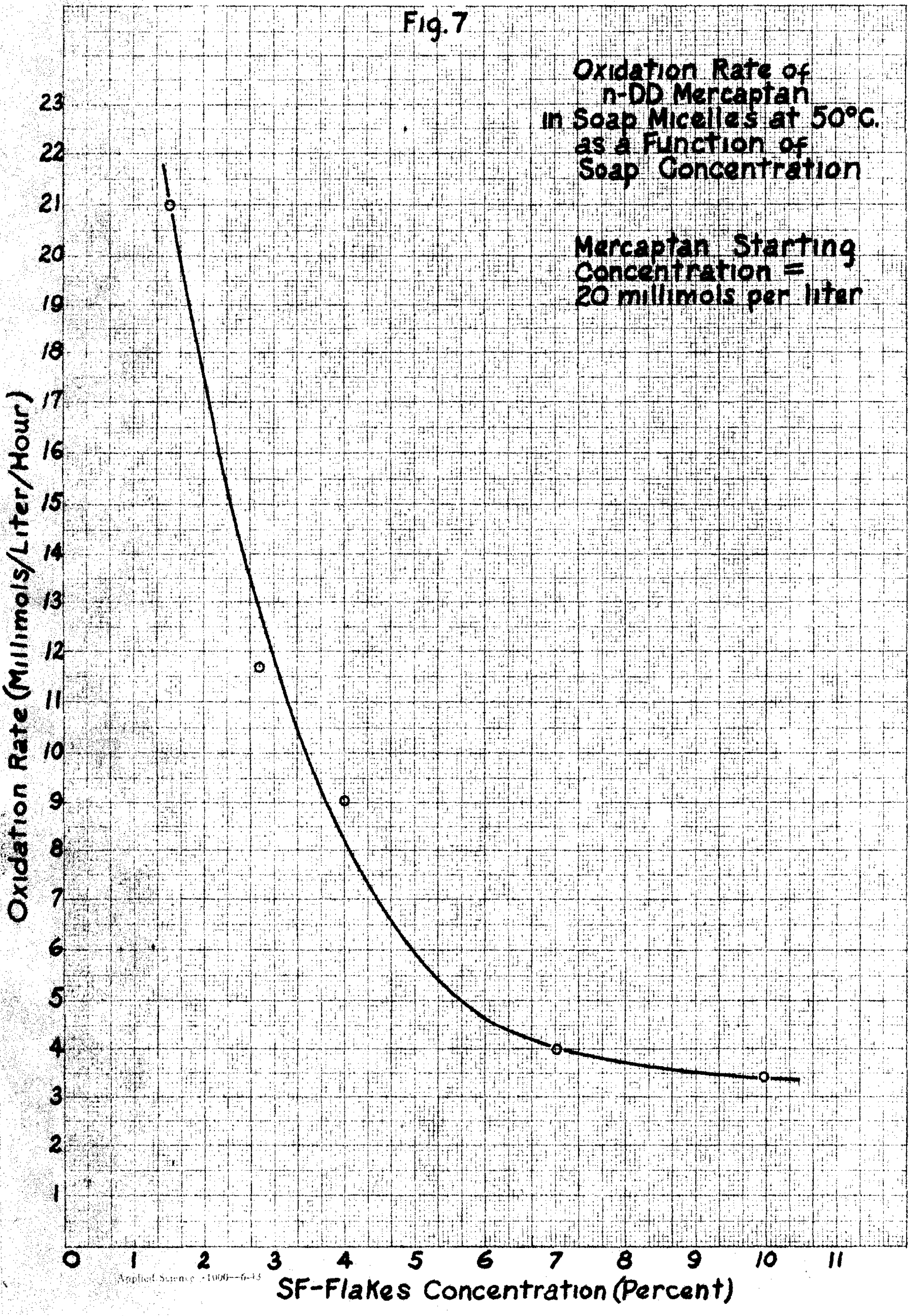
dissolved in the micelles is doubled, the slope of the line is exactly doubled, and when the starting amount of mercaptan is reduced to one-half, the slope of the line is exactly halved. This relationship holds regardless of the particular soap, mercaptan, or persulfate concentration used.

These data are given in Table IV, and plotted in Figure 5. This figure shows oxidation rate as a function of mercaptan starting concentration for the oxidation of n-DD mercaptan in 5% Standard Lot RR soap buffered to pH 10. The persulfate concentration is 3%. This system is the so-called "standard oxidation system", which will be discussed later.

Effect of Persulfate Concentration.-The oxidation rate is proportional to the persulfate concentration. Figure 6 shows oxidation rate (expressed as millimols oxidized per liter of solution per hour) of n-DD mercaptan in 5% SF-Flakes solution and a starting concentration of 20 millimols per liter as a function of persulfate concentration. The results are listed in Table V.

Effect of Soap Concentration.-The effect of soap concentration is summarized in Table VI, and is expressed graphically in Figure 7. It is seen that the effect of varying the soap concentration is unexpected -the oxidation rates, everything else being equal, decrease rapidly with increasing soap concentration. In other words, the rates depend upon the concentration of the mercaptan in

Fig. 7



Oxidation Rate of n-DD Mercaptan in Soap Micelles at 50°C. as a Function of Soap Concentration

Mercaptan Starting Concentration = 20 millimols per liter the micelle.

Since the oxidation rate increases with increasing mercaptan starting concentratio and with decreasing soap concentration it would appear that the rate is proportional to the ratio of mols of mercaptan per mol of soap. When data of Figure 5 (varying mercaptan concentration) and Figure 7 (varying soap concentration) are combined and the oxidation rate is plotted as a function of the starting ratio -moles mercaptan/mol soap, a straight line function is obtained as shown in Figure 8.

Effect of pH.-In the absence of buffer the pH changes during the oxidation because of the formation of $KHSO_4$. The drop in unbuffered systems from the beginning to the end of the oxidation is about 0.3 units- i.e., from 1010 to 9.7. This suggests the possibility that the reason for the pseudo first order reaction might be that the decrease in pH exactly compensates for the decrease in mercaptan concentration. Accordingly, various buffered systems were evaluated. It was possible by means of a carbonate-bicarbonate buffer, to hold the pH to within 0.1 unit at pH 10.0 throughout the oxidation. Although the rates in the buffered systems differed from the rates in the unbuffered systems, the same zero-order rates were obtained and the differences could be attributed to the "salt effect" of the buffer on the soap. Table VIII gives the rates of oxidation of several mercaptans in unbuffered solutions. These may

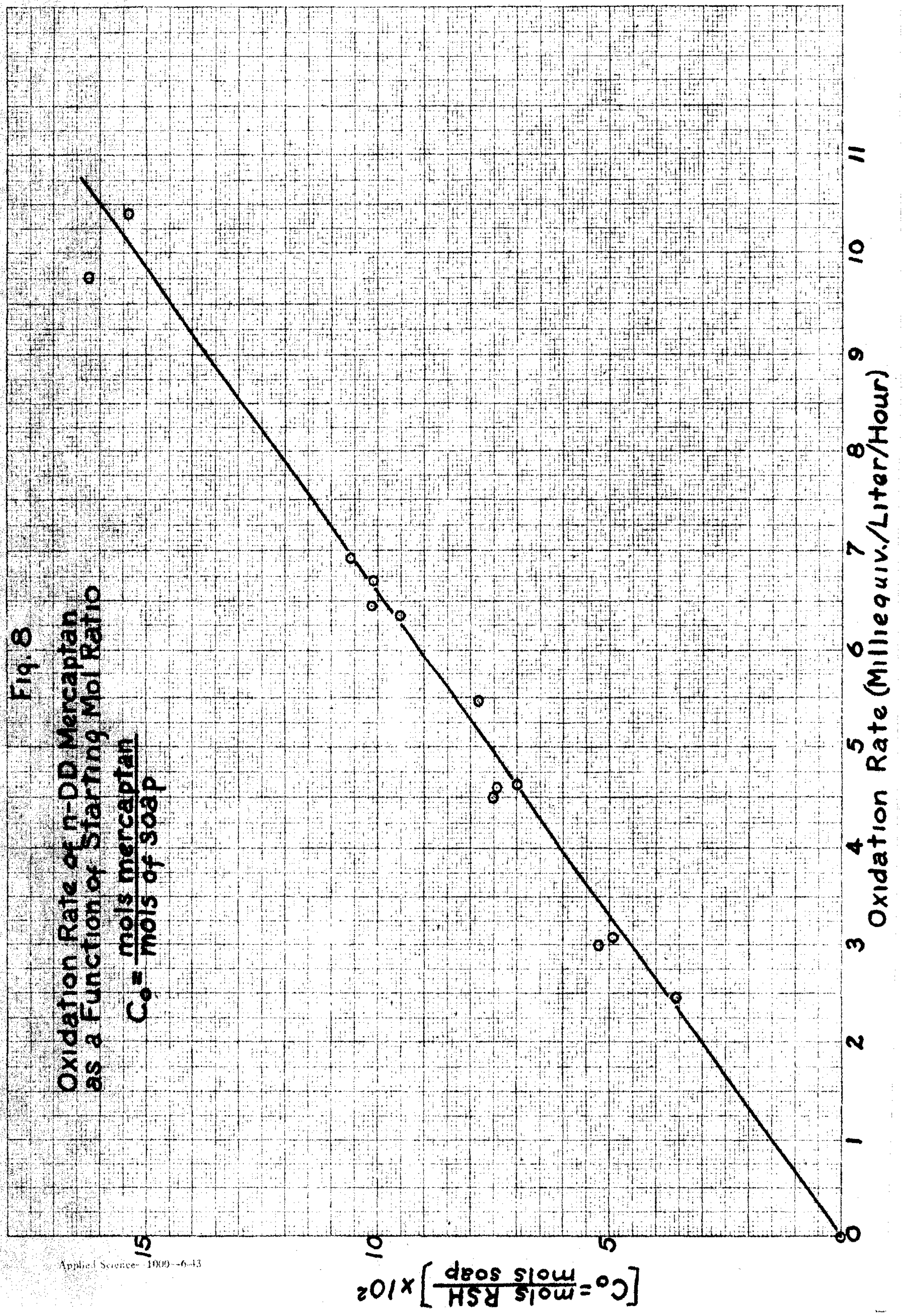


Fig. 8

Oxidation Rate of n-DD Mercaptan as a Function of Starting Mol Ratio

$C_0 = \frac{\text{mols mercaptan}}{\text{mols of soap}}$

be compared with the values in the buffered system in Table X.

When 10% excess caustic was used in an unbuffered system the rate was about 25% higher than that for 100% neutralized soap. When the soap was only 90% neutralized, the zero order curve was no longer obtained; in this case the reaction was approximately first order (Figure 9). Addition of 0.5% NaCl instead of the caustic also resulted in an increase in the oxidation rate (Table VII).

Kinetics of the Reaction.-Combining the effects of the variables discussed above, the amount of mercaptan reacting as a function of time can be expressed as follows:

$$dx/dt = kC_o(a-x)$$

where $x =$ amount reacted

$a =$ persulfate concentration (initial)

$C_o =$ RSH starting concentration expressed as mols RSH/mol soap

When a large excess of potassium persulfate is used,

$$dx/dt = kaC_o$$

Integrating,

$$x = kaC_ot$$

and

$$k = \frac{x}{a}\,\frac{1}{C_ot}$$

$$= \frac{\text{mols soap}}{a} \cdot \frac{x}{\text{initial mols mercaptan}} \cdot \frac{1}{t}$$

Now, if a standard system is chosen so that in all

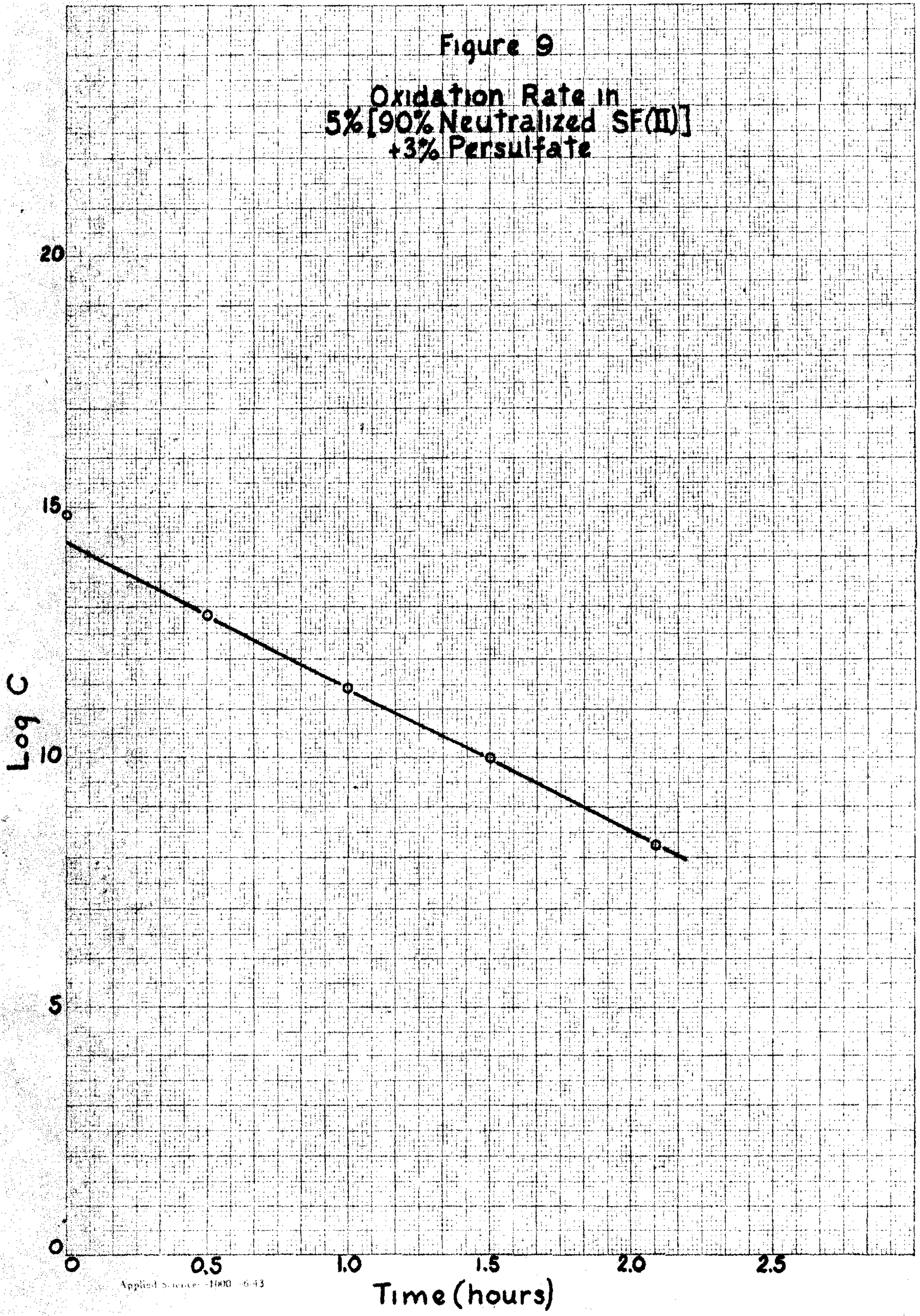


Figure 9

Oxidation Rate in 5% [90% Neutralized SF(II)] +3% Persulfate experiments the initial mols of soap and the persulfate concentration are constant and noting that x/initial mols of mercaptan is the fraction of mercaptan oxidized at time t, we have for the rate constant:

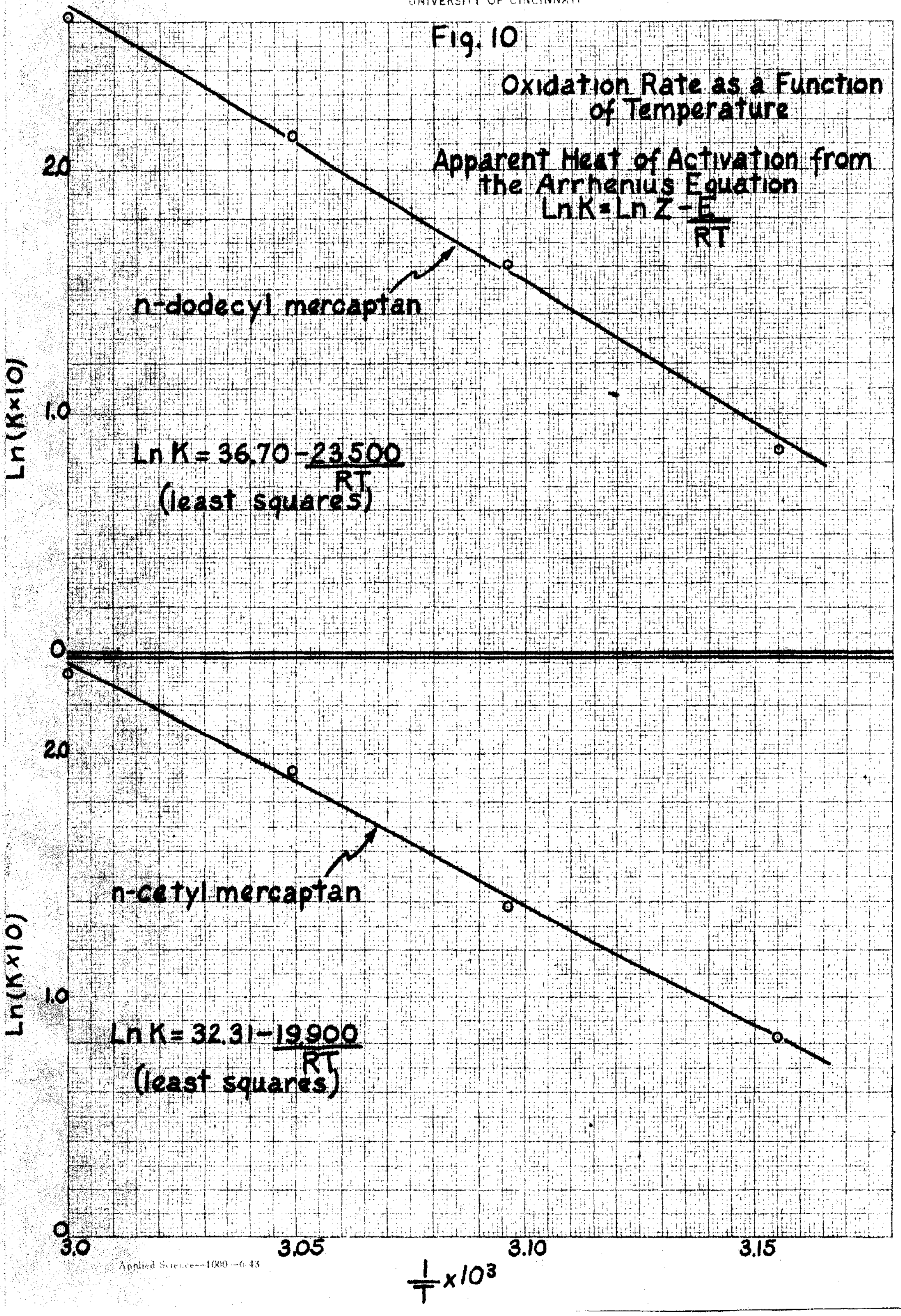
$$K = \frac{1}{t}(\text{fraction of mercaptan oxidized})$$

Thus, if the straight-line portion of Figure 4 is extrapolated to zero mercaptan concentration, the value of K is given by the reciprocal of the time ~~*~~i.e., 3.8×10^{-1} hrs^{-1}. This value is for SF-Flakes without buffer and is less than the value given for the oxidation of n-DD mercaptan in the standard RR soap system buffered to pH 10.0.

Since K in the above derivation includes the factors of soap and persulfate concentrations, it was more convenient to compare the various mercaptans in a <u>standard oxidation system</u>. Consequently, the standard system chosen for the comparison of different mercaptans is as follows: Standard Lot RR soap, 5%; potassium persulfate, 3%; buffer, 0.5% (an equimolar mixture of sodium carbonate and sodium bicarbonate) to give a pH of 10. Although the K as defined above is independent of the starting concentration of mercaptan, in practice the starting concentration was always approximately 20 millimols per liter.

<u>Effect of Temperature</u>.-The apparent activation energy was determined from the Arrhenius equation for n-DD mercaptan and for n-cetyl (C_{16}) mercaptan by measuring the value of K at four different temperatures.

Fig. 10



Oxidation Rate as a Function of Temperature

Apparent Heat of Activation from the Arrhenius Equation

$$\ln K = \ln Z - \frac{E}{RT}$$

These data are given in Table IX.

The variation with temperature of the velocity constant for a thermal reaction occurring in solution may be expressed in the form

$$k = Ze^{-E/RT}$$

or $$\ln k = \ln Z - E/RT \ .$$

The constants Z and E, which are specific for any reaction may then be determined by plotting ln k against 1/T. The slope of the curve is -E/R and the intercept on the ln k axis is the ln Z. In practice, it is more convenient to find only E from the graph; ln Z can be found by inserting into the equation the values of k and T corresponding to any point on the curve. In Figure 10, the values from Table IX are so treated, and the best straight line drawn through the data by the method of least squares. This gives a value of E for n-DD of 23,500 calories per gram mole and for n-C_{16} mercaptan of 19,900 calories per gram mole.

Effect of Mercaptan Structure on the Oxidation Rates.- The oxidation rates for the various mercaptans in the standard system are given in Table X. The rates are expressed in two ways. In the second column the rates are given in millimols oxidized per liter of solution per hour calculated to a mercaptan starting concentration of exactly 20 millimols per liter. Since the rate is exactly proportional to the starting concentration (see Figure 5), this procedure is justified as a basis for comparing rates where the starting concentrations differ. In column 3 the rate constants $K = 1/t \cdot$(fraction oxidized) are given. This is a more logical basis for comparison but leads to precisely the same relative oxidation rates, as the method of column 2. In column 4 are given the relative oxidation rates, assigning a value of one to the purified n-DD mercaptan from the University of Illinois, which thereby becomes the basis of comparison for the entire series.

It will be noted from the table that there is a very fundamental difference in the rates of primary and tertiary mercaptans. Except for the very short-chain mercaptans (e.g. n-hexyl and t-butyl) the rates for the primary mercaptans fall into one group where K is approximately 0.5 $hrs.^{-1}$ and the tertiary mercaptans fall into another group where K is of the order of 0.04 $hrs.^{-1}$. In other words, as a class the primary mercaptans oxidize about twelve times as rapidly as do the tertiary mercaptans. There is a somewhat greater variation among the tertiary mercaptans than among the primary due, perhaps, to steric effects. The one example of a secondary mercaptan included (6-dodecyl mercaptan) has an oxidation about twice that for the tertiary mercaptans but less than 1/5 that of the primary mercaptans.

Conclusions

As pointed out in the introduction it appears that mercaptan modifier efficiency is determined by two inherent properties -i.e., ease of oxidation, and rate of diffusion into soap solutions. The total solubility of mercaptan in the soap solution seems to be relatively unimportant. This can be seen, since in the mutual formula there is used only 0.5 g. of mercaptan to 100 g. of monomer and 180 g. of 2.8% SF-Flakes. There is not nearly enough mercaptan present to saturate the soap solution. Moreover, the partition coefficient very likely decreases the amount of mercaptan dissolved in the micelle still further. In view of this, the total solubility of mercaptans in the micelle of the soap is a negligible factor and need not be taken into account in determining its efficiency as a modifier.

Relative Diffox Product.-If the diffusion rate and oxidation rate of mercaptans are the only two factors which are involved in the ability of a given mercaptan to act as modifier, then a function of the two should give a quantitative measurement of the modifying effect of that mercaptan. One difficulty is that there is no way of knowing what constitutes a good modifier. O.E.I. (a mixture composed mainly of DDM with small amounts of both higher and lower normal mercaptans) is being used in the mutual recipe, and is found to give fairly satisfactory modification. Then, as a method for comparison of the various mercaptans, we will make modification by n-DD mercaptan (pure) the basis for assigning each mercaptan a definite value.

The mercaptan disappearance curves give a fairly reliable measure of the modifying effect. From the disappearance curves of the mercaptan, the regulating index can be calculated (see Historical Development for discussion of regulating index). This may be found by plotting log of unreacted mercaptan versus per-cent conversion of the monomer. The slope of this line multiplied by 2.3 gives the regulating index.

Since the modifying efficiency depends on the oxidation and diffusion rates of the mercaptan, then the regulating index may be expressed as a function of these two properties:

$$r = \text{const.}(\text{ox. rate})^{\alpha}(\text{diff. rate})^{\beta}$$

where alpha and beta are both assigned a value of one since no exact value can be given them on the basis of the present data. The product of the relative oxidation rate and relative diffusion rate is termed the <u>relative diffox product</u>. In the table on the following page, the regulating indices for the seventeen mercaptans are given in column one and the relative regulating indices (pure n-dodecyl mercaptan equals 1) in column 2.

Regulating Indices and Diffox Values

Mercaptan	Regulating index	Rel. Reg. index	Relative Diffox Product
n-hexyl mercaptan	> 24	>13	138
n-octyl mercaptan	24.2	13.0	38.2
n-decyl mercaptan	15.6	8.4	19.2
n-dodecyl mercaptan (Illinois pure)	1.86	1.00	1.00
n-dodecyl mercaptan (Fr. from OEI)	2.48	1.34	1.01
4-n-butyl-1-octyl mercaptan	2.74	1.47	1.95
n-cetyl mercaptan	0.41	0.22	0.013
6-dodecyl mercaptan	1.63	0.88	0.38
t-butyl mercaptan	6.36	3.42	930
t-octyl mercaptan	3.84	2.06	3.74
t-decyl mercaptan	2.74	1.48	0.48
t-dodecyl mercaptan	3.01	1.62	0.30
di-n-butyl-n-propyl-carbinthiol	1.63	0.83	0.24
dimethyl-n-nonylcarbinthiol	1.38	0.74	0.24
t-tetradecyl mercaptan	0.30	0.16	0.08
t-hexadecyl mercaptan	0.09	0.05	0.01
*OPME	21.2	11.4	11.5

*This is beta-p-octylphenoxy-beta prime-mercaptodiethyl ether.

This is compared with the relative diffox product in column 3.

The values for the regulating index are all based upon the mercaptan consumption curves contained in various Rubber Reserve Company reports[9,10,11]. The values are all calculated from the percent of mercaptan remaining at 10% conversion by the following equation:

$$r = 2.3\ (2.00 - \log_{10} \text{percent remaining})(10)$$

Unfortunately, except for the five Illinois mercaptans, the regulating indices and the diffox values were obtained on samples of different purity. Also in finding r, the mercaptan lost in non-modifying reactions is not taken into account.

Discussion of the Table.- Although the correlation of relative diffox values with mercaptan disappearance is only approximate, there are some rather striking

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[9] Kolthoff and Harris, Technical Report to Rubber Reserve Company No.CR-355, from University of Minnesota, June 13,1944.

[10] Thompson, Technical Report to Rubber Reserve Company No.CR-213 from U.S. Rubber Company, Nov. 29,1943.

[11] Kolthoff, Progress Report to Rubber Reserve Company No.CR-387 from University of Minnesota, 1944.

observations that can be made. It is safe to say, for instance, that any mercaptan having a diffox value greater than 10 will have an exceedingly rapid disappearance, i.e., high regulating index. Thus n-hexyl, n-octyl, n-decyl, t-butyl mercaptans, and OPME all have less than 25% mercaptan remaining at 10% conversion. On the other hand, if the diffox value is less than 0.2, the mercaptan will have low modifier activity. In this category fall n-cetyl, t-tetradecyl, and t-hexadecyl mercaptans. The mercaptans are arranged in three groups below according to their activities:

Group 1	Group 2	Group 3
Diffox range (<0.2)	Diffox Range (0.2-10)	Diffox Range (>10)
Rel. Reg. Index (<0.5)	Rel. Reg. Index (.5-2.1)	Rel.Reg. Ind.(>2)
n-Cetyl	n-Dodecyl mercaptan	n-Hexyl merc.
t-Tetradecyl	4-n-Butyl-1-octyl mer.	n-Octyl merc.
t-Hexadecyl	6-Dodecyl mercaptan	n-Decyl merc.
	t-Octyl mercaptan	t-butyl merc.
	t-Decyl mercaptan	OPME
	t-Dodecyl mercaptan	
	Di-n-butyl-n-propylcarbinthiol	
	Dimethyl-n-nonylcarbinthiol	

Within Group 2 certain comparisons can be made. t-Octyl mercaptan has the highest diffox value of the group and also the highest regulating index. The first two members listed offer an interesting comparison between two primary C_{12} mercaptans. The branched-chain mercaptan has a diffox product 1.95 times that of the n-product. Its regulating index is 1.47 times that of the n-product.

It will be noted that the diffox product values of the tertiary mercaptans (t-C_8 to t-C_{16}) fall within a narrow range, while the normal mercaptans (n-C_8 to n-C_{16}) have a range at least ten times as broad. This same spread is found in the disappearance curves of the primary and tertiary mercaptans.

When the diffox product is too high, the mercaptan functions as an inhibitor. This is actually found to be true when t-butyl and n-hexyl mercaptans are used in an emulsion polymerization.

It is unfortunate that the diffox product can be correlated only with the mercaptan disappearance in order to evaluate its usefulness as a more quantitative measurement of the modifying efficiency of a mercaptan. As has already been pointed out, mercaptans of different purity were used to find the mercaptan disappearance in actual polymerizations. Also, it must be borne in mind that although there is a close relation between mercaptan disappearance and modification, mercaptan disappearance can be affected by numerous variables such as rate of stirring, change in pH, change in the composition of soap, presence of oxygen, purity of monomers, and even order of mixing of the ingredients.

Therefore, since there is as yet no absolute measurement of modifying effect of a mercaptan in emulsion polymerization, the diffox product can be considered now only as a promising approach to a quantitative relation between the properties inherent to a mercaptan, and its modifying effect.

Experimental Part

Technique for Diffusion Measurements.-All diffusion rate measurements were made by the Vinograd microscopic technique. An oil droplet of 0.3 to 0.8 mm in diameter was placed in a soap solution and the decrease in diameter with time was observed.

A 5 ml pH-meter cup was used to hold the solution. The top of this cell was precision ground so that the cover glass fitted tightly and did not need to be sealed on with cement. A special microscope, water-circulation hot-stage was constructed which held two 5 ml cells in order to permit the measurement of two rates simultaneously without disturbing the cells. The temperature in the hot-stage was regulated by pumping water through it from a constant-temperature bath.

The measurements were made at 100x by means of a calibrated ocular scale in the microscope eyepiece. The scale was calibrated against a standard-ruled slide obtained from Bausch and Lomb. The microscope used was a Bausch and Lomb DDE, with movable platform which permitted the hot stage to be moved in order to follow the drop.

In making a determination, the cell was filled to the brim with soap solution, and then a cover glass was placed over the top in such a manner as to introduce no air bubbles. Then the cover glass was slipped back a few millimeters, and by means of a flexible capillary, a droplet of mercaptan of 0.3 to 0.8 mm in diameter was formed under the soap solution, well beneath the cover glass. One or two more drops of soap solution were added and the cover glass slipped back on, care being taken to avoid air bubbles. The hot stage was then placed under the microscope, and the diameter of the drop was measured at regular intervals.

Technique for Measurement of Oxidation Rates.-The oxidation rates were measured by dissolving the mercaptan in soap solution, adding persulfate and a buffer, and following the disappearance of mercaptan by means of the Kolthoff amperometric procedure[12].

The equipment for carrying out the amperometric titrations consists of a reference electrode whose potential is -0.25 V with regards to the standard calomel electrode, a rotating platinum wire electrode, and a Rawson Electrical Instrument Co. (type 507B)

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[12] Kolthoff and Harris, "The Determination of Mercaptan in Latex by Amperometric Titration with Silver Nitrate in Ammoniacal Alcoholic Medium", Technical report to Rubber Reserve Company No. CR-62 from the University of Minnesota.

micro-ammeter. The rotating platinum wire electrode is connected to the reference electrode through the ammeter; a salt bridge between the reference electrode and the solution to be titrated completes the circuit.

The electrolyte for the reference electrode is prepared by dissolving 4.2 g of potassium iodide and 1.3 g of mercuric iodide in 100 ml of saturated potassium chloride solution. This solution is held by a wide-mouthed bottle. A layer of mercury on the bottom serves as the electrode. Electrical contact is made by means of a platinum wire sealed in the end of a piece of glass tubing. This glass tube is partly filled with mercury and a copper wire dipped into the mercury.

The salt bridge for making the electrical connection between the reference electrode and the half cell in which the titration is being carried out consists of about two feet of soft rubber tubing of 6 mm (i.d.) filled with saturated potassium chloride solution. The rubber tubing is then connected to a sintered glass filter stick containing a jell made of 3% agar and 30% potassium chloride.

The theory of the rotating platinum wire electrode with regards to amperometric titrations is described by Laitinen and Kolthoff[13]. The electrode used is similar

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[13] J. Phys. Chem. 45 1079 (1941); for a review see Kolthoff and Lingane, *Polarography*, Interscience Publishers, Inc., New York, 1941: page 475.

to that described in the above reference: it consists of a short length of platinum wire sealed in the side of a soft-glass tube about 1.5 cm from the end. The end of the glass tubing (6mm i.d.) had two ears which served to agitate the solution thoroughly during the titration. Electrical connection is made by dipping a wire into the mercury inside the electrode. The electrode is attached to a hollow shaft driven by a motor at 600 revolutions per minute.

The micrometer has a full-scale deflection of four micro amperes. The scale is divided into units of 0.05 microamperes.

The titration is carried out by placing the rotating electrode and the arm of the salt bridge in the solution to be titrated. The current read on the ammeter is zero, or very nearly zero. Then 0.005 N silver nitrate is added from a burette.As long as the silver n nitrate is not in excess, the current remains zero. As soon as there is an excess of silver nitrate, it is reduced at the platinum electrode, and the microammeter shows a current. Then two or three small increments of silver nitrate are added, and the current read. The current is plotted on graph paper against the volume of silver nitrate solution added, and the point at which the resulting straight line crosses the zero current axis, is the end point.

Procedure for Oxidation Rate.-A 10% soap solution is made up from freshly distilled water. To this is added the mercaptan in sufficient quantity to give approximately 40 millimols of mercaptan per liter of solution. This solution is placed in a glass-stoppered flask, the air above the solution is swept out with nitrogen, and the flask stoppered, shaken well to emulsify the mercaptan, and finally placed in a thermostat at 50° C overnight. The next morning the mercaptan is entirely in solution and any soap peroxides have been reduced by the mercaptan. In case of long-chain mercaptans a slight turbidity may remain due to undissolved mercaptan.

The mercaptan-soap solution is next filtered through two fluted filter-papers to remove disulfide and any undissolved mercaptan. A solution of only slight turbidity is thus obtained. If the turbidity is more than slight, the solution should be filtered again.

To a 100 ml volumetric flask is now added 6 g of potassium persulfate. Freshly distilled water is added to dissolve the solids and the solution is warmed to 50° C in a thermostat after which it is brought to exactly 100 ml volume. When using buffer, for the standard system, 1 gram of a 50 mol percent mixture of anhydrous sodium carbonate and sodium bicarbonate is first added to the volumetric flask, dissolved in about 50 ml of water, then the persulfate added, and the volume brought up to 100 ml as above.

Into a 300 ml glass-stoppered flask is pipetted 100 ml of the mercaptan-soap solution, then the buffer-persulfate solution, also at 50° C, is added and zero time is taken as the moment of mixing. The solution is then kept in a thermostat at 50.1± 0.005° C, and a ten ml aliquot withdrawn by pipette at intervals for mercaptan analysis. After each time that it was opened, the flask was flushed out with nitrogen.

Mercaptan Analysis.-For the standard oxidation system, the 10ml aliquot from the above is run into 150 ml of 95% alcohol, and is immediately followed by 3 ml of 12 N H_2SO_4 and 5 ml of 20% ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) solution. After standing for 10 minutes, 5 ml of 15 N NH_4OH is added and the solution is stirred to the disappearance of the green color (10 minutes). The mercaptan is then titrated as described previously.

The amounts of sulfuric acid, ammonium hydroxide and ferrous ammonium sulfate varied for the systems not using buffer, using different quantities of soaps, or varying the amount of potassium persulfate. The amount of ferrous ammonium sulfate added was always such that it would destroy completely any persulfate. The sulfuric acid added was enough to free the fatty acids of the soap and give a solution 0.1 N in sulfuric acid. The ammonium hydroxide added was designed to give a solution about 0.25 N.

To measure the oxidation rate of n-DD in the absence of a solubilizing soap, the procedure was varied a little. The mercaptan (30 millimols) was added to 200 cc of 10% freshly prepared sodium acetate and placed in a thermostat at 50° C overnight after flushing out the air with nitrogen. Then the bottle was shaken very vigorously, and 100 cc of the solution was pipetted into a crown-capped bottle. To this was added 100 cc of persulfate-buffer solution (6 g $K_2S_2O_8$, 1 g buffer). The bottle was then fitted with a crown cap which had had the cork replaced by a self-sealing rubber gasket. The bottle was placed in the thermostat at 50° and rotated end over end at 50 r.p.m. To obtain an aliquot for titration a hypodermic syringe filled with nitrogen was inserted through a small puncture in the top of the crown cap, and the bottle was shaken vigorously to insure uniform sampling. The bottle was then turned up-side down, the nitrogen from the syringe emptied into it, and a sample of the solution drawn out. This sample was weighed, and then poured into 150 cc of alcohol and titrated for mercaptan as described previously.

Soap Solutions.--The soap solutions for the diffusion and oxidation measurements were made up immediately before using. The water used was always freshly distilled. A 5% soap solution would contain 5 g of soap in 100 ml of solution.

Mercaptans.-The sources and methods of purification of the mercaptans used are summarized below:

n-Hexyl Mercaptan (Eastman) was fractionated through a 15 plate column at 745 mm pressure. B.R. 149-50°C.

n-Octyl Mercaptan.(Conn. Hard Rubber) was fractionated through a 15 plate column at 745 mm B.R. 194-5°C.

n-Decyl (Conn. Hard Rubber) was fractionated through a 15 plate column at 15 mm B.R. 106-7°C.

n-Dodecyl Mercaptan (U.S.Rubber) OEI was fractionated through a 15 plate column at 1.5 mm. The cut was used distilling from 96-97°C.

n-Dodecyl Mercaptan (Illinois) A specially purified sample of n-DD from the University of Illinois was included for comparison. B.R. 127-9°C/9mm (R.L. Frank)

n-Cetyl Mercaptan (U.S. Rubber) A sample of high-purity n-cetyl mercaptan (99%) from the U. S. Rubber Co. was redistilled through a modified Claissen flask just prior to using. B.R. 130-4/1 mm.

t-Butyl Mercaptan (Phillips) was fractionated through a 15 plate column at 745 mm. B.R. 62.8-63.2° C.

t-Octyl Mercaptan (Sharples) was fractionated through a 15 plate column at 745 mm. B.R. 158.5-159°C.

t-Decyl Mercaptan(Sharples) was fractionated through a 15 plate column at 6 mm. B.R. 73.5-75°C.

t-Dodecyl Mercaptan (Sharples)3B) was fractionated through a 15 plate column at 4 mm. B.R. 71.5-73°C.

6-Dodecyl Mercaptan (Illinois) B.R. 130-35°/9-10 mm (R. L. Frank)

4-n-Butyl-1-Octyl Mercaptan (Illinois) B.R. 98-99°/2.5mm. (R.L. Frank)

di-n-Butyl-n-propylcarbinthiol (Illinois) B.P. 84°/2-3mm. (R. L. Frank)

Dimethyl-n-nonylcarbinthiol (Illinois) B.R. 75°/1.5 mm. (R.L.Frank)

t-Tetradecyl Mercaptan (Phillips) A specially purified sample was obtained from Dr. W.A. Schulze. B.R. 104.5-106.5/1.8 mm. Mercaptan sulfur 13.9%, molecular weight 228, purity 99%.

t-Hexadecyl Mercaptan (Sharples) was fractionated through a 15 plate column. B.R. 113-4°/4 mm.

OPME (Goodrich) This product was evaluated as received without further purification. OPME is beta-p-octylphenoxy-beta prime-mercaptodiethylether. The sample evaluated had a mercaptan sulfur content of 10.05%.

Summary

1. The product of the diffusion rate and oxidation rate of a given mercaptan, called diffox product, has been correlated with mercaptan, disappearance in actual emulsion polymerizations.

2. A study of diffusion rates of mercaptans in soap solutions has been made. It has been found that:

(a) The rate of volume change of a mercaptan drop in an acqueous soap solution is proportional to the surface area of the drop, and equals -dr/dt.

(b) pH is an important variable. Solution rates are at a minimum at approximately 100% fatty acid neutralization. In excess caustic the normal mercaptans show a large increase, while tertiary show only a small increase, In partially neutralized soaps, both show surprisingly high diffusion rates.

(c) The diffusion rates of tertiary and primary mercaptans increase with increasing soap concentration.

(d) Difference in diffusion rates of tertiary and primary mercaptans results from branching and probably does not represent an inherent difference between the two classes of mercaptans.

(e) Diffusion rates show a temperature coefficient of about 1.5.

3. A study of the oxidation rates of mercaptans has been made, and the following found:

(a) Oxidation rates are proportional to the initial concentration of the mercaptan.

(b) Oxidation rates are inversely proportional to the soap concentration, and vary from soap to soap.

(c) Oxidation rates are directly proportional to the concentration of persulfate.

(d) The oxidation reaction has a high temperature coefficient (appr. 2.8) which is a fair indication that the reaction is of a colloidal nature and probably takes place at the micelle boundaries.

(e) There is a very fundamental difference in the oxidation rates of primary and tertiary mercaptans. The normal mercaptans oxidize about twelve times as fast as the tertiary. The secondary mercaptan falls into a class between these two.

(f) The equation

$$k = \frac{x}{a} \cdot \frac{1}{C_c t}$$

where $C_o = \frac{\text{moles of mercaptan}}{\text{moles of soap}}$

a = persulfate concentration

t = time

x = amount of mercaptan oxidized

describes the oxidation (by a large excess of persulfate) of a normal mercaptan dissolved in soap micelles.

Experimental Results

In the next section are tabulated the experimental results.

1. Table I. The Effect of pH on Solution Rates of Mercaptans in 5% Na Laurate Solutions
2. Table II. Mercaptan Diffusion Rates into 10% Potassium Laurate at 30°C, pH 10
3. Table III. Diffusion Rates of University of Illinois Isomeric C_{12} Mercaptans
4. Table IV Oxidation Rates in 5% RRS (buffered solution, varying initial mercaptan concentration)
5. Table V Effect of Persulfate Concentration on Oxidation Rate
6. Table VI Effect of Soap Concentration on Oxidation Rate of n-DD.
7. Table VII Effect of pH on Oxidation Rate
8. TableVIII Oxidation Rates of Mercaptans in 5% RRS with no Buffer
9. Table IX Effect of Temperature on K
10. Table X Mercaptan Oxidation Rates -Standard System

Table I

Effect of pH on Solution Rates of Mercaptans in 5 % (5 gr/100 ml) Na Laurate Solutions

(Grams/cm^2-hr x 10^4)

Neutralization of 5 % Na Laurate	pH at 30°	pH at 50°	Mercaptan Rates	
			n-C_{12}	t-C_{12}
90 %	8.85	8.36	11.	78
95 %	9.18	8.78	6.0	--
100 %	10.36	9.82	3.6	14
110 %	11.74	11.16	9.4	15
144 % (0.1 N NaOH)			31.0	21

Table II

Mercaptan Diffusion Rates
10% Potassium Laurate, 30°C, pH 10

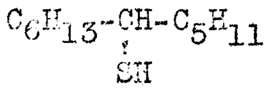
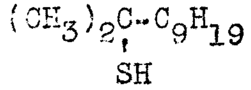
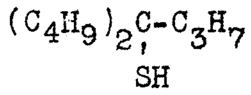
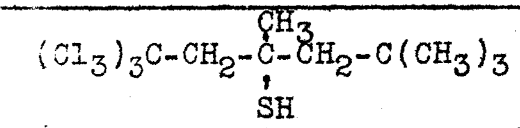
	Mercaptan	Diffusion Rates		
		gr/cm^2/hr. x 10^4	millimoles/ cm^2/hr x 10^4	Relative rates. Pure n-DD = 1.00
Primary	n-hexyl mercaptan	36	305	50.5
	n-octyl mercaptan	30[a]	206[a]	34.1
	n-decyl mercaptan	23.5	135	22.3
	n-dodecyl mercaptan (Illinois pure)	1.22	6.05	1.00
	n-dodecyl mercaptan (Fr. from OEI)	1.32	6.55	1.08
	4-n-butyl-1-octyl mercaptan	3.12	15.4	2.54
	n-cetyl mercaptan	0.028	0.11	0.018
Sec.	s-dodecyl mercaptan	2.09	10.2	1.70
Tertiary	t-butyl mercaptan	81	900	149
	t-octyl mercaptan	30	206	34.0
	t-decyl mercaptan	13.6	78	12.9
	t-dodecyl mercaptan	6.25	31	5.1
	di-n-butyl-n-propyl-carbinthiol	3.13	15.5	2.56
	dimethyl-n-nonylcarbinthiol	2.37	11.7	1.93
	t-tetradecyl mercaptan	2.36	10.3	1.70
	t-hexadecyl mercaptan	0.17	0.61	0.10
	OPME	8.15	26.3	4.35

[a] Value estimated--represents minimum value

Table III

Diffusion Rates

University of Illinois Isomeric C_{12} Mercaptans

No.	Mercaptan Structure	Mercaptan density 30°	Diffusion Rate grams/cm²/hr x 10^4	Longest chain
1)	$H_3C(CH_2)_{10}CH_2SH$ (From OEI)	0.843	1.32	13
2)	" (Illinois)	0.837	1.22	13
3)	 $C_6H_{13}\text{-}\underset{SH}{CH}\text{-}C_5H_{11}$	0.849	2.09	12
4)	 $(CH_3)_2\underset{SH}{C}\text{-}C_9H_{19}$	0.835	2.37	11
5)	$(C_4H_9)_2CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}SH$	0.847	3.12	9
6)	 $(C_4H_9)_2\underset{SH}{C}\text{-}C_3H_7$	0.853	3.13	8
7)	 $(Cl_3)_3C\text{-}CH_2\text{-}\overset{CH_3}{\underset{SH}{C}}\text{-}CH_2\text{-}C(CH_3)_3$ (Fractionated Sharples 3B)[a]	0.853	6.25	7

[a] Sharples 3B mercaptan is probably a mixture of the above mercaptan with $(CH_3)_3C\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}SH$--private communication from Mr. H.I. Cramer.

Table IV

Oxidation Rates in 5% RRS

(Buffered Solution - Varying n-DD initial concentration)

Initial Conc. of n-C_{12} mercaptan	Rate in millimoles/l/hr	$K=\frac{1}{t}$
45.0	12.0	.535
33.5	8.5	.508
34.8	8.7	.500
40.8	9.6	.472
63.0	16.9	.535
50.0	13.5	.541
28.8	7.3	.508
18.6	4.83	.513
39.6	9.2	.484

Table V

Effect of Persulfate Concentration on Reaction Rate

System: 5% SF - no buffer

% $K_2S_2O_8$	Rate - millimoles/l/hr
0.5	0.71
1.0	1.42
2.0	2.5
2.95	3.6
4.0	4.85

Table VI

Effect of Soap Conc. on Oxidation Rate of n-DD

SF Conc. (in g/100 cc sol'n)	Rate in millimoles/l/hr	t = hours required for complete oxidation (extrapolated)
0	0.17	93.0
1.5	21.30	0.96
2.8	11.7	1.80
4	9.05	2.75
7	4.0	4.8
10.0	3.48	5.8

Table VII

Effect of pH on Oxidation Rate of n-DD

% Soap Neutralized (SF)	Rate in millimoles/l/hr	t = hours required for complete oxidation
90	first order reaction	---
100	6.7	3.02
110	8.45	2.42
5% SF + 0.5% NaCl	7.55	2.66

Table VIII

Oxidation Rates of Mercaptans in 5% RRS + 3% $K_2S_2O_8$
(no buffer)

Mercaptan	Rate in millimoles/l/hr	Rate: K = 1/t
n-octyl	14.2	0.714
n-decyl	12.3	0.613
n-dodecyl (from OEI)	11.6	0.563
n-dodecyl (Illinois)	11.1	0.549
n-hexadecyl	7.56	0.377
6-dodecyl	2.46	0.122
t-octyl	0.95	0.048
t-decyl	0.26	0.013
t-dodecyl	0.89	0.042
t-tetradecyl	0.46	0.023
t-hexadecyl	0.64	0.040

Table IX

Effect of Temperature on K

Mercaptan	Time to complete oxidation	K = 1/t	ln(K x 10)	Temp. °C	1/T x 1000
n-DD	0.73(hrs)	1.37	2.620	60.1	3.000
"	1.20 "	0.835	2.122	54.8	3.049
"	2.00 "	0.500	1.609	50.1	3.096
"	4.20 "	0.236	0.859	44.3	3.155
n-C_{16}	0.96 "	1.04	2.342	60.1	3.000
"	1.45 "	0.690	1.932	54.8	3.049
"	2.50 "	0.400	1.386	50.1	3.096
"	4.30 "	0.232	0.832	44.3	3.155

Table X

Mercaptan Oxidation Rates--Standard System
RR Soap 5%, persulfate 3%, buffered to pH 10, 50°C

	Mercaptan ↓	Oxidation Rates		
		Millimols per liter per hr. Calc. to starting conc. of 20 millimols/liter	$K = \frac{1}{t} = \text{hrs}^{-1}$	Relative rates. Pure n-DD mercaptan = 1.00
Primary	n-hexyl mercaptan	30	1.49	2.73
	n-octyl mercaptan	12	0.615	1.12
	n-decyl mercaptan	9.4	0.468	0.86
	n-dodecyl mercaptan (Illinois pure)	11	0.546	1.00
	n-dodecyl mercaptan (Fr. from OEI)	10	0.510	0.93
	4-n-butyl-1-octyl mercaptan	8.5	0.422	0.77
	n-cetyl mercaptan	8.0	0.400	0.73
Sec.	6-dodecyl mercaptan	2.4	0.121	0.22
Tertiary	t-butyl mercaptan	66	3.42	6.26
	t-octyl mercaptan	1.2	0.059	0.11
	t-decyl mercaptan	0.24	0.020	0.037
	t-dodecyl mercaptan	0.64	0.032	0.058
	di-n-butyl-n-propylcarbinthiol	1.0	0.051	0.093
	dimethyl-n-nonylcarbinthiol	1.3	0.067	0.12
	t-tetradecyl mercaptan	0.5	0.025	0.046
	t-hexadecyl mercaptan	0.89	0.045	0.082
	DPME	29	1.44	2.64