

THE ABSORPTIOMETRIC DETERMINATION
OF SODIUM SULPHIDE AND
THE KINETICS OF ITS OXIDATION

by

CHARLES CHUAN-CHI HONG

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Department of Chemical Engineering

The University of British Columbia,
Vancouver 8, Canada.

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ABSTRACT

A study of the Lauth's Violet absorptiometric method for the analysis of sodium sulphide was carried out. The order of adding the reactants in the development of the color, the use of three different methods of titration for standardizing the solutions used for determining the calibration factor, and the effects of varying the concentrations of the reagents were all investigated. In the formation of Lauth's Violet from sodium sulphide, addition of reactants in the order base electrolyte, sodium sulphide, and p-phenylenediamine was shown to be best. The arsenious oxide method of titration was selected for determining the concentration of sodium sulphide in standard solutions used for calibration. If the reagents: base electrolyte containing ferric chloride, and p-phenylenediamine, were used at the concentrations of 0.16% and 5% by weight, respectively, the calibration factor remained constant up to concentrations 16 grams per litre of sodium sulphide. The applicability of the Lambert-Beer law and the effect of sodium thiosulphate on the absorptiometric method also were studied in detail.

The oxidation of sodium sulphide was studied under atmospheric pressure at various temperatures by use of two different apparatuses. From the measurements of the amounts of oxygen absorbed, the oxidation of sodium sulphide probably gives disulphide, thiosulphate, sulphite

and sulphate. The stoichiometry corresponds to thiosulphate being the main product of this reaction. The rate of absorption of oxygen with simultaneous oxidation of sodium sulphide was observed to decrease with increasing temperature from 25° to 45°C. Nevertheless, the maximum absorption rate was found at 55°C, and the absorption rate decreases again with temperature at least to 85°C. The reaction orders for the oxidation of sodium sulphide depend upon temperature, being second order at 25°C., order of 1.5 at 35° and 45°C., and first order from 55° to 85° C. The reaction order with respect to oxygen is first order, irrespective of temperature. The maximum rate of oxidation also occurs at 55° C.

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PREFACE

This thesis consists of two parts: Part I, The Absorptiometric Determination of Sodium Sulphide; and Part II, The Kinetics of the Oxidation of Sodium Sulphide.

In Part I, various effects were investigated to improve the Lauth's Violet absorptiometric method for the analysis of sodium sulphide. In Part II, the kinetics of the oxidation of sodium sulphide were studied by use of the modified absorptiometric method obtained from Part I.

The Nomenclature and the Literature Cited, which appear at the end of the thesis, refer to Parts I and II taken together.

PART I

THE ABSORPTIOMETRIC DETERMINATION

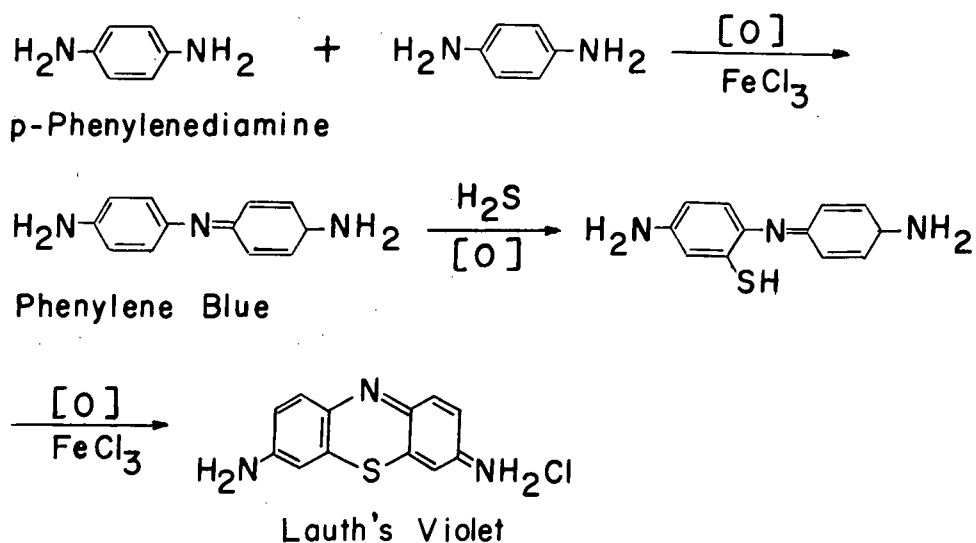
OF

SODIUM SULPHIDE

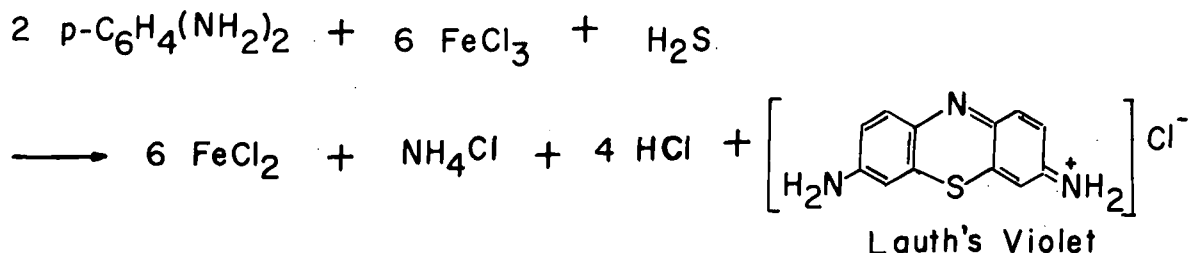
INTRODUCTION

Sodium sulphide can be estimated by developing it into a purple solution containing Lauth's Violet, by means of p-phenylenediamine and a base electrolyte containing ferric chloride as an oxidizing agent (1). Strickland and Risk (1) applied the method to the problem of the determination of sulphide in Kraft pulp process black liquor. However, the present work is restricted to the analysis of solutions of hydrogen sulphide in aqueous sodium hydroxide solutions. Accordingly, the problems associated with the presence of lignin and the like do not arise here.

The reaction mechanisms taking place in the formation of Lauth's Violet could not be found in the literature. However, the following steps would represent its formation if this proceeds similarly to that of methylene blue (2):



The overall stoichiometric equation was proposed by Werner (3) as follows:



INITIAL PROCEDURE

Samples of sulphide solution were taken by means of a 1-ml. tuberculin syringe fitted with a brass stop attached to the plunger so that the volume delivered each time was the same. In the present work this volume was 0.1590 ml., in accordance with the recommendations of Strickland and Risk. The tuberculin syringe was calibrated with distilled water of known temperature, as shown in Table 1. This syringe was rinsed three times with the

Table 1. Calibration of Tuberculin Syringe

Run	Wt. H ₂ O Delivered	Temp. of H ₂ O	Density of H ₂ O	Volume
1	0.1587 g.	25° C.	0.9971	0.1592 ml.
2	0.1586 "	"	"	0.1591 "
3	0.1575 "	"	"	0.1580 "
4	0.1593 "	"	"	0.1598 "
Average Volume of Tuberculin Syringe				= 0.1590 ml.

solution to be analyzed and was then used to deliver the exact volume of sample quoted above under the surface of 45 ml. of base electrolyte 0.08% * by weight ferric chloride (1) contained in a glass-stoppered graduated cylinder. The mixture was

* See footnote on P. 3

swirled two or three times and allowed to stand for two minutes. Next 2 - ml. of 1% * by weight p-phenylenediamine was added by means of a blow pipet. The solution was thoroughly mixed. After ten minutes, the resulting Lauth's Violet solution had reached the maximum intensity of colour. It was then diluted to a suitable volume with distilled water, and its extinction, or optical density, was measured. In the present study a Beckman DU spectrophotometer was used at a wavelength of 600 millimicrons and a slit width of 0.24-mm. Silica cells with a thickness of 1 cm. were used. The concentration of sodium sulphide was calculated from the following expression (1):

$$C = EVF/50$$

1

where C is the concentration of sodium sulphide in grams per litre, E the extinction corrected by subtracting the extinction of a blank solution (1), V the volume in ml. to which the solution has been diluted after colour development but prior to extinction measurement, and F a calibration factor determined experimentally by titrating freshly-prepared oxygen-free samples of sodium sulphide and also analyzing these same solutions absorptiometrically. Before dilution the solution has a volume near 50 ml. (actually close to 47 ml.) and the ratio V/50 is then approximately the factor by which the

* The concentrations of ferric chloride and p-phenylenediamine mentioned here are those of Strickland and Risk. These were used initially in this work. However, as shown later, others are more suitable and for the kinetics studies the latter were used.

Lauth's Violet solution has been diluted. The ratio V/50 is called the dilution in this thesis.

The absorption spectrum of Lauth's Violet solution at 3.55 grams per litre sodium sulphide was measured. The extinction reached a sharp maximum at 600 millimicrons, as shown in Figure 1. This result confirms the recommendation of Strickland and Risk (1) that a wavelength of 600 millimicrons be used.

In preparing the base electrolyte the "Roccal" wetting agent suggested by Strickland and Risk (1) was left out for the present case of analysis of sodium sulphide solutions. ("Roccal" is necessary in the analysis of black liquor which forms a precipitate on acidification (1).) The volume of diluted Lauth's Violet solution can be measured more accurately without the wetting agent present because of a marked reduction in foaming.

For obtaining the calibration factor F , sodium sulphide solutions were prepared by injecting hydrogen sulphide into a standard sodium hydroxide solution. Stoichiometric calculations revealed that 0.2 N sodium hydroxide, proposed by Wright et al (2) is too dilute for preparing samples of sodium sulphide with concentrations higher than 7.8 gms. per litre. Therefore, 0.4 N sodium hydroxide has been used in the present work. To freshly boiled distilled water, sufficient carbonate-free sodium hydroxide solution of 50% by weight concentration (4) was added to prepare a solution of 0.4 N sodium hydroxide. A

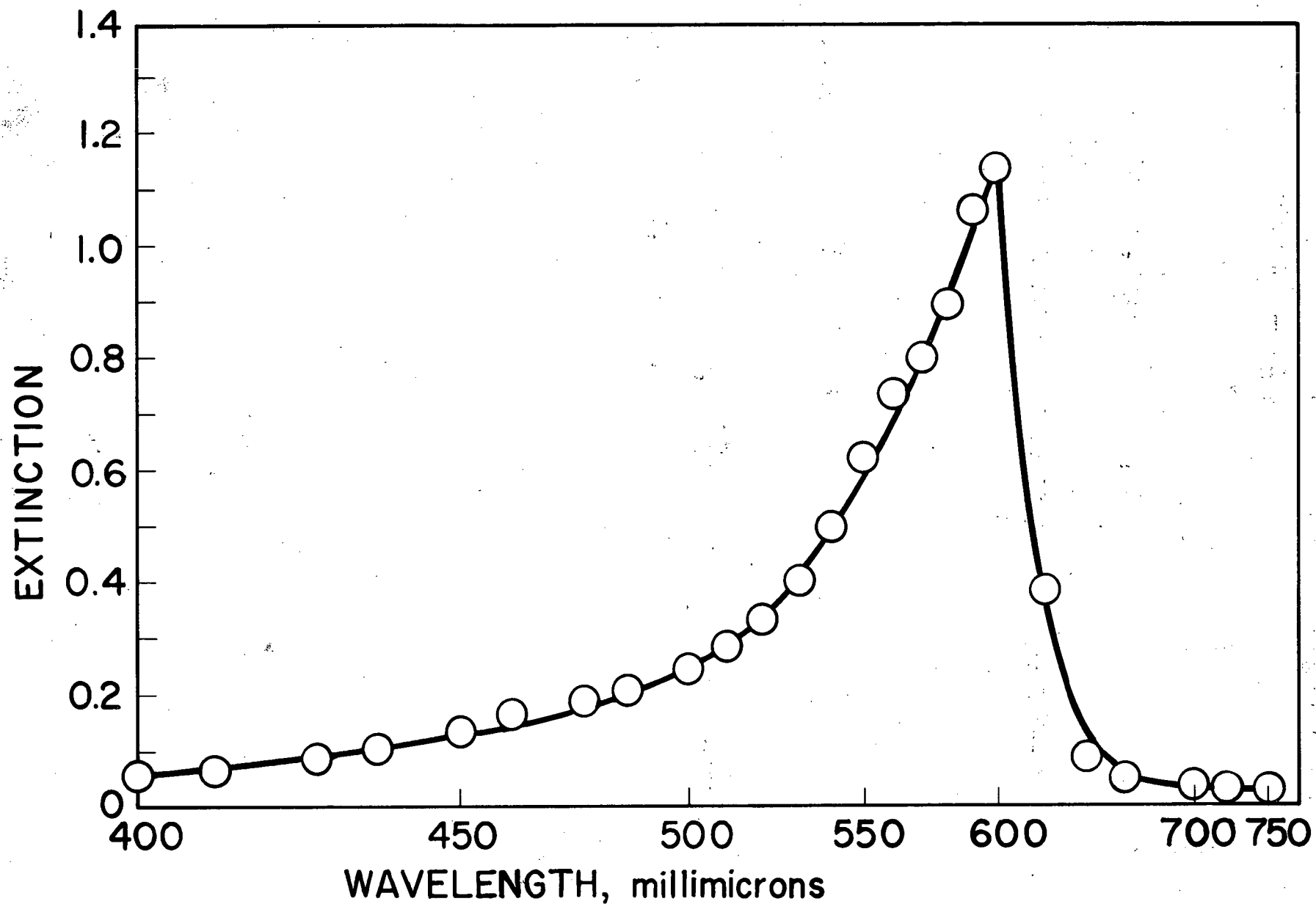


Figure 1. Absorption Spectrum of Lauth's Violet Solution.

30-ml. vial was filled with the 0.4 N sodium hydroxide solution and nitrogen (99.993% purity) was bubbled through the solution by being passed through two syringe needles, one below and the other above the surface of the solution, for twenty minutes in order to strip the oxygen from the solution. Pure hydrogen sulphide from a gas cylinder was then injected into the solution by means of a 100-ml. hypodermic syringe. The sodium sulphide solutions thus prepared were used immediately for calibration, in an attempt to prevent any possible oxidation of sodium sulphide by air. If the solutions are contaminated with oxygen, the sodium sulphide is gradually oxidized to sodium thiosulphate (5). As shown later, the thiosulphate interferes with the titration method by which the final calibration has been made.

To obtain the value of the calibration factor F , the sodium sulphide solutions initially were standardized by an iodimetric method as proposed by Wright et al (2). However, an investigation of this and other methods of standardization of sodium sulphide solutions indicated that a much better method of analysis of these could be used. This involved the use of arsenious oxide followed by back titration with iodine solution to a starch end point (6). The present work was done to investigate the Lauth's Violet method from two points of view: the method of standardizing the solutions of sodium sulphide used in determining the calibration factor F , and the absorptiometric method itself.

The latter part of the work consisted of studying the order of adding together the reagents in the colour formation of Lauth's Violet, the applicability of the Lambert-Beer law, the effect of concentrations of p-phenylenediamine and ferric chloride on the extinction, and the effect of any sodium thiosulphate present in the solutions analyzed.

METHODS OF TITRATION

Titration is necessary to establish the value of calibration factor F . Many methods of titrating sulphide, both chemical and potentiometric (7), have been published in the literature. Three methods of chemical titration were considered in the present work: the iodimetric method (2), the Volhard method (4), and the arsenious oxide method (6).

A. Iodimetric Method:

The use of the iodimetric method as proposed by Wright et al (2) produced a curve of calibration factor F versus the concentration of sodium sulphide, which was a concave upward. In other words, high values of the calibration factor were obtained for both high and low concentrations of sodium sulphide in the vials of sodium sulphide solutions prepared as previously described. Furthermore, the curve was found to be not reproducible.

In view of the poor reproducibility of the calibration curve, the stability of the Beckman DU spectrophotometer used was doubted. To check its stability, a red glass filter, which

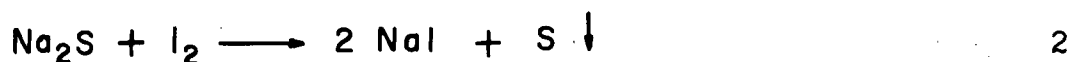
transmits radiation mainly in the range 580 to 640 millimicrons, was used as a standard "solution" of constant optical density. The spectrophotometer was found to be quite stable: the readings of extinction of the filter kept essentially constant on different days. Thus the doubt of the stability of the spectrophotometer was dissipated. The Lauth's Violet solution was found stable also, as its extinction reading remained constant for several hours after it was diluted with distilled water.

As a check on the reliability of the results obtained by the iodimetric method, the concentration of sodium sulphide in each vial used as a standard was obtained by accurately measuring the increase in weight resulting from the injection of the hydrogen sulphide into the solution of sodium hydroxide of measured volume in the vial. The concentration of sodium sulphide was calculated, and the result was compared with that obtained iodimetrically. The concentrations found by the iodimetric method were always higher than those calculated from weighing. The difference was as much as 100% at 0.5-gm. per litre sodium sulphide, and decreased with increasing concentration, being only 3% at 7.3 gm. per litre.

The iodimetric method involves the oxidation of sodium sulphide by iodine to form precipitated sulphur, and the back titration of the iodine in excess with sodium

thiosulphate solution, starch being used as an indicator.

The first reaction proceeds as follows:



Two major sources of error are believed to be the cause of the high F values already noted as being obtained by this method. These are vaporization of iodine into air (4), and enclosure of iodine by the sulphur precipitated in the solution (6). The former was probably more important at low concentrations of sodium sulphide, whereas the latter was probably the major cause of the high values of F at large concentrations. Loss of iodine by enclosure by the precipitated sulphur is known to be important at sulphide concentrations greater than 0.80-gm. per litre (6). The highest concentration of sulphide solution prepared for the present work was 15.72 gms. per litre, much higher than the limiting concentration. The iodine loss can be minimized by using concentration of iodine of 0.02 N * rather than the concentration of 0.1 N proposed by Wright et al (2). In addition, the iodine loss can be kept down to a minimum when iodine is used as slightly in excess as possible. The fact that this suggestion was not always followed at low concentrations of sodium sulphide in the present work probably explains the high F values at such concentrations.

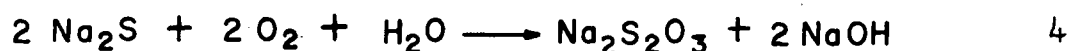
* 0.02 N iodine solution was suggested verbally by Dr. J. B. Risk of B.C. Research Council.

B. Volhard Method:

The use of Volhard method (4) produced more accurate results than did the iodimetric method when the weighing method was taken as the standard for comparison. However, the end point in the back titration of the Volhard procedure is not easily detectable, because of the presence of white silver thiocyanate precipitate:



In addition, the method is time consuming as compared with the other two methods. The Volhard method has one advantage over the iodimetric method or the arsenious oxide method to be described shortly in that it may be used to measure the concentration of sodium sulphide in solutions which have undergone partial air oxidation. In both the iodimetric method and the arsenious oxide method the presence of sodium thiosulphate, produced as a result of air oxidation of sodium sulphide according to the equation (3):



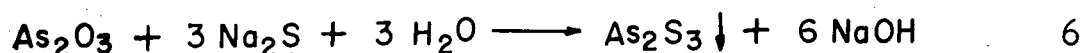
means that, in the iodimetric method, less than the proper amount of sodium thiosulphate would be added in the back titration, and that, in the arsenious oxide method, extra standard iodine solution would be required in the back titration step to oxidize the thiosulphate. This difficulty does not arise when the Volhard method is used, since redox reactions are not involved in either the precipitation of the sulphide,



or the back titration of the extra silver ions added (Equation 3).

C. Arsenious Oxide Method:

In the present study, the arsenious oxide method was found to be an excellent one for the titration involved in determining the calibration factor F. Accordingly, the calibration factors reported in this work have been determined in this way. A known volume (5 ml.) of the sodium sulphide solution prepared as described earlier, is added by a calibrated syringe to an excess of standard sodium arsenite solution (0.02 N) below the surface in order to prevent any possibility of air oxidation of sodium sulphide, and the mixture is then acidified with hydrochloric acid. The mixture of the precipitate which is formed and the solution is then diluted to 200 ml. in a volumetric flask, and shaken thoroughly. The reaction taking place is



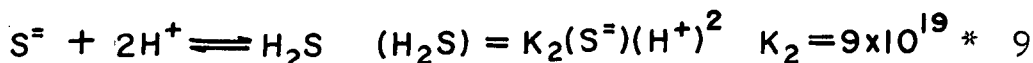
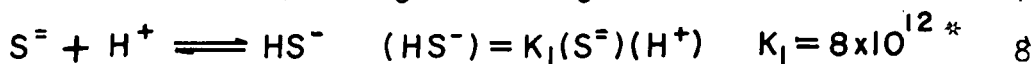
The mixture is filtered into a dry vessel through a dry filter paper. One hundred ml. of the filtrate is removed, neutralized with sodium bicarbonate, and back titrated with standard 0.02 N iodine in the presence of starch to the first blue colour. The quantity of the arsenious oxide consumed is calculated by subtracting the amount of the residual oxide from that originally employed.

The arsenious oxide method was found to give concentrations of sodium sulphide only slightly less than

those obtained by the weighing method. This result is in contrast to the results obtained iodimetrically which were higher than those of the weighing method. The negative discrepancy seems to be more reasonable than the positive one in the results for the sodium sulphide concentration, since part of the hydrogen sulphide injected is probably present in the gas phase in the vial.

HYDROLYSIS OF SODIUM SULPHIDE

Since sodium sulphide is a salt of weak acid and strong base, it has a tendency to hydrolyze in aqueous solution. The equilibria involved are



A material balance for the total sulphur in the solution is

$$C = (S^{2-}) + (HS^-) + (H_2S) \quad 10$$

where C = total concentration of sulphur, moles / litre.

Substitution of equations 7, 8, and 9 into 10 gives

$$C = (S^{2-}) [1 + 8 \times 10^{12} (H^+) + 9 \times 10^{19} (H^+)^2]$$

By definition mole fractions of the three sulphur-containing components in the solution are defined as

$$X_{S^{2-}} = (S^{2-}) / C, \quad X_{HS^-} = (HS^-) / C, \quad X_{H_2S} = (H_2S) / C.$$

Therefore,

$$X_{S^{2-}} = \frac{1}{1 + 8 \times 10^{12} (H^+) + 9 \times 10^{19} (H^+)^2} \quad 11$$

* K_1 is calculated from the data of Reference 8 and K_2 , from that of References 8 and 4.

$$X_{HS^-} = \frac{8 \times 10^{12} (H^+)}{1 + 8 \times 10^{12} (H^+) + 9 \times 10^{19} (H^+)^2} \quad 12$$

$$X_{H_2S} = \frac{9 \times 10^{19} (H^+)^2}{1 + 8 \times 10^{12} (H^+) + 9 \times 10^{19} (H^+)^2} \quad 13$$

The three equations above are graphically represented in Figure 2. The hydrogen ion concentration (H^+) in these equations is, of course, the equilibrium value. It is seen from Figure 2 that at pH's less than 4, the sulphur is present essentially as hydrogen sulphide molecules. Similarly the sulphur is almost completely in the hydro-sulphide form at pH equal to 10, and in the sulphide form at pH's greater than 15.

The equilibrium value of hydroxyl ion concentration (OH^-) or of hydrogen ion concentration (H^+) can be related to the initial concentration of sodium hydroxide solution and the total moles of sulphur present. When hydrogen sulphide is injected into an excess of sodium hydroxide solution, the hydroxyl ion concentration will decrease by an amount equal to the hydrogen ion produced per unit volume due to the formation of sulphur-containing ions from hydrogen sulphide. Therefore,

$$(OH^-)_0 - (OH^-) = (HS^-) + 2(S^{2-}) \quad 14$$

where $(OH^-)_0$ = the initial concentration of hydroxyl ion.

When the pH is greater than ten, hydrogen sulphide dissolved in the solution is negligible. Thus,

$$C = (HS^-) + (S^{2-}) \quad 15$$

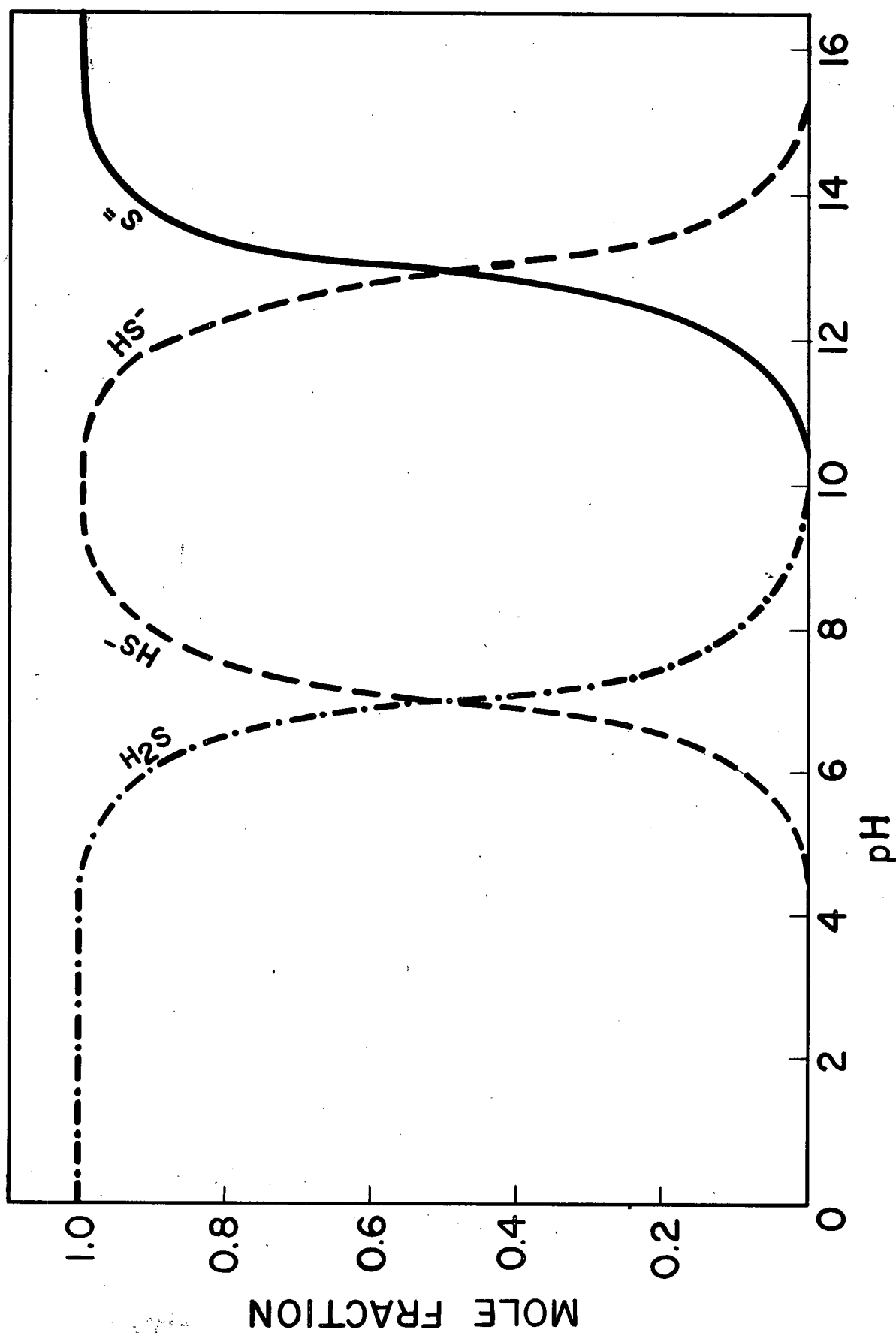
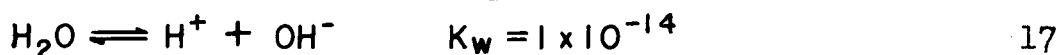
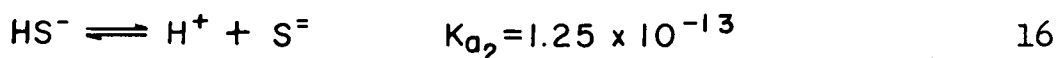


Figure 2. Mole Fractions vs. pH for the System Na_2S - NaHS - H_2S .

Equations for the ionization of the hydrosulphide ion and for the ionization of water, with their respective ionization constants (8,4), are



Subtracting equation 17 from equation 16 and rearranging gives



Now,

$$K = \frac{K_w}{K_{a2}} = \frac{1 \times 10^{-14}}{1.25 \times 10^{-13}} = 8 \times 10^{-2} \quad 18a$$

i.e.

$$\frac{(\text{HS}^-)(\text{OH}^-)}{(\text{S}^{2-})} = 8 \times 10^{-2}$$

$$\text{or } \frac{(\text{S}^{2-})}{(\text{HS}^-)} = \frac{(\text{OH}^-)}{8 \times 10^{-2}} \quad 19$$

Combining equations 14, 15 and 19 to eliminate (HS^-) and (S^{2-}) yields

$$(\text{OH}^-)^2 + [2C - (\text{OH}^-)_0 + 0.08](\text{OH}^-) + 0.08 [C - (\text{OH}^-)_0] = 0 \quad 20$$

By use of equation 20 it is possible to calculate the equilibrium hydroxyl ion concentration (OH^-) if the concentration of the total sulphur C and the initial concentration of sodium hydroxide $(\text{OH}^-)_0$ are known. The ratio of the concentrations of sulphide to hydrosulphide ions can be estimated by substituting the calculated (OH^-) into equation 19 or reading directly from Fig. 2. In this work, the initial concentration of sodium hydroxide solution used was

0.4 M. The ratios of $(S^{2-})/(HS^-)$ corresponding to this initial concentration were calculated as 1.16 and 45.4 for $C = 0.2$ M and 0.02 M, respectively. In view of the fact that the concentration of sulphide is higher than that of hydro-sulphide, the latter will be calculated as sodium sulphide for the purpose of reporting results. (On this basis the concentrations C of 0.2 M and 0.02 M respectively, just quoted, are 15.6 gm./l. and 1.56 gm./l. of sodium sulphide, respectively.)

CALIBRATION FACTORS

The calibration factors obtained by means of the arsenious oxide method are shown in Table 2. These apply to the concentrations of reagents used initially as mentioned earlier. Between 0 and 6 gm./l. of sodium sulphide F remains constant at a value of 0.614 with a standard deviation of 0.015 (corresponding to a coefficient of variability of 2.4%). A best line was drawn by use of the method of least squares in this range of concentrations. Since the line passes through the origin, it is completely specified by its slope, which is determined, in accordance with the principle of least squares (9), by dividing the ~~sum~~ of concentrations by the sum of the products of extinction and dilution. The slope is equal to the calibration factor F .

$$\sum C = 42.63, \quad \sum (EV/50) = 69.46 \quad (\text{below } 6.03 \text{ g./l.})$$

$$F = \frac{\sum C}{\sum (EV/50)} = 0.614$$

Table 2. Calibration Factors, Initial Procedure
(Volume of Na_2S solution: 0.159 ml.)

gm./l. Na_2S	EV/50.	F
0.86	1.35	0.637
1.30	2.06	0.631
1.49	2.30	0.648
2.54	4.10	0.620
2.59	4.11	0.630
3.55	5.83	0.609
3.89	6.44	0.604
4.49	7.28	0.617
4.62	7.41	0.623
5.52	9.20	0.600
5.75	9.64	0.596
6.03	9.74	0.619
6.71	10.84	0.619
7.28	11.42	0.637
7.44	12.02	0.619
7.62	11.97	0.637
8.22	12.80	0.642
9.90	14.55	0.680
10.08	14.62	0.680
11.24	16.35	0.687
11.39	16.24	0.701
12.34	17.43	0.708
12.41	17.38	0.714
13.10	18.80	0.697
13.71	18.98	0.722

When the concentrations are greater than 6 gm./l., F increases with increasing concentration of sodium sulphide. Figure 3 shows the concentration of sodium sulphide in the various vials plotted against the product of extinction and dilution: $\frac{EV}{50}$. A straight line relationship exists even

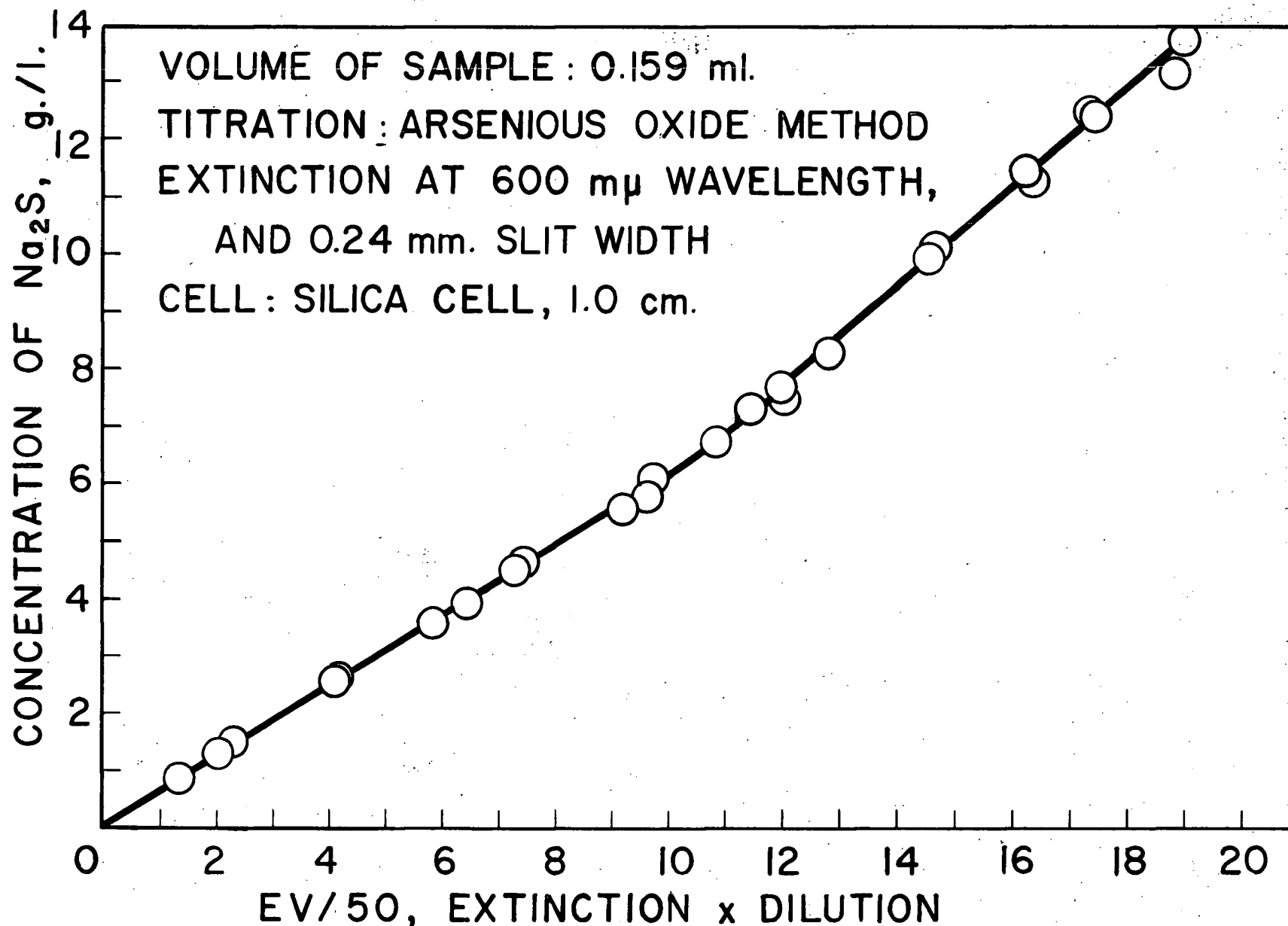


Figure 3. Calibration Curve, Initial Procedure.

at concentrations greater than 6 gm./l. However, the straight line does not pass through the origin at such concentrations.

The calibration curve of Fig. 3 is reproducible within the experimental error. It is based on a tuberculin syringe delivering a sample volume of 0.159 ml. It is possible to calculate the calibration factors based on other sample volumes, since the product of the calibration factor and the sample volume is a constant if the sample volume taken is in the neighbourhood of 0.15 ml. (1).

In an attempt to explain why the calibration factors increase at high concentration levels, the absorptiometric method was investigated in more detail.

ORDER OF ADDING REAGENTS IN FORMING LAUTH'S VIOLET

With three reagents, there are six possible orders in which these reagents can be brought together. These orders are listed in Table 3 together with an indication of

Table 3. Comparisons of Orders of Adding Reagents in Forming Lauth's Violet.

Order	Mutual Destruction of B and P	Oxidation of Na ₂ S by Air
B-P-N	X	
P-B-N	X	
N-B-P		X
N-P-B		X
B-N-P		
P-N-B		

B = Base Electrolyte, P=p-Phenylenediamine, N = Na₂S

certain difficulties that arise for various orders. As pointed out by Strickland and Risk (1), p-phenylenediamine and ferric chloride react with each other very rapidly, so that when they have been together for less than thirty seconds, sufficient mutual destruction has taken place for a low extinction to be found after subsequently adding sulphide. Therefore the orders B-P-N, and P-B-N, in Table 3 can be discarded. The orders N-B-P, and N-P-B, in which the other reagents are added to the sodium sulphide, result in oxidation of the sodium sulphide by air. Low extinction readings result as a consequence of this oxidation so that these orders are also to be rejected. Only the two orders: B-N-P, and P-N-B, remain for consideration.

The calibration factors F were determined experimentally as a function of concentration for each of these two orders. The arsenious oxide method of titration and the concentrations of reagents given under Initial Procedure were used. The results are shown in Fig. 4 which indicates that the calibration factors for the B-N-P order remain essentially constant over the range of concentrations investigated, but that the calibration factors for the P-N-B order increase with concentration. Also, the values of F for the P-N-B order are somewhat lower than those for the B-N-P order. In other words, the P-N-B order yields higher extinction values. These results strongly suggest that when the B-N-P order is used, part of the sodium sulphide is oxidized by ferric chloride to compounds, perhaps

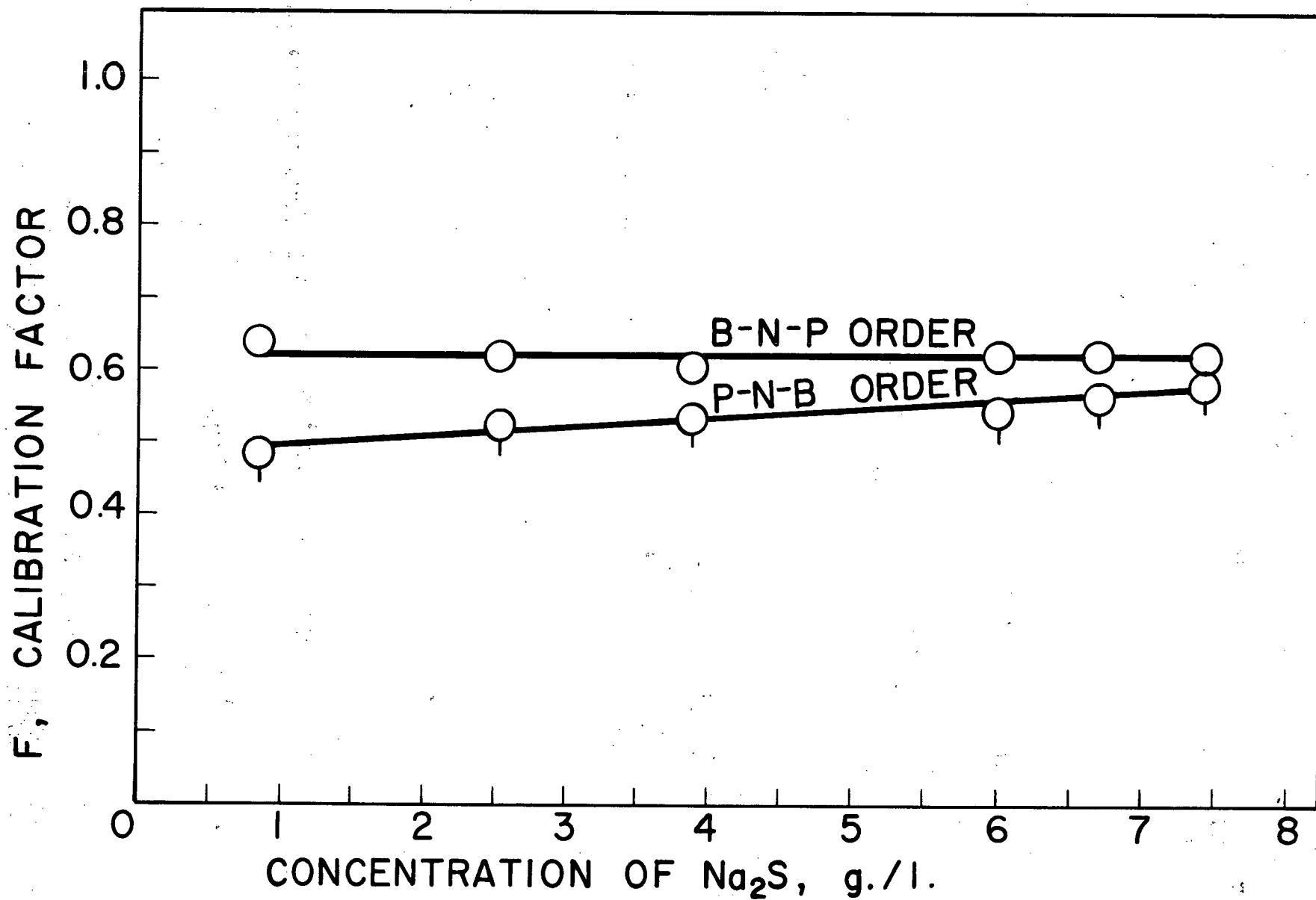


Figure 4. Calibration Factors Obtained from Two Different Orders.

sodium thiosulphate for instance, which do not give Lauth's Violet when p-phenylenediamine is added. For both the B-N-P and the P-N-B orders the odour of hydrogen sulphide could be detected during the addition of p-phenylenediamine and base electrolyte to the respective mixtures. However, since the minimum perceptible concentration of hydrogen sulphide is approximately one part per billion (10), the loss of sulphide in the form of hydrogen sulphide gas is probably negligible. Therefore, even if the loss should not be reproducible, it should not affect the constancy of the calibration factor F.

For the B-N-P order, the calibration factors are approximately constant in the region of concentrations investigated, as shown in Fig. 4. Hence the sulphide lost as hydrogen sulphide is either a constant proportion of that originally present or the losses are negligible as suggested.

The B-N-P order is believed to be preferable to the P-N-B order even though the latter produces higher extinctions. A constant value of F implies a linear relationship between extinction and concentration. The advantage of such a linear relationship is considered to be preferable to that of the existence of higher extinctions. Admittedly, however, the B-N-P order is probably only very slightly better than the P-N-B order when it is recalled that the former provides a linear relationship between concentration and the product of extinction and dilution up to only about 6 gms./l. of sodium sulphide, as shown in Fig. 3. (This remark applies

only to the reagent concentrations given under the Initial Procedure. The P-N-B order has not been tested with the higher reagent concentrations proposed in a later section.) The B-N-P order was that used by Strickland and Risk (1), that used in obtaining the calibration factors reported earlier in this thesis, and that used in all the work described from this point onward.

APPLICABILITY OF LAMBERT-BEER LAW

According to the Lambert-Beer law (11), the extinction E , corrected by subtracting the extinction of a blank (1), of the sample is directly proportional to concentration C :

$$\log \frac{I_0}{I} = E = k b C \quad 21$$

If the law is obeyed, the specific extinction k should be a constant, irrespective of the concentration C of Lauth's Violet. Lauth's Violet solutions, prepared from sodium sulphide solutions at 1.14, 4.55, 5.70, 7.25, 8.74, 12.36, 14.10 gms./l. respectively, by means of the procedure already described (Initial Procedure), were each diluted to several different volumes. The extinction of each diluted solution was measured by use of cells with thickness 1.0 cm., or of 0.1 cm. if the extinction was high. The results are summarized in Table 4 and Fig. 5, in which the concentration of the Lauth's Violet is expressed as p.p.m. of sodium sulphide which means that in the diluted solution whose extinction was measured the concentration of sodium sulphide would have been the value quoted had the sodium sulphide not

Table 4. Test of Lambert-Beer Law
(sample volume = 0.159 ml.)

Conc. Na_2S in standard solution, gms./l.	Diluted Volume, ml.	Conc. Lauth's Violet, pp.m. Na_2S	Cell Thickness b, cm.	Extinction E (corrected for the ex- tinction of a blank)	Specific Extinction k, (p.p.m.) ⁻¹ (cm.) ⁻¹
1.14	100	1.81	1.0	0.900	0.585
	200	0.92	"	0.463	0.590
	400	0.46	"	0.238	0.604
	800	0.23	"	0.125	0.631
4.55	250	2.89	1.0	1.376	0.498
	500	1.45	"	0.726	0.523
	1,000	0.72	"	0.372	0.539
	2,000	0.36	"	0.193	0.558
5.70	50	18.24	0.1	0.603	0.330
	100	9.12	"	0.355	0.389
	200	4.56	"	0.207	0.453
	400	2.28	"	0.115	0.504
	800	1.14	1.0	0.583	0.511
	1,600	0.57	"	0.290	0.508
	3,200	0.29	"	0.146	0.512
7.25	100	11.50	0.1	0.436	0.388
	200	5.75	"	0.262	0.455
	400	2.88	"	0.142	0.483
	800	1.44	1.0	0.698	0.485
	1,600	0.72	"	0.360	0.500
	3,200	0.36	"	0.183	0.508
8.74	100	13.92	0.1	0.513	0.368
	200	6.96	"	0.300	0.431
	400	3.48	"	0.161	0.463
	800	1.74	1.0	0.837	0.481
	1,600	0.87	"	0.435	0.500
	3,200	0.44	"	0.221	0.508
12.36	1,000	1.96	1.0	0.849	0.441
	2,000	0.98	"	0.434	0.451
	4,000	0.49	"	0.223	0.463
14.10	1,000	2.24	1.0	0.952	0.432
	2,000	1.12	"	0.484	0.440
	4,000	0.56	"	0.245	0.437

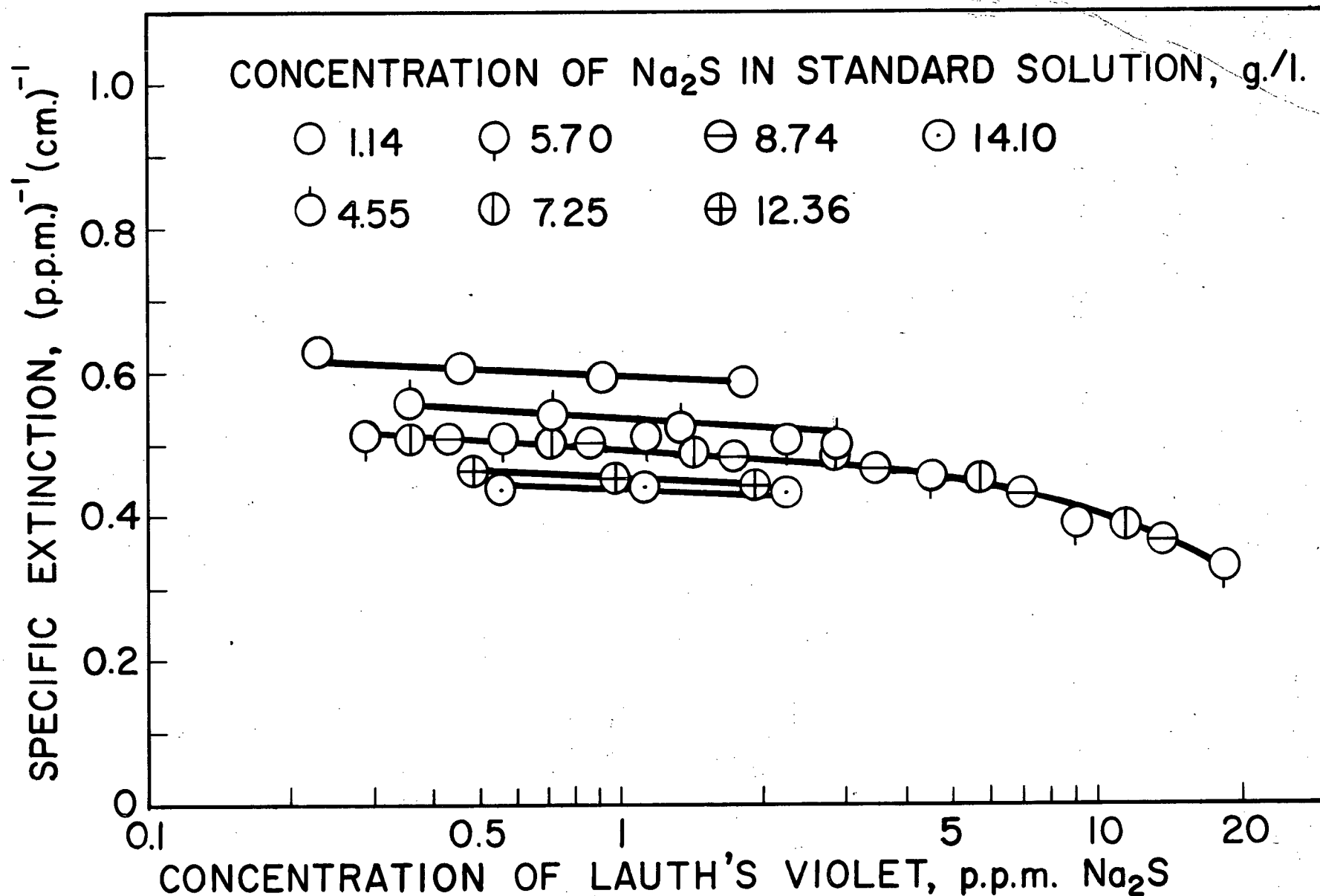


Figure 5. Specific Extinction versus Concentration of Lauth's Violet (calculated as parts per million of sodium sulphide in the diluted solution).

been converted into Lauth's Violet. Fig. 5 shows that the Lambert-Beer law is obeyed fairly well with respect to the concentration of the Lauth's Violet up to concentrations less than 3 p.p.m. (expressed as sodium sulphide), the constant slope of the family of the parallel lines indicating the deviation of the law with respect to Lauth's Violet concentrations. The maximum deviation between values of k 's for a given concentration of standard sodium sulphide solution was estimated from Fig. 5 as only 5.3% if the Lauth's Violet solution was so diluted that the extinction readings fell in the range of 0.9 to 0.2 when cells with a thickness of 1.0 cm. were used. The curve shows a falling off at high concentration of the Lauth's Violet, and the Lambert-Beer law breaks down, as shown in Fig. 5. The Lambert-Beer law, however, appears not to be obeyed with respect to the concentration of sodium sulphide in the standard solution, since the parallel lines shown in Fig. 5 fail to coincide with one another. It is of interest to note that the low concentrations of sodium sulphide in the standard solutions used yield high values of specific extinction, and vice versa, if the amounts of reagents used are those suggested by Strickland and Risk (1). Therefore, it becomes apparent that the concentrations of reagents, p-phenylenediamine and base electrolyte, are not sufficiently high to convert all of the sodium sulphide into Lauth's Violet, and this fact results in the increase described previously, of the calibration factor F at high levels of

sodium sulphide concentration in the standard solution.

EFFECT OF CONCENTRATIONS OF REAGENTS

A study was made of the effect on the extinction of changing the concentrations of p-phenylenediamine and ferric chloride in the analytical procedure. Strickland and Risk (1) suggested the use of 45 ml. of 0.08% by weight ferric chloride and 2 ml. of 1% by weight p-phenylenediamine, to develop 0.15 ml. of sodium sulphide solution into Lauth's Violet. When these concentrations were used the calibration factors were found to be high at high concentration levels of sodium sulphide, as mentioned earlier. If the concentration of ferric chloride is kept at 0.08% by weight, the extinction times dilution, $EV/50$, is found to increase with increasing concentrations of p-phenylenediamine used, as shown in Fig. 6. This is especially so at high concentrations of sodium sulphide. If, now, the concentration of p-phenylenediamine is kept at 1% by weight, the extinction times dilution is found to increase, then decrease, with increasing concentrations of ferric chloride, as shown in Fig. 7. The maximum extinction times dilution occurs very roughly at 0.16% by weight of ferric chloride. The increasing ordinate portion of the curves is consistent with ferric chloride being one of the active agents in the formation of Lauth's Violet from sodium sulphide. However, if the concentration of ferric chloride used is increased beyond about 0.16%, perhaps oxidation takes place of some of the sodium sulphide to a compound which gives

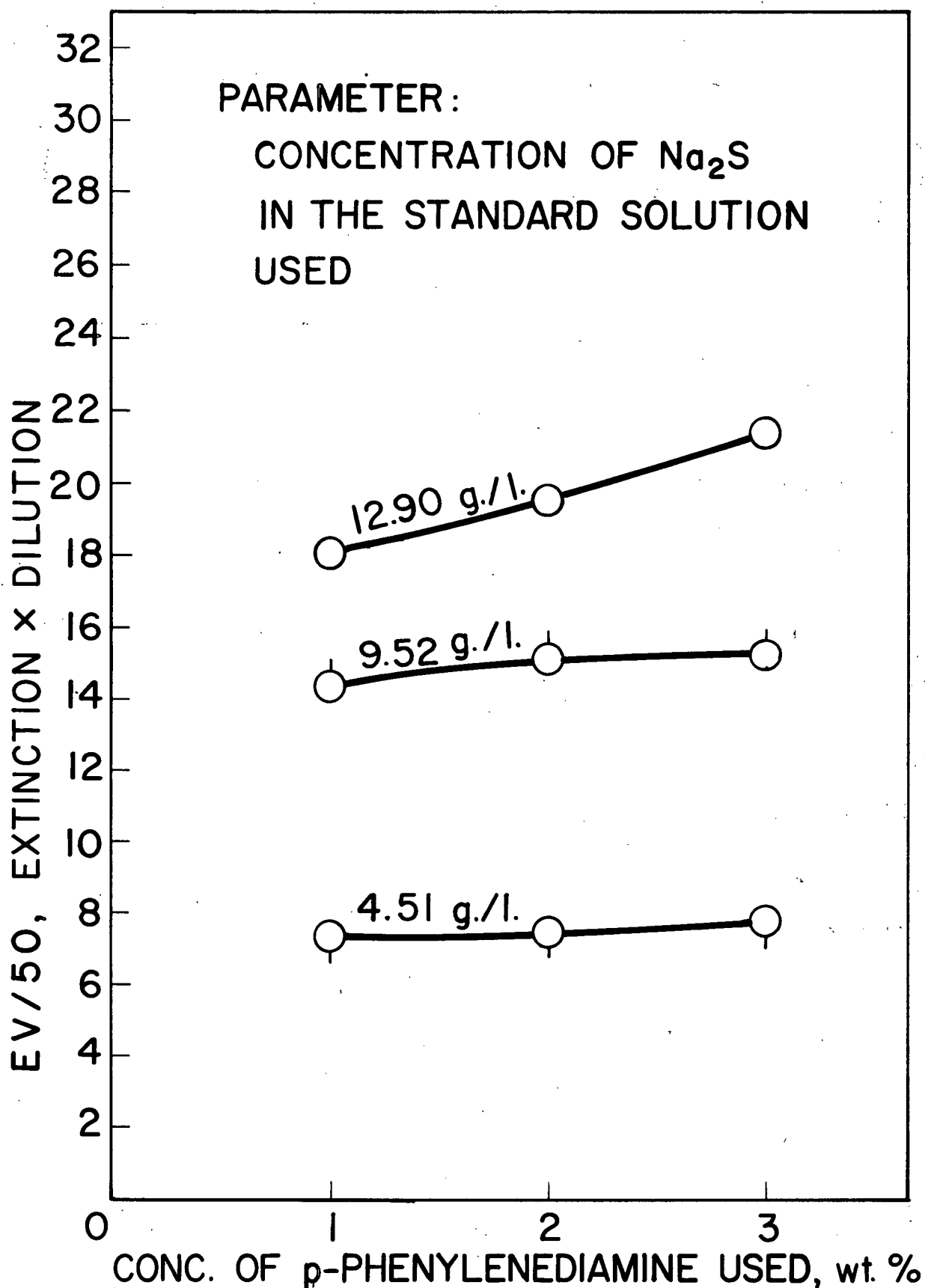


Figure 6. Effect of Concentration of p-Phenylenediamine on Extinction (0.08% by wt. of FeCl_3 solution used)

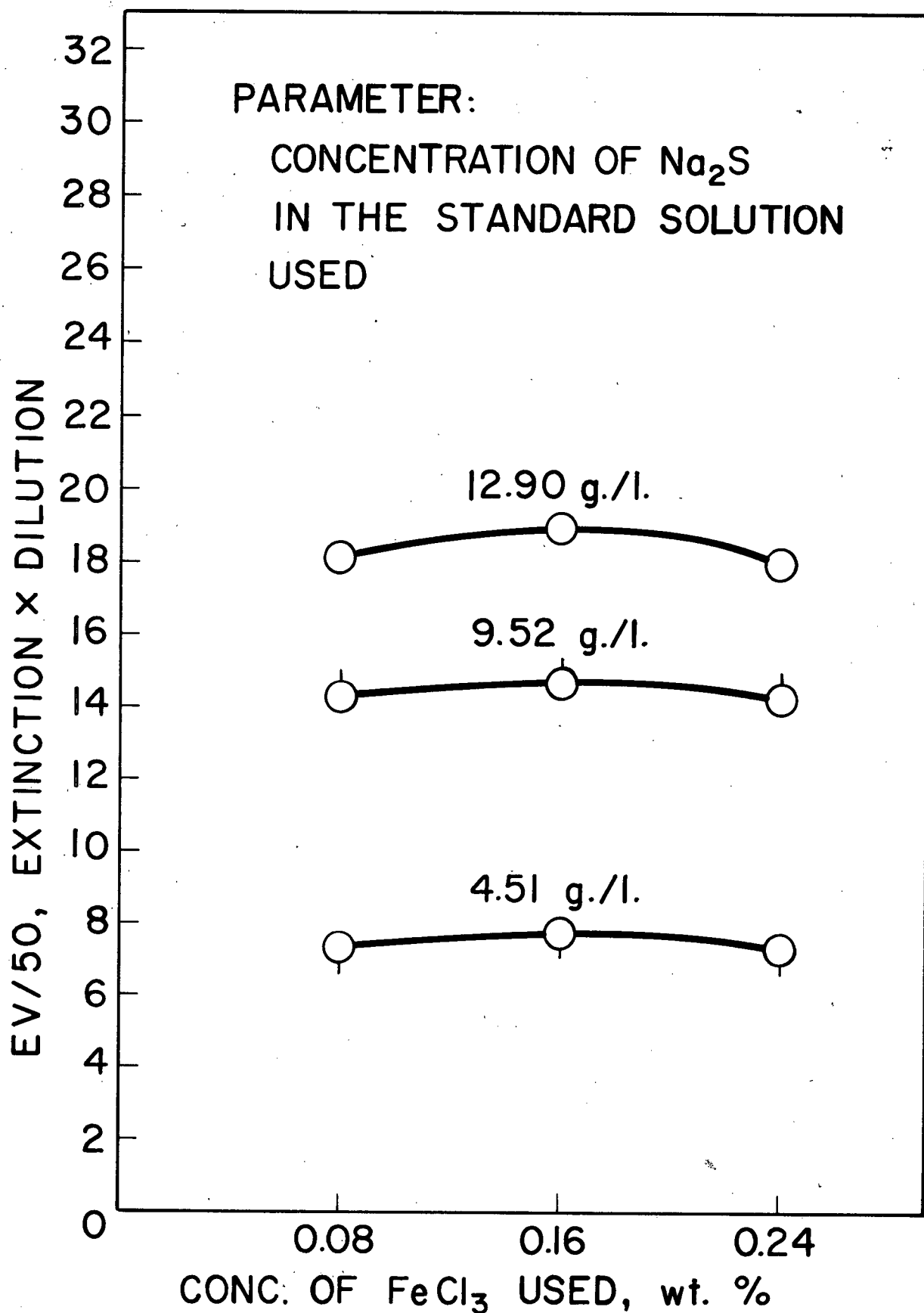


Figure 7. Effect of Concentration of Ferric Chloride on Extinction.
(1% by wt. of p-phenylenediamine used)

no colour when p-phenylenediamine is added and the extinction at a given dilution decreases as implied in Fig. 7.

It was expected from Fig. 6 that, if the concentration of ferric chloride were kept at 0.16% by weight, the extinction times dilution would increase from the values predicted by Fig. 7 if the concentration of the p-phenylenediamine used were increased above the value of 1% which applied to Fig. 7. The results of experiments to test this assumption appear in Fig. 8. The results expected were obtained and Fig. 8 shows also that at 5% by weight of p-phenylenediamine, the extinction times dilution is beginning to level out. In fact, this is the maximum extinction obtained by using the B-N-P order in this work. The numerical data corresponding to Figures 6, 7, and 8 are summarized in Tables 5, 6, and 7.

Table 5. Effect of Concentration of p-Phenylenediamine
(FeCl_3 = 0.08% by wt., 45 ml. used)

Conc. of Na ₂ S in Standard Solution, gms./l.	Values of Extinction X Dilution for Three Concs. of p-Phenylenediamine (2 ml. used)	1%	2%	3%
4.51	7.38	7.44	7.78	
9.52	14.32	15.12	15.24	
12.90	18.10	19.55	21.40	

Table 6. Effect of Concentration of Ferric Chloride
(p-phenylenediamine = 1% by wt., 2 ml. used)

Conc. of Na ₂ S in Standard Solution, Three Concs. of Ferric Chloride (45 ml. used)		Values of Extinction X Dilution for		
gms./l.	0.08%	0.16%	0.24%	
4.51	7.38	7.74	7.34	
9.52	14.32	14.66	14.26	
12.90	18.10	18.95	18.00	

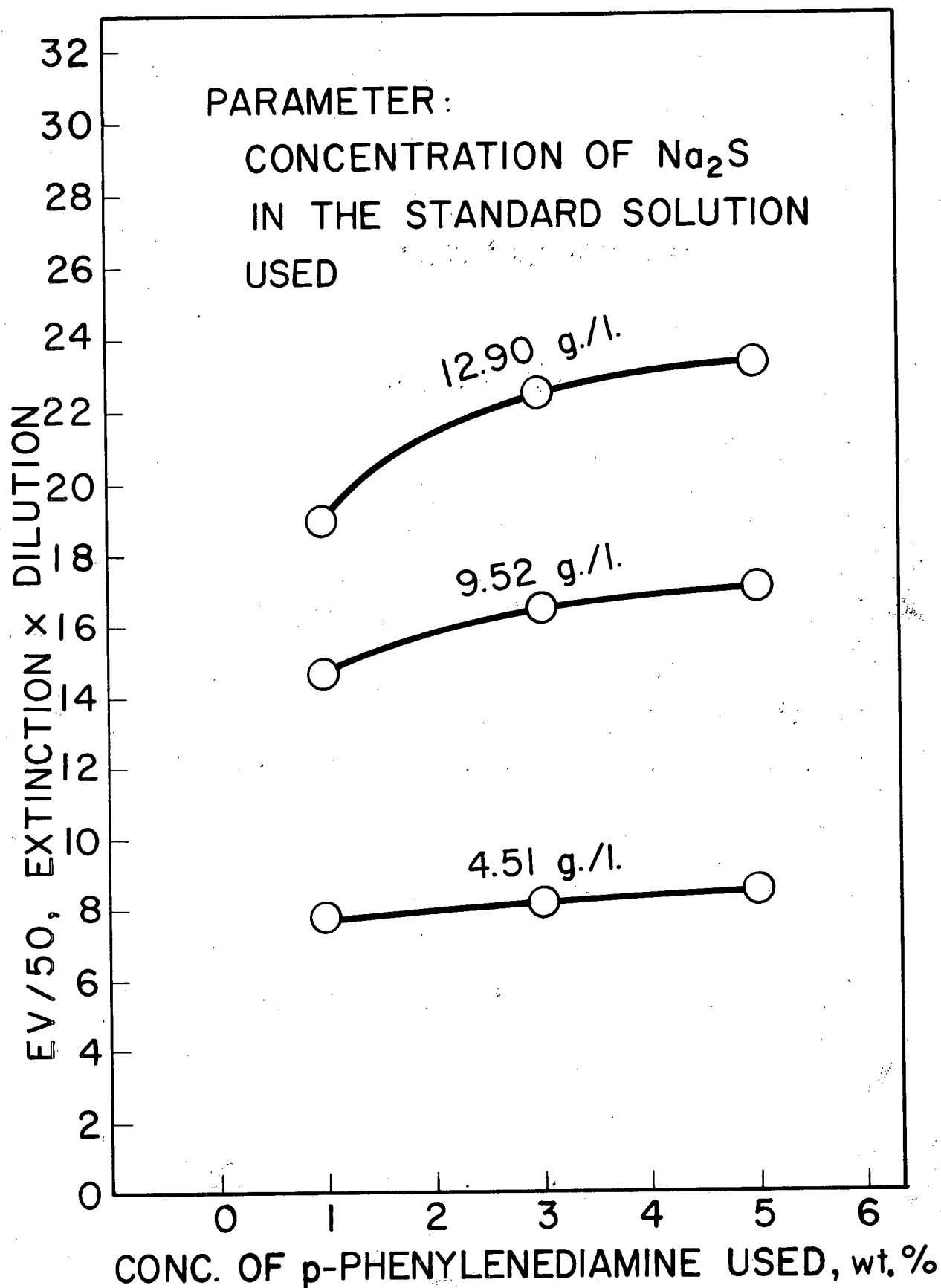


Figure 8. Effect of Concentration of p-Phenylenediamine on Extinction (0.16% FeCl_3 solution used).

Table 7. Effect of Concentration of p-Phenylenediamine
(FeCl_3 = 0.16% by wt., 45 ml. used)

Conc. of Na_2S in Standard Solution, gms./l.	Values of Extinction X Dilution for Three Concs. of p-Phenylenediamine (2 ml. used)		
	1%	3%	5%
4.51	7.74	8.08	8.48
9.52	14.66	16.46	17.06
12.90	18.95	22.50	23.28

A new calibration giving the concentration of sodium sulphide as a function of the product of extinction and dilution was made by using 45 ml. of 0.16% by weight ferric chloride and 2 ml. of 5% by weight p-phenylenediamine instead of the lower concentrations of these reagents given under the heading Initial Procedure. A linear relationship was established throughout all of the concentrations investigated, from 0 up to 15.72 gms. per litre of sodium sulphide. These results are given in Figure 9 and Table 8. Based on a sample volume of 0.159 ml., the average calibration factor is 0.541, with a standard deviation of 0.011 and a co-efficient of variance of 2.0%.

As a colour-developing reagent, p-phenylenediamine will shift the reaction equilibrium forward to form more Lauth's Violet if it is used in more concentrated form. In order to reproduce the calibration completely it is suggested that p-phenylenediamine in the form of dihydrochloride be weighed accurately with a chemical balance and diluted with distilled water by use of a pipet. It is possible in this way to prepare the p-phenylenediamine at the

Table 8. Calibration Factors for 0.16% by Wt. FeCl_3
and 5% by Wt. p-Phenylenediamine
(Volume of Na_2S sample = 0.159 ml.)

Conc. of Na_2S in Standard Solution gms./l.	$\frac{\text{EV}}{50}$	F	Remarks
1.12	2.12	0.528	
2.62	4.40	0.592	
3.14	6.12	0.513	*
4.52	8.48	0.533	
4.60	8.44	0.545	
5.78	10.56	0.547	
6.29	11.60	0.542	*
7.60	14.55	0.523	
9.43	17.37	0.543	*
9.53	17.06	0.551	
10.80	19.76	0.546	
12.35	22.96	0.538	
12.58	23.46	0.536	*
12.89	23.28	0.554	
14.10	26.56	0.531	
15.72	29.20	0.538	

Average Calibration Factor F = 0.541

* represents the sodium sulphide solution with the presence of sodium thiosulphate.

same concentration each time. This procedure was used in obtaining the calibration curve of Figure 9.

In the case of ferric chloride, the shift of the equilibrium cannot explain the experimental results fully, since a secondary reaction involving oxidation of sodium sulphide by ferric chloride probably occurs also.

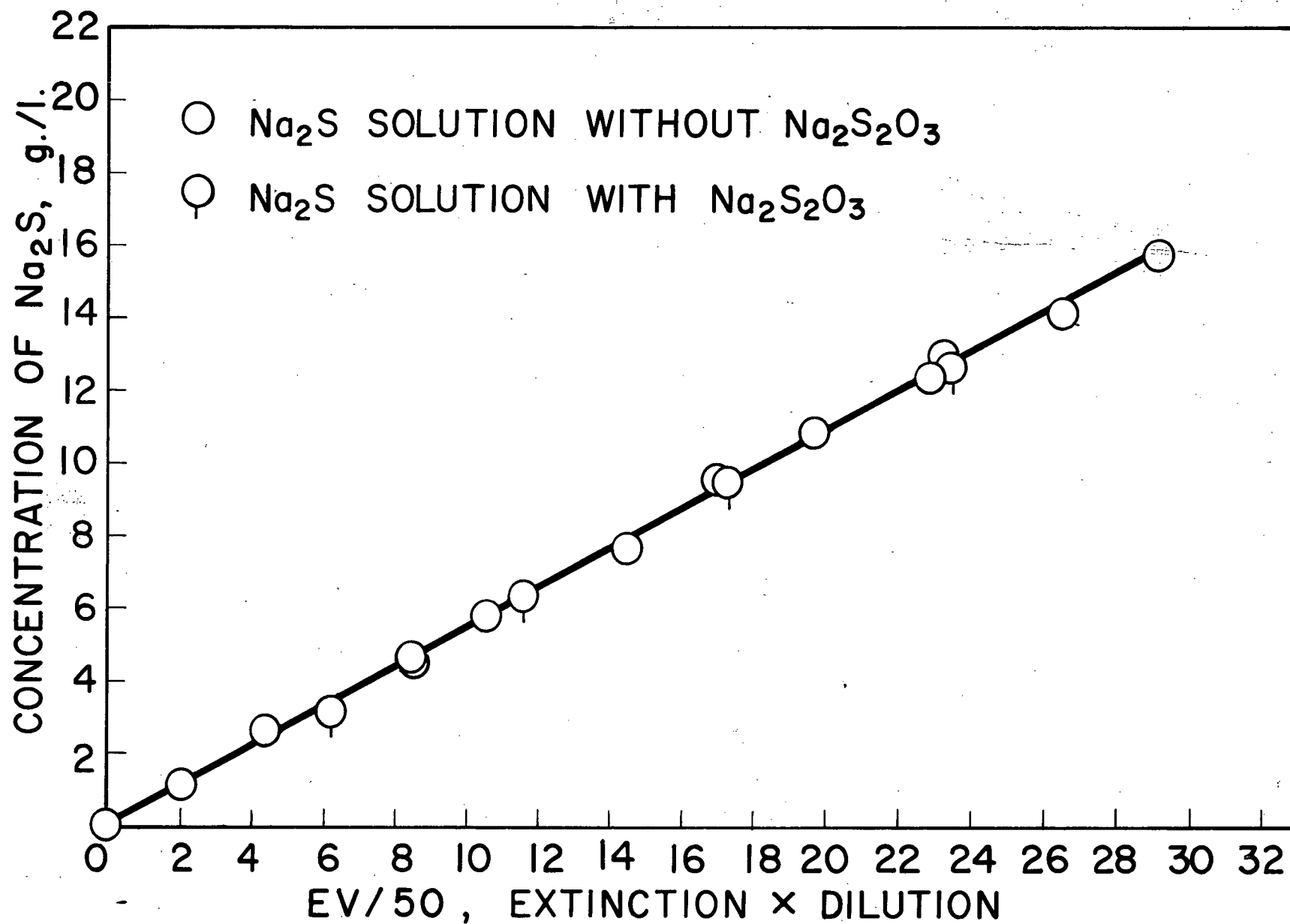


Figure 9. Calibration for Use of 0.16% Ferric Chloride and 5% p-Phenylenediamine.

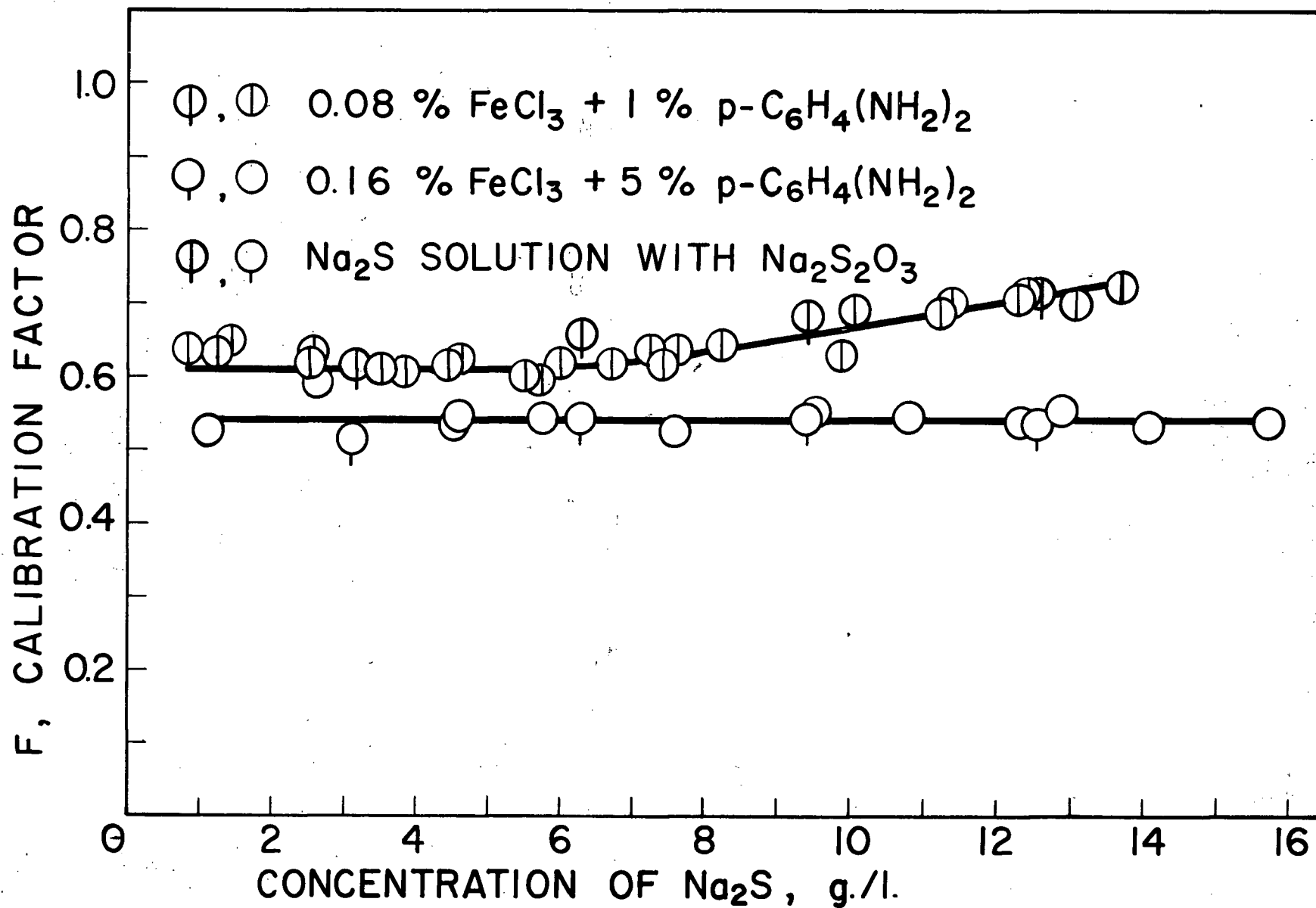


Figure 10. Effect of the Concentration of p-Phenylenediamine and Ferric Chloride Used, on the Calibration Factor.

The effect of the concentrations of p-phenylenediamine and ferric chloride is visualized by plotting the calibration factors against the concentrations of sodium sulphide with the concentrations of the two reagents as a parameter, as shown in Fig. 10. The calibration factors obtained by use of 5% p-phenylenediamine and 0.16% ferric chloride remain at a constant value up to 15.72 gms./l. of sodium sulphide. For the kinetics studies of the oxidation of sodium sulphide, these concentrations of the reagents were used to determine the concentration of sodium sulphide in the reaction solution. The following equation was applied.

$$C = 0.541 (EV/50)$$

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EFFECT OF SODIUM THIOSULPHATE ON THE ABSORPTIOMETRIC METHOD

Upon oxidation of sodium sulphide, the compound formed is sodium thiosulphate, as shown in Equation 4. Sodium thiosulphate was studied to see whether it would interfere with the determination of sodium sulphide by the absorptiometric method. Stoichiometric calculations based on Equation 4 showed that complete oxidation of 156 grams of sodium sulphide gives 158 grams of sodium thiosulphate. Since the weight ratio of sodium thiosulphate to sodium sulphide oxidized is nearly unity, a solution of sodium sulphide and a solution of sodium thiosulphate were prepared separately, each having the same concentration expressed as

grams per litre of the respective compound. Mixing these solutions then gave a solution which simulated a partially oxidized sodium sulphide solution.

The sodium sulphide solution was prepared first. As usual, hydrogen sulphide was injected into a 0.4 N sodium hydroxide. This solution was found to contain 15.72 grams per litre of sodium sulphide by the absorptiometric method (5% p-phenylenediamine and 0.16% ferric chloride). The sodium thiosulphate solution was prepared at this same concentration (15.72 gms./l. of sodium thiosulphate) by slightly diluting a standard 0.1 N sodium thiosulphate solution. The two solutions then were mixed in various proportions, by use of a calibrated syringe, in serum bottles in which the air had been replaced by pure nitrogen. The concentrations of sodium sulphide and sodium thiosulphate in each resulting mixed solution were calculated from the known volumes and the concentrations of the two compounds which had been mixed.

The value of EV/50 corresponding to the calculated concentration of sodium sulphide in each mixed solution was then read from the calibrations in Figures 3 and 9. The EV/50 thus obtained represented the extinction times dilution of sodium sulphide without thiosulphate. The actual EV/50 also was determined by the absorptiometric method, and this represented the extinction times dilution of sodium sulphide with thiosulphate present. The effect of sodium thiosulphate

on the absorptiometric method can be observed by comparing the EV/50's obtained from the calibration curve and with those obtained by actual analyses. The results are shown in Table 9, which indicates that the presence of sodium

Table 9. Effect of Sodium Thiosulphate on Extinction

Na ₂ S and Na ₂ S ₂ O ₃ in Mixed Solution		Results of EV/50 for 0.08% FeCl ₃ + 1% p-phenylenediamine		Results of EV/50 for 0.16% FeCl ₃ + 5% p-phenylenediamine	
g./l. Na ₂ S	g./l. Na ₂ S ₂ O ₃	Na ₂ S with- out Na ₂ S ₂ O ₃	Na ₂ S with Na ₂ S ₂ O ₃	Na ₂ S with- out Na ₂ S ₂ O ₃	Na ₂ S with Na ₂ S ₂ O ₃
0	15.72	0	0	0	0
3.14	12.58	5.14	5.12	5.80	6.12
6.29	9.43	10.22	9.62	11.60	11.60
9.43	6.29	14.23	13.86	17.37	17.37
12.58	3.14	17.75	17.64	23.20	23.46
15.72	0	21.12	21.12	29.20	29.20

thiosulphate in the solution decreased the extinction somewhat if 0.08% ferric chloride and 1% p-phenylenediamine are used; but does not affect the extinction significantly if 0.16% ferric chloride and 5% p-phenylenediamine are employed. Thiosulphate acts as a chain breaker in the chain reaction occurring in the oxidation of p-phenylenediamine by ferric chloride during the formation of Lauth's Violet (12). The induction time is approximately proportional to the concentration of the thiosulphate in the solution, as shown in Fig. 11. If the colour development was prolonged from the time of 10 minutes, used routinely, to 15 minutes, the increase in extinction was found to be negligible, only 1.4% on the average.

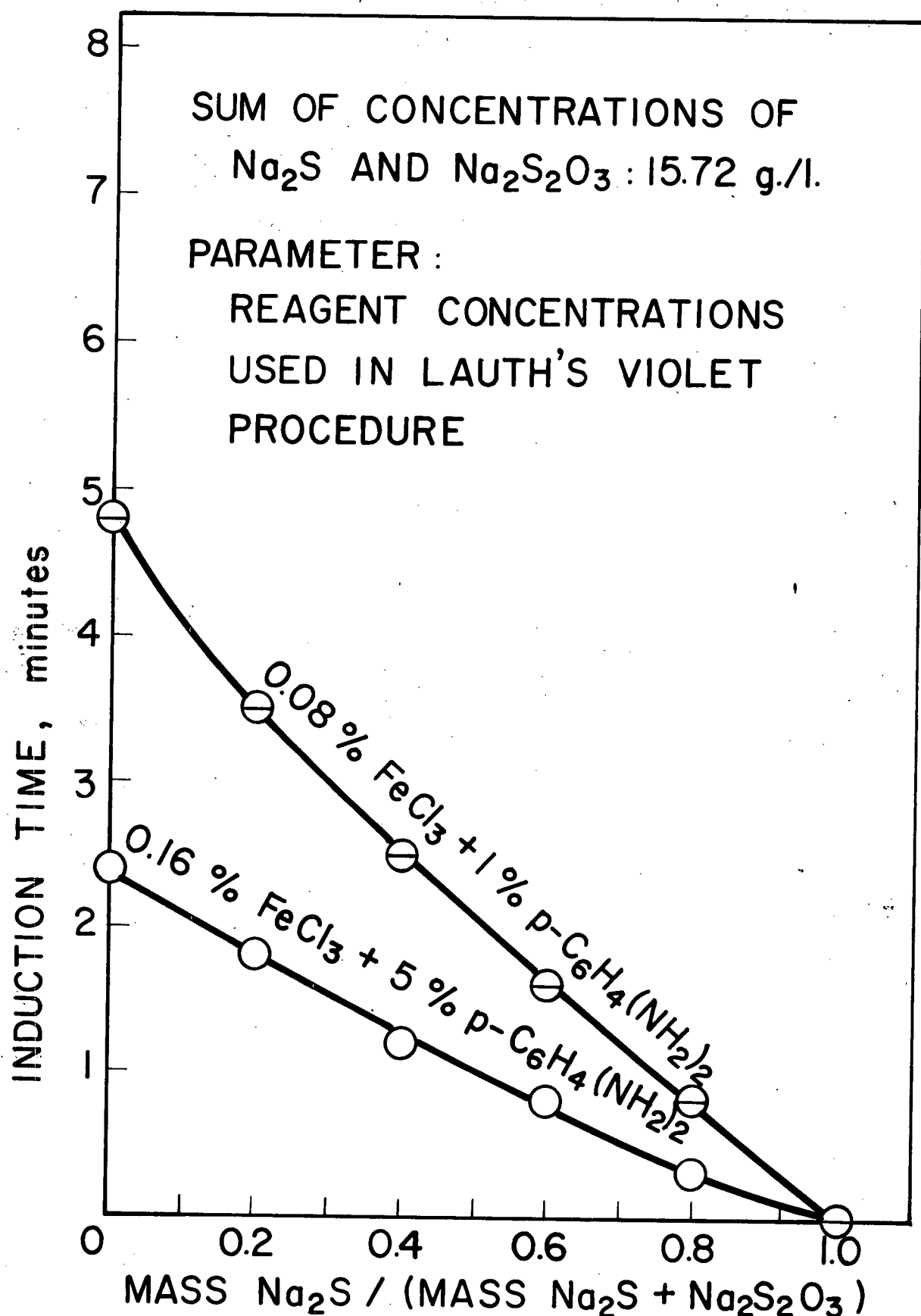


Figure 11. Induction Time for the Formation of Lauth's Violet.

Equation 4 shows sodium hydroxide is a product of the oxidation of sodium sulphide also. However, the change in the concentration of sodium hydroxide seems to have little effect.

The sodium sulphide solutions prepared as standards are apparently subject to air oxidation even though the solutions removed from the vials are replaced with nitrogen. It was found that if such a solution was allowed to stand in the vial for days, the extinction tended to decrease with time. The use for calibration purposes of freshly prepared (and oxygen-free) sodium sulphide solution is therefore important, in order that no thiosulphate be present to conflict with arsenious oxide in the back titration with iodine. The fact that the Lauth's Violet method produces, for a given vial of standard sodium sulphide solution, decreasing concentrations with time is consistent with the fact that the method is independent of the presence of sodium thiosulphate.

CONCLUSIONS

In determining the calibration factors for use with the Lauth's Violet absorptiometric determination of soluble sulphides, the arsenious oxide method of titration (6) is certainly more satisfactory than is the iodimetric method (2) and is probably better than the Volhard method (4). In this calibration procedure the sodium sulphide solutions

should be prepared oxygen free, and should be used when freshly prepared in order that thiosulphate produced by air oxidation of the sulphide does not destroy the accuracy of the arsenious oxide determination.

The reagents are best brought together in the order: base electrolyte, sodium sulphide and p-phenylenediamine. If 45 ml. of 0.16% by weight ferric chloride base electrolyte, and 2 ml. of 5% by weight p-phenylenediamine are used for a volume of sodium sulphide of 0.15 ml., the calibration factor is constant up to 16 gms. per litre of sodium sulphide.

The Lauth's Violet method itself is independent of the presence of sodium thiosulphate in the solution.

PART II

THE KINETICS

OF

THE OXIDATION OF SODIUM SULPHIDE

INTRODUCTION

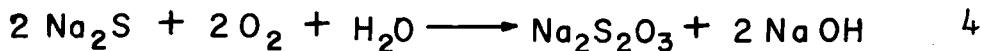
Odour control in the Kraft pulping process has been a subject of interest for several decades. In 1939 Bergstrom and Trobeck (13) first proposed the oxidation of black liquor to reduce the malodour from the pulping operations. The advantages for the oxidation of sulphate black liquor, outlined by Collins (14), include:

1. Maintenance of the sulphidity of cooking liquor.
2. Reduction in the amount of lime required for causticizing.
3. Reduction of the odour nuisance from evaporators and the recovery furnace.
4. Possibility of substitution for salt cake of soda ash or caustic soda as partial alkali make-up.
5. Improving the suitability for rubber compounding of lignin precipitated from black liquor.
6. More uniform operation of the vacuum evaporators.
7. Reduction of corrosion in evaporators and scrubbers.
8. Production of a fuel in the form of dry liquor which is more suitable than that prepared from unoxidized liquor.

In regard to the kinetics of the oxidation of black liquor, insufficient knowledge is available so far, even though many contributors have published their experimental results. Wright (15) found that the reaction is pseudo first order by measuring the rate of absorption

of oxygen from moist air at one atmosphere total pressure by sulphate black liquor between 40° and 90°C. He also found that sodium sulphide is oxidized more rapidly in black liquor than in aqueous alkali, probably because of the presence of catalysts derived from the wood. Murray (16) found that the rates of oxidation varied in a complex manner depending upon the partial pressure of oxygen, the sodium sulphide concentration, the rate of liquor stirring, and the chemical reaction taking place under the prevailing experimental conditions.

Ziegelmeyer and Feischl (5) found the full agreement for the process occurring during the oxidation with the supposed reaction equation.



However, Bilberg and Landmark (17) found the oxidation products of black liquor contain polysulphides, thiosulphate, sulphite, and small amounts of sulphate.

Since the black liquor contains a variety of organic and inorganic compounds, a complete analysis of black liquor is difficult. In view of this complexity, the present study was restricted to the oxidation of sodium sulphide, which is the main component of the black liquor oxidized. The present work is aimed at the determinations of reaction orders with respect to both sodium sulphide and oxygen, rates of oxygen absorption, and the stoichiometry of reactions taking place during the oxidation of sodium

sulphide at different temperatures. A brief comparison is made between the oxidations of sodium sulphide and of black liquor publicized in the literature.

EXPERIMENTAL METHODS

1. Apparatus

The two different apparatuses used in this work are shown in Figures 12 and 13. The apparatus in Fig. 12 was used to study the kinetics of the oxidation of sodium sulphide by bubbling oxygen or air whereby the overall reaction orders with respect to the concentrations of sodium sulphide and oxygen could be determined. The apparatus in Fig. 13 was used to determine the rate of oxygen absorption with simultaneous oxidation of sodium sulphide, and its stoichiometry at various temperatures. The key to Figures 12 and 13 is shown in Table 10.

Table 10. Key to Figures 12 and 13

1, 2, 3, 4, 5	-	stopcocks
A	-	pressure regulator
B	-	purge meter
C	-	saturator
D	-	reactor
E	-	soap bubble meter
F	-	water bath
G	-	stirrer for water bath
H	-	thermometer
I	-	fritted disk
J	-	magnet
K	-	thermoregulator
L	-	heating element
M	-	magnetic stirrer
N	-	water reservoir
O	-	gas buret

Table 10. - (Continued)

P	-	manometer
Q	-	glass tube
R	-	preheating coil
S	-	breaker
T	-	Allen screw

2. Procedure

The reaction orders for the oxidation of sodium sulphide were determined by means of the apparatus shown in Fig. 12. Oxygen or air was used as gas feed. The gas from a cylinder was passed through a pressure regulator A, a purge meter B with a brass differential pressure regulator to control the constant flow rates, and an absorption bulb C which contained water and was used as a saturator. The gas was bubbled through a fritted disc I of coarse porosity (nominal maximum pore size: 40 - 60 microns), 20 mm. in diameter, into the reactor D. The reactor was a Pyrex round-bottom flask of 500 ml. capacity, and contained 250 ml. of sodium sulphide solution. (The sulphide solution was prepared by bubbling hydrogen sulphide through a glass tube into 0.4 N sodium hydroxide solution in a storage bottle. Air was purged out of the bottle through another glass tube above the surface of the solution by this stream of hydrogen sulphide. It took very roughly one minute to purge out air from the bottle. 250 ml. of the sulphide solution were poured into the reactor. The run was started immediately). The gas flow rates were measured with a soap bubble meter E by measuring the time with a stop-watch

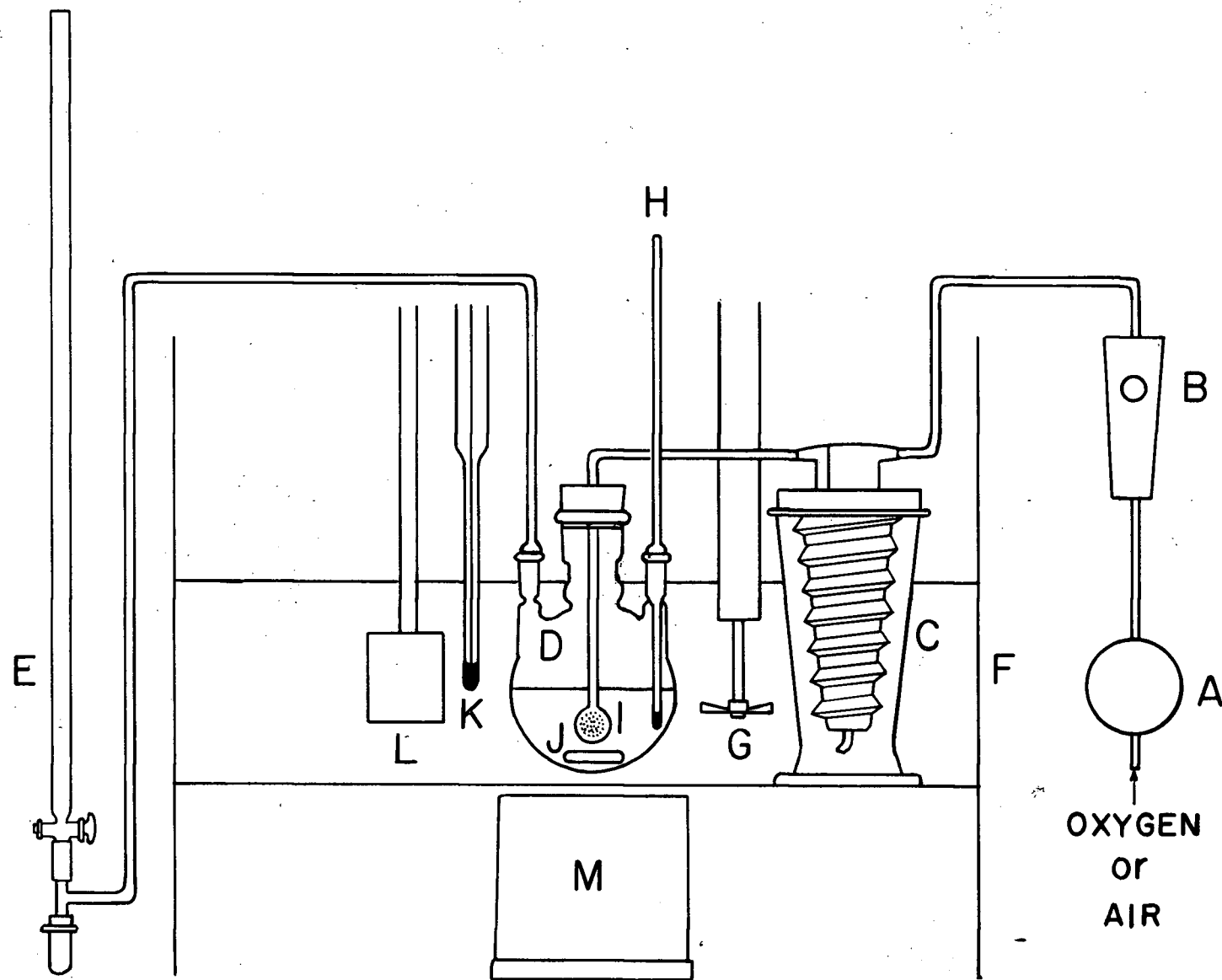


Figure 12. Apparatus for Determining Reaction Orders with Respect to Sodium Sulphide and Oxygen. 47

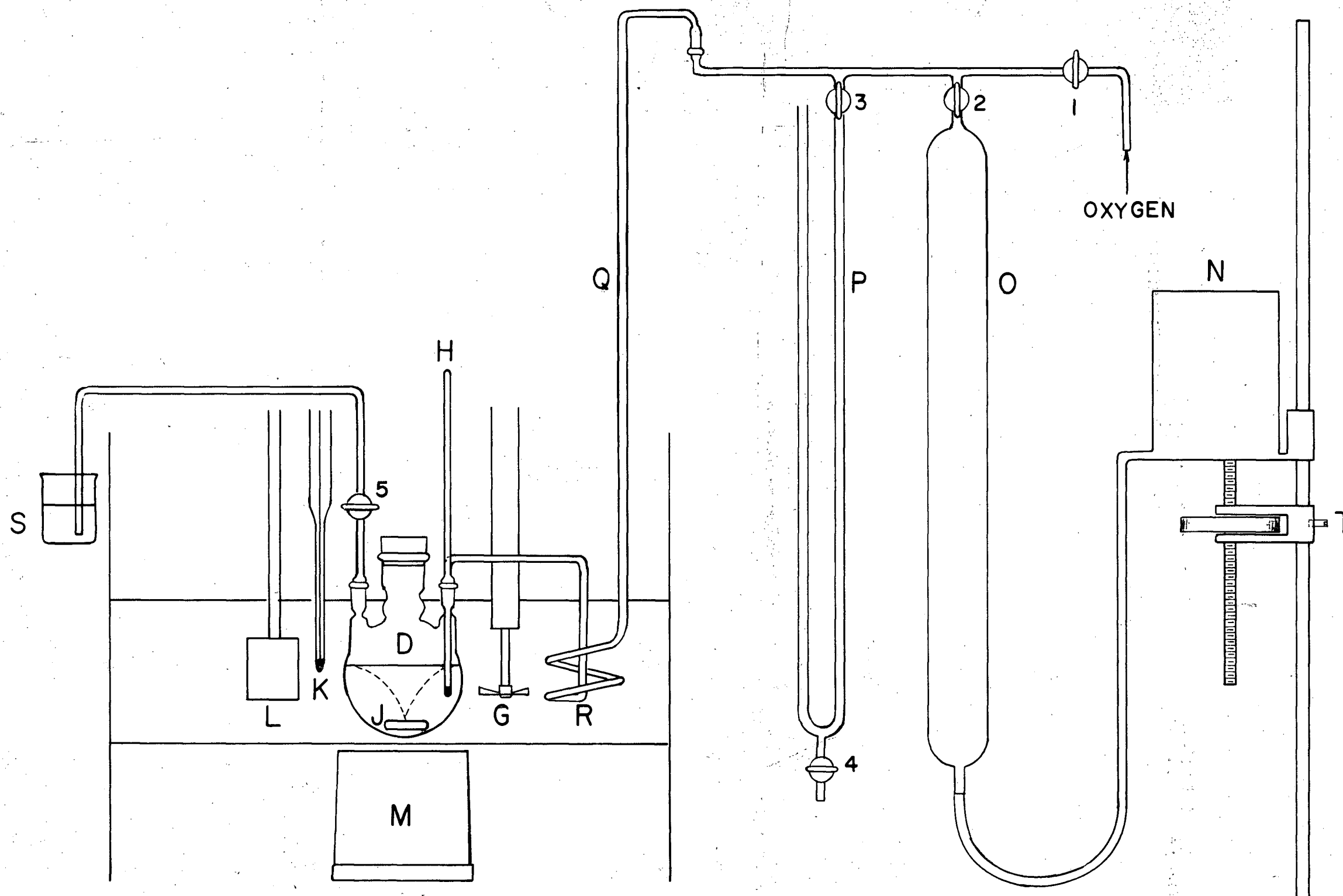


Figure 13. Apparatus for Determining Stoichiometry and Oxygen Absorption.

required for a soap film to pass through 50 ml. The gas flow rates were calculated from the reaction temperatures and the barometric pressure on a dry-gas basis (the gas as measured was assumed to be saturated with water).

The reaction temperature was controlled with a Colara Ultra Thermostat, with an accuracy of $\pm 0.01^{\circ}\text{C}$. It consisted of a thermo-regulator K, two heating elements L, and a high-speed stirrer G for the water bath. The water bath F had a dimension of 12 in. x 20 in. x 11 in. high, and was filled with 5 in. of water. It was made of glass so that the stirring rate of the magnet J in the solution could be measured with a Nichols probostrobe. The magnet, 5/16 in. diam. x 1.5 in., was plastic-coated, and stirred with a magnetic stirrer M below the water bath.

The samples of sodium sulphide solution were withdrawn at 30-min. intervals. The sampling was done by use of a calibrated tuberculin syringe (volume: 0.159 ml.) through a rubber serum bottle cap attached to one of the four 10/30 taper seal joints on the reactor. The concentrations of the sodium sulphide solutions were determined by the absorptiometric method using 0.16 % ferric chloride and 5% p-phenylenediamine as reagents, as already described in Part I. The concentrations of sodium sulphide, in gram moles per litre, were calculated from the following equation:

$$C = 0.006936 (EV/50)$$

The apparatus of Fig. 13 was used to study the rate of oxygen absorption and the stoichiometry for the oxidation of sodium sulphide. Both the gas buret O (1,000 ml. in capacity and having 10-ml. divisions), and the manometer P were filled with water. Oxygen from a cylinder was passed through the system for a few minutes, with stopcocks 1 and 5 opened, and 2, 3, and 4 closed. When the air in the glass tube Q ($1/4$ in. I.D.), and in the reactor D had been replaced by oxygen, stopcock 2 was opened, and the water reservoir N (4.5 in. diam. and 6 in. high) was lowered slowly. Care was taken that no air was sucked into the system by observing the bubbling of oxygen in the water contained in the beaker S. When the gas buret had been filled with oxygen, stopcocks 1 and 5 were closed simultaneously. By means of stopcock 4 the water then was drained partially from the manometer. The pressure in the system was adjusted by turning the knurled wheel below the water reservoir. The gas buret reading was recorded when the pressure in the system was the same as the atmospheric pressure. The sodium sulphide solution in the reactor was stirred immediately at a rate of 1,320 r.p.m. The stirring rates and the sodium sulphide analyses were determined by the same methods used for the apparatus of Fig. 12.

When the pressure in the system had decreased by an inch or so of water, because of the absorption of oxygen by the sodium sulphide solution, the pressure was restored

to atmospheric pressure by raising the water reservoir. The gas buret reading was recorded with the corresponding reading time.

Before the apparatus in Fig. 13 was used for experiments, it had been tested for leaks. The system was sealed, and brought to 3.24 in. of water below atmospheric pressure. After eleven hours, the same pressure difference was observed. The absence of leaks was the result of the fact that the whole system was made of glassware, with taper-seal joints each coated with Dow Corning high vacuum grease. The joints also were sealed tightly by use of Teflon sleeves. In addition, rubber bands were connected between hooks on each side of the joints.

For the apparatus of Fig. 13 only oxygen was used as gas feed. Therefore, there is no resistance in the gas phase except, perhaps, at the beginning of a run before the oxygen has had time to reach saturation. Air was not used as gas feed for the apparatus of Fig. 13, since the partial pressure of oxygen in the gas phase would change persistently with time as the oxidation of sodium sulphide proceeded in the reaction zone. The interfacial area between the two phases was supposed to be the same in each run at constant stirring speed, even though a vortex was formed. The diffusional resistance occurs mainly in the liquid phase.

The installation of coil R in the apparatus of Fig. 13, had the purpose of preheating the entering oxygen. The glass tube connecting the heating coil and the reactor was not immersed in the water bath except in a trial run. In this run, the high-vacuum grease coated between the joints melted and flowed to the reactor. The presence of a surface active agent at the gas-liquid interface in the reactor could cause marked reduction in the rate of mass transfer of oxygen across the interface. Therefore the tube was not immersed for the runs for which data have been reported.

For each run, the temperature in the reactor remained constant when the air above the liquid in the reactor was replaced with the preheated oxygen. No condensation on water vapor was found in the coil, in the tube between the coil and the reactor, or in the tube Q, even at the highest temperature, 85°C., investigated.

THEORY

Since equation 4 is the dominant reaction in the oxidation of sodium sulphide, it is necessary to calculate the chemical equilibrium constant for this reaction to see if the reaction is reversible or irreversible. Thermodynamically, the equilibrium constant, calculated from the free energy of formation, was found to be 1×10^{159} at 25°C. The equilibrium constant is so large that the reaction may be regarded as unidirectional. The experimentally determined

data for the concentrations of sodium sulphide as functions of reaction time were treated accordingly.

When the concentration of oxygen in the solution is constant, the rate of oxidation of sodium sulphide may be expressed by the following equation (11):

$$-\frac{dC}{dt} = k_n C^n \quad 24$$

where C = concentration of sodium sulphide at time t.

n = reaction order with respect to sodium sulphide.

k_n = specific reaction rate.

t = reaction time.

Integration of equation 24 and substitution of the initial condition, C = C₀ at t = 0, gives

$$C^{1-n} - C_0^{1-n} = (n-1)k_n t \quad 25$$

The value of n may be any positive number not necessarily an integer (except one in Equation 25). For the first order, n = 1, equation 24 gives

$$\ln C = k_1 t + \ln C_0 \quad 26$$

The reaction order with respect to the concentration of oxygen may be determined by comparing the ratio of the specific reaction rate obtained by using oxygen as a gas feed bubbling into the sulphide solution with that obtained by similarly using air.

When the oxidation of sodium sulphide occurs, the rate of oxygen absorption is increased as compared to the

physical absorption into pure water without a simultaneous chemical reaction. From the amount of oxygen absorbed and the amount of sodium sulphide oxidized, it is possible to evaluate the stoichiometry of the reactions as the oxidation of sodium sulphide proceeds.

All of the experimental concentration versus time data will be handled by the approach of the integration method (11).

RESULTS AND DISCUSSION

1. The Kinetics of the Oxidation of Sodium Sulphide

In order to study the reaction kinetics of the oxidation of sodium sulphide the experiments were carried out with the apparatus shown in Fig. 12. In ordinary heterogeneous gas-liquid reactions, the overall rates may be controlled by the physical transport of the gas from the gas phase to the liquid phase, by the chemical reaction itself, or by both factors working together. The experimental conditions for the apparatus in Fig. 12 were established in such a way that the mass transfer resistance would not complicate the overall reaction rate by consideration of two factors (20):

- (a) The influence of stirring rate on the oxidation rate.
- (b) The influence of oxygen feed rate on the oxidation rate.

Both the stirring rate and the oxygen feed rate

were increased to certain respective values; from these values onward the reaction rate was found to be independent of them. Under such conditions, the sodium sulphide solution may be regarded as saturated with the gas, and the concentration of the gas dissolved in the solution may be taken as constant at a given temperature. Since the rate of the diffusion of gas is low at low temperature, the two factors were established at 25°C., rather than at higher temperatures. The initial specific reaction rates were compared at various stirring rates with a fixed oxygen feed rate, and also, at various oxygen feed rates with a fixed stirring rate. Since the reaction order with respect to sodium sulphide at 25°C. was still uncertain at this stage, this was taken to be first order at this temperature for convenience.

The influence of stirring rates on oxidation rate was studied at an arbitrary oxygen feed rate of 314 ml./min. (on a dry-gas basis) at standard conditions (0°C. and 760 mm. Hg). The results are summarized in Table 11 and graphically represented in Fig. 14. The initial specific reaction rates

Table 11. Influence of Stirring Rates on Oxidation Rate

Temp.: 25°C; Oxygen Feed Rate: 314 ml./min.				
Time, min.	Conc. of Na ₂ S, gm. mole/litre			
	135 r.p.m.	800 r.p.m.	1,030 r.p.m.	1,220 r.p.m.
0	0.0668	0.0733	0.0761	0.0771
30	0.0535	0.0590	0.0621	0.0621
60	0.0442	0.0480	0.0496	0.0488
90	0.0365	0.0411	0.0420	0.0424

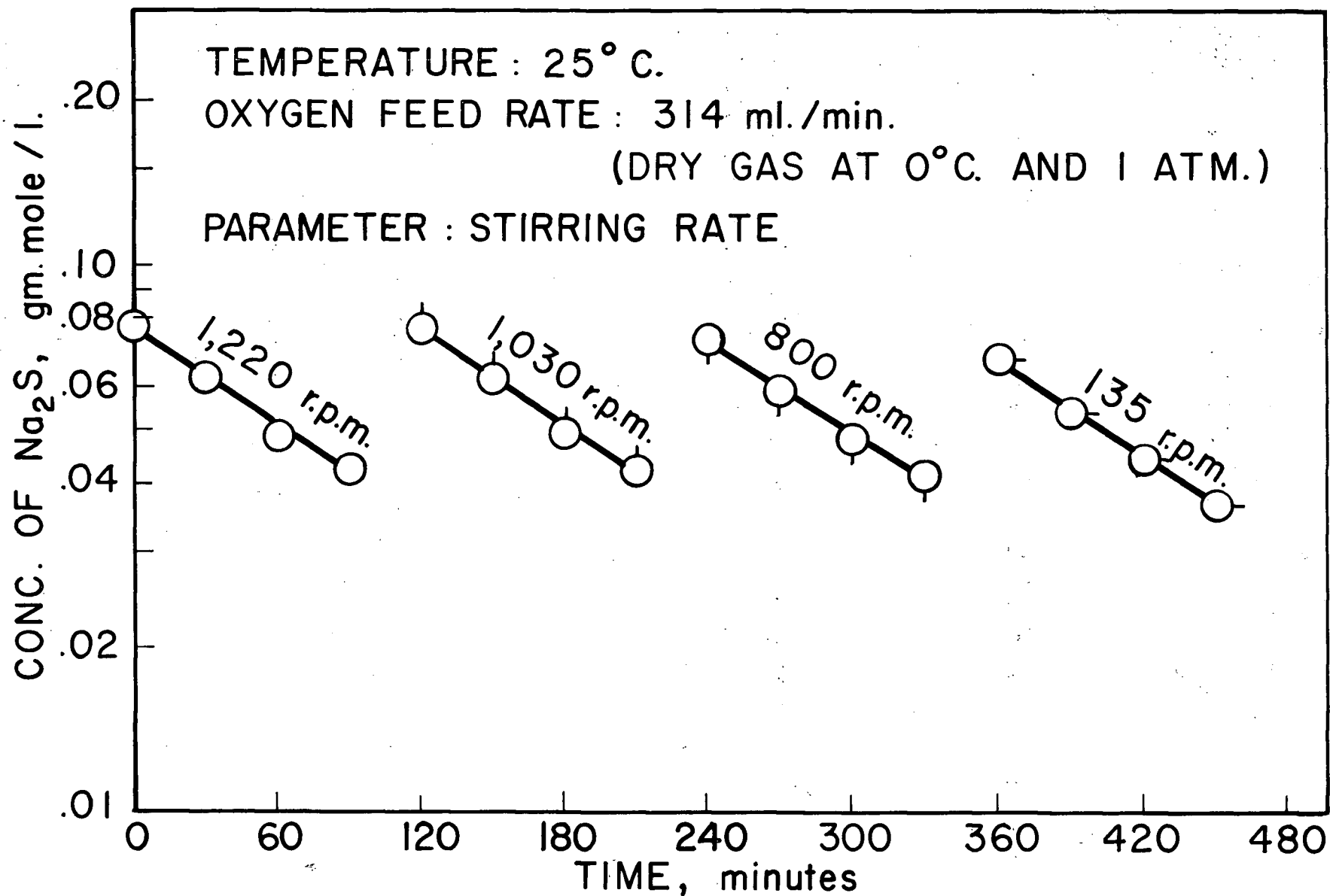


Figure 14. Influence of Stirring Rates on the Oxidation Rate of Sodium Sulphide.

were calculated and shown in Table 12 and Fig. 15, which show that when oxygen was bubbled into the sulphide solution at 314 ml./min., the reaction rate was independent of the

Table 12. Influence of Stirring Rates on Oxidation Rate

Temp.: 25°C.; Oxygen Feed Rate: 314 ml./min.

r.p.m.	135	800	1,030	1,220
initial $k \times 10^3, \text{min}^{-1}$	6.68	6.47	6.70	6.84

stirring rates between 135 and 1,220 r.p.m. In other words, when the solution was stirred at rates between 135 and 1,220 r.p.m., sufficient liquid turbulence was obtained for thorough mixing of the solution with the bubbling oxygen. The stirring rate was kept at 1,000 r.p.m. while studying the influence of oxygen feed rates on the oxidation rates of sodium sulphide.

At 1,000 r.p.m. of the stirrer, the rate of oxidation was found to depend on the oxygen feed rates up to 450 ml./min. However, beyond 450 ml./min., the initial specific reaction rate remains constant, as shown in Tables 13 and 14, and Figures 16 and 17. The 0 ml./min. of oxygen feed rate corresponded to the use of oxygen above the liquid phase without bubbling it through the solution.

From the experimental results illustrated in Tables 13 and 14, it may be concluded that at oxygen feed rates higher than 450 ml./min. and at stirring rates higher

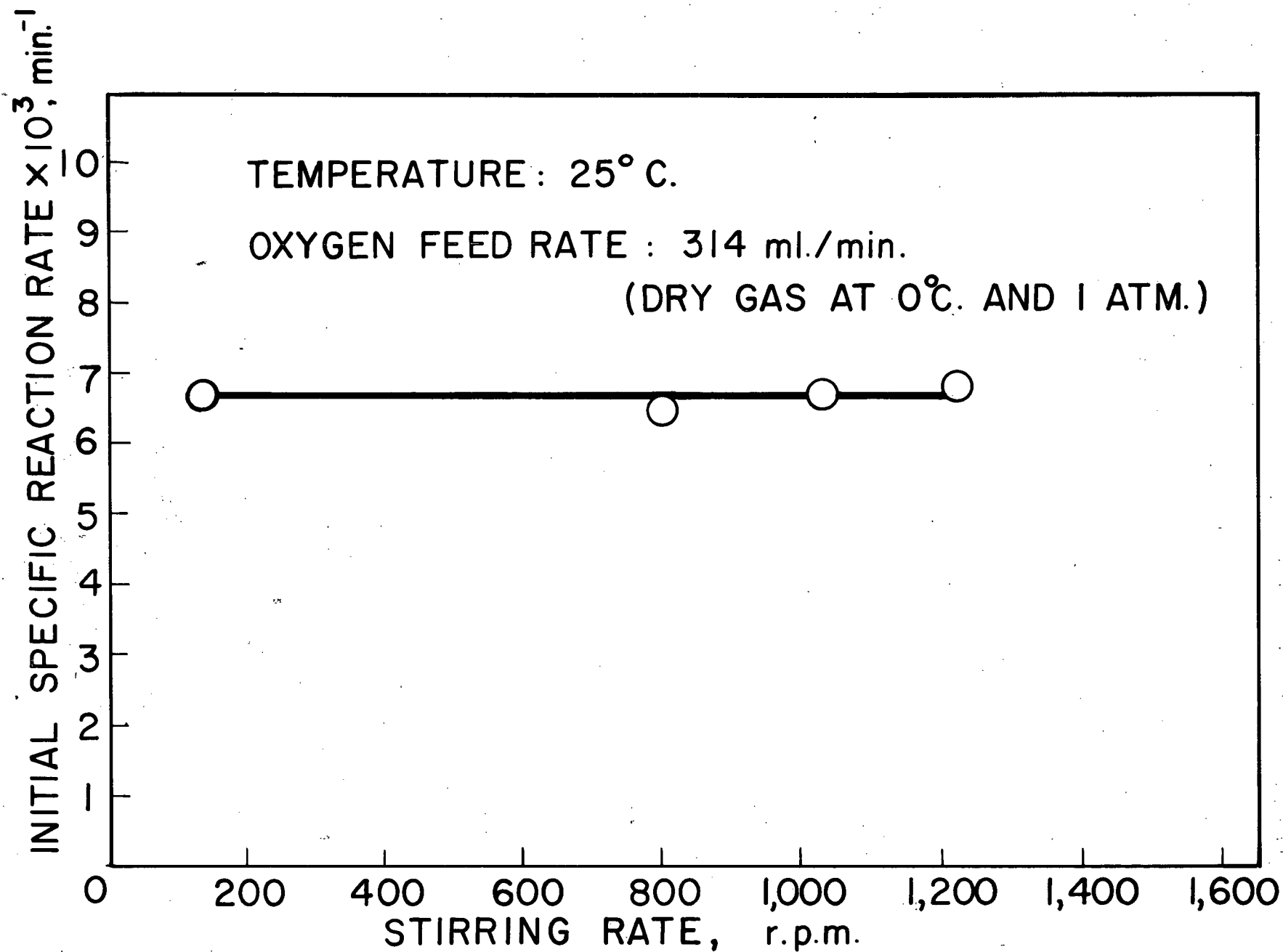


Figure 15. Influence of Stirring Rates on the Oxidation Rate of Sodium Sulphide.

Table 13. Influence of Oxygen Feed Rates on Oxidation Rate

Temp.: 25°C.; Stirring rate: 1,000 r.p.m.					
Time, min.	Conc. of Na ₂ S, gm. mole/litre				
	0 ml./min.	46 ml./min.	168 ml./min.	314 ml./min.	709 ml./min.
0	0.228	0.237	0.237	0.243	0.224
30	0.225	0.211	0.208	0.209	0.190
60	0.221	0.192	0.178	0.172	0.144
90	0.214	0.167	0.154	0.139	0.120
120	0.220	0.154	0.137	0.118	0.102
150	0.206	0.139	0.115	0.0999	0.0840
180	0.206	0.121	0.0985	0.0849	0.0756
210	0.201	0.110	0.0857	0.0749	0.0660

Table 14. Influence of Oxygen Feed Rates on Oxidation Rate

Temp.: 25°C.; Stirring rate: 1,000 r.p.m.					
O ₂ Feed Rate, ml./min.	0	46	168	314	709
Initial kx10 ³ , min. ⁻¹	0.488	3.65	4.88	5.77	6.05

than 135 r.p.m., no rate determining influence of mass transfer is to be expected. For studying the effect of temperature on the oxidation rate of sodium sulphide, the stirring rate and the oxygen feed rate therefore were maintained at 1,000 r.p.m. and 500 ml./min. of dry gas at 0°C. and 1 atm., respectively. Although the experiments just described were made with oxygen as a gas feed, and although a mass transfer resistance could have been present in the gas phase when air was so used, the same feed rate and the same stirring rate were used with air as with oxygen. It is shown later that no mass transfer resistance was present under these conditions even when air was the feed.

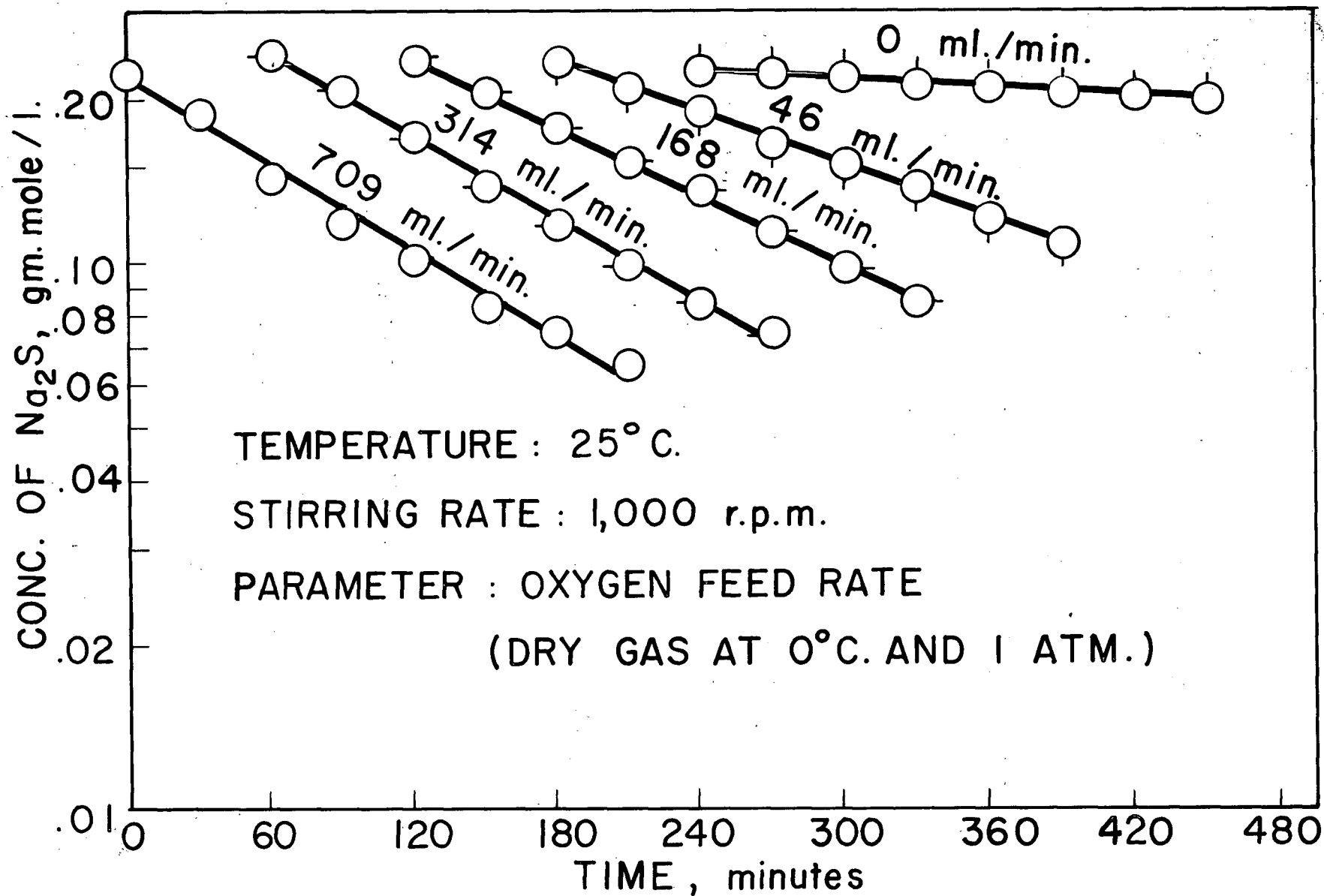


Figure 16. Influence of Oxygen Feed Rates on the Oxidation Rate of Sodium Sulphide.

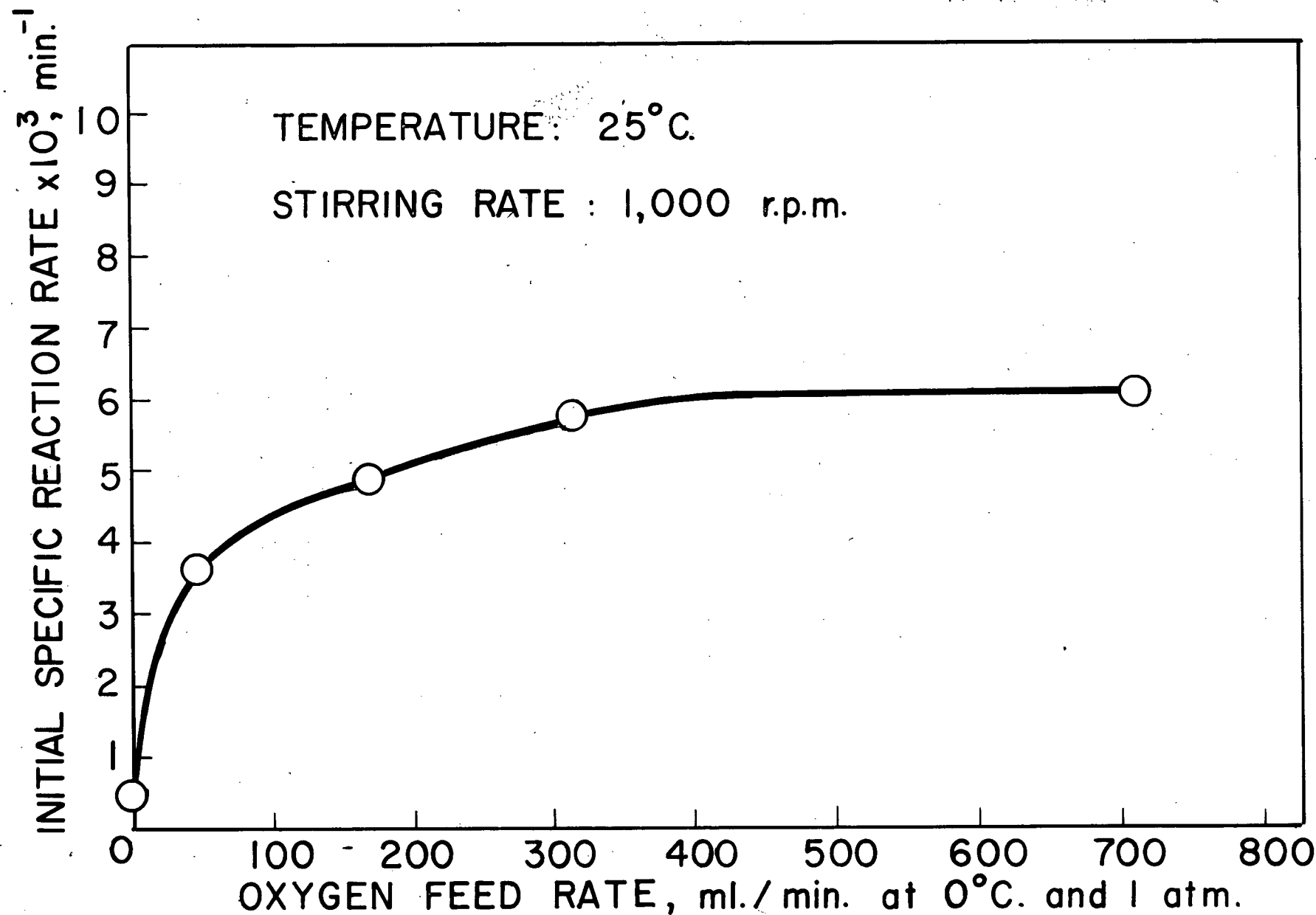


Figure 17. Influence of Oxygen Feed Rates on the Oxidation Rate of Sodium Sulphide.

The effect of temperature on the oxidation rates of sodium sulphide was investigated between 25°C. and 85°C. for each of oxygen and air as gas feeds to the sulphide solution. The concentration versus time data are given in Tables 15 and 16.

Table 15. Effect of Temperature on Oxidation Rate
(Oxygen used)

Stirring rate: 1,000 r.p.m.;
Feed Rate: 500 ml./min.

Time, min.	Conc. of Na ₂ S, gm. mole/litre						
	25°C.	35°C.	45°C.	55°C.	65°C.	75°C.	85°C.
0	0.181	0.170	0.178	0.181	0.181	0.180	0.185
30	0.145	0.120	0.128	0.128	0.129	0.120	0.137
60	0.112	0.0835	0.0918	0.0860	0.0878	0.0892	0.102
90	0.0970	0.0603	0.0675	0.0611	0.0668	0.0617	0.0779
120	0.0804	0.0455	0.0521	0.0417	0.0499	0.0431	0.0571
150	0.0726	0.0359	0.0406	0.0261	0.0353	0.0315	0.0411
180	0.0640	0.0275	0.0325	0.0137	0.0287	0.0166	0.0250
210	0.0564		0.0251		0.0211		0.0200
240	0.0520		0.0226		0.0160		
270	0.0484		0.0191		0.0119		
300	0.0433		0.0161		0.0068		

Table 16. Effect of Temperature on Oxidation Rate
(Air used)

Stirring rate: 1,000 r.p.m.; Air Feed Rate: 500 ml./min.

Time, min.	Conc. of Na ₂ S, gm. mole/litre						
	25°C.	35°C.	45°C.	55°C.	65°C.	75°C.	85°C.
0	0.170	0.169	0.169	0.161	0.172	0.174	0.173
30	0.160	0.155	0.158	0.152	0.157	0.160	0.159
60	0.149	0.139	0.142	0.135	0.145	0.147	0.153
90	0.135	0.125	0.129	0.126	0.133	0.134	0.140
120	0.130	0.114	0.120	0.115	0.121	0.122	0.133
150	0.120	0.106	0.109	0.106	0.116	0.116	0.123
180	0.111	0.0990	0.103	0.0961	0.105	0.103	0.111
210	0.106	0.0931	0.0954	0.0873	0.100	0.0950	0.104
240	0.100	0.0840	0.0873	0.0813	0.0951	0.0920	0.100
270	0.0940	0.0774	0.0821	0.0738	0.0885	0.0869	0.0980
300	0.0907	0.0713	0.0762	0.0677	0.0833		0.0850

Since part of the water in the sulphide solution was evaporated at temperatures higher than 65°C., the concentrations reported in Tables 15 and 16 at 65°, 75°, and 85° C. have been corrected for evaporation, which amounted at the end of the runs to 3% to 14% of the original 250 ml. of solution. (These percentages refer to evaporation only. An additional percentage, approximately 2%, was removed as samples). The percentage evaporation at each temperature is given in Table 17 for each gas feed used. At the end of

Table 17. Percentage Evaporation of Water from Solution

Gas Feed	Percentage Evaporation		
	65°C	75°C	85°C
Oxygen	4%	3%	14%
Air	3%	9%	5%

each run, the volume of the solution was measured with a graduated cylinder. This volume was subtracted from 250 ml. (250 ml. of sodium sulphide solution was placed in a graduated cylinder and poured from this into the reaction vessel at the start of a run). The evaporation of water from the sulphide solution was estimated by subtracting the volume of the samples withdrawn from the difference calculated. Since the gas flow rate was maintained constant, the evaporation was assumed directly proportional to time for the purpose of correcting concentrations.

The evaporation of water from the sulphide solution at temperatures higher than 65°C took place because of the

fact that the entering gas was only partially saturated with water vapor in the saturator. At the temperatures between 25°C and 55°C, the evaporation of water from the reaction vessel was negligible. The decrease in volume of the solution was only 2%, mainly because of the volume of samples taken for analyses (no correction was applied).

The data given in Tables 15 and 16 for the temperatures from 25° to 45°C did not yield straight lines on semi-logarithmic charts. Since the formation of thio-sulphate is the main reaction in the oxidation of sodium sulphide, and since the chemical equilibrium constant, calculated from thermodynamic data, is very large, the decreasing slope* on the semi-logarithmic charts of the curves relating concentration to reaction time for 25°, 35°, and 45°C (Figures 18 and 19), is believed to have been caused, not by reversibility of the reaction, but rather by mechanisms being involved over this temperature range different from those applicable from 55° to 85°C, since for the latter range the semi-logarithmic plots were straight lines (See Figs. 23 to 26 inclusive).

A good straight line was obtained for 25°C when the data were plotted as $1/C$ versus time (Fig. 20). These results indicate that the reaction is of second order with respect to sulphide at 25°C. The data are given in Table 18.

* The slope of each curve of Figures 18 and 19 decreases with time.

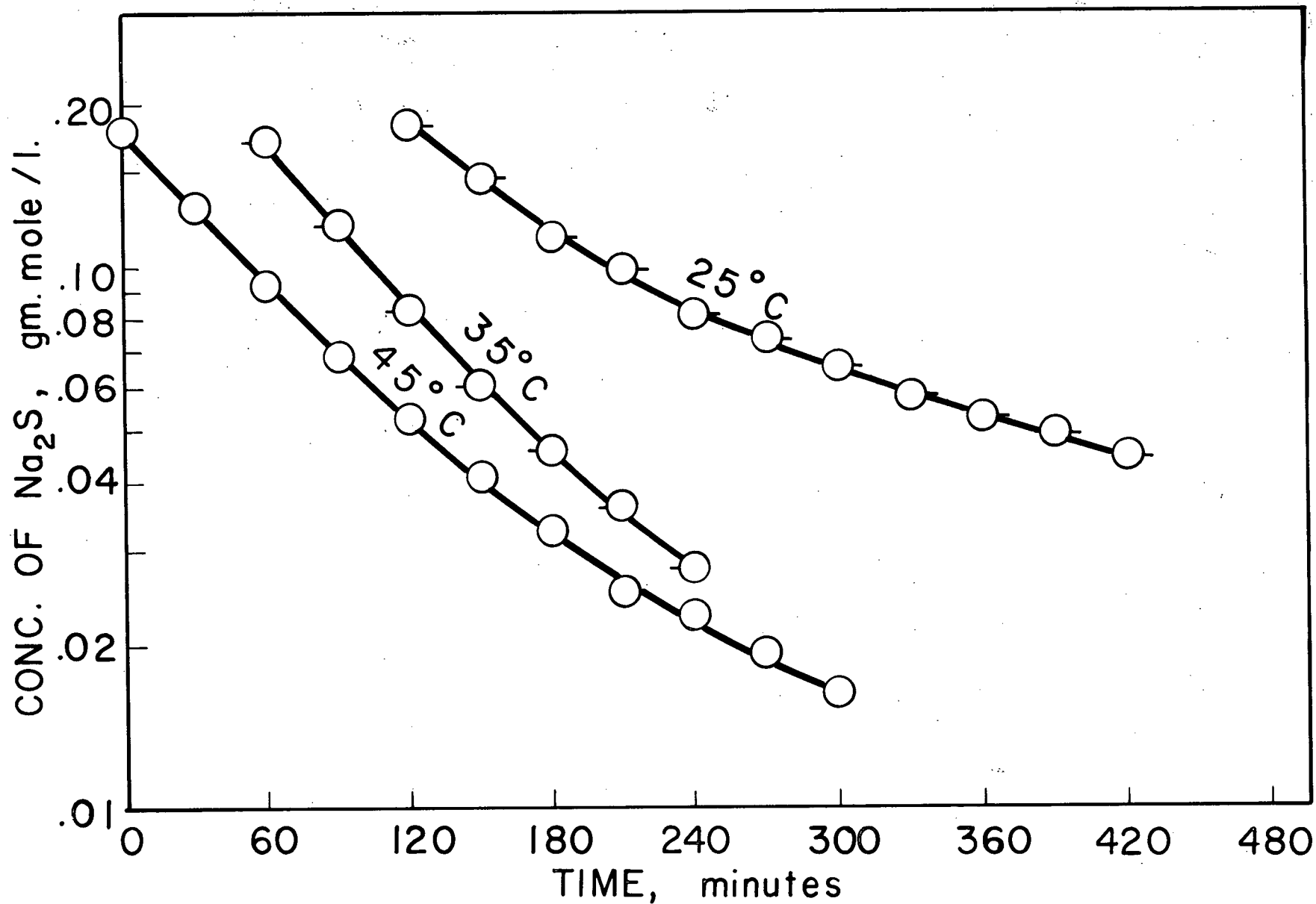


Figure 18. Oxidation of Sodium Sulphide at 25°, 35°, and 45°C. (Oxygen Used).

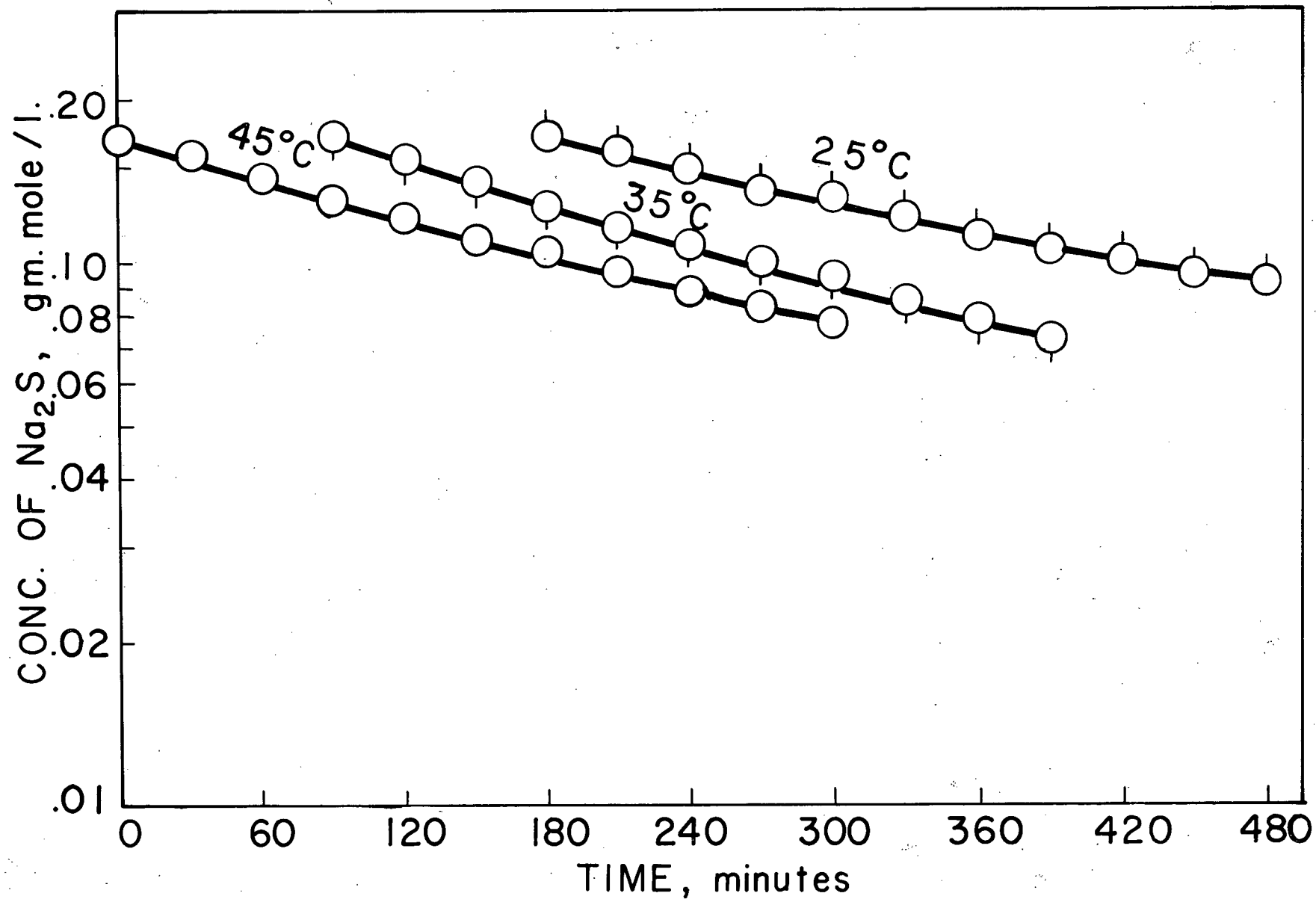


Figure 19. Oxidation of Sodium Sulphide at 25°, 35°, and 45°C. (Air Used).

Table 18. Data Showing Second Order at 25°C.

Stirring Rate: 1,000 r.p.m.; Gas Feed Rate: 500 ml./min.

Time, min.	Oxidation with O ₂		Oxidation with Air	
	C, gm.mole/l.*	1/C, l./gm.mole	C, gm.mole/l.*	1/C, l./gm.mole
0	0.181	5.52	0.170	5.88
30	0.145	6.90	0.160	6.25
60	0.112	8.93	0.149	6.71
90	0.0970	10.31	0.135	7.41
120	0.0804	12.44	0.130	7.69
150	0.0726	13.78	0.120	8.33
180	0.0640	15.63	0.111	9.01
210	0.0564	17.73	0.106	9.44
240	0.0520	19.23	0.100	10.00
270	0.0484	20.66	0.0940	10.64
300	0.0433	23.09	0.0907	11.02

* Data transferred from Tables 15 and 16.

However, for 35°C and 45°C, the data did not give straight lines on 1/C versus time charts. A reaction order of 1.5 was assumed, and the order was confirmed when the concentration versus time data did yield excellent straight lines on plots of $1/C^{0.5}$ versus time, as shown in Figures 21 and 22. Tables 19 and 20 give the corresponding data.

Table 19. Data Showing Order of 1.5 at 35°C

Stirring Rate: 1,000 r.p.m.; Gas Feed Rate: 500 ml./min.

Time, min.	Oxidation with O ₂		Oxidation with Air	
	C, gm.mole/l.*	$1/C^{0.5}$ (l./gm.mole) ^{0.5}	C, gm.mole/l.*	$1/C^{0.5}$ (l./gm.mole) ^{0.5}
0	0.170	2.42	0.169	2.41
30	0.120	2.88	0.155	2.54
60	0.0835	3.46	0.139	2.68
90	0.0603	4.06	0.125	2.83
120	0.0455	4.69	0.114	2.96
150	0.0359	5.28	0.106	3.07
180	0.0275	6.03	0.0990	3.18
210			0.0931	3.28
240			0.0840	3.44
270			0.0774	3.59
300			0.0713	3.74

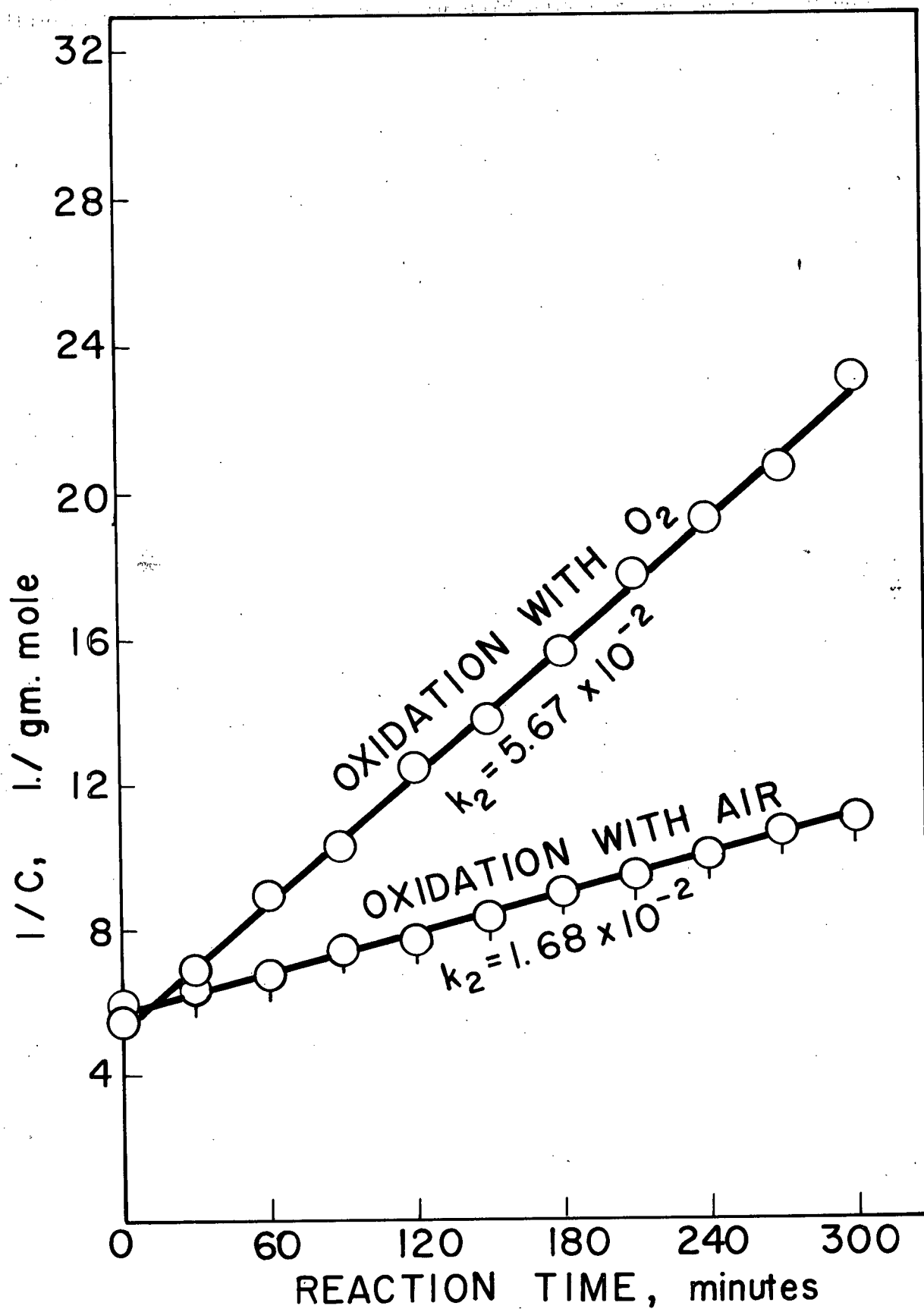


Figure 20. Second Order Reaction at 25°C .

Table 20. Data Showing Order of 1.5 at 45°C

Stirring Rate: 1,000 r.p.m.; Gas Feed Rate: 500 ml./min.

Time, min.	Oxidation with O ₂		Oxidation with Air	
	C, gm.mole/l.*	$1/C^{0.5}, (1./gm.mole)^{0.5}$	C, gm.mole/l.*	$1/C^{0.5}, (1./gm.mole)^{0.5}$
0	0.178	2.37	0.169	2.43
30	0.128	2.80	0.158	2.52
60	0.0918	3.30	0.142	2.65
90	0.0675	3.86	0.129	2.78
120	0.0521	4.38	0.120	2.88
150	0.0406	4.96	0.109	3.03
180	0.0325	5.55	0.103	3.11
210	0.0251	6.31	0.0954	3.24
240	0.0226	6.65	0.0873	3.38
270	0.0191	7.23	0.0821	3.49
300	0.0161	7.87	0.0762	3.62

* Data transferred from Tables 15 and 16.

For the temperatures from 55° to 85°C, the oxidation of sodium sulphide follows the first order with respect to the concentration of sodium sulphide, as illustrated in Figures 23 to 26.

The specific reaction rates for the oxidation of sodium sulphide by use of oxygen and air as gas feeds at various temperatures are summarized in Table 21. If the Henry's law is assumed, and if the reaction is of the first order with respect to the concentration of oxygen in the sulphide solution, the ratio of the specific reaction rates with oxygen and with air as gas feeds will be 4.76. This reasoning makes it a first order reaction, since the ratio of solubilities of oxygen in the solution by bubbling

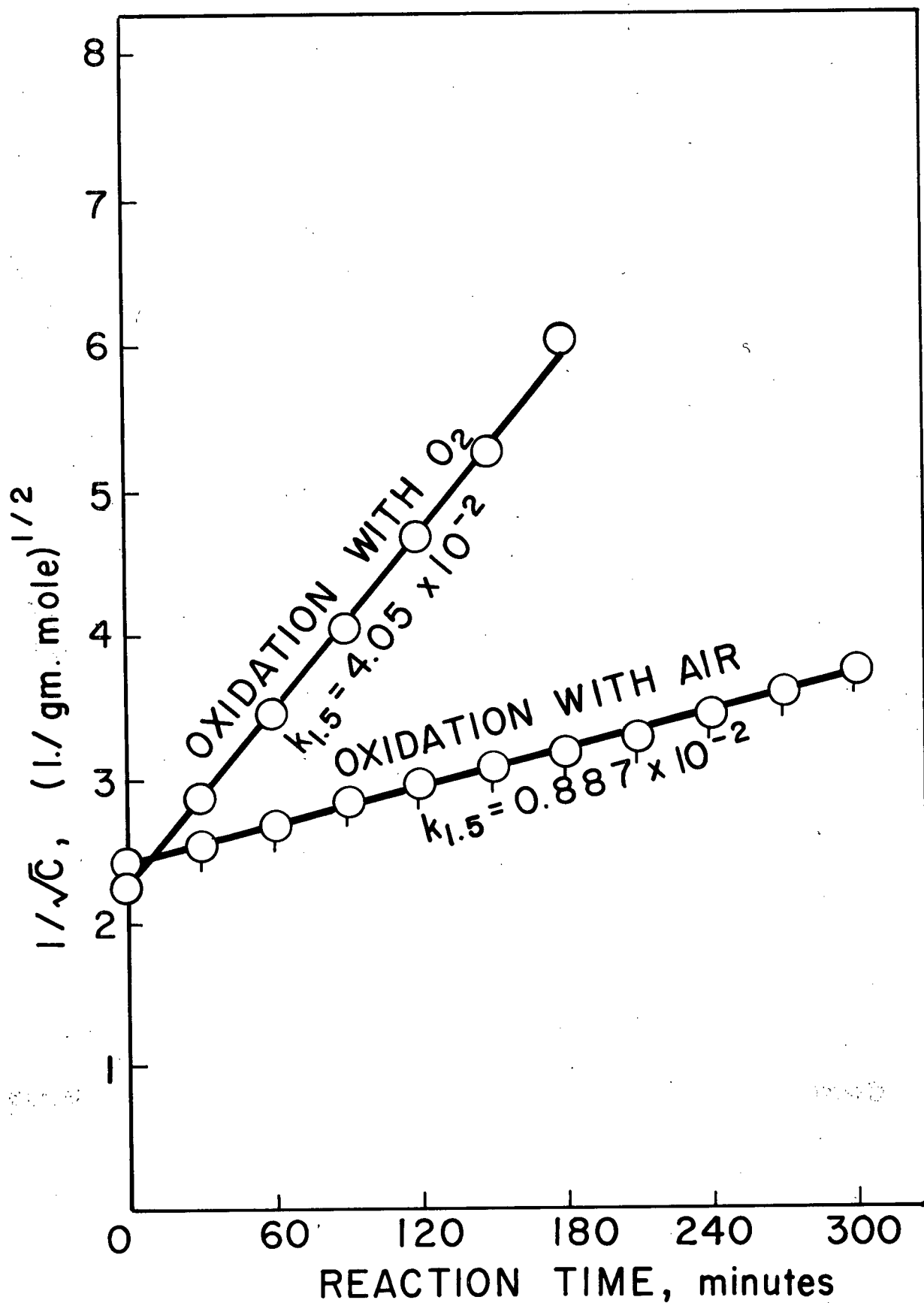


Figure 21. Order of 1.5 at 35°C.

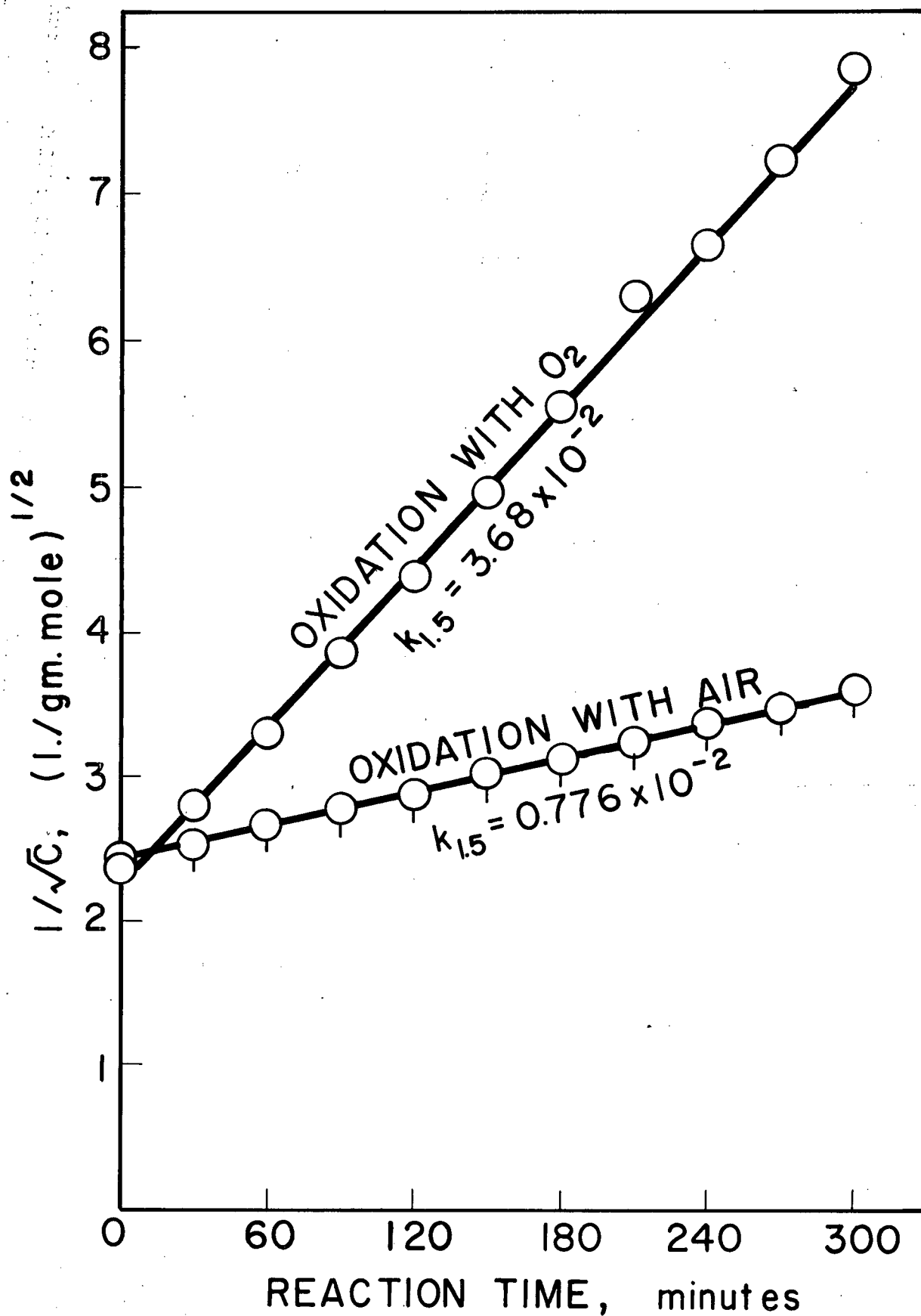


Figure 22. Order of 1.5 at 45°C.

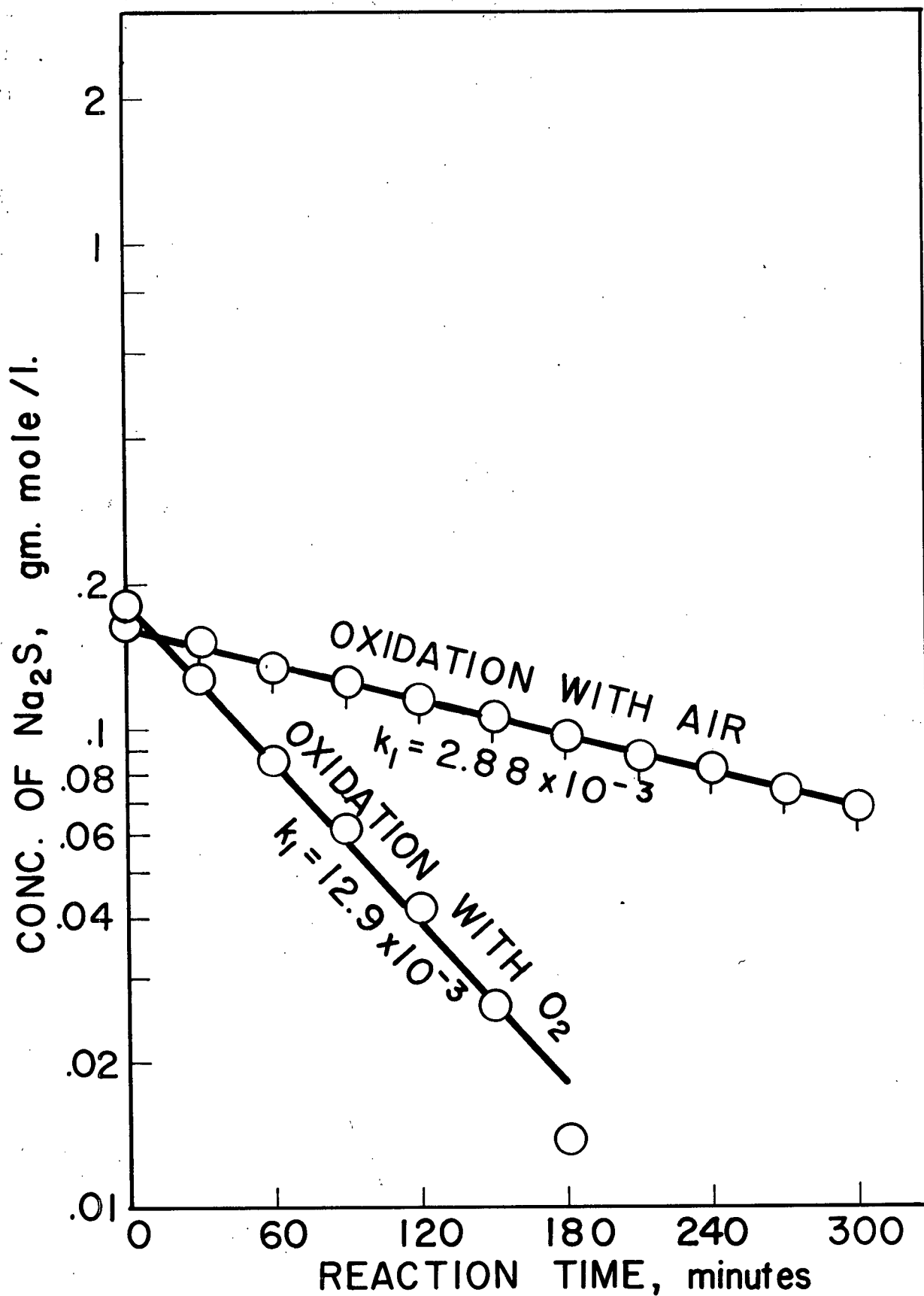


Figure 23. First Order Reaction at 55°C .

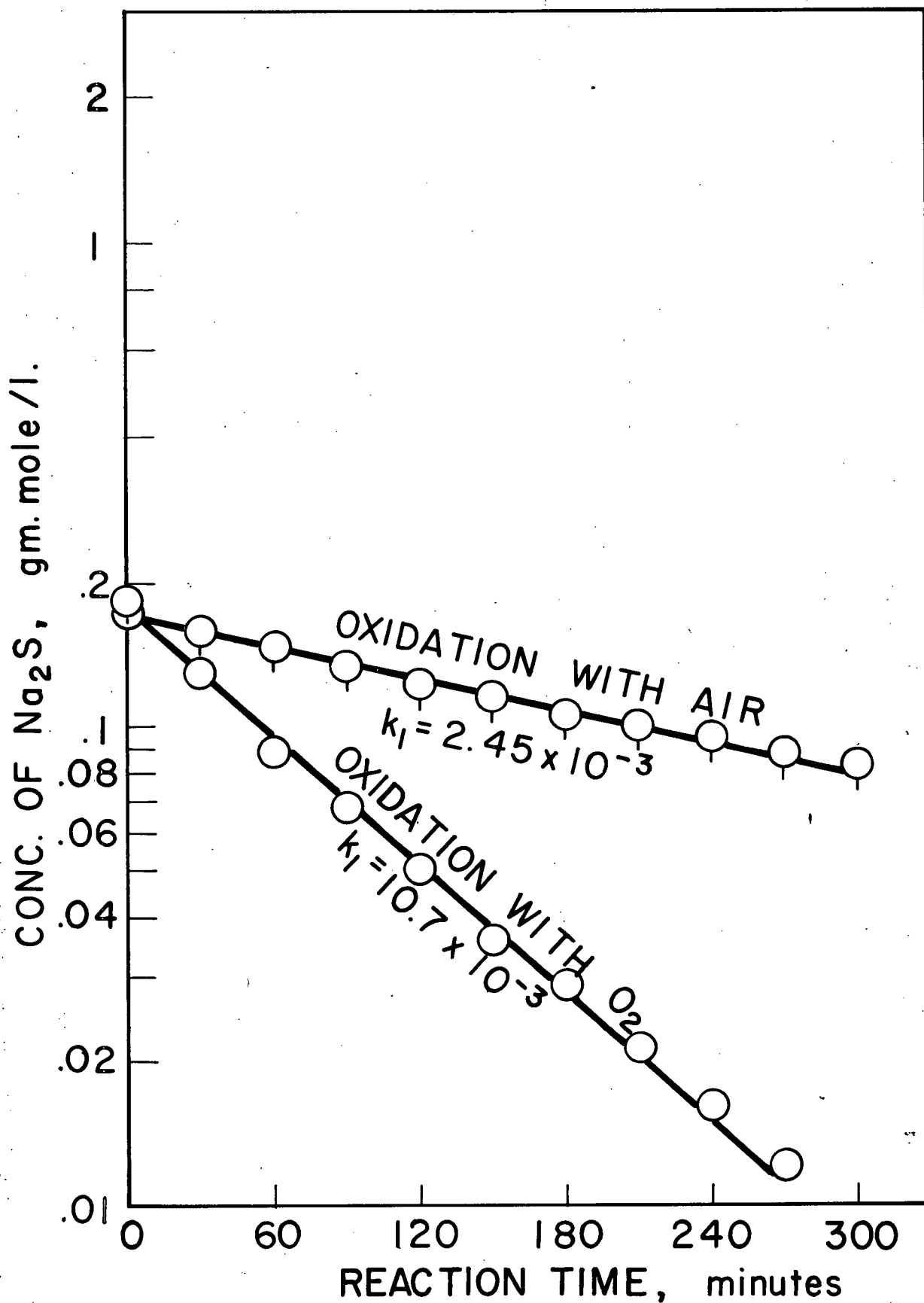


Figure 24. First Order Reaction at 65°C .

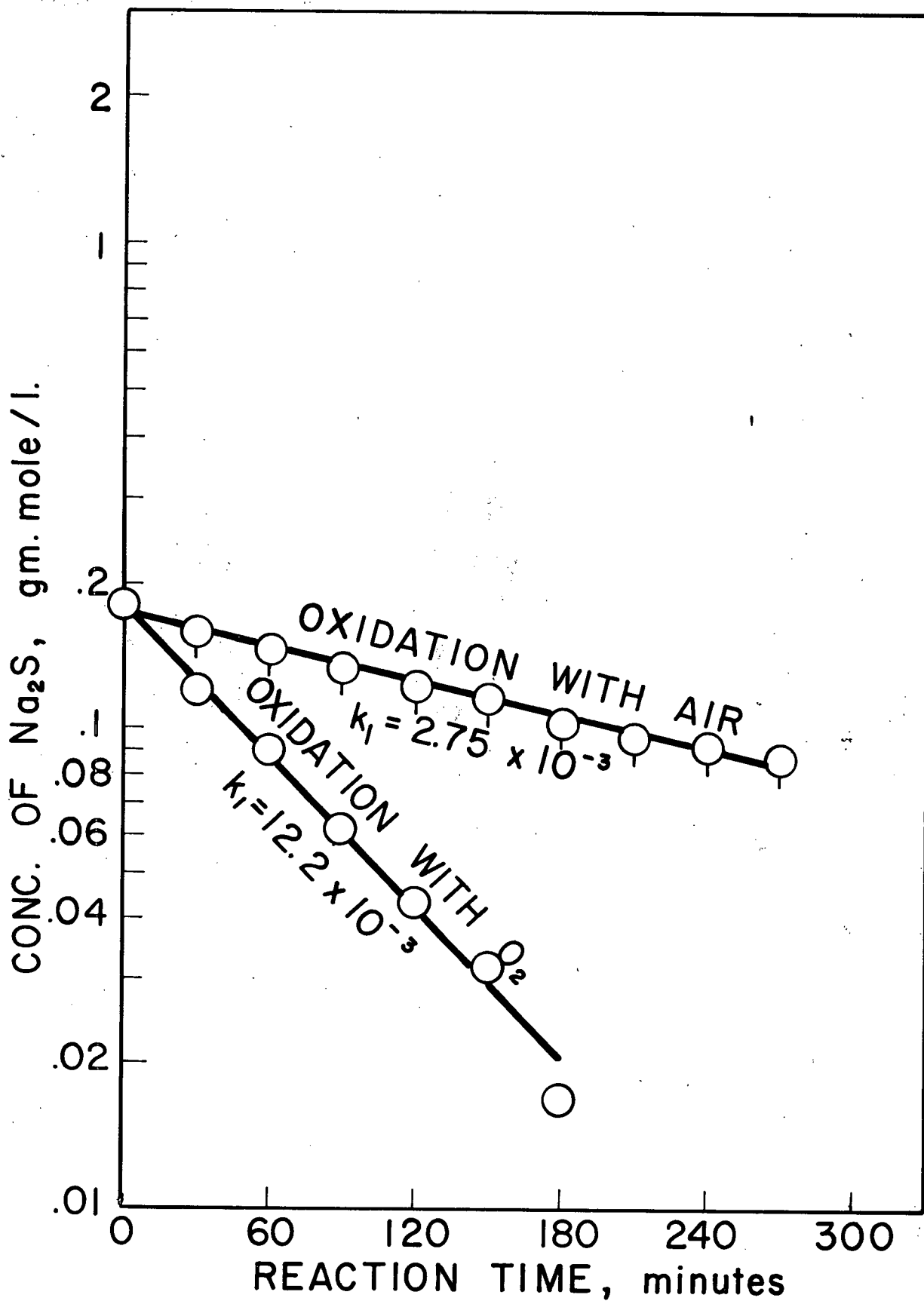


Figure 25. First Order Reaction at 75°C .

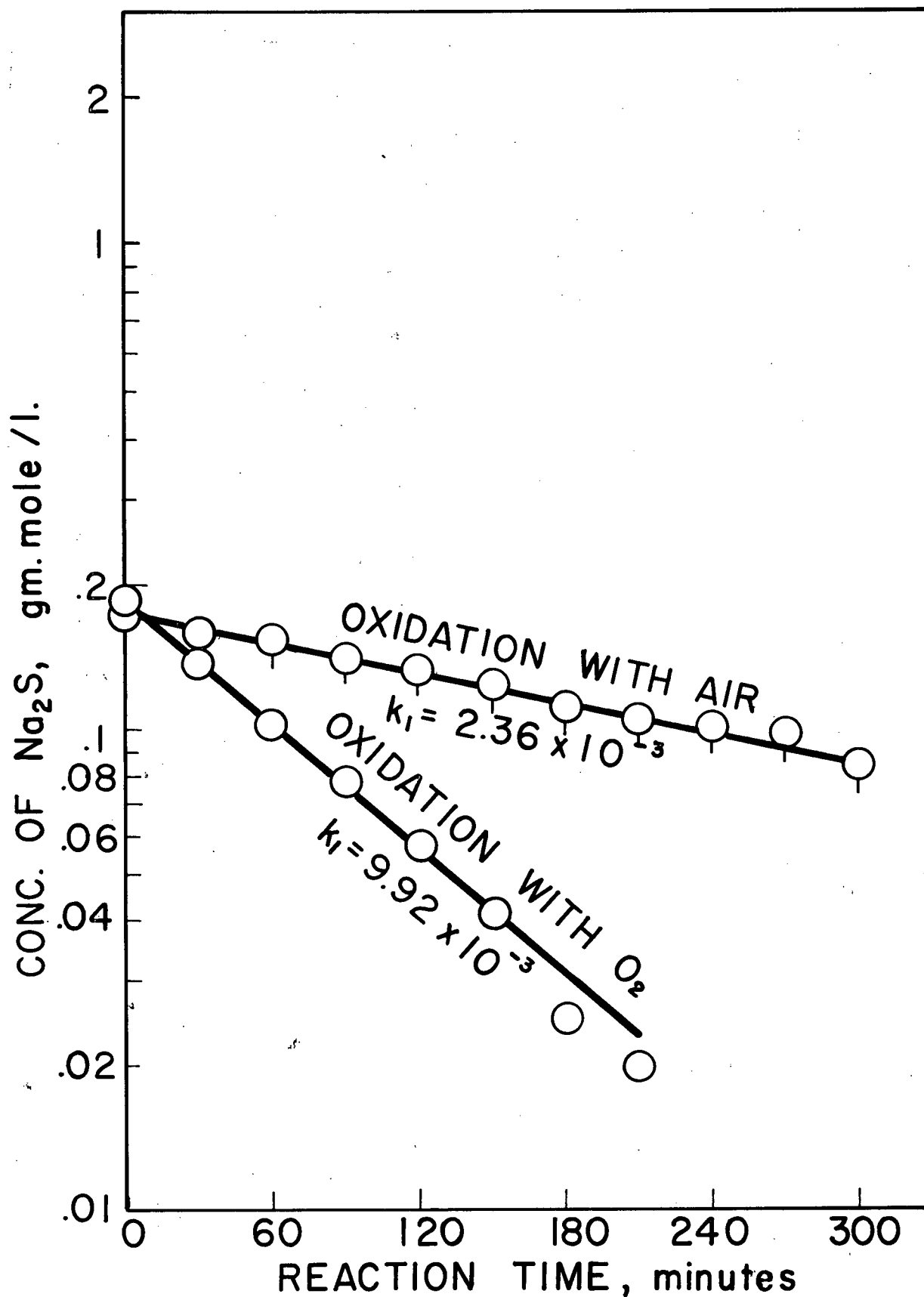


Figure 26. First Order Reaction at 85°C .

Table 21. Specific Reaction Rates at Various Temperatures

Stirring Rate: 1,000 r.p.m.; Gas Feed Rate: 500 ml./min.

Temp., °C	Reaction Order w.r.t. Na ₂ S	Oxidation with O ₂ (k) _{O₂}	Oxidation with Air (k) _{air}	$\frac{(k)_{O_2}}{(k)_{air}}^*$
25	2	5.67×10^{-2}	1.68×10^{-2}	3.38
35	1.5	4.05×10^{-2}	0.887×10^{-2}	4.56
45	1.5	3.68×10^{-2}	0.776×10^{-2}	4.74
55	1	12.9×10^{-3}	2.88×10^{-3}	4.48
65	1	10.7×10^{-3}	2.45×10^{-3}	4.36
75	1	12.2×10^{-3}	2.75×10^{-3}	4.44
85	1	9.92×10^{-3}	2.36×10^{-3}	4.20

Units of k's: 2nd order: $1./(\text{gm.mole})(\text{min.})$
 order of 1.5: $1.0.5/(\text{gm.mole})^{0.5}(\text{min.})$
 1st order: min.^{-1}

* If Henry's law is applicable, this ratio is 4.76

pure oxygen and air (containing 21% of oxygen by volume), respectively, is 4.76. The experimental results obtained for this ratio at various temperatures show that the oxidation of sodium sulphide follows the first order with respect to oxygen, irrespective of the temperature investigated. The ratios are all very close to 4.76, except for the somewhat smaller value at 25°C. The good agreement of the experimental values of the ratios with the theoretically predicted value shows not only that the reaction is of first order with respect to oxygen, but also that the solution is saturated with oxygen, whether the feed is oxygen or air, for a stirring rate of 1,000 r.p.m. and a gas feed rate of 500 ml./min. Therefore the mass transfer resistance in the gas phase

can be ignored even when air is used as the gas feed for these conditions of contacting.

It can be seen from Table 21 that the influence of temperature on the oxidation rate of sodium sulphide is not very pronounced. There are two opposing effects involved in the heterogeneous gas-liquid reaction: reaction of solutes and solubility of oxygen. At high temperature the reaction rate may be increased; however, the solubility of the gas in the solution will be decreased. The maximum oxidation rate of sodium sulphide occurs at 55°C. As will be seen later, the maximum absorption rate observed for oxygen also occurred at 55°C when the apparatus shown in Fig. 13 was used.

2. Effect of Initial Concentration of Sodium Sulphide on the Oxidation Rate.

The experimental results for various initial concentrations of sodium sulphide are shown in Tables 22, 23 and 24 for 25°, 35°, and 55°C. The data are shown also in Figures 27, 28, and 29. These results show that at low initial concentrations the specific reaction rate is comparatively high. This phenomenon suggests that the oxidation of sodium sulphide probably involves reactions in addition to that described by equation 4. This statement is justified later in the determination of the stoichiometry.

Table 22. Effect of Initial Concentration of Sodium Sulphide on Oxidation at 25°C
(Oxygen used)

Stirring Rate: 1,000 r.p.m.; Oxygen Feed Rate: 500 ml./min.

Time, min.	C,* gm.mole/l.	1/C, l./gm. mole	C, gm. mole/l.	1/C, l./gm. mole	C, gm. mole/l.	1/C, l./gm. mole
0	0.181	5.52	0.0990	10.10	0.0485	20.6
30	0.145	6.90	0.0704	14.20	0.0400	25.0
60	0.112	8.93	0.0535	18.70	0.0323	31.0
90	0.0970	10.31	0.0437	22.90	0.0266	37.6
120	0.0804	12.44	0.0349	28.65	0.0232	43.1
150	0.0726	13.78	0.0298	33.55	0.0193	51.8
180	0.0640	15.63	0.0277	36.10	0.0169	59.1
210	0.0564	17.73	0.0219	45.70		
240	0.0520	19.23				
270	0.0484	20.66				
300	0.0433	23.09				
k_2 , l./gm. mole) (min.)	5.67×10^{-2}		15.2×10^{-2}		19.6×10^{-2}	

* Data transferred from Table 15.

Table 23. Effect of Initial Concentration of Sodium Sulphide on Oxidation at 35°C
(Oxygen used)

Stirring Rate: 1,000 r.p.m.; Oxygen Feed Rate: 500 ml./min.

Time, min.	C,* gm.mole/l.	1/C ^{0.5} , (l./gm. mole) ^{0.5}	C, gm.mole/l.	1/C ^{0.5} , (l./gm. mole) ^{0.5}
0	0.170	2.42	0.0737	3.68
30	0.120	2.88	0.0525	4.36
60	0.0835	3.46	0.0368	5.21
90	0.0603	4.06	0.0305	5.73
120	0.0455	4.69	0.0238	6.48
150	0.0359	5.28	0.0196	7.15
180	0.0275	6.03	0.0158	7.95
$k_{1.5}$, (l.) ^{0.5} /(gm. mole) ^{0.5} (min.)	4.05×10^{-2}		4.63×10^{-2}	

Table 24. Effect of Initial Concentration of Sodium Sulphide on Oxidation at 55° C
(Oxygen used)

Stirring Rate: 1,000 r.p.m.; Oxygen Feed Rate: 500 ml./min.

Time, min.	Conc. of Na ₂ S, gm. mole/l.		
0	0.181 *	0.116	0.0559
30	0.128	0.0762	0.0287
60	0.0860	0.0475	0.0186
90	0.0611	0.0277	0.0135
120	0.0417	0.0195	
150	0.0261		
180	0.0137		
k ₁ , min. ⁻¹	12.9 x 10 ⁻³	14.8 x 10 ⁻³	17.1 x 10 ⁻³

* Data in this column transferred from Table 15.

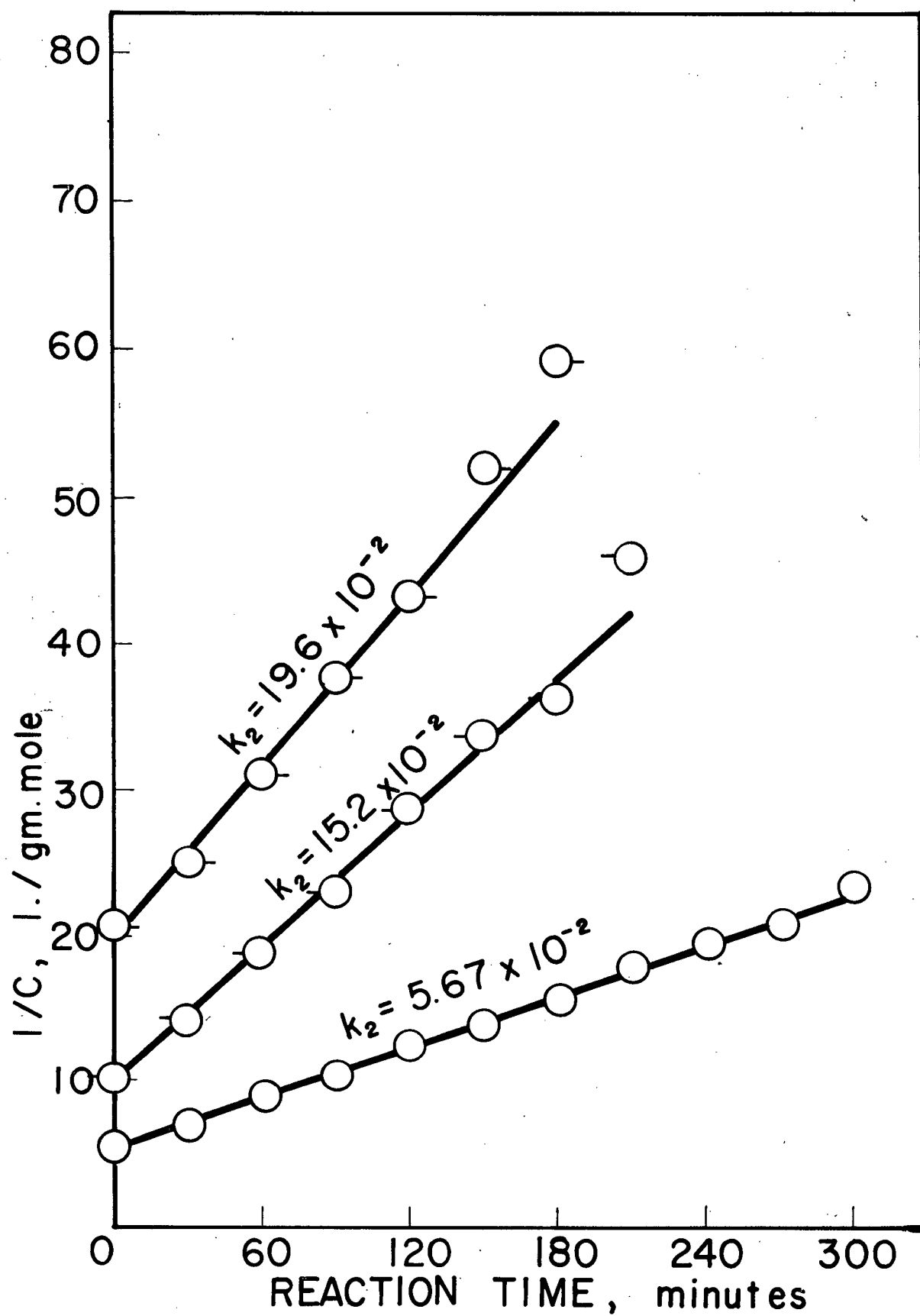


Figure 27. Effect of Initial Concentration of Sodium Sulphide on Oxidation at 25°C . (Oxygen Feed).

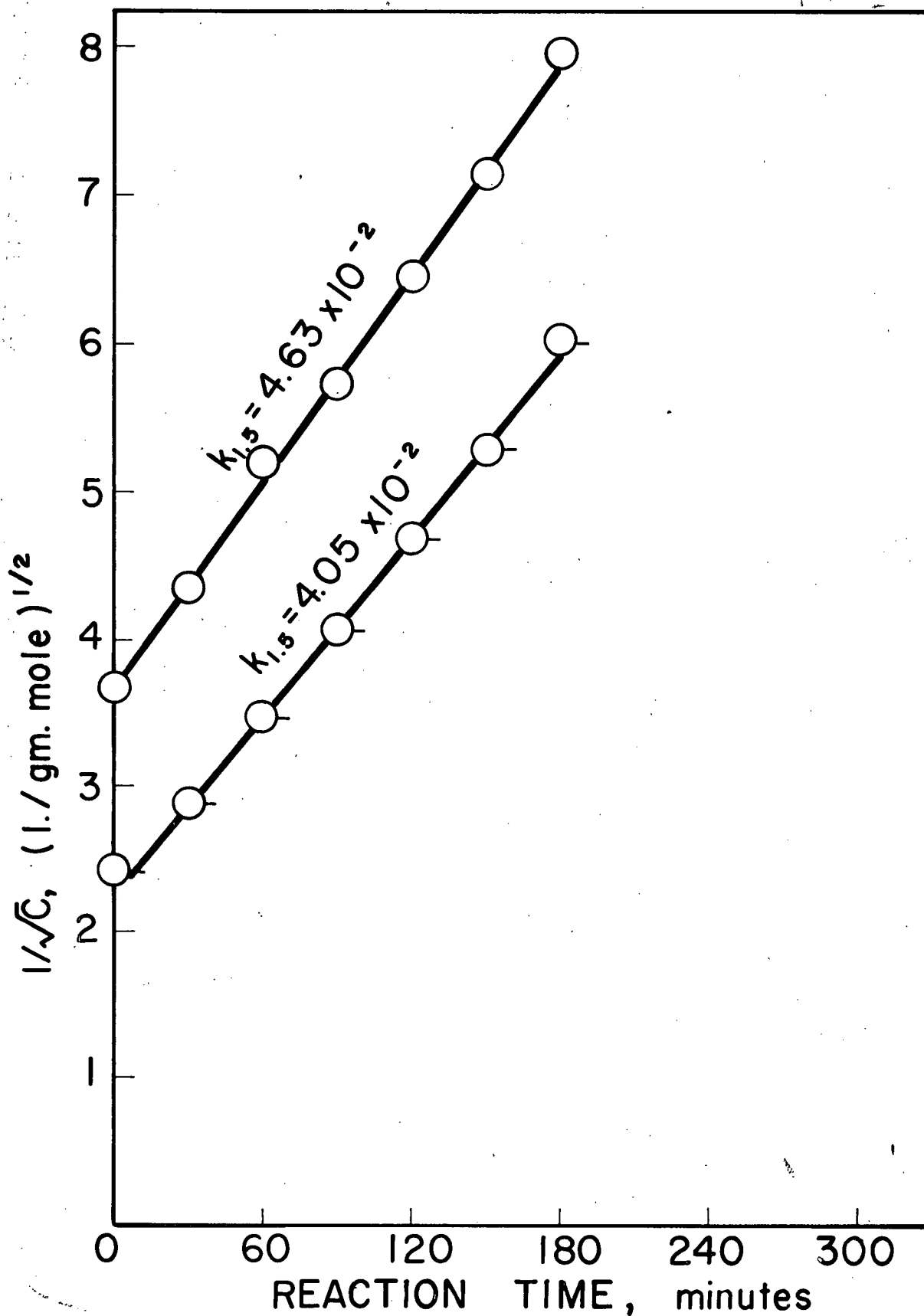


Figure 28. Effect of Initial Concentration of Sodium Sulphide on Oxidation at 35°C. (Oxygen Feed).

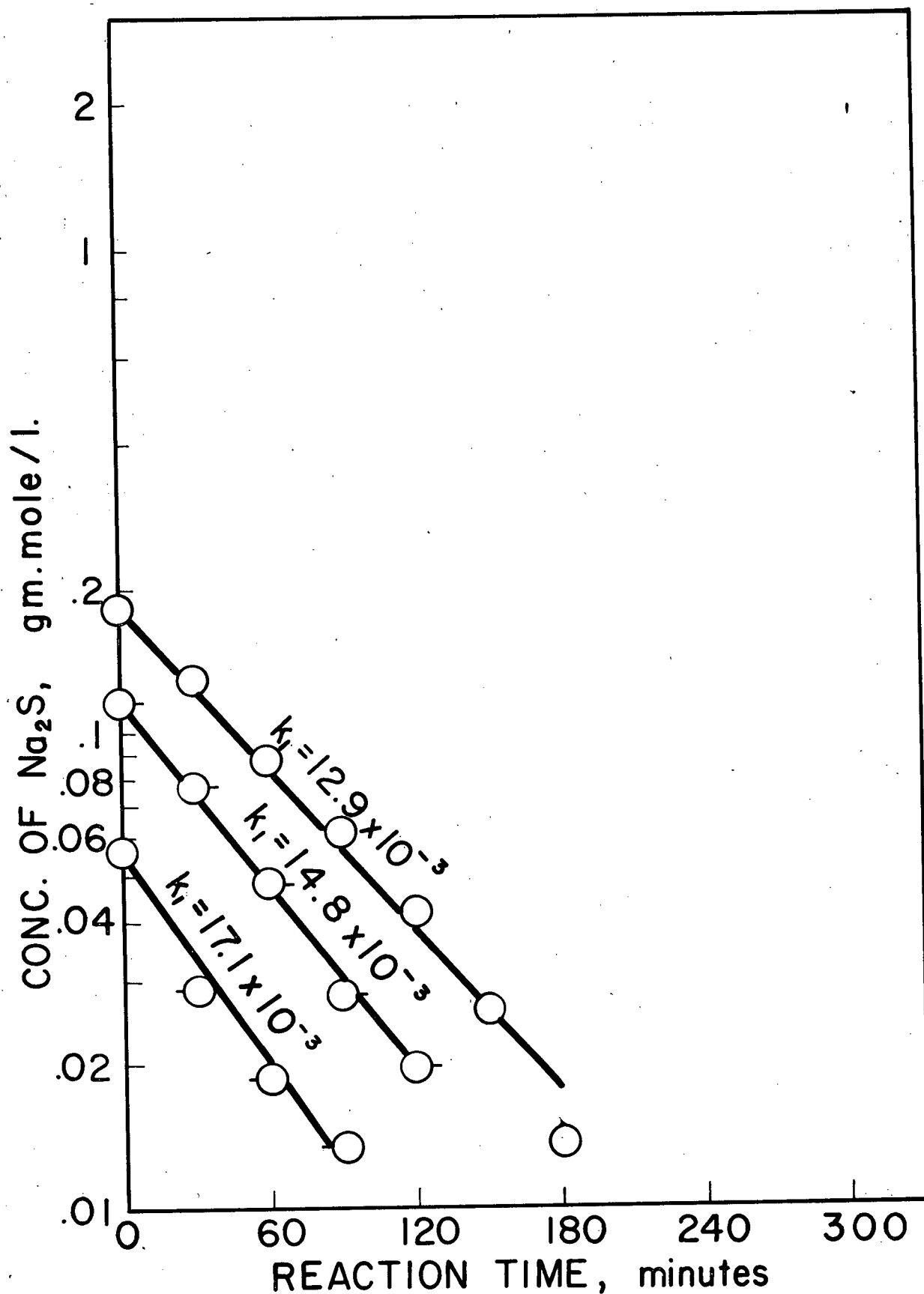


Figure 29. Effect of Initial Concentration of Sodium Sulphide on Oxidation at 55°C. (Oxygen Feed).

3. Effect of Addition of Glass Beads

To test whether glass will catalyze the oxidation of sodium sulphide, two runs were done by adding refined glass beads (supplied by A.S. LaPine & Co., Chicago) to the solution in the Pyrex reactor. In the first run, 2.68 gms. of 500 microns average diameter were added, and in the second, 0.023 gm. of 42 microns maximum diameter. In both runs, the addition of the glass beads increased the area of contact between the solution and glass by about ten times. The oxidation of sodium sulphide was carried out at 55°C by the use of oxygen as gas feed in the apparatus shown in Fig. 12. The observed first order specific reaction rates were 5.79×10^{-3} , and $5.88 \times 10^{-3} \text{ min.}^{-1}$. When compared with the oxidation without the presence of glass beads at 55°C ($12.9 \times 10^{-3} \text{ min.}^{-1}$), the addition of glass beads to the solution did not increase the reaction rate. In fact, the reaction rate was decreased by 55% and 54%, respectively, by the addition. Therefore, the oxidation of sodium sulphide was not catalyzed by glass. The decrease in the oxidation rate in the presence of glass beads may have been due to the inhibition by glass of the oxidation of sodium sulphide. However, in view of the fact that increasing the area of contact by ten times, a whole order of magnitude, decreases the specific reaction rate only by a factor of two, suggests that for present purposes any inhibition perhaps can be ignored.

4. Reproducibility

To test the reproducibility of the work, the run at 55°C in the apparatus of Fig. 12 with no glass beads present was done a second time. The specific reaction rates was $12.5 \times 10^{-3} \text{ min.}^{-1}$ whereas, in the earlier run, the value was $12.9 \times 10^{-3} \text{ min.}^{-1}$ as mentioned in connection with the work where glass beads were added. Agreement of the two values of the specific reaction rate was thus within 4%. The good reproducibility is reflected also in the constancy of the ratio of specific reaction rates obtained by using oxygen and air as respective gas feeds.

5. The Absorption of Oxygen.

The absorption of oxygen into sodium sulphide solutions was investigated by use of the apparatus shown in Fig. 13 with a stirring rate of 1,320 * r.p.m. As implied by Fig. 16, the rate of oxygen absorption as well as the rate of the oxidation of sodium sulphide, measured by this apparatus, include the effect of reaction kinetics plus that of a mass transfer resistance in the liquid phase. (Although Fig. 16 applies to a stirring rate of 1,000 r.p.m. instead of 1,320 r.p.m., it would seem quite likely that a mass transfer resistance would still be involved at the higher rate of stirring, since bubbling at 450 ml./min. of oxygen was needed to remove the mass transfer resistance at 1,000 r.p.m. That mass transfer resistance is involved is confirmed later.) The rate of oxygen absorption was evaluated

* applies to Figures 30 to 41 inclusive.

by finding the volume of oxygen absorbed measured at the known room temperature and barometric pressure. The results, obtained at various reaction temperatures, are given in Tables 25 to 31, together with the amounts of sodium sulphide oxidized calculated from the analyses. The results are shown graphically in Figures 30 to 36. Both tables and graphs are labelled "stoichiometry" although their use in this connection is described later.

A comparison of the slopes of the absorption curves of oxygen in Figures 30 to 36 shows that the overall average rate of absorption of oxygen into the sodium sulphide solution decreases with temperature from 25° to 45°C. However, when the temperature is increased to 55°C, the absorption rate increases abruptly to a maximum, 1.06×10^{-4} gm. mole/min. for an initial concentration of 0.164 gm. mole/litre of sodium sulphide. The absorption rate then decreases again with increasing temperature.

This phenomenon is consistent with the assumption, mentioned in the first section of Results and Discussion, that different reaction mechanisms are involved for each of the two temperature ranges, 25° to 45° C, and 55° to 85°C. Accordingly, different orders of reaction with respect to sodium sulphide were observed for these two temperature ranges, as already described.

Table 25. Stoichiometry at 25°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.185 gm. mole

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed ²
0	0	0	0
30	0.0028	25	0.0016
60	0.0088	43	0.0034
90	0.0108	63	0.0054
120	0.0143	83	0.0071
150	0.0163	100	0.0088
180	0.0188	120	0.0107
210	0.0201	145	0.0131
240	0.0213	166	0.0151
270	0.0230	185	0.0169
300	0.0244	206	0.0188
330	0.0260	229	0.0208
360	0.0267	256	0.0229
		279	0.0247
		301	0.0264
		324	0.0282
		346	0.0299
		360	0.0309

Table 26. Stoichiometry at 35°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.198 gm.mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0018	51	0.0019
60	0.0052	75	0.0041
90	0.0088	94	0.0059
120	0.0121	113	0.0076
150	0.0151	138	0.0099
180	0.0181	165	0.0123
210	0.0203	185	0.0141
240	0.0228	203	0.0158
270	0.0240	226	0.0177
300	0.0256	248	0.0196
330	0.0271	266	0.0213
360	0.0285	287	0.0230
		309	0.0248
		335	0.0271
		360	0.0292

Table 27. Stoichiometry at 45°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.191 gm.mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0015	55	0.0018
60	0.0040	83	0.0038
90	0.0060	110	0.0058
120	0.0090	136	0.0078
150	0.0123	167	0.0102
180	0.0153	190	0.0121
210	0.0180	215	0.0141
240	0.0193	244	0.0163
270	0.0213	269	0.0183
300	0.0223	294	0.0202
330	0.0237	319	0.0221
360	0.0251	344	0.0239
		360	0.0253

Table 28. Stoichiometry at 55°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.164 gm.mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0035	31	0.0019
60	0.0083	50	0.0039
90	0.0110	65	0.0056
120	0.0143	83	0.0075
150	0.0164	104	0.0097
180	0.0175	124	0.0119
210	0.0194	143	0.0140
240	0.0215	167	0.0164
270	0.0233	185	0.0182
300	0.0235	204	0.0202
330	0.0264	222	0.0222
360	0.0268	235	0.0233
		257	0.0256
		278	0.0278
		302	0.0301
		325	0.0324
		345	0.0343
		360	0.0358

Table 29. Stoichiometry at 65°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.169 gm.mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0045	22	0.0020
60	0.0080	46	0.0043
90	0.0108	65	0.0061
120	0.0123	87	0.0083
150	0.0158	110	0.0101
180	0.0168	136	0.0127
210	0.0180	160	0.0148
240	0.0200	175	0.0164
270	0.0226	194	0.0184
300	0.0232	215	0.0206
330	0.0241	230	0.0223
360	0.0252	251	0.0243
		274	0.0264
		298	0.0286
		319	0.0306
		338	0.0322
		360	0.0337

Table 30. Stoichiometry at 75°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.171 gm.mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0035	30	0.0018
60	0.0073	50	0.0036
90	0.0105	75	0.0062
120	0.0128	93	0.0082
150	0.0153	113	0.0102
180	0.0173	141	0.0134
210	0.0188	158	0.0151
240	0.0206	174	0.0168
270	0.0214	194	0.0186
300	0.0221	220	0.0203
330	0.0235	267	0.0228
360	0.0243	290	0.0244
		321	0.0261
		360	0.0283

Table 31. Stoichiometry at 85°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.172 gm. mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0020	41	0.0019
60	0.0038	80	0.0041
90	0.0050	110	0.0060
120	0.0063	156	0.0083
150	0.0075	210	0.0102
180	0.0085	255	0.0125
210	0.0098	293	0.0141
240	0.0110	335	0.0160
270	0.0128	360	0.0172
300	0.0130		
330	0.0133		
360	0.0158		

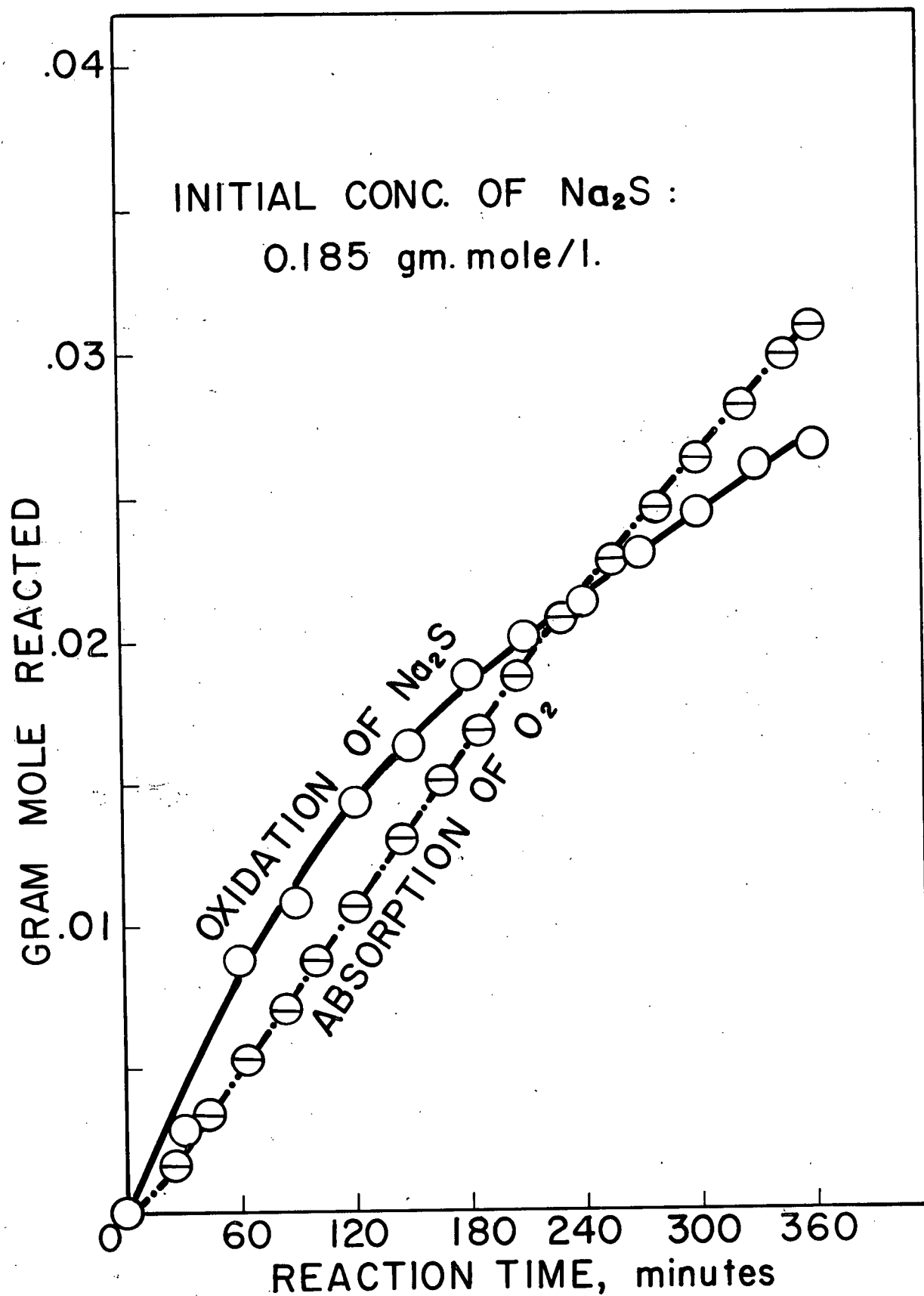


Figure 30. Stoichiometry at 25°C.

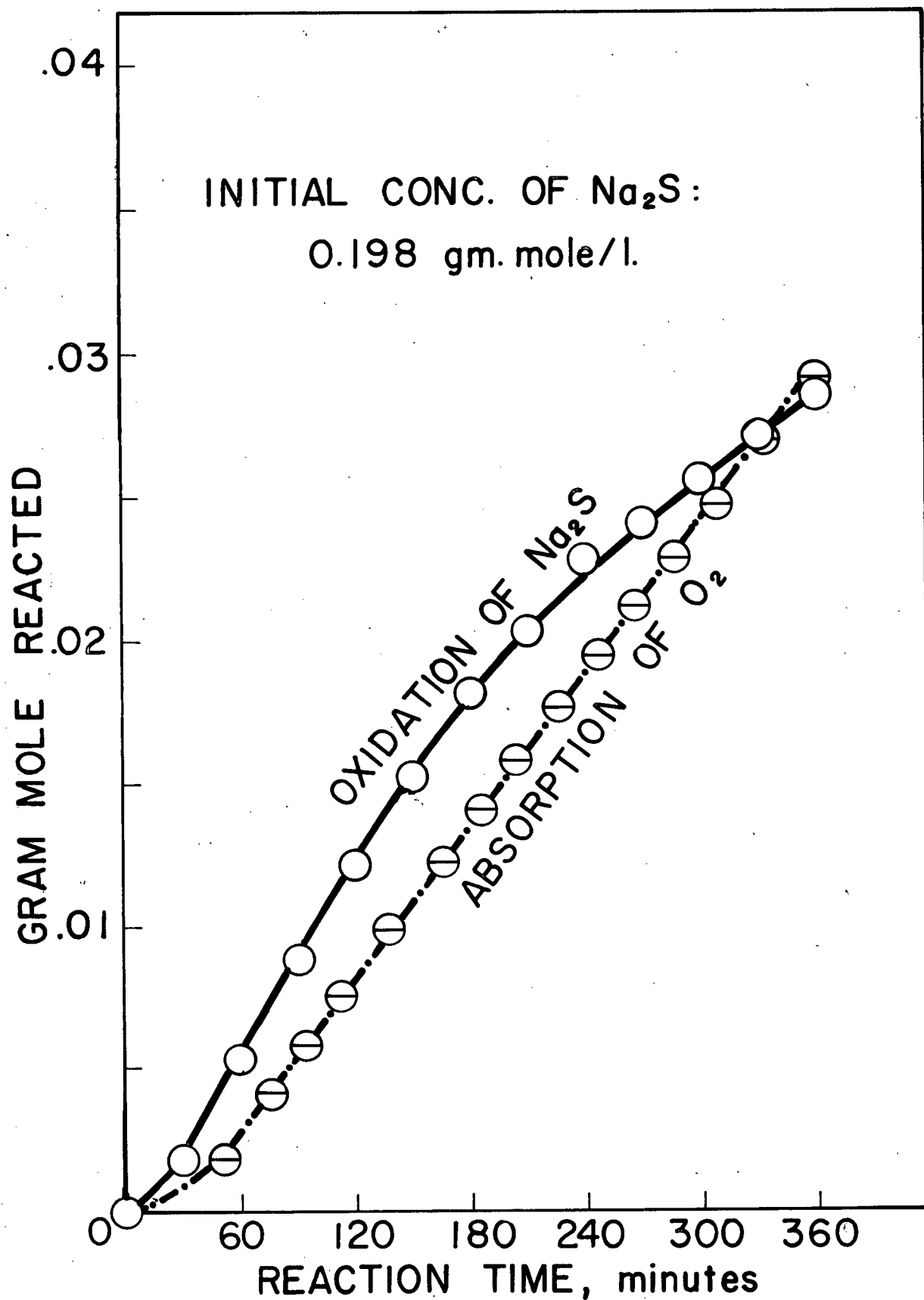


Figure 31. Stoichiometry at 35°C.

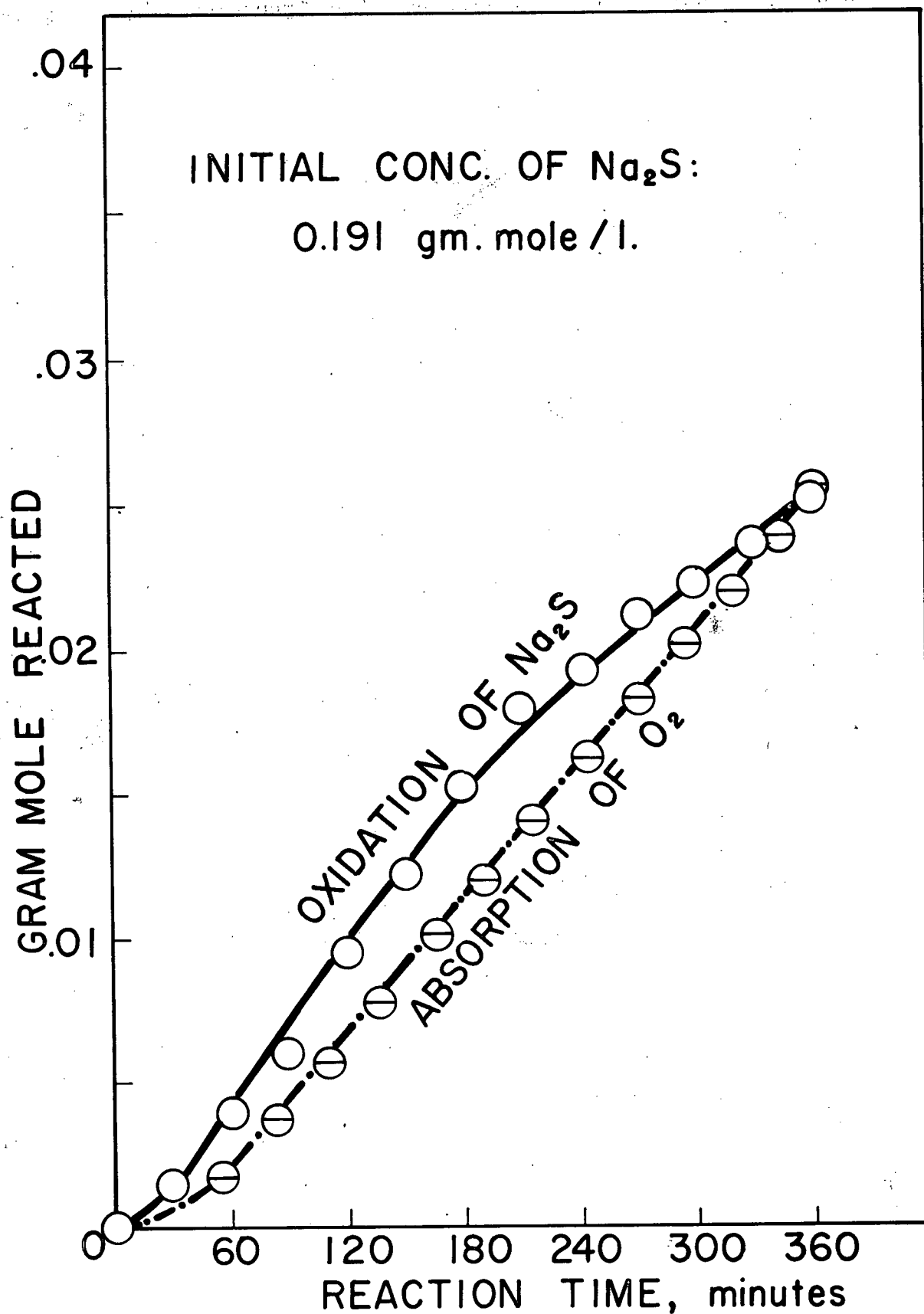


Figure 32. Stoichiometry at 45°C.

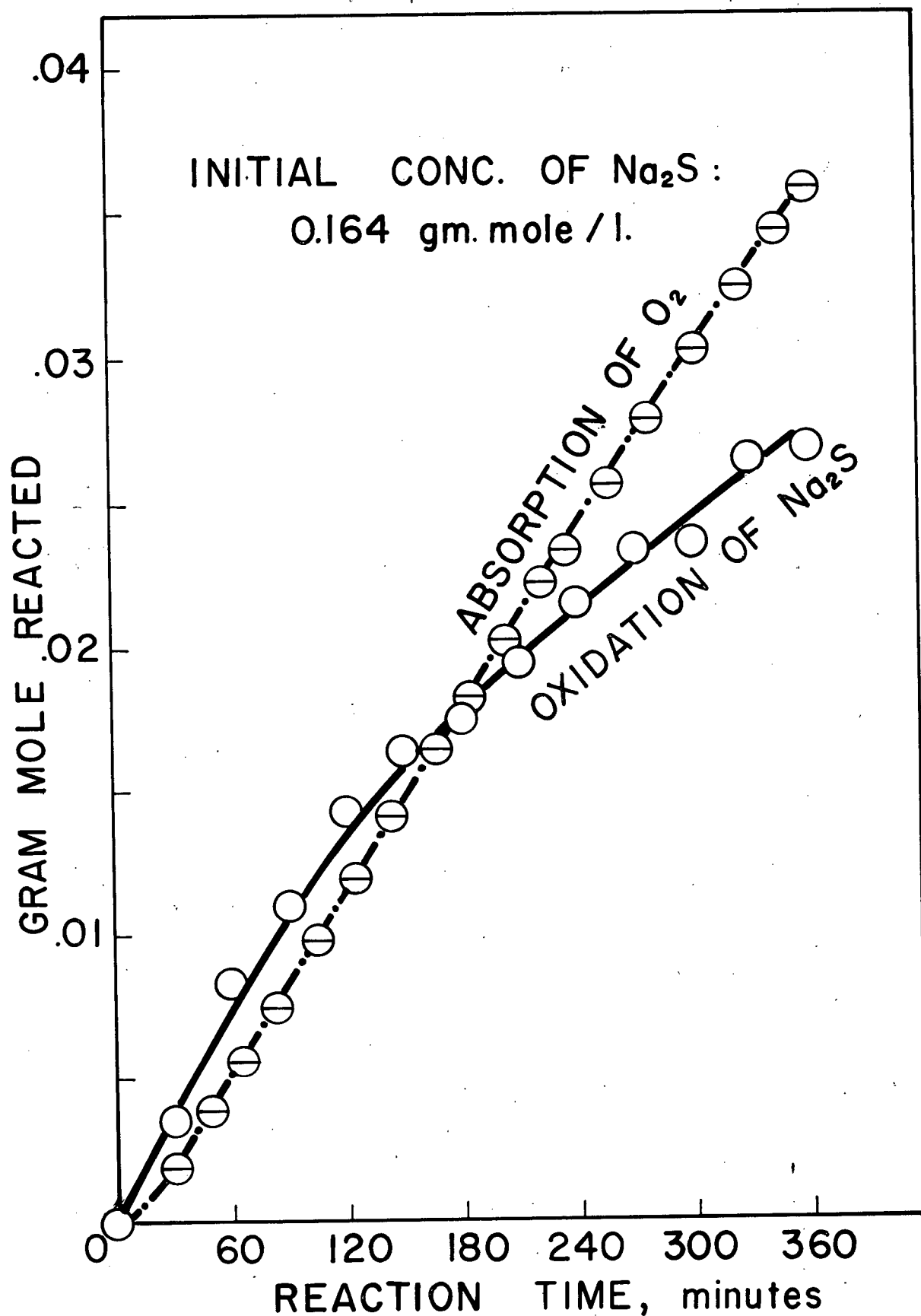


Figure 33. Stoichiometry at 55°C.

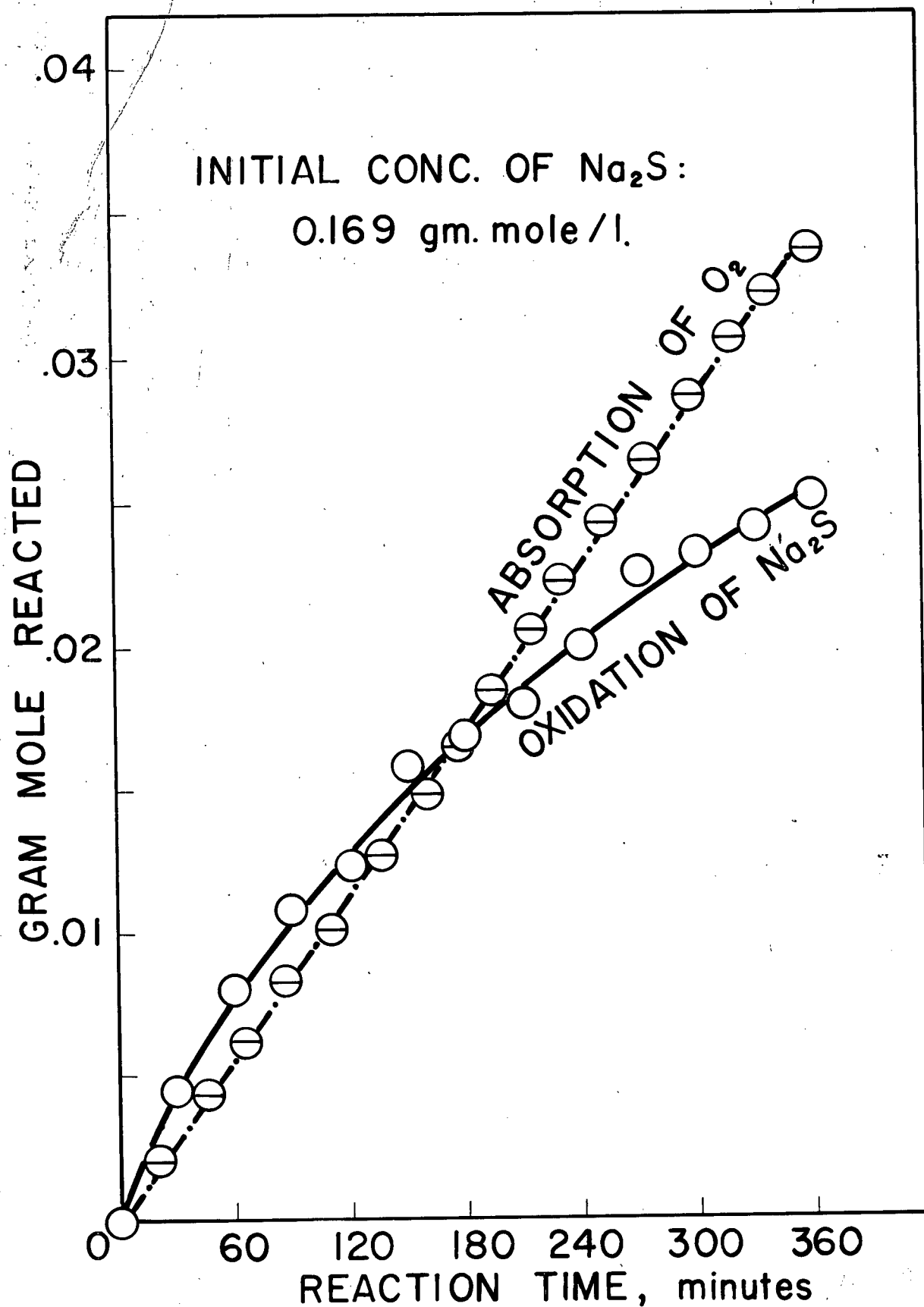


Figure 34. Stoichiometry at 65°C.

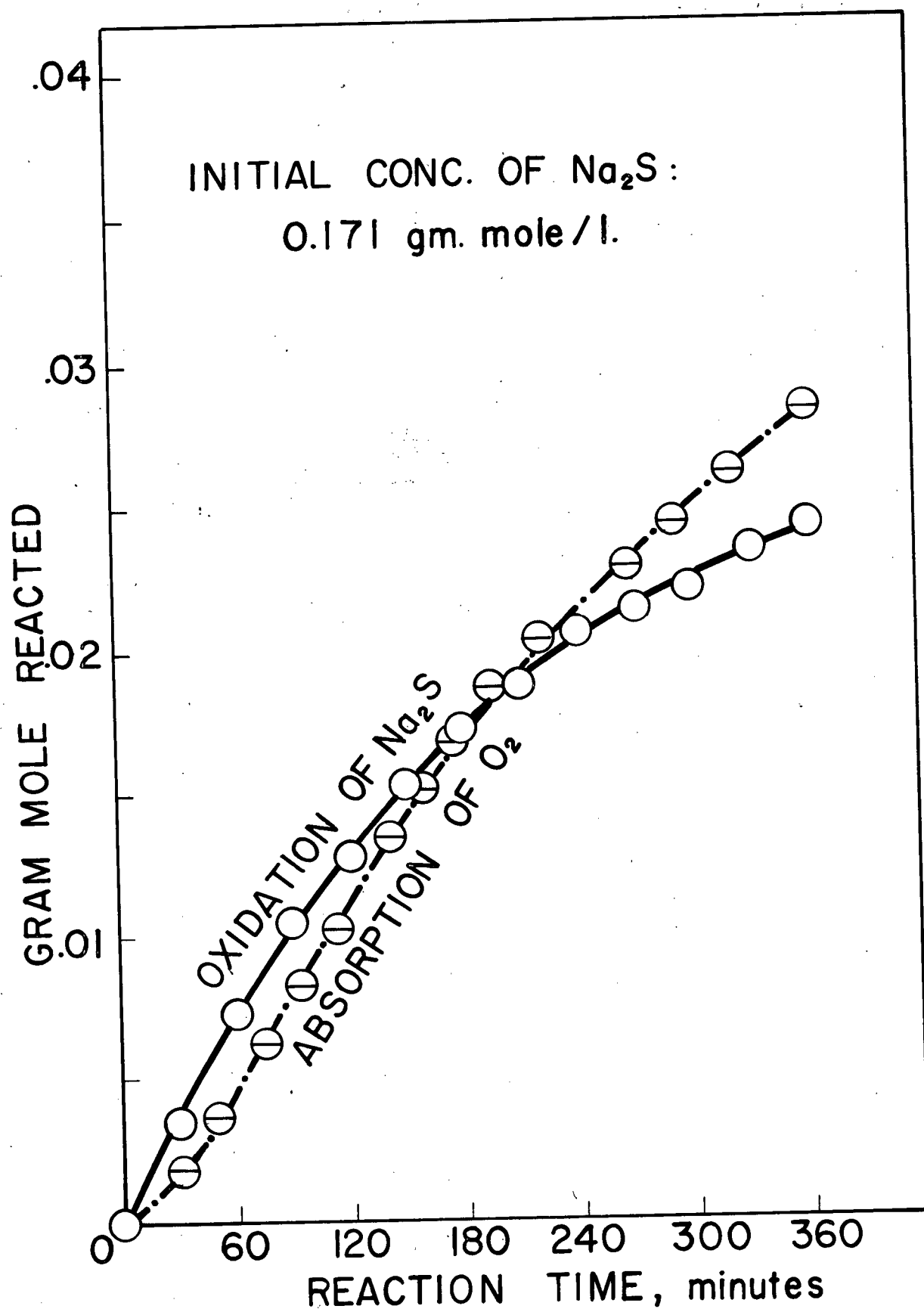


Figure 35. Stoichiometry at 75°C.

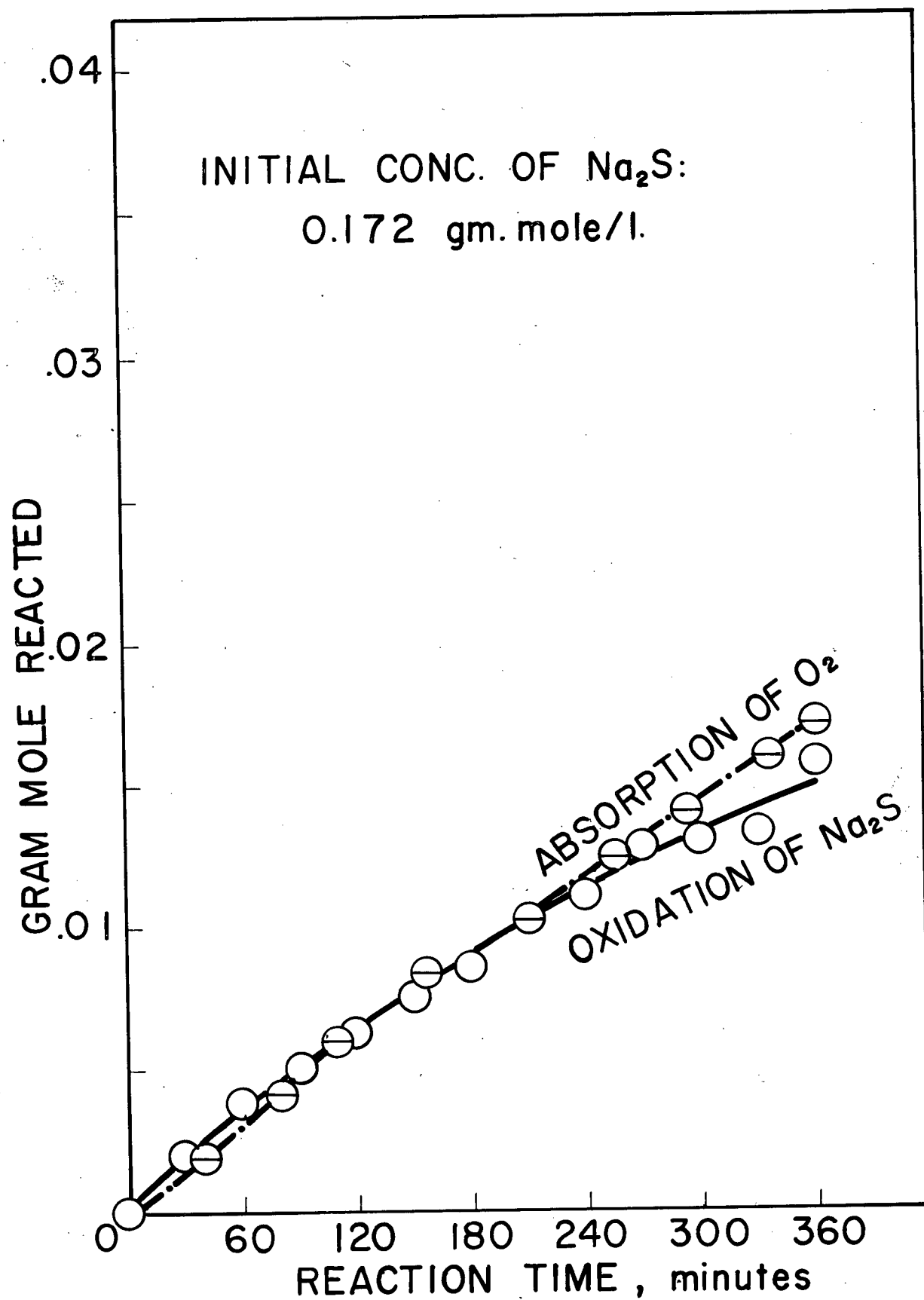


Figure 36. Stoichiometry at 85°C.

The rate of oxygen absorption was found to be slow in the first hour of reaction. The rate then increased to a constant value which was maintained for several hours, and then decreased gradually as the oxidation of sodium sulphide continued. High initial concentrations of sodium sulphide produce a comparatively high absorption rate. As the initial concentration decreases so does the absorption rate as implied by Fig. 37. The curve marked with 0 gm. moles/litre of sodium sulphide in Fig. 37 was obtained by using 250 ml. of 0.4 N sodium hydroxide solution without the injection of hydrogen sulphide.* This curve represents the rate of absorption of oxygen without a simultaneous oxidation of sodium sulphide. Figures 30, 38, and 39 show the oxidation of sodium sulphide and the absorption of oxygen for initial concentrations of 0.185, 0.0906, and 0.040 gm. moles/litre of sodium sulphide. The experimental data are summarized in Table 25, 32, 33, and 34. (The oxygen absorption data are the same as that shown in Fig. 37).

It has been mentioned already that at low initial concentrations of sodium sulphide the specific reaction rate for the disappearance of sodium sulphide is comparatively high. This result is in contrast with the result for the rate of oxygen absorption. This paradox also suggests that the oxidation of sodium sulphide does not involve a single reaction, a statement which will be justified in the next section.

* Only in this case has oxygen not been partially stripped from the solution by hydrogen sulphide.

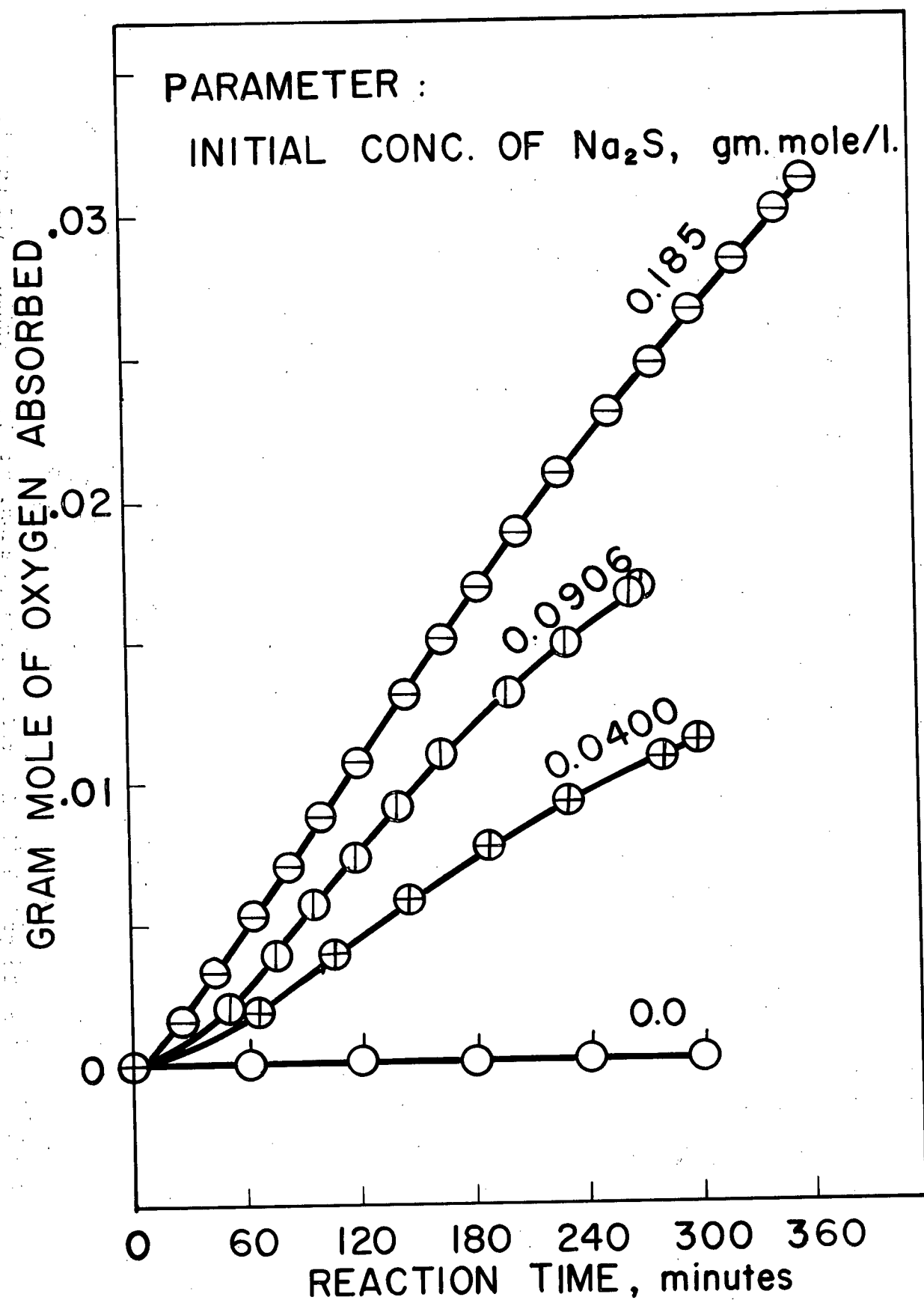


Figure 37. Effect of Initial Concentration of Sodium Sulphide on Absorption of Oxygen at 25°C .

The decrease in the volume of sodium sulphide solution, due to the withdrawals of samples for analyses, was negligible, being less than 2% when the apparatus of Fig. 13 was used. This small decrease in the volume of solution would have little effect on either the absorption rate or the oxidation rate.

Table 32. Effect of Initial Concentration of Sodium Sulphide on the Absorption and on the Oxidation at 25°C.

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.0906 gm.mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0009	50	0.0020
60	0.0035	75	0.0039
90	0.0055	95	0.0057
120	0.0072	117	0.0074
150	0.0090	140	0.0091
180	0.0095	164	0.0110
210	0.0117	200	0.0131
240	0.0119	230	0.0148
270	0.0124	265	0.0166
		270	0.0168

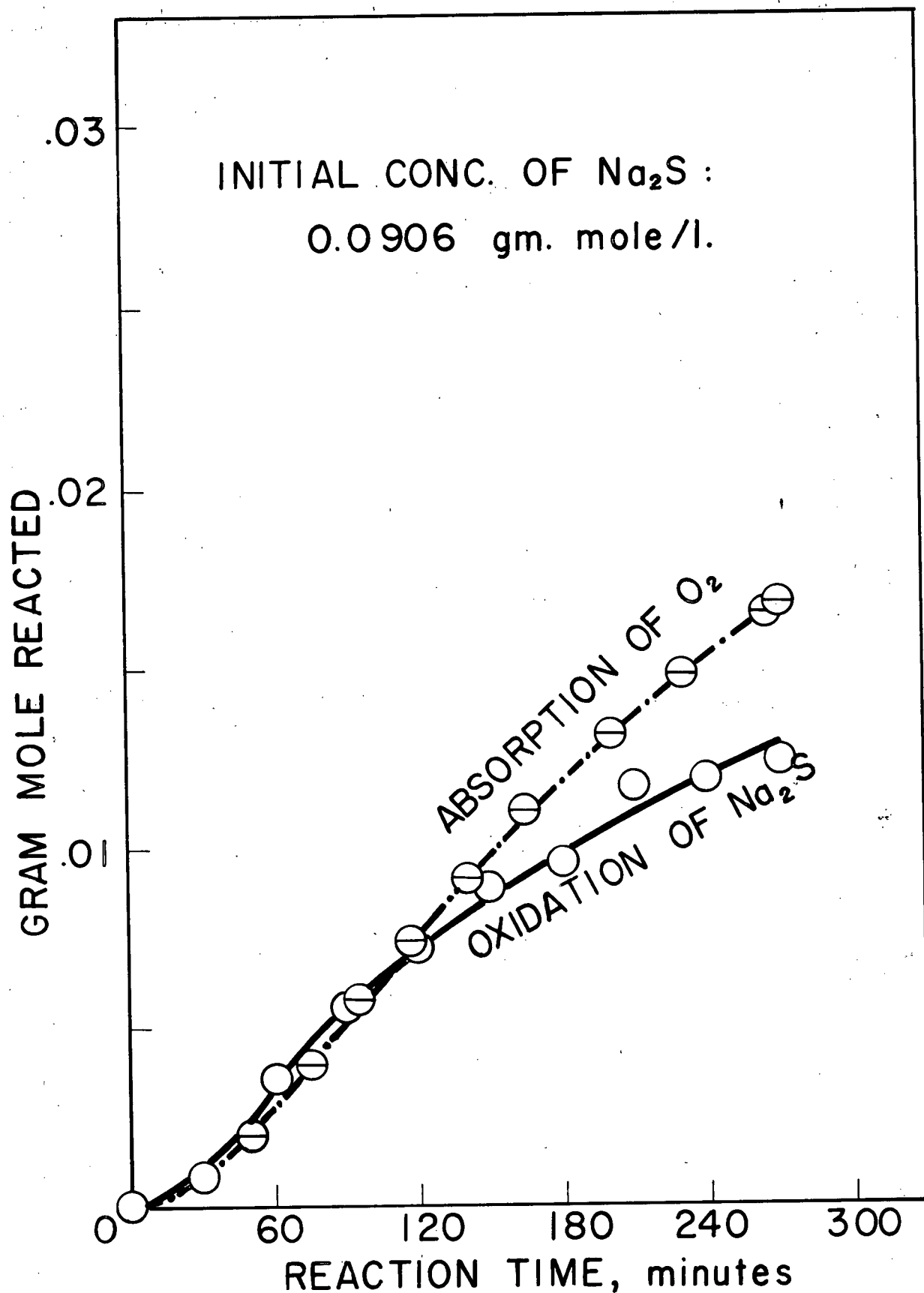


Figure 38. Effect of Initial Concentration of Sodium Sulphide on Absorption and on the Oxidation at 25°C .

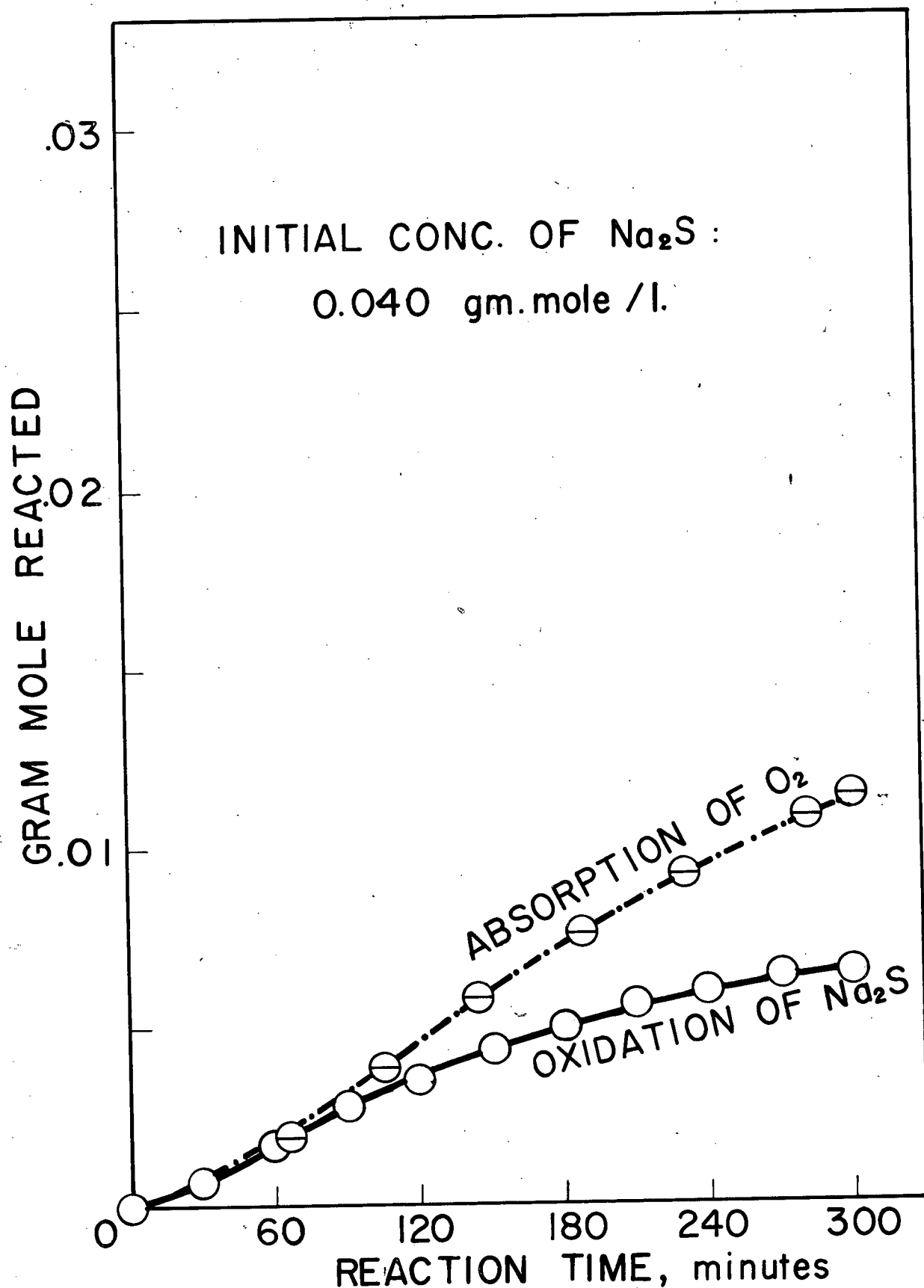


Figure 39. Effect of Initial Concentration of Sodium Sulphide on Absorption and on the Oxidation at 25 C.

Table 33. Effect of Initial Concentration of Sodium Sulphide on the Absorption and on the Oxidation at 25°C

Stirring rate: 1,320 r.p.m.; Initial conc.: 0.040 gm. mole/l.

Time, min.	Cumulative gm. mole Na ₂ S Oxidized	Time, min.	Cumulative gm. mole O ₂ Absorbed
0	0	0	0
30	0.0007	65	0.0019
60	0.0017	105	0.0039
90	0.0028	145	0.0058
120	0.0035	187	0.0076
150	0.0044	230	0.0092
180	0.0050	281	0.0108
210	0.0056	300	0.0114
240	0.0060		
270	0.0064		
300	0.0065		

Table 34. Absorption of Oxygen Without a Chemical Reaction at 25°C

Stirring rate: 1,320 r.p.m.; 0.4 N NaOH: 250 ml.

Time, min.	0	60	120	180	240	300
Cumulative gm. mole O ₂ Absorbed x 10 ⁵	0	1.2	1.6	3.3	4.9	7.0

6. Determination of Stoichiometry

From Figures 30 to 36, it is seen that sodium thiosulphate is the main product when the oxidation of sodium sulphide proceeds, since one mole of oxygen is required per mole of sodium sulphide oxidized (equation 4). However, in the initial stages of oxidation, the actual quantity of oxygen absorbed is less than the theoretical value for the formation of the thiosulphate. This indicates that at least

one parallel reaction, which consumes less oxygen, takes place in competition with the formation of the thiosulphate. Booth (18) gives the equation for the formation of disulphide for which reaction only $1/4$ mole of oxygen is required per mole of sodium sulphide oxidized, and perhaps this reaction is the one in competition here with the formation of thiosulphate. Of course, when disulphide ions move to the interface or more oxygenated part of the solution, they will be oxidized further instantly (18).

In the later stages of oxidation, in contrast to the early stages, the consumption of oxygen is greater than the theoretical value for the formation of sodium thiosulphate, perhaps because the sodium sulphide also is oxidized to sodium sulphite and sulphate. (19)

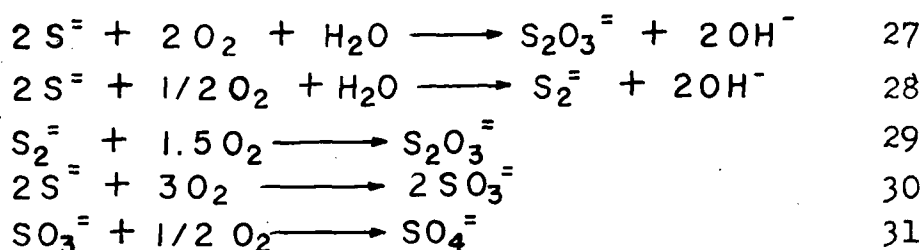
It should be emphasized here that when the pH of a sodium sulphide solution lies between 10 and 15, as shown in Fig. 2, the solution, in fact, consists of a mixture of sulphide and hydrosulphide. Similar reactions to the oxidation of sodium sulphide are expected for the oxidation of the hydrosulphide. All of the probable reactions for the oxidation of sulphide and hydrosulphide are summarized in Table 35.

The fact that at least ten reactions of different importance probably are involved in the oxidation of sodium sulphide solution, as given in Table 35, presumably explains

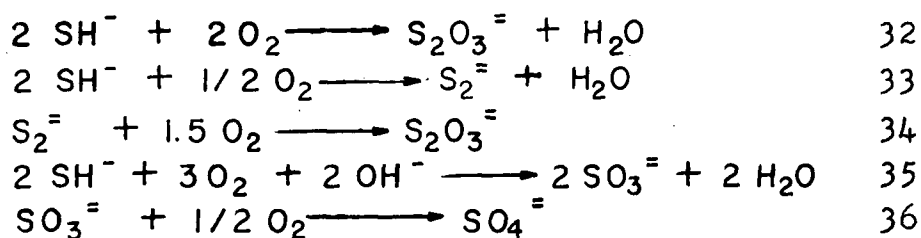
the phenomenon that the oxidation rate of sulphide increases as the initial concentration of sodium sulphide is decreased, in contrast to the decrease in the rate of absorption of oxygen observed as the concentration of sodium sulphide is decreased.

Table 35. Probable Reactions in the Oxidation of Na_2S and NaHS

A. For Na_2S :



B. For NaHS :



Instead of a single reaction giving sodium thiosulphate as the product, the oxidation of sodium sulphide, in fact, likely involves a series of reactions, parallel, consecutive, irreversible, and probably reversible. These reactions, although of minor importance as compared to the formation of the thiosulphate, complicate the study of the reaction. Furthermore, in the range of pH investigated, the solution actually contains both sulphide and hydrosulphide. This also renders the investigation difficult.

It was described already that the use of the apparatus in Fig. 13 involves the effect of reaction kinetics plus a mass transfer resistance of oxygen in the liquid phase. This is confirmed by comparing the slopes of the curves in Fig. 40 with those of the corresponding curves appearing in Figures 18, 23, 24, 25, and 26. The former is always less than the latter. This result indicates that mass transfer resistance is involved in affecting the overall rate besides the reaction kinetics. The experimental data corresponding to Fig. 40 are shown in Table 36.

The use of the apparatus in Fig. 13 also shows that the specific reaction rate increases as the initial concentration of sodium sulphide is decreased, as implied by the data of Table 37 which are plotted in Fig. 41.

The effect of temperature on the oxidation rate is difficult to correlate by means of an Arrhenius equation, since the temperature effect is not pronounced, and since the results depend upon the initial concentrations of sodium sulphide.

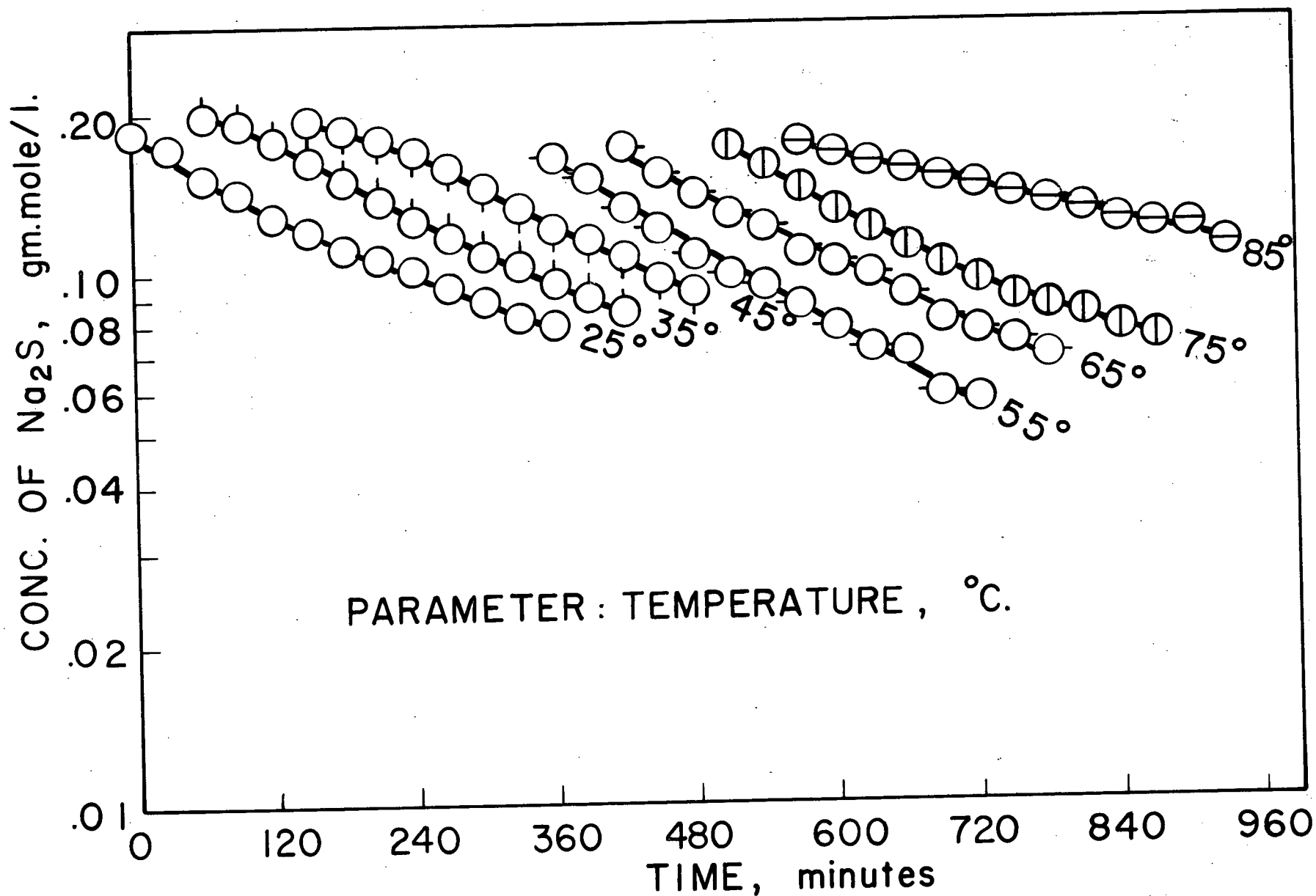


Figure 40. Oxidation of Sodium Sulphide at Various Temperatures for Apparatus in Figure 13.

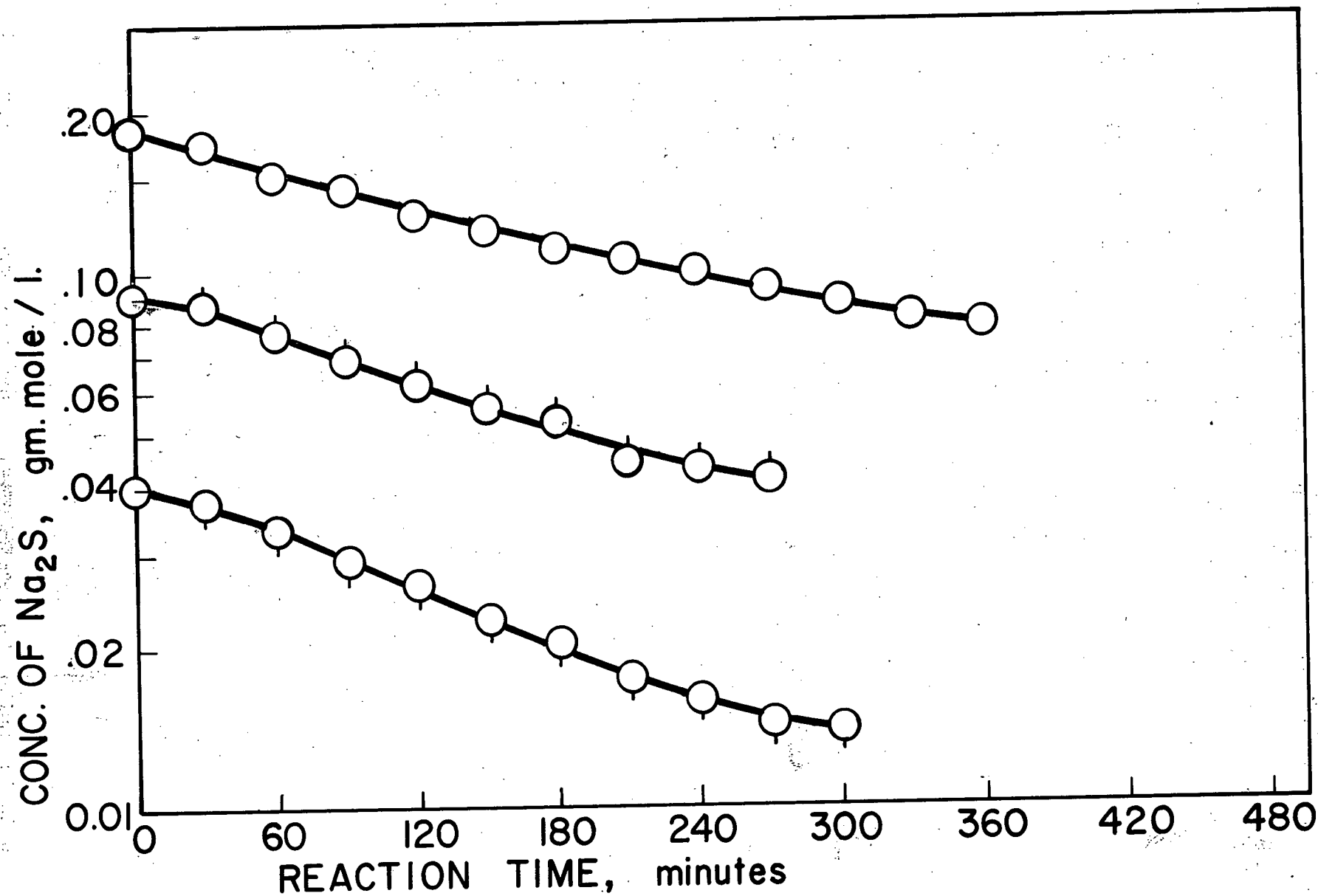


Figure 41. Oxidation of Sodium Sulphide at 25°C. as a Function of Initial Concentration.

Table 36. Oxidation of Sodium Sulphide at Various Temperatures for Apparatus in Fig. 13.

Stirring rate = 1,320 r.p.m.

Time, min.	Conc. of Na ₂ S, gm. mole/litre						
	25°C	35°C	45°C	55°C	65°C	75°C	85°C
0	0.185	0.198	0.191	0.164	0.169	0.171	0.172
30	0.174	0.191	0.185	0.150	0.151	0.157	0.164
60	0.150	0.178	0.175	0.131	0.137	0.142	0.157
90	0.142	0.163	0.167	0.120	0.126	0.129	0.132
120	0.128	0.150	0.155	0.107	0.120	0.120	0.147
150	0.120	0.138	0.142	0.0984	0.106	0.110	0.142
180	0.110	0.126	0.130	0.0940	0.102	0.102	0.138
210	0.105	0.117	0.119	0.0865	0.0970	0.0960	0.133
240	0.100	0.107	0.114	0.0780	0.0892	0.0885	0.128
270	0.0935	0.102	0.106	0.0710	0.0795	0.0855	0.121
300	0.0879	0.0956	0.102	0.0700	0.0762	0.0826	0.120
330	0.0815	0.0896	0.0961	0.0585	0.0725	0.0771	0.119
360	0.0785	0.0840	0.0905	0.0570	0.0681	0.0737	0.109

Table 37. Oxidation of Sodium Sulphide at 25°C as a Function of Initial Concentration.

Stirring rate = 1,320 r.p.m.

Time, min.	Conc. of Na ₂ S, gm. mole/l.		
0	0.185	0.0906	0.0400
30	0.174	0.0871	0.0373
60	0.150	0.0765	0.0333
90	0.142	0.0685	0.0289
120	0.128	0.0618	0.0262
150	0.120	0.0552	0.0223
180	0.110	0.0525	0.0202
210	0.105	0.0438	0.0175
240	0.100	0.0430	0.0160
270	0.0935	0.0409	0.0144
300	0.0879		0.0140
330	0.0815		
360	0.0785		

7. Comparison of the Oxidations of Sodium Sulphide and Black Liquor.

The oxidation of hydrogen sulphide dissolved in sodium hydroxide solution behaves similarly to the oxidation of sodium sulphide in black liquor. The main difference lies in the rates of oxidation. Ziegelmeyer and Feischl (5) showed that black liquors contain organic substances, which increase the rate of oxidation by 20 to 30 times.

Bilberg and Landmark (17) found that the oxidation products of black liquor include polysulphides, thiosulphate, sulphite, and small amounts of sulphate. In the present work, from the stoichiometric determination of oxygen absorbed, the formation of the same products of the oxidation of the sulphide solution is implied.

Venemark (21) found that the rate of oxygen absorption into black liquor in each run is to a large extent independent of time from the beginning of oxidation, a result which is in agreement with the results obtained from the present work for the treatment of solutions of sulphide.

Murray (15) studied the oxidation of black liquor between 50° and 91°C. Although catalysis in his studies may result in quite different mechanisms of reaction from those applicable in the present work, it would seem interesting to compare his results with those of the present

work. Murray (15) found that the rate of the oxidation of weak black liquor may be expressed by a semi-empirical first order equation with respect to sulphide. In the present work at temperatures between 550 and 850°C the oxidation of sodium sulphide also was found to be of first order with respect to the concentration of sodium sulphide. Murray (15) did not study the oxidation at lower temperatures. Shchukarev and Kireeva-Tuzulakhova (19) studied the oxidation of sodium sulphide at 200 and 400°C, and found that the reaction order was anomalous.

In regard to the reaction order with respect to the concentration of oxygen, the present work establishes it as first order, irrespective of the temperature, for the oxidation of sulphide. Murray (15), however, gave the ratio of oxidation rates with oxygen to those obtained using air as feed gas as a function of temperature and the concentration. The ratio ranged from 1.71 to 3.11. The way Murray calculated this ratio was ineffective. He obtained the oxidation rates in the units of grams per unit time. Only if the reaction were of zero order would the values of the ratio be expected to remain constant. In the present work the specific reaction rates were compared. The specific reaction rate is independent of time and concentration, whereas the oxidation rate, expressed as mass per unit time, is a strong function of both time and concentration.

Murray (15) used the method of analysis of the present work for determining the content of sulphide in black liquor except that the concentrations of base electrolyte and p-phenylenediamine were those suggested by Strickland and Risk (1) instead of the higher concentrations used here. This fact may account for the different results in the two studies with respect to the reaction order for oxygen. Murray (15) correlated his data by adding the partial pressure of oxygen in the gas phase, multiplied by an arbitrary constant, to the concentration of sulphide. This approach is entirely empirical, and the order with respect to oxygen is not easy to visualize.

Murray (15) found that the change with temperature in the rate of the oxidation of sodium sulphide in black liquor is very slight. His results show that the maximum oxidation rate occurs at a temperature between 61° and 71°C. For the oxidation of sodium sulphide, the maximum rate was found from this work to be at 55°C.

CONCLUSIONS

The experimental results, as a whole, are satisfactory, since the two different apparatuses gave the consistent results.

The use of the higher concentrations of reagents, base electrolyte and p-phenylenediamine, for the development

of Lauth's Violet from sulphide solution, is satisfactory for the study of the kinetics of the oxidation of sodium sulphide. One advantage is that the concentration of sodium sulphide can be calculated directly from the calibration factor without using the calibration curve, since the calibration factor remains constant up to 16 gms. per litre of sodium sulphide.

The oxidation of sodium sulphide is similar to that of black liquor, except that the reaction is much slower, due to the absence of the organic substances which catalyze the reaction. Besides the thiosulphate, oxidation of sodium sulphide may give disulphide, sulphite and sulphate. The rate of oxygen absorption is increased appreciably by the simultaneous oxidation of sodium sulphide in the solution. The rate of oxygen absorption decreases with temperature from 25° to 45°C, but increases abruptly to a maximum at 55°C, and then decreases again. Although the absorption rate of oxygen is to a great extent independent of the concentration change of sodium sulphide during an oxidation experiment, it does depend upon the initial concentration of the sulphide.

The reaction orders with respect to sodium sulphide depend upon the temperature: second order at 25°C, order of 1.5 at 35° and 45°C, and first order from 55° to 85°C. The reaction order with respect to oxygen is always first order, independent of the temperature. The maximum oxidation rate also occurs at 55°C.

RECOMMENDATIONS

The following recommendations are proposed for further experimental work on the oxidation of sodium sulphide or of black liquor:

(a) For the study of reaction kinetics, the apparatus shown in Fig. 12 can be modified by replacing the saturator with a condenser connected to the outlets of the gas. In this way, the water vapor carried by the gas from the solution will reflux to the reactor without causing serious change of the concentration of the sulphide due to evaporation at high temperature. (Calculations show a loss of only 0.5% of a 250 ml. volume from the reactor in 5 hours if the exit gas were cooled to 70°C.)

(b) A study of the oxidation of sodium sulphide could be carried out with various appropriate organic substances present to catalyze the oxidation. Perhaps information would result as to those compounds which are important in the oxidation of sodium sulphide in black liquor.

(c) The reason, why the reaction orders with respect to the concentration of sodium sulphide depend upon the temperatures, may be clarified by use of the E.S.R. technique to detect and determine the different unpaired free radicals which probably are involved at different temperatures.

NOMENCLATURE

Symbols

B	Base Electrolyte
b	Cell Thickness, cm.
C	Concentration of Sodium Sulphide, gms./l. or gm.moles, /l. or concentration of Lauth's Violet, p.p.m. Na_2S .
C_0	Initial Concentration of Sodium Sulphide, gms./l. or gm. moles/l.
E	Extinction = $\log I_0/I = kbC$ = Absorbance
F	Calibration Factor = $50 C / E V$
I	Intensity of transmitted light or radiant energy at single wavelength
I_0	Intensity of incident light or radiant energy at single wavelength
k	Specific extinction or specific absorbance, (p.p.m.) ⁻¹ (cm.) ⁻¹
K	Chemical equilibrium constant
k_n	Specific reaction rate, (gm. moles/l.) ¹⁻ⁿ (min.) ⁻¹
N	Sodium sulphide
n	Reaction order
P	p-Phenylenediamine
t	Reaction time, min.
V	Diluted volume of Lauth's Violet solution, ml.
V/50	Dilution
x	Mole fraction

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APPENDIX

The correction of the concentration of sodium sulphide for the evaporation of water from the reactor in a few of the runs compensates for the fact that, without the correction, the concentration at any time would be the result not only of reaction, but also of evaporation. However, the reaction rate observed at any time is that corresponding to the actual concentrations in the reactor which are higher than the corrected ones. This defect in the correction is probably not serious except toward the ends of two or three of the runs.

The experimental conditions for negligible resistance to mass transfer in the apparatus of Fig. 12 were established at low temperature under saturated conditions. At higher temperatures, diffusion may be important since the gas is not saturated in the saturator. The evaporation of water into a gas bubble might here present a significant resistance to mass transfer. In any further work this point should be checked.

Operation with a condenser following the reactor, suggested in Recommendations, would not be possible with a saturator ahead of the reactor since a gain of water in the reactor with time would result. Hence if a condenser were used dry gas would be needed, and the problem of possible mass transfer resistance as a result of evaporation of water into the gas bubbles in the reaction would need even more careful examination.