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HYDROLYSIS OF SODIUM SILICOFLUORIDE

By

FRANK A. GRAF, JR.

A THESIS
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ABSTRACT

HYDROLYSIS OF SODIUM SILICOFLUORIDE

The kinetics of an apparent solubility decrease of commercial sodium fluoride encountered in a piece of equipment designed to produce saturated sodium fluoride solution was investigated, in order to understand why a consistently saturated solution was not possible to achieve with plain tap water as solvent.

The main impurity, about 1 percent sodium silicofluoride, coats the sodium fluoride crystals, resulting in an equilibrium shift during dissolution of the salt in water; and under certain conditions results in the formation of a protective gel. Therefore, in order to produce a constant strength sodium fluoride solution, this coated impurity must be decomposed under conditions which are unfavorable to the formation of the silica gel.

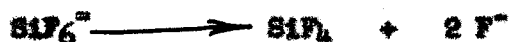
The investigation was concerned specifically with the kinetics of the hydrolysis of sodium silicofluoride in water and in saturated sodium fluoride solutions.

Two different mechanisms for the hydrolytic decomposition of the silicofluoride ion in water have been proposed by previous authors. Ryss and Slutskaya¹ and Kubelka and Pristoupil² postulate the reaction:

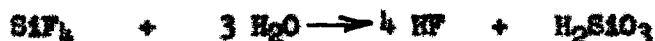
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1. Ryss, I. G. and Slutskaya, M. M., J. Phys. Chem. (USSR) 14 (1940) p. 701.
 2. Kulbelka, V. P. and Pristoupil, V., Z. Anorg. Allgem. Chem. 197, 393 (1931).



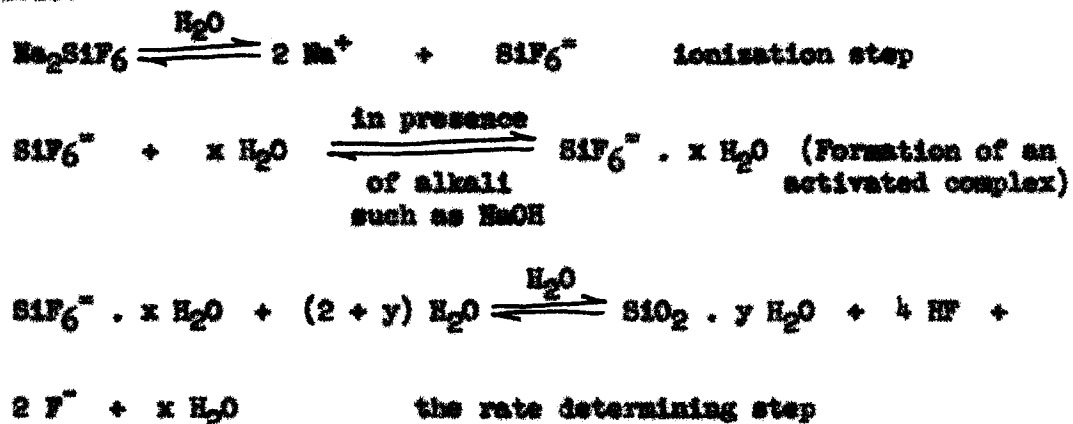
A two step mechanism is offered by Hudleston and Bassett³ and also by Rees and Hudleston⁴, a slow reaction,



followed by a rapid reaction,



This author has shown from experimental considerations of the primary and secondary salt effects, the effect of dielectric constant of the media on the reaction rate constant, and from theoretical calculations of the entropy factor that the following mechanism is more probable:



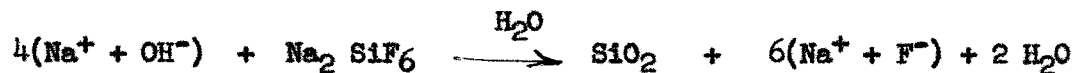
followed by the rapid neutralization of the HF formed by the alkali (sodium hydroxide) that has been added



3. Hudleston, J. and Bassett, H., J. Chem. Soc. (1921) p. 403.

4. Rees, A. G. and Hudleston, J. L., J. Chem. Soc. (1921) p. 1334.

The overall stoichiometric equation would be



In this mechanism x and y are unknown due to the difficulty of determining their exact values.

A minimum alkalinity, pH of 10.2, is apparently necessary in order that the silica produced from the $\text{Na}_2 \text{SiF}_6$ present is not activated to form a gel. Equilibrium shift cannot explain entirely the required high alkaline conditions necessary in the effluent for complete dissolution of the commercial sodium fluoride in a continuous dissolution bed.

APPROVAL OF THESIS

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TEXT

A. Introduction

During the development of a sodium fluoride saturator for use as a means of fluoridating potable waters, a solubility problem was encountered when a consistent sodium fluoride solution was attempted to be produced from the dissolution of a commercial grade of sodium fluoride salt.

The saturator is primarily a sodium fluoride bed through which water is drawn at a very slow rate, in order to produce a saturated sodium fluoride solution. Saturated solution was produced at first, but the concentration of the salt in the effluent decreased steadily as shown by Figure 1.

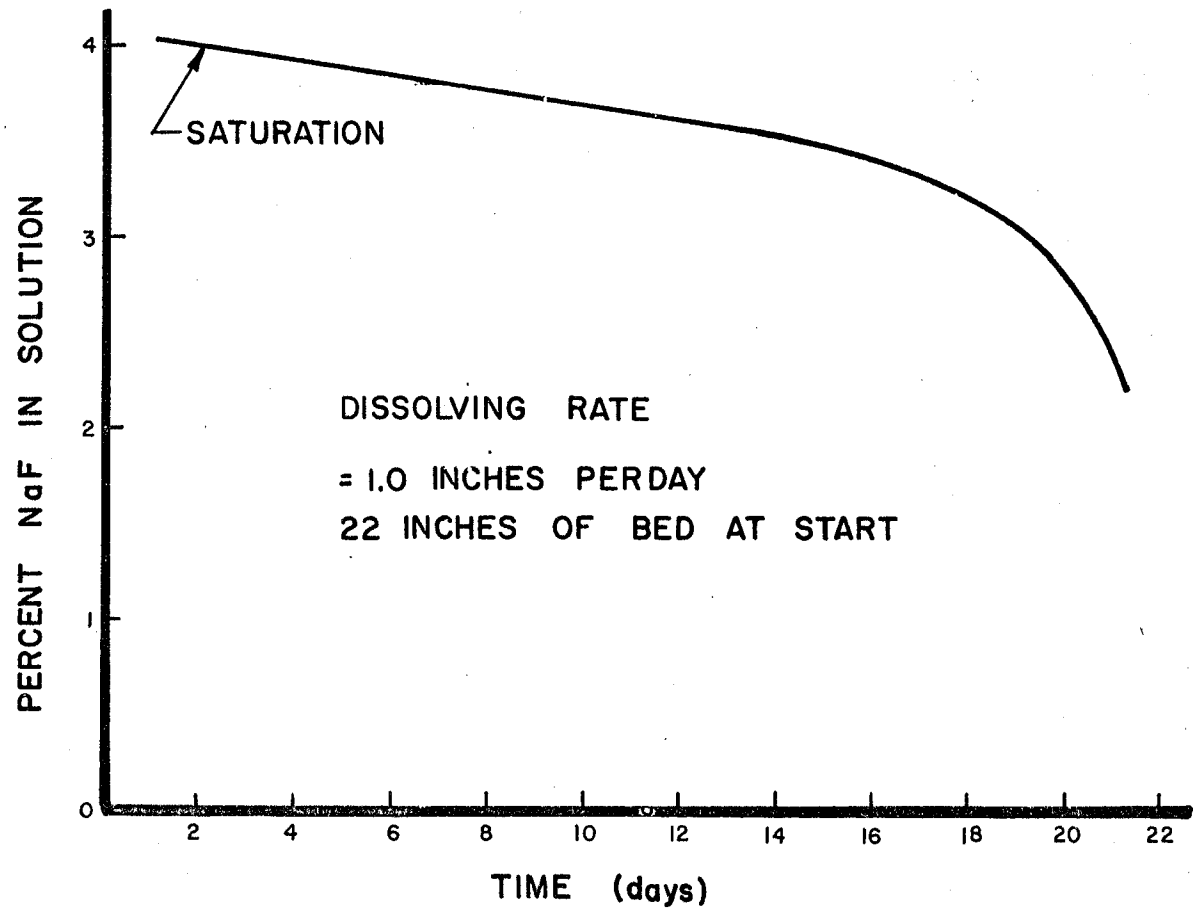
At first it was thought that the throughput time was a factor so the water rate was decreased to a negligible amount, but it did not restore the concentration of sodium fluoride to its original value. By comparison, pure sodium fluoride produced a constant strength effluent, and a synthetic commercial grade, consisting of pure sodium fluoride and the various impurities added, also gave a consistent concentration. It was evident that a problem of impurities coating the surface of the sodium fluoride crystals existed. The largest impurity present in the commercial grade of sodium fluoride is sodium silicofluoride, which averages about one percent in the best product available.

FIGURE 1

A TYPICAL DISSOLVING CURVE FOR A
COMMERCIAL GRADE OF SODIUM FLUORIDE
IN PLAIN TAP WATER AT 23° C

SODIUM FLUORIDE ASSAY
98% MINIMUM NaF
1% MAXIMUM Na₂SiF₆

TAP WATER — APPROX. 20 P.P.M. TOTAL
DISSOLVED SOLIDS



By using a synthetic salt, composed of high purity sodium fluoride and one percent sodium silicofluoride which was recrystallized under reduced pressure in a Lucite container, a comparable solubility curve was obtained. The curve was similar to that which was plotted for a commercial grade sodium fluoride salt in Figure 1.

From Figure 2, the solubility of Na_2SiF_6 is 0.725 grams per 100 grams of water at 23°C , then the Na_2SiF_6 concentration, $[\text{Na}_2\text{SiF}_6]$, is equal to,

$$[\text{Na}_2\text{SiF}_6] = \frac{725}{100.7} \times 1000 \times \frac{1}{188.05} = .0386 \text{ molar}$$

$$\text{and } [\text{Na}_2\text{SiF}_6] = [\text{SiF}_6^{=}] = 1/2 [\text{Na}^+]$$

assuming additive volumes of water and sodium silicofluoride.

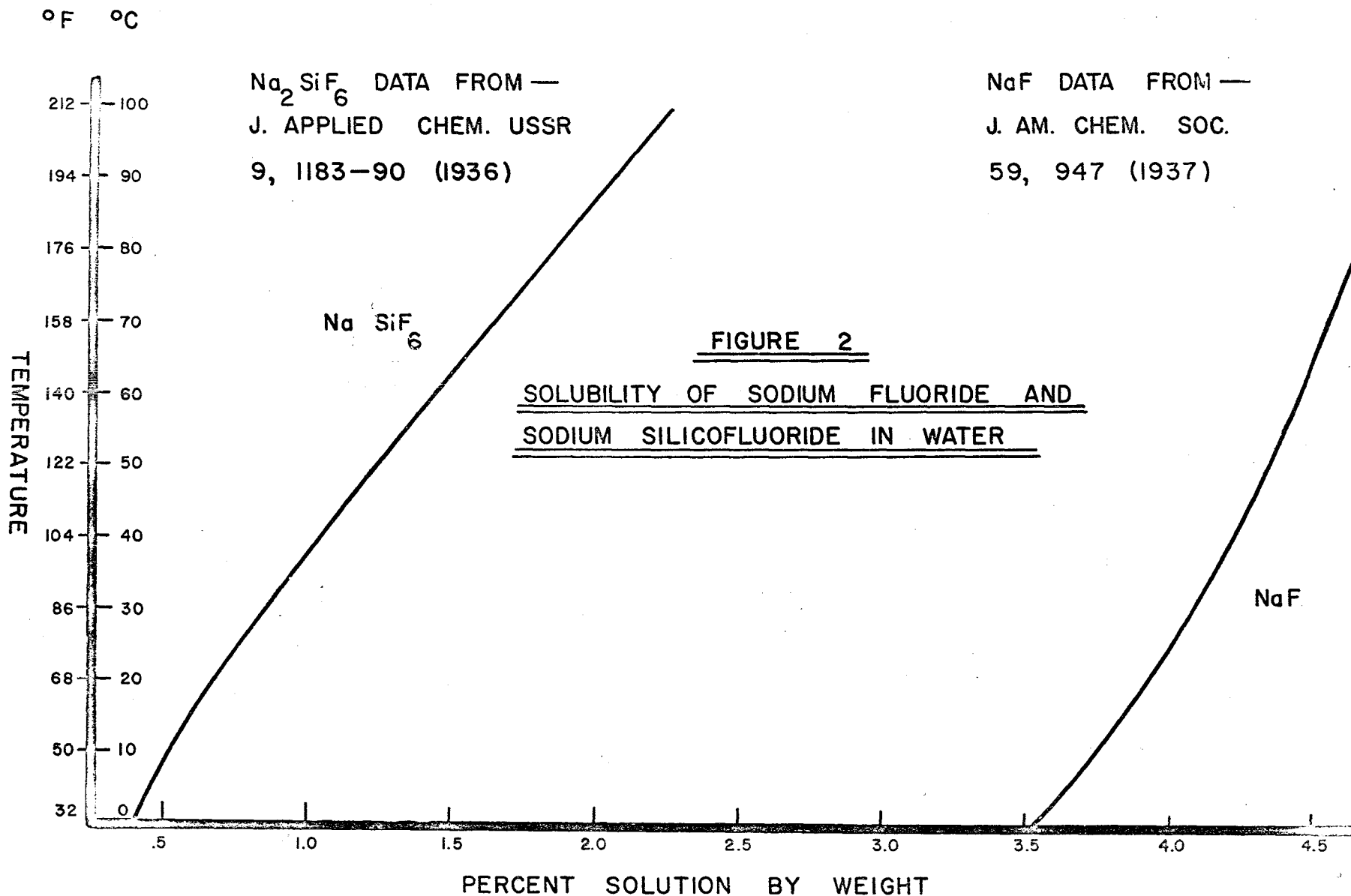
The concentration solubility product, L, then is equal to:

$$L = (.0386)(.0772)^2 = 2.30 \times 10^{-4} \text{ at } 23^\circ\text{C}$$

For this discussion the author feels that the use of the solubility product simplifies the problem and does not introduce an excessive error.

With a commercial grade of NaF, a saturated solution at 23°C would contain 4.0 percent NaF which would be 0.952 molar

$$\frac{4.0}{100} \times \frac{1}{42.0} \times 1000 = 0.952 \text{ moles of NaF per liter}$$



Since the NaF concentration is 0.952 molar, then the sodium ion concentration contributed by the NaF is also 0.952 molar. However, one percent of the total salt is sodium silicofluoride, so that

$$\begin{aligned} [\text{Na}_2\text{SiF}_6] &= [\text{SiF}_6^{=}] = 1/2 [\text{Na}^+] \text{ from the Na}_2\text{SiF}_6 \\ \text{or } [\text{Na}_2\text{SiF}_6] &= .01(0.952) = .00952 \text{ molar} \end{aligned}$$

assuming that all of the silicofluoride is in solution.

The total sodium ion concentration from all contributing molecules is then

$$[\text{Na}^+] = \left\{ 0.952 + 2 [\text{SiF}_6^{=}] \right\}$$

Employing the solubility product relationship

$$L = [\text{Na}^+]^2 [\text{SiF}_6^{=}] = 2.30 \times 10^{-4} \text{ at } 23^\circ\text{C}$$

$$2.30 \times 10^{-4} = \left\{ .952 + 2 [\text{SiF}_6^{=}] \right\} \times [\text{SiF}_6^{=}]$$

$$[\text{SiF}_6^{=}] = 2.53 \times 10^{-4} \text{ molar}$$

but .00917 molar is present assuming it all dissolved, so that it can be seen that the solubility of the sodium silicofluoride has been reduced to 2.65 percent of the amount present.

$$\frac{2.53 \times 10^{-4}}{.00953} \times 100 = 2.65\%$$

From the above calculations, it can be seen that the sodium silicofluoride has been rendered practically insoluble by the common-ion effect.

The drop in solubility of the commercial sodium fluoride can be accounted for by the presence of the almost insoluble coating of the silicofluoride on the sodium fluoride crystals which hinders dissolution.

Kubelka and Pristoupil¹ have shown that the equilibrium constant for the hydrolysis reaction is:

$$K = \frac{[H^+]^4 [F^-]^6}{[SiF_6^{2-}]} = 2 \times 10^{-27} \text{ at } 23^\circ C$$

A sodium fluoride solution made from commercial sodium fluoride would contain 2.5×10^{-4} moles per liter of sodium silicofluoride as shown previously. From Figure 3 it can be seen that a silicofluoride solution of this concentration in water has a pH of 3.35 and therefore would be 78 percent hydrolyzed.

$$K = \frac{[H^+]^4 [F^-]^6}{[SiF_6^{2-}]} = 2 \times 10^{-27}$$

$$x = \text{amount of } SiF_6^{2-} \text{ that hydrolyzes}$$

$$6x = \text{amount of } F^- \text{ from the hydrolysis}$$

$$pH = 3.35 = 4.47 \times 10^{-4} = [H^+]$$

therefore,

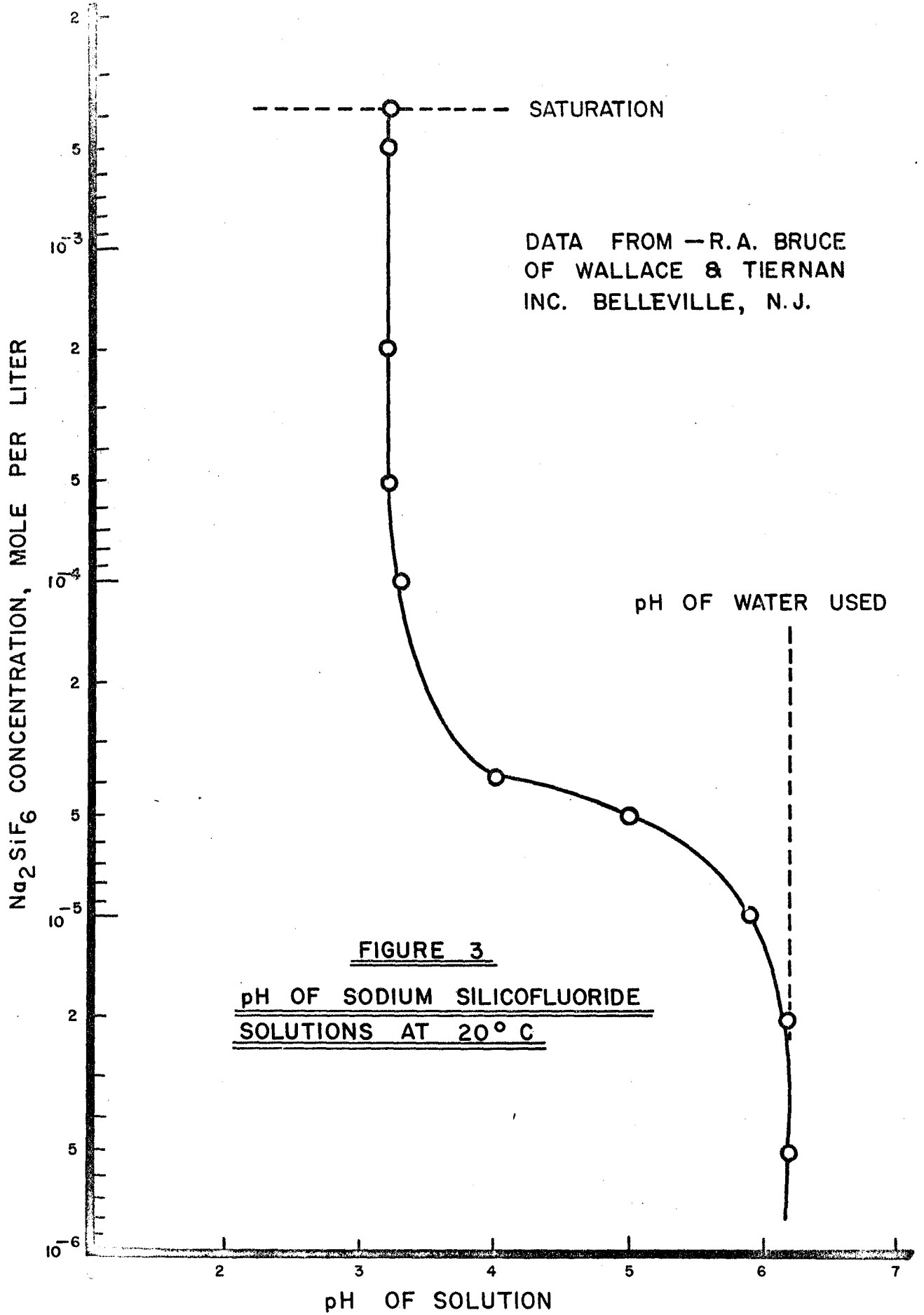
$$2 \times 10^{-27} = \frac{(4.47 \times 10^{-4})^4 (6x)^6}{(2.53 \times 10^{-4} - x)}$$

$$x = 1.97 \times 10^{-4} = \text{amount of } SiF_6^{2-}$$

that hydrolyzes

$$\% x = 100 \frac{1.97 \times 10^{-4}}{2.53 \times 10^{-4}} = 78.0\%$$

1. Kubelka, V. P. and Pristoupil, V., A. Anorg. Allgem. Chem. 197, 393 (1931).



However, there is 0.952 molar sodium fluoride present and the pH from experimental measurements is 7.4, in a solution made from commercial NaF. Therefore the fraction of hydrolyzed material is calculated:

$$\frac{(2.51 \times 10^{-8})^4 (.952 + 6x)^6}{(2.53 \times 10^{-4} - x)} = 2 \times 10^{-27}$$

where x = the amount that hydrolyzes. By trial and error,

$$x = 1.04 \times 10^{-4} \text{ molar.}$$

From the above calculations it can be seen that the sodium fluoride that is present reduces the degree of hydrolysis of the sodium silicofluoride by 52.8 percent.

$$\frac{1.04 \times 10^{-4}}{1.97 \times 10^{-4}} \times 100 = 52.8\%$$

Using the same equilibrium relationships, the effect of raising the pH of a NaF solution made from commercial grade salt was calculated and can be seen in Figure 4.

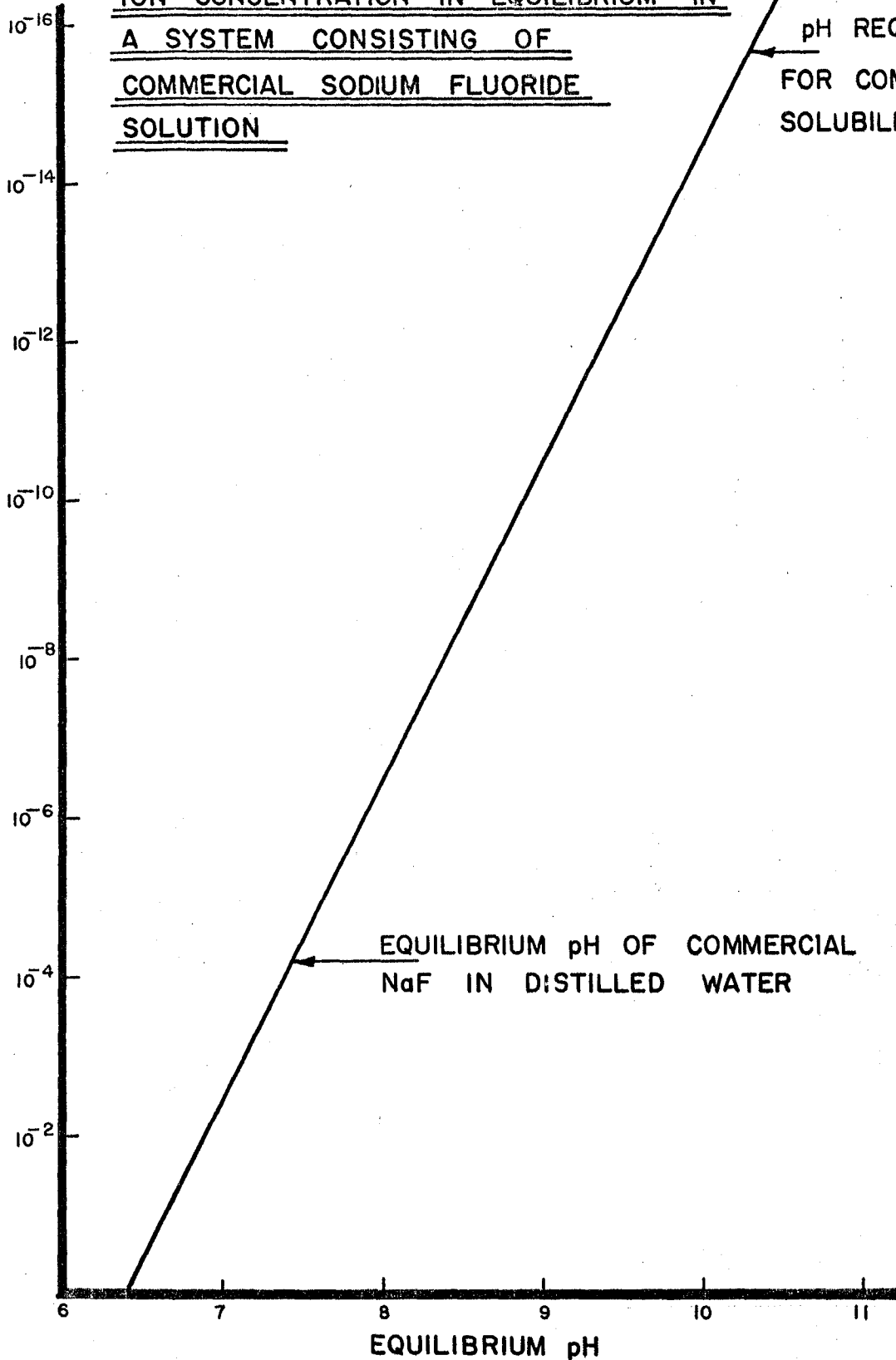
In practice, it was found that a pH of 10.2 was necessary before complete dissolution of the sodium fluoride bed and a constant solubility was produced. It is apparent from Figure 4 that a pH lower than 10.2 could shift the equilibrium sufficiently so that the amount of Na_2SiF_6 present is negligible. Therefore, there must be another contributing cause for the solubility fall-off that is encountered.

The only other thing that could effect the solubility would be the formation of a silica gel on the sodium fluoride crystals. The effect of activated silica gel, which can cover the NaF crystals and thereby

FIGURE 4

THE EFFECT OF pH ON THE SILICOFLUORIDE
ION CONCENTRATION IN EQUILIBRIUM IN
A SYSTEM CONSISTING OF
COMMERCIAL SODIUM FLUORIDE
SOLUTION

SILICOFLUORIDE ION CONCENTRATION IN EQUILIBRIUM WITH THE FLUORIDE AND HYDROGEN IONS



change the dissolution characteristics, will be shown in this thesis to be the cause of the necessity of maintaining a minimum pH of 10.2 in a sodium fluoride saturator.

The method of maintaining a pH of 10.2 in practice in a saturator is by treatment with sodium carbonate rather than sodium hydroxide. Sodium carbonate has been chosen because it is a common water-works chemical that Public Health officials would not object to and it is safer to handle by water plant personnel.

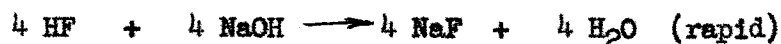
Since all previous work was done using plain sodium silicofluoride and sodium hydroxide with no agreement on the mechanism of the hydrolysis, this thesis is concerned with:

1. Checking the rate constants with sodium hydroxide and sodium silicofluoride.
2. Determining the mechanism of the reaction by experimental means and theoretical considerations.
3. Determining the effect of high sodium fluoride concentrations on the hydrolysis reaction rate constants.
4. Checking the rate constants using sodium carbonate as alkali.
5. Show that silica gel accounts for the minimum pH of 10.2 that is required for constant strength NaF in a saturator.

B. Review of Previous Investigators

The earliest work done on the kinetics of the hydrolysis of sodium silicofluoride is that of Hudleston and Bassett² (1921) who measured the velocity constants by using fluosilicic acid. These authors proposed the following mechanism:

(In the presence of NaOH) $\text{SiF}_6^{=}$ \rightarrow $2 \text{F}^- + \text{SiF}_4$ (the rate determining step)



The rate was measured at various temperatures and for the reaction:

$$\ln k = \frac{-9662}{T} + 29.82 \quad \text{was given}$$

in which T is the temperature in °K

k = velocity constant (natural log-sec)

The rate constants are summarized in Table I along with the values obtained by the other authors. Table II shows a compilation of pertinent equilibrium data available.

Rees and Hudleston³ (1931), working with sodium silicofluoride at 20°C, determined the rate and equilibrium constants. They also contend that the mechanism proposed earlier by Hudleston and Bassett was satisfactory.

2. Hudleston, J. and Bassett, H., J. Chem. Soc. (1921) p. 403.

3. Rees, A. G. and Hudleston, J. L., J. Chem. Soc. (1921) p. 1334.

Table I

A Summary of All Kinetics Data Available on the
Hydrolysis of the Silicofluoride Ion

Author	Temp. °C	Rate Constant k <u>Common Logs and Seconds</u>	Rate Equation
Hudleston and Bassett (1921)	15.2	.0109	$\ln k = \frac{-9662}{T} + 29.83$
	15.0	.0104	
	25.0	.0326	
	0	.00167	
Rees and Hudleston (1931)	20.0	.0163	
Ryss and Slutskaya (1940)	10	.00458	$\log k = \frac{-4248}{T} + 13.033$
	10	.00460	
	20	.0154	
	30	.0447	
	40	.149	
	50	.566	
Graf (1955)	1.0 ± .3	.0014	$\ln k = \frac{-9840}{T} + 29.44$
	10.0 ± .3	.00498	
	20.0 ± .3	.0156	
	25.0 ± .3	.0327	
	30.0 ± .3	.0467	

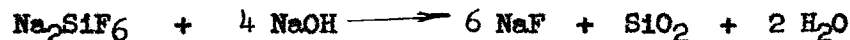
Table IIA Summary of All Equilibrium Data Available

<u>Author</u>	<u>Temp. °C</u>	<u>Equilibrium Constant, k</u>
Ruiss and Bakina (1936)	20	1.2×10^{-27}
I. G. Ryss (1951)	15	1.46×10^{-27}
	20	2.50×10^{-27}
	25	4.10×10^{-27}
	30	6.62×10^{-27}
	35	10.2×10^{-27}
I. G. Ryss (1946)	11	5.4×10^{-27}
Kubelka and Pristoupil (1931)	23	2×10^{-27}

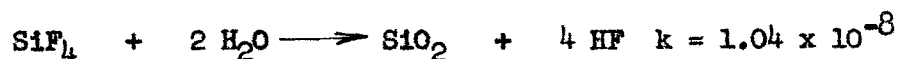
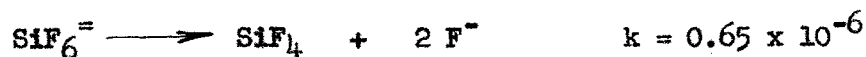
Kubelka and Pristoupil¹ (1931) working with fluosillicic acid proposed the following hydrolysis equilibrium:



and the overall reaction:



J. G. Ryss⁴ (1946) agrees with Hudleston and Bassett² and Rees and Hudleston³ in that he gives the following mechanism:



and the overall reaction:



Ryss⁴ determined the equilibrium constants for both steps in the proposed mechanism and for the overall reaction at 11°C.

Ryss and Slutskaya⁵ (1940) derive from their data,

$$\ln k = \frac{-4248}{T} + 13.033$$

1. p. 391

4. Ryss, I. G., J. Gen. Chem. (USSR) 16 (1946) p. 331

2. p. 403

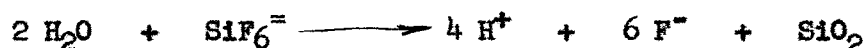
3. p. 1334

4. p. 331

5. Ryss, I. G. and Slutskaya M. M., J. Phys. Chem. (USSR) 14 (1940) p. 701

The rate constants were determined between 10 and 50°C and the rate controlling step was shown to follow a first order mechanism.

These authors agree with Kubelka and Pristoupil's¹ mechanism:



Ryss⁶ recalculated the equilibrium constant using the latest values of the sodium fluoride activity.

Ruiss and Bakina⁷ give the equilibrium constant from pH measurement of mixtures of sodium fluoride, sodium silicofluoride, silica, and water.

C. Discussion of Previous Work

Rees and Hudleston³ state that,

"They eliminated the possibility of the rate determining step as being a hydrolysis by determining the rate constant in mixed media-water containing up to 20 percent alcohol or acetone, but the data was not published due to a slight error caused by the indicator used"

They did show one rate constant and how it was increased in the mixed media-water. Their conclusion is not consistent with Glasstone, Laidler, and Eyring⁸ who have shown that hydrolysis reactions involving a neutral solvent molecule, should increase when the dielectric strength of the medium is decreased as would be the case in alcohol-water mixtures.

1. p. 391

6. Ryss, I. G. Zhur. Fiz. Khim 25, 655 (1951).

7. Ruiss, I. G. and Bakina, N. P., Compt. rend. acad. SCI. (URSS) N.S. 2 22, 1936.

3. p. 1335

8. Glasstone, S., Laidler, K. J., and Eyring, H., The Theory of Rate Processes, (1941) p. 442.

Rees and Hudleston³ also determined the rate constants in the presence of non-participating ions. Their data indicates that the rate constant was not affected in dilute solutions of electrolytes. However, they conclude that, "the data constitutes the most searching proof of the correctness of the postulated mechanism." According to modern theory, a constant rate constant in low concentrations (less than .01M) of non-participating ions indicates that the sum of the charges ($Z_A Z_B$) of the reacting particles in the rate determining step should equal zero.⁸ Furthermore, if $Z_A Z_B$ is zero, the rate determining step must involve a neutral molecule.

Rees and Hudleston also state that their mechanism,

"Is in agreement with the modern theory of hydrolysis (Sidgwick, "The Electronic Theory of Valency" 1929, pp. 156-158), according to which the SiF_6^- ion would not be open to attack since the co-ordination number of the silicon atom is fully satisfied, whereas the silicon tetrafluoride can co-ordinate two molecules of water, the silicon atom acting as acceptor, after which hydrogen fluoride would split off from the resulting complex."

However, Hudleston and Bassett² never proved that SiF_4 did exist in sodium silicofluoride solution; they merely stated that a small amount must be present in solution.

Hudleston and Bassett² base their mechanism on the fact,

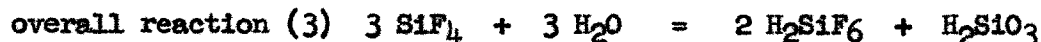
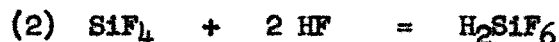
"That since the following reactions occur when silicon tetrafluoride is passed into water:

3. p. 1337

8. p. 429

2. p. 408

2. p. 412



the reactions must be reversible, since hydrofluosilicic acid is formed equally by the action of silicon tetrafluoride on water and of hydrofluoric acid on silica, and also hydrofluosilicic acid with sufficient alkali yields, ultimately, sodium fluoride and silicic acid."

They, therefore, conclude that "all four substances must be present in finite, even though possibly very small, concentrations in these solutions." However, silicon tetrafluoride was never chemically shown to exist in silicofluoride solutions or water.

None of the other authors presented any experimental or theoretical proof of their mechanisms.

D. Experimental Method

The method adopted was similar to that used by Hudleston and Bassett except that quantities were larger.² Into each of a series of 250 cc flasks was measured the same amount of sodium silicofluoride, as the salt, which was allowed sufficient time to dissolve completely.* Into each of another series of flasks were measured volumetrically various amounts of NaOH but not enough for complete neutralization of the sodium silicofluoride. The sodium silicofluoride solution was poured into a 600 cc wax-lined beaker that was provided with a stirrer and pH electrodes

2. p. 404

*Since dissolution was extremely slow in most cases, the flasks were heated in the temperature bath to increase the dissolving rate.

after both solutions were brought to constant temperature. The alkali was then poured rapidly into the beaker and the time required for neutralization (pH 8 on the pH meter) was determined for each. The amount of alkali required for complete neutralization of the silicofluoride was determined by mixing various proportions of the reagents together in the same concentrations as used in determining the rate constants so that the equilibrium curve could be obtained. Since the concentration of the silicofluoride affected the amount of alkali slightly, equilibrium curves for each different run were required. Previous authors used the back titration method, but the reaction is rather slow at low temperatures and thus the possibility of reaching a false end-point persists.

The time, t , from the moment of mixing to the instant a pH of 8.00 was reached was measured with a stopwatch. If the amount of silicofluoride required N cc of alkali for permanent neutralization, and only a smaller quantity, n cc., had been put into the beaker, then at the moment when the pH fell to 8.00, the amount of silicofluoride ion present was equivalent to $(N-n)$ cc of alkali. Thus the fraction $(N-n)/N = R$ measures the proportion of the stoichiometrical amount of fluosilicate existing at the time t . According to the ordinary unimolecular law, $\log R$ is a linear function of t , and by plotting $\log R$ versus t , the rate constants may be obtained.

The above method of following the course of reaction is based on the rate at which the hydrofluoric acid is produced from the decomposition of the activated complex. Since the decomposition is rapid along with the

neutralization of the hydrofluoric acid by the alkali, the reaction rate that is actually being followed is the rate determining step, or the activation of the silicofluoride ion.

E. Discussion

The rate constants were redetermined and found to check those of the previous authors with the expected results.

Using the new values of the rate constants the temperature can be related to the rate constant, by the integrated form of the Arrhenius Equation,⁸

$$\ln k = -E/RT + C$$

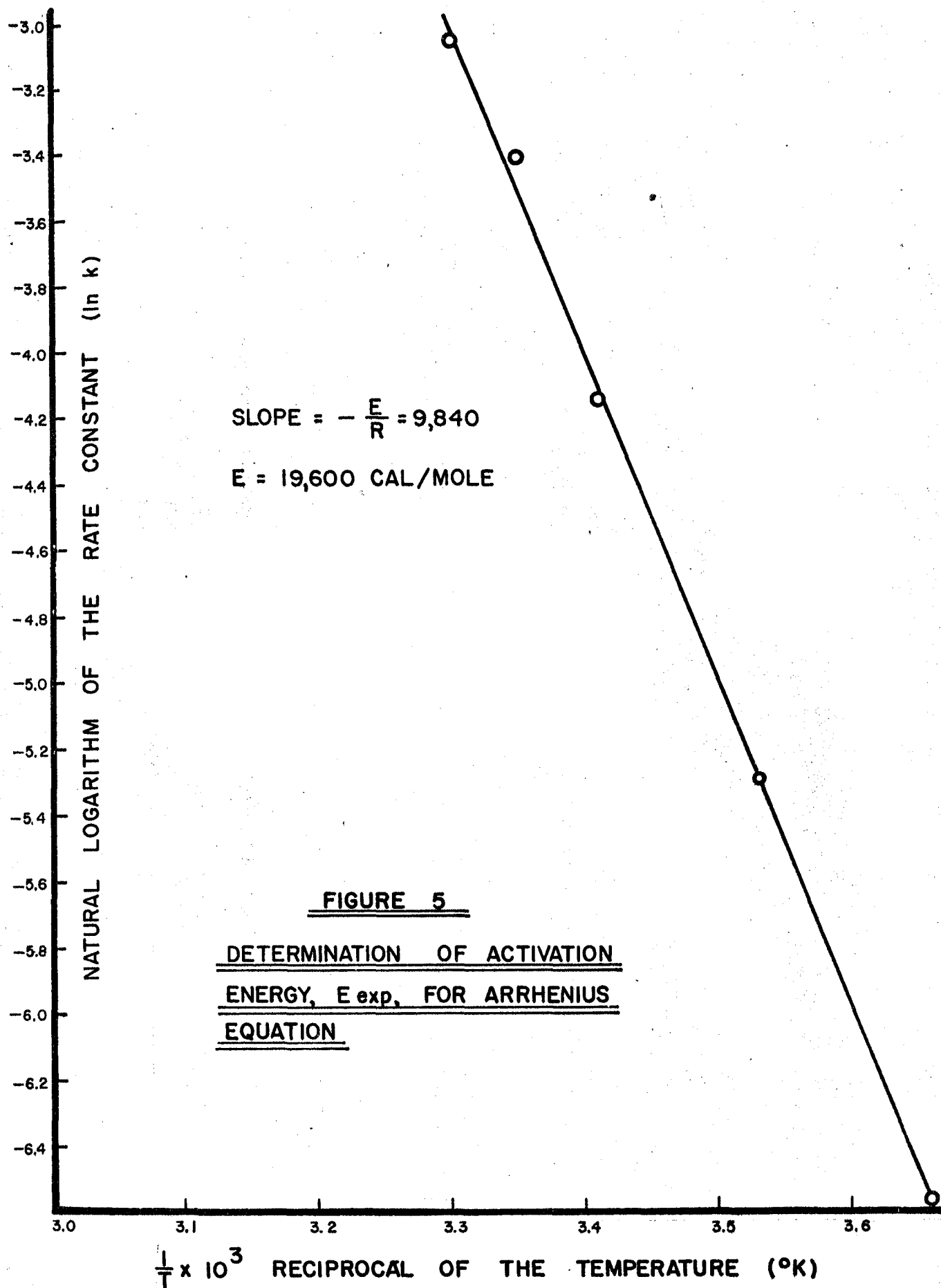
where,

- k = rate constant
- E = activation energy in cal. per mole
- R = gas constant
- T = temperature in °K
- C = constant

The value $-E/R$ is equal to the slope of the curve $1/T$ versus $\ln k$ as shown in Figure 5. By substitution of data for several temperatures into the equation, the constant C can be evaluated and the complete equation may be written:

$$\ln k = \frac{-9840}{T} + 29.44$$

8. p. 1



Glasstone, Laidler, and Eyring⁸ have shown that the relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant should be a straight line of positive slope for reactions involving a neutral molecule and an ion. In Figure 3, such a curve has been obtained from experimental data on the silicofluoride ion hydrolysis reaction.

Glasstone, Laidler, and Eyring⁸ have shown that the product of the charges of the reacting particles, $Z_A Z_B$, in the rate determining step, can be determined theoretically by evaluation of the entropy factor.

Since,

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

where,

k = rate constant

A = frequency factor

$e^{-E/R}$ = experimentally determined value from the modified Arrhenius Equation which has already been determined

T = temperature in °K

for 1°C then

$$A = \frac{k}{e^{-E/RT}} = \frac{.0014 \times 2.303}{e^{-19350/1.99 \times 274}} = 8.22 \times 10^{12}$$

and $k = \frac{KT}{h} = e^{4S/R} (e^{-E/RT})$

but $\frac{k}{e^{-E/RT}} = A = 8.22 \times 10^{12}$

8. p. 439

8. p. 435

$$\text{and } \frac{KT}{h} = 2.085 \times 10^{10} T$$

$$\text{and } e^{\Delta S/R} = \text{entropy factor}$$

$$\text{Therefore, } e^{\Delta S/R} = \frac{A}{(KT/h)} = \frac{8.22 \times 10^{12}}{2.085 \times 10^{10} \times 274} = 1.44$$

The average of all entropy factors calculated is 1.59.

Glasstone, Laidler and Eyring⁸ have shown that the entropy factor should be about 1 for an ionic reaction in which the product of the charges on the reactants is equal to zero. This appears to be the case here since the entropy factor is 1.59.

Frost and Pearson¹⁰ have tabulated the frequency factors for many neutral molecule-ion type reactions. The frequency factor varied from 10^7 to 7×10^{12} . Above this author has shown that a frequency factor of 8×10^{12} for the silicofluoride hydrolysis reaction. This author's frequency factor is somewhat higher than most of those listed by Frost and Pearson as would be expected if the rate determining step were the formation of an activated complex between the water and the silicofluoride ion, since there would be more encounters between the two, due to the fact that the media is water.

The effect of various low ionic strength solutions on the reaction rate constant was shown by Rees and Hudleston³ and also by this author to have no measurable effect in dilute solutions. Glasstone, Laidler

8. p. 435

10. Frost, A. A. and Pearson, R. G., Kinetics and Mechanisms (1953) p. 136.

3. p. 1337

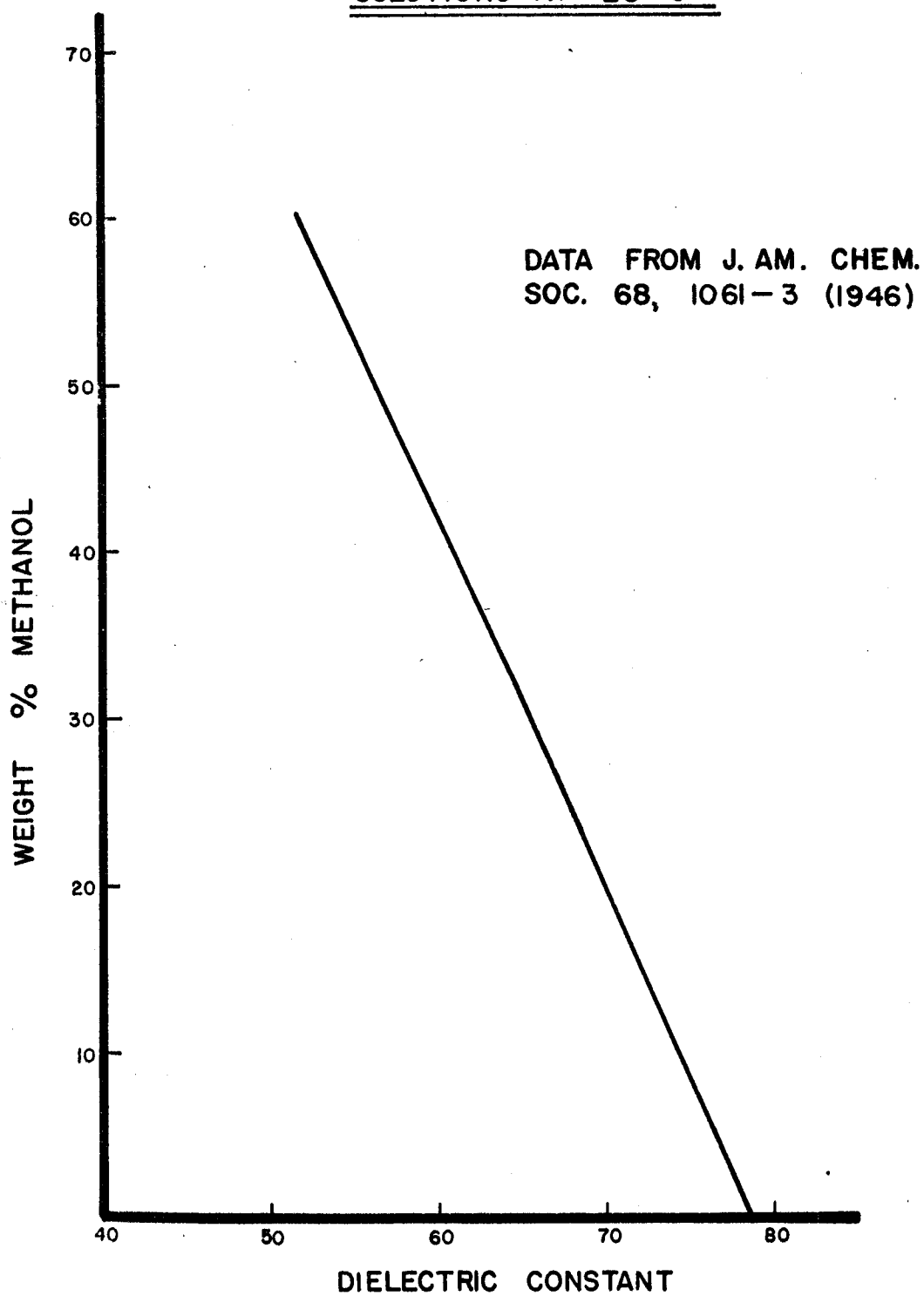
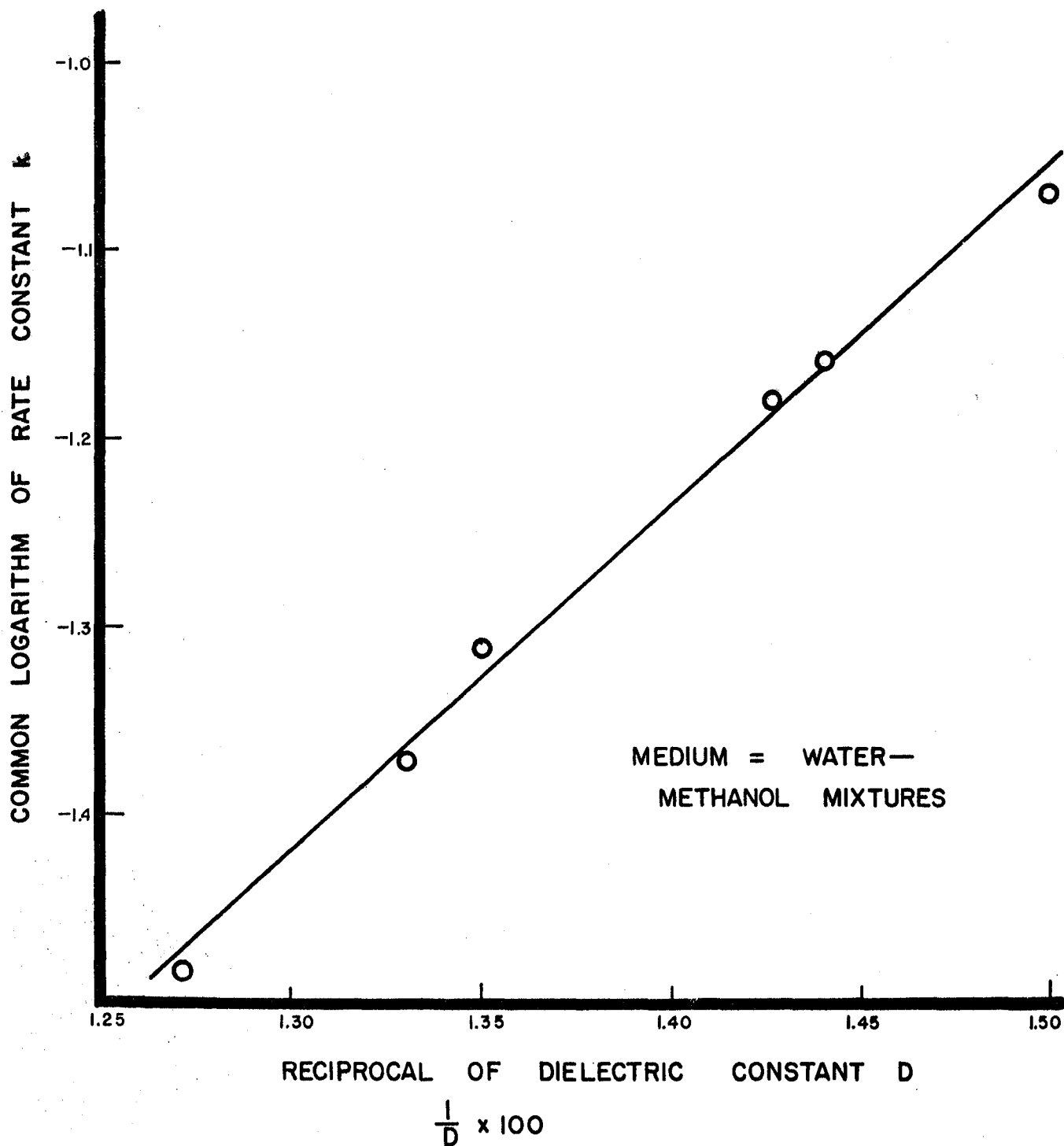
FIGURE 6DIELECTRIC CONSTANT
OF METHANOL - WATER
SOLUTIONS AT 25° C

FIGURE 7

VARIATION OF THE SPECIFIC RATE OF THE
SILICOFLUORIDE HYDROLYSIS REACTION WITH
THE DIELECTRIC CONSTANT OF THE MEDIUM



and Eyring have shown that when this is the case that $Z_A Z_B$, the product of the charges on the reactants in the rate determining step, should be equal to zero.

In higher concentrations of electrolytes, however, the rate constant is effected by the ionic strength since it changes the activity coefficients of the reactants. The above mentioned authors have shown that if the Kirkwood and electrostatic terms are small, then, for a medium of definite dielectric constant, the following relationship holds fairly well:

$$\log k = \log k_p + b\mu$$

in which

k = specific reaction rate constant obtained

k_p = specific reaction rate constant extrapolated to zero ionic strength

μ = ionic strength

b = a constant consisting of several empirical constants

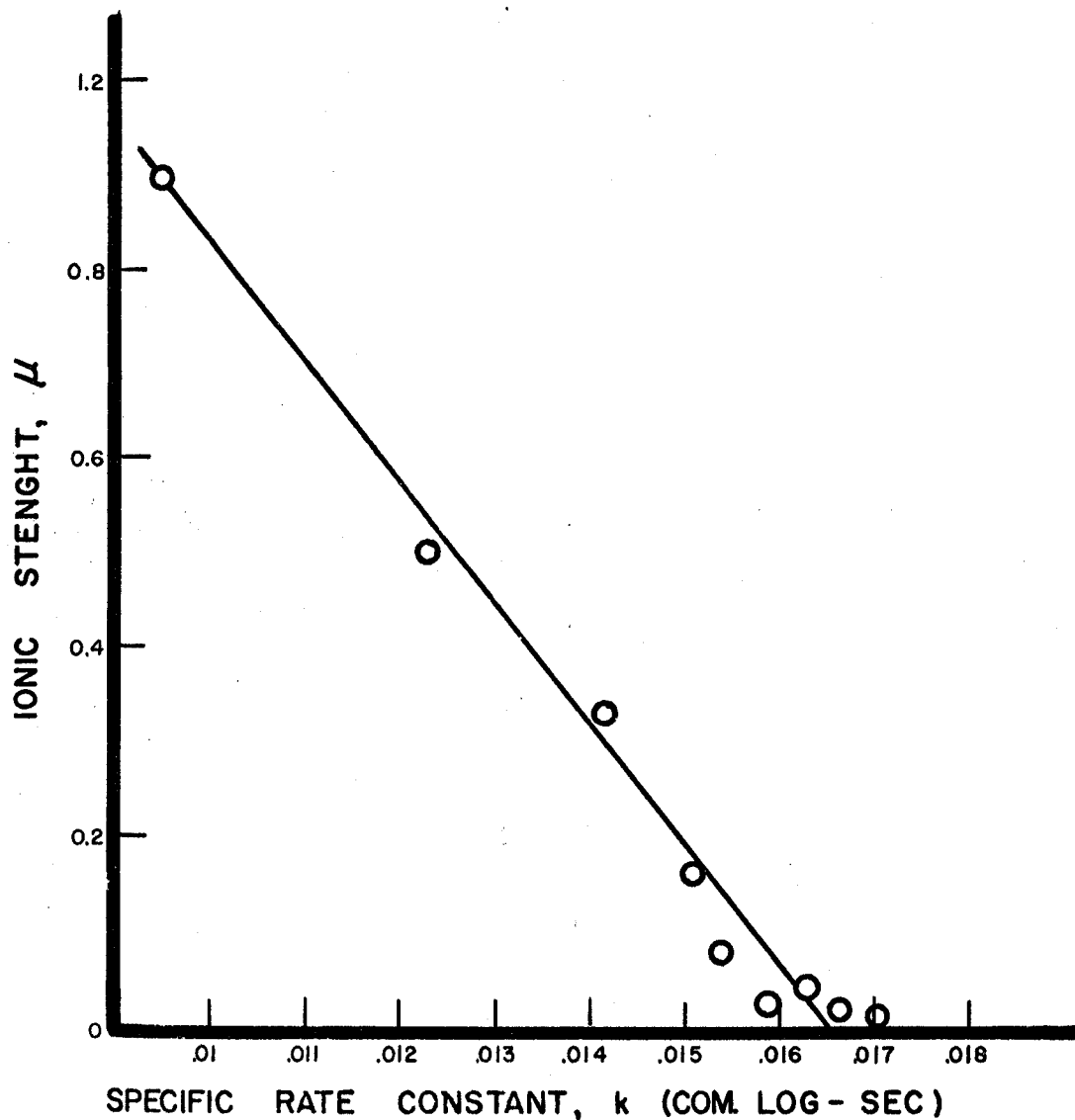
If $b\mu$ is small, then all terms involving powers of b higher than the first may be neglected so that the relationship reduces to

$$k = k_p (1 + b\mu)$$

Under these conditions a plot of k against μ should be a straight line which is shown in Figure 8 to be so for the silicofluoride hydrolysis reaction.

FIGURE 8

THE EFFECT OF THE IONIC STRENGTH
OF THE MEDIA ON THE SPECIFIC
RATE CONSTANT, k



Previous authors have not calculated the entropy factor for the reaction nor have they determined the rates constants in high ionic strength mediums.

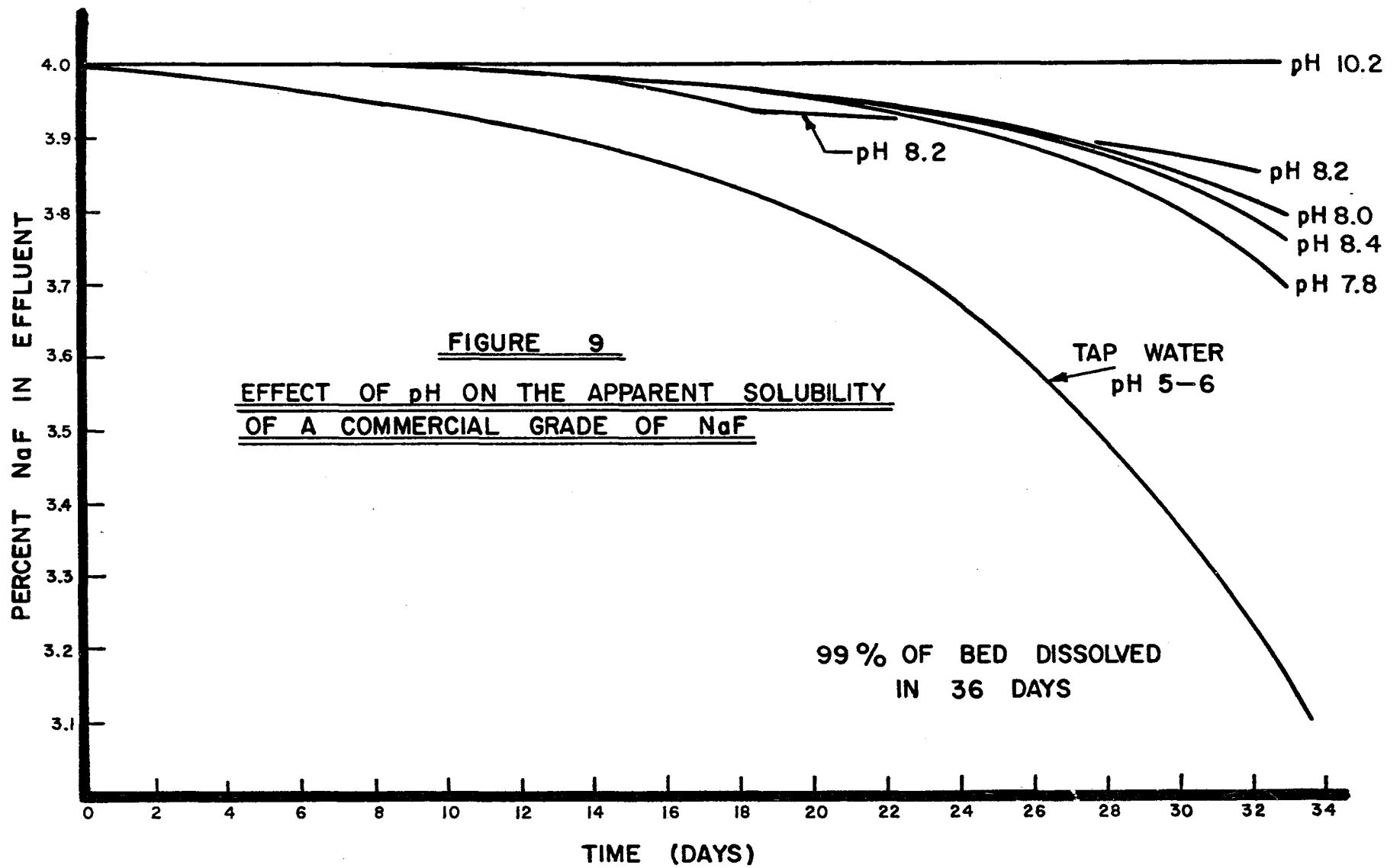
The rate constants were also determined by using sodium carbonate as alkali, but due to the side reactions occurring simultaneously, consistent results were not obtainable. However, the results were in the same order of magnitude as those obtained by using caustic as alkali which this author believes to be sufficient in this problem.

In the introduction it was pointed out that the equilibrium shift could not fully explain the reason for the required influent pH of 10.2 before constant solubility was had. It was mentioned that silica gel could cause the problem encountered. Figure 9 shows the effect of several pH influents on the apparent solubility of a commercial grade of sodium fluoride. It can clearly be seen that in the pH range of 7.8-8.4 some improvement was noted but it took a 10.2 pH for complete solubility. Since the silicofluoride ion is being hydrolyzed in the pH range of 7.8-8.4 as Figure 9 indicates, then the formation of the SiO_2 must be the offender in this alkalinity range.

Silica can become "activated" when it is produced under certain conditions. Some of the variables are:¹¹

1. The concentration of silica
2. Temperature
3. Acid used
4. Hydrogen ion concentration
5. Concentration of other materials present

11. Hurd, Charles B., "Theories of the Mechanism of the Setting of Silicic Acid Gels," Chem. Reviews, 22, (1938) p. 407.



Alexander¹² has pointed out that the polymerization of the activated silica to form a gel is catalyzed by the fluoride ion at moderate pH's. Gelation of silica is not a phenomenon that is very exact and depends on many factors as has been pointed out. Since no data exists for silica gel formation in the particular environment that this thesis is concerned with, the data available must be examined to show the trend of the situation only.

Hurd¹³ has stated that in general, the effect of salts on the silica gelation is not particularly marked unless present in great quantity. This is the case with the commercial sodium fluoride that has about one percent sodium silicofluoride. The sodium fluoride is in great excess compared to the silica formed and also the catalysis effect of the fluoride ion is present.

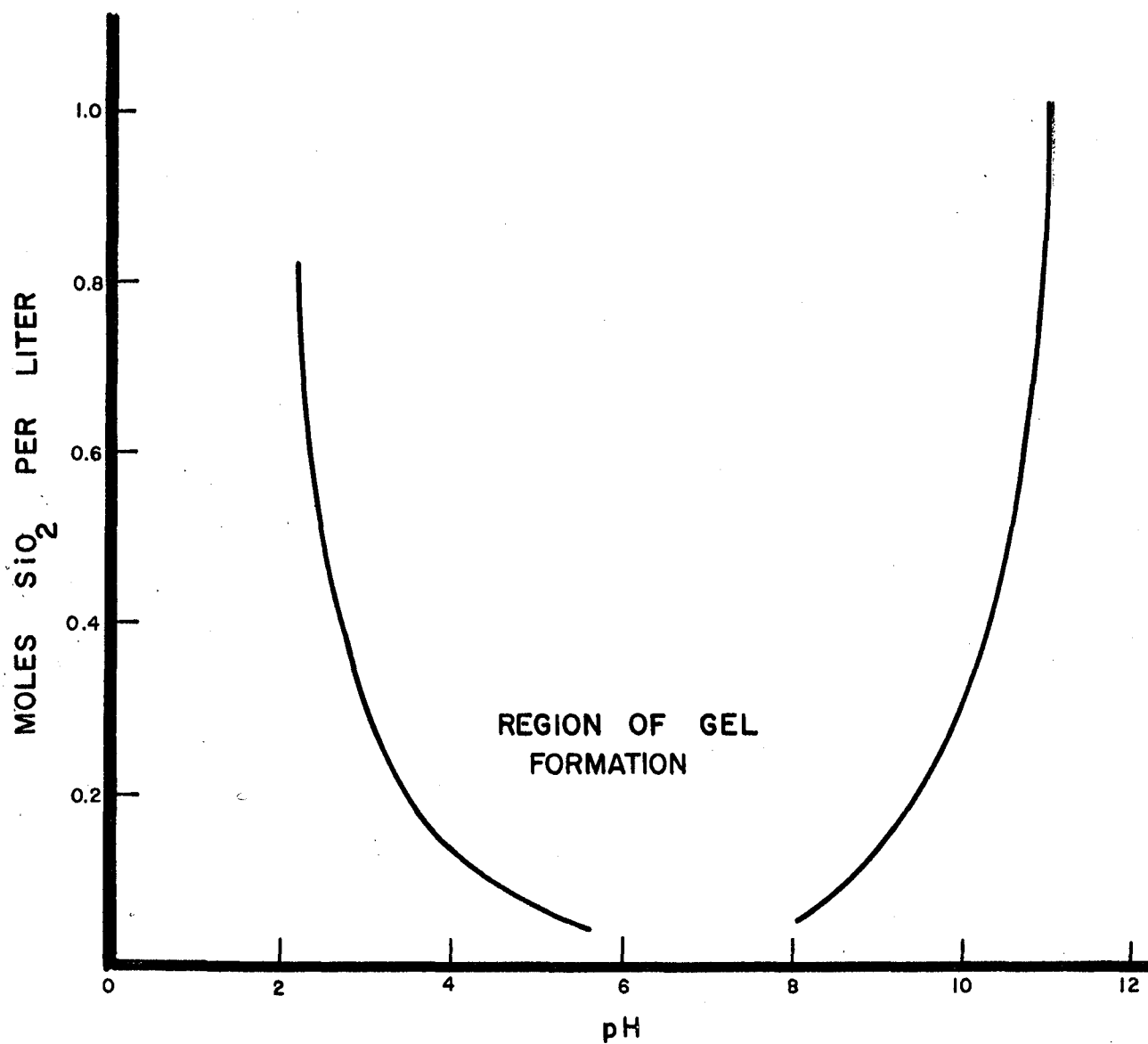
Figure 10 shows the region of gel formation for various concentrations of silica for a particular system. The trend can clearly be seen as to what effect pH does have.

12. Alexander, G. G., "The Polymerization of Monosilicic Acid," J. Am. Chem. Soc. 76 (1954) p. 2094.

11. p. 408

FIGURE 10
LIMITING pH FOR GEL FORMATION

DATA FROM - J. PHYS. CHEM.
35, 596 (1931)



F. Conclusions

The effect of varying the dielectric constant of the medium has been shown by this author to be consistent with modern theory as outlined by Glasstone, Laidler, and Eyring⁸ who show that ions of the opposite sign or a neutral molecule must be involved in the rate determining step. Since reactions of the silicofluoride ion with any positive ions in solution is highly improbable, the neutral molecule mechanism must be present.

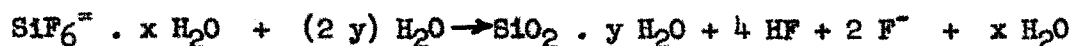
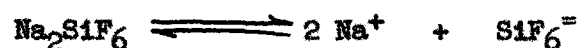
Studies of the rate constant in various low ionic strength solutions indicate that the product of the charges of the reacting particles in the rate determining step, $Z_A Z_B$, must equal zero so that a neutral molecule-ion reaction mechanism theory is further strengthened.

In high ionic concentration solutions, a linear relationship between the rate constant and the ionic strength has also been shown consistent with the neutral molecule-ion reaction mechanism.

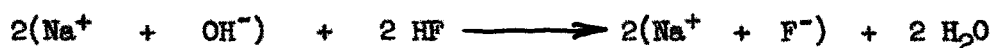
The entropy factor was evaluated for the reaction and it was shown to be very close to the theoretical expected value for the proposed theory.

This author, therefore, feels that this data and the calculations show in this thesis constitute overwhelming proof for the activated complex formation of water and the silicofluoride ion theory as shown in the following equations:

8. p. 442



followed by the rapid neutralization of the HF by the alkali present



In this mechanism, x and y remain unknown due to the difficulty of determining their exact values.

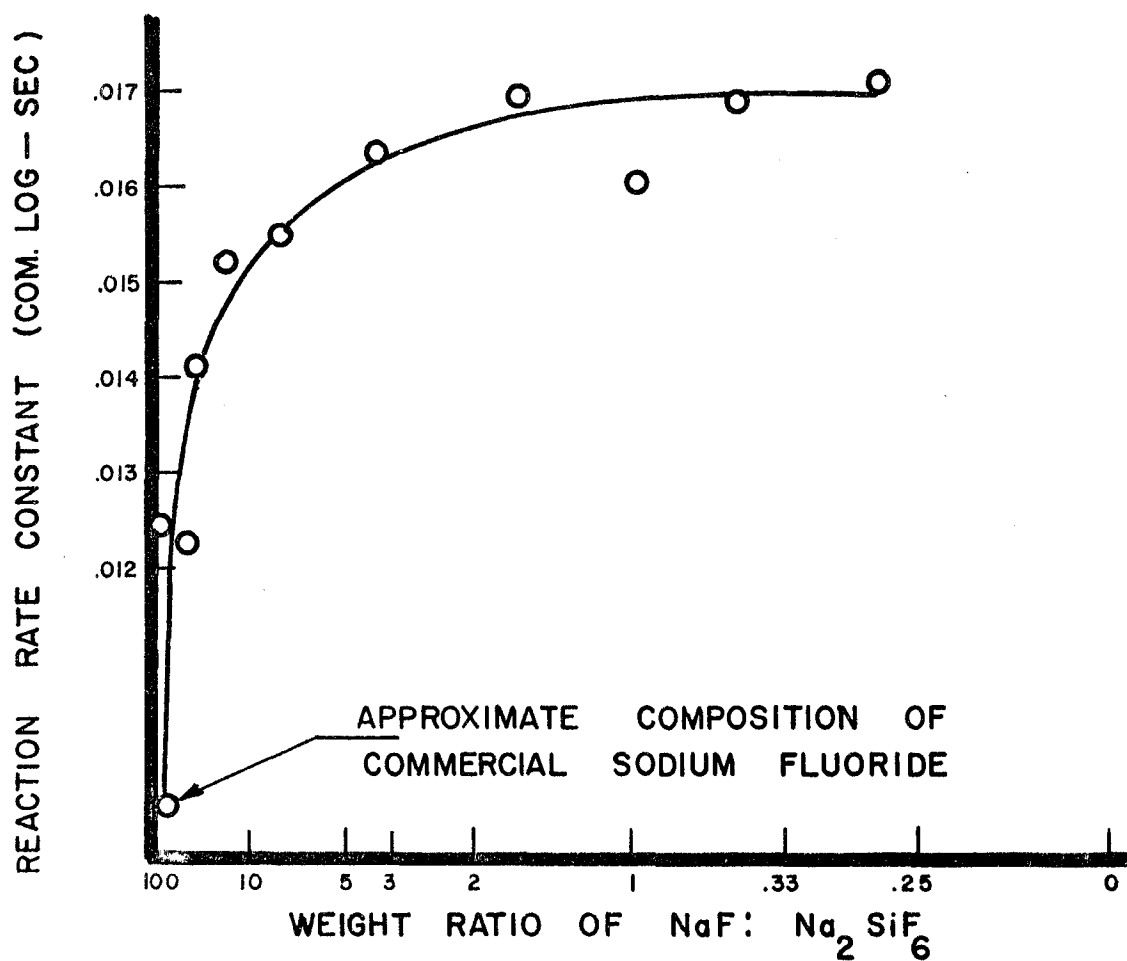
The above reaction then would be pseudo-unimolecular, since the water is in large excess.

The effect of a large amount of sodium fluoride, as exists in a commercial grade of sodium fluoride has been shown in Figure 11 to decrease the rate of hydrolysis of the silicofluoride ion to about one-half of its normal value.

With sodium carbonate as alkali, reaction rates comparable to those obtained with caustic were found which indicates that the hydrolysis reaction proceeds at the same rate.

The reaction with caustic or carbonate proceed at such a rate that it would never be a limiting factor in a sodium fluoride saturator since solution rates of the sodium fluoride are much slower.

FIGURE II
EFFECT OF SODIUM FLUORIDE
CONCENTRATION ON THE
REACTION RATE AT 20°C



By calculations, it has been shown that the equilibrium shift that occurs from the presence of the sodium silicofluoride impurity does not account entirely for the minimum alkalinity, pH 10.2, that is required for complete dissolution. The only other contributing cause is the formation of silica gel which was shown to be possible in the pH range of 6 to about 10.

G. Recommendations

For a constant strength sodium fluoride solution from a saturator utilizing commercial sodium fluoride containing sodium silicofluoride impurity, an alkaline influent (pH = 10.2 minimum) must be maintained constantly in order to hydrolyze the impurity and to prevent activated silica formation.

Although the rate constants with sodium carbonate were not consistent and only the mention of the fact that the constants are in the same range as those obtained by using sodium hydroxide is made, this author feels that this is sufficient from the practical aspect. However, from an academic point of view, more work on the determination of the rate constants for sodium carbonate might be enlightening because it affords a possible method of evaluating the rate of hydrolysis of the sodium carbonate since the rate of the silicofluoride ion hydrolysis includes the rate of hydrolysis of the unhydrolyzed sodium carbonate too.

APPENDIXTable IIIEquilibrium Study

.00186 Molar Na_2SiF_6
 .100 gm Na_2SiF_6
 350 ml Total Volume
 .3182 N NaOH

<u>ML</u> <u>NaOH</u>	<u>1°C pH</u> <u>After 24 Hrs</u>	<u>10°C</u> <u>pH</u>	<u>20°C</u> <u>pH</u>	<u>30°C</u> <u>pH</u>	<u>Molar</u> <u>Ratio</u>	<u>25°C</u>
1	3.45	3.53	3.35	3.50	.60	3.38
2	3.88	3.88	3.60	3.70	1.20	3.66
3	4.20	4.13	3.80	3.93	1.80	3.90
4	4.44	4.35	3.90	4.11	2.40	4.11
5	4.65	4.58	4.15	4.32	3.00	4.33
6	4.98	4.90	4.40	4.67	3.60	4.70
6.2	5.20	5.13	5.03	5.03	3.72	5.02
6.4	5.05	4.95	4.75	4.80	3.84	4.81
6.6	5.47	5.43	5.30	5.47	3.96	5.45
6.8	8.25	8.25	7.60	7.35	4.08	6.63
7.0	9.80	--	--	--	4.20	--
7.2	10.00	9.80	9.50	9.45	4.32	9.48
7.4	10.17	10.05	9.70	9.65	4.43	9.65
8.0	10.80	10.53	10.20	10.10	4.80	10.15

Table IV
Equilibrium Study

.300 gm Sodium Silicofluoride
.1155N NaOH
Total Volume = 350 ml

<u>Ml .1155N</u> <u>NaOH</u>	<u>Molar Ratio</u> <u>NaOH/Na₂SiF₆</u>	<u>pH at</u> <u>1°C</u>	<u>pH at</u> <u>10°C</u>	<u>pH at</u> <u>20°C</u>	<u>pH at</u> <u>25°C</u>	<u>pH at</u> <u>30°C</u>
5	.36	3.50	3.55	3.73	3.72	3.63
10	.725	4.04	4.07	4.07	4.07	3.92
20	1.45	4.57	4.53	4.50	4.42	4.33
30	2.17	4.90	4.87	4.82	4.82	4.67
35	2.54	5.05	4.96	4.93	4.96	4.78
40	2.90	5.30	5.13	5.11	5.12	4.94
45	3.26	5.45	5.30	5.21	5.26	5.13
50	3.62	5.57	5.53	5.42	5.40	5.30
55	3.99	7.13	7.15	7.03	6.97	6.85
60	4.35	9.80	9.75	9.55	9.55	9.37
42	3.05	5.43	5.20	5.20	5.17	5.03
44	3.19	5.43	5.30	5.20	5.22	5.10
46	3.33	5.43	5.35	5.25	5.22	5.16
48	3.48	5.63	5.46	5.30	5.25	5.20
52	3.77	8.15	6.13	6.13	6.20	6.20
53	3.84	7.80	5.63	5.50	5.47	5.47
51	3.69	5.75	5.76	5.63	5.65	5.55
70	5.07	11.15	10.87	10.67	10.48	10.30
54	3.91	--	5.95	5.84	5.87	5.85

Table V
Equilibrium Study

.500 gm Na_2SiF_6
.1155N NaOH
350 ml Total Volume

<u>ml NaOH</u>	<u>1°C pH</u>	<u>Molar Ratio</u>	<u>10°C pH</u>	<u>20°C pH</u>	<u>25°C pH</u>	<u>30°C pH</u>
10	4.23	.435	4.25	4.06	4.04	4.00
20	4.85	.868	4.70	4.47	4.44	4.35
30	5.07	1.305	4.90	4.73	4.67	4.55
40	5.17	1.74	5.15	4.97	4.90	4.75
50	5.55	2.17	5.40	5.13	5.10	4.90
60	5.57	2.61	5.50	5.27	5.18	5.00
70	5.80	3.04	5.60	5.40	5.35	5.15
80	5.87	3.38	5.75	5.55	5.50	5.30
85	5.95	3.69	5.80	5.62	5.55	5.60
87	5.95	3.79	5.87	5.70	5.65	5.75
90	6.26	3.91	6.10	5.95	5.90	6.25
92	7.58	4.00	7.50	7.50	7.40	7.31
95	9.52	4.13	9.40	9.30	9.13	9.03
100	10.25	4.35	9.85	9.73	9.60	9.48

FIGURE 17

EQUILIBRIUM pH CURVES
1°C

EQUILIBRIUM pH

11
10
9
8
7
6
5
4
3

1 2 3 4 5 6

MOLAR RATIO $\text{NH}_4\text{OH} : \text{NH}_4\text{SiF}_6$

.0025M NH_4SiF_6

.0050M NH_4SiF_6

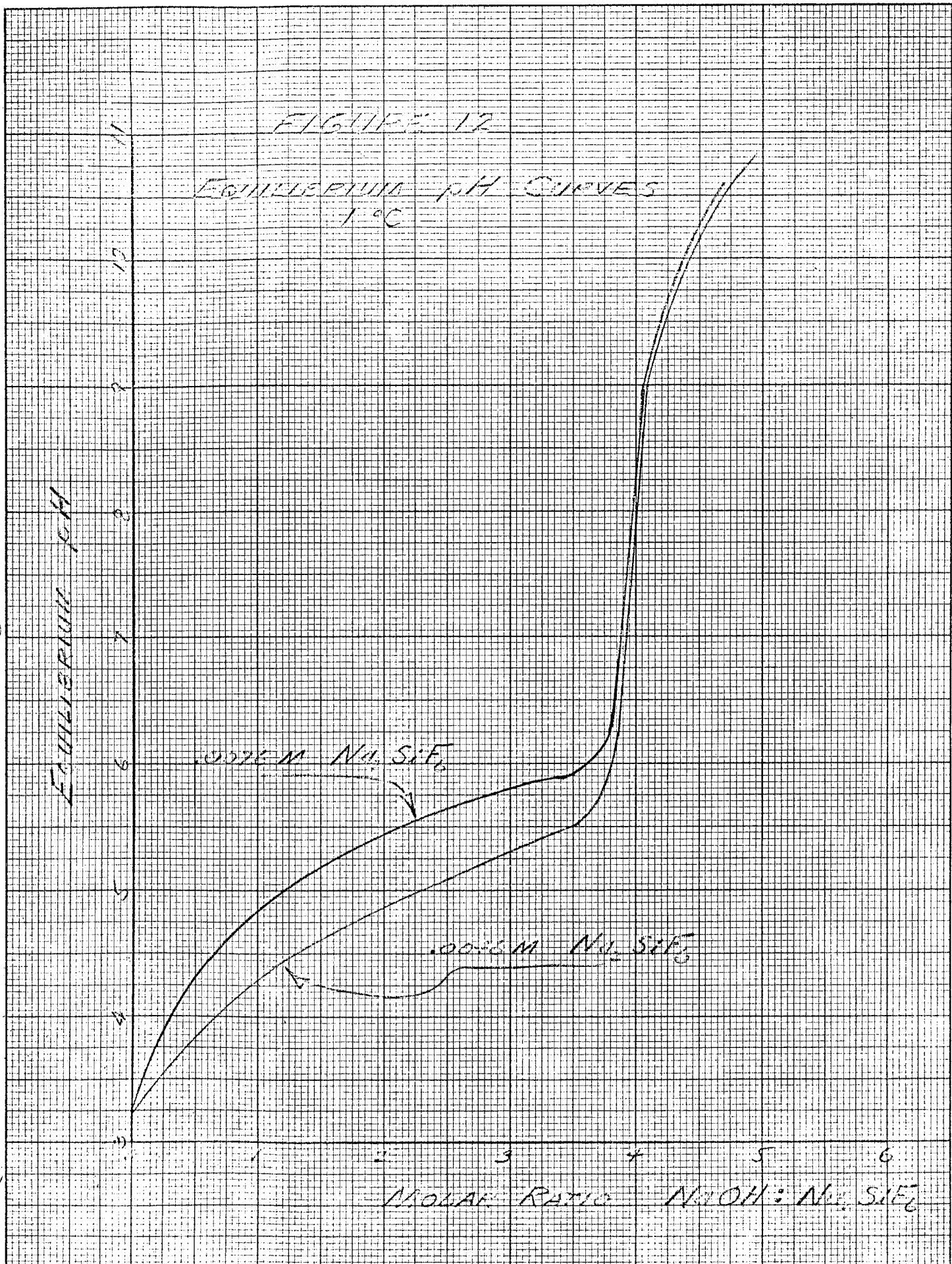


FIGURE 13

EQUILIBRIUM pH CURVES

10 °C

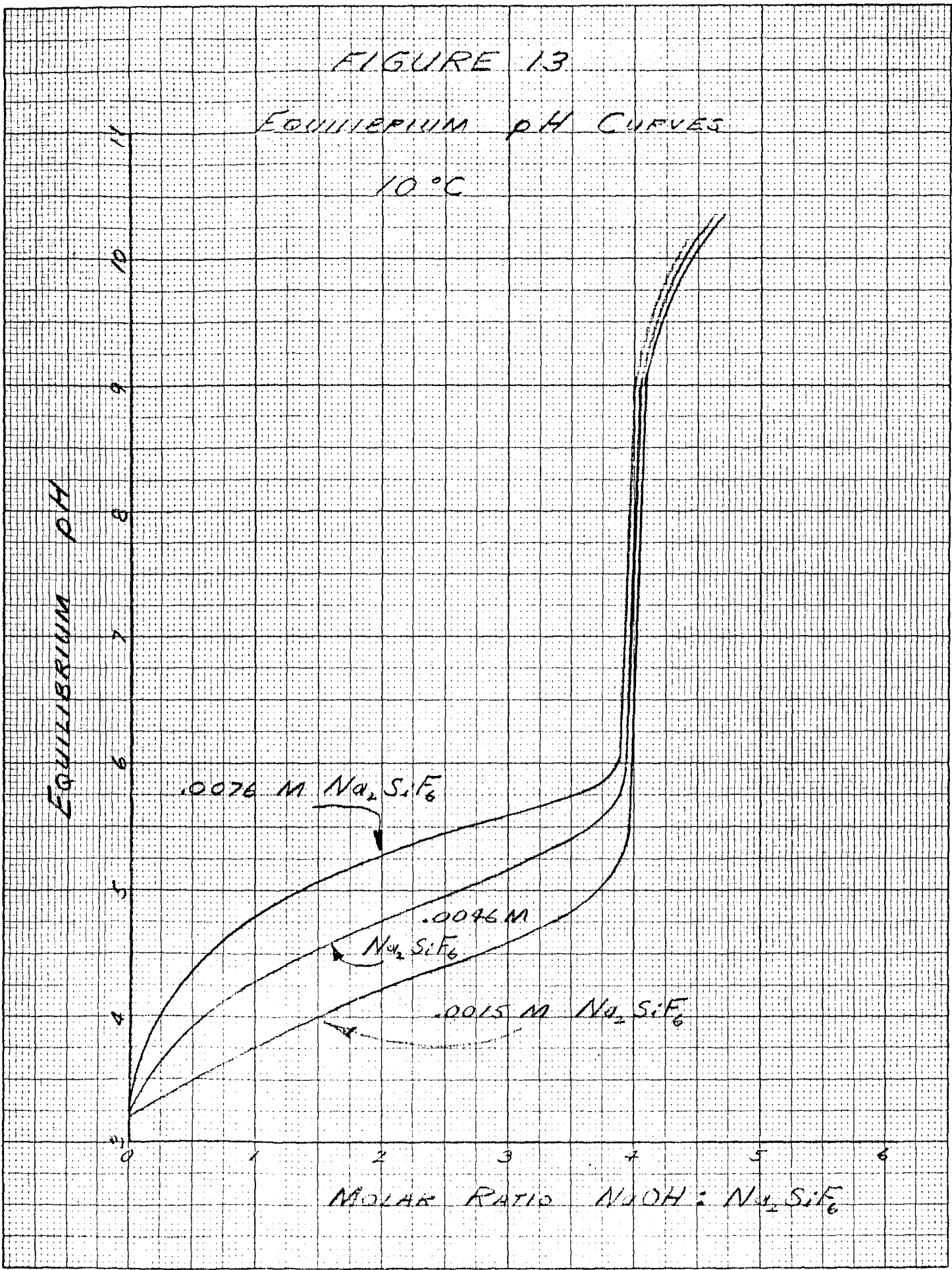


FIGURE 14

EQUILIBRIUM PH CURVES

20 °C

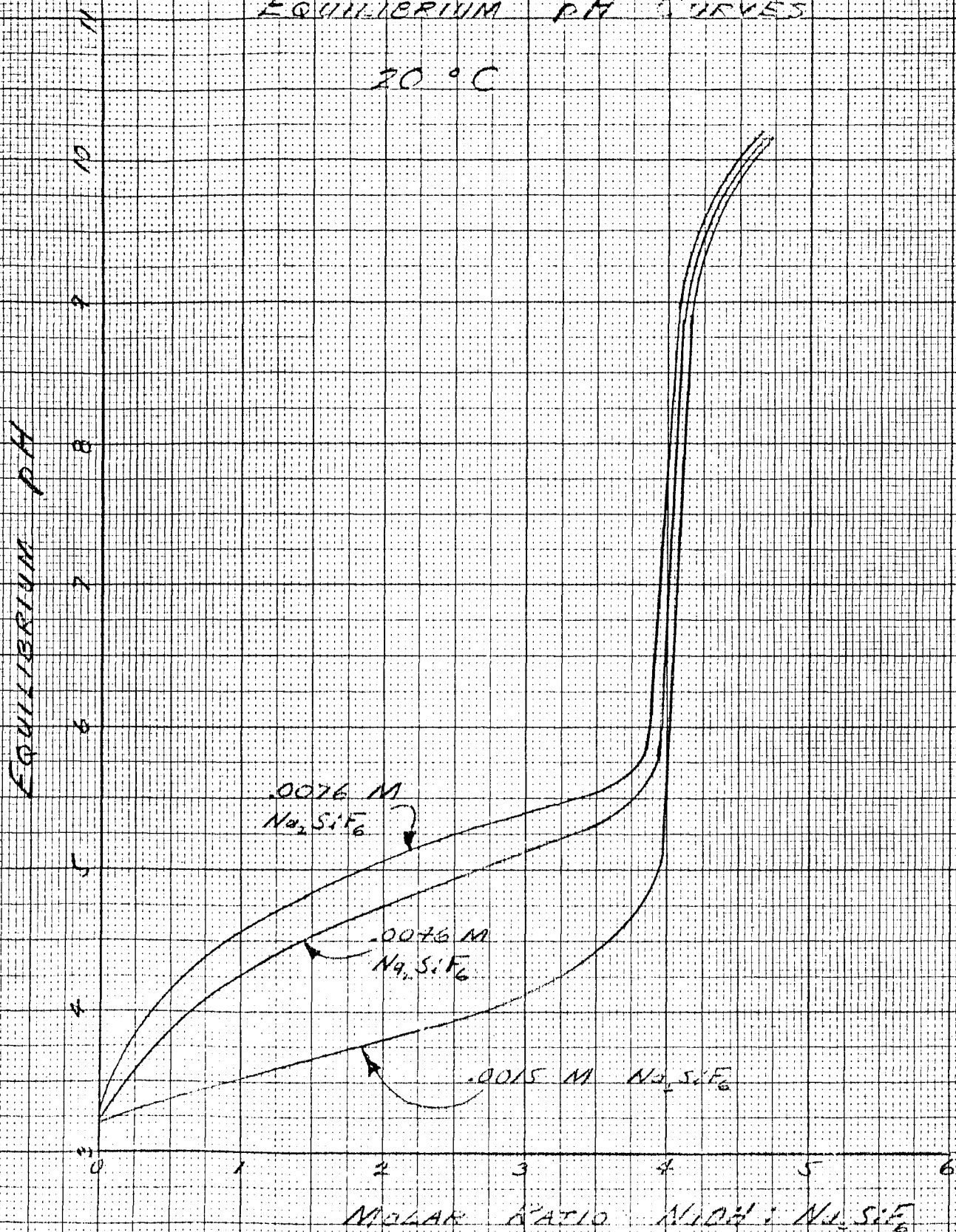
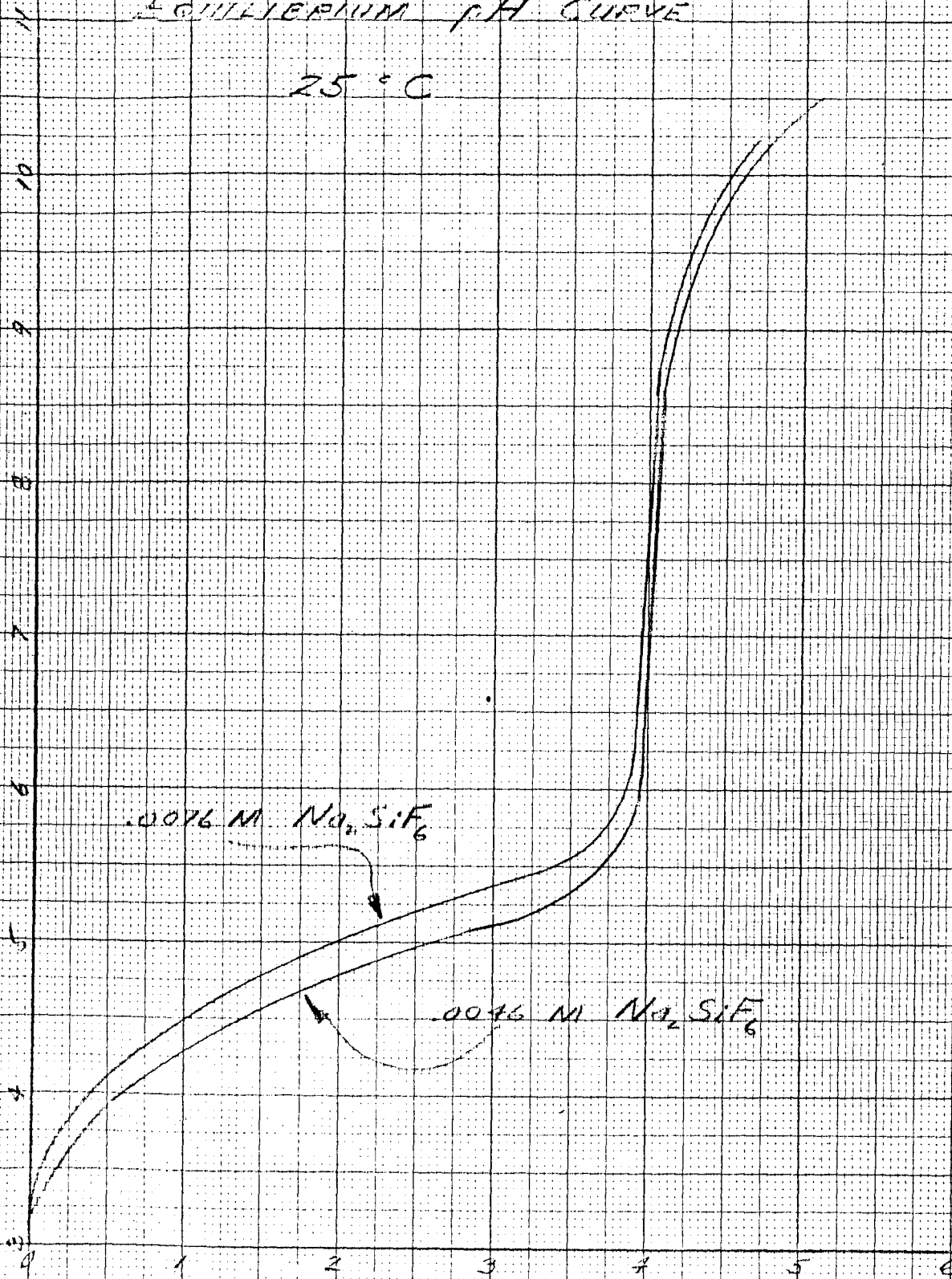


FIGURE 15

EQUILIBRIUM pH CURVE

25 °C

EQUILIBRIUM pH



0.0076 M Na₂SiF₆

0.0046 M Na₂SiF₆

MOLAR RATIO NaOH : Na₂SiF₆

FIGURE 16

EQUILIBRIUM pH CURVES

30 ° C

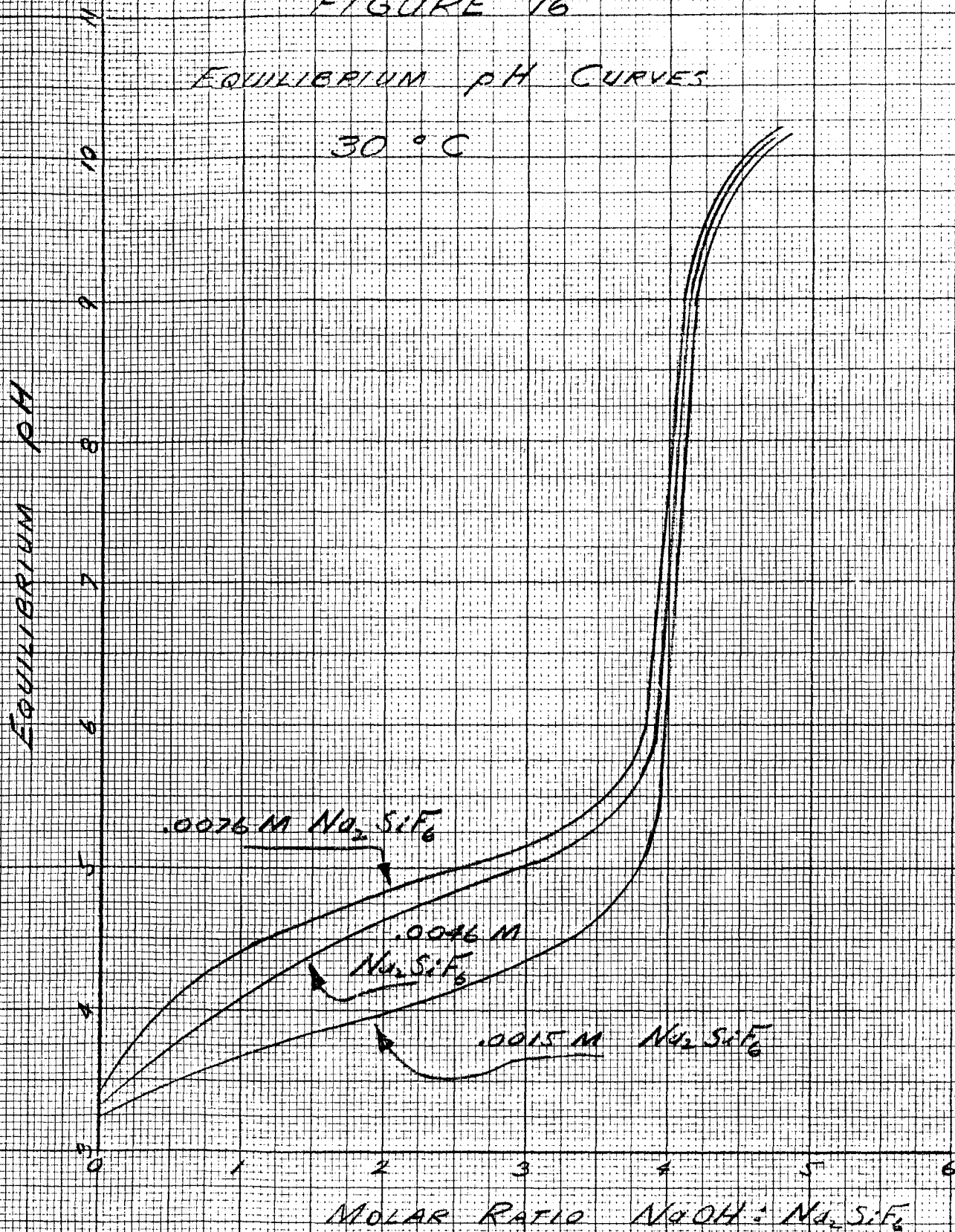


Table VIReaction Rate

25°C
 .300 gm Na₂SiF₆
 350 ml Total Volume
 .1103N NaOH

<u>Ml NaOH</u> <u>.1103 N</u>	<u>Time</u> <u>to pH 8</u>	<u>R</u>	<u>1 + log R</u>
10	--	--	--
10	--	--	--
15	1.1	.743	.871
15	1.2	--	--
20	3.7	.658	.818
20	3.5	--	--
25	5.7	.572	.757
25	5.7	--	--
30	8.0	.487	.687
30	8.1	--	--
35	10.8	.402	.605
35	10.7	--	--
40	13.9	.316	.500
40	13.5	--	--
45	17.8	.231	.363
45	17.4	--	--
50	24.0	.145	.161
50	24.2	--	--

FIGURE IV

DETERMINATION OF THE
RATE CONSTANT, k .

.0046 M NO_2SiF_6

25 °C

$k = .0344$

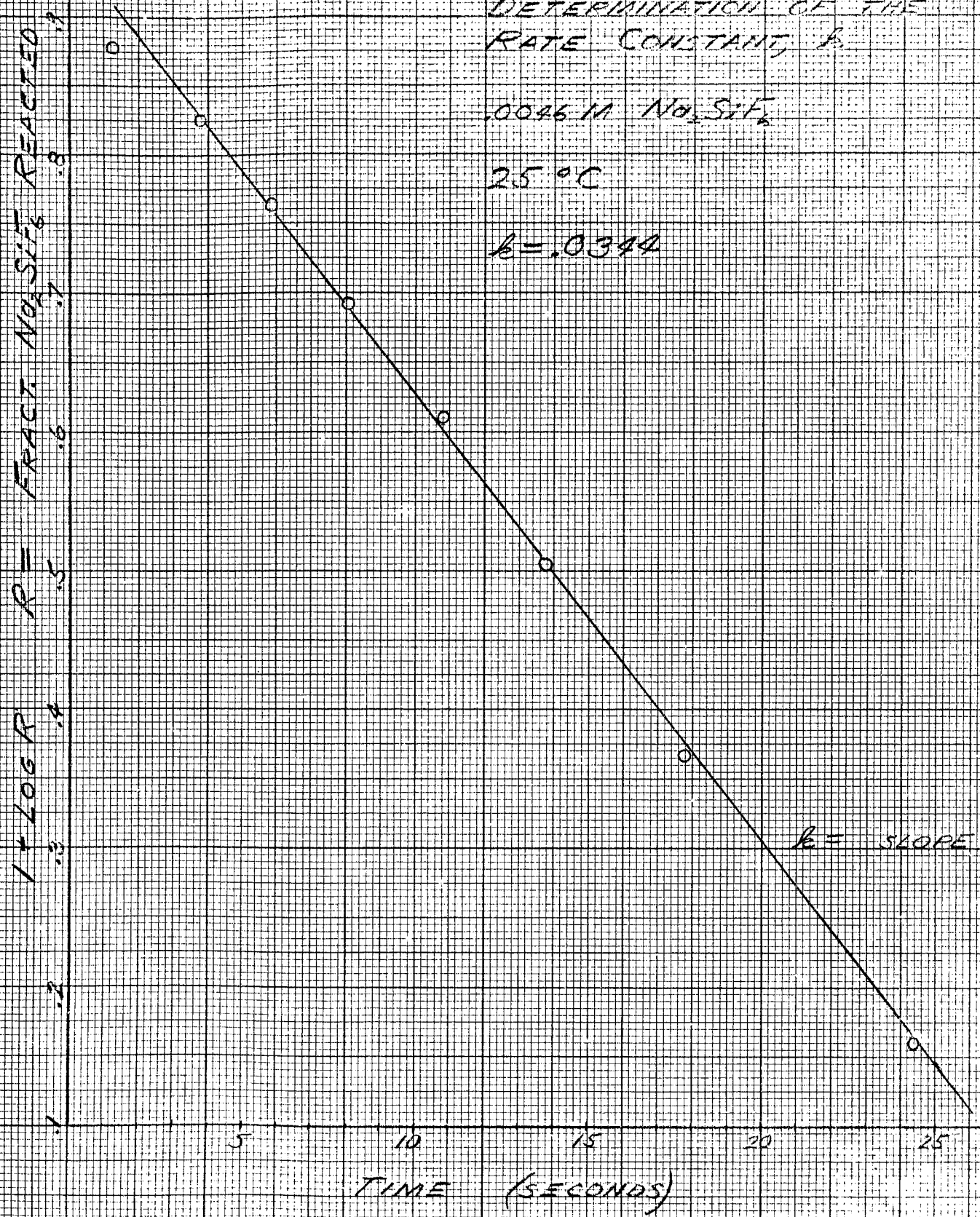


Table VIIReaction Rate

25°C
 .400 gm Na₂SiF₆
 350 ml Total Volume
 .1135N NaOH

<u>ML NaOH</u>	<u>Time to pH 8.0 sec.</u>	<u>R(avg)</u>	<u>1 + log R</u>
10	1	--	--
10	1.4	.875	.942
20	3.0	--	--
20	3.3	.757	.879
30	6.0	--	--
30	6.0	.621	.793
40	9.1	--	--
40	9.5	.492	.693
50	14.5	--	--
50	14.5	.366	.563
60	20.4	--	--
60	20.4	.240	.380
70	35.5	--	--
70	35.5	.113	.053
80	--	--	--
80	--	--	--

FIGURE 18

DETERMINATION OF THE
RATE CONSTANT, k

.061 M Na_2SiF_6

25 °C

$k = .0310$

$1 + \log R$
 $R = \text{FRACT. } \text{Na}_2\text{SiF}_6 \text{ REACTED}$

1.0
.9
.8
.7
.6
.5
.4

0 2 4 6 8 10 12 14 16 18 20 22 24

TIME (SECONDS)

$k = \text{SLOPE}$

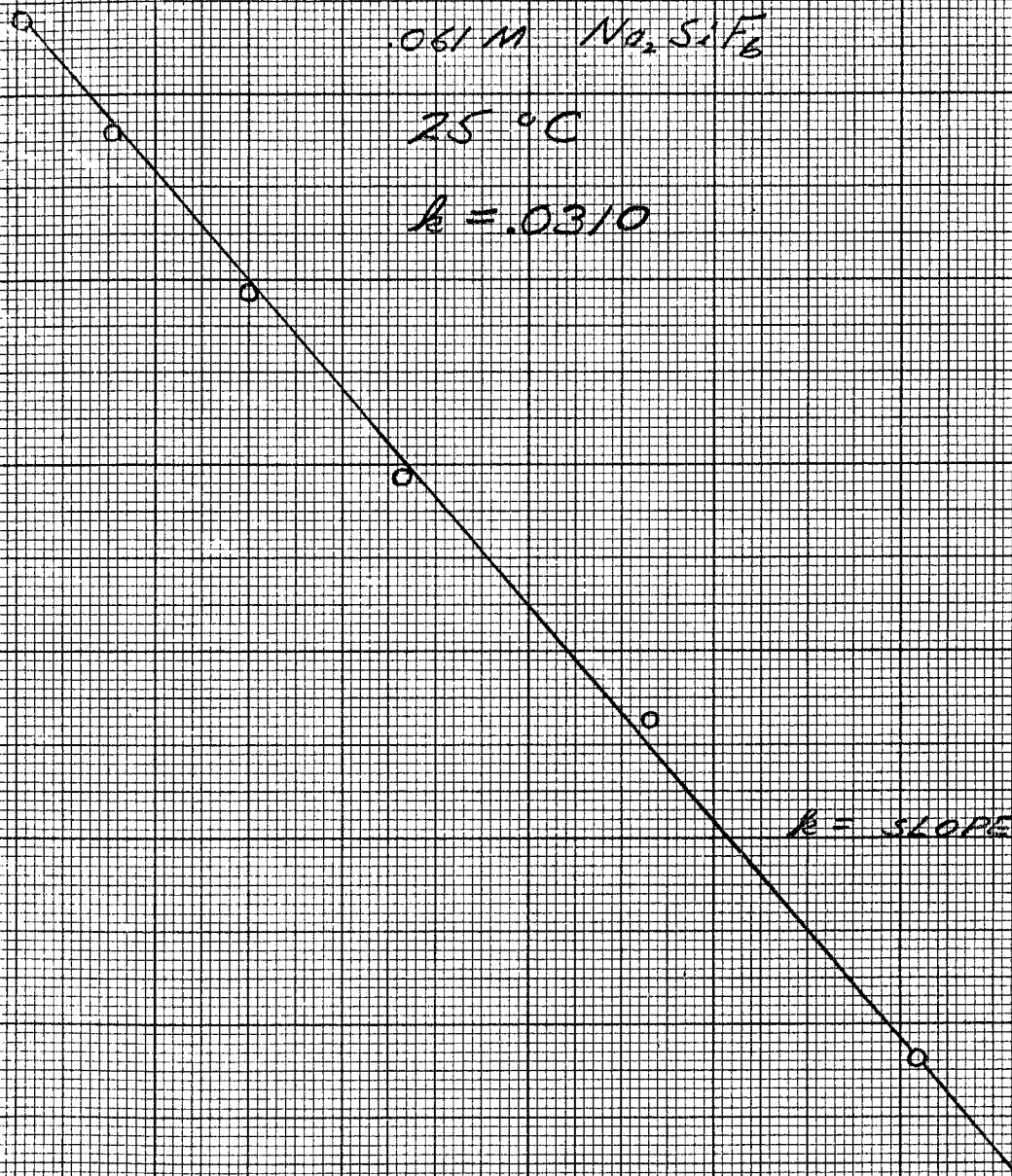


Table VIIIReaction Rate

1°C
 .500 gm Na₂SIF₆
 350 ml Total Volume
 .1155N NaOH

<u>Ml NaOH</u>	<u>Time to pH 8.0 sec.</u>	<u>R</u>	<u>1 + log R</u>
30	76	.673	.828
60	257.7	.348	.541
50	196.2	.456	.659
50	195.1	.456	.659
40	138.9	.565	.752
45	168.7	.512	.709
39	133.8	.576	.760
35	116.2	.630	.799
35	112.7	.630	.799
33	101.8	.641	.807
33	103.5	.641	.807
27	68.1	.706	.849
25	71.0	.728	.862
25	69.3	.728	.862
20	48.1	.782	.893
19	44.8	.793	.899
15	23.5	.836	.922
18	38.1	.803	.905
13	21.0	.857	.933
12	15.7	.868	.939

FIGURE 19

DETERMINATION OF THE
RATE CONSTANT, k

.0076 M Na_2SiF_6

1°C

$k = .0014$

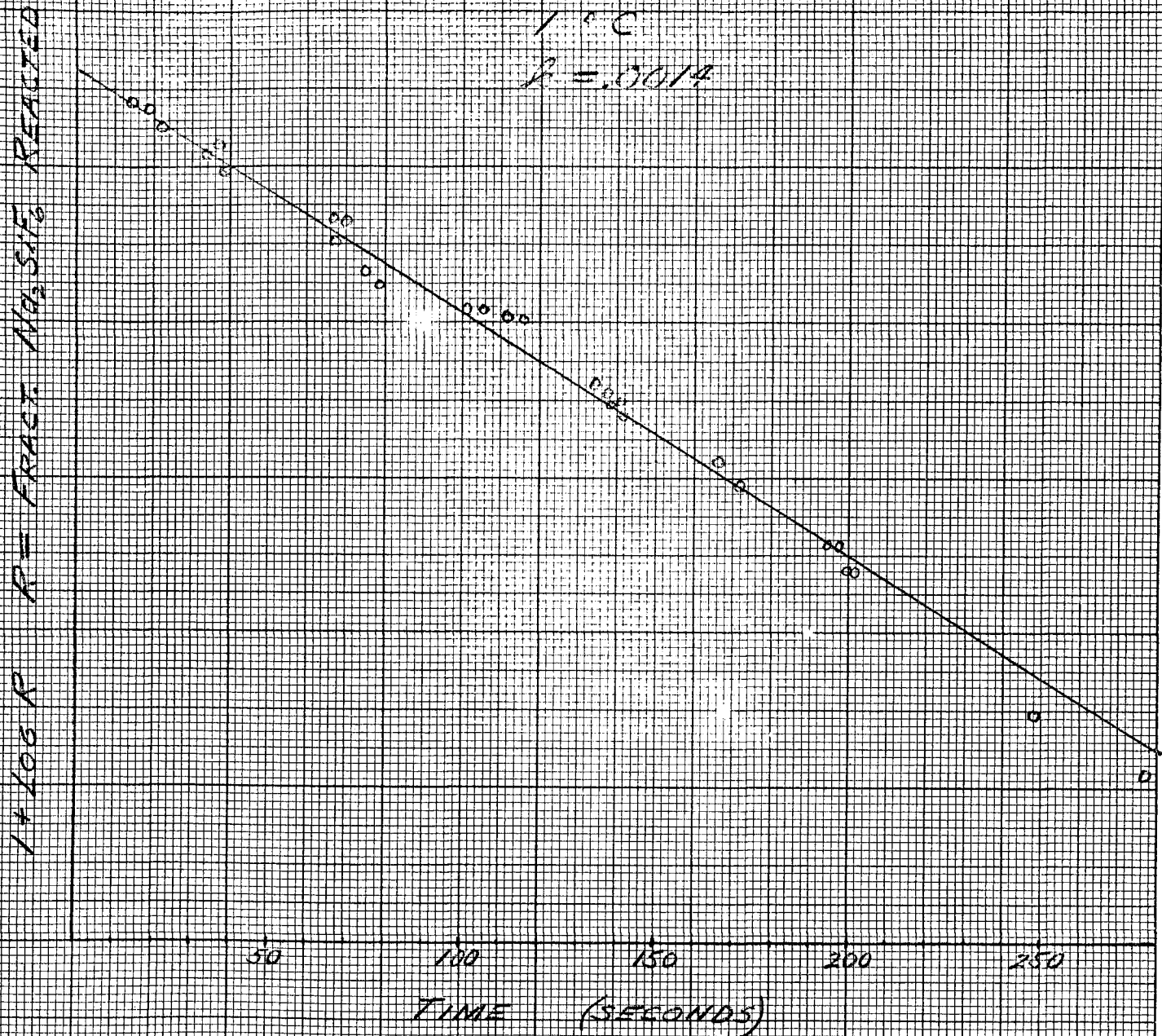


Table IX
10°C Reaction Rate

.300 gm Na_2SiF_6
350 ml Total Volume
.1155N NaOH

<u>ml NaOH</u>	<u>Time to pH 8</u>	<u>R</u>	<u>1 + log R</u>
10	6.1	.820	.914
10	--	--	--
15	15.0	.730	.853
15	15.7	--	--
20	27.0	.641	.807
20	27.7	--	--
25	36.8	.552	.742
25	39.1	--	--
30	53.7	.462	.664
30	53.8	--	--
35	70.4	.372	.571
35	74.3	--	--
40	95.0	.283	.451
40	91.8	--	--
45	128.0	.1935	.286
45	127.0	--	--
50	181.7	.1040	.017
50	164.0	--	--

FIGURE 10

DETERMINATION OF THE RATE CONSTANT, k

COAL M. 14H2SO4

10 °C

$k = .0058$

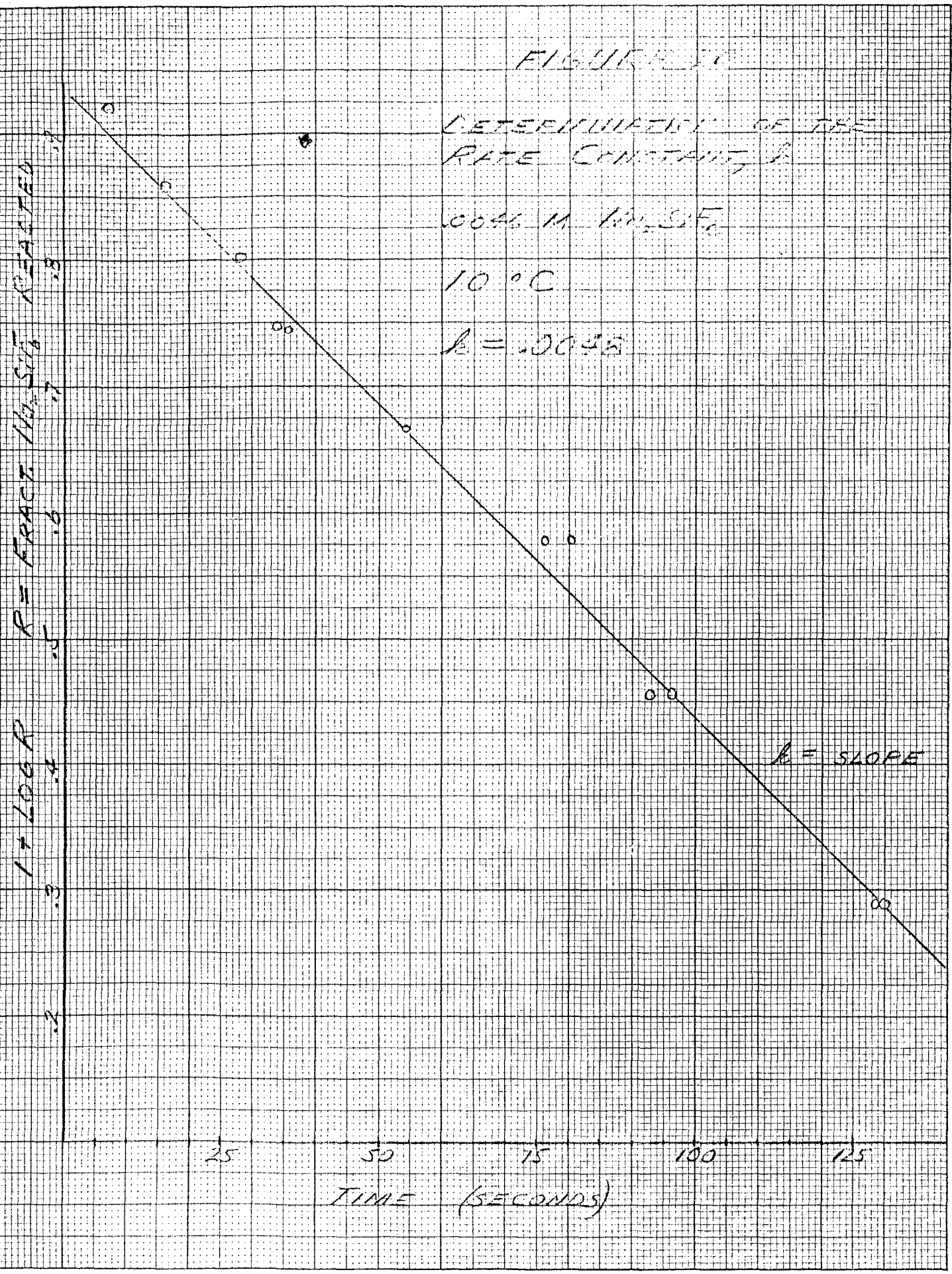


Table X
Reaction Rate

10°C
.500 gm Na_2SiF_6
350 ml Total Volume
.1155N NaOH

<u>ml NaOH</u> <u>.1155 N</u>	<u>Time to</u> <u>pH 8</u>	<u>R</u>	<u>1 + log R</u>
35	29.1	.615	.789
40	39.5	.562	.750
13	5.3	.851	.930
15	7.5	.808	.907
25	19.0	.722	.859
27	21.8	.700	.845
50	56.2	.454	.657
35	30.5	.615	.789
21	13.7	.658	.818
33	28.5	.636	.804
50	55.0	.454	.657
45	46.6	.508	.706
31	26.5	.658	.818
60	69.2	.347	.540
33	29.6	.636	.803
25	19.3	.722	.859
33	29.3	.636	.803
20	18.5	.776	.890

FIGURE 21

DETERMINATION OF THE
RATE CONSTANT, k

.0076 M Na_2SiF_6

10°C

$k = .0055$

$k = \text{SLOPE}$

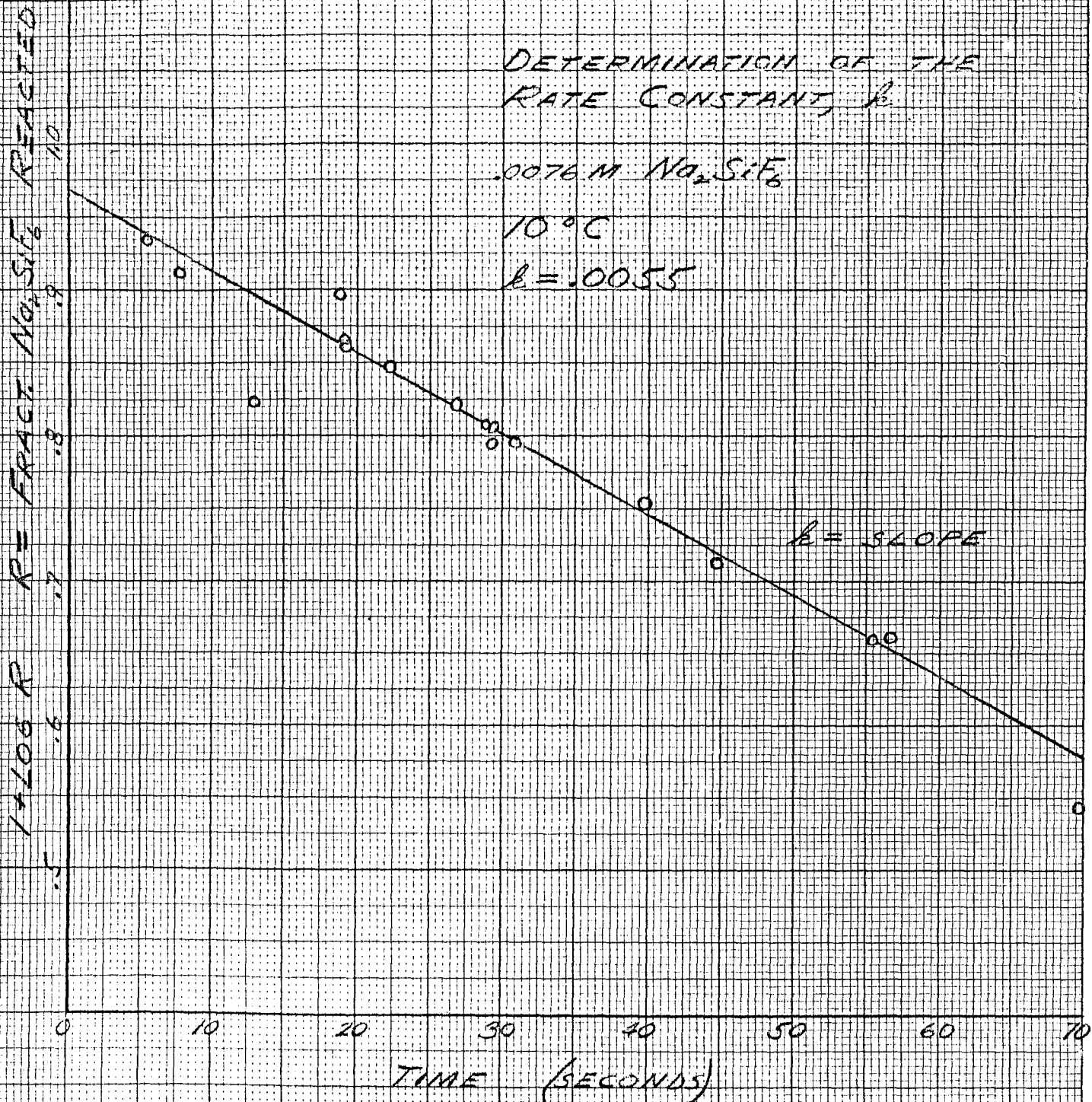


Table XI
Reaction Rate

20° C
.300 gm Na₂SiF₆
350 ml Total Volume
.1155N NaOH

<u>ml NaOH</u>	<u>Time to pH 8</u>	<u>R</u>	<u>1 + log R</u>
15	4.5	.734	.866
15	4.5	--	--
20	8.5	.645	.810
20	7.9	--	--
25	12.7	.656	.817
25	12.5	--	--
30	18.0	.467	.670
30	18.0	--	--
35	23.8	.378	.578
35	23.6	--	--
40	31.8	.289	.461
40	31.3	--	--
45	41.9	.200	.301
45	41.7	--	--
50	59.6	.1105	.044
50	60.2	.1105	--
55	300+	--	--
55	300+	--	--
19	6.5	.663	.822

FIGURE 27

DETERMINATION OF THE
RATE CONSTANT, k

0.0046 M Na_2SiF_6
70 °C
 $k = 0.0197$

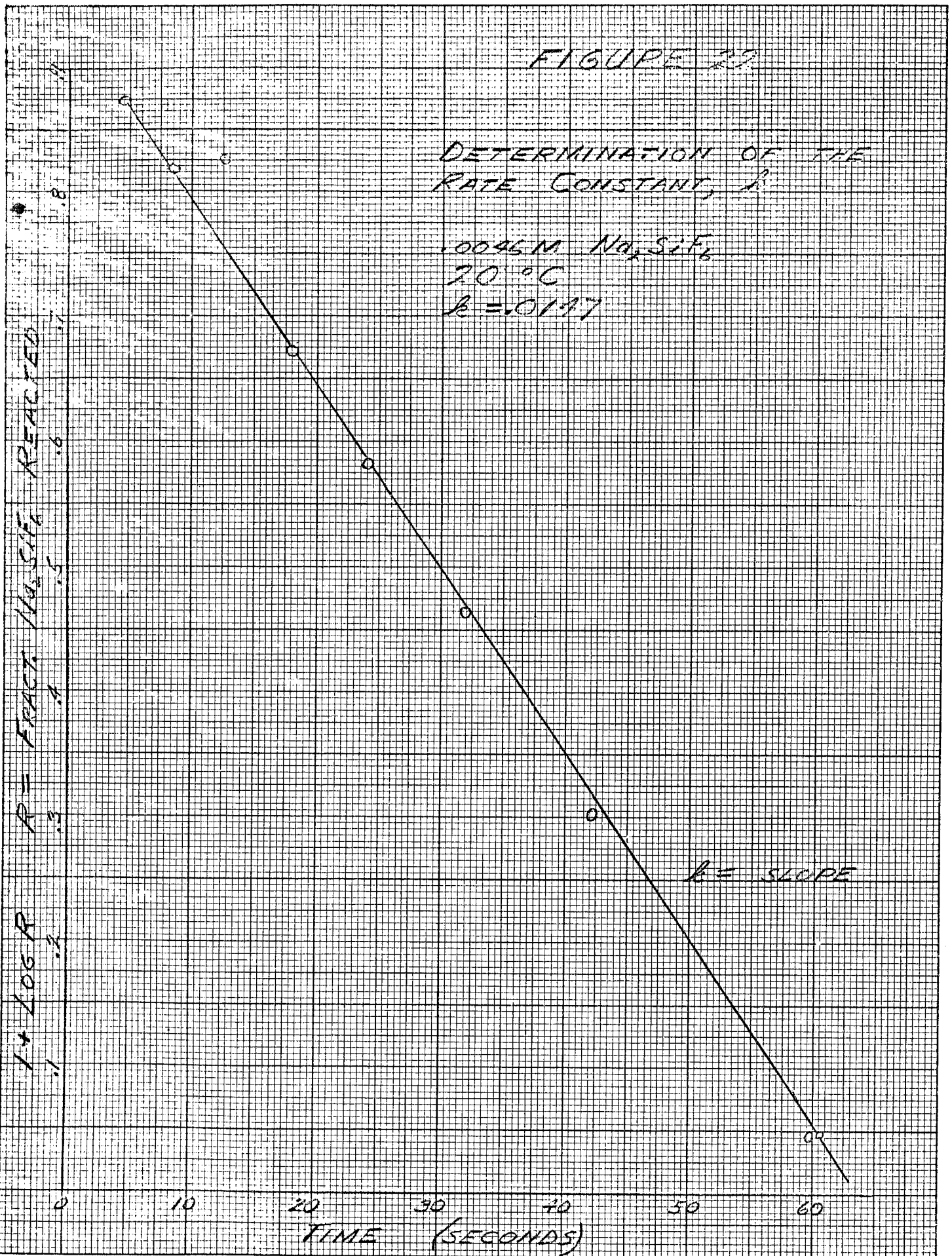


Table XII

Reaction Rate

20°C
 .500 gm Na₂SiF₆
 350 ml Total Volume
 .1103N NaOH

<u>ml NaOH</u> <u>.1103 N</u>	<u>Time to</u> <u>pH 8</u>	<u>R</u>	<u>1 + log R</u>
20	3.5	.793	.900
20	3.5	--	--
25	5.3	.740	.859
25	5.3	--	--
30	7.3	.689	.838
30	7.3	--	--
35	9.5	.637	.804
35	9.3	--	--
40	11.7	.587	.769
40	11.7	--	--
45	14.1	.533	.727
45	14.2	--	--
50	16.9	.482	.683
50	16.7	--	--
55	19.3	.432	.635
55	19.6	--	--
60	22.8	.379	.578
60	23.4	--	--
65	26.4	.328	.516
65	--	--	--
70	30.3	.276	.441
70	30.3	--	--

FIGURE 23

DETERMINATION OF THE RATE CONSTANT, k

.0076 M $\text{HNO}_3/\text{SiF}_6$
20 °C

$k = .0165$

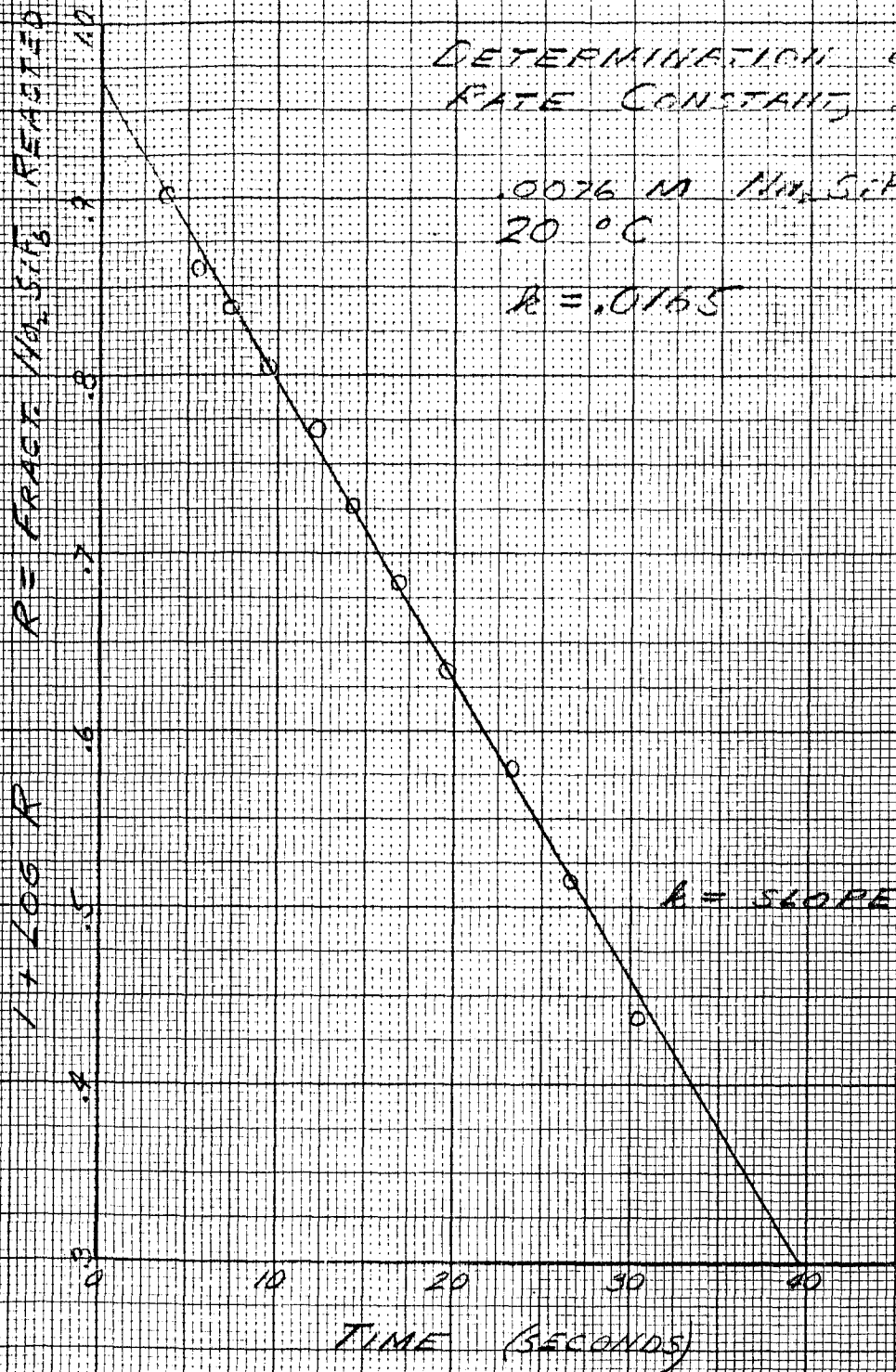


Table XIIIReaction Rate

30°C
 .300 gm Na₂SiF₆
 350 ml Total Volume

<u>ml NaOH</u> <u>.1103 N</u>	<u>Time to</u> <u>pH 8</u>	<u>R</u>	<u>1 + log R</u>
20	2.1	.660	.819
20	1.9	--	--
25	3.0	.575	.760
25	3.6	--	--
30	4.7	.489	.689
30	4.6	--	--
30	4.7	--	--
30	5.1	--	--
35	6.7	.405	.607
35	6.9	--	--
40	8.8	.320	.505
45	11.5	.235	.370
50	15.7	.1495	.175
50	16.0	.1495	.175
40	10.3	.320	.505
50	15.5	.1495	.174
50	13.5	.1495	--
50	15.4	.1495	--

FIGURE 21

DETERMINATION OF THE RATE CONSTANT, k

.0046 M NO_2SiF_6

30 °C

$k = .0466$

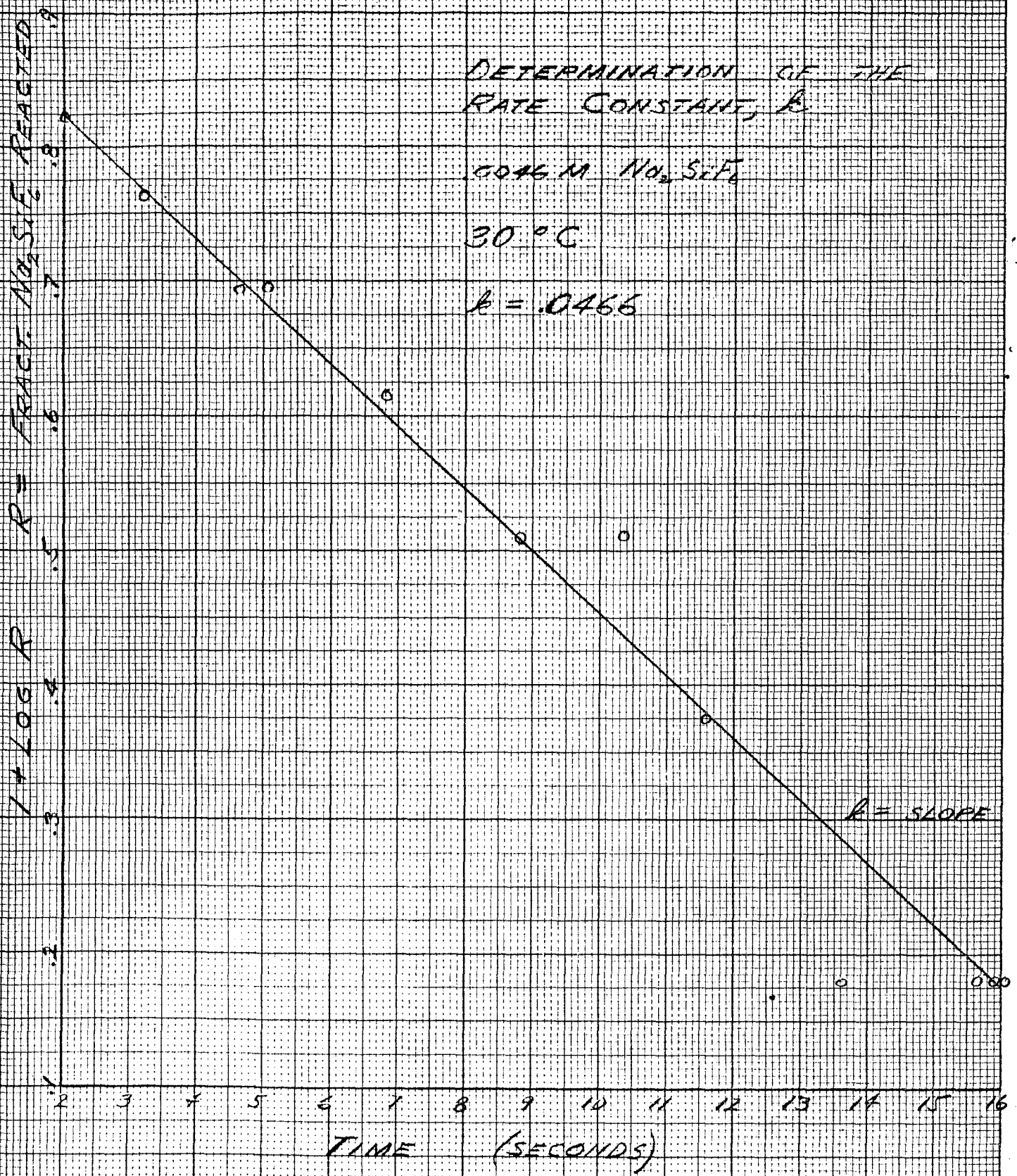


Table XIVReaction Rate

30°C

.500 gm Na₂SiF₆

350 ml Total Volume

<u>ml NaOH</u> <u>.1103 N</u>	<u>Time to</u> <u>pH 8</u>	<u>R</u>	<u>1 + log R</u>
30	2.5	.693	.841
35	3.3	.642	.807
35	3.0	.642	.807
45	4.5	.539	.731
45	4.5	.539	.731
50	5.5	.488	.689
50	5.3	.488	.689
55	6.3	.437	.641
55	6.7	.437	.641
60	7.1	.386	.587
60	6.9	.386	.587
65	7.9	.335	.525
65	8.3	.335	.525
70	9.1	.284	.453
70	9.3	.284	.453
75	10.9	.232	.366
75	10.9	.232	.366
85	15.1	.130	.114
85	15.6	.130	.114
90	20.0	.0788	.104
90	19.6	--	--

FIGURE 3

DETERMINATION OF THE
RATE CONSTANT, k

.0076 M Na_2SiF_6
30 °C

$k = .0948$

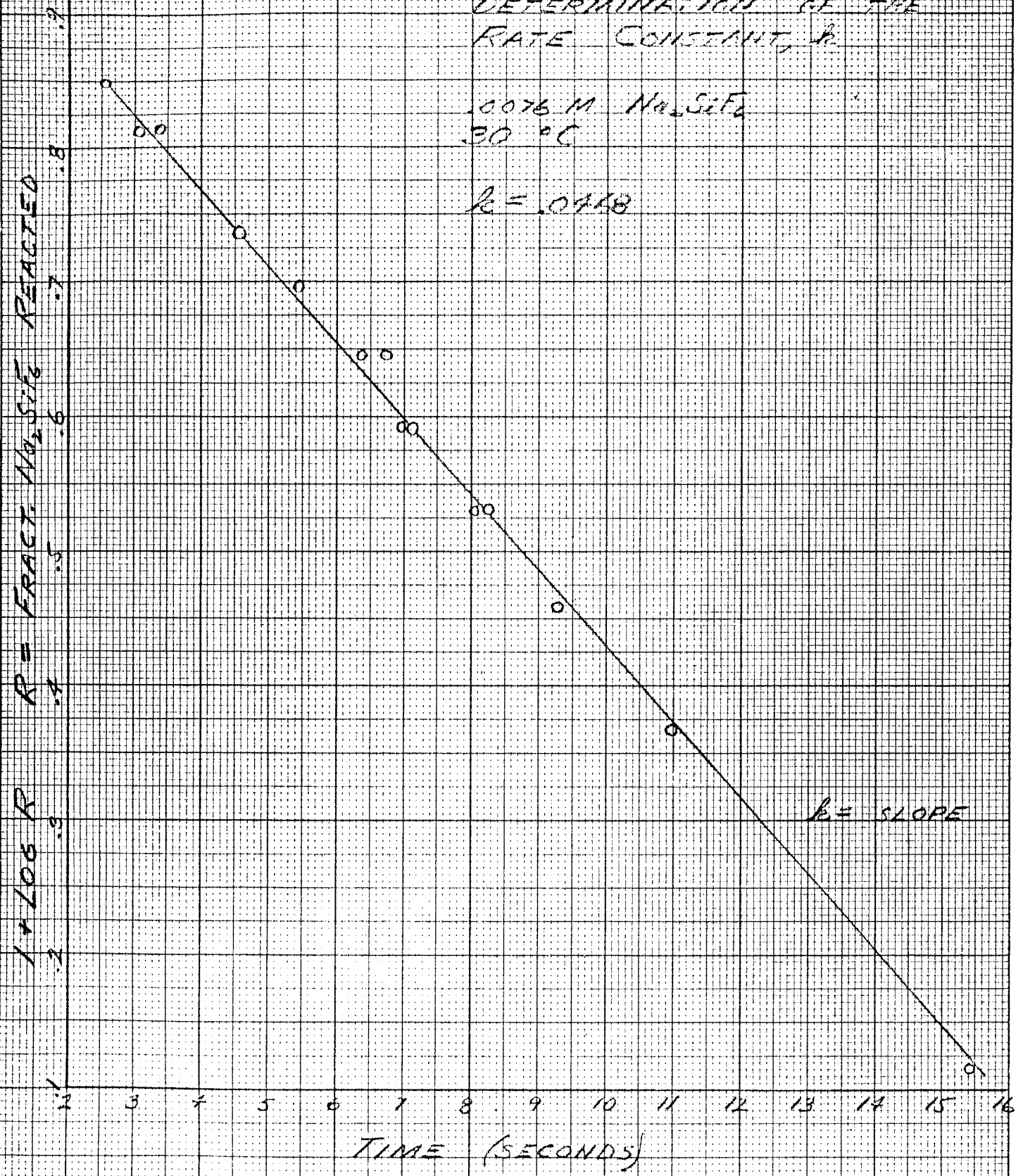


Table XV

Reaction Rate at 20°C in Presence of NaF

.300 gm Na_2SiF_6
350 ml Total Volume

<u>ML NaOH</u> <u>.1103 N</u>	<u>Gms NaF</u>	<u>Time to</u> <u>pH 8</u>	<u>pH</u> <u>NaF +</u> <u>Na_2SiF_6</u>	<u>End Pt.</u> <u>Titration</u>	<u>R</u>	<u>1 +</u> <u>log R</u>	<u>k</u>
25	.100	13.1	4.25	---	.567	.753	.017
25	.100	13.5	4.25	---	--	--	--
25	.100	13.6	4.25	---	--	--	--
50	.100	50.6	--	57.65	.135	.130	--
50	.100	49.1	--	58.00	--	--	--
50	.100	50.2	--	---	--	--	--
25	.200	14.1	4.67	---	.572	.758	.167
25	.200	14.3	4.66	---	--	--	--
25	.200	14.2	4.70	---	--	--	--
50	.200	50.2	4.67	58.50	.142	.152	--
50	.200	50.8	--	58.30	--	--	--
50	.200	52.5	--	58.00	--	--	--
25	.300	14.7	4.90	---	.573	.759	.0159
25	.300	15.0	4.90	---	--	--	--
25	.300	15.0	--	---	--	--	--
50	.300	52.5	--	58.5	.144	.158	--
50	.300	54.2	--	58.2	--	--	--
50	.300	51.0	--	58.6	--	--	--
25	.500	15.1	5.23	---	.572	.757	.0169
25	.500	14.9	5.23	---	--	--	--
25	.500	15.0	5.23	---	--	--	--
50	.500	50.9	--	58.8	.143	.155	--
50	.500	50.7	--	58.4	--	--	--
50	.500	50.0	--	57.8	--	--	--
25	1.000	15.1	5.70	---	.572	.757	.0163
25	1.000	15.6	--	---	--	--	--
25	1.000	15.0	--	---	--	--	--
50	1.000	52.0	5.60	58.7	.147	.168	--
50	1.000	51.2	5.60	58.2	.147	--	--
50	1.000	51.4	5.70	59.0	.147	--	--

Table XVIReaction Rate at 20°C in Presence of NaF

<u>Ml NaOH</u> <u>.1103 N</u>	<u>Gms</u> <u>NaF</u>	<u>Time to</u> <u>pH 8</u>	<u>Initial</u> <u>pH NaF</u> <u>Na₂SiF₆</u>	<u>End Point</u> <u>Titration</u>	<u>End</u> <u>Point</u> <u>pH</u>	<u>R</u>	<u>1 +</u> <u>Log R</u>	<u>k</u>
25	2.000	15.0	6.16	--	--	.576	.761	--
25	2.000	15.3	6.14	--	--	.576	--	.0154
25	2.000	15.5	6.17	--	--	.576	--	--
50	2.000	52.3	6.18	59.0	--	.151	.179	--
50	2.000	54.2	--	58.7	--	--	--	--
50	2.000	52.7	--	59.0	--	--	--	--
25	4.000	15.8	6.65	--	--	.580	.763	--
25	4.000	16.1	6.63	--	--	--	--	.0151
25	4.000	15.7	6.65	--	--	--	--	--
50	4.000	57.5	--	58.5	--	.160	.204	--
50	4.000	51.0	--	59.5	--	--	--	--
50	4.000	50.2	--	60.5	--	--	--	--
25	6.000	14.5	6.95	--	--	.590	.771	--
25	6.000	15.6	6.95	--	--	--	--	.0142
25	6.000	16.1	--	--	6.95	--	--	--
50	6.000	50.0	--	61.2	--	.172	.236	--
50	6.000	51.8	--	60.6	--	--	--	--
50	6.000	53.6	--	59.5	--	--	--	--
25	8.000	17.3	7.25	--	7.25	.587	.769	--
25	8.000	19.4	7.23	--	7.25	--	--	--
25	8.000	18.2	7.28	--	7.28	--	--	.0123
50	8.000	59.4	7.25	60.5	7.40	.174	.241	--
50	8.000	59.4	7.30	60.5	7.40	--	--	--
50	8.000	65.4	7.25	--	7.40	--	--	--

Table XVIIReaction Rate at 20°C in Presence of NaF

<u>Ml NaOH</u> <u>.1103 N</u>	<u>Gms NaF</u>	<u>Time to</u> <u>pH 8</u>	<u>Initial</u> <u>pH</u>	<u>End Point</u> <u>Titration</u>	<u>End</u> <u>pH</u>	<u>Gms</u> <u>Na₂SiF₆</u>	<u>R</u>	<u>1 +</u> <u>Log R</u>
30.00	8.000	46.8	7.23	39.8	7.35	.200	.257	.410
30.00	8.000	47.8	7.25	41.0	--	.200	--	--
30.00	8.000	48.1	--	--	--	.200	--	--
10.0	8.000	10.1	--	--	--	.200	.752	.876
10.0	8.000	9.9	--	--	--	.200	--	--
10.0	8.000	9.8	--	--	--	.200	--	--
20	8.000	65.6	7.25	23.0	7.45	.100	.13	.114
20	8.000	63.3	7.33	23.0	--	.100	--	--
20	8.000	62.5	7.28	23.2	--	.100	--	--
10	8.000	18.0	--	--	--	.100	.567	.754
10	8.000	17.8	--	--	--	.100	--	--
10	8.000	17.8	--	--	--	.100	--	--

Table XVIII
A Check of Several Points
of Reaction Rate in Presence of NaCl

Total Volume = 350 ml
 Temperature = 20°C

<u>Ml NaOH</u> <u>.1103 N</u>	<u>Gms</u> <u>NaCl</u>	<u>Gms</u> <u>Na₂SiF₆</u>	<u>Time to</u> <u>pH 8</u>	<u>Initial</u> <u>pH</u>	<u>End Point</u> <u>Titration</u>
20	1.00	.500	3.5	3.4	96.0
25	1.00	.500	5.5	3.4	97.0
35	1.00	.500	9.4	3.4	96.7
50	1.00	.500	17.0	3.4	96.9
70	1.00	.500	30.1	3.4	--
20	2.000	.500	3.3	3.4	96.5
25	2.000	.500	5.8	--	--
35	2.000	.500	9.3	--	--
50	2.000	.500	16.7	--	--
70	2.000	.500	30.5	--	--
20	1.000	.300	8.3	3.4	56.0
25	1.000	.300	12.4	3.4	55.9
35	1.000	.300	23.5	3.4	56.4
40	1.000	.300	31.3	--	--
50	1.000	.300	60.0	--	--
20	2.000	.300	8.5	3.4	56.2
25	2.000	.300	12.5	--	--
35	2.000	.300	23.2	--	--
40	2.000	.300	31.0	--	--
50	2.000	.300	59.9	--	--

Table XVIIEffect of pH on Apparent Solubility of NaF

<u>Solubility in % With pH 7.8 Influent</u>	<u>Time Days</u>	<u>Solubility in % With pH 8.0 Influent</u>	<u>Time Days</u>	<u>Solubility in % With pH 8.2 Influent</u>	<u>Time Days</u>	<u>Solubility in % With pH 8.4 Influent</u>	<u>Time Days</u>
4.0	2	4.0	2	4.00	2	4.00	2
4.0	8	4.0	6	4.00	6	3.99	9
3.995	11	3.995	8	3.995	8	3.985	12
3.995	12	3.995	9	3.995	9	3.98	13
3.98	16	3.98	12	3.98	12	3.96	17
3.97	17	3.98	13	3.98	13	3.95	19
3.95	20	3.97	15	3.97	15	3.93	22
3.90	25	3.95	19	3.93	19	3.88	27
3.85	28	3.93	21	3.92	21	3.83	30
3.80	30	3.92	23	3.91	23	2.76	33
3.70	33	3.90	25	3.90	25		
		3.89	28	3.90	28		
		3.88	30	3.88	30		
		3.80	33	3.75	33		

Table XXThe Effect of the Ionic Strength of the Media
on the Specific Rate Constant

<u>Grams NaF Per 350 cc of Solution</u>	<u>Ionic Strength</u>	<u>k</u>
.1	.0083	.017
.2	.0167	.0167
.3	.025	.0159
.5	.042	.0163
1.0	.083	.0154
2.0	.167	.0151
4.0	.333	.0142
6.0	.500	.0123
8.0	1.00	.0095

Table XXICalculation of the Frequency Factor, A

<u>Temperature</u>	<u>E/RT</u>	<u>$e^{-E/RT}$</u>	<u>$\frac{k}{e^{-E/RT}} = A$</u>
1	35.5	3.92×10^{-16}	8.22×10^{12}
10	34.4	1.12×10^{-15}	1.02×10^{13}
20	33.1	4.26×10^{-15}	8.43×10^{13}
25	32.7	6.3×10^{-15}	1.2×10^{14}
30	32.1	1.15×10^{-14}	9.3×10^{14}

Table XXII

Calculation of Entropy Factor, $e^{\Delta S/R}$

$$e^{\Delta S/R} = A/kT/h = \frac{A}{2.085 \times 10^{10} \times T}$$

<u>Temperature °C</u>	<u>T°k</u>	<u>$2.085 \times 10^{10} \times T$</u>	<u>A</u>	<u>$e^{\Delta S/R}$</u>
1	274	5.72×10^{12}	8.22×10^{12}	1.44
10	283	5.9×10^{12}	1.02×10^{13}	1.73
20	293	6.1×10^{12}	8.43×10^{13}	1.38
25	298	6.22×10^{12}	1.2×10^{14}	1.93
30	303	6.32×10^{12}	9.3×10^{14}	<u>1.47</u>
				<u>7.95</u> Total

$$\frac{7.95}{5} = 1.59 \text{ average entropy factor}$$

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