

THE RATE OF CONVERSION OF AMMONIUM CYANATE TO UREA  
IN VARIOUS ALCOHOL SOLVENTS

By

Selmer W. Peterson

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## INTRODUCTION

Studies of the rate of conversion of ammonium cyanate into urea have been carried out in a number of laboratories<sup>1,2,3,4,5,6,7,8,9,10,11,12</sup>. The earliest investigations<sup>1,2,3,4</sup> showed that the reaction is bimolecular, that equilibrium is reached at a low concentration of ammonium cyanate, that a slight side reaction leading to the formation of carbonate occurs but is not important until the later stages of the reaction, and that the reaction rate varies from solvent to solvent. Further, the work of Walker and Hambly<sup>1</sup>, Walker and Kay<sup>2</sup>, and Ross<sup>3</sup> indicated that the reaction rate depended on collisions between ammonium and cyanate ions. This ionic mechanism was later supported by the work of Warner and Stitt<sup>6</sup> on the kinetic salt effect displayed by the reaction.

Up until 1935 practically no systematic studies had been made on the influence of the dielectric constant of the solvent on ionic reaction rates. Warner and Warrick<sup>7</sup> in 1935 studied the ammonium cyanate reaction in water and in alcohol-water mixtures of known dielectric constants at 50°. However, since this work was carried out at one temperature only, the effect of the dielectric constant of the solvent on the activation energy of the reaction could not be determined. The work of Svirbely and Warner<sup>8</sup> in 1935 on the ammonium cyanate reaction in isodielectric methanol-water mixtures was the first example of reaction rate measurements carried out in isodielectric media over a temperature range. All previous temperature coefficient measurements had been carried out in constant composition solvents, whose dielectric constants varied with temperature. This new isodielectric work led to new activation energy concepts and resulted in a considerable advance in our understanding of reaction rates of ionic

species in solution.

9,10,11,12

More recently Svrbely and coworkers have made systematic studies of the ammonium cyanate reaction in several isodielectric solvent-water mixtures over a wide dielectric constant range and over a temperature range of 30°.

However water is the only pure solvent in which accurate, constant composition, velocity constant measurements have been made on this reaction over a temperature range. It seemed desirable to study the reaction in order to complete the previous work and to observe whether any new effects, peculiar to the particular solvent, would appear. This thesis reports measurements made on the ammonium cyanate reaction in various non-aqueous solvents, namely methanol, ethanol, isopropanol, and ethylene glycol over a temperature range of 30°.

## THEORETICAL DISCUSSION

The mathematical expressions for the rates of simple first, second and third order reactions as a function of concentration have long been known. The expression for a simple bimolecular reaction of the type



is

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \quad (1)$$

where  $-dC_A/dt$  and  $-dC_B/dt$  are the time rates of change of concentration of species A and B respectively and  $k$  is a constant known as the specific rate constant or velocity constant. Obviously this equation expresses only the concentration dependence of the reaction velocity.

It has also long been known that temperature has a very important effect on the rates of chemical reactions. Many reactions double or even treble their velocity for a  $10^\circ$  temperature rise. Arrhenius proposed a quantitative relation for this effect, namely

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad (2)$$

where  $k$  is the specific reaction rate constant,  $R$  is the gas constant,  $T$  the absolute temperature, and  $E$  a constant which is interpreted as the activation energy which must be supplied to molecules before they will react.

Integrating and putting into the exponential form, equation (2) becomes

$$k = Ze^{-E/RT} \quad (3)$$

where  $Z$  is an integration constant. This constant  $Z$  has the dimensions of a frequency and for many second order reactions has been shown to be equal to the number of molecules colliding in unit time. Thus the rate of a chemical reaction is equal to the collision rate multiplied by the fraction

of the molecules which are in the activated state. From this it appears that the rate of a chemical reaction at any temperature could be calculated knowing  $E$  and  $Z$  for the reaction.  $Z$  can be calculated from collision theory, while  $E$  can be obtained from experimental measurements of the temperature coefficient of the reaction rate. Applied to gaseous reactions, this theory has met with considerable success. However when attempts are made to apply it to reactions in solution, it is quite inadequate. Moelwyn-Hughes in a review article<sup>13</sup> revealed values of  $k_{\text{obs.}}/k_{\text{calc.}}$  which varied from  $10^2$  to  $10^{-9}$ . Attempts have been made, with little justification, to obtain better agreement by including a probability term  $F$ , which could sometimes be theoretically estimated. Thus the resulting equation

$$k = PZe^{-E/RT} \quad (4)$$

is valuable more as a pictorial approximation than as a quantitative relationship.

It is not surprising that the kinetic equation obtained from the collision theory of gas reactions falls down when applied to solution reactions, when it is realized that the activation energies for solution reactions are obtained under the most diverse experimental conditions.

It is well known that for a specific reaction, the ordinary Arrhenius energy of activation obtained from the variation of the rate constant with temperature depends upon the solvent used, upon whether the solvent is one of constant composition or one of constant dielectric constant, and upon the ionic strength. This is especially true for ionic reactions in solution. Any effect of ionic strength may be eliminated by using rate constants which have been extrapolated to zero ionic strength. Thus this leaves the dielectric constant and temperature as the known important

factors having an effect upon  $k_0$ , the rate constant at zero ionic strength. Starting with the assumption that these are the only important factors, Svirebely and Warner<sup>8</sup> derived the following:

$$\log k_0 = f(D, T)$$

$$\frac{d \log k_0}{dT} = \left( \frac{\partial \log k_0}{\partial T} \right)_D + \left( \frac{\partial \log k_0}{\partial D} \right)_T \frac{dD}{dT} \quad (5)$$

multiplying by  $2.3RT^2$  and integrating

$$(E^0)_{P.C.} = (E^{0*})_D + 2.3RT^2 \left( \frac{\partial \log k_0}{\partial D} \right)_T \frac{dT}{dT} \quad (6)$$

$E^0_{P.C.}$  is interpreted as the ordinary activation energy obtained in a solvent of fixed composition.  $E^{0*}$  is interpreted as the activation energy obtained in isodielectric mixtures over the whole temperature range.

Experimentally this condition can be realized by varying the  $H_2O$  content in a solvent-water mixture at each temperature in such a way as to maintain the same dielectric constant.  $\left( \frac{\partial \log k_0}{\partial D} \right)_T$  is a measure of the way  $k_0$  varies with changing dielectric constant at a constant temperature.  $\frac{dD}{dT}$  is a measure of the way the dielectric constant of the fixed composition solvent varies with temperature.

Since the dielectric constants of all common solvents decrease with increasing temperature and if the rate constants also decrease with increasing dielectric constant, equation (6) predicts that  $E^0$  should be greater than  $E^{0*}$ .

The dielectric constants of most solvents and solvent mixtures may be expressed in the form

$$D = ae^{-bT} \quad (7)$$

where  $a$  and  $b$  are empirical constants. Hence at any given temperature

$$\frac{dD}{dT} = -abe^{-bT} = -bD \quad (8)$$

Since the term  $\left(\frac{\partial \log k_0}{\partial D}\right)_T$  of equation (6) is simply the slope of a plot of  $\log k_0$  versus  $D$ , equation (6) may be written

$$E^{\circ}_{F.C.} - E^{\circ*}_D = 2.3RT^2 \cdot (\text{slope}) (-bD)$$

Thus from experiments to determine the variation of  $k_0$  with  $D$  at constant temperature,  $\left(\frac{\partial \log k_0}{\partial D}\right)_T$  may be evaluated and then  $E^{\circ}_{F.C.} - E^{\circ*}_D$  calculated.

The Scatchard theory<sup>14</sup> for the effect of dielectric constant on  $k_0$ , the velocity constant at zero ionic strength, yields the relation

$$\ln k_0^r - \ln k_0 = \frac{E^2 Z_A Z_B}{k' T r} \left( \frac{1}{D_0} - \frac{1}{D} \right) \quad (9)$$

where  $k_0^r$  is the limiting velocity constant in the reference solvent,  $E$  is the electronic charge,  $Z_A$  and  $Z_B$  are the valences of the reacting ions,  $k'$  is the Boltzmann constant,  $D_0$  is the dielectric constant of the reference solvent, and  $D$  is the dielectric constant of the particular solvent in which the  $k_0$  values are obtained. Differentiation with respect to  $D$  with the restriction of constant temperature yields

$$\left(\frac{\partial \log k_0}{\partial D}\right)_T = \frac{E^2 Z_A Z_B}{2.3rkD^2T} \quad (10)$$

which enables a theoretical calculation of the slope of  $\log k_0$  plotted against  $D$  for a reaction carried out over a range of dielectric constant values at a single temperature. If the value of  $\left(\frac{\partial \log k_0}{\partial D}\right)_T$  from equation (10) is substituted in equation (6) we obtain

$$E^{\circ}_{F.C.} - E^{\circ*}_D = - \frac{N E^2 Z_A Z_B}{r} \frac{T}{D} \quad (b) \quad (11)$$

Thus  $E^{\circ}_{F.C.} - E^{\circ*}_D$  can be directly calculated from physical constants and the results compared with experimentally determined  $E^{\circ}_{F.C.} - E^{\circ*}_D$  values obtained from temperature coefficient studies in constant composition and isodielectric media.

Equation (10) shows that  $\left(\frac{\partial \log k_0}{\partial D}\right)_T$  is a function of  $D$ , hence a straight line would not be obtained from a  $\log k_0$  versus  $D$  plot. However multiplying through by  $D^2$  leads to

$$\left(\frac{\partial \log k_0}{\partial 1/D}\right)_T = \frac{E^2 Z_A Z_B}{2.3rk'T} \quad (12)$$

from which it can be seen that a plot of  $\log k_0$  versus  $1/D$  should give a straight line. Thus since

$$D^2 \left(\frac{\partial \log k_0}{\partial D}\right)_T = \left(\frac{\partial \log k_0}{\partial 1/D}\right)_T$$

we find that

$$E^{\circ}_{F.C.} - E^{\circ*}_D = \frac{2.3RT^2}{D} \cdot \frac{\partial \log k_0(-b)}{\partial 1/D}$$

or

$$E^{\circ}_{F.C.} - E^{\circ*}_D = -2.3Rb \frac{T \partial \log k_0}{\partial 1/D} \cdot \frac{T}{D} \quad (13)$$

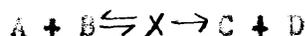
Thus another and somewhat more preferable method of calculating  $E^{\circ}_{F.C.} - E^{\circ*}_D$  is by evaluating the slope of a  $\log k_0$  versus  $1/D$  plot and substituting this value into the right side of equation (13). Equation (11) also predicts that if  $Z_A Z_B$  is negative, which is true for reactions between ions of opposite charge,

$$E^{\circ}_{F.C.} > E^{\circ}_D \quad (14)$$

while if  $Z_A Z_B$  is positive, which is true for ions of like charge

$$E^{\circ}_{F.C.} < E^{\circ}_D \quad (15)$$

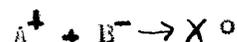
So far we have confined ourselves to dielectric constant effects. If however we know velocity constants at a fixed temperature and dielectric constant as a function of the ionic strength ( $\mu$ ) we can find relations between activation energies at zero ionic strength and some fixed ionic strength. The effect of the ionic strength of the medium upon the rate of reaction has been treated by Bronsted<sup>15</sup> for the type reaction



yielding the equation

$$k = k_0 \frac{f_A f_B}{f_X} \quad (16)$$

where  $k$  is the observed velocity constant at a definite ionic strength,  $k_0$  is the velocity constant at zero ionic strength, and the  $f$  terms are the activity coefficients of the species designated. Equation (16) for the case of the primary salt effect on a reaction of the type



becomes

$$k = \frac{k_0}{1 + 2A\sqrt{u}} \quad (17)$$

where  $A$  is the Debye-Huckel constant in the relation

$$\ln f_i = -AZ_i^2\sqrt{u} \quad (18)$$

Christiansen<sup>16</sup> and Scatchard<sup>17</sup> later treated the problem theoretically and arrived at identical equations which may be written

$$\log k = \log k_0 + \frac{E^2 Z_A Z_B K}{Dk^2 T(1 + KE)} \quad (19)$$

where  $K = \sqrt{\frac{8N}{1000DK^2 T} E^2 u}$  is the usual Debye-Huckel value. Differentiating equation (19) and multiplying by  $RT^2$  a relation between  $E^0$  and  $E$  at a fixed ionic strength is obtained which for the ammonium cyanate reaction may be written

$$E = E^0 + 8.35 \times 10^6 RT^2 \sqrt{u} \left[ \frac{3/2 T^{1/2} D^{3/2} + 100.6 D \sqrt{u}}{(T^{3/2} D^{3/2} + 100.6 D T \sqrt{u})^2} \right] \left[ 1 + \frac{d \ln D}{d \ln T} \right] \quad (20)$$

For isodielectric work  $d \ln D / d \ln T = 0$ , hence the relation between  $(E)_D$  and  $(E^0)_D$  in this case becomes

$$(E^*)_D = (E^0)_D + 8.35 \times 10^6 RT^2 \sqrt{u} \left[ \frac{3/2 T^{1/2} D^{3/2} + 100.6 D \sqrt{u}}{(T^{3/2} D^{3/2} + 100.6 D T \sqrt{u})^2} \right] \quad (21)$$

The values for  $(E - E^0)$  calculated from equations (20) and (21) may be

compared with experimentally obtained values. A somewhat simpler equation may be obtained by putting equation (17) in the logarithmic form, differentiating, and multiplying by  $RT^2$ . The result is

$$E = E^0 + \frac{12.5 \times 10^6 \sqrt{u} RT}{(TD)^{3/2} + 8.36 \times 10^6 \sqrt{u}} \left( 1 + \frac{d \ln D}{d \ln T} \right) \quad (22)$$

A thermodynamic theory of reaction rates has been developed by Eyring<sup>18</sup>, La Mer<sup>19</sup> and others. This theory leads to the equation

$$k = \frac{RT}{Nh} e^{S/R} e^{-E/RT} \quad (23)$$

for the specific reaction rate, where  $S$  is the entropy of activation and the other terms have their usual significance. The collision theory on the other hand gave the equation

$$k = PZ e^{-E/RT} \quad (4)$$

On comparison of equations (23) and (4) one observes that

$$PZ = \frac{RT}{Nh} e^{S/R} \quad (24)$$

is the condition that the two theories lead to identical results.  $Z$ , the collision frequency of gas kinetics, is given by the equation

$$Z = \frac{N}{1000} \sigma_{12}^2 \left[ 8\pi RT \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} \quad (25)$$

where  $\sigma_{12}$  is the collision diameter and  $M_1$  and  $M_2$  are the molecular weights of the reacting particles. If the assumption is made that  $P = 1$ , then equation (24) and (25) combine to

$$\frac{RT}{Nh} e^{S/R} = \frac{N}{1000} \sigma_{12}^2 \left[ 8\pi RT \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} \quad (26)$$

On solving equation (26) for  $\sigma_{12}$  and substituting in appropriate values for the physical constants, one obtains for the ammonium cyanate at 50° the following relation

$$\log \sigma_{12} = \frac{1}{2} \left( \frac{S}{2.3R} \right) - \frac{6.713}{14.020} \quad (27)$$

Now  $\frac{S}{2.3R}$  can be shown to be equal to B, the frequency factor, of the equation (minus  $\log \frac{kT}{h}$ )

$$\log k_0 = - \frac{E^0}{2.3RT} + B \quad (28)$$

for the case of reactions in isodielectric media. Hence

$$\log \sigma_{12} = \frac{B}{2} - 14.020 \quad (29)$$

Equation (29) may be used to test the collision theory in terms of the thermodynamic theory by calculating  $\sigma_{12}$  from experimentally obtained B values. If the collision diameters so calculated are physically reasonable, the two theories may be said to be in substantial agreement.

## REAGENTS AND APPARATUS

## I. Reagents

Silver cyanate was prepared as follows: 50 grams of C. P.  $\text{AgNO}_3$  was dissolved in 250 cc. of water, and 90 grams of a good grade of urea was dissolved in 350 cc. of water. The solutions were filtered, heated separately to near boiling, mixed in a darkened flask, and heated for a short time on a steam bath. The mixture was then cooled to room temperature and filtered through a Buchner funnel into a darkened suction flask. The first small crop of crystals thus obtained were always discolored, hence discarded. Sometimes a second filtration was carried out at this point to purify the filtrate as much as possible. The filtrate was then returned to the darkened Florence flask and heated under reflux on a steam bath for a period of an hour. After cooling to room temperature the solution was again filtered, and the silver cyanate crystals were washed with several portions of ice water. The crystals were sucked as dry as possible and placed in a dessicator over calcium chloride. The filtrate was then returned to the steam bath and the above procedure was repeated as long as any appreciable quantity of silver cyanate crystals was obtained. The silver cyanate crystals were of a long needle like shape and were usually quite white in color.

An exactly 0.02000 molar solution of  $\text{KSCN}$  was prepared by dissolving the proper quantity of the carefully dried C. P. reagent in distilled water and making up to volume. Similarly, an exactly 0.02800 molar solution of  $\text{AgNO}_3$  was prepared by dissolving dried and fused C. P.  $\text{AgNO}_3$  in distilled water and making up to volume. Experimental comparison of the strengths of the two solutions using ferric alum indicator led to exact

agreement with the calculated ratio. Furthermore, the exact strengths of the two solutions were checked by titration against weighed samples of pure NaCl. The results obtained were 0.2800, 0.2800, 0.2802 for the molarity of the  $\text{AgNO}_3$  solution. Since the strength of the  $\text{AgNO}_3$  solution changed slightly with time, frequent determinations of the  $\text{AgNO}_3/\text{KSCN}$  ratio were made and the experimental value obtained was used in the experiments carried out during that day. The strength of the KSCN solution showed no variation with time. In some of the earlier experiments carried out an 0.03530 molar solution of  $\text{AgNO}_3$  was used.

The solvents used were purified, insofar as possible, by Akerlof's<sup>21</sup> methods, since his values for the dielectric constants were to be used. Absolute methanol was fractionally distilled, rejecting the first and last one-tenth portions. The middle portion was refluxed with enough sodium metal to react with five per cent of water, and then fractionated again. The middle eighty per cent was collected. The entire sample distilled at a constant temperature, and had a refractive index of 1.3280 at 22°. Absolute ethanol was treated in an identical manner. The purified material distilled at a constant temperature and had a refractive index of 1.3573 at 32°. Isopropanol was purified by two successive fractional distillations, discarding each time the first and last cuts. The material distilled constantly at 81.5°(uncorr.) during both fractionations and showed no change in refractive index, which was 1.3758 at 24°. Ethylene glycol was dried over  $\text{Na}_2\text{SO}_4$  for several weeks and then vacuum distilled, collecting the middle eighty per cent. This middle portion was then fractionally distilled at atmospheric pressure and the middle cut again taken. This middle portion distilled at a constant temperature and gave a refractive index of 1.4292 at 24°. All fractional distillations were carried out in a three foot column. All refractive indices quoted above agree, within a deviation

of  $\pm 0.0002$ , with literature values after reducing them to  $20^{\circ}$ .

The indicator solution was prepared by saturating 3 molar nitric acid with C. P. ferric nitrate or alternatively by saturating 3 molar nitric acid with C. P. ferric ammonium sulfate.

Analytical grade C. P. ammonium chloride was used for the preparation of ammonium cyanate from silver cyanate.

## II. Apparatus

The velocity constant measurements were carried out in a water thermostat provided with efficient stirring and excellent temperature regulation. The bath was heated by a Cenco blade heater, and stirred with a motor-attached propeller stirrer. The temperature was regulated by means of a mercury regulator. The combination of heater and mercury regulator were capable of maintaining the temperature constant to  $\pm 0.02^{\circ}$ . For the measurements at  $20^{\circ}$  it was necessary to provide the bath with a copper cooling coil. By passing a slow stream of water through the coil the bath temperature could easily be brought to the desired temperature.

The thermometer used was a Fisher, nitrogen filled thermometer with a  $100^{\circ}$  range calibrated in tenths of degrees. This thermometer was checked with a Bureau of Standards calibrated thermometer at the temperatures used in the experimental work. Furthermore, it was provided with a glass jacket which surrounded the exposed part of the mercury column, maintaining it at reasonably constant temperature, and protecting it from sudden fluctuations in room temperature. An auxiliary thermometer was placed inside the glass jacket with the bulb slightly below the middle of the exposed mercury column. The thermometer gave the mean temperature of the exposed mercury column, which then was used for stem correction calculations. The true temperature was then found by adding the stem correction and cal-

ibration correction to the thermometer reading. By constructing tables of the corrections involved, the thermometer reading corresponding to the desired temperature could quickly be ascertained. A Beckmann thermometer calibrated in  $0.01^{\circ}$  steps was also placed in the bath to facilitate observation of temperature fluctuations.

The reaction flasks were 250 cc. glass stoppered Erlenmeyer flasks. The pipettes and burettes used in the analytical method were all carefully calibrated. All weighings were made with a previously calibrated set of weights. Since the corrections on the weights were very small, they were never used.

## EXPERIMENTAL METHOD AND DATA

The general method involved in conducting a velocity experiment on the ammonium cyanate reaction was to prepare ammonium cyanate solutions of the desired concentration by agitating a known amount of ammonium chloride with an excess of silver cyanate in the chosen solvent. When the resulting solution was free of chloride ion, it was filtered into the reaction flask, heated over an open flame to approximately the thermostat temperature, and then placed in the thermostat. After allowing sufficient time for establishment of temperature equilibrium an initial sample was withdrawn from the reaction flask and pipetted into a weighed flask containing an excess of standard silver nitrate solution. The flask was then again weighed in order to obtain the amount of sample withdrawn from the reaction flask. As soon as possible the precipitated silver cyanate was filtered off and the filtrate analyzed for excess silver nitrate by titration with standard ammonium thiocyanate using ferric nitrate or ferric alum as indicator. As the reaction proceeded samples were withdrawn at known time intervals and treated in a similar manner to that described above. The run was usually continued for a long enough time to allow the reaction to reach about seventy per cent conversion of ammonium cyanate to urea. It was stopped at that point because previous work had shown that the back reaction becomes appreciable at seventy per cent conversion.

The method outlined above was approximately the method followed in the experiments, but for each solvent many of the details had to be considerably modified. A detailed account of the method that was employed, when methanol was the solvent, follows. Modifications which were found to be necessary or desirable for the other solvents will be described

later.

An amount of ammonium chloride, calculated to give an ammonium ion concentration of about 0.07M, was weighed out and added to 130 cc. of methanol contained in a 250 cc. Erlenmeyer flask. The flask was clamped into position and the contents stirred with a motor-driven stirrer, mounted so as to keep out moisture during the process. When the salt had dissolved, a weighed excess of silver cyanate was added to the flask and the stirring continued. After a period of ten minutes the stirring was interrupted and a small sample of the supernatant liquid was withdrawn to be tested for the presence of chloride ion. This sample was filtered into a few cc. of 0.1 M. silver nitrate solution acidified with 8 to 10 drops of nitric acid. If a precipitate was obtained, a little more silver cyanate was added and the stirring continued for a few minutes more. Usually no chloride ion remained, however. When a negative test for chloride ion was obtained, the flask and its contents were cooled in ice to slow down the conversion of ammonium cyanate. The solution was then filtered through dry filter paper into dried reaction flask. During the filtration moisture was eliminated insofar as possible by covering the filter funnel with a watch glass and closing the neck of the reaction flask with absorbent cotton. The filtered solution was then heated over an open flame to approximately the thermostat temperature and placed in the thermostat. After fifteen to twenty minutes a 10 cc. sample (approximate) was withdrawn and pipetted into a weighed flask containing 24.95 cc. of standard  $\text{AgNO}_3$ . As the reaction proceeded, 10 cc. samples were withdrawn at times so chosen that similar concentration decrements would result. After reweighing the flasks, the solutions were filtered, and the flasks and precipitates were carefully washed with several portions of ice water. Then 5 cc. of 6M.  $\text{HNO}_3$  and 1

cc. of the indicator solution were added to each filtrate, and the mixture was titrated with standard KSCN to determine the excess silver ion.

In some of the first runs a volumetric procedure was used entirely. Samples were withdrawn from the reaction flask with a calibrated pipette and aliquot portions of the filtered solutions were taken for analysis. However pipette errors were considerable due to faulty drainage, and concordant results were difficult to obtain. The method was finally discarded in favor of the weighing method described above, where a measuring pipette was used to withdraw the sample and the amount of sample was determined by weighing. The weighing method not only eliminated the drainage error, but also reduced somewhat the possible error due to drop in temperature of the sample during the time consumed in pipetting. This reduction in error due to the shorter drainage time for a measuring pipette as compared with an exact volumetric pipette may be quite significant in some of the faster runs. Another advantage was that the reaction flask was open a much shorter time leaving less chance for evaporation of solvent and for introduction of moisture.

When ethanol was used as solvent the experimental method used was almost identical to that described above. The lower solubility of ammonium chloride in ethanol as compared with methanol made it impossible to completely dissolve the salt before adding the silver cyanate. However, the reaction between silver cyanate and ammonium chloride forming silver chloride quickly reduces the ammonium chloride concentration so the undissolved material can go into solution and react, finally removing all chloride ion. A period of ten to fifteen minutes was usually sufficient to remove all chloride ion. Since the rate of conversion of ammonium cyanate is more rapid in ethanol than in methanol due to its lower dielectric constant, it was difficult to obtain starting concentrations as high as desired. How-

ever by cooling the solution after the first few minutes of stirring, and by allowing less time in the thermostat before beginning to withdraw samples, the initial concentration could be brought to a reasonably high value. In the case of the reaction carried out in ethanol at  $50^{\circ}$  the time allowed to reach equilibrium was lowered to five minutes. However the temperature of the solution was brought very close to  $50^{\circ}$  before placing in the thermostat, and it was shaken vigorously during the five minute period. The results obtained by this method were quite satisfactory.

When isopropanol was used as solvent, the experimental difficulties became much greater. The very low solubility of ammonium chloride in isopropanol coupled with the increased speed of conversion in this solvent made it quite impossible to obtain starting concentrations of the desired magnitude. Since good experimental results on the ammonium cyanate reaction are rarely obtained at concentrations much below 0.02M., some method of obtaining a starting concentration somewhat above this value had to be evolved. The method finally arrived at was to increase the solubility of ammonium chloride by warming the isopropanol to  $50^{\circ}$ . The silver cyanate was then added and the mixture agitated for twenty minutes while maintaining the temperature at  $50^{\circ}$ . Then the mixture was cooled quickly by surrounding the flask with ice meanwhile continuing the stirring for ten to fifteen minutes. By this method starting concentrations of ammonium cyanate in the neighborhood of 0.03M. were obtained when using enough ammonium chloride to give theoretically a starting concentration of 0.06M. to 0.08M. Heating at higher or lower temperatures for longer or shorter periods of time usually gave poorer results. The isopropanol also gave difficulty in the silver ion titrations. It had some effect on the indicator, making the endpoint more difficult to ascertain, and also caused fading endpoints

doubtless due to some adsorption effect. After considerable experience, however, reproducible results were obtained.

Ethylene glycol, due to the high viscosity of the pure solvent gave difficulty in the usual filtration methods. The method finally used to filter the ammonium cyanate solutions in glycol was one involving suction filtration with a Buchner funnel. A very tight grade of quantitative paper (no. 50) had to be used to prevent silver chloride being pulled through. The material was filtered directly into the reaction flask taking precautions to preclude moisture.

Attempts were also made to run the reaction in glycerol and in dioxane by the same general method. However ammonium chloride was found to be almost completely insoluble in dioxane, and attempts to filter or centrifuge glycerol solutions met with failure.

All the experimental data obtained are tabulated in Tables I through XVI. The method of using this data to calculate the other columns in the Tables will be described in the next section.

TABLE I

METHYL ALCOHOL at 20° D = 32.55

Run #1								
TIME (min)	WT. of SAMPLE	VOL. of SAMPLE	cc. KSCN (corr)	34.85-cc*	CONC. NH <sub>4</sub> CNO	$\frac{1+4A\sqrt{C}}{C}$	k <sub>ot</sub>	k <sub>o</sub>
0	7.813gm	9.87cc	2.14	32.71	0.06632M	85.3		
60	8.477	10.71	2.50	32.35	.06040	90.0	4.7	0.0783
91	8.257	10.44	4.55	30.30	.05805	92.3	7.0	.0769
121	8.313	10.51	5.63	29.22	.05560	94.6	9.3	.0768
200	8.156	10.31	9.02	25.83	.05012	100.7	15.4	.0770
250	8.192	10.35	10.53	24.32	.04702	104.6	19.3	.0772
300	8.110	10.25	12.09	22.76	.04441	108.3	23.0	<u>.0766</u>
								av. 0.0771

Run #2								
TIME (min)	WT. of SAMPLE	VOL. of SAMPLE	cc. KSCN (corr)	34.85-cc*	CONC. NH <sub>4</sub> CNO	$\frac{1+4A\sqrt{C}}{C}$	k <sub>ot</sub>	k <sub>o</sub>
0	7.493gm	9.46cc	7.85	27.00	0.05713M	93.1		
60	8.002	10.11	8.29	26.56	.05253	97.8	4.7	0.0783
125	7.823	19.89	10.94	23.91	.04832	102.8	9.7	.0776
165	8.035	10.15	11.40	23.45	.04619	105.8	12.7	.0770
216	8.163	10.31	12.40	22.45	.04354	109.7	16.6	.0768
250	7.947	10.04	13.57	21.28	.04181	112.3	19.2	<u>.0768</u>
								av. 0.0773

Average k<sub>o</sub> = 0.0773

\*34.85 is the cc. of 0.02M KSCN = 24.95 cc. AgNO<sub>3</sub> into which volume the samples were pipetted.

TABLE II

METHYL ALCOHOL at 30° D = 30.68

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	44.08-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.98cc	16.22cc	27.86cc	0.05582M		
17	9.98	18.46	25.62	.05133	4.9	0.288
44	9.98	21.19	22.89	.04586	11.9	.271
45	9.98	21.21	22.87	.04581	12.0	.266
84	9.98	24.37	19.71	.03950	22.2	.264
144	9.98	28.23	15.85	.03177	39.3	.273
146	9.98	28.20	16.08	.03222	38.1	<u>.261</u>
						av. 0.2705

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	44.08-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.98cc	26.92cc	17.16cc	0.03439M		
15.1	9.98	27.76	16.32	.03271	4.1	0.272
45	9.98	29.30	14.78	.02963	12.4	.275
46	9.98	29.30	14.78	.02963	12.4	.270
90	9.98	31.08	13.00	.02606	24.2	.269
155	9.98	33.06	11.02	.02210	41.0	.264
156	9.98	33.17	10.91	.02188	42.1	<u>.270</u>
						av. 0.270

Average k<sub>0</sub> = 0.270\*44.08cc. KSCN = 24.95cc. AgNO<sub>3</sub>

TABLE III

METHYL ALCOHOL at 40° D = 29.03

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.93-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	10.26cc	13.20	21.73	0.04235M		
5	10.21	14.63	20.30	.03978	4.5	0.90
27	9.83	19.83	15.10	.03052	24.8	.918
34	10.14	20.27	14.66	.02892	30.7	.903
44	11.44	19.94	14.99	.02620	40.4	.918
56	11.39	21.34	13.59	.02386	49.4	.883
69	11.35	22.80	12.13	.02137	61.4	<u>.890</u>
					av.	0.887
Run #2						
0	12.18 cc	9.68	25.25	0.04147M		
5	11.08	13.32	21.61	.03902	4.4	0.88
24	11.37	16.88	18.05	.03175	20.9	.871
30	11.91	17.06	17.87	.03001	25.8	.861
37	11.68	18.59	16.34	.02798	32.2	.870
44	11.59	19.61	15.32	.02643	37.6	<u>.855</u>
					av.	0.865

Average k<sub>0</sub> = 0.876\*34.93 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE IV

METHYL ALCOHOL at 50° D = 27.44

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.86-cc.*KSCN	CONC. NH <sub>4</sub> CNO	k <sub>ot</sub>	k <sub>o</sub>
0	10.94cc	8.90cc	25.96cc	0.04749M		
1	10.64	10.62	24.24	.04560	2.7	2.70
10	10.39	17.63	17.23	.03317	27.2	2.72
13	10.65	18.44	16.32	.03063	34.3	2.64
16	10.63	19.83	15.03	.02828	41.7	2.61
19	10.44	21.18	13.68	.02620	49.6	<u>2.61</u>
						av. 2.66
Run #2						
0	10.31cc	10.46cc	24.40cc	0.04732M		
6	10.33	15.28	19.58	.03790	16.1	2.68
13	10.57	18.90	15.96	.03051	34.3	2.64
18	10.39	21.27	13.59	.02616	48.8	2.71
21	10.26	22.42	12.44	.02424	56.8	2.706
24	11.09	22.28	12.58	.02270	63.8	<u>2.66</u>
						av. 2.68

Average k<sub>o</sub> = 2.67\*34.86 cc.KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE V

ETHYL ALCOHOL at 20° D = 25.00

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.88-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>o</sub> t	k <sub>o</sub>
0	10.18cc	3.01cc	31.87cc	0.06261M		
34	10.79	4.30	30.58	.05667	7.1	0.208
54	10.66	6.02	28.80	.05417	10.5	.188
74	10.80	6.93	27.95	.05174	14.4	.194
102	9.59	11.63	23.25	.04965	19.2	.188
134	10.02	12.33	22.55	.04499	25.4	.190
175	10.34	13.69	21.19	.04096	33.6	.192
226	4.83	25.86	9.02	.03731	42.3	<u>.187</u>
						av. 0.193

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.88-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>o</sub> t	k <sub>o</sub>
0	10.62cc	3.93cc	30.95cc	0.05826M		
45	10.39	8.03	26.85	.05166	9.0	0.200
80	9.73	11.87	23.01	.04728	16.1	.201
105	10.08	12.43	22.45	.04454	21.2	.202
130	9.38	15.12	19.76	.04212	26.0	.200
161	10.08	15.12	19.76	.03921	32.5	.201
185	10.31	15.66	19.22	.03728	37.3	<u>.201</u>
						av. 0.201

Average k<sub>o</sub> = 0.197\*34.88 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE VI

ETHYL ALCOHOL at 30° D = 23.55

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.85-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	10.52cc	5.79cc	29.06cc	0.05526M		
2	10.54	6.09	28.76	.05457	1.2	0.60
30	10.72	11.17	23.68	.04416	18.5	.616
57	10.38	15.72	19.13	.03687	35.3	.608
71	10.24	17.39	17.46	.03412	43.2	.609
86	10.50	18.20	16.65	.03170	51.0	.593
100	10.05	20.06	14.79	.02943	59.5	.595
121	9.58	22.06	12.79	.02672	70.9	<u>.586</u>
						av. 0.601
Run #2						
0	10.31cc	10.04cc	24.81cc	0.04814M		
2	10.21	10.65	24.20	.04740	1.2	0.60
30	10.35	14.46	20.39	.03940	17.7	.590
36	10.45	15.08	19.77	.03785	21.7	.603
45	10.18	16.58	18.27	.03590	26.9	.597
60	10.12	17.95	16.90	.03340	34.6	.576
75	10.58	18.59	16.26	.03071	43.6	<u>.582</u>
						av. 0.591

Average k<sub>0</sub> = 0.596\*34.85 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE VII

ETHYL ALCOHOL at 40° D = 22.20

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.93-cc.KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	8.61cc	19.27cc	15.66cc	0.03638M		
19	11.30	19.45	15.48	.02740	32.1	1.69
24	11.16	20.60	14.33	.02569	40.2	1.675
29	10.96	21.76	13.17	.02403	49.0	1.69
35	11.09	22.54	12.39	.02234	59.0	1.686
42	10.37	24.23	10.70	.02063	70.6	1.68
49	9.17	26.11	8.82	.01924	81.2	<u>1.66</u>
						av. 1.68

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.93-cc.KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	4.703cc	3.87cc	10.09cc	0.04291M		
23	7.705	2.79	11.17	.02899	41.3	1.79
28	7.113	3.97	9.99	.02809	45.1	1.61
40	9.168	3.14	10.82	.02360	67.5	1.69
50	10.352	3.18	10.78	.02083	85.3	<u>1.70</u>
						av. 1.70

Average k<sub>0</sub> = 1.69\*34.93 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE VIII

ETHYL ALCOHOL at 50° D = 20.87

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.93-cc. KSCN	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.89cc	15.32cc	19.61cc	0.03964M		
1	10.16	15.66	19.27	.03788	4.5	4.50
7	10.30	19.54	15.39	.02990	31.2	4.46
8	10.67	19.68	15.25	.02857	36.7	4.59
9	10.24	20.72	14.21	.02776	40.3	4.47
10	10.18	21.22	13.65	.02682	44.6	<u>4.46</u>
						av. 4.495

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.93-cc. KSCN	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	10.70cc	18.13cc	16.80cc	0.03140M		
8	11.30	21.47	13.46	.02383	35.2	4.42
10	10.75	22.97	11.96	.02226	45.0	4.50
11	11.69	22.35	12.58	.02152	50.0	4.55
13	12.10	22.62	12.31	.02035	58.5	<u>4.50</u>
						av. 4.49

Average k<sub>0</sub> = 4.49

TABLE IX

ISOPROPYL ALCOHOL at 20°  $D = 18.62$ 

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.88-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.52cc	21.05cc	13.83cc	0.02905M		
30	9.84	21.05	13.83	.02810	5.4	0.180
50	9.03	22.52	12.36	.02738	9.2	.184
70	9.24	22.50	12.38	.02679	13.0	.186
100	9.41	22.68	12.20	.02593	18.2	.182
190	9.13	24.15	10.73	.02350	35.1	<u>.185</u>
						av. 0.1834

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.88-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.515cc	21.25cc	13.63cc	0.02864M		
20	9.85	21.12	13.76	.02795	3.7	0.185
40	9.875	21.38	13.50	.02733	7.3	.183
60	9.74	21.86	13.02	.02682	11.0	.1835
85	9.46	22.52	12.36	.02612	15.1	.1775
120	10.15	22.14	12.74	.02509	21.8	<u>.182</u>
						av. 0.182

Average k<sub>0</sub> = 0.183\*34.88 cc. KSCN = 24.95cc. AgNO<sub>3</sub>

TABLE X

ISOPROPYL ALCOHOL at 30° D = 17.38

TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	Run #1		k <sub>o</sub> t	k <sub>o</sub>
			34.86-cc. KSCN*	CONC. NH <sub>4</sub> CNO		
0	10.52cc	20.26cc	14.60cc	0.02774M		
5	10.30	20.80	14.06	.02730	3.0	0.60
40	10.51	22.19	12.67	.02411	24.5	.612
50	10.33	22.79	12.07	.02336	29.8	.596
65	10.21	23.44	11.42	.02237	38.7	.595
80	10.40	23.76	11.10	.02134	47.7	.596
100	10.58	24.18	10.68	.02020	58.6	.586
120	10.51	24.84	10.02	.01907	70.5	<u>.588</u>
						av. 0.595
			Run #2			
0	10.23cc	21.40cc	13.46cc	0.02630M		
38	10.17	23.10	11.76	.02313	23.0	0.605
58	10.45	23.49	11.37	.02175	34.7	.598
72	10.36	24.03	10.83	.02092	42.2	.587
88	10.47	24.51	10.35	.01977	53.9	.613
108	9.96	25.49	9.37	.01883	64.2	.595
130	10.17	25.86	9.00	.01770	77.5	<u>.596</u>
						av. 0.599

Average k<sub>o</sub> = 0.597\*34.86 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE XI

ISOPROPYL ALCOHOL at 40° D = 16.23

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.93-cc KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.83cc	20.44cc	14.49cc	0.02949M		
5	10.27	20.60	14.33	.02790	9.5	0.190
15	10.07	22.27	12.66	.02513	28.2	.188
18	10.01	22.75	12.18	.02434	34.0	.189
22	10.66	22.39	12.54	.02352	40.8	.186
27	10.88	22.76	12.17	.02236	51.7	.192
33	10.77	23.36	11.57	.02149	58.7	.178
40	10.41	24.44	10.49	.02015	72.0	<u>.180</u>
						av. 0.186

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.86-cc KSCN**	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	10.29cc	20.84cc	14.02cc	0.02726M		
12	10.18	22.55	12.31	.02418	22.1	0.184
16	10.45	22.69	12.17	.02330	29.2	.1825
21	10.42	23.32	11.54	.02214	38.7	.184
27	10.35	24.06	10.80	.02088	51.0	.188
34	10.38	24.52	10.34	.01992	60.9	.179
42	9.95	25.58	9.28	.01865	75.1	.179
50	10.75	25.40	9.46	.01760	88.1	<u>.176</u>
						av. 0.182

Average k<sub>0</sub> = 0.184\*34.93 cc. KSCN = 24.95cc. AgNO<sub>3</sub>\*\*34.86cc. KSCN = 24.95cc. AgNO<sub>3</sub>

TABLE XII

ISOPROPYL ALCOHOL at 50° D = 15.06

TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	Run #1		k <sub>0t</sub>	k <sub>0</sub>
			34.93-cc. KSCN*	CONC. NH <sub>4</sub> CNO		
0	10.20cc	22.90cc	12.03cc	0.02358M		
4	10.33	23.90	11.03	.02134	20.5	5.13
6	10.42	24.38	10.55	.02024	32.1	5.34
8	10.21	25.07	9.86	.01931	42.4	5.30
9	10.32	25.14	9.79	.01897	46.8	5.20
10	10.17	25.51	9.42	.01853	52.5	5.25
12	10.26	25.90	9.02	.01761	63.5	<u>5.28</u>
						av. 5.25

Run #2						
0	10.61cc	21.25cc	13.68cc	0.02578M		
1	10.56	21.71	13.22	.02504	5.2	5.2
4	10.56	22.80	12.13	.02314	21.1	5.27
6	10.35	23.56	11.37	.02197	32.1	5.35
9	10.44	24.20	10.73	.02054	46.8	5.20
10	10.80	24.12	10.81	.02002	52.6	5.26
11	10.91	24.32	10.61	.01946	59.1	<u>5.37</u>
						av. 5.27

Average k<sub>0</sub> = 5.26\*34.93cc. KSCN = 24.95cc. AgNO<sub>3</sub>

TABLE XIII

ETHYLENE GLYCOL at 30° D = 36.80

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.85-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	8.70cc	5.06cc	29.79cc	0.06847M		
70	9.00	6.64	28.21	.06272	3.77	0.0538
100	8.93	7.87	26.98	.06040	5.45	.0545
135	9.04	8.65	26.20	.05798	7.32	.0542
211	9.065	10.70	24.15	.05327	11.4	.0540
250	8.89	12.10	22.75	.05119	13.4	.0537
300	8.85	13.38	21.47	.04850	16.2	.0540
372	7.52	17.87	16.98	.04513	20.03	<u>.0539</u>
						av. 0.0540

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.85-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	9.14cc	7.32cc	27.53cc	0.06026M		
105	9.07	10.90	23.95	.05345	5.7	0.0543
140	8.81	12.23	22.62	.05136	7.6	.0543
175	9.09	12.38	22.47	.04945	9.5	.0543
210	8.99	13.39	21.46	.04774	11.4	.0543
255	8.83	14.67	20.18	.04571	13.8	.0541
295	7.88	17.60	17.25	.04377	16.2	<u>.0550</u>
						av. 0.0544

Average k<sub>0</sub> = 0.0542\*34.85 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>

TABLE XIV

ETHYLENE GLYCOL at 40° D = 34.94

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.86-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>ot</sub>	k <sub>o</sub>
0	9.47cc	6.91cc	27.95cc	0.05904M		
5	9.40	7.70	27.16	.05778	.95	0.190
30	9.46	9.99	24.87	.05259	5.5	.183
38	9.67	10.00	24.86	.05140	6.8	.179
48	9.60	11.03	23.83	.04962	8.6	.179
60	9.63	11.95	22.91	.04758	11.0	.1834
76	9.56	13.17	21.69	.04535	13.6	.179
95	9.49	14.53	20.33	.04280	17.0	<u>.179</u>

av. 0.182

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.85-cc. KSCN**	CONC. NH <sub>4</sub> CNO	k <sub>ot</sub>	k <sub>o</sub>
0	9.87cc	2.87cc	31.98cc	0.06480M		
40	9.69	7.97	26.88	.05550	7.2	0.180
60	9.46	10.21	24.64	.05210	10.8	.180
75	9.56	11.31	23.54	.04920	13.3	.1775
95	9.56	12.85	22.00	.04600	17.0	.177
110	9.62	13.70	21.15	.04397	19.5	.177
130	9.14	15.89	18.96	.04150	22.9	.176
150	9.11	17.05	17.80	.03907	26.6	.1775
180	7.97	20.54	14.31	.03593	32.0	<u>.178</u>

av. 0.178

Average k<sub>o</sub> = 0.180\*34.86 cc. KSCN = 24.95 cc. AgNO<sub>3</sub>      \*\*34.85 cc. KSCN = 24.95cc. AgNO<sub>3</sub>

TABLE XV

ETHYLENE GLYCOL at 50° D = 33.21

Run #1						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.86-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	10.36cc	4.69cc	30.17cc	0.05822M		
12	10.11	9.29	25.57	.05056	7.3	0.608
16	9.96	10.70	24.16	.04846	9.7	.606
20	9.81	12.13	22.73	.04632	12.0	.600
25	10.25	12.38	22.48	.04387	15.2	.608
30	10.00	14.05	20.81	.04162	18.3	.610
42	10.15	16.10	18.76	.03698	25.4	<u>.605</u>
						av. 0.606

Run #2						
TIME (min)	VOL. of SAMPLE	cc. KSCN (corr)	34.86-cc. KSCN*	CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
0	10.37cc	8.83cc	26.03cc	0.05020M		
2	9.77	10.84	24.02	.04915	1.17	0.585
17	9.59	14.76	20.10	.04191	10.15	.597
23	9.79	15.40	19.46	.03974	13.5	.587
30	9.36	17.43	17.43	.03724	17.8	.593
40	9.39	18.81	16.05	.03418	23.5	.587
48	9.53	19.63	15.23	.03194	28.3	.590
70	9.56	21.91	12.95	.02710	41.2	<u>.589</u>
						av. 0.590

Average k<sub>0</sub> = 0.598\*34.86 cc. KSCN = 24.95cc. AgNO<sub>3</sub>

TABLE XVI

ETHYLENE GLYCOL at 60° D = 31.58

TIME (min)	VOL. of SAMPLE	Run #1		CONC. NH <sub>4</sub> CNO	k <sub>0</sub> t	k <sub>0</sub>
		cc. KSCN (corr)	34.86-cc. KSCN			
0	9.79cc	9.83cc	25.03cc	0.05116M		
8	9.60	15.80	19.06	.03972	14.8	1.85
11	9.55	17.48	17.38	.03640	20.7	1.88
14	9.30	19.33	15.53	.03341	26.6	1.90
18	10.04	19.63	15.23	.03034	33.8	1.88
22	9.40	21.86	13.00	.02767	41.3	1.88
26	9.065	23.35	11.51	.02540	48.6	1.87
30	9.41	23.82	11.04	.02347	55.7	1.86
35	10.42	23.79	11.07	.02125	65.3	<u>1.87</u>
						av. 1.87

Run #2						
0	9.83cc	9.92cc	24.94cc	0.05074M		
1	9.83	10.73	24.13	.04910	1.7	1.70
7	9.24	15.85	19.01	.04115	12.1	1.73
9	10.00	15.32	19.54	.03908	15.4	1.71
12	9.80	17.20	17.66	.03604	20.7	1.72
15	9.84	18.26	16.60	.03374	25.4	1.69
18	9.86	19.39	15.47	.03138	31.0	1.71
26	9.99	21.65	13.21	.02644	45.2	1.74
30	9.87	22.89	11.97	.02425	52.2	<u>1.74</u>
						av. 1.72

Average k<sub>0</sub> = 1.80

## CALCULATIONS AND DISCUSSION

The method of calculating  $k_0$ , the reaction rate constant, at zero ionic strength can be followed by referring to the data in Table I. The columns headed Time, Weight, and cc. of KSCN consist of recorded experimental data. The data in the column headed Vol. of Sample is calculated from the weight data using the density of the pure solvent at the specified temperature. All density data was either taken from the International Critical Tables or calculated from formulas given in the same tables. The data in the fifth column is obtained by subtracting the number of cc. of KSCN used in titration from the cc. of KSCN equivalent to the added excess of  $\text{AgNO}_3$ . The resulting figures are the cc. of 0.02M KSCN equivalent to the amount of  $\text{NH}_4\text{CNO}$  present in the withdrawn sample. The concentrations of  $\text{NH}_4\text{CNO}$  are calculated by multiplying the cc. of KSCN(0.02) and dividing by the volume of the sample. The limiting velocity constants were then calculated by means of the equation

$$k_0 t = \frac{1+4A\sqrt{C}}{C} - \frac{1+4A\sqrt{C_0}}{C_0}$$

which previous work<sup>7</sup> has shown holds reasonably well for reactions between unlike univalent ions in a changing ionic environment.  $A$  in this equation is the Debye-Huckel constant previously referred to,  $C_0$  is the initial concentration of  $\text{NH}_4\text{CNO}$ , and  $C$  is the concentration of  $\text{NH}_4\text{CNO}$  at any time  $t$ . Thus in the seventh column in Table I the first value of  $\frac{1+4A\sqrt{C}}{C}$ , which corresponds to zero time, becomes  $\frac{1+4A\sqrt{C_0}}{C_0}$ . Subtracting this figure from the subsequent values of  $\frac{1+4A\sqrt{C}}{C}$  gives the  $k_0 t$  values of the next column. Dividing  $k_0 t$  by the corresponding time yields  $k_0$  values for each experimental concentration following the initial one. Constancy of the  $k_0$  values throughout a run is a measure of the reliability of the experimental data.

The average value of the averaged  $k_0$ 's for two duplicate runs is taken to be the true  $k_0$  for that solvent and temperature. Tables II through XVI omit the weight and  $\frac{1+4A\sqrt{C}}{C}$  columns in order to eliminate the crowding of data.

In the derivation of the equation for calculation of  $k_0$  just described, the limiting Debye-Huckel theory has been used. The validity of this Debye-Huckel theory in low dielectric constant media is questionable. It is possible to treat the data by graphical means to calculate  $k_0$  and thus compare these methods. The graphical method is described in the material which follows. Since the rate equation for a simple bimolecular reaction may be written

$$-\frac{dC}{dt} = kC^2$$

for the case of equal starting concentrations, it is obvious that a plot of  $\frac{1}{C}$  vs.  $t$  should be independent of concentration and give a straight line of slope equal to  $k$ . However in reactions between ions, the ionic strength of the medium affects the reaction rate and the  $\frac{1}{C}$  vs.  $t$  plot is found to be curved. The slope of this plot at zero ionic strength would give  $k_0$  for the reaction, if it were possible to determine it accurately. The slope at any other point on the curve would give a  $k$  value for the corresponding ionic strength. If the values of  $k_1$  obtained from the slopes are now plotted against the corresponding value of  $\sqrt{u}$ , then on extrapolation to  $\sqrt{u}=0$ , it is possible to obtain a value of  $k_0$ . Previous work has shown that this method leads to essentially the same values as those obtained by the analytical calculation method in solvents of not too low a dielectric constant. The use of the Debye-Huckel limiting law in such solvents is thus upheld by experimental evidence within the limit of experimental error.

Equation (17) also gives us a relation between  $k_0$  and the  $k_1$  value

at any ionic strength. It is possible by means of equation (17) to calculate from the analytical  $k_0$  the corresponding  $k_1$  value at any desired ionic strength. Table XVII compares the  $k_1$  values, at  $\sqrt{u} = 0.194$ , calculated by equation (17) with those obtained by the graphical methods described above.

TABLE XVII

SOLVENT	T	$k_1$ (graphical)	$k_1$ (calc. by eq. 17)
Ethylene Glycol	50°	.246	.243
Ethylene Glycol	60°	.720	.718
Ethyl Alcohol	30°	.162	.162
Methyl Alcohol	20°	.276	.280

The agreement is good and so for all future calculations of  $k$ , at  $\sqrt{u} = 0.194$ , equation (17) will be used regardless of whether or not the experiment has been carried out at that particular concentration.

Table XVIII contains the complete list of  $k_0$  and  $k_1$  ( $\sqrt{u} = 0.194$ ) values obtained in the four solvents at the various temperatures.

TABLE XVIII

SOLVENT	20°		30°		40°		50°	
	$k_0$	$k_1$	$k_0$	$k_1$	$k_0$	$k_1$	$k_0$	$k_1$
Methanol	0.0772	0.0280	0.270	0.0962	0.876	0.305	2.67	0.907
Ethanol	0.197	0.0550	0.596	0.162	1.69	0.445	4.49	1.14
Isopropanol	0.183	0.0364	0.597	0.114	1.84	0.336	5.26	0.910
Glycol	—	—	0.542	0.0228	0.180	0.0746	0.598	0.243
								<u>60°</u>
Glycol							1.80	0.718

Graphs of  $-\log k_0$  vs.  $1/T$  and of  $-\log k_1$  vs.  $1/T$  for the four solvents are given in figures I, II, III, and IV. It may be observed that the points lie on a straight line in every case. The activation energy (E) and frequency factor (B) terms for each solvent, as obtained from these graphs using equation (28), are given in Table XIX.

TABLE XIX

SOLVENT	$\sqrt{u} = 0$		$\sqrt{u} = 0.194$	
	$E^\circ$	B	E	B
Methyl Alcohol	22230	15.45	20390	13.71
Ethyl Alcohol	19650	13.92	15300	10.27
Isopropyl Alcohol	21100	14.97	18930	12.70
Ethylene Glycol	23620	16.27	23320	15.15

The ammonium cyanate reaction has been carried out in isodielectric solvent-water mixtures by Svrbely and coworkers. By application of equation (19), using a slope taken from a  $\log k_0$  vs.  $1/D$  plot, the empirical equation

$$E^\circ_{P.C.} - E^{\circ*} = \underline{a} T/D \quad (30)$$

relating the fixed composition and isodielectric activation energies is obtained. The empirical constant,  $\underline{a}$ , was found to be equal to 1050, 620, and 605 for methanol-water, isopropanol-water, and glycol-water mixtures respectively referred to water at  $50^\circ$ . Direct calculation from equation (11) yields a constant = 778 referred to water at  $50^\circ$ , if a reasonable value for  $r$  ( $2 \times 10^{-8}$  cm) is assumed. In the next table experimental  $E^\circ_{H_2O} - E^{\circ*}$  values, obtained from previous work,<sup>9,10,11</sup> are given for several dielectric constant values in three different isodielectric solvent-water media. Comparison is made with values of  $E^\circ_{H_2O} - E^{\circ*}$  calculated by

Figure I

- Log  $k_0$  vs.  $1/T$

(1) Methyl Alcohol

(2) Isopropyl Alcohol

(3) Ethyl Alcohol

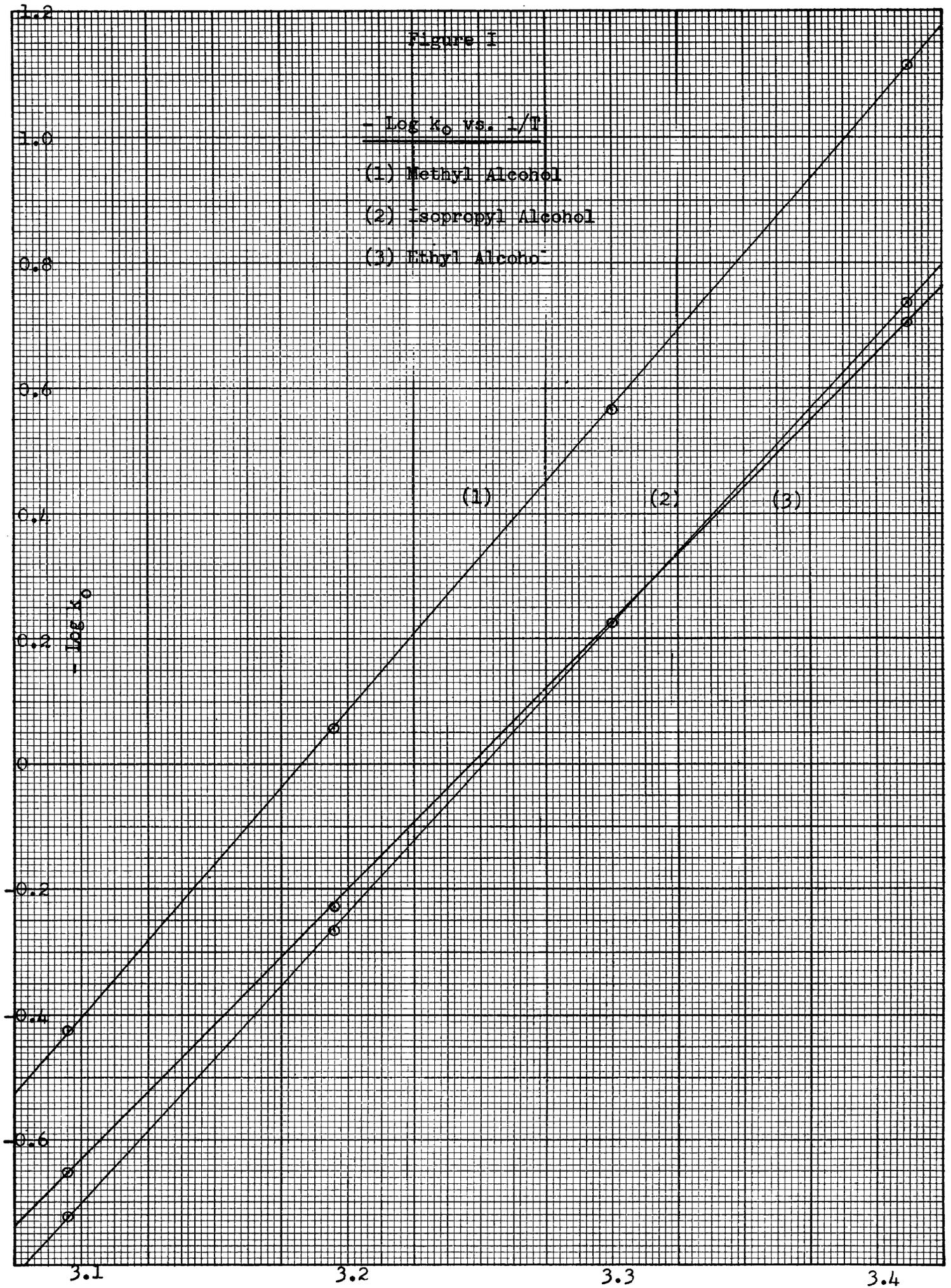


Figure II

$-\log k_0$  vs.  $1/T$   
for  
Ethylene Glycol

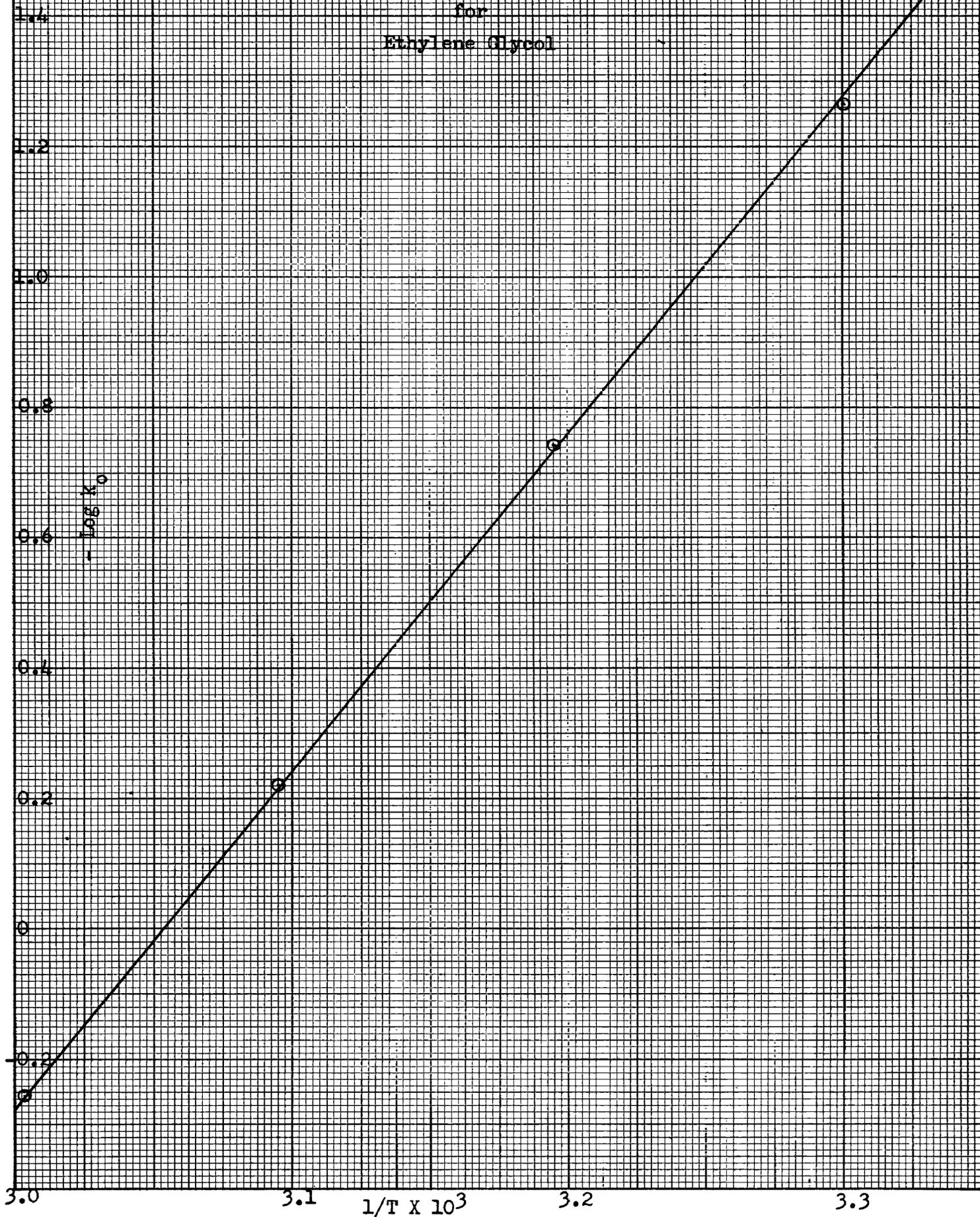


Figure III

Log  $k_1$  vs.  $1/T$

- (1) Methyl Alcohol
- (2) Isopropyl Alcohol
- (3) Ethyl Alcohol

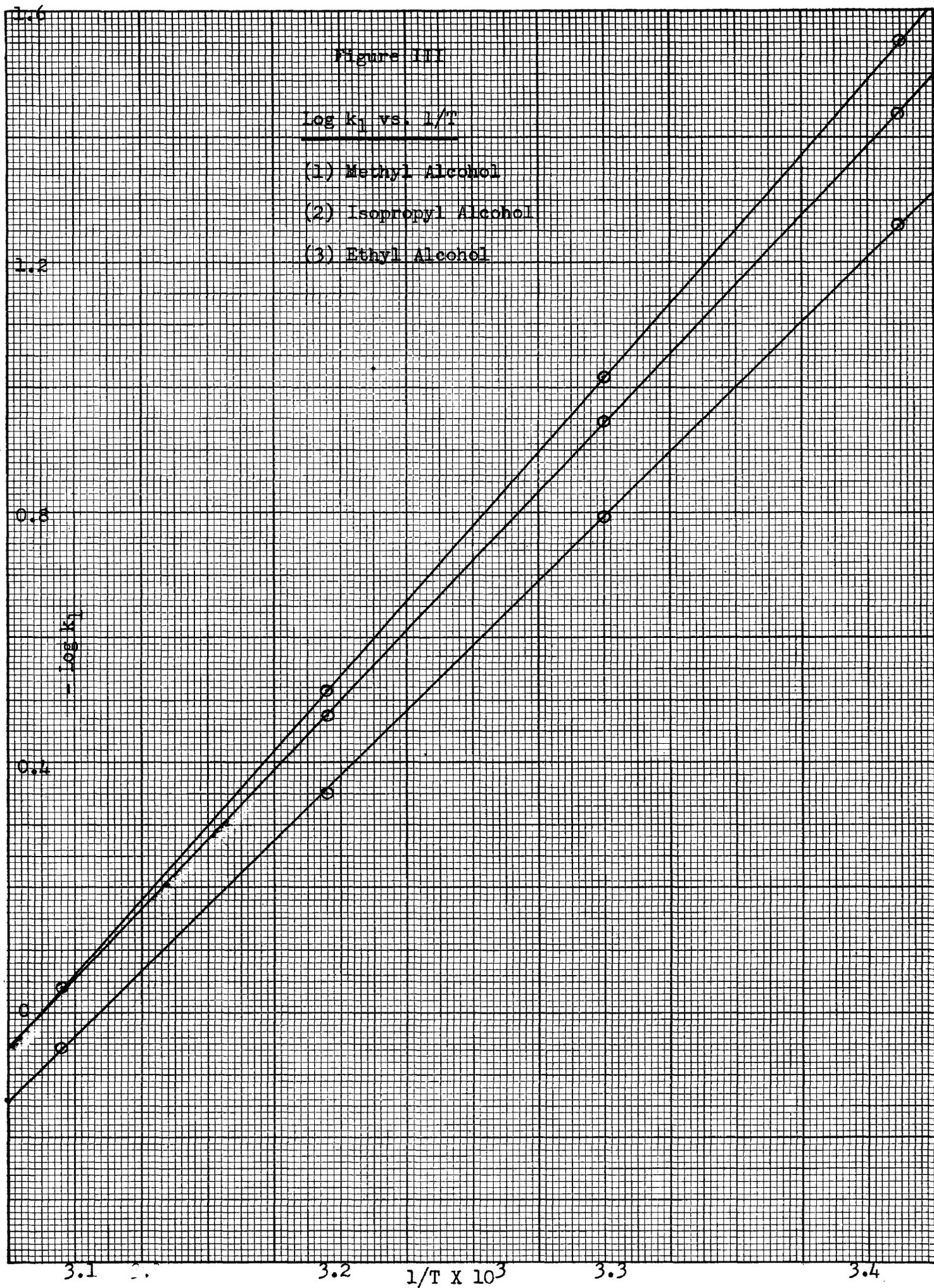


Figure IV

$-\log k_1$  vs.  $1/T$

for

Ethylene Glycol

1.6

1.2

0.8

0.4

0

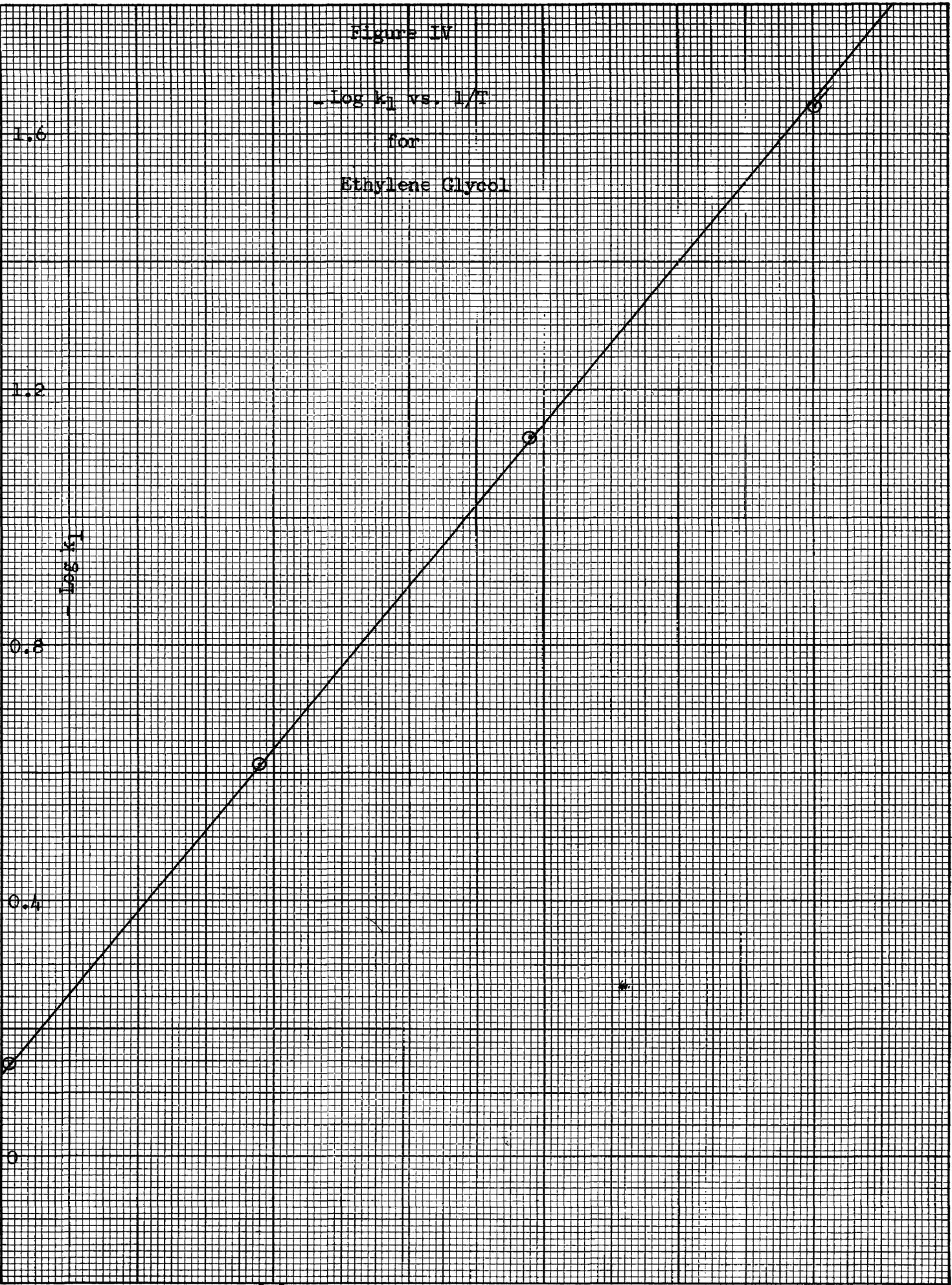
$-\log k_1$

3.1

$1/T \times 10^3$

3.2

3.3



means of the constants given above.

TABLE XX

 $E^{\circ}_{H_2O} - E^{\circ*}$  Values

SOLVENTS	D of Isodielectric Media						$E^{\circ}_{H_2O} - E^{\circ*}$ slope method	$E^{\circ}_{H_2O} - E^{\circ*}$ equation (11)
	63.5	55	150	40	30	20		
CH <sub>3</sub> OH-H <sub>2</sub> O	4740	5040	5740	5990			4860	3600
iso-C <sub>3</sub> H <sub>7</sub> OH-H <sub>2</sub> O	2830	2750	2840	2830	2700	5800	2860	3600
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> -H <sub>2</sub> O	3520	3590	3680	3660			2800	3600

It can be seen that the agreement in  $\Delta E^{\circ}$  values obtained experimentally and by the method of slopes is reasonably good in the higher isodielectric media. This slope method may be inspected by referring to Figure V. This graph contains plots of  $\log k_0$  vs.  $1/D$  for three solvent-water mixtures at  $50^{\circ}$ . It can be seen that contrary to the predictions of equation (12)  $\log k_0$  does vary with  $1/D$  and a constant slope is not obtained. The only term on the right side of equation (12) which could conceivably vary with  $1/D$  is  $r$ , the distance of closest approach. In applying the slope method to  $E^{\circ}_{H_2O} - E^{\circ*}$  calculations it was necessary to take slope values from the high dielectric constant portion of the curve in order to obtain results in agreement with theory. This corresponds to selecting from experiment the correct  $r$  value for the medium of that particular dielectric constant. It is interesting to note that the curves in Figure V tend to straighten out at both upper and lower ends giving reasonably constant  $r$  values for solutions as the mixed solvent approaches either of the pure components of the mixture.

Values of  $r$  for  $NH_4CNO$  have been calculated by means of equation (12) for slopes taken from both the high and low dielectric constants portions

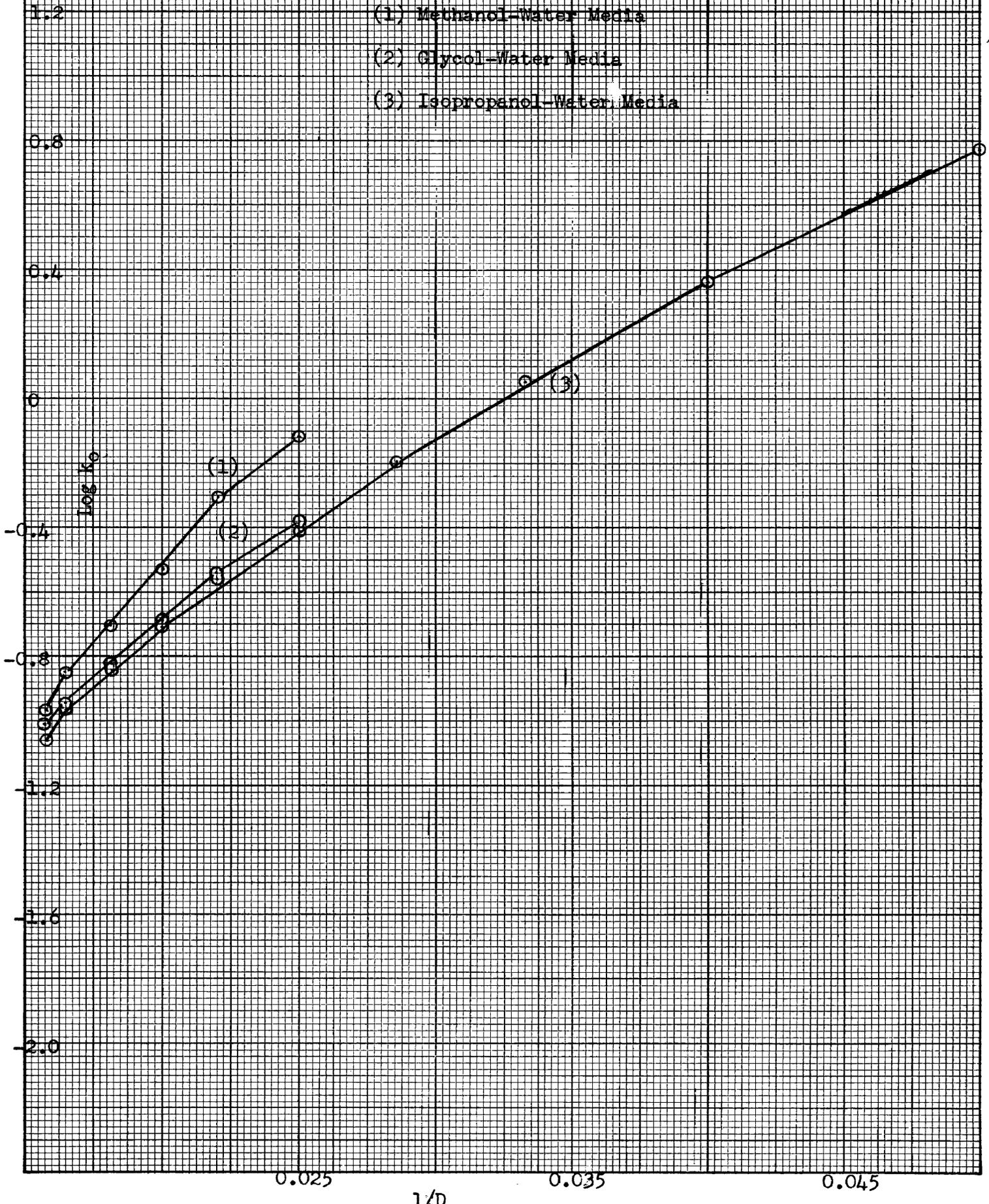
Figure 7

Log  $k_0$  vs.  $1/D$

(1) Methanol-Water Media

(2) Glycol-Water Media

(3) Isopropanol-Water Media



of the curve. These values should correspond approximately to the  $r$  values of  $\text{NH}_4\text{CNO}$  in pure water and pure non-aqueous solvent. Using these values of  $r$ , new  $a$  values have been calculated with the aid of equation (12).  $E^\circ_{\text{F.C.}} - E^{0*}$  values have also been determined by means of equation (30) for each reference solvent. Table XXI tabulates the values of  $r$  and  $a$  and  $E^\circ_{\text{F.C.}} - E^{0*}$  calculated by the methods described above. It also contains, for comparison purposes, values of  $E^\circ_{\text{F.C.}} - E^{0*}$  calculated for a value of  $r = 2 \times 10^{-8}$  cm., as well as experimental values of  $E^\circ_{\text{F.C.}} - E^{0*}$ .

TABLE XXI

SOLVENT MIXTURE	REFERENCE SOLVENT	$r$	$a$	$E^\circ_{\text{F.C.}} - E^{0*}$	$E^\circ_{\text{F.C.}} - E^{0*}$ ( $r=2 \times 10^{-8}$ cm)	$E^\circ - E^{0*}$ (exper.)
Methanol-Water	Methanol	3.86	460	5420	10460	4120
	Water	1.61	967	4470	3600	5470
Isopropanol-Water	Isopropanol	5.88	401	8600	25300	350
	Water	2.31	674	3120	3600	2850
Glycol-Water	Glycol	4.41	386	3750	8270	3670
	Water	2.43	640	2970	3600	3620

It is easily seen that when experimentally obtained  $r$  values are used in  $E^\circ_{\text{F.C.}} - E^{0*}$  calculations, the agreement with experimental  $\Delta E$  values is considerably better than when a constant  $r$  value ( $2 \times 10^{-8}$ ) is used. Furthermore the  $r$  values are all of the right order of magnitude and the agreement between  $r$  values based on high dielectric constant slopes for the different solvent-water mixtures is fairly good.

Equation (20) has been used to calculate theoretically the differences between the activation energies at  $\bar{v}_u = 0$  and at  $\bar{v}_u = 0.194$  for the ammonium cyanate reaction in various pure solvents. The theoretical  $E - E^0$  values are compared with experimentally obtained ones in Table XXII.

The data for water is taken from previous work<sup>8</sup>. The calculations are based on a temperature of 50°.

TABLE XXII

SOLVENT	E-E°(exper.)	E-E°(calc.)
Water	- 340	- 210
Methanol	-1840	-1080
Ethanol	-4350	-2060
Isopropanol	-2170	-6990
Glycol	- 300	- 745

It can be seen that while the agreement is reasonably good for water, it becomes poorer as we go to solvents of lower dielectric constant. This is not at all surprising since equation (20) is based on Debye-Huckel activity coefficient relations, which are known to be inadequate at low dielectric constants.

Equation (29) has been used to calculate  $\sigma_{12}$  values from the experimentally obtained B values which are listed in Table XIX. The calculations have been made for the various pure solvents, and also for several isodielectric mixtures, taking data from previous work<sup>9,10,11,12</sup>. Since B changed with dielectric constant for most of the isodielectric media, B values corresponding to intermediate dielectric constants were chosen for this comparison. The results are shown in Table XXIII, which is given on the next page.

It is immediately apparent from this table that equation (29) is valid only for isodielectric media. The  $\sigma_{12}$  values are of the correct order of magnitude only in the case of isodielectric solvents where conditions are more nearly comparable to those in the gas phase. These

results are in agreement with the prediction of La Mer<sup>19</sup>.

TABLE AXIII

Fixed Composition Solvents	12	Isodielectric Solvents	12
Water	$23.2 \times 10^{-8}$	Dioxane-water	$2.40 \times 10^{-8}$
Methanol	50.7	Methanol-water	0.74
Ethanol	8.7		
Isopropanol	29.2	Isopropanol-water	4.79
Glycol	130.3	Glycol-water	2.29

The comparisons which have been made between theory and experiment in the preceding material are fairly satisfactory considering the approximate nature of many of the equations. The assumption that dielectric constant, temperature, and ionic strength are the only important factors affecting ionic reaction velocities may not be entirely valid. Other solution properties such as viscosity and density may conceivably have some effect. The fact that limiting rate constants determined at the same dielectric constant and temperature in two different solvents often show little agreement argues that there are factors specific for each solvent that affect reaction rates. Figure VI shows a plot of  $\log k_0$  vs.  $1/D$  for the five pure solvents in which data on the ammonium cyanate reaction is now available. Since the plotted  $\log k_0$  values are for a single temperature, and since we have previously shown that a plot of  $\log k_0$  vs.  $1/D$  should be independent of dielectric constant, the points should fall on a straight line if  $D$  and  $T$  are the only factors affecting  $k_0$ . It may be observed that three of the points fall on a straight line while the other two fall on either side of the curve. The fact that water, glycol, and ethanol fall on a straight line seems to argue a fundamental

similarity between these solvents, at least in their effects on reaction rates. Since all electrostatic effects have been eliminated in this treatment, the properties causing methanol and isopropanol to deviate from the other solvents must be primarily due to physical properties of the respective molecules, such as shape, size, degree of association, degree of solvation, and polar characteristics.

It was previously noted that Figure V, which is a plot of  $\log k_0$  against  $1/D$  for solvent-water mixtures, does not give a straight line relation. The explanation has been advanced that this type of behavior is due to the salting out of the less polar component of the mixture by the added ions. Scatchard<sup>20</sup> suggested that this salting out explanation could be tested by velocity constant data obtained in pure solvents. If it should be found that the plot of  $\log k_0$  vs.  $1/D$  for the reaction measured in pure solvents gives a constant slope, the deviations from linearity shown in Figure V may be adequately explained purely on the basis of the salting out effect. Figure VI shows how well this requirement of constancy of slope is met. Apparently salting out does occur in solvent-water mixtures, but in addition complicating factors, such as were previously mentioned, are probably present.

## DISCUSSION OF ERRORS

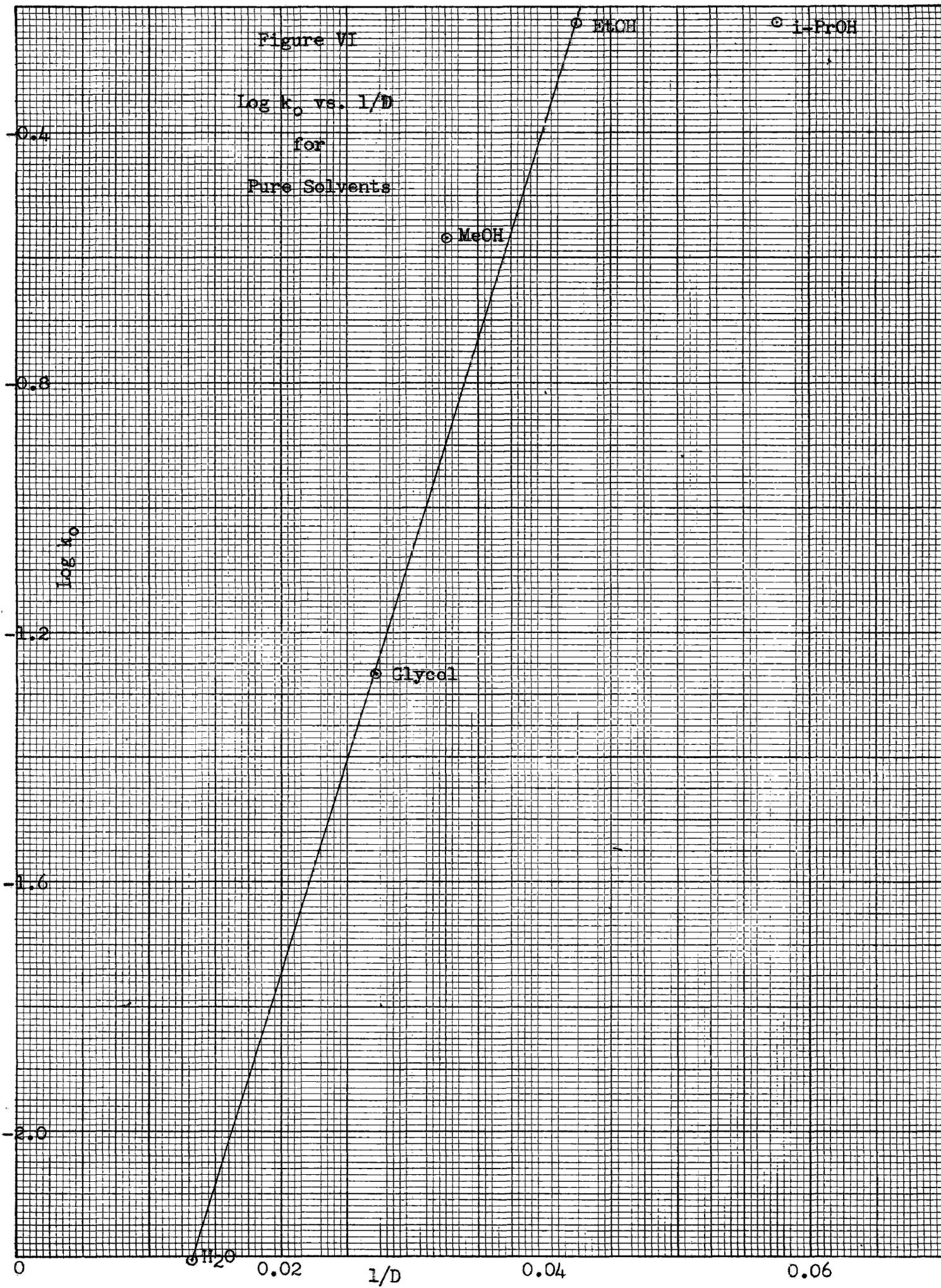
The possible sources of error in the experimental determinations are numerous. They may be summarized as errors in temperature control, time reading, weighing, and analytical method. Since the temperature was constant to within  $\pm 0.02^\circ$ , except at rare instances, and since great care was taken to assure its correct absolute value, the error involved in the temperature should be insignificant. However the drop in temperature of the withdrawn sample during the time consumed in pipetting may have caused an appreciable error in the measurements at the higher temperatures. Since the recorded times, which were times for half drainage of the sample into the silver nitrate solution, were read from an accurate stop watch, the timing errors should be small except for the very fast runs. Since the weighing involved large samples, weighing errors also should be inappreciable. In contrast, however, the errors involved in the analytical method were probably of considerable magnitude. Solubility of silver cyanate, insufficient washing of the silver cyanate precipitate, and adsorption of silver ions by the silver thiocyanate precipitate during titration were probably the chief analytical errors.

It is difficult to evaluate the probable magnitude of the analytical errors. The consistency of the experimental results is probably the best check on the reliability of the methods involved. In the worst case duplicate  $k_0$  values, obtained from separate runs, agree within a precision of 4.2 per cent. The usual agreement is considerably better than this, and in the average case the precision of duplicate results is about 0.5 per cent.

There are two systematic errors that should be discussed. One is the

Figure VI

log  $k_0$  vs.  $1/D$   
for  
Pure Solvents



use of pure solvent densities in calculating the volumes of the samples withdrawn. For the dilute solutions involved in these experiments, the error involved in this approximation is small in comparison to experimental error. The other possible error is involved in the use of Akerlof's dielectric constant values for the pure solvents. Because of the possibility of moisture absorption by the purified solvents on standing and during an experiment, it is conceivable that the actual dielectric constant of the solvent might vary somewhat from Akerlof's value. Furthermore, the presence of ammonium cyanate ions has some effect on the dielectric constant of the solvent, hence the dielectric constant of the medium is not identical with that of the pure solvent. The exact magnitude of this effect is not known at present, but is probably small.

The degree of reliability of the activation energies which have been determined is difficult to estimate. However they probably are correct within  $\pm 150$  calories, which is the reliability claimed by other investigators working on the same reaction.

## SUMMARY

1. The rate of conversion of ammonium cyanate to urea has been studied over a temperature range of  $30^{\circ}$  in the pure solvents, methanol, ethanol, isopropanol, and ethylene glycol.
2. The experimental results have been compared with results previously obtained for the same reaction in water and in isodielectric mixtures.
3. The observed influences of dielectric constant and ionic strength upon the activation energy for the reaction in the pure solvents are in good agreement with theory only in ethylene glycol and water (previously studied).
4. Values of  $r$ , the distance of closest approach, are found to vary with the solvent, becoming larger for lower dielectric constants.
5. The collision and thermodynamic theories of reaction rates are shown to be in substantial agreement when compared under similar conditions.
6. The salting out effect explanation for deviations from linearity in plots of  $\log k_0$  vs.  $1/D$  for solvent water mixtures has been substantially verified, however the situation is complicated by other disturbing factors in some solvents.

#### LITERATURE CITED

- (1) J. Walker and Hambly, *J. Chem. Soc.*, 67, 746 (1895)
- (2) J. Walker and Kay, *J. Chem. Soc.*, 71, 489 (1897)
- (3) Ross, *J. Chem. Soc.*, 105, 690 (1914)
- (4) E. B. Walker, *Proc. Royal Soc. (London)*, A87, 539 (1912)
- (5) J. S. Peake, Thesis, Carnegie Institute of Technology, 1932
- (6) Warner and Stitt, *J. Am. Chem. Soc.*, 55, 4807 (1933)
- (7) Warner and Warrick, *J. Am. Chem. Soc.*, 57, 1491 (1935)
- (8) Warner and Svirbely, *J. Am. Chem. Soc.*, 57, 1883 (1935)
- (9) Svirbely and Schramm, *J. Am. Chem. Soc.*, 60, 330 (1938)
- (10) Svirbely and Lander, *J. Am. Chem. Soc.*, 60, 1613 (1938)
- (11) Svirbely and Lander, *J. Am. Chem. Soc.*, 61, 3538 (1939)
- (12) Svirbely and Rampino, *J. Am. Chem. Soc.*, 61, 3534 (1939)
- (13) Moelwyn-Hughes, *Chem. Rev.*, 10, 244 (1932)
- (14) Scatchard, *Chem. Rev.*, 10, 229 (1932)
- (15) Bronsted, *Chem. Rev.*, 5, 231 (1928)
- (16) Christiansen, *Z. Physik. Chem.*, 113, 35 (1924)
- (17) Scatchard, *Chem. Rev.*, 10, 229 (1932)
- (18) Glasstone, Laidler and Eyring, Theory of Rate Processes, New York: McGraw Hill Book Co., 1941
- (19) La Mer, *J. Am. Chem. Soc.*, 61, 905 (1939)
- (20) Scatchard, *J. Chem. Phys.*, 7, 657 (1939)
- (21) Akerlof, *J. Am. Chem. Soc.*, 54, 4125 (1932)