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Title "A Study of the Transformation of Hydrazine Cyanate
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The rate of reaction of the conversion of hydrazine cyanate into semicarbazide has been measured, and the velocity constant, k at 15°C . and 25°C . has been determined. The limiting rate constant at 25°C . has been calculated. The dependence of the velocity constant has been determined in the presence of foreign salts.

The negative primary salt effect upon the velocity constant has been observed and according to the Bronsted theory indicates a bimolecular reaction which depends upon collisions between hydrazine and cyanate ions and not upon the collisions between the undissociated molecules of hydrazine chloride and potassium cyanate or between two molecules of hydrazine cyanate.

The classical equilibrium constant at 15° and 25°C has been determined from an analysis of the concentration of cyanate ions in solutions which have reacted for long periods of time. Determinations have been made from both decomposition of the pure semicarbazide and the reaction of the hydrazine and cyanate ions.

From the equilibrium constant and the bimolecular constant for the forward reaction of hydrazine cyanate, the unimolecular constant k' , for the reverse reaction has been calculated.

Determination of the bimolecular constant k at 15° and 25°C . has made it possible to calculate the temperature coefficient. The energy of activation of the hydrazine and cyanate ions necessary to cause their reaction has been calculated with the aid of the theories of Arrhenius and modern chemistry.

A STUDY OF THE TRANSFORMATION OF
HYDRAZINE CYANATE TO SEMICARBAZIDE

by

ELTON MURRAY BAKER

A THESIS

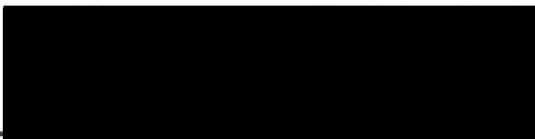
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degree of

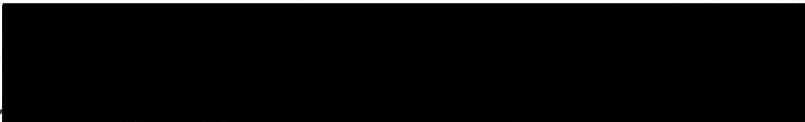
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A STUDY OF THE TRANSFORMATION OF HYDRAZINE CYANATE TO SEMICARBAZIDE

INTRODUCTION

One of the most interesting chemical reactions, historically, was the formation of urea from ammonium cyanate demonstrated by Wöhler in 1828. At that time it was important because it showed that an organic compound could be synthesized from purely inorganic substances, and hence it attracted considerable attention.

The interest in this reaction was soon shifted to more important organic syntheses and the reaction was largely forgotten. When interest in the physical aspects of chemistry began in the latter part of the nineteenth century, however, Walker and Hambly (26) chose this reaction to study its chemical kinetics. The rate was measurable at controlled temperatures and indicated it to be a bimolecular or second order reaction between the ammonium and cyanate ions. Again the reaction was replaced with other more important ones.

With the revival of interest in the application of newer theories to chemical kinetics, especially in Brønsted's (6) explanation of apparent irregularities due to salt effects and the change of reaction velocity with temperature, the ammonium cyanate rearrangement to

urea was again revived by Warner and Stitt (29) in 1933 and studied anew in the light of modern reaction rate theory.

It has been pointed out that since hydrazine is really a substituted ammonia, its reactions should be similar to those of ammonia. This led Thiele and Stange (25) in 1894 to use hydrazine instead of ammonia to react with cyanate to give semicarbazide.

The similarity of the two reactions led us to believe that this heretofore unstudied reaction of the formation of semicarbazide would be similar in its chemical kinetics to that of the urea synthesis.

This thesis therefore constitutes a comprehensive examination of the reaction of hydrazine cyanate to produce semicarbazide, including a study of the reaction kinetics, equilibrium measurements, temperature coefficient and effect of foreign salts. No similar studies of this reaction have been made.

THEORETICAL DISCUSSION

Any study in chemical kinetics should include the rates at which the substances react as well as the influence of the environmental conditions. It was shown by Wilhelmy (31) in 1850 that the rate of inversion of sucrose was proportional to the amount of sucrose remaining unchanged at any particular instant. If this is true, then the rate of the reaction of the involved substances should become less as the time of the reaction increases, and while half of the reactants may disappear in a short time, the remainder of the reaction may require days or weeks to reach completion. Complete reaction may not be possible should there be a reverse reaction resulting in an equilibrium.

The probability of more than three molecules entering into a reaction and colliding at the same instant is very small. Most homogeneous reactions may be placed in one of a few groups, i.e. first order, second order, or third order reaction. The second order reaction is one in which the concentration of only two molecules determines the velocity of the reaction. First and third order reactions involve concentrations of one and three molecules respectively.

The rate of any reaction may be expressed as follows, depending upon the number of reacting molecules,

$$(1) \quad \frac{dx}{dt} = k c_1 c_2 c_3$$

x is the amount of reactant which has disappeared, k is the velocity constant, and c the concentration (assuming the concentration to be a measure of the reactive masses) in mols per liter of reactant at a definite time, t . If a is taken as the concentration of the original reactant, then the equation becomes for a second order reaction,

$$(2) \quad \frac{dx}{dt} = k (a_1 - x)(a_2 - x)$$

If the two reactants have the same original concentration, it becomes,

$$(3) \quad \frac{dx}{dt} = k (a - x)^2$$

On integration this gives,

$$(4) \quad kt = \frac{x}{a(a - x)}$$

which may be written in the following form,

$$(5) \quad t = \frac{1}{k(a - x)} - \frac{1}{ka}$$

If time is plotted against $1/(a-x)$, then a straight line should be obtained with slope equal to $1/k$. A first or third order reaction would not be linear.

Should the products react to give the original reactants, this would constitute an opposing reaction to the one shown above, and the concentration of the reactants would not decrease as rapidly. The total rate of the reaction would be expressed as,

$$(6) \quad \frac{dx}{dt} = k (a - x)^2 - k' x$$

k' being the velocity constant for the reverse reaction which is a first order reaction opposing one of a second order. A plot of time against the reciprocal of the concentration would not be a straight line after the concentration of the products has become sizable. However, as long as the ratio of the concentration of the reactants to that of the products is very large, which is the case at the beginning of the reaction, the plot of the reaction as a second order will be linear.

When the forward and reverse reactions are moving at the same rate, i.e. at equilibrium, then

$$(7) \quad k (a - e)^2 = k' e$$

e being the value of x at the point of equilibrium, rearranging,

$$(8) \quad \frac{k'}{k} = \frac{(a - e)^2}{e} = K$$

According to Walker and Appleyard (27) the rate equation may be integrated in the following manner using partial fractions,

$$(9) \quad \frac{dx}{dt} = k [(a - x)^2 - K x]$$

$$(10) \quad k dt = \frac{dx}{x^2 - (2a + K) x + a^2}$$

$$(11) \quad k = \frac{1}{2t \sqrt{(a+\frac{K}{2})^2 - a^2}} \ln \frac{a^2 - x \left[a + \frac{K}{2} - \sqrt{(a+\frac{K}{2})^2 - a^2} \right]}{a^2 - x \left[a + \frac{K}{2} + \sqrt{(a+\frac{K}{2})^2 - a^2} \right]}$$

Having the "classical equilibrium constant" K , the initial concentration of reactants a , and the concentration of products x at any time t , the velocity constant k , may be calculated. It must be remembered that K as given above is not the same as the thermodynamic equilibrium constant. The latter is expressed using the activities of the various substances. The two constants become the same in ideal solutions, where the activities and concentrations are the same. A dilute solution approaches this ideal state.

However, since the reaction under study is one involving ions and not atoms or molecules in a solution containing a salt which does not enter into the reaction, it is necessary to consider the possibility of the activity coefficients varying in solutions of different ionic

strength (calculated according to Lewis and Randall (18). According to Bronsted (6,7), this may be shown as follows. By this theory the reaction involves the formation of an activated complex as the first stage of the process, followed by the decomposition of this complex to yield the products. Then,

$$(12) \quad K = \frac{a_x}{a^2} = \frac{c_x f_x}{c_1 c_2 f_1 f_2}$$

K is the thermodynamic equilibrium constant, a is the activity of the reactants, c is the concentration in mols per liter and f is the activity coefficient, while the subscript x refers to the complex. The rate of the reaction is proportional to the concentration of the complex,

$$(13) \quad \frac{dx}{dt} = k_x c_x$$

combining equations (12) and (13),

$$(14) \quad \frac{dx}{dt} = \frac{k_x K c_1 c_2 f_1 f_2}{f_x}$$

substituting k_o for $k_x K$,

$$(15) \quad \frac{dx}{dt} = \frac{k_o c_1 c_2 f_1 f_2}{f_x}$$

If equation (1) containing the ordinary observed velocity constant is combined with (15) then,

$$(16) \quad k = k_0 \frac{f_1 f_2}{f_x}$$

and the constant k_0 becomes the same as the velocity constant which is determined, if the solution is ideal or the activity coefficients are one, as is usually assumed in very dilute solutions.

Using the Debye-Huckel equation, the activity coefficient may be calculated as a function of the ionic strength, at 25° C.

$$(17) \quad -\log f = 0.5 Z_1 Z_2 \sqrt{\mu}$$

μ is the ionic strength with Z_1 and Z_2 the charge of the reacting ions. Substituting for the activity coefficients,

$$(18) \quad \log \frac{f_1 f_2}{f_x} = -0.5 \sqrt{\mu} (Z_1^2 + Z_2^2 - Z_x^2)$$

Since the charge Z_x is composed of the charges of the two reacting ions, then the above equation becomes,

$$(19) \quad \log \frac{f_1 f_2}{f_x} = Z_1 Z_2 \sqrt{\mu}$$

and substituting in (16)

$$(20) \quad k = k_0 10^{Z_1 Z_2 \sqrt{\mu}}$$

If a plot of $\log k$ against $\sqrt{\mu}$ is made, the slope of the line should be the product of the charges of the ions, and the point of intersection on the ordinate will give the velocity constant, k_0 for an infinitely dilute solution. It will also be observed that for two reacting ions of opposite charge, the observed velocity constant k will decrease with an increase in ionic strength of the solution, but it would remain unchanged in the case of uncharged reacting particles.

Most reactions which proceed at a measurable rate are slower at lower temperatures. This change in the speed of a reaction may be expressed by comparing the velocity constants at temperatures, differing by ten degrees. Most reactions fall within a range between 2 and 3 in this quantity. An attempt to explain this change in the velocity has been made by considering that only molecules having energy above a certain lower limit will react when they collide. Those molecules which have this excess energy are "activated", and the energy is known as energy of activation.

Since there are many molecules involved, it is possible to use a form of the Maxwell distribution law to express the number of molecules having the necessary energy of activation,

$$(21) \quad A_e = A e^{-\frac{E}{RT}}$$

where A_e is the total number of molecules, R the gas constant, T is the absolute temperature, and E the activation energy. If two molecules are reacting, it is generally assumed that the total excess energy of both molecules must be equal to the activation energy. If we define A as the number of molecules colliding in 1 cubic centimeter, which in turn is twice the number of collisions per second, the number reacting is,

$$(22) \quad \frac{dx}{dt} = A e^{-\frac{E}{RT}} = k c_1 c_2$$

if c^2 expresses the number of molecules per cubic centimeter, we may divide both sides of the equation by c^2 obtaining k , also with the term Z as the collision number, equivalent to the number of collisions per second when only one molecule is present,

$$(23) \quad k = Z e^{-\frac{E}{RT}}$$

If this equation is placed in the logarithmic form and differentiated, we obtain the same equation derived by Arrhenius (14),

$$(24) \quad \frac{d \ln k}{dt} = -\frac{E}{RT^2}$$

In the equation form before integration,

$$(25) \quad \log k = B - \frac{E}{2.303 RT}$$

$\log k$ may be plotted against $1/T$ giving $E/2.303 R$ for the slope of the straight line. With R expressed in calories, E may be determined in calories per mol.

The intersection of the above plotted line with the ordinate should give a value for B which involves the entropy of activation. The collision number does not vary greatly from one substance to another, so it is safe to assume that the energy of activation is the determining factor influencing the velocity of a reaction.

Many reactions seem to be much less than the calculated value, and it is necessary to add a correction factor or probability factor, P to the derived equation (23) of the velocity constant,

$$(27) \quad k = PZ e^{-\frac{E}{RT}}$$

This factor may be as high as 10^6 for the reaction between oppositely charged ions in solution x . In explanation one must assume that the molecules must be in the proper "condition" to cause the reaction to produce the activated complex, which in turn decomposes at a measured rate.

MATERIALS

The materials used were prepared and purified as follows:

Potassium Cyanate. Baker's C.P. potassium cyanate was suspended in absolute ethyl alcohol by shaking for several minutes. Since potassium cyanide is more soluble than potassium cyanate in alcohol, any cyanide impurity was removed. The remaining potassium cyanate was filtered, dried, and washed with ether to remove any water. The partly dried salt was placed in a desiccator and dried over sulfuric acid in a partial vacuum. The potassium cyanate thus prepared and stored in the dark and away from moisture, would keep for two to three weeks. It was analyzed by the Volhard method.

Hydrazine monohydrochloride. Kahlbaum hydrazine hydrate was neutralized with Baker's C.P. hydrochloric acid to a methyl orange endpoint in a solvent of methyl alcohol. After cooling, the crystals of hydrazine monohydrochloride separated. They were recrystallized from 80% methyl alcohol-water solution, washed with ethyl alcohol and dried over sulfuric acid. The salt was analyzed by a standard iodate method.

Semicarbazide monohydrochloride. Eastman's semicarbazide hydrochloride was recrystallized from an 80%

methyl alcohol-water solution. It was analyzed for chloride by the Volhard method.

Hydrazine perchlorate. Kahlbaum hydrazine hydrate was neutralized with C.P. perchloric acid to a methyl orange endpoint in methyl alcohol. After cooling, the hydrazine salt which crystallized out was recrystallized from a 80% methyl alcohol-water solution. The salt was analyzed by a standard iodate method.

Silver nitrate. Baker's C.P. silver nitrate was used for a standard solution. It was standardized against standard sodium chloride by using an excess of silver nitrate which was titrated after filtering with potassium thiocyanate using ferric alum as an indicator.

Sodium chloride. Baker's C.P. sodium chloride was dissolved in water to form a saturated solution. The solution was saturated with hydrogen chloride. The pure sodium chloride which crystallized from the solution was dried and used as a primary standard.

Potassium thiocyanate. Baker's C.P. potassium thiocyanate was used for a standard solution and standardized against a previously standardized silver nitrate solution using ferric alum as an indicator.

Ferric Ammonium Alum. Coleman and Bell ferric ammonium alum was used as an indicator in the Volhard method of analysis.

Sodium hydroxide. A solution of Baker's pellet sodium hydroxide C.P. was used to adjust the pH of the semicarbazide hydrochloride solution.

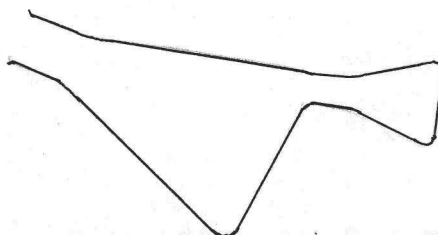
Hydrochloric acid. Baker's C.P.

Nitric Acid. Baker's C.P.

APPARATUS

The temperature of the reactions was maintained constant within 0.05° C. by placing the reaction flask in a constant temperature water bath. The thermostat consisted of a toluene and mercury filled regulator whose expansion caused a mercury column to close a relay circuit. The relay operated a carbon filament light bulb which heated the circulating water.

The reaction flask consisted of a 250 ml. Erylenmeyer pyrex flask at the bottom of which was joined a 25 ml. Erylenmeyer flask as shown in Fig. 1. The construction



Reaction Flask

Figure 1

of this flask made it possible to place both solutions of the reacting substances in the flask when suspended horizontally without mixing them until their temperature was constant to that of the controlled bath. It was also

possible to pipet all of the solution from the small flask. To start the reaction the flask was turned in a vertical position, allowing the solutions to mix thoroughly and almost instantaneously.

A Brenet stop watch was used to measure the time of the reactions to within one second.

A Beckmann pH Meter, Laboratory Model G, was used to measure the pH of some of the solutions containing the reacting substances.

A Normax pipet was calibrated and used to measure the standard silver nitrate solutions, the samples of reacting mixture, and the samples to be analyzed for excess silver nitrate.

A microburet was used for the titration of the silver nitrate with potassium thiocyanate. It could be read easily to within 0.005 ml.

METHOD OF ANALYSIS

The rate of the reaction was followed by determining the cyanate concentration at several time intervals. This was done by pipetting a definite volume of the reaction mixture into an excess of silver nitrate and filtering. An aliquot of the filtrate was analyzed for silver ions by titrating with standard potassium thiocyanate solution using ferric alum as an indicator.

Standard solutions of the reacting substances were made so that either 10 ml. of the cyanate or hydrazine could be placed in the small bulb of the reaction flask. The other solution was placed in the large part of the flask. The part of the flask containing the solutions was suspended in a horizontal position in the constant temperature bath. When the solutions were mixed by turning the flask in a vertical position with shaking, the stop watch was started. The mixed solution had a concentration which was used as the initial concentration, a. The exact time in seconds was taken when one half of a 10 ml. pipetted portion of the reaction mixture had left the pipet. Part of it would still be reacting while the precipitation of the cyanate would have stopped that part of the reaction mixture in the flask containing silver ions. Exactly 40 ml. of standard silver nitrate made

acid with nitric acid to the red color of methyl orange was used in the latter flask. All chloride and unreacted cyanate were precipitated. The solution was filtered immediately to prevent further precipitation of the silver ions which might follow after any of the silver chloride was reduced by light. All silver solutions were covered to prevent as much as possible the reduction of silver. A drop of concentrated nitric acid was usually sufficient to cause complete coagulation of any colloidal silver chloride, which occasionally formed.

A ten milliliter aliquot portion of the filtered solution was analyzed within 2 hours for silver ions. The cyanate present, was precipitated as silver cyanate with the silver chloride, providing the pH of the silver was not lower than 4. Cyanate decomposes rapidly in acid solutions of low pH. With the chloride concentration always constant, the unprecipitated silver ion concentration varies with the concentration of unreacted cyanate ions. Since some of the solution was lost by filtering, an analysis of an aliquot portion of the filtrate gives the concentration of silver ions. From this, the concentration of unreacted cyanate could be obtained. The Volhard method was used. This method depends upon the precipitation of the excess silver ions as silver thiocyanate with the formation of red ferric thiocyanate as the endpoint indicator.

ESTABLISHING THE REACTION

The use of hydrazine monochloride has not been reported in the literature. It was necessary to establish definitely that the proposed reaction did proceed as follows,



instead of a decomposition of the cyanate ion.

To a sample of the reaction mixture which had reacted for 30 minutes, one-half milliliter of benzaldehyde was added. After shaking the mixture vigorously for several minutes a light yellow precipitate appeared along with larger particles of a white precipitate. This mixture was filtered and washed several times with water. After drying, a portion of ether was used to extract the yellow compound which gave crystals from the ether. M.P. 94.5°-95.5° C. The remaining pure white compound was dried and recrystallized from ethyl alcohol. M.P. 211-213. These compounds had identical melting points with those formed from the reaction of benzaldehyde with hydrazine and with semicarbazide. A mixed melting point of each of the knowns with the unknowns did not show a difference in the melting points. This was evidence that the yellow compound was benzalazine and the white one was benzaldehyde semicarbazone.

An examination of the precipitates obtained by pipetting samples of the reaction mixture into benzaldehyde solutions at definite time intervals, showed qualitatively a definite decrease in the yellow color intensity indicating the disappearance of the hydrazine. At the same time the amount of benzal semicarbazone precipitate increased.

Table I

Effect of Temperature on the Reaction Rate

Run 63. Initial molality of hydrazine cyanate 0.0403 M.

25° C. Foreign salt concentration 0.0403 M.

Time (sec.)	Molality of Hydrazine Cyanate	Reciprocal of Cyanate Concentration
0	0.0403	24.8
79	0.0360	27.8
206	0.0322	31.1
370	0.0281	35.5
600	0.0238	41.9
925	0.0198	50.6
1511	0.0148	67.7

Run 65. Initial molality of hydrazine cyanate 0.0403 M.

15° C. Foreign salt concentration 0.0403 M.

0	0.0403	24.8
173	0.0372	26.9
379	0.0343	29.1
668	0.0306	32.7
1099	0.0268	37.4
1530	0.0242	41.4
2466	0.0194	51.5

Change in Reaction Rate at Different Temperatures

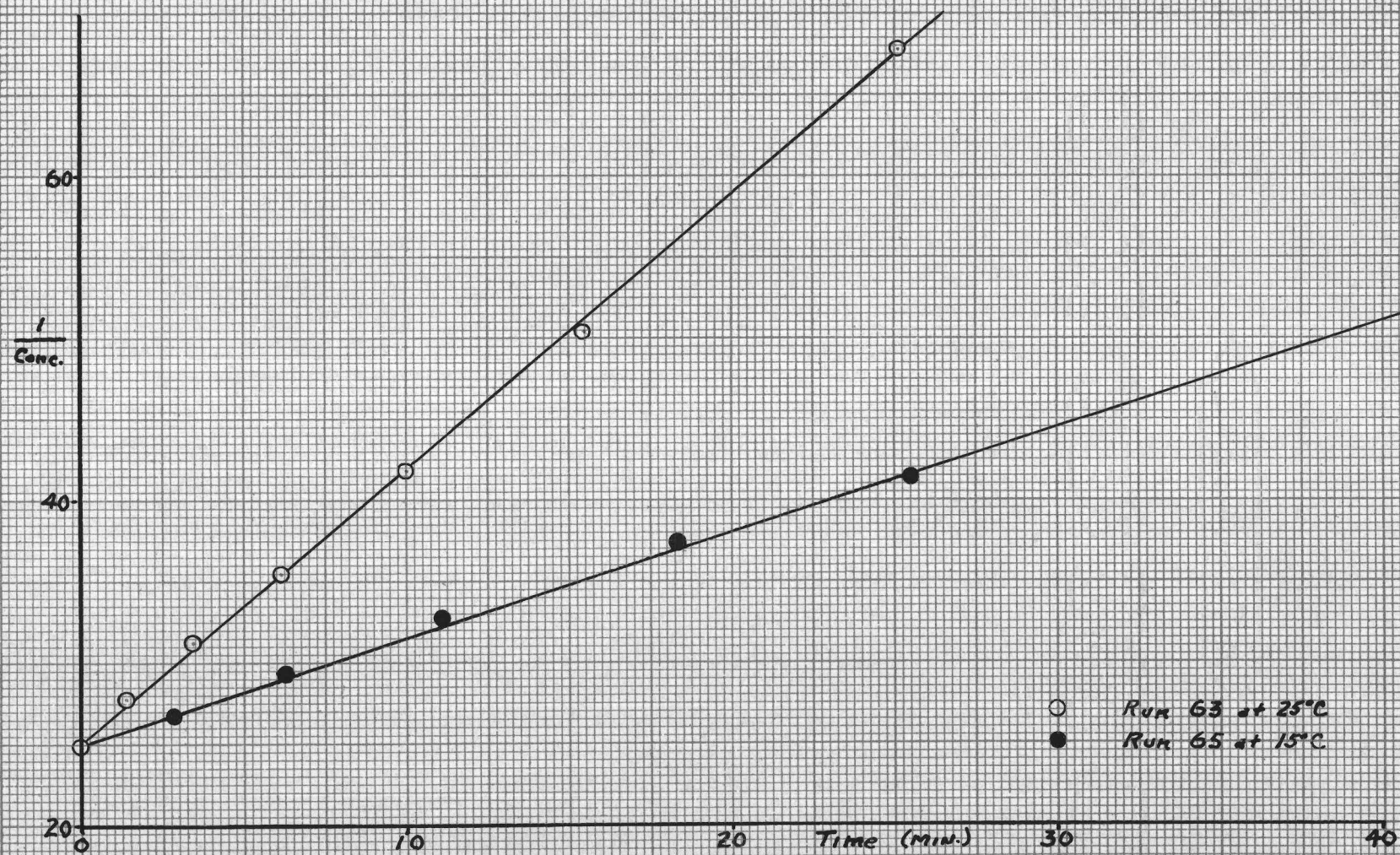


Figure 2

Table II

Effect of Temperature on the Rate of the Reaction

Run 25. Initial molality of hydrazine cyanate 0.0250 M.
25° C. Foreign salt concentration 0.0250 M. (Hydrazine perchlorate used in this run instead of hydrazine hydrochloride).

Time (sec.)	Molality of Hydrazine Cyanate	Reciprocal of Cyanate Concentration
0	0.0250	40.0
70	0.0234	42.7
188	0.0217	46.1
360	0.0197	50.8
610	0.0173	57.8
912	0.0155	64.5
1263	0.0137	73.0
1809	0.0114	87.7

Run 74. Initial molality of hydrazine cyanate 0.0250 M.
15° C. Foreign salt concentration 0.0250 M.

0	0.0250	40.0
200	0.0233	42.9
409	0.0223	44.9
728	0.0208	48.2
1206	0.0189	52.8
1870	0.0168	59.7
2918	0.0145	68.9

Change in Reaction Rate at Different Temperatures

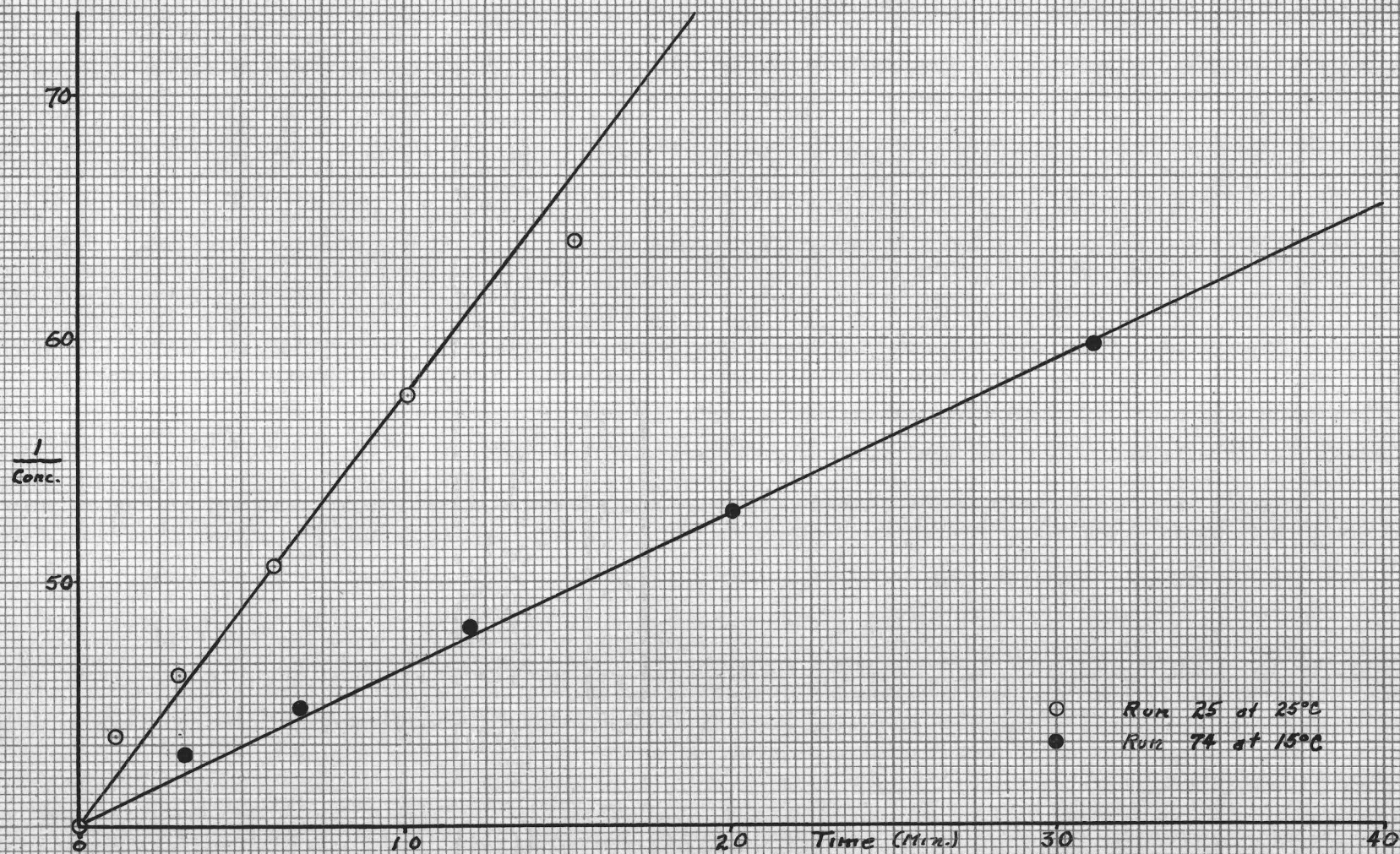


Figure 3

Table III

Effect of Reactant Concentration on the Reaction Rate

Run 12. Initial molality of hydrazine cyanate 0.0500 M.

25° C. Foreign salt concentration 0.0500 M.

Time (sec.)	Molality of Hydrazine Cyanate	Reciprocal of Cyanate Concentration
0	0.0500	20.0
65	0.0435	23.0
184	0.0383	26.14
382	0.0322	31.25
606	0.0267	37.45
899	0.0220	45.45
1254	0.0179	55.80
1894	0.0139	71.90

Run 24. Initial molality of hydrazine cyanate 0.0250 M.

25° C. Foreign salt concentration 0.0250 M.

0	0.0250	40.0
70	0.0239	41.8
188	0.0217	46.1
363	0.0192	52.1
603	0.0172	58.1
925	0.0155	64.5
1266	0.0131	76.3
1807	0.0113	88.5

Reaction Rates at Different Concentrations of Reactants

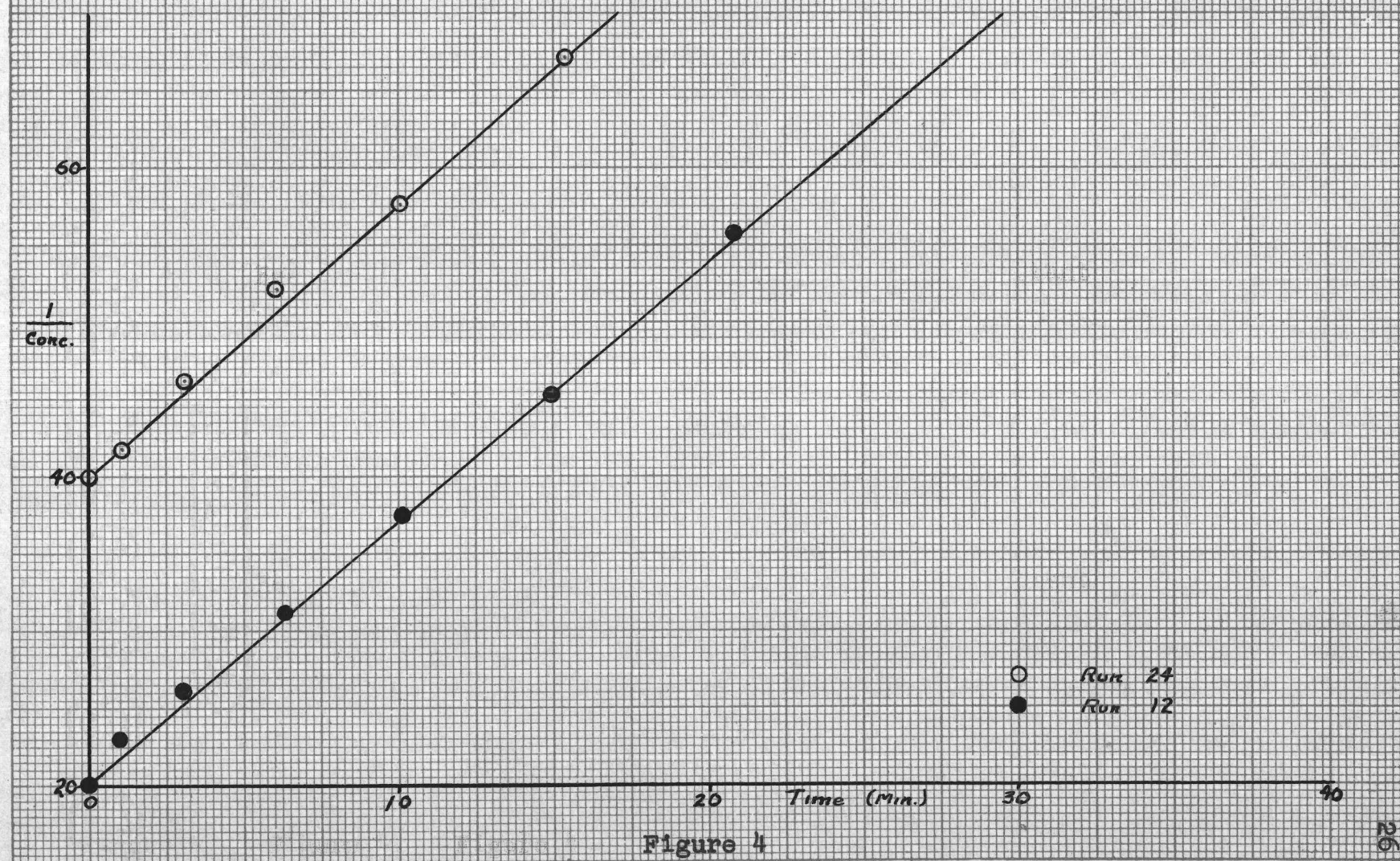


Table IV

Effect of Foreign Salt on the Reaction Rate

Run 14. Initial molality of hydrazine cyanate 0.0500 M.

25° C. Foreign salt concentration 0.4500 M.

Time (sec.)	Molality of Hydrazine Cyanate	Reciprocal of Cyanate Concentration
0	0.0500	20.0
66	0.0428	23.3
189	0.0392	25.5
369	0.0340	29.4
609	0.0296	33.8
894	0.0253	39.5
1267	0.0211	47.4
1801	0.0167	59.8

Run 15. Initial molality of hydrazine cyanate 0.0500 M.

25° C. Foreign salt concentration 0.2500 M.

0	0.0500	20.0
64	0.0427	23.4
192	0.0384	26.0
358	0.0342	29.2
613	0.0289	34.6
897	0.0242	41.3
1283	0.0200	50.0
1812	0.0159	62.9

Table V

Effect of Foreign Salt Concentration
on the Reaction Rate

Run 16. Initial molality of hydrazine cyanate 0.0500 M.

25° C. Foreign salt concentration 0.1500 M.

Time (sec.)	Molality of Hydrazine Cyanate	Reciprocal of Cyanate Concentration
0	0.0500	20.0
67	0.0425	23.5
194	0.0385	26.0
365	0.0337	29.7
608	0.0277	36.1
910	0.0230	43.5
1257	0.0189	52.9
1810	0.0145	68.9

Run 17. Initial molality of hydrazine cyanate 0.0500 M.

25° C. Foreign salt concentration 0.1000 M.

0	0.0500	20.0
75	0.0420	23.8
202	0.0375	26.7
364	0.0326	30.7
609	0.0272	36.8
911	0.0220	45.5
1261	0.0187	53.5
1810	0.0147	68.0

Reaction Rates with Different Concentrations of Foreign Salt

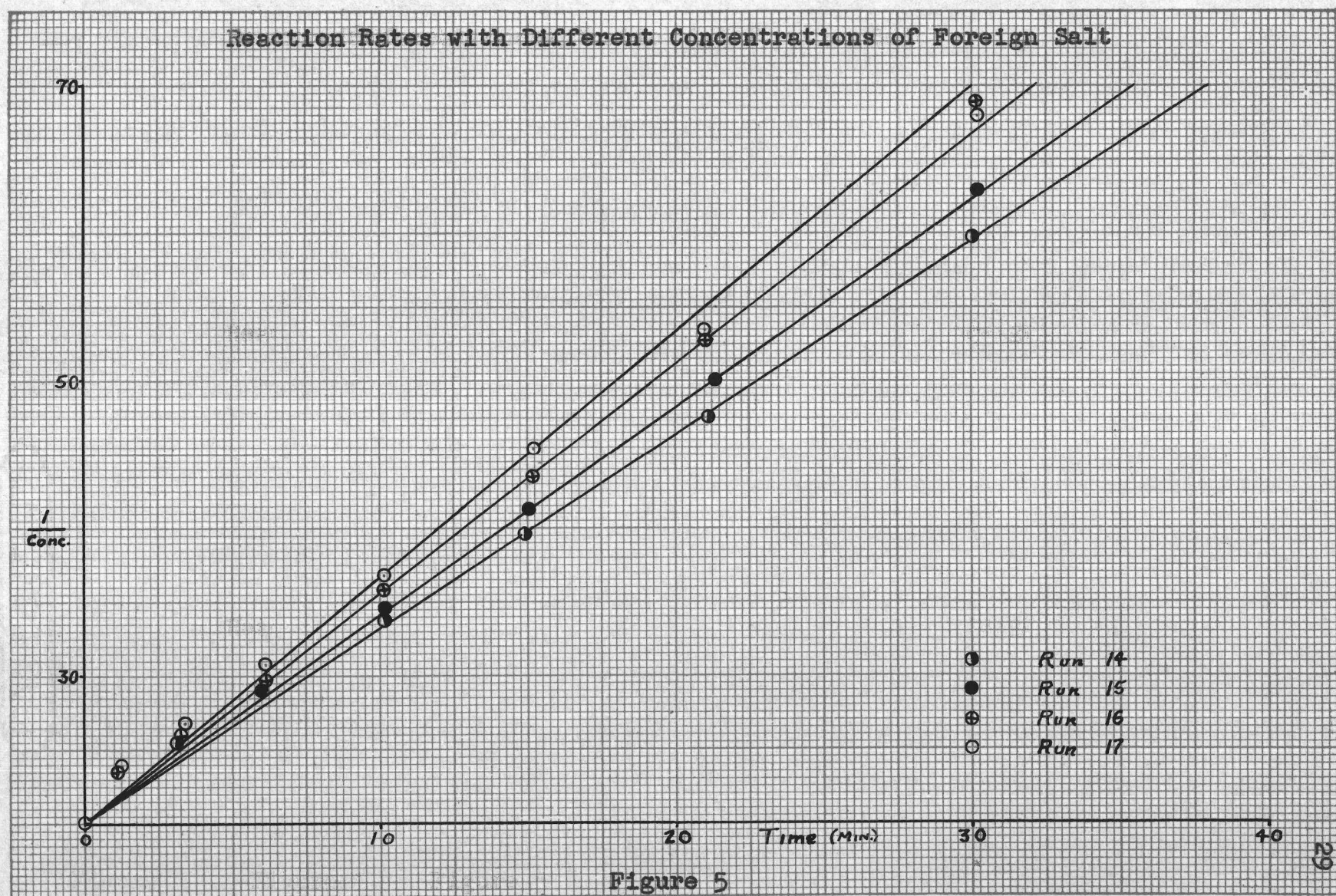


Figure 5

Table VI

$$\text{Equilibrium Constant, } K = \frac{(\text{Molality of Cyanate})^2}{(\text{Molality of Semicarbazide})}$$

Run	Molality of Semicarbazide	Molality of Cyanate	T	K x 10 ⁵
60	0.02409	0.00091	25	3.44
*61	0.03903	0.00124	25	3.94
*62	0.03924	0.00111	25	3.14
*62	0.03927	0.00108	25	2.97
64	0.03907	0.00128	25	4.19
*68	0.03940	0.00095	15	2.29
70	0.03914	0.00121	15	3.74
*69	0.03952	0.00083	15	1.74
71	0.03912	0.00123	15	3.87

* Semicarbazide was allowed to decompose into hydrazine cyanate. In all other runs the reactant was hydrazine cyanate.

Table VII

Difference in bimolecular k at temperatures 15° and 25° C.

Run	T	1/T	k	minus log k
75	15	3.472	0.0107	1.972
72	15	3.472	0.0108	1.967
65	15	3.472	0.0108	1.967
73	15	3.472	0.0107	1.972
74	15	3.472	0.0106	1.975
10	25	3.356	0.0286	1.544
63	25	3.356	0.0285	1.545
18	25	3.356	0.0283	1.548
12	25	3.356	0.0282	1.549

Change of the Velocity Constant with Temperature

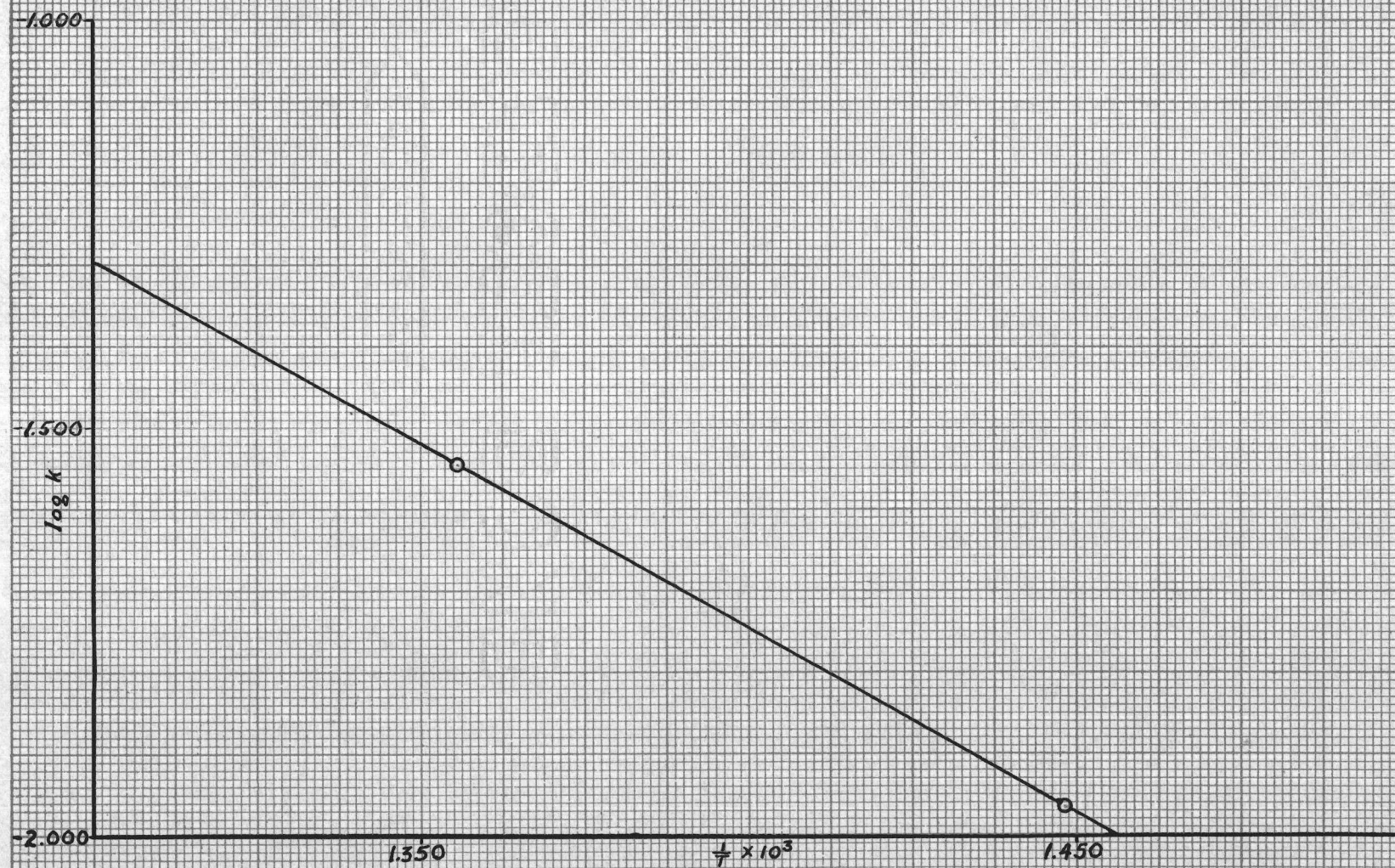


Figure 6

Table VIII

Dependence of the Bimolecular Rate Constant upon the Ionic Strength

Run	Initial Molality $\text{N}_2\text{H}_5\text{OCN}$	Molality of added salts	*Mean μ	μ	Bimolecular k (sec)	minus log k
19	0.0250	0.0250	0.0448	0.2116	0.0309	1.510
24	0.0250	0.0250	0.0453	0.2130	0.0300	1.522
25	0.0250	0.0250	0.0453	0.2130	0.0298	1.526
63	0.0403	0.0403	0.0700	0.2650	0.0286	1.543
10	0.0500	0.0500	0.0858	0.2930	0.0286	1.543
18	0.0500	0.0500	0.0860	0.2930	0.0283	1.549
12	0.0500	0.0500	0.0860	0.2930	0.0282	1.550
11	0.0500	0.0500	0.0860	0.2930	0.0278	1.556
17	0.0500	0.1000	0.1360	0.3690	0.0275	1.561
16	0.0500	0.1500	0.1865	0.4320	0.0260	1.585
15	0.0500	0.2500	0.2870	0.5360	0.0238	1.624
14	0.0500	0.4500	0.4887	0.6990	0.0220	1.658

* Mean ionic strength taking into account salts present plus mean concentration of cyanate ions over time used in establishing bimolecular constant, \bar{k} .

Change of the Bimolecular Velocity Constant with Ionic Strength

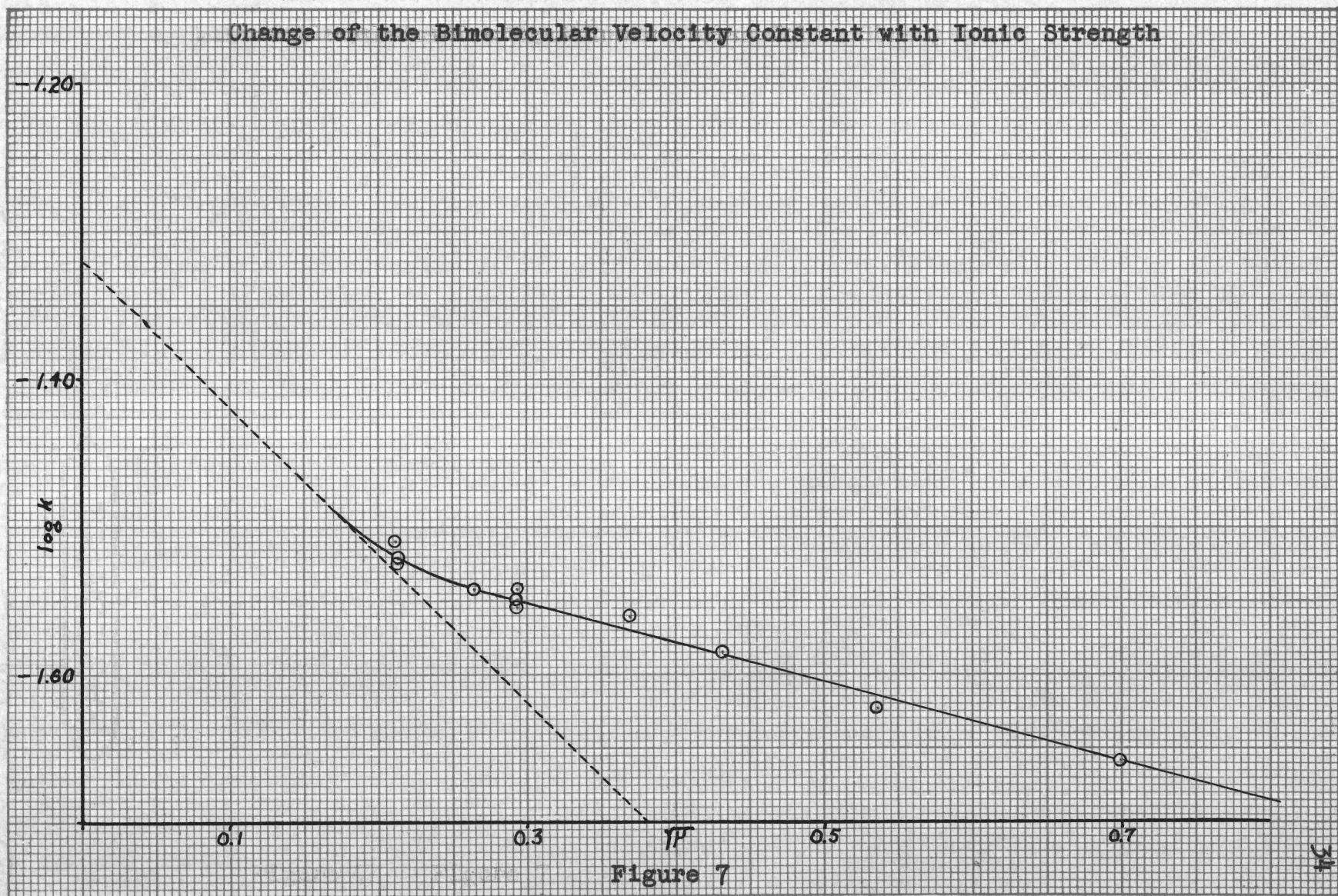


Figure 7

Table IX

Summary of Constants

Reaction of Hydrazine Cyanate to Semicarbazide

Equilibrium Constant, K_{25}	3.5×10^{-5}
Equilibrium Constant, K_{15}	2.9×10^{-5}
*Bimolecular k , at 25°C .	2.85×10^{-2}
*Unimolecular k' , at 25°C .	9.98×10^{-7}
Bimolecular k , at 15°C .	1.07×10^{-2}
Unimolecular k' , at 15°C .	4.93×10^{-8}
Bimolecular k_0 , at infinite dilution	4.76×10^{-2}
Temperature coefficient, $\frac{k_{25}}{k_{15}}$	2.65
Energy of Activation	16600 cal./mol

* k is rate constant for the forward reaction, and k' is the rate constant for the reverse reaction.

DISCUSSION OF RESULTS

In the determination of velocity constants from the data, consideration has been given to the effect of the back reaction, the effect of the side reaction, if any, and the changing of ionic strength during the course of the reaction. The effect of the back reaction is less than the experimental error up to at least 50% conversion of hydrazine cyanate to semicarbazide. An examination of Figures 2,3,4, and 5 indicate a straight line in the early part of the bimolecular reaction. The points obtained in the first few minutes are sometimes in error due to the time necessary to allow the reaction mixture to run into the flask containing the silver nitrate, where the reaction is stopped. A side reaction involving formation of carbonate is possible, since semicarbazide decomposes easily above 35° C. and in alkaline solutions. The presence of any carbonate was not indicated until after 48 hours and that only in the case of a determination made of the equilibrium constant from a solution containing semicarbazide decomposing to cyanate and hydrazine. A slight milkiness was observed in the semicarbazide solution on the addition of calcium ions to the solution.

If the reaction of hydrazine cyanate to form semicarbazide is a bimolecular reaction, then a plot of $1/OCN$

against time should give a straight line. This is the case shown in the accompanying graphs. From the slopes of the lines were obtained the bimolecular velocity constants, k as given in Table VIII.

It will be observed in Figure 7 that no determinations were made at low ionic strengths. This was because too large an excess of silver nitrate used in the analysis might cause an increase in the solubility of the silver chloride and silver cyanate. This would result in velocity constants which were too high.

From an observation of Figure 7 it is evident that the velocity constants at various ionic strengths form a fairly smooth curve. In the region of low ionic strength the line bends and joins a theoretical line of slope -1.00. By using the extrapolated value to $\sqrt{u} = 0$, a value of $k_0 = 0.0476$ is obtained. This represents a velocity constant at 25° C. free from all salt effects. Due to the difficulty in obtaining results in solutions of low ionic strength we have been guided in our extrapolation of the theoretical limiting slope indicated by the Bronsted theory and expressed in equation,

$$(2) \quad \log k = \log k_0 - Z_1 Z_2 \sqrt{\mu}$$

There is a negative primary salt effect upon the rate constant in accordance with theory, since the above

equation predicts that the velocity constant should decrease with an increase in the ionic strength. This is only true of the collision of two particles having opposite charges as would be the case of the cyanate ion and hydrazine ion, and not the collisions of two hydrazine cyanate molecules. In the latter case there would be very little observed primary salt effect.

The reaction rate is faster than might be expected from the directions for making semicarbazide as given in the literature.

In the determination of the equilibrium constant, it is necessary to obtain the point at which transformation of reactants and product is proceeding at the same rate. This point should be the same, whether approached from the hydrazine cyanate end or the semicarbazide end of the reaction. As the rate at which hydrazine cyanate is converted into semicarbazide is much greater with equal concentrations than the reverse reaction, it is evident that the equilibrium point must lie near the semicarbazide end.

Analysis of solutions containing hydrazine and cyanate ions as reactants for cyanate was made at intervals of from six to eight hours until two consecutive analyses were the same. Knowing the original concentra-

tions, the amount of reactive masses could be obtained for use in calculating the equilibrium constant. A solution of the same original concentration of semicarbazide was analyzed in a similar manner. Table VII shows the results obtained at 25° and 15° C. Any inconsistent results may be due to a slight error in the estimation of the cyanate concentration which when assumed to be equal to the hydrazine concentration and substituted in the equation,

$$K = \frac{(\text{Molality of Cyanate})(\text{Molality of Hydrazine})}{(\text{Molality of Semicarbazide})}$$

gives a squared term, and the possible original error causes a wider variation in the final calculation of the constant.

It was stated earlier that carbonate formation was possible from the decomposition of semicarbazide, but this was not detected, except in one solution after 48 hours of reaction. This possible decomposition necessitated care in using and storing well dried and purified semicarbazide samples.

The true equilibrium point must be very close to the value obtained using hydrazine and cyanate solutions, since that reaction is much faster and less chance of side reactions is possible through waiting for longer time for equilibrium to be reached than when using semicarbazide solutions.

The effect of temperature upon the reaction may be studied through a comparison from Table VII of the velocity constants obtained at 25° and 15° C. It is to be expected that the reaction would progress at a slower rate at 15° C. The calculation of the temperature coefficient indicates that the reaction would take place about 2.65 times faster with a ten degree increase in temperature. From the equation of Arrhenius,

$$(25) \quad \log k = B - E/2.303 RT$$

the activation energy may be obtained if one considers the fact that a plot of $\log k$ against the reciprocal of the different temperatures will give a straight line, Fig. 6, with a slope of $-E/2.303 R$ from which E , the activation energy may be calculated in calories. This was found to be 16,600 cal./mol. at room temperature. Most bimolecular reactions range from this value to 60 or 70 kcal./mol. The value is in keeping with the rapid rate at which the reaction proceeds at room temperatures. One may say that the reaction proceeds more rapidly as a result of an increase in the number of effective collisions, produced by an increase in the concentration of positive and negative ions. If one considers the meaning of the constant in the Arrhenius equation in the light of

modern theory, then that term according to Eyring (11,12) becomes

$$B = \frac{\Delta S}{2.3 R} - \log k \frac{T}{Nh}$$

and an increase in B may be attributed to an increase in the entropy of activation, ΔS . This means that the number of systems crossing the potential energy barrier per second is increased as an increase in the number of reactive complexes per liter.

SUMMARY

The rate of reaction of the conversion of hydrazine cyanate into semicarbazide has been measured, and the velocity constant, k at 15° C. and 25° C. has been determined. The limiting rate constant at 25° C. has been calculated. The dependence of the velocity constant has been determined in the presence of foreign salts.

The negative primary salt effect upon the velocity constant has been observed and according to the Bronsted theory indicates a bimolecular reaction which depends upon collisions between hydrazine and cyanate ions and not upon the collisions between the undissociated molecules of hydrazine chloride and potassium cyanate or between two molecules of hydrazine cyanate.

The classical equilibrium constant at 15° and 25° C. has been determined from an analysis of the concentration of cyanate ions in solutions which have reacted for long periods of time. Determinations have been made from both decomposition of the pure semicarbazide and the reaction of the hydrazine and cyanate ions.

From the equilibrium constant and the bimolecular constant for the forward reaction of hydrazine cyanate, the unimolecular constant k' , for the reverse reaction has been calculated.

Determination of the bimolecular constant k at 15° and 25° C. has made it possible to calculate the temperature coefficient. The energy of activation of the hydrazine and cyanate ions necessary to cause their reaction has been calculated with the aid of the theories of Arrhenius and modern chemistry.

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