

## TESTING OF SOME DYNAMIC KINETIC EQUATIONS

### PART II. SECOND-ORDER REACTION

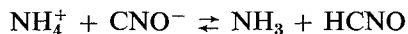
D. T. Y. CHEN and P. H. FONG

*Department of Chemistry, The Chinese University of Hong Kong,  
Shatin, Hong Kong*

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The conversion of ammonium cyanate into urea in aqueous solution was used to test three dynamic kinetic methods. It is concluded that the Freeman and Carroll method is the most satisfactory.

In a recent paper [1] we tested four dynamic kinetic equations, using our own data on the catalytic decomposition of hydrogen peroxide in aqueous solution. It was concluded that the Freeman and Carroll treatment was the most satisfactory. The intercept on the *Y* axis gives the theoretical order of reaction, unity, but the activation energy differs from that of isothermal kinetics by 4 kcal per mole, which may be due to the decomposition of the catalyst solution as well as to experimental error. In a later paper [2] the alkaline fading of bromophenol blue in aqueous solution was also treated by the Freeman and Carroll method. The order of reaction and the energy of activation agree well with those obtained from classical kinetics. The orders of these two reactions are both unity. It is desirable to use a reaction of order other than unity to test these equations. The difficulty lies in the facts that under the primitive working conditions, a suitable reaction for testing must be completed in between half an hour and three hours, and that the reaction should not be reversible to a great extent. In the present work, the ammonium cyanate-urea conversion was chosen for this purpose. The kinetics of this reaction have been extensively studied and summarized by Frost and Pearson [3]. The first kinetic studies of this reaction were made by Walker and co-workers [4], who found that the reaction was of second-order: first-order with respect to both  $\text{NH}_4^+$  and  $\text{CNO}^-$  ions. Chattaway [5] pointed out that the reaction could also be considered as a second-order reaction between  $\text{NH}_3$  and  $\text{HCNO}$ , because of the following fast equilibrium:



Many workers have since investigated the effects of ionic strength, dielectric constant, etc. on the rate, with the aim of proving that the reaction is ionic, but Weil and Morris [6] pointed out that all the evidence supporting the ionic mechanism could also be used to explain the molecular mechanism. This kinetic

ambiguity, however, is immaterial in the present case, because we are interested in only the reaction order and activation energy, but not the reaction mechanism.

The activation energies of this reaction in different media and ionic strengths were investigated by Svrbely and co-workers [7]. From their data it can be summarized that in mixed solvents of glycol and water the activation energy does not vary much with dielectric constant, while in mixed solvents of methanol and water the activation energy decreases significantly as the dielectric constant of the medium decreases. In various pure solvents the activation energy decreases as the ionic strength increases, but in mixed solvents it increases slightly with the ionic strength. With pure water as solvent, the activation energy of this reaction was found to be 23.5 kcal per mole at zero ionic strength and 23.2 kcal per mole at an ionic strength of 0.194. Walker [4] and co-workers also determined rate constants in water and alcohols at different temperatures. From their data we calculated an activation energy of 23.1 kcal per mole in pure water.

### Experimental

Experimental procedures follow those of Warner and Stitt [8] with slight modification.

#### *Preparation of silver cyanate*

50 g reagent grade  $\text{AgNO}_3$  was dissolved in 250 ml water in a 800 ml beaker, the outside of which was painted with black paint. The solution was heated to near boiling on a water bath. 90 g reagent grade urea (about five times the equivalent of  $\text{AgNO}_3$ ) was dissolved in 350 ml water in another beaker. When this solution had also been heated to near boiling, it was poured into the  $\text{AgNO}_3$  solution with stirring. The mixture was filtered to remove some precipitate immediately formed and the clear solution was again heated on the water bath. Silver cyanate precipitate formed gradually on digestion and was collected at about half-hour intervals on a filter paper, washed three times with ice-cold water and dried in a vacuum desiccator over calcium chloride for three days. It was then kept in a dark glass-stoppered bottle.

#### *Preparation of ammonium cyanate and the kinetic run*

1.5 g reagent grade  $\text{NH}_4\text{Cl}$  was dissolved in 80 ml water in a 250 ml beaker cooled with ice water. 4.7 g of the prepared  $\text{AgCNO}$  crystal was added slowly. The mixture was stirred until the filtrate was tested to be free of chloride; this usually takes about half an hour. The mixture was filtered to remove silverchloride and some unreacted  $\text{AgCNO}$ . The freshly-prepared  $\text{NH}_4\text{CNO}$  solution was then heated to the same temperature as the water bath and divided into two portions, each in a 100 ml Erlenmeyer flask, which were placed in the water bath. After about five minutes, to equilibrate the temperature of the solution with that of the

water bath, the latter was heated by manual control of a rheostat to increase the temperature at a linear rate of  $1^\circ$  every three minutes. The flasks were shaken from time to time so as to keep the temperature difference between the inside and outside of the flasks at a minimum. Two ml of sample was taken at about ten-minute intervals, and delivered into a 50 ml dry beaker containing 10 ml standard  $\text{AgNO}_3$  solution (0.1435 N) cooled in ice-water to stop reaction. The precipitated  $\text{AgCNO}$  was filtered off using dry funnels and dry filter papers. The middle portion of the filtrate was collected in a dry container. 5 ml aliquot was taken and the excess  $\text{Ag}^+$  ion was determined immediately by the Volhard method. The unreacted  $\text{NH}_4\text{CNO}$  was calculated therefrom. Isothermal kinetic runs were also carried out at 30.0, 40.2, 50.0 and 60.0° by the same procedure.

### Results and discussion

Figure 1 shows the results of isothermal kinetics:  $\frac{x}{a(a-x)}$  is plotted against time in minutes, where  $a$  is the initial concentration of  $\text{NH}_4\text{CNO}$  and  $x$ , the concentration of  $\text{NH}_4\text{CNO}$  converted. The plots are linear, indicating that the reaction is of second-order. The side-reaction of the formation of carbonate was also observed [4, 8, 9]. However, this side-reaction would not change the kinetics of disappearance of  $\text{CNO}^-$ , as explained by Wyatt and Kornberg [9]. From the slopes of the straight lines, the rate constants at 30.0, 40.2, 50.0 and 60.0° are calculated to be 0.0033, 0.010, 0.032 and 0.079 liter  $\cdot$  mole $^{-1} \cdot$  min $^{-1}$ , respectively. The energy of activation calculated from the slope of the Arrhenius plot is 92.0 kJ (22.0 kcal) per mole as compared to the literature value of 23.2 kcal per mole [7]. The discrepancy may be attributed to experimental error.

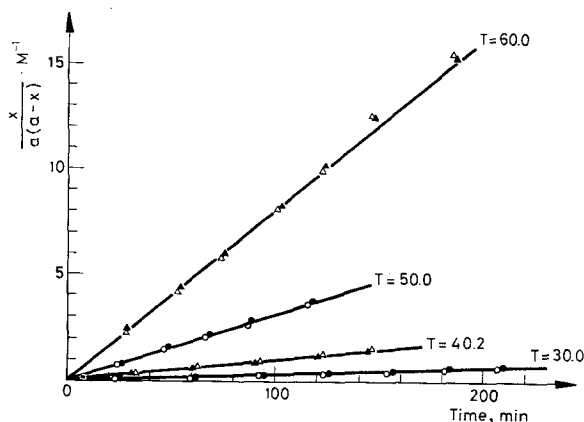


Fig. 1. Isothermal kinetics of ammonium cyanate-urea conversion

Data for duplicate dynamic kinetic runs are shown in Tables 1 and 2 and are plotted in Fig. 2. A smooth curve is drawn to represent the course of reaction; this is done by inspection. The rate of reaction,  $\frac{dx}{dt}$ , at any time is taken as the slope of the tangent to the curve at that point. Corresponding values of  $(a - x)$  are also taken from the curve. Treatment of the data by the Freeman and Carroll method is shown in Table 3, with a plot in Fig. 3. It is seen that a straight line can be drawn through the theoretical intercept of two on the ordinate and most

Table 1  
Dynamic kinetic run of ammonium cyanate—urea conversion

Time (min)	0.02263 N KCNS added (ml)	[CNO <sup>-</sup> ] M
10.75	12.80	0.3699
20.03	12.90	0.3672
30.72	13.10	0.3618
40.08	13.40	0.3536
50.13	13.95	0.3387
60.48	14.55	0.3224
69.68	15.30	0.3020
80.39	16.30	0.2749
90.35	17.45	0.2436
100.15	18.80	0.2070
110.80	20.10	0.1717
121.12	21.20	0.1418

Table 2  
Another dynamic kinetic run of ammonium cyanate—urea conversion

Time (min)	0.02263 N KCNS added (ml)	[CNO <sup>-</sup> ] M
11.52	12.95	0.3658
20.79	13.10	0.3618
31.51	13.30	0.3563
40.90	13.60	0.3482
51.14	14.10	0.3346
61.25	14.85	0.3142
70.55	15.55	0.2952
81.26	16.55	0.2681
91.30	17.75	0.2355
101.06	18.90	0.2043
111.67	20.30	0.1662
122.03	21.40	0.1364

of the experimental points, with the exception of the first two points. The activation energy calculated from the slope of the straight line is 103.3 kJ per mole. If we do not know the theoretical order, the straight line portion of the curve leads to a reaction order of 2.2 and an activation energy of 107.1 kJ per mole.

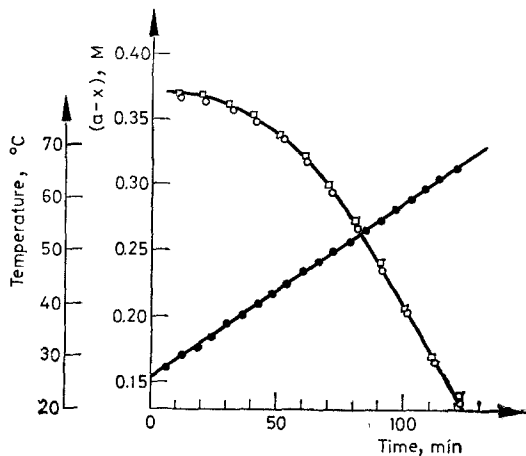


Fig. 2. Dynamic kinetic runs for ammonium cyanate-urea conversion

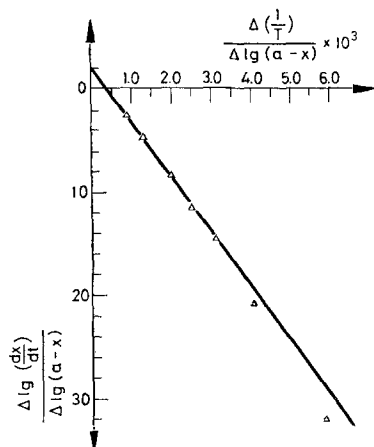


Fig. 3. Freeman and Carroll treatment for ammonium cyanate-urea conversion (Figures on the ordinate are negative)

Treatment of the data by the method of Achar et al. is shown in Table 4, with a plot in Fig. 4. The points with  $n = 2$  and  $n = 2.5$  can both be fitted in straight lines. The activation energies calculated from the slopes of the lines are 103.3 and 113.0 kJ per mole, respectively. It is interesting to note here that all the lines do not intersect; in the first part of this paper [1] they do intersect at a common point.

Table 3

Freeman and Carroll's treatment for the ammonium cyanate-urea conversion  
 $a=0.373$

Time (min)	Temp. (K)	(a-x)	$\frac{dx}{dt} \times 10^4$	$\frac{\Delta \log \frac{dx}{dt}}{\Delta \log(a-x)}$	$\frac{\frac{1}{T} \times 10^3}{\Delta \log(a-x)}$
20	305.7	0.365	4.66		
30	309.0	0.360	7.27	32.24	5.843
40	312.3	0.351	10.6	21.01	4.061
50	315.7	0.338	14.9	15.12	3.086
60	319.0	0.322	20.2	11.70	2.498
70	322.3	0.300	25.0	8.57	1.973
90	329.0	0.241	33.8	4.77	1.281
110	335.7	0.171	32.6	2.56	0.887

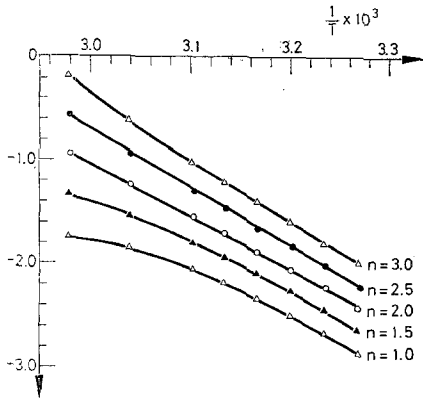


Fig. 4. Achar, Brindley and Sharp treatment for ammonium cyanate-urea conversion

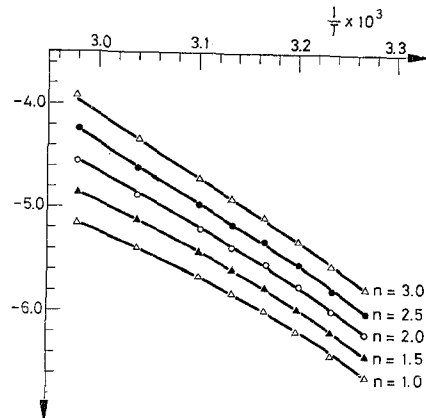


Fig. 5. Coats and Redfern treatment for ammonium cyanate-urea conversion

Treatment of the data by the Coats and Redfern's method is shown in Table 5, with the plot in Fig. 5;  $\log \left[ - \left\{ \ln \left( \frac{a-x}{a} \right) \right\} / T^2 \right]$  is plotted against  $\frac{1}{T}$  as suggested by Ozawa [10]. Judd and Pope [11,] mistakenly plotted  $\log \left[ - \log \left\{ \left( \frac{a-x}{a} \right) / T^2 \right\} \right]$  instead of  $\log \left[ - \left\{ \ln \left( \frac{a-x}{a} \right) \right\} / T^2 \right]$  against  $\frac{1}{T}$ . There is a big difference between these two quantities. According to our calculation, the former quantity varies only very slightly throughout the experimental temperature range, and the values are all positive. It is seen from the Figure that all the lines are curved. The points representing  $n = 2.5$  fit better as a straight line. The slope of the straight line por-

Table 4  
Treatment of data for ammonium cyanate — urea conversion by the method of Achar et al.

Time (min)	$\frac{I}{T} \times 10^3$	$n = 1.0$ $\log \frac{dx/dt}{a-x}$	$n = 1.5$ $\log \frac{dx/dt}{(a-x)^{1.5}}$	$n = 2.0$ $\log \frac{dx/dt}{(a-x)^{2.0}}$	$n = 2.5$ $\log \frac{dx/dt}{(a-x)^{2.5}}$	$n = 3.0$ $\log \frac{dx/dt}{(a-x)^{3.0}}$
20	3.271	-2.893	-2.675	-2.456	-2.237	-2.018
30	3.236	-2.694	-2.472	-2.251	-2.029	-1.807
40	3.202	-2.520	-2.292	-2.065	-1.838	-1.611
50	3.168	-2.354	-2.119	-1.883	-1.648	-1.412
60	3.135	-2.202	-1.956	-1.710	-1.464	-1.218
70	3.103	-2.079	-1.818	-1.556	-1.295	-1.033
90	3.040	-1.853	-1.545	-1.235	-0.927	-0.618
110	2.979	-1.720	-1.337	-0.953	-0.570	-0.186

Table 5  
Coats and Redfern's treatment of data for ammonium cyanate — urea conversion

Time (min)	$n = 1.0$ $\log \left[ - \left\{ \ln \frac{(a-x)}{a} \right\} / T^2 \right]$	$n = 1.5$ $\log \left[ \frac{a^{-0.5} - (a-x)^{-0.5}}{-0.5 T^2} \right]$	$n = 2.0$ $\log \left[ \frac{a^{-1} - (a-x)^{-1}}{-T^2} \right]$	$n = 2.5$ $\log \left[ \frac{a^{-1.5} - (a-x)^{-1.5}}{-1.5 T^2} \right]$	$n = 3.0$ $\log \left[ \frac{a^{-2} - (a-x)^{-2}}{-2 T^2} \right]$
20	-6.652	-6.448	-6.222	-6.010	-5.792
30	-6.444	-6.222	-6.005	-5.788	-5.571
40	-6.214	-5.992	-5.771	-5.549	-5.328
50	-6.010	-5.784	-5.558	-5.332	-5.106
60	-5.840	-5.610	-5.380	-5.150	-4.920
70	-5.680	-5.441	-5.202	-4.963	-4.724
90	-5.393	-5.132	-4.868	-4.603	-4.334
110	-5.159	-4.859	-4.551	-4.238	-3.921

tion (excluding the first two low-temperature points) corresponds to an activation energy of 113.4 kJ permole. The straight line portion for the points representing  $n = 2.0$  (excluding the first three low-temperature points) gives an activation energy of 106.3 kJ per mole.

### Conclusion

It is seen from these results that the Freeman and Carroll method predicts the right order of reaction. The first few low-temperature points do not lie on the straight line. This could be attributed to error in experiment, error in curve fitting, as well as error in slope measurement. At the beginning of the reaction the rates are very small, so the differences in  $(a - x)$  and  $\frac{dx}{dt}$  values are also very small.

Small errors in these would lead to large deviations. It can also be seen from Fig. 2 that the duplicate runs do not coincide very well at the start of the experiment. However, such a departure from linearity would not lead to a wrong prediction of the reaction order; we could simply use the straight portion of the curve. The activation energy obtained by the Freeman and Carroll treatment differs from that obtained from isothermal kinetics by approximately ten per cent; this error is the same as that obtained by the Achar method for  $n = 2$ . The latter method, however, cannot distinguish between  $n = 2$  and  $n = 2.5$ . As for the Coats and Redfern method, all the lines are curved. If we exclude the first two low-temperature points, this method leads to a wrong reaction order and activation energy ( $n = 2.5$ ,  $E = 113.0$  kJ per mole). It is therefore concluded that the Freeman and Carroll method is the best of the three dynamic kinetic methods tested. This conclusion is in accord with that derived in the previous paper [1].

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RÉSUMÉ — Trois méthodes ont été utilisées pour étudier la cinétique de la transformation du cyanate d'ammonium en urée. Celle de Freeman et Carroll donne les résultats les plus satisfaisants.

ZUSAMMENFASSUNG — Die Umwandlung des Ammoniumcyanats zu Harnstoff in wäßriger Lösung diente zur Untersuchung von drei dynamischen kinetischen Methoden. Man fand, daß die Freeman-Carrollsche Methode die zuverlässigste ist.

Резюме — На примере реакции превращения цианата аммония в водном растворе до мочевины были проверены три динамические кинетические методы. Было установлено, что наиболее приемлемым является метод Фримена и Кэррлла.