Urea–Formaldehyde Reaction System. An Experimental Investigation

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Synopsis

Batch production of urea–formaldehyde resins at temperatures up to 100°C takes several hours for completion. Reduction of the batch time may be possible with the higher reaction rates obtained at higher temperatures and increased pressures. In order to investigate this possibility, an experimental technique to obtain the necessary kinetic data, without loss of formaldehyde by evaporation, was developed. The results are compared with earlier low-temperature data extrapolated to the present range of interest. The results were interpreted on the basis of the successive reaction of two or three molecules of formaldehyde with a molecule of urea.

Rate Equations

In order to carry out the chemical engineering design procedure for a reactor producing UF (urea–formaldehyde) resins, appropriate rate equations would be required of the form

$$r = \pm \frac{dc}{dt} = f[k(T), \text{concentrations}] \tag{1}$$

where r = rate of appearance or disappearance of a chemical, c = concentration of that chemical, and t = time elapsed from start of reaction.

It has been established[1] that the combination of urea and formaldehyde begins with a series of addition reactions[2] followed by condensation reactions[3]; that the speed and extent of reaction are dependent on temperature, pH, and U:F ratio, although the reaction rate is essentially constant in the pH range 4–9 at constant temperature[4] and that UF_3 is produced in significant quantities only at low U:F ratios.[5] Therefore, since the commercial process usually involves U:F molar ratios between 1:1.33 and 1:2.2, within the pH range 4–9, it is reasonable to assume initially that the reactions taking place are

$$\mathrm{U} + \mathrm{F} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{UF_1} \tag{2}$$

$$\mathrm{UF_1} + \mathrm{F} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{UF_2} \tag{3}$$

so that the rate equations become

$$r_F = \frac{-d[\mathrm{F}]}{dt} = k_1[\mathrm{U}][\mathrm{F}] - k_2[\mathrm{UF_1}] + k_3[\mathrm{F}][\mathrm{UF_1}] - k_4[\mathrm{UF_2}] \tag{4}$$

$$r_U = \frac{-d[\mathrm{U}]}{dt} = k_1[\mathrm{U}][\mathrm{F}] - k_2[\mathrm{UF_1}] \tag{5}$$

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where [ ] denotes concentration in moles per unit volume. A mass balance on formaldehyde and urea gives

$$[F] + [F]_{UF_1} + [F]_{UF_2} = [F_0] = [F] + [UF_1] + 2[UF_2] \quad (6)$$

$$[U] + [U]_{UF_1} + [U]_{UF_2} = [U_0] = [U] + [UF_1] + [UF_2] \quad (7)$$

Solving eqs. (6) and (7) in terms of UF_1 and UF_2 gives

$$[UF_1] = 2[U_0] - 2[U] - [F_0] + [F] \quad (8)$$

$$[UF_2] = [U] - [F] - [U_0] + [F_0] \quad (9)$$

Substituting eqs. (8) and (9) into (4) and (5) yields

$$r_F = \frac{-d[F]}{dt} = k_1[U][F] - k_2(4[U_0] - 2[U] - 2[F_0] + 2[F])$$

$$+ k_3[F](2[U_0] - 2[U] - [F_0] + [F] - k_4[U] - [F] - [U_0] + [F_0]) \quad (10)$$

$$r_U = \frac{-d[U]}{dt} = k_1[U][F] - k_2 (4[U_0] - 4[U] - 2[F_0] + 2[F]) \quad (11)$$

At a particular temperature, solution of the second-order nonlinear simultaneous differential eqs. (10) and (11) is possible using a computer, providing that values of the rate constants k_1 to k_4 are available. These were obtained by evaluating the data of de Jong and de Jonge[6,7] plotted as ln k vs. $1/T$, using the Arrhenius equation

$$k = A \exp\left(\frac{-\Delta E}{RT}\right)$$

or

$$\ln k = \ln A - \left(\frac{\Delta E}{R} \cdot \frac{1}{T}\right) \quad (12)$$

Errors in estimating the intercept, ln A, were reduced by calculating the slopes of the curves from a knowledge of the activation energy ΔE. The following values were obtained:

$$k_1^0 = 10^{5.81} \exp\left(-\frac{6542.5}{T}\right) \text{ l./mole sec} \quad (13)$$

$$k_2^0 = 10^{6.31} \exp\left(-\frac{9562.15}{T}\right) \text{ 1/sec} \quad (14)$$

$$k_3^0 = 10^{4.26} \exp\left(-\frac{7045.8}{T}\right) \text{ l./mole sec} \quad (15)$$

$$k_4^0 = 10^{7.15} \exp\left(-\frac{9562.15}{T}\right) \text{ 1/sec} \quad (16)$$

where the superscript 0 indicates that the rate constant originated from the data of de Jong and de Jonge.

Values for [U] and [F] were obtained[1] by integrating eqs. (10) and (11) and inserting eqs. (13)–(16) on a Honeywell 316 computer using the package Aston Simulation Program[8] and the Runga-Kutta fourth-order routine.[9] A flow sheet for the program is shown in Figure 1.

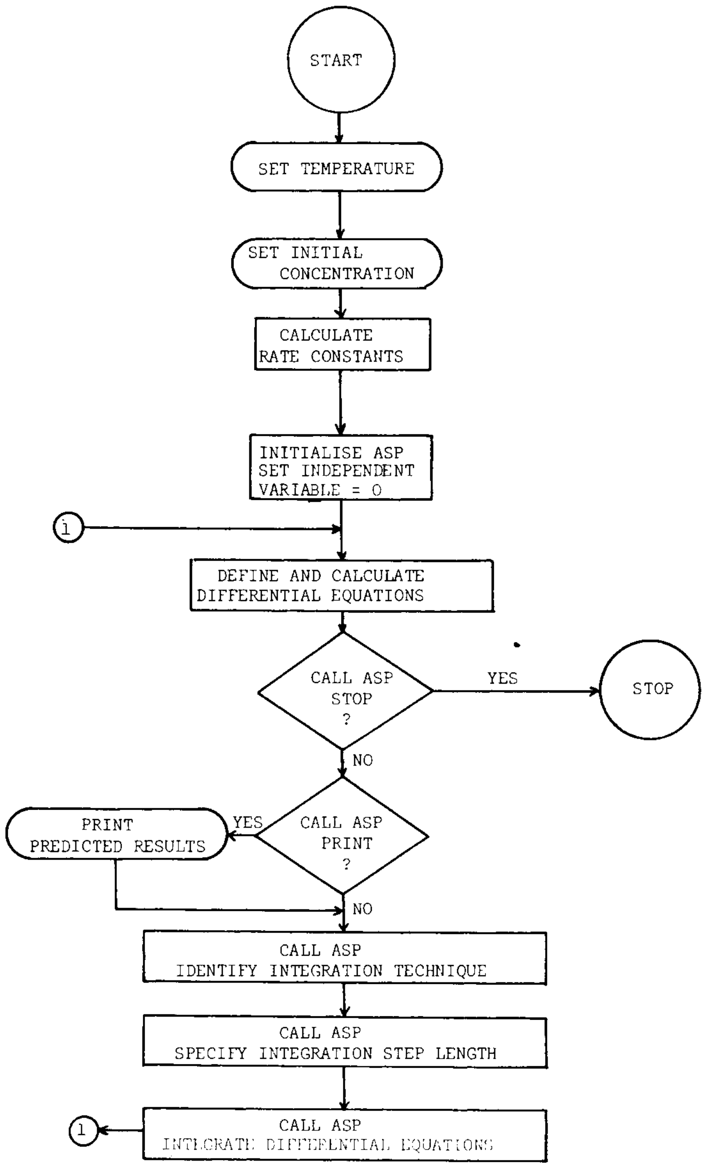

Fig. 1. Logic diagram for solution of kinetics.

EXPERIMENTAL RESULTS AND DISCUSSION

The data of de Jong and de Jonge used in the kinetic model were obtained under conditions where the condensation reactions were minimized. Since this is unlikely to be the case in the industrial production situation, experimental results were obtained to test the model.[1] Commercial 36% formalin and urea were charged to a glass reactor fitted with stirrer and condenser. The pH was adjusted and the temperature controlled in the range of 20–80°C. Samples taken from the reactor at selected intervals were analyzed for free formaldehyde by the acidimetric sulfite method. The initial U:F ratio in the charge was always

1:1.33. Results are listed in Table I and shown in Figure 2. Comparison of predicted and experimental results at 25 and 80°C in Figure 3 is very good at low temperatures, but divergence occurs at higher temperatures.

The discrepancies noted at higher temperatures could arise from the following factors:

(1) inaccuracy caused by the loss of the more volatile component, formaldehyde, from the reactor either in the form of a gas or a solid paraformaldehyde deposited on cold surfaces,

(2) the effect of the unavoidable reaction occurring while the reactor contents are being heated to the selected temperature,

(3) the reaction scheme suggested in eqs. (2) and (3) may not be adequate at higher temperatures because of further reactions of the addition or condensation type.

It was apparent that extrapolation of the model to temperatures higher than 60°C would be unwise and that an experimental method capable of avoiding items (1) and (2) above would be advantageous.

TABLE I
Experimental Results in Open Reactor[a]

Temp, °C	Time, min	[F], %
	0	23.40
	60	13.10
25	120	9.90
	240	6.60
	360	4.75
	0	23.40
	15	14.50
	30	11.30
40	60	7.60
	120	4.70
	240	2.25
	360	1.75
	0	23.40
	10	8.80
	20	5.40
	30	3.75
60	60	1.90
	120	1.00
	240	0.50
	360	0.25
	0	23.40
	5	7.40
	10	3.75
	20	1.70
80	30	1.00
	60	0.70
	120	0.60
	240	0.50
	360	0.50

[a] U:F Ratio 1:1.33.

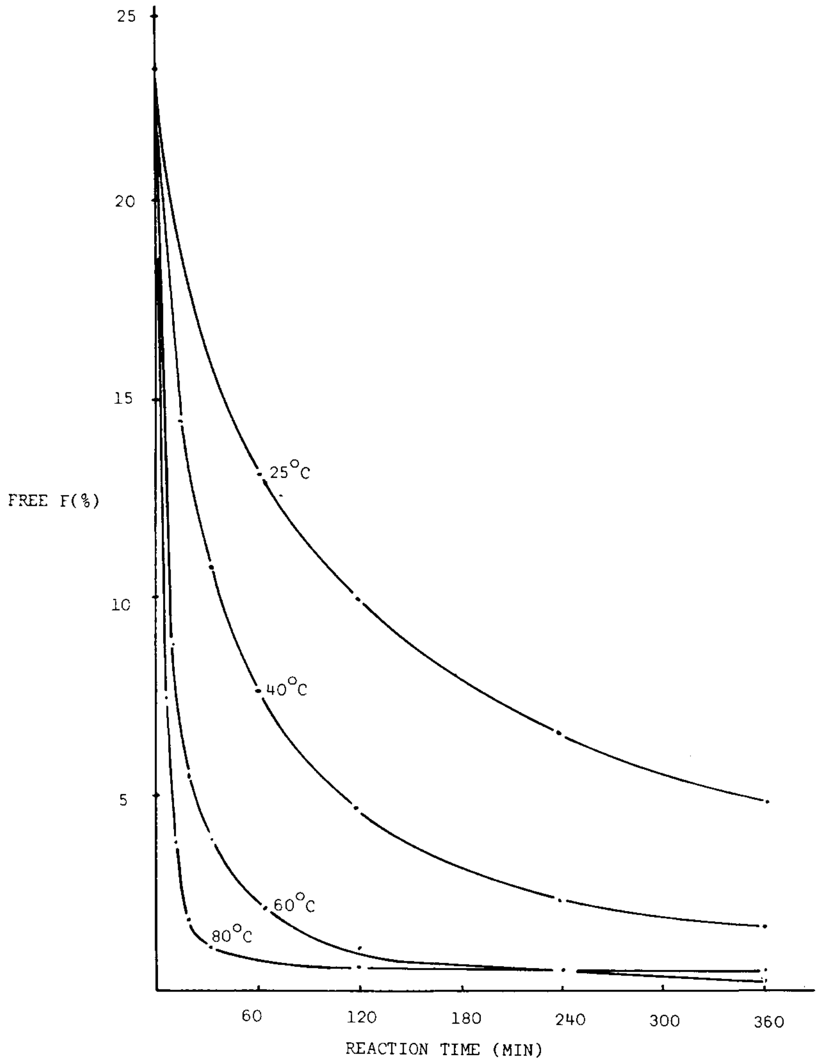

Fig. 2. Concentration–time curves for formaldehyde. Initial pH 8, U:F 1:1.33.

Modified Experimental Procedure for UF Reactions

The method used by Gordunov[10] was modified to avoid the problems in timing the reaction and controlling the temperature of the reaction. The static sealed tube was replaced by a Y-shaped reactor made of glass (Fig. 4). Its size was chosen to ensure that an adequate sample was available for formaldehyde analysis with minimum vapor space. The latter allowed minimum vaporization to pressurize the system, thus avoiding loss of formaldehyde.

A predetermined quantity of prilled urea was charged to one arm of the reactor. Formalin at a chosen pH was carefully charged to the other arm using a hypodermic syringe to avoid contact with the urea. The charging arm was then sealed in a flame in such a way that the pressure generated on heating the contents would not break the reactor. It was then held in a laboratory clamp which also acted as the shaft to a suitable electric stirrer motor. This was carefully posi-

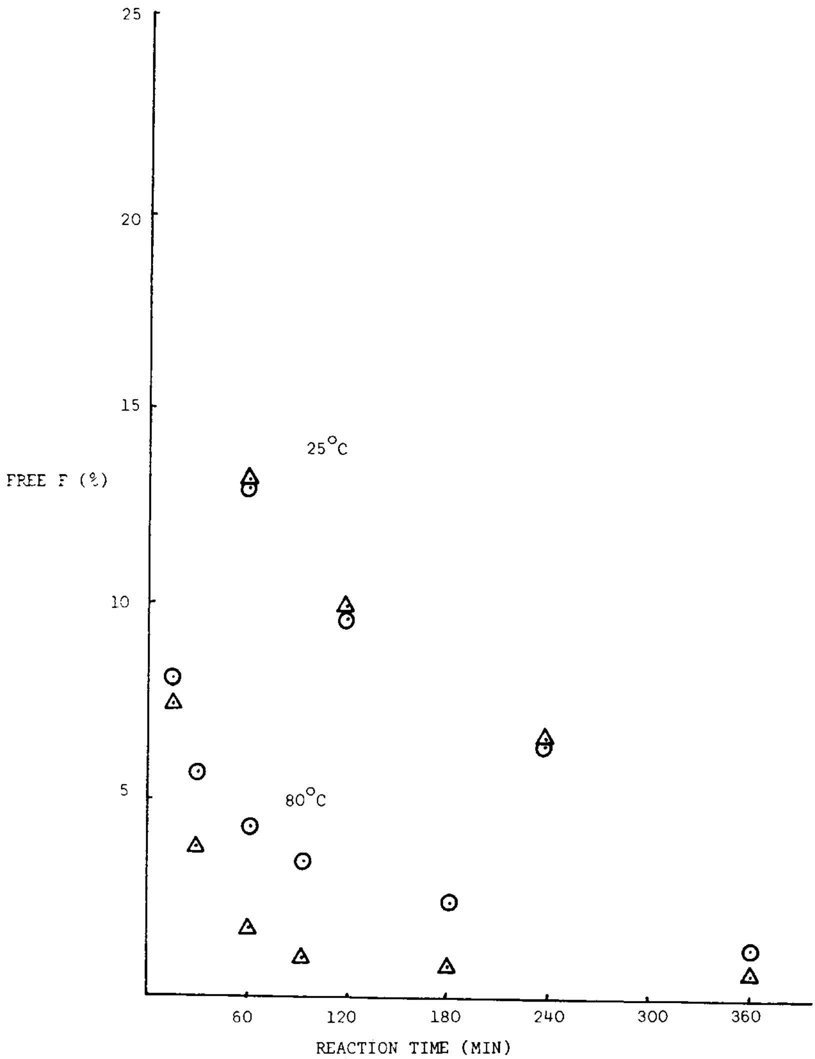

Fig. 3. Prediction of low-temperature UF kinetics: (△) experimental data; (⊙) predicted data.

tioned so that the reactants were well immersed in a constant-temperature bath without contacting one another. After a sufficient period of time for the reactants to reach the required temperature, the motor was switched on to mix the reactants together, with the reactor now behaving as a "Y-cone blender." At the end of the required period, the reactor was removed and broken immediately into a quantity of ice water to quench the reaction. (The ice water also served as part of the water required in the analytical procedure.)

Experiments were carried out at U:F molar ratios of 1:1.33 and 1:2.2 over the temperature range of 25–160°C with the pH in the band 4–9. Results for formaldehyde[11] are shown in Table II and representative values are shown in Figure 5. Comparison with Table I indicates that the present method produces slightly higher formaldehyde concentrations than the conventional open reactor, suggesting that loss of formaldehyde from the system has been prevented.

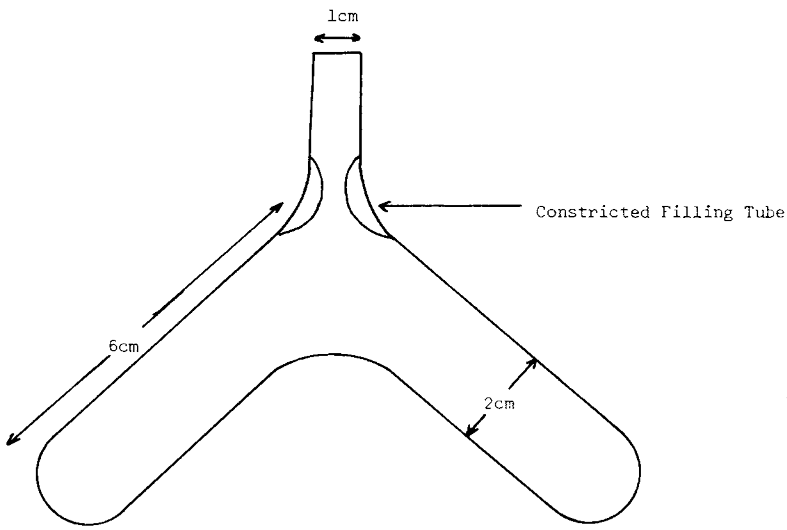

Fig. 4. Glass reactor.

Modeling of Experimental Results

Since eqs. (2) and (3) proved to be inadequate over the entire temperature range examined, the third addition reaction was included in the mechanism:

$$UF_2 + F \underset{k_6}{\overset{k_5}{\rightleftharpoons}} UF_3 \tag{17}$$

The rate equations then become

$$r_F = \frac{-d[F]}{dt} = k_1\,[U][F] - k_2\,[UF_1] + k_3[F][UF_1] - k_4[UF_2] + k_5[F][UF_2] - k_6[UF_3] \tag{18}$$

$$r_U = \frac{-d[U]}{dt} = k_1[U][F] - k_2[UF_1] \tag{19}$$

$$r_{UF_1} = \frac{d[UF_1]}{dt} = k_2[UF_1] - k_1[U][F] + k_3[F][UF_1] - k_4[UF_2] \tag{20}$$

and the mass balances become

$$[U] + [UF_1] + [UF_2] + [UF_3] = [U_0] \tag{21}$$

$$[F] + [UF_1] + 2[UF_2] + 3[UF_3] = [F_0] \tag{22}$$

so that

$$[UF_2] = 3([U_0] - [U] + [F] - [F_0] - 2[UF_1]) \tag{23}$$

$$[UF_3] = 2([U] - [U_0]) + [F_0] - [F] + [UF_1] \tag{24}$$

Substitution of eqs. (23) and (24) into (18), (19), and (20) provides the necessary rate equations for U, F, and UF_1 and can be treated as before if values of the rate constants in eq. (17) are available. Lack of data prevents k_5 and k_6 being calculated in the same manner as eqs. (13)–(16), but de Jong and de Jonge[12] quote approximate values for k_5 and the equilibrium constant for reaction (17) at 35°C. Using these values gives the following expressions for k_5 and k_6:

TABLE II
Experimental and Predicted Results

Temp., °C	Time, min	Experimental [F] %	Experimental [F], mole/l.	Predicted [F], mole/l.	$\frac{k_1}{k_1^0}$	$\frac{k_2}{k_2^0}$	$\frac{k_3}{k_3^0}$	$\frac{k_4}{k_4^0}$	$\frac{k_5}{k_5^0}$	$\frac{k_6}{k_6^0}$
				U:F Ratio 1:1.33						
25	0.0	23.32	9.1867	9.1867	0.8534	1.0034	0.1034	1.0144	—	—
	10.0	20.18	7.9500	7.9590						
	20.0	17.90	7.0500	7.0626						
	30.0	16.18	6.3750	6.3801						
	40.0	14.95	5.8875	5.8437						
	50.0	13.90	5.4750	5.4114						
	60.0	12.98	5.1052	5.0561						
	120.0	10.04	3.9490	—						
	240.0	6.75	2.6549	—						
	360.0	5.78	2.2733							
40	0.0	23.32	9.1867	9.1867	0.9030	1.0034	1.0034	1.0144	—	—
	10.0	16.18	6.3750	6.3454						
	20.0	12.75	5.0250	4.9933						
	30.0	10.85	4.2750	4.2033						
	40.0	9.52	3.7500	3.6858						
	50.0	8.57	3.3750	3.3208						
	60.0	7.87	3.0953	3.0494						
	120.0	5.43	2.1357	—						
	180.0	3.47	1.3648	—						
	240.0	2.45	0.9636	—						
	360.0	1.63	0.6411	—						
60	0.0	23.32	9.1867	9.1867	1.0068	1.0068	4.0068	1.0289	—	—
	10.0	8.75	3.4415	3.4306						
	20.0	5.45	2.1489	2.1930						
	30.0	4.50	1.7699	1.6078						
	40.0	3.24	1.2750	1.2524						
	50.0	2.66	1.0500	1.0090						
	60.0	2.57	1.0108	0.8307						
	90.0	1.42	0.5585	—						
	120.0	1.21	0.4759	—						
	180.0	0.58	0.2281	—						
80	0.0	23.32	9.1867	9.1867	1.0136	1.0136	5.0136	5.0578	—	—
	5.0	6.37	2.5093	2.4630						
	10.0	3.58	1.4109	1.3902						
	15.0	2.51	0.9900	0.9305						
	20.0	1.88	0.7394	0.6821						
	25.0	1.52	0.6000	0.5341						
	30.0	1.36	0.5349	0.4413						
	60.0	0.98	0.3854	—						
	120.0	0.86	0.3382	—						
120	0.0	23.32	9.1867	9.1867	1.0000	1.0000	5.0000	1.0000	0.8333	1.2000
	1.17	2.96	1.1642	—						
	2.5	1.49	0.5860	0.6138						
	5.0	0.55	0.2160	0.2011						
	7.5	0.34	0.1350	0.1332						
	10.0	0.33	0.1284	0.1208						
	12.5	0.30	0.1195	0.1185						
	15.0	0.27	0.1048	0.1176						

TABLE II (*Continued from previous page.*)

Temp., °C	Time, min	Experimental [F] %	Experimental [F], mole/l.	Predicted [F], mole/l.	$\frac{k_1}{k_1^0}$	$\frac{k_2}{k_2^0}$	$\frac{k_3}{k_3^0}$	$\frac{k_4}{k_4^0}$	$\frac{k_5}{k_5^0}$	$\frac{k_6}{k_6^0}$
	20.0	0.32	0.1259	—						
	30.0	0.15	0.0590	—						
160	0.0	23.32	9.1867	9.1867	1.0000	1.0000	8.0000	4.0000	0.8333	1.2000
	1.0	0.95	0.3736	0.3761						
	2.0	0.90	0.3562	0.3423						
	3.0	0.86	0.3375	0.3330						
	4.0	0.85	0.3337	0.3292						
	5.0	0.84	0.3325	0.3275						
	6.0	0.83	0.3287	0.3268						
	10.0	0.72	0.2832	—						
	20.0	0.62	0.2438	—						
	30.0	0.62	0.2438	—						
U:F Ratio 1:2.2										
40	0.0	27.12	10.4970	10.4970	1.0000	1.0000	1.0000	1.0000	0.8333	1.2000
	5.0	21.96	8.4998	—						
	10.0	21.10	8.1669	8.0954						
	20.0	18.29	7.0793	7.0166						
	30.0	16.86	6.5250	6.4295						
	40.0	15.70	6.0750	6.0714						
	50.0	14.92	5.7750	5.8345						
	60.0	14.10	5.4575	5.6665						
	90.0	11.35	4.3931	—						
	120.0	10.95	4.2383	—						
60	0.0	27.12	10.4970	10.4970	0.6000	5.0000	5.0000	10.0000	16.6667	24.0000
	2.5	23.16	8.9625	8.8844						
	5.0	20.15	7.7988	7.7547						
	7.5	17.79	6.8875	6.8982						
	10.0	15.88	6.1439	6.2200						
	20.0	13.19	5.1038	—						
	30.0	11.43	4.4233	—						
	60.0	7.91	3.0623	—						
	120.0	7.96	3.0816	—						
80	0.0	27.12	10.4970	10.4970	5.0000	5.0000	40.0000	40.0000	0.0083	0.0120
	5.0	6.23	2.4127	2.4430						
	10.0	5.70	2.2050	2.1210						
	15.0	5.52	2.1375	2.0690						
	20.0	5.37	2.0775	2.0579						
	25.0	5.31	2.0550	2.0535						
	30.0	5.28	2.0454	2.0504						
	60.0	3.91	1.5118	—						
	120.0	4.10	1.5858	—						
100	0.0	27.12	10.4970	10.4970	1.0000	1.0000	80.0000	30.0000	16.6667	12.0000
	1.25	5.77	2.2345	2.2965						
	2.50	3.00	1.1625	1.0890						
	3.75	2.34	0.9075	0.8134						
	5.00	1.87	0.7240	0.7207						
	6.25	1.63	0.6300	0.6743						
	7.50	1.41	0.5475	0.6443						
	8.75	1.32	0.5100	0.6227						

TABLE II (*Continued from previous page.*)

Temp., °C	Temp, min	Experimental [F] %	Experimental [F], mole/l.	Predicted [F], mole/l.	$\frac{k_1}{k_1^0}$	$\frac{k_2}{k_2^0}$	$\frac{k_3}{k_3^0}$	$\frac{k_4}{k_4^0}$	$\frac{k_5}{k_5^0}$	$\frac{k_6}{k_6^0}$
	10.0	1.19	0.4600	0.6062						
	20.0	1.19	0.4600	—						
	30.0	1.17	0.4524	—						
	60.0	1.19	0.4600	—						
120	0.0	27.12	10.4970	10.4970	1.2000	1.0000	150.0000	40.0000	50.0000	12.0000
	1.0	1.96	0.7575	0.7643						
	2.0	1.06	0.4125	0.4949						
	3.0	0.86	0.3337	0.4312						
	4.0	0.78	0.3000	0.3980						
	5.0	0.77	0.2977	0.3774						
	10.0	0.47	0.1817	—						
	20.0	0.32	0.1237	—						
	30.0	0.17	0.0657	—						
160	0.0	27.12	10.4970	10.4970	0.7000	1.0000	8.0000	4.0000	1.0833	1.5600
	1.0	3.72	1.4412	1.4869						
	2.0	3.29	1.2740	1.1963						
	3.0	3.10	1.2000	1.1500						
	4.0	2.89	1.1175	1.1395						
	5.0	2.77	1.0727	1.1369						
	6.0	2.62	1.0125	1.1363						
	10.0	2.19	0.8492	—						
	20.0	1.15	0.4470	—						
	30.0	0.92	0.3577	—						

$$k_5^0 = \frac{1.2}{9} k_1^0 \tag{25}$$

$$k_6^0 = \frac{1}{9} k_1^0 \tag{26}$$

Solution of eqs. (18)–(20) produced only a marginal improvement in the comparison of experimental and predicted results at higher temperatures, emphasizing the possible inadequacy of the reaction mechanism proposed. In fact, Sato[13] during a study of the thermodynamics of the urea–formaldehyde reaction concluded that the rate constants remain constant only over narrow conversion limits, because of the change in functionality of urea as the reaction progressed. If, therefore, the rate constants vary with composition as well as temperature, solution of the problem necessitates a simultaneous search for four or six rate constant values at each temperature. The kinetic model then becomes inappropriate, particularly if significant condensation takes place, but it can be used as the basic model to which the experimental data are fitted.

The technique of nonlinear regression analysis was applied[1] to the data to estimate the best values of the rate constants which would predict the experimental data within a specified limit of accuracy. It was assumed that the result

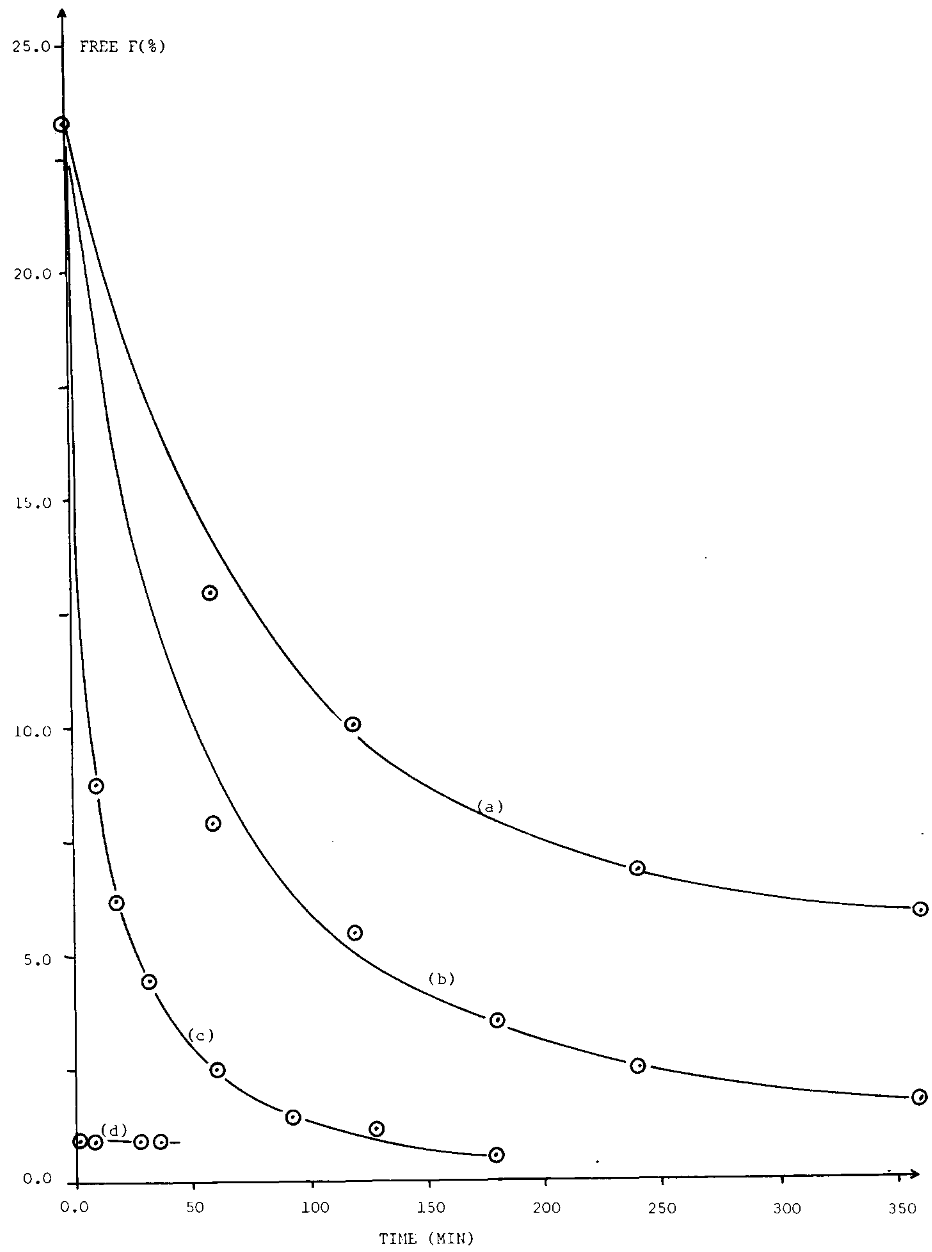

Fig. 5. Sample experimental data; U:F = 1:1.33: (a) 25°C; (b) 40°C; (c) 80°C; (d) 160°C.

at a particular temperature could be applied with acceptable accuracy to a 10-K band around that temperature. The criterion adopted was that the difference between experimentally determined and model predicted values of formaldehyde concentration should be less than the error expected in the chemical determination of free formaldehyde, i.e., 0.1% by weight. Preliminary work with a Honeywell 316 computer indicated that at a U:F ratio of 1:1.33, eqs. (2) and (3) would give satisfactory results for temperatures up to and including 80°C, pro-

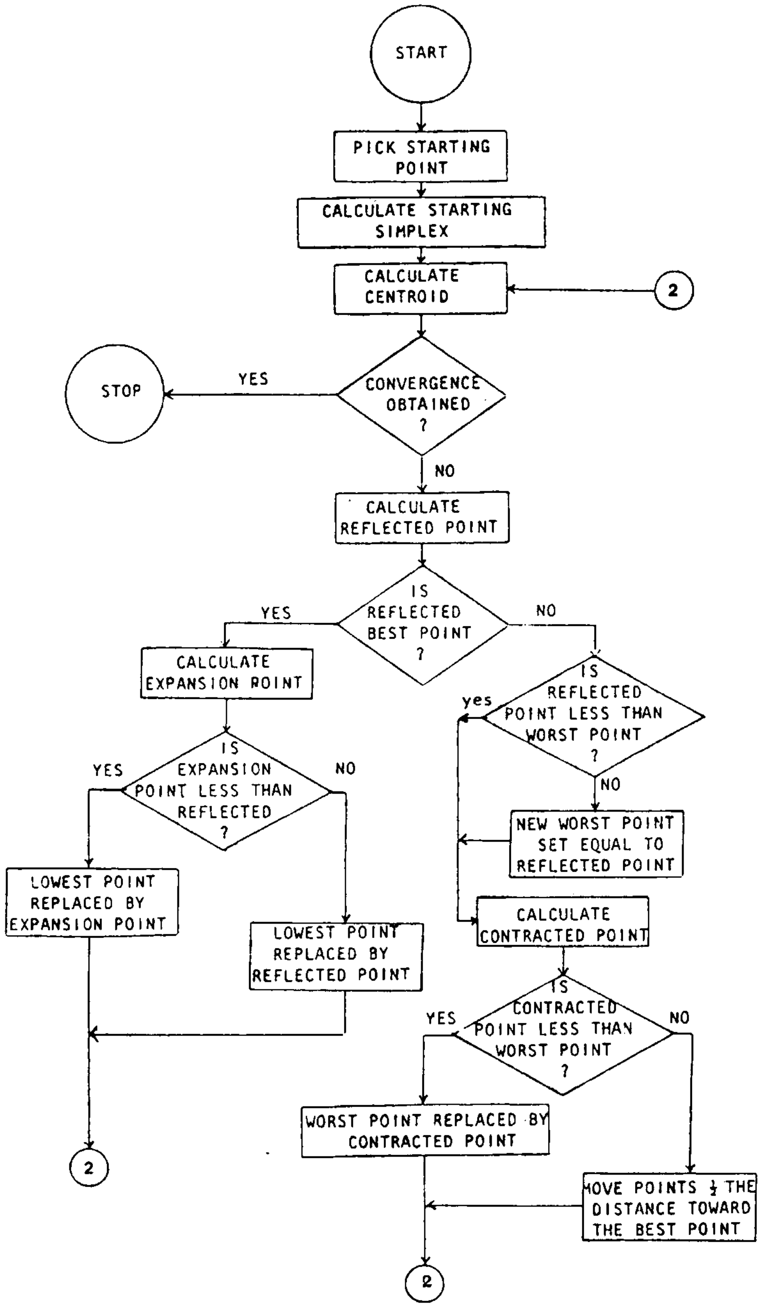

Fig. 6. Nelder and Mead logic diagram.

vided that the rate constants were modified. Higher temperatures and all temperatures at a U:F ratio of 1:2.2 required the inclusion of eq. (17).

The optimization exercise was carried out on an ICL 1904S computer using a FORTRAN package[14] which made use of an improved simplex search routine due to Nelder and Mead.[15] The flow sheet is shown in Figure 6. The following inputs were required:

(1) A subroutine for description of the objective function to be minimized:

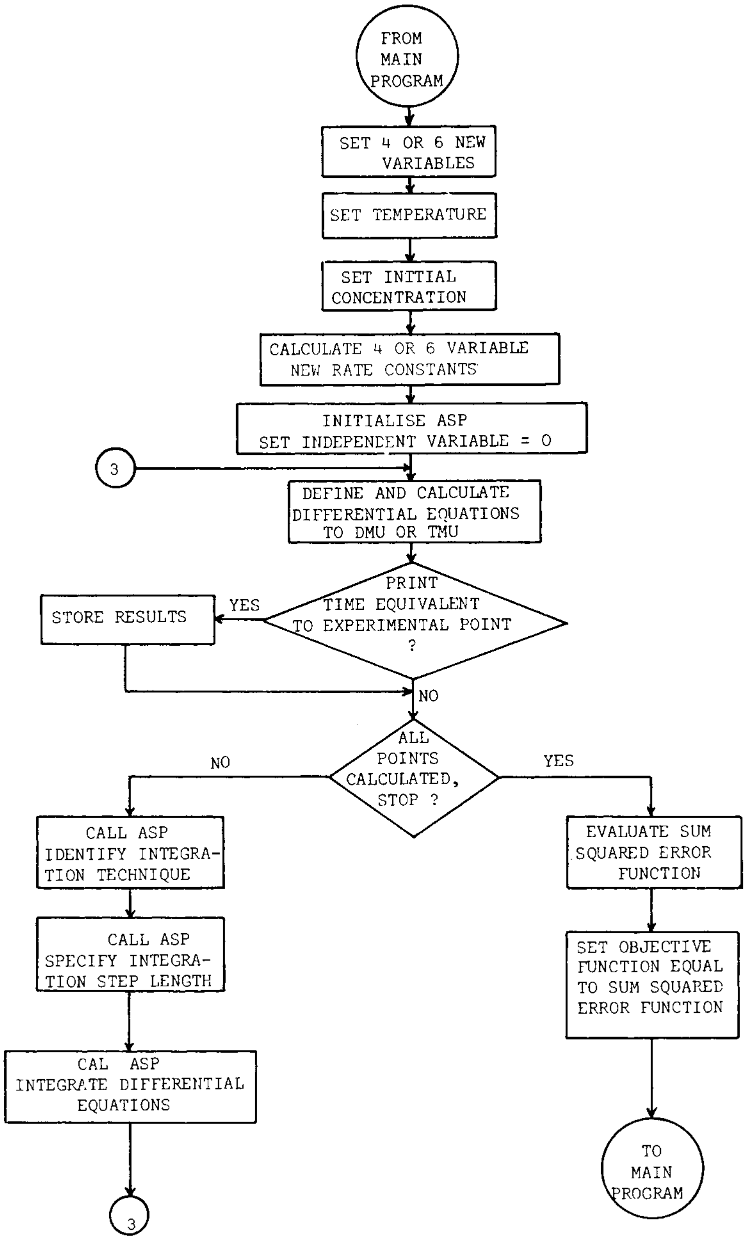

Fig. 7. Logic diagram for subroutine to define objective function for minimization.

$$S = \sum_{j=1}^{j=n} (E_j - F_j)^2$$

where S = sum squared error function, E_j = experimental value of free formaldehyde for the jth observation, F_j = predicted value of free formaldehyde for the jth observation, and n = number of experimental points available. A flow sheet, which also allows for the calculation of predicted formaldehyde concentrations, for the subroutine is shown in Figure 7.

(2) The following variables: number of independent variables; initial starting

values for the rate constants; side length of simplex; reflection coefficient; contraction coefficient; expansion coefficient; and accuracy.

Results are shown in Table II in the form of optimized rate constants relative to those defined in eqs. (13)–(16), (25), and (26). It is apparent that there is no correlation between the optimized rate constants. Therefore each set can only be used to predict formaldehyde concentration variation with time over a narrow temperature range of less than ±10 K. Nevertheless, predictions can be made by this method to an acceptable level of accuracy for the early stages of the reaction.

NOMENCLATURE

A	constant in Arrhenius eq. (12)
c	concentration of reacting specie
d	differential operator
E_j	experimental value of free formaldehyde for jth observation
ΔE	activation energy
F	formaldehyde
F_j	predicted value of free formaldehyde for jth observation
k_1–k_6	reaction rate constants, eqs. (2), (3) and (17)
n	number of experimental points
r	rate of chemical reaction
R	universal gas constant
S	sum squared error function
T	absolute temperature, K
t	time elapsed from start of reaction
U	urea
UF_1	monomethylolurea
UF_2	dimethylolurea
UF_3	trimethylolurea
[ ]	concentration of

Superscript

^{0}	applies to rate constant originating from the data of de Jong and de Jonge

Subscript

$_0$	initial condition

References

1. A. S. Meskin, Ph.D. thesis, Chemical Engineering Dept., University of Aston, Birmingham, England, 1977.
2. Y. Ito, *Kogyo Kagaku Zasshi,* **64,** 382 (1961).
3. G. Zigeneur and R. Pitter, *Monatsh. Chem.,* **86,** 57 (1955).
4. J. I. De Jong and J. De Jonge, *Rec. Trav. Chim.,* **72,** 88 (1953).
5. A. Iliceto, *Ann. Chim.* (Rome), **43,** 625, (1953).
6. J. I. De Jong and J. De Jonge, *Rec. Trav. Chim.,* **71,** 643 (1952).
7. J. I. De Jong and J. De Jonge, *Rec. Trav. Chim.,* **71,** 661 (1952).
8. B. Gay and S. Payne, *Comput. J.,* **16** (2), 118 (1973).
9. V. G. Jensen and G. V. Jeffreys, *Mathematical Methods in Chemical Engineering,* Academic, New York, 1965.

10. Y. N. Gordunov and V. Z. Yashina, *Plast. Massy,* **No. 4,** (1960).

11. B. P. Fernando, M.Sc. thesis, Chemical Engineering Dept., University of Aston, Birmingham, England 1976.

12. J. I. De Jong and J. De Jonge, *Rec. Trav. Chim.,* **72,** 88 (1953).

13. K. Sato, *Bull. Chem. Soc. Jpn.,* **40,** 724 (1967).

14. J. L. Kuster and J. H. Mize, *Optimization Techniques with FORTRAN,* McGraw-Hill, New York, 1973.

15. J. A. Nelder and R. Mead, *Comput. J.,* **7,** 308 (1964).

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