Appendix

I. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM SIMULATED DATA

a. PRODUCT FORMATION IN TWO–STEP REACTIONS

10 REM PROGRAM IN BASIC, WRITTEN BY R. SIVARAMAKRISHNAN, FOR RECOVERING THE
11 REM TWO FIRST-ORDER RATE COEFFICIENTS OF A TWO-STEP, CONSECUTIVE REACTION
12 REM FROM DATA OF PRODUCT CONCENTRATION (SIMULATED INCORPORATING RANDOM,
13 REM NORMAL ERRORS AT A SPECIFIED LEVEL, SIGMA) VERSUS TIME BY THE NELDER-
14 REM MEAD DOWNHILL SIMPLEX MINIMIZATION ROUTINE. THE PROGRAM USES UP TO 100
15 REM ITERATIONS IN CYCLES OF FIVE "RE-ITERATIONS" AND MAKES TWO RESTARTS IN
16 REM TRYING TO REACH A GENUINE MINIMUM. IT ALSO EMPLOYS FOUR PAIRS OF
17 REM INITIAL INPUTS (J0 AND K0) OF THE TWO RATE COEFFICIENTS IN ORDER TO
18 REM LOCATE THE TWIN MINIMA IN THE SYMMETRIC ERROR SURFACE. THERE IS ALSO
19 REM A PROVISION FOR CHECKING WHETHER THE OPTIMIZED ESTIMATES, J AND K,
20 REM INDEED CORRESPOND TO A MINIMUM ON THE ERROR MAP BY CHECKING THE SAME
21 REM WITH THE SUM OF SQUARES OF DEVIATIONS (S) COMPUTED FOR EIGHT ADJACENT
22 REM POINTS. IT FINALLY EMPLOYS THE DEMING ROUTINE, A GRADIENT METHOD, TO
23 REM CONFIRM THE VALIDITY OF THE NELDER-MEAD OUTPUT, ALSO ASSESSING THE
24 REM STANDARD DEVIATIONS IN THE ESTIMATES OF THE RATE COEFFICIENTS
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM JO(10): DIM K1(10): DIM X(100): DIM Y(100): DIM Z(100): DIM R(100):
   DIM V(510)
50 FOR E = 1 TO 4
60 READ JO(E), K0(E)
70 NEXT E
80 INPUT "KS, KF, DT, N, SIGMA"; KS, KF, DT, N, SIGMA
90 FOR I = 1 TO 24
100 READ V(I)
110 X(I) = I * DT
120 Z(I) = (KF / (KF - KS)) * EXP(-KS * X(I)) - (KS / (KF - KS)) * EXP(-KF * X(I))
   - SIGMA * V(I)
130 Y(I) = INT((10000 * (Z(I) + .00005)) / 10000)
131 REM PRINT "Y"; Y(I)
135 PRINT #1, I, Y(I)
140 NEXT I
145 PRINT "KS"; KS; "KF"; KF; "DT"; DT; "N"; N; "Y"; Y(N); "SIGMA"; SIGMA
150 PRINT #1, "KS"; KS; "KF"; KF; "DT"; DT; "N"; N; "Y"; Y(N); "SIGMA"; SIGMA
155 FOR E = 1 TO 4
160 J(1) = JO(E): K(1) = K0(E)
165 REM PRINT "JO"; JO(E); "K0"; K0(E)
168 REM PRINT #1, "JO"; JO(E); "K0"; K0(E)
170 FOR G = 1 TO 3
190 FOR ITER = 1 TO 5
200 FOR P = 1 TO 3
205 FOR Q = P + 1 TO N
210 IF S(Q) >= S(P) THEN GOTO 480
215 S(P) = S(P) + R(I) * R(I)
220 NEXT I
225 NEXT P
230 FOR ITER = 1 TO 100
240 FOR P = 1 TO 2
245 FOR Q = P + 1 TO 3
250 IF S(Q) >= S(P) THEN GOTO 480
255 S(P) = S(P) + R(I) * R(I)
260 NEXT I
265 NEXT P
270 FOR ITER = 1 TO 100
280 FOR P = 1 TO 2
285 FOR Q = P + 1 TO 3
290 IF S(Q) >= S(P) THEN GOTO 480
295 S(P) = S(P) + R(I) * R(I)
300 NEXT I
305 NEXT P
310 FOR Q = P + 1 TO 3
320 IF S(Q) >= S(P) THEN GOTO 480
325 S(P) = S(P) + R(I) * R(I)
330 NEXT I
335 NEXT P
340 FOR E = 1 TO 4
345 FOR I = 1 TO 24
350 IF S(Q) >= S(P) THEN GOTO 480
355 S(P) = S(P) + R(I) * R(I)
360 NEXT I
365 NEXT E
370 FOR Q = P + 1 TO 3
380 IF S(Q) >= S(P) THEN GOTO 480
385 S(P) = S(P) + R(I) * R(I)
390 NEXT Q
395 NEXT Q
400 FOR ITER = 1 TO 100
410 FOR P = 1 TO 2
415 FOR Q = P + 1 TO 3
420 IF S(Q) >= S(P) THEN GOTO 480
425 S(P) = S(P) + R(I) * R(I)
430 NEXT Q
435 NEXT P
440 FOR Q = P + 1 TO 3
450 IF S(Q) >= S(P) THEN GOTO 480
455 S(P) = S(P) + R(I) * R(I)
460 NEXT Q
465 NEXT Q
470 NEXT ITER
480 GOTO 170
500 END
350 \( S = S(P) \)
360 \( S(P) = S(Q) \)
370 \( S(Q) = S \)
380 NEXT Q
390 NEXT P
400 \( J(4) = J(1) + J(2) - J(3); \ K(4) = K(1) + K(2) - K(3) \)
410 \( S(4) = 0 \)
420 FOR I = 1 TO N
430 \( R(I) = Y(I) - (K(4) \times \text{EXP}(-J(4) \times X(I)) - J(4) \times \text{EXP}(-K(4) \times X(I))) / (K(4) - J(4)) \)
440 \( S(4) = S(4) + R(I) \times R(I) \)
450 NEXT I
460 IF \( S(4) \geq S(2) \) THEN GOTO 680
470 IF \( S(4) < S(1) \) THEN GOTO 590
480 \( J(3) = J(4); \ K(3) = K(4); \ S(3) = S(4); \ GOTO 880 \)
490 \( J(5) = 1.5 \times J(1) + 1.5 \times J(2) - 2 \times J(3); \ K(5) = 1.5 \times K(1) + 1.5 \times K(2) - 2 \times K(3) \)
500 \( S(5) = 0 \)
510 FOR I = 1 TO N
520 \( R(I) = Y(I) - (K(5) \times \text{EXP}(-J(5) \times X(I)) - J(5) \times \text{EXP}(-K(5) \times X(I))) / (K(5) - J(5)) \)
530 \( S(5) = S(5) + R(I) \times R(I) \)
540 NEXT I
550 IF \( S(5) > S(1) \) THEN GOTO 670
560 J(3) = J(5);
570 K(3) = K(5);
580 S(3) = S(5);
590 GOTO 880
600 \( S(6) = 0 \)
610 FOR I = 1 TO N
620 \( R(I) = Y(I) - (K(6) \times \text{EXP}(-J(6) \times X(I)) - J(6) \times \text{EXP}(-K(6) \times X(I))) / (K(6) - J(6)) \)
630 \( S(6) = S(6) + R(I) \times R(I) \)
640 NEXT I
650 IF \( S(6) < S(3) \) THEN GOTO 760
660 \( J(6) = .75 \times J(1) + .75 \times J(2) - .5 \times J(3); \ K(6) = .75 \times K(1) + .75 \times K(2) - .5 \times K(3) \)
670 \( S(7) = 0 \)
680 FOR I = 1 TO N
690 \( R(I) = Y(I) - (K(7) \times \text{EXP}(-J(7) \times X(I)) - J(7) \times \text{EXP}(-K(7) \times X(I))) / (K(7) - J(7)) \)
700 \( S(7) = S(7) + R(I) \times R(I) \)
710 NEXT I
720 IF \( S(7) < S(3) \) THEN GOTO 880
730 \( J(2) = .5 \times (J(1) + J(2)); \ K(2) = .5 \times (K(1) + K(2)) \)
740 \( J(3) = .5 \times (J(1) + J(3)); \ K(3) = .5 \times (K(1) + K(3)) \)
750 GOTO 890
760 NEXT ITER
770 NEXT REIT
780 NEXT G
790 PRINT "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
800 PRINT #1, "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
920 NEXT E

1000 F = .0001
1005 REM INPUT "F"; F
1010 PRINT "MINIMUM CHECK:"; " F"; F
1015 PRINT #1, "MINIMUM CHECK:"; " F"; F
1020 INPUT "J, K"; J(1), K(1)
1030 FOR H = 1 TO 9
1040 S = 0
1041 IF H = 1 THEN J = (1 - F) * J(1): K = (1 - F) * K(1)
1042 IF H = 2 THEN J = (1 - F) * J(1): K = K(1)
1043 IF H = 3 THEN J = (1 - F) * J(1): K = (1 + F) * K(1)
1044 IF H = 4 THEN J = J(1): K = (1 - F) * K(1)
1045 IF H = 5 THEN J = J(1): K = K(1)
1046 IF H = 6 THEN J = J(1): K = (1 + F) * K(1)
1047 IF H = 7 THEN J = (1 + F) * J(1): K = (1 - F) * K(1)
1048 IF H = 8 THEN J = (1 + F) * J(1): K = K(1)
1049 IF H = 9 THEN J = (1 + F) * J(1): K = (1 + F) * K(1)
1130 FOR I = 1 TO N
1140 REM D = (J / (J - K)) * EXP(-K * X(I)) - (K / (J - K)) * EXP(-J * X(I)) - Y(I)
1141 D = Y(I) - (K * EXP(-J * X(I)) - J * EXP(-K * X(I))) / (K - J)
1150 S = S + D * D
1160 NEXT I
1170 PRINT "H"; H; "J"; J; "K"; K; "S"; S
1175 PRINT #1, "H"; H; "J"; J; "K"; K; "S"; S
1180 NEXT H

1200 PRINT "DEMING:
1205 PRINT #1, "DEMING:
1210 INPUT "J, K"; J, K
1220 FOR M = 1 TO 6
1230 SKK = 0: SJJ = 0: SJK = 0: SKO = 0: SJO = 0: S = 0
1240 FOR I = 1 TO N
1250 FO = Y(I) - (K / (K - J)) * EXP(-J * X(I)) + (J / (K - J)) * EXP(-K * X(I))
1260 FJ = (K / (K - J)) * X(I) * EXP(-J * X(I)) - (K / ((K - J) * (K - J))) * (EXP(-J * X(I)) - EXP(-K * X(I)))
1270 FK = -(J / ((K - J) * (K - J))) * (EXP(-K * X(I)) - EXP(-J * X(I))) - (J / (K - J)) * X(I) * EXP(-K * X(I))
1280 SKK = SKK + FK * FK
1290 SJJ = SJJ + FJ * FJ
1300 SJK = SJK + FJ * FK
1310 SKO = SKO + FK * FO
1320 SJO = SJO + FJ * FO
1330 S = S + FO * FO
1340 NEXT I
1350 Q = SKK * SJJ - SJK * SJK
1360 KK = (SKO * SJJ - SJO * SJK) / Q
1370 JJ = (SJO * SKK - SKO * SJK) / Q
1380 T = S - SKO * KK - SJO * JJ
1390 DK = SQR(ABS((SJJ * T) / ((N - 2) * Q)))
1400 DJ = SQR(ABS((SKK * T) / ((N - 2) * Q)))
1410 PRINT "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1415 PRINT #1, "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1420 K = K - KK: J = J - JJ
1430 NEXT M
1500 REM LISTING J0, K0 FOR FOUR DIFFERENT STARTS (E)
1510 DATA .01,2,2, .01,5,.1,.1,1,5
2000 REM LISTING SIX RANDOMLY-SELECTED SEQUENCES OF 24 RANDOM, NORMAL DEVIATES
2010 REM SET I: FROM BURINGTON & MAY, TABLE XXIII, COL. 20, LINE 16, DOWNWARDS
2011 DATA 0.592, -0.395, -0.825, 2.362, 1.060, 0.298, -0.726, -1.483
2012 DATA -0.224, -0.386, 0.238, -1.273, 2.399, 0.118, -2.277, 0.655
2013 DATA 0.977, 0.052, -0.799, 0.672, -0.639, -1.389, 1.759, 0.426
2020 REM SET II: FROM COL. 73, LINE 26, UPWARDS
2021 REM DATA 0.919, -0.866, 1.283, -0.762, 0.639, -1.206, -0.209, 1.001
2022 REM DATA -0.012, 0.335, -2.099, 1.284, -0.013, 0.531, -1.757, -0.255
2023 REM DATA 1.829, 1.677, 0.066, 0.471, -0.131, 0.206, 0.893, -1.071
2030 REM SET III: FROM COL. 59, LINE 38, DOWNWARDS
2031 REM DATA 0.750, 2.105, -0.066, -0.252, 1.070, 0.196, 0.438, -1.135
2032 REM DATA -0.303, 0.782, -0.611, 1.683, 0.350, 1.156, -0.155, 0.654
2033 REM DATA 0.527, -1.432, -2.205, -0.850, 0.622, 0.844, -0.974, 0.058
2040 REM SET IV: FROM COL. 52, LINE 06, DOWNWARDS
2041 REM DATA 0.402, -0.833, -1.315, 1.701, 0.708, -0.390, -1.422, -1.727
2042 REM DATA 1.848, 0.412, -1.503, 1.224, -0.790, 0.129, 2.155, 0.181
2043 REM DATA 0.579, -0.243, 0.558, -0.309, -0.129, -0.875, -0.118, -0.746
2050 REM SET V: FROM COL. 46, LINE 33, DOWNWARDS
2051 REM DATA 0.883, 0.397, 1.759, 0.090, 0.079, 1.116, -0.383, 0.371
2052 REM DATA 0.436, 1.934, -0.421, 0.448, 1.371, -1.414, -0.467, 0.364
2053 REM DATA 0.355, -0.126, 1.623, 0.365, -1.134, -0.739, 1.559, 0.092
2060 REM SET VI: FROM COL. 95, LINE 37, DOWNWARDS
2061 REM DATA -1.639, -1.948, -1.272, -0.055, -0.029, -0.757, -1.701, -0.446
2062 REM DATA -2.853, 1.633, 0.667, 0.435, 0.690, -0.462, -0.559, 1.275
2063 REM DATA -0.052, -1.148, 1.148, 0.872, -0.245, 0.371, -0.197, 0.005
Appendix

I. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM SIMULATED DATA

b. CO-PRODUCT FORMATION IN TWO-STEP REACTIONS

10 REM PROGRAM IN BASIC FOR RECOVERING THE TWO FIRST-ORDER RATE COEFFICIENTS
11 REM OF A TWO-STEP, CONSECUTIVE REACTION FROM DATA OF CO-PRODUCT CONCENTRATIONS.
12 REMITION, SIMULATED INORPORATING RANDOM, NORMAL ERRORS AT A SPECIFIED LEVEL
13 REM SIGMA, VERSUS TIME BY THE NELDER-MEAD DOWNHILL SIMPLEX MINIMIZATION
14 REM ROUTINE. THE PROGRAM CHECKS WHETHER THE OPTIMIZED ESTIMATES CORRESPOND
15 REM TO A MINIMUM AND ALSO EMPLOYS THE DEMING ROUTINE TO CONFIRM THE NELDER-
16 REM MEAD OUTPUT.
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM J0(10): DIM K0(10): DIM X(100): DIM Y(100): DIM Z(100): DIM R(100):
DIM V(S10)
50 FOR E = 1 TO 4
60 READ J0(E), K0(E)
70 NEXT E
80 INPUT "K1, K2, DT, N, SIGMA": K1, K2, DT, N, SIGMA
90 FOR I = 1 TO 24
100 READ V(I)
110 X(I) = I * DT
120 Z(I) = ((2 * K2 - K1) / (K2 - K1)) * EXP(-K1 * X(I)) - (K1 / (K2 - K1)) * EXP(-K2 * X(I)) - 2 * SIGMA * V(I)
130 Y(I) = INT(10000 * (Z(I) + .00005)) / 10000
135 PRINT #1, I, X(I), Y(I)
140 NEXT I
150 PRINT "K1"; K1; "K2"; K2; "DT"; DT; "N"; N; "Y"; Y(N); "SIGMA";
SIGMA
155 PRINT #1, "K1"; K1; "K2"; K2; "DT"; DT; "N"; N; "Y"; Y(N); "SIGMA";
SIGMA
160 FOR E = 1 TO 4
170 J(1) = J0(E): K(1) = K0(E)
180 REM PRINT "J0"; J0(E); "K0"; K0(E)
185 REM PRINT #1, "J0"; J0(E); "K0"; K0(E)
190 FOR G = 1 TO 3
210 FOR REI = 1 TO 5
220 FOR P = 1 TO 3
230 S(P) = 0
240 FOR I = 1 TO N
250 R(I) = Y(I) - ((2 * K(P) - J(P)) * EXP(-J(P) * X(I)) - J(P) * EXP(-K(P) * X(I))) / (K(P) - J(P))
260 S(P) = S(P) + R(I) * R(I)
270 NEXT I
280 NEXT P
290 FOR ITER = 1 TO 100
300 FOR P = 1 TO 2
310 FOR Q = P + 1 TO 3
320 IF S(Q) >= S(P) THEN GOTO 480
330 J = J(P)
340 J(P) = J(Q)
350 J(Q) = J
360 K = K(P)
370 K(P) = K(Q)
380 K(Q) = K
390 S = S(P)
400 S(P) = S(Q)
410 S(Q) = S
420 NEXT Q
430 NEXT P
440 S(4) = 0
450 FOR I = 1 TO N
460 R(I) = Y(I) - ((2 * K(4) - J(4)) * EXP(-J(4) * X(I)) - J(4) * EXP(-K(4) * X(I))) / (K(4) - J(4))
470 S(4) = S(4) + R(I) * R(I)
480 NEXT I
490 NEXT P
500 J(4) = J(1) + J(2) - J(3): K(4) = K(1) + K(2) - K(3)
510 S(4) = 0
520 FOR I = 1 TO N
530 R(I) = Y(I) - ((2 * K(4) - J(4)) * EXP(-J(4) * X(I)) - J(4) * EXP(-K(4) * X(I))) / (K(4) - J(4))
540 S(4) = S(4) + R(I) * R(I)
550 NEXT I
560 IF S(4) >= S(2) THEN GOTO 680
570 IF S(4) < S(1) THEN GOTO 590
590 J(5) = 1.5 * J(1) + 1.5 * J(2) - 2 * J(3): K(5) = 1.5 * K(1) + 1.5 * K(2) - 2 * K(3)
600 S(5) = 0
610 FOR I = 1 TO N
620 R(I) = Y(I) - ((2 * K(5) - J(5)) * EXP(-J(5) * X(I)) - J(5) * EXP(-K(5) * X(I))) / (K(5) - J(5))
630 S(5) = S(5) + R(I) * R(I)
640 NEXT I
650 IF S(5) > S(1) THEN GOTO 670
680 IF S(4) >= S(3) THEN GOTO 880
690 J(6) = .75 * J(1) + .75 * J(2) - .5 * J(3): K(6) = .75 * K(1) + .75 * K(2) - .5 * K(3)
700 S(6) = 0
710 FOR I = 1 TO N
720 R(I) = Y(I) - ((2 * K(6) - J(6)) * EXP(-J(6) * X(I)) - J(6) * EXP(-K(6) * X(I))) / (K(6) - J(6))
730 S(6) = S(6) + R(I) * R(I)
740 NEXT I
760 J(7) = .25 * J(1) + .25 * J(2) + .5 * J(3): K(7) = .25 * K(1) + .25 * K(2) + .5 * K(3)
770 S(7) = 0
780 FOR I = 1 TO N
790 R(I) = Y(I) - ((2 * K(7) - J(7)) * EXP(-J(7) * X(I)) - J(7) * EXP(-K(7) * X(I))) / (K(7) - J(7))
800 S(7) = S(7) + R(I) * R(I)
810 NEXT I
830 J(2) = .5 * (J(1) + J(2)): K(2) = .5 * (K(1) + K(2))
840 J(3) = .5 * (J(1) + J(3)): K(3) = .5 * (K(1) + K(3))
870 GOTO 890
880 NEXT ITER
890 NEXT REIT
900 NEXT G
910 PRINT "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
915 PRINT #1, "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
920 NEXT E

1000 F = .0001
1005 REM INPUT "F"; F
1010 PRINT "MINIMUM CHECK:"; " F"; F
1015 PRINT #1, "MINIMUM CHECK:"; " F"; F
1020 REM INPUT "J, K"; J(1), K(1)
1030 FOR H = 1 TO 9
1040 S = 0
1041 IF H = 1 THEN J = (1 - F) * J(1): K = (1 - F) * K(1)
1042 IF H = 2 THEN J = (1 - F) * J(1): K = K(1)
1043 IF H = 3 THEN J = (1 - F) * J(1): K = (1 + F) * K(1)
1044 IF H = 4 THEN J = J(1): K = (1 - F) * K(1)
1045 IF H = 5 THEN J = J(1):   K = K(1)
1046 IF H = 6 THEN J = J(1):   K = (1 + F) * K(1)
1047 IF H = 7 THEN J = (1 + F) * J(1):  K = (1 - F) * K(1)
1048 IF H = 8 THEN J = (1 + F) * J(1):  K = K(1)
1049 IF H = 9 THEN J = (1 + F) * J(1):  K = (1 + F) * K(1)
1130 FOR I = 1 TO N
1140 D = Y(I) - ((2 * K - J) * EXP(-J * X(I)) - J * EXP(-K * X(I))) / (K - J)
1150 S = S + D^2
1160 NEXT I
1170 PRINT "H"; H; "J"; J; "K"; K; "S"; S
1180 NEXT H
1200 PRINT "DEMING:"
1205 PRINT #1, "DEMING:"
1210 INPUT "J", K
1220 FOR M = 1 TO 10
1230 SKK = 0: SJJ = 0: SJK = 0: SKO = 0: SJO = 0: S = 0
1240 FOR I = 1 TO N
1250 FO = ((J - 2 * K) * EXP(-J * X(I)) + J * EXP(-K * X(I))) / (J - K) - Y(I)
1260 FJ = K * (EXP(-J * X(I)) - EXP(-K * X(I))) / ((J - K) * (J - K)) - (J - 2 * K) * X(I) * EXP(-J * X(I)) / (J - K)
1270 FK = J * (EXP(-K * X(I)) - EXP(-J * X(I))) / ((J - K) * (J - K)) - J * X(I) * EXP(-K * X(I)) / (J - K)
1280 SKK = SKK + FK * FK
1290 SJJ = SJJ + FJ * FJ
1300 SJK = SJK + FJ * FK
1310 SKO = SKO + FK * FO
1320 SJO = SJO + FJ * FO
1330 S = S + FO * FO
1340 NEXT I
1350 Q = SKK * SJJ - SJK * SJK
1360 KK = (SKO * SJJ - SJO * SJK) / Q
1370 JJ = (SJO * SKK - SKO * SJK) / Q
1380 T = S - SKO * KK - SJO * JJ
1390 DK = SQR(ABS((SJ J * T) / ((N - 2) * Q)))
1400 DJ = SQR(ABS((SKK * T) / ((N - 2) * Q)))
1410 PRINT "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1415 PRINT #1, "M"; M; "J"; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1420 K = K - KK: J = J - JJ
1430 NEXT M
1500 REM LISTING J0, K0 FOR FOUR DIFFERENT STARTS (E)
1510 DATA .01, 2, 2, .01, .1, 5, 5, .1
2000 REM LISTING SIX RANDOMLY-SELECTED SEQUENCES OF 24 RANDOM, NORMAL DEVIATES

2010 REM SET I: FROM BURINGTON & MAY, TABLE XXIII, COL. 20, LINE 16, DOWNWARDS
DATA 0.592, -0.395, -0.825, 2.362, 1.060, 0.298, -0.726, -1.483
DATA -0.224, -0.386, 0.238, -1.273, 2.399, 0.118, -2.277, 0.655
DATA 0.977, 0.052, -0.799, 0.672, -0.639, -1.389, 1.759, 0.426
Appendix

I. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM SIMULATED DATA

.. INTERMEDIATE CONCENTRATION IN TWO-STEP REACTIONS

10 REM PROGRAM IN BASIC FOR RECOVERING THE TWO FIRST-ORDER RATE COEFFICIENTS
11 REM OF A TWO-STEP, CONSECUTIVE REACTION FROM DATA OF INTERMEDIATE
12 REM CONCENTRATION, SIMULATED INORPORATING RANDOM, NORMAL ERRORS AT A
13 REM SPECIFIED LEVEL, SIGMA, VERSUS TIME BY THE NELDER-MEAD DOWNHILL
14 REM SIMPLEX MINIMIZATION ROUTINE. THE PROGRAM ALSO CHECKS WHETHER THE
15 REM OPTIMIZED ESTIMATES OF J AND K INDEED CORRESPOND TO A MINIMUM.
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM JO(10): DIM KO(10): DIM X(100): DIM Y(100): DIM Z(100): DIM R(100): DIM V(510)
50 FOR E = 1 TO 8
60 READ JO(E), KO(E)
70 NEXT E
80 INPUT "K1, K2, N, SIGMA"; K1, K2, N, SIGMA
86 RR = K2 / K1
87 TM = LOG(RR) / (RR - 1)
88 BM = (EXP(-TM) - EXP(-TM * RR)) / (RR - 1)
89 PRINT "TM"; TM; "BM"; BM
90 FOR I = 1 TO N
100 READ V(I)
110 X(I) = I * TM
120 Z(I) = K1 * (EXP(-K1 * X(I)) - EXP(-K2 * X(I))) / (K2 - K1) + BM * SIGMA * V(I)
130 Y(I) = INT(10000 * (Z(I) + .00005)) / 10000
135 REM PRINT #1, I, X(I), Y(I)
140 NEXT I
FOR I = 1 TO N
R(I) = Y(I) - (J(S) * (EXP(-J(S) * X(I)) - EXP(-K(S) * X(I)))/ (K(S) - J(S))
REM R(I) = Y(I) - (K(S) * EXP(-J(S) * X(I)) - J(S) * EXP(-K(S) * X(I)))/ (K(S) - J(S))
S(S) = S(S) + R(I) * R(I)
NEXT I
IF S(S) > S(1) THEN GOTO 670
K(3) = K(S): J(3) = J(S): S(3) = S(S): GOTO 880
IF S(4) >= S(3) THEN GOT0 760
J(6) = .75 * J(1) + .75 * J(2) - .5 * J(3): K(6) = .75 * K(1) + .75 * K(2) - .5 * K(3)
S(6) = 0
FOR I = 1 TO N
R(I) = Y(I) - (J(6) * (EXP(-J(6) * X(I)) - EXP(-K(6) * X(I)))/ (K(6) - J(6))
REM R(I) = Y(I) - (K(6) * EXP(-J(6) * X(I)) - J(6) * EXP(-K(6) * X(I)))/ (K(6) - J(6))
S(6) = S(6) + R(I) * R(I)
NEXT I
J(7) = .25 * J(1) + .25 * J(2) + .5 * J(3): K(7) = .25 * K(1) + .25 * K(2) + .5 * K(3)
S(7) = 0
FOR I = 1 TO N
R(I) = Y(I) - (J(7) * (EXP(-J(7) * X(I)) - EXP(-K(7) * X(I)))/ (K(7) - J(7))
REM R(I) = Y(I) - (K(7) * EXP(-J(7) * X(I)) - J(7) * EXP(-K(7) * X(I)))/ (K(7) - J(7))
S(7) = S(7) + R(I) * R(I)
NEXT I
J(2) = .5 * (J(1) + J(2)): K(2) = .5 * (K(1) + K(2))
J(3) = .5 * (J(1) + J(3)): K(3) = .5 * (K(1) + K(3))
GOTO 890
NEXT ITER
NEXT REIT
NEXT G
PRINT "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
PRINT #1, "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
NEXT E
F = .001
REM INPUT "F"; F
PRINT "MINIMUM CHECK:"; " F"; F
INPUT "J, K"; J(1), K(1)
FOR H = 1 TO 9
S = 0
IF H = 1 THEN J = (1 - F) * J(1): K = (1 - F) * K(1)
IF H = 2 THEN J = (1 - F) * J(1): K = K(1)
IF H = 3 THEN J = (1 - F) * J(1): K = (1 + F) * K(1)
IF \( H = 4 \) THEN \( J = J(1) \): \( K = (1 - F) \times K(1) \)

IF \( H = 5 \) THEN \( J = J(1) \): \( K = K(1) \)

IF \( H = 6 \) THEN \( J = J(1) \): \( K = (1 + F) \times K(1) \)

IF \( H = 7 \) THEN \( J = (1 + F) \times J(1) \): \( K = (1 - F) \times K(1) \)

IF \( H = 8 \) THEN \( J = (1 + F) \times J(1) \): \( K = K(1) \)

IF \( H = 9 \) THEN \( J = (1 + F) \times J(1) \): \( K = (1 + F) \times K(1) \)

FOR \( I = 1 \) TO \( N \)

\[ D = Y(I) - (J \times \exp(-J \times X(I)) - \exp(-K \times X(I))) / (K - J) \]

\[ S = S + D \times D \]

NEXT \( I \)

PRINT "H": \( H \); "J": \( J \); "K": \( K \); "S": \( S \)

NEXT \( H \)

CLOSE #1

REM CO-ORDINATES, \( J0 \) AND \( K0 \), OF EIGHT STARTS

DATA .05, 1, 1, .05, 1, 2, 2, .1, 4, 4, .2, 5, 5

REM SET \( I \): FROM BURINGTON & MAY, TABLE XXIII, COL. 20, LINE 16, DOWNWARDS

DATA 0.592, -0.395, -0.825, 2.362, 1.060, 0.298, -0.726, -1.483

DATA -0.224, -0.386, 0.238, -1.273, 2.399, 0.118, -2.277, 0.655

DATA 0.977, 0.052, -0.799, 0.672, -0.639, -1.389, 1.759, 0.426
Appendix

I. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM SIMULATED DATA

d. PRODUCT FORMATION IN THREE - STEP REACTIONS

10 REM PROGRAM IN QBASIC FOR RECOVERING THE THREE FIRST-ORDER RATE COEFFICIENTS,
11 REM KS, KM AND KF, OF A THREE-STEP, CONSECUTIVE REACTION FROM DATA OF
12 REM PRODUCT CONCENTRATION, SIMULATED INCORPORATING RANDOM, NORMAL DEVIATES
13 REM AT A GIVEN LEVEL SIGMA, BY THE NELDER-MEAD DOWNHILL SIMPLEX MINIMIZATION
14 REM ROUTINE. THE PROGRAM STARTS THE SEARCH FOR THE MINIMA SUCCESSIVELY FROM
15 REM FIVE POINTS, SPECIFIED AS DATA. THE PROGRAM CAN ALSO VERIFY THE
16 REM AUTHENTICITY OF ANY PARTICULAR MINIMUM MINIMUM.
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM J0(20): DIM K0(20): DIM L0(20): DIM X(100): DIM Y(100): DIM Z(100):
DIM V(100): DIM R(100)
50 FOR E = 1 TO 5
60 READ J0(E), K0(E), L0(E)
70 NEXT E
80 INPUT "KS, KM, KF, DT, N, SIGMA"; KS, KM, KF, DT, N, SIGMA
90 FOR I = 1 TO 24
100 READ V(I)
110 X(I) = I * DT
130 Y(I) = INT(10000 * (Z(I) + .00005)) / 10000
135 REM PRINT X(I), Y(I)
140 NEXT I
150 PRINT "KS"; KS; "KM"; KM; "KF"; KF; "DT"; DT; "N"; N; "SIGMA"; SIGMA; "Y(N)"; Y(N)
155 PRINT #1, "KS"; KS; "KM"; KM; "KF"; KF; "DT"; DT; "N"; N; "SIGMA"; SIGMA; "Y(N)"; Y(N)
160 FOR E = 1 TO 5
170 J(1) = J0(E): K(1) = K0(E): L(1) = L0(E)
180 REM PRINT "JO"; JO(E); "KO"; KO(E); "LO"; LO(E)
185 REM PRINT #1, "JO"; J0(E); "KO"; K0(E); "LO"; L0(E)
190 FOR G = 1 TO 4
210 FOR REIT = 1 TO 10
220 FOR P = 1 TO 4
230 S(P) = 0
240 FOR I = 1 TO N
250 R(I) = Y(I) - ((L(P) - K(P)) * L(P) * K(P) * EXP(-J(P) * X(I)) + (J(P) - L(P)) * J(P) * L(P) * EXP(-K(P) * X(I))) / ((J(P) - K(P)) * (K(P) - L(P)) * (L(P) - J(P))))
260 S(P) = S(P) + R(I) * R(I)
270 NEXT I
280 NEXT P
290 FOR ITER = 1 TO 100
300 FOR P = 1 TO 3
310 FOR Q = P + 1 TO 4
320 IF S(Q) >= S(P) THEN GOTO 480
330 J = J(P)
340 J(P) = J(Q)
350 J(Q) = J
360 K = K(P)
370 K(P) = K(Q)
380 K(Q) = K
390 L = L(P)
400 L(P) = L(Q)
410 L(Q) = L
450 S = S(P)
460 S(P) = S(Q)
470 S(Q) = S
480 NEXT Q
490 NEXT P
500 J(5) = 2 * (J(1) + J(2) + J(3)) / 3 - J(4): K(5) = 2 * (K(1) + K(2) + K(3)) / 3 - K(4): L(5) = 2 * (L(1) + L(2) + L(3)) / 3 - L(4)
510 S(5) = 0
520 FOR I = 1 TO N
530 R(I) = Y(I) - ((L(5) - K(5)) * L(5) * K(5) * EXP(-J(5) * X(I)) + (J(5) - L(5)) * J(5) * L(5) * EXP(-K(5) * X(I))) / ((J(5) - K(5)) * (K(5) - L(5)) * (L(5) - J(5))))
540 S(5) = S(5) + R(1) * R(1)
550 NEXT I
560 IF S(5) >= S(2) THEN GOTO 680
570 IF S(5) < S(1) THEN GOTO 590
600 S(6) = 0
610 FOR I = 1 TO N
620 R(I) = Y(I) - (((L(I) - K(I)) * L(I) * K(I) * EXP(-J(I) * X(I)) + (J(I) - L(I)) * J(I) * L(I) * EXP(-K(I) * X(I))) / ((J(I) - K(I)) * (K(I) - L(I)) * (L(I) - J(I))))
630 S(6) = S(6) + R(I) * R(I)
640 NEXT I
650 IF S(6) > S(1) THEN GOTO 670
680 IF S(5) >= S(4) THEN GOTO 760
690 J(7) = .5 * (J(1) + J(2) + J(3) - J(4)): K(7) = .5 * (K(1) + K(2) + K(3) - K(4)): L(7) = .5 * (L(1) + L(2) + L(3) - L(4))
700 S(7) = 0
710 FOR I = 1 TO N
720 R(I) = Y(I) - (((L(I) - K(I)) * L(I) * K(I) * EXP(-J(I) * X(I)) + (J(I) - L(I)) * J(I) * L(I) * EXP(-K(I) * X(I))) / ((J(I) - K(I)) * (K(I) - L(I)) * (L(I) - J(I))))
730 S(7) = S(7) + R(I) * R(I)
740 NEXT I
760 J(8) = .5 * J(4) + (J(1) + J(2) + J(3)) / 6: K(8) = .5 * K(4) + (K(1) + K(2) + K(3)) / 6: L(8) = .5 * L(4) + (L(1) + L(2) + L(3)) / 6
770 S(8) = 0
780 FOR I = 1 TO N
790 R(I) = Y(I) - (((L(I) - K(I)) * L(I) * K(I) * EXP(-J(I) * X(I)) + (J(I) - L(I)) * J(I) * L(I) * EXP(-K(I) * X(I))) / ((J(I) - K(I)) * (K(I) - L(I)) * (L(I) - J(I))))
800 S(8) = S(8) + R(I) * R(I)
810 NEXT I
830 J(2) = .5 * (J(1) + J(2)): K(2) = .5 * (K(1) + K(2)): L(2) = .5 * (L(1) + L(2))
840 J(3) = .5 * (J(1) + J(3)): K(3) = .5 * (K(1) + K(3)): L(3) = .5 * (L(1) + L(3))
850 J(4) = .5 * (J(1) + J(4)): K(4) = .5 * (K(1) + K(4)): L(4) = .5 * (L(1) + L(4))
870 GOTO 890
880 NEXT ITER
890 NEXT REIT
1000 F = .00001
1005 REM INPUT "F"; F
1010 PRINT #1, "MINIMUM CHECK"; "F"; F
1020 INPUT "J, K, L"; J(I), K(I), L(I)
1030 FOR H = 1 TO 27
1040 S = 0
1041 IF H = 1 THEN J = (1 - F) * J(1): K = (1 - F) * K(1): L = (1 - F) * L(1)
1044 IF H = 4 THEN J = (1 - F) * J(1): K = K(1):     L = (1 - F) * L(1)
1045 IF H = 5 THEN J = J(1):  K = K(1):     L = (1 - F) * L(1)
1046 IF H = 6 THEN J = (1 + F) * J(1): K = K(1):     L = (1 - F) * L(1)
1049 IF H = 9 THEN J = (1 + F) * J(1): K = (1 + F) * K(1): L = (1 - F) * L(1)
1060 IF H = 20 THEN J = J(1):  K = (1 - F) * K(1): L = (1 + F) * L(1)
1061 IF H = 21 THEN J = (1 + F) * J(1): K = (1 - F) * K(1): L = (1 + F) * L(1)
1062 IF H = 22 THEN J = (1 - F) * J(1): K = K(1):     L = (1 + F) * L(1)
1064 IF H = 24 THEN J = (1 + F) * J(1): K = K(1):     L = (1 + F) * L(1)
1066 IF H = 26 THEN J = J(1):  K = (1 + F) * K(1): L = (1 + F) * L(1)
1067 IF H = 27 THEN J = (1 + F) * J(1): K = (1 + F) * K(1): L = (1 + F) * L(1)
1130 FOR I = 1 TO N
1140 D = Y(I) - (((L - K) * L * K * EXP(-J * X(I)) + (J - L) * J * L * EXP(-K * X(I)) ) + (K - J) * K * J * EXP(-L * X(I)) / ((J - K) * (K - L) * (L - J)))
1150 S = S + D * D
1160 NEXT I
1170 PRINT #1, "H"; H; "J"; J(I); "K"; K(I); "L"; L(I); "S"; S
1180 NEXT H
1190 CLOSE #1
1500 REM COMBINATIONS FOR J0, K0 AND L0 FOR FIVE DIFFERENT STARTS
1510 DATA .05, .5, .05, .5, .05, .5, .05, .5, .05, .5, .05, .5

2010 REM SET I: FROM BURINGTON & MAY, TABLE XXIII, COL. 20, LINE 16, DOWNWARDS
2011 DATA 0.592, -0.395, -0.825, 2.362, 1.060, 0.298, -0.726, -1.483
2012 DATA -0.224, -0.386, 0.238, -1.273, 2.399, 0.118, -2.277, 0.655
2013 DATA 0.977, 0.052, -0.799, 0.672, -0.639, -1.389, 1.759, 0.426

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Appendix

1. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM SIMULATED DATA

e. SYSTEM PROPERTY DATA IN TWO-STEP REACTIONS

10 REM PROGRAM IN QBASIC, WRITTEN BY R. SIVARAMAKRISHNAN, FOR THE OPTIMIZATION
11 REM BY THE NELDER-MEAD DOWNHILL SIMPLEX ROUTINE, OF THE FOUR PARAMETERS \( J, \)
12 REM \( K, L \) AND \( M \) OF THE RATE EQUATION \( Y = L \times \exp(-J \times T) + M \times \exp(-K \times T) \)
13 REM OF A TWO-STEP, CONSECUTIVE, FIRST-ORDER REACTION FROM (N) DATA OF A
14 REM SYSTEM PROPERTY (SUCH AS ABSORBANCE) VERSUS TIME (X), SIMULATED INCORPORATING RANDOM, NORMAL ERRORS AT A GIVEN LEVEL SIGMA. THE PROGRAM
15 REM STARTS SUCCESSIVELY FROM TEN LATIN HYPERCUBE SETS OF INITIAL INPUTS OF
16 REM THE PARAMETERS, LISTED AS DATA. IT CARRIES OUT UP TO 100 ITERATIONS IN
17 REM EACH OF TEN CYCLES (REIT), THEN RESTARTS NINE TIMES IN AN EFFORT TO
18 REM REACH A MINIMUM. IT ALSO VERIFIES WHETHER A GIVEN OUTPUT CORRESPONDS
19 REM TO A MINIMUM OF THE SUM OF SQUARES OF DEVIATIONS.
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
DIM Z(100): DIM V(100): DIM R(100)
50 FOR E = 1 TO 10
60 READ JO(E), KO(E), LO(E), MO(E)
70 NEXT E
80 INPUT "KS, KF, CS, CF, DT, N, SIGMA": KS, KF, CS, CF, DT, N, SIGMA
90 FOR I = 1 TO 24
100 READ V(I)
110 X(I) = I * DT
120 \( Z(I) = CS \times \exp(-KS \times X(I)) + CF \times \exp(-KF \times X(I)) - V(I) \times \sigma \)
130 \( Y(I) = \text{INT}(10000 \times (Z(I) + 0.00005)) / 10000 \)
135 REM PRINT "X("; I; ")"; X(I); "Y"; Y(I)
140 NEXT I
150 PRINT "KS"; KS; "KF"; KF; "CS"; CS; "CF"; CF; "DT"; DT; "N"; N; "Y"; Y(N); "SIGMA"; SIGMA
155 PRINT #1, "KS"; KS; "KF"; KF; "CS"; CS; "CF"; CF; "DT"; DT; "N"; N; "Y"; Y(N); "SIGMA"; SIGMA
160 FOR E = 1 TO 10
170 J(1) = J0(E): K(1) = K0(E): L(1) = L0(E): M(1) = M0(E)
180 REM PRINT "J0"; J0(E); "K0"; K0(E); "L0"; L0(E); "M0"; M0(E)
185 REM PRINT #1, "J0"; J0(E); "K0"; K0(E); "L0"; L0(E); "M0"; M0(E)
190 FOR G = 1 TO 10
210 FOR ITER = 1 TO 10
220 FOR P = 1 TO 5
230 S(P) = 0
240 FOR I = 1 TO N
250 R(I) = L(P) \times \exp(-J(P) \times X(I)) + M(P) \times \exp(-K(P) \times X(I)) - Y(I)
260 S(P) = S(P) + R(I) \times R(I)
270 NEXT I
280 NEXT P
290 FOR ITER = 1 TO 100
300 FOR P = 1 TO 4
310 FOR Q = P + 1 TO 5
320 IF S(Q) >= S(P) THEN GOTO 480
330 J = J(P)
340 J(P) = J(Q)
350 J(Q) = J
360 K = K(P)
370 K(P) = K(Q)
380 K(Q) = K
390 L = L(P)
400 L(P) = L(Q)
410 L(Q) = L
420 M = M(P)
430 M(P) = M(Q)
440 M(Q) = M
450 S = S(P)
460 S(P) = S(Q)
470 S(Q) = S
480 NEXT Q
490 NEXT P
510 S(6) = 0
520 FOR I = 1 TO N
530 R(I) = L(I) * EXP(-J(6) * X(I)) + M(6) * EXP(-K(6) * X(I)) - Y(I)
540 S(6) = S(6) + R(I) * R(I)
550 NEXT I
560 IF S(6) >= S(2) THEN GOTO 680
570 IF S(6) < S(1) THEN GOTO 590
600 S(7) = 0
610 FOR I = 1 TO N
620 R(I) = L(I) * EXP(-J(7) * X(I)) + M(7) * EXP(-K(7) * X(I)) - Y(I)
630 S(7) = S(7) + R(I) * R(I)
640 NEXT I
650 IF S(7) > S(1) THEN GOTO 670
680 IF S(6) >= S(5) THEN GOTO 760
690 J(8) = 3 * (J(1) + J(2) + J(3) + J(4)) / 8 - .5 * J(5): K(8) = 3 * (K(1) + K(2) + K(3) + K(4)) / 8 - .5 * K(5): L(8) = 3 * (L(1) + L(2) + L(3) + L(4)) / 8 - .5 * L(5): M(8) = 3 * (M(1) + M(2) + M(3) + M(4)) / 8 - .5 * M(5)
700 S(8) = 0
710 FOR I = 1 TO N
720 R(I) = L(I) * EXP(-J(8) * X(I)) + M(8) * EXP(-K(8) * X(I)) - Y(I)
730 S(8) = S(8) + R(I) * R(I)
740 NEXT I
770 S(9) = 0
780 FOR I = 1 TO N
790 R(I) = L(I) * EXP(-J(9) * X(I)) + M(9) * EXP(-K(9) * X(I)) - Y(I)
800 S(9) = S(9) + R(I) * R(I)
810 NEXT I
830 J(2) = .5 * (J(1) + J(2)): K(2) = .5 * (K(1) + K(2)): L(2) = .5 * (L(1) + L(2)): M(2) = .5 * (M(1) + M(2))
840 J(3) = .5 * (J(1) + J(3)); K(3) = .5 * (K(1) + K(3)); L(3) = .5 * (L(1) + L(3)); M(3) = .5 * (M(1) + M(3))
850 J(4) = .5 * (J(1) + J(4)); K(4) = .5 * (K(1) + K(4)); L(4) = .5 * (L(1) + L(4)); M(4) = .5 * (M(1) + M(4))
860 J(5) = .5 * (J(1) + J(5)); K(5) = .5 * (K(1) + K(5)); L(5) = .5 * (L(1) + L(5)); M(5) = .5 * (M(1) + M(5))
870 GOTO 890
880 NEXT ITER
890 NEXT REIT
900 NEXT G
910 PRINT "E"; E; "J"; J(1); "K"; K(1); "L"; L(1); "M"; M(1); "S"; S(1)
915 PRINT #1, "E"; E; "J"; J(1); "K"; K(1); "L"; L(1); "M"; M(1); "S"; S(1)
920 NEXT E

1000 F = .00001
1005 REM INPUT "F"; F
1010 PRINT #1, "MINIMUM CHECK"; "F"; F
1020 INPUT "J, K, L, M"; J(1), K(1), L(1), M(1)
1030 FOR H = 1 TO 81
1040 S = 0
1104 IF H = 64 THEN J = (1 - F) * J(1); K = (1 - F) * K(1); L = L(1): M = (1 + F) * M(1)
1105 IF H = 65 THEN J = J(1): K = (1 - F) * K(1); L = L(1): M = (1 + F) * M(1)
1106 IF H = 66 THEN J = (1 + F) * J(1); K = (1 - F) * K(1); L = L(1): M = (1 + F) * M(1)
1110 IF H = 70 THEN J = (1 - F) * J(1); K = (1 + F) * K(1); L = L(1): M = (1 + F) * M(1)
1111 IF H = 71 THEN J = J(1): K = (1 + F) * K(1); L = L(1): M = (1 + F) * M(1)
1112 IF H = 72 THEN J = (1 + F) * J(1): K = (1 + F) * K(1); L = L(1): M = (1 + F) * M(1)
1113 IF H = 73 THEN J = (1 - F) * J(1); K = (1 - F) * K(1); L = (1 + F) * L(1): M = (1 + F) * M(1)
1114 IF H = 74 THEN J = J(1): K = (1 - F) * K(1); L = (1 + F) * L(1): M = (1 + F) * M(1)
1115 IF H = 75 THEN J = (1 + F) * J(1); K = (1 - F) * K(1); L = (1 + F) * L(1): M = (1 + F) * M(1)
1119 IF H = 79 THEN J = (1 - F) * J(1); K = (1 + F) * K(1); L = (1 + F) * L(1): M = (1 + F) * M(1)
1120 IF H = 80 THEN J = J(1): K = (1 + F) * K(1); L = (1 + F) * L(1): M = (1 + F) * M(1)
1121 IF H = 81 THEN J = (1 + F) * J(1): K = (1 + F) * K(1); L = (1 + F) * L(1): M = (1 + F) * M(1)
1130 FOR I = 1 TO N
1140 D = L * EXP(-J * X(I)) + M * EXP(-K * X(I)) - Y(I)
1150 S = S + D * D
1160 NEXT I
1170 PRINT #1, "H"; H; "J"; J; "K"; K; "L"; L; "M"; M; "S"; S
1180 NEXT H
1190 CLOSE #1

1500 REM TEN LATIN HYPERCUBE STARTS, LISTING THE INITIAL INPUTS OF J, K, L AND M
1510 DATA .75, .45, .45, .55, .05, .35, .95, .05, .85, .75, .35, .65
1520 DATA .25, .95, .55, .45, .15, .65, .65, .35, .35, .05, .75, .25
1530 DATA .65, .85, .05, .95, .45, .15, .15, .85, .95, .55, .85, .15
1540 DATA .55, .25, .25, .75

2000 REM LISTING SIX RANDOMLY-SELECTED SEQUENCES OF 24 RANDOM, NORMAL DEVIATES
2010 REM SET I: FROM BURINGTON & MAY, TABLE XXIII, COL. 20, LINE 16, DOWNWARDS
2011 DATA 0.592, -0.395, -0.825, 2.362, 1.060, 0.298, -0.726, -1.483
2012 DATA -0.224, -0.386, 0.238, -1.273, 2.399, 0.118, -2.277, 0.655
2013 DATA 0.977, 0.052, -0.799, 0.672, -0.639, -1.389, 1.759, 0.426
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<th>X-Positions</th>
<th>Y-Positions</th>
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II. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM REAL DATA

1. PRODUCT FORMATION IN TWO STEP REACTIONS

10 REM PROGRAM IN BASIC FOR OPTIMIZING THE TWO FIRST-ORDER RATE COEFFICIENTS
11 REM OF A TWO-STEP, CONSECUTIVE REACTION FROM EXPERIMENTAL DATA OF PRODUCT
12 REM CONCENTRATION VERSUS TIME BY THE NELDER-MEAD DOWNHILL SIMPLEX MINIMIZATION ROUTINE, AS ADOPTED IN THIS THESIS, ILLUSTRATED BY APPLICATION TO
13 REM GALE AND EADIE'S DATA [46] ON THE HYDROLYSIS OF UREA PRODUCING CARBON
14 REM DIOXIDE; CONFIRMED BY THE DEMING ROUTINE
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM JO(10): DIM KO(10): DIM X(100): DIM Y(100): DIM Z(100): DIM R(100):
DIM V(510)
50 FOR E = 1 TO 4
60 READ JO(E), KO(E)
70 NEXT E
80 INPUT "N", N
90 FOR I = 1 TO N
100 READ X(I), Y(I)
140 NEXT I
160 FOR E = 1 TO 4
170 J(1) = JO(E); K(1) = K0(E)
180 REM PRINT "JO"; J0(E); "K0"; K0(E)
185 REM PRINT #1, "JO"; J0(E); "K0"; K0(E)
190 FOR G = 1 TO 3
210 FOR REIT = 1 TO 5
220 FOR P = 1 TO 3
230 S(P) = 0
240 FOR I = 1 TO N
250 R(I) = Y(I) - (K(P) * EXP(-J(P) * X(I)) - J(P) * EXP(-K(P) * X(I))) / (K(P) - J(P))
260 S(P) = S(P) + R(I) * R(I)
270 NEXT I
280 NEXT P
290 FOR ITER = 1 TO 100
300 FOR P = 1 TO 2
310 FOR Q = P + 1 TO 3
320 IF S(Q) >= S(P) THEN GOTO 480
330 J = J(P)
340 J(P) = J(Q)
350 J(Q) = J
360 K = K(P)
370 K(P) = K(Q)
380 K(Q) = K
390 S = S(P)
400 S(P) = S(Q)
410 S(Q) = S
420 NEXT Q
430 NEXT P
500  J(4) = J(1) + J(2) - J(3):  K(4) = K(1) + K(2) - K(3)
510  S(4) = 0
520  FOR I = 1 TO N
530   R(I) = Y(I) - (K(4) * EXP(-J(4) * X(I))) - J(4) * EXP(-K(4) * X(I))) / (K(4) - J(4))
540  S(4) = S(4) + R(I) * R(I)
550  NEXT I
560  IF S(4) >= S(2) THEN GOTO 680
570  IF S(4) < S(1) THEN GOTO 590
590  J(5) = 1.5 * J(1) + 1.5 * J(2) - 2 * J(3):  K(5) = 1.5 * K(1) + 1.5 * K(2) - 2 * K(3)
600  S(5) = 0
610  FOR I = 1 TO N
620   R(I) = Y(I) - (K(5) * EXP(-J(5) * X(I))) - J(5) * EXP(-K(5) * X(I))) / (K(5) - J(5))
630  S(5) = S(5) + R(I) * R(I)
640  NEXT I
650  IF S(5) > S(1) THEN GOTO 670
680  IF S(4) >= S(3) THEN GOTO 760
690  J(6) = .75 * J(1) + .75 * J(2) - .5 * J(3):  K(6) = .75 * K(1) + .75 * K(2) - .5 * K(3)
700  S(6) = 0
710  FOR I = 1 TO N
720   R(I) = Y(I) - (K(6) * EXP(-J(6) * X(I))) - J(6) * EXP(-K(6) * X(I))) / (K(6) - J(6))
730  S(6) = S(6) + R(I) * R(I)
740  NEXT I
760  J(7) = .25 * J(1) + .25 * J(2) + .5 * J(3):  K(7) = .25 * K(1) + .25 * K(2) + .5 * K(3)
770  S(7) = 0
780  FOR I = 1 TO N
790   R(I) = Y(I) - (K(7) * EXP(-J(7) * X(I))) - J(7) * EXP(-K(7) * X(I))) / (K(7) - J(7))
800  S(7) = S(7) + R(I) * R(I)
810 NEXT I
830 J(2) = .5 * (J(1) + J(2)): K(2) = .5 * (K(1) + K(2))
840 J(3) = .5 * (J(1) + J(3)): K(3) = .5 * (K(1) + K(3))
870 GOTO 890
880 NEXT ITER
890 NEXT G
900 NEXT E
910 PRINT "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
915 PRINT #1, "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
920 NEXT E

1000 F = .0001
1005 REM INPUT "F"; F
1010 PRINT "MINIMUM CHECK:"; "F"; F
1015 PRINT #1, "MINIMUM CHECK:"; "F"; F
1020 INPUT "J, K"; J(1), K(1)
1030 FOR H = 1 TO 9
1040 S = 0
1041 IF H = 1 THEN J = (1 - F) * J(1): K = (1 - F) * K(1)
1042 IF H = 2 THEN J = (1 - F) * J(1): K = K(1)
1043 IF H = 3 THEN J = (1 - F) * J(1): K = (1 + F) * K(1)
1044 IF H = 4 THEN J = J(1): K = (1 - F) * K(1)
1045 IF H = 5 THEN J = J(1): K = K(1)
1046 IF H = 6 THEN J = J(1): K = (1 + F) * K(1)
1047 IF H = 7 THEN J = (1 + F) * J(1): K = (1 - F) * K(1)
1048 IF H = 8 THEN J = (1 + F) * J(1): K = K(1)
1049 IF H = 9 THEN J = (1 + F) * J(1): K = (1 + F) * K(1)
1130 FOR I = 1 TO N
1140 REM D = (J / (J - K)) * EXP(-K * X(I)) - (K / (J - K)) * EXP(-J * X(I)) - Y(I)
1141 D = Y(I) - (K * EXP(-J * X(I)) - J * EXP(-K * X(I))) / (K - J)
1150 S = S + D * D
1160 NEXT I
1170 PRINT "H"; H; "J"; J; "K"; K; "S"; S
1175 PRINT #I, "H"; H; "J"; J; "K"; K; "S"; S
1180 NEXT H

1200 PRINT "DEMING;"
1205 PRINT #I, "DEMING;"
1210 INPUT "J, K"; J, K
1220 FORM = 1 TO 6
1230 SKK = 0: SJJ = 0: SJK = 0: SKO = 0: SJO = 0: S = 0
1240 FOR I = 1 TO N
1250 FO = Y(I) - (K / (K - J)) * EXP(-J * X(I)) + (J / (K - J)) * EXP(-K * X(I))
1260 FJ = (K / (K - J)) * X(I) * EXP(-J * X(I)) - (K / ((K - J) * (K - J))) * (EXP(-J * X(I)) - EXP(-K * X(I)))
1270 FK = -(J / ((K - J) * (K - J))) * (EXP(-K * X(I)) - EXP(-J * X(I))) - (J / (K - J)) * X(I) * EXP(-K * X(I))
1280 SKK = SKK + FK * FK
1290 SJJ = SJJ + FJ * FJ
1300 SJK = SJK + FJ * FK
1310 SKO = SKO + FK * FO
1320 SJO = SJO + FJ * FO
1330 S = S + FO * FO
1340 NEXT I
1350 Q = SKK * SJJ - SJK * SJK
1360 KK = (SKO * SJJ - SJO * SJK) / Q
1370 JJ = (SJO * SKK - SKO * SJK) / Q
1380 T = S - SKO * KK - SJO * JJ
1390 DK = SQR(ABS((SJJ * T) / ((N - 2) * Q)))
1400 DJ = SQR(ABS((SKK * T) / ((N - 2) * Q)))
1410 PRINT "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1415 PRINT #1, "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1420 K = K - KK: J = J - JJ
1430 NEXT M

1500 REM LISTING J0, K0 FOR FOUR DIFFERENT STARTS (E)
1510 DATA .05, 1, 1, .05, .2, 4, 4, .2

2000 DATA 2, 0.908, 4, 0.776, 6, 0.644, 8, 0.530, 10, 0.424
2010 DATA 12, 0.341, 14, 0.271, 16, 0.214, 18, 0.166, 20, 0.139
Appendix

II. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM REAL DATA

2. CO-PRODUCT FORMATION IN TWO STEP REACTIONS

10 REM PROGRAM IN BASIC FOR OPTIMIZING THE TWO FIRST-ORDER RATE COEFFICIENTS
11 REM OF A TWO-STEP, CONSECUTIVE REACTION FROM DATA OF CO-PRODUCT CONCENTRATION
12 REM TIME VERSUS TIME BY THE NELDER-MEAD DOWNHILL SIMPLEX MINIMIZATION
13 REM ROUTINE AS ADOPTED IN THIS THESIS, ILLUSTRATED WITH KAUFER'S CLASSIC
14 REM EXPERIMENT (1906) [9] ON THE HYDROLYSIS OF 2,7-DICYANONAPHTHALENE
15 REM AMMONIA IN BOTH THE STEPS; CONFIRMED BY THE DEMING ROUTINE
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM J0(10): DIM K0(10): DIM X(100): DIM Y(100): DIM Z(100): DIM R(100): DIM V(510)
50 FOR E = 1 TO 4
60 READ J0(E), K0(E)
70 NEXT E
80 INPUT "N"; N
90 FOR I = 1 TO N
100 READ X(I), Y(I)
110 NEXT I
120 FOR E = 1 TO 4
130 J(1) = J0(E); K(1) = K0(E)
140 REM PRINT "J0"; J0(E); "K0"; K0(E)
150 REM PRINT #1, "J0"; J0(E); "K0"; K0(E)
160 FOR G = 1 TO 3
180 FOR REIT = 1 TO 5
190 FOR P = 1 TO 3
200 S(P) = 0
210 FOR I = 1 TO N
250 R(I) = Y(I) - ((2 * K(P) - J(P)) * EXP(-J(P) * X(I)) - J(P) * EXP(-K(P) * X(I))) / (K(P) - J(P))
260 S(P) = S(P) + R(I) * R(I)
270 NEXT I
280 NEXT P
290 FOR ITER = 1 TO 100
300 FOR P = 1 TO 2
310 FOR Q = P + 1 TO 3
320 IF S(Q) >= S(P) THEN GOTO 480
330 J = J(P)
340 J(P) = J(Q)
350 J(Q) = J
360 K = K(P)
370 K(P) = K(Q)
380 K(Q) = K
390 S = S(P)
400 S(P) = S(Q)
410 S(Q) = S
420 NEXT Q
430 NEXT P
450 J(4) = J(1) + J(2) - J(3): K(4) = K(1) + K(2) - K(3)
460 S(4) = 0
470 FOR I = 1 TO N
480 R(I) = Y(I) - ((2 * K(4) - J(4)) * EXP(-J(4) * X(I)) - J(4) * EXP(-K(4) * X(I))) / (K(4) - J(4))
490 S(4) = S(4) + R(I) * R(I)
500 NEXT I
510 IF S(4) >= S(2) THEN GOTO 680
520 IF S(4) < S(1) THEN GOTO 590
540 J(5) = 1.5 * J(1) + 1.5 * J(2) - 2 * J(3): K(5) = 1.5 * K(1) + 1.5 * K(2) - 2 * K(3)
550 S(5) = 0
560 FOR I = 1 TO N
570 R(I) = Y(I) - ((2 * K(5) - J(5)) * EXP(-J(5) * X(I)) - J(5) * EXP(-K(5) * X(I))) / (K(5) - J(5))
580 S(5) = S(5) + R(I) * R(I)
590 NEXT I
600 IF S(5) >= S(1) THEN GOTO 670
610 IF S(5) > S(1) THEN GOTO 660
630 J(6) = .75 * J(1) + .75 * J(2) - .5 * J(3): K(6) = .75 * K(1) + .75 * K(2) - .5 * K(3)
640 S(6) = 0
650 FOR I = 1 TO N
660 R(I) = Y(I) - ((2 * K(6) - J(6)) * EXP(-J(6) * X(I)) - J(6) * EXP(-K(6) * X(I))) / (K(6) - J(6))
670 NEXT I
680 FOR Q = P + 1 TO 3
690 IF S(Q) >= S(P) THEN GOTO 480
700 J = J(P)
710 J(P) = J(Q)
720 J(Q) = J
730 K = K(P)
740 K(P) = K(Q)
750 K(Q) = K
760 S = S(P)
770 S(P) = S(Q)
780 S(Q) = S
790 NEXT Q
800 NEXT P
810 J(4) = J(1) + J(2) - J(3): K(4) = K(1) + K(2) - K(3)
820 S(4) = 0
830 FOR I = 1 TO N
840 R(I) = Y(I) - ((2 * K(4) - J(4)) * EXP(-J(4) * X(I)) - J(4) * EXP(-K(4) * X(I))) / (K(4) - J(4))
850 S(4) = S(4) + R(I) * R(I)
860 NEXT I
870 IF S(4) >= S(2) THEN GOTO 680
880 IF S(4) < S(1) THEN GOTO 590
900 J(5) = 1.5 * J(1) + 1.5 * J(2) - 2 * J(3): K(5) = 1.5 * K(1) + 1.5 * K(2) - 2 * K(3)
910 S(5) = 0
920 FOR I = 1 TO N
930 R(I) = Y(I) - ((2 * K(5) - J(5)) * EXP(-J(5) * X(I)) - J(5) * EXP(-K(5) * X(I))) / (K(5) - J(5))
940 S(5) = S(5) + R(I) * R(I)
950 NEXT I
960 IF S(5) >= S(1) THEN GOTO 670
970 IF S(5) > S(1) THEN GOTO 660
990 J(6) = .75 * J(1) + .75 * J(2) - .5 * J(3): K(6) = .75 * K(1) + .75 * K(2) - .5 * K(3)
1000 S(6) = 0
1010 FOR I = 1 TO N
1020 R(I) = Y(I) - ((2 * K(6) - J(6)) * EXP(-J(6) * X(I)) - J(6) * EXP(-K(6) * X(I))) / (K(6) - J(6))
730 S(6) = S(6) + R(I) * R(I)
740 NEXT I
760 J(7) = .25 * J(1) + .25 * J(2) + .5 * J(3): K(7) = .25 * K(1) + .25 * K(2) + .5 * K(3)
770 S(7) = 0
780 FOR I = 1 TO N
790 R(I) = Y(I) - ((2 * K(7) - J(7)) * EXP(-J(7) * X(I)) - J(7) * EXP(-K(7) * X(I))) / (K(7) - J(7))
800 S(7) = S(7) + R(I) * R(I)
810 NEXT I
830 J(2) = .5 * (J(1) + J(2)): K(2) = .5 * (K(1) + K(2))
840 J(3) = .5 * (J(1) + J(3)): K(3) = .5 * (K(1) + K(3))
870 GOTO 890
880 NEXT ITER
890 NEXT REIT
900 NEXT G
910 PRINT "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
915 PRINT #I, "E"; E; "J"; J(1); "K"; K(1); "S"; S(1)
920 NEXT E
1000 F = .0001
1005 REM INPUT "F"; F
1010 PRINT "MINIMUM CHECK:"; " F"; F
1015 PRINT #I, "MINIMUM CHECK:"; " F"; F
1020 INPUT "J, K"; J(I), K(I)
1030 FOR H = 1 TO 9
1040 S = 0
1041 IF H = 1 THEN J = (1 - F) * J(1): K = (1 - F) * K(1)
1042 IF H = 2 THEN J = (1 - F) * J(1): K = K(1)
1043 IF H = 3 THEN J = (1 - F) * J(1): K = (1 + F) * K(1)
1044 IF H = 4 THEN J = J(1): K = (1 - F) * K(1)
1045 IF H = 5 THEN J = J(1): K = K(1)
1046 IF H = 6 THEN J = J(1): K = (1 + F) * K(1)
1047 IF H = 7 THEN J = (1 + F) * J(1): K = (1 - F) * K(1)
1048 IF H = 8 THEN J = (1 + F) * J(1): K = K(1)
1049 IF H = 9 THEN J = (1 + F) * J(1): K = (1 + F) * K(1)
1130 FOR I = 1 TO N
1140 D = Y(I) - ((2 * K - J) * EXP(-J * X(I)) - J * EXP(-K * X(I))) / (K - J)
1150 S = S + D * D
1160 NEXT I
1170 PRINT "H"; H; "J"; J; "K"; K; "S"; S
1175 PRINT #I, "H"; H; "J"; J; "K"; K; "S"; S
1180 NEXT H
1200 PRINT "DEMING:"
1205 PRINT #1, "DEMING:"
1210 INPUT "J, K"; J, K
1220 FOR M = 1 TO 10
1230 SKK = 0: SJJ = 0: SJK = 0: SKO = 0: SJO = 0: S = 0
1240 FOR I = 1 TO N
1250 FO = ((J - 2 * K) * EXP(-J * X(I)) + J * EXP(-K * X(I))) / (J - K) - Y(I)
1260 FJ = K * (EXP(-J * X(I)) - EXP(-K * X(I))) / ((J - K) * (J - K)) - (J - 2 * K) * X(I) * EXP(-J * X(I)) / (J - K)
1270 FK = J * (EXP(-K * X(I)) - EXP(-J * X(I))) / ((J - K) * (J - K)) - J * X(I) * EXP(-K * X(I)) / (J - K)
1280 SKK = SKK + FK * FK
1290 SJJ = SJJ + FJ * FJ
1300 SJK = SJK + FJ * FK
1310 SKO = SKO + FK * FO
1320 SJO = SJO + FJ * FO
1330 S = S + FO * FO
1340 NEXT I
1350 Q = SKK * SJJ - SJK * SJK
1360 KK = (SKO * SJJ - SJO * SJK) / Q
1370 JJ = (SJO * SKK - SKO * SJK) / Q
1380 T = S - SKO * KK - SJO * JJ
1390 DK = SQR(ABS((SJJ * T) / ((N - 2) * Q)))
1400 DJ = SQR(ABS((SKK * T) / ((N - 2) * Q)))
1410 PRINT "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1415 PRINT #1, "M"; M; "J"; J; "+/-"; DJ; "K"; K; "+/-"; DK; "S"; S
1420 K = K - KK: J = J - JJ
1430 NEXT M

1500 REM LISTING J0, K0 FOR FOUR DIFFERENT STARTS (E)
1510 DATA .1, 2, 2, .1, .4, 8, 8, .4
2000 DATA 0.5, 1.729, 1, 1.373, 1.5, 1.136, 2, 0.965, 3, 0.758, 4, 0.616, 5, 0.525, 6, 0.455
Appendix

II. THE PROGRAM LISTINGS FOR OPTIMIZATION FROM REAL DATA

3. SYSTEM PROPERTY DATA IN TWO-STEP REACTIONS

10 REM PROGRAM IN QBASIC FOR THE OPTIMIZATION BY THE NELDER-MEAD DOWNHILL
11 REM SIMPLEX ROUTINE OF THE FOUR PARAMETERS J, K, L AND M OF THE RATE
12 REM EQUATION \( Y = L \times \exp(-J \times T) + M \times \exp(-K \times T) \) OF A TWO-STEP,
13 REM CONSECUTIVE, FIRST-ORDER REACTION FROM (N) EXPERIMENTAL DATA OF A
14 REM SYSTEM PROPERTY Y (SUCH AS ABSORBANCE) VERSUS TIME (X). THE PROGRAM
15 REM STARTS SUCCESSIVELY FROM TEN LATIN HYPERCUBE SETS OF INITIAL INPUTS
16 REM OF THE PARAMETERS TO LOCATER AS MANY MINIMA AS POSSIBLE. IT ALSO
17 REM VERIFIES WHETHER A GIVEN OUTPUT CORRESPONDS TO A MINIMUM OF THE SUM
18 REM OF SQUARES OF DEVIATIONS. THE PROGRAM IS ILLUSTRATED HERE WITH SINDHU-
19 REM JAYARAJAN'S [61] ABSORBANCE DATA ON THE TWO-STEP, CONSECUTIVE FIRST-
20 REM ORDER SUBSTITUTION REACTIONS IN A CHARGE-TRANSFER COMPLEX AND WITH
21 REM LOWRY AND TRAILL'S [107] POLARIMETRIC DATA ON THE MUTAROTATION OF
22 REM ALUMINIUM BENZOYLCAMPHOR.
30 REM CLS
35 OPEN "OUT.DAT" FOR OUTPUT AS #1
40 DIM J0(20): DIM K0(20): DIM L0(20): DIM M0(20): DIM X(100): DIM Y(100):
DIM Z(100): DIM V(100): DIM R(100)
50 FOR E = 1 TO 10
60 READ J0(E), K0(E), L0(E), M0(E)
70 NEXT E
85 N = 30: ZINF = 1244.5
90 FOR I = 1 TO N
100 READ X(I), Z(I)
105 Y(I) = ZINF - Z(I)
140 NEXT I
160 FOR E = 1 TO 10
170 J(1) = J0(E): K(1) = K0(E): L(1) = .6 * ZINF * L0(E): M(1) = .4 * ZINF * M0(E)
180 REM PRINT "J0"; J0(E); "K0"; K0(E); "L0"; L0(E); "M0"; M0(E)
185 REM PRINT #1, "J0"; J0(E); "K0"; K0(E); "L0"; L0(E); "M0"; M0(E)
190 FOR G = 1 TO 10
210 FOR REIT = 1 TO 10
220 FOR P = 1 TO 5
230 IF S(P) >= S(P) THEN GOTO 480
270 NEXT I
280 NEXT P
290 FOR ITER = 1 TO 100
300 FOR P = 1 TO 4
310 FOR Q = P + 1 TO 5
320 IF S(Q) >= S(P) THEN GOTO 480
330 J = J(P)
340 J(P) = J(Q)
350 J(Q) = J
360 K = K(P)
370 K(P) = K(Q)
380 K(Q) = K
390 L = L(P)
400 L(P) = L(Q)
410 L(Q) = L
420 M = M(P)
430 M(P) = M(Q)
440 M(Q) = M
450 S = S(P)
460 S(P) = S(Q)
470 S(Q) = S
480 NEXT Q
490 NEXT P
500 J(6) = (J(1) + J(2) + J(3) + J(4)) / 2 - J(5): K(6) = (K(1) + K(2) + K(3) + K(4)) / 2 -
K(5): L(6) = (L(1) + L(2) + L(3) + L(4)) / 2 - L(5): M(6) = (M(1) + M(2) + M(3) +
M(4)) / 2 - M(5)
510 S(6) = 0
520 FOR I = 1 TO N
530 R(I) = L(6) * EXP(-J(6) * X(I)) + M(6) * EXP(-K(6) * X(I)) - Y(I)
540 S(6) = S(6) + R(I) * R(I)
550 NEXT I
560 IF S(6) >= S(2) THEN GOTO 680
570 IF S(6) < S(1) THEN GOTO 590
580 J(5) = J(6); K(5) = K(6); L(5) = L(6); M(5) = M(6); S(5) = S(6); GOTO 880
590 J(7) = 3 * (J(1) + J(2) + J(3) + J(4)) / 4 - 2 * J(5); K(7) = 3 * (K(1) + K(2) + K(3) + K(4)) / 4 - 2 * K(5); L(7) = 3 * (L(1) + L(2) + L(3) + L(4)) / 4 - 2 * L(5); M(7) = 3 * (M(1) + M(2) + M(3) + M(4)) / 4 - 2 * M(5)
600 S(7) = 0
610 FOR I = 1 TO N
620 R(I) = L(7) * EXP(-J(7) * X(I)) + M(7) * EXP(-K(7) * X(I)) - Y(I)
630 S(7) = S(7) + R(I) * R(I)
640 NEXT I
650 IF S(7) > S(1) THEN GOTO 670
660 J(5) = J(7); K(5) = K(7); L(5) = L(7); M(5) = M(7); S(5) = S(7); GOTO 880
670 J(5) = J(6); K(5) = K(6); L(5) = L(6); M(5) = M(6); S(5) = S(6); GOTO 880
680 IF S(6) >= S(5) THEN GOTO 760
690 J(8) = 3 * (J(1) + J(2) + J(3) + J(4)) / 8 - .5 * J(5); K(8) = 3 * (K(1) + K(2) + K(3) + K(4)) / 8 - .5 * K(5); L(8) = 3 * (L(1) + L(2) + L(3) + L(4)) / 8 - .5 * L(5); M(8) = 3 * (M(1) + M(2) + M(3) + M(4)) / 8 - .5 * M(5)
700 S(8) = 0
710 FOR I = 1 TO N
720 R(I) = L(8) * EXP(-J(8) * X(I)) + M(8) * EXP(-K(8) * X(I)) - Y(I)
730 S(8) = S(8) + R(I) * R(I)
740 NEXT I
750 IF S(8) < S(5) THEN GOTO 880
760 J(9) = (J(1) + J(2) + J(3) + J(4)) / 8 + .5 * J(5); K(9) = (K(1) + K(2) + K(3) + K(4)) / 8 + .5 * K(5); L(9) = (L(1) + L(2) + L(3) + L(4)) / 8 + .5 * L(5); M(9) = (M(1) + M(2) + M(3) + M(4)) / 8 + .5 * M(5)
770 S(9) = 0
780 FOR I = 1 TO N
790 R(I) = L(9) * EXP(-J(9) * X(I)) + M(9) * EXP(-K(9) * X(I)) - Y(I)
800 S(9) = S(9) + R(I) * R(I)
810 NEXT I
820 IF S(9) < S(5) THEN GOTO 880
830 J(2) = .5 * (J(1) + J(2)); K(2) = .5 * (K(1) + K(2)); L(2) = .5 * (L(1) + L(2)); M(2) = .5 * (M(1) + M(2))
840 J(3) = .5 * (J(1) + J(3)); K(3) = .5 * (K(1) + K(3)); L(3) = .5 * (L(1) + L(3)); M(3) = .5 * (M(1) + M(3))
850 J(4) = .5 * (J(1) + J(4)); K(4) = .5 * (K(1) + K(4)); L(4) = .5 * (L(1) + L(4)); M(4) = .5 * (M(1) + M(4))
860 J(5) = .5 * (J(1) + J(5)); K(5) = .5 * (K(1) + K(5)); L(5) = .5 * (L(1) + L(5)); M(5) = .5 * (M(1) + M(5))
870 GOTO 890
880 NEXT ITER
890 NEXT RElT
900 NEXT G
910 PRINT "E"; E; "J"; J(1); "K"; K(1); "L"; L(1); "M"; M(1); "S"; S(1)
915 PRINT #1, "E"; E; "J"; J(1); "K"; K(1); "L"; L(1); "M"; M(1); "S"; S(1)
920 NEXT E

1000 F = .00001
1005 REM INPUT "F"; F
1010 PRINT #1, "MINIMUM CHECK"; "F"; F
1020 INPUT "J, K, L, M"; J(1), K(1), L(1), M(1)
1030 FOR H = I TO 81
1040 S = 0
1084 IF H = 44 THEN J = J(1): \[ K = (1 + F) \times K(1): \] \[ L = L(1): \] \[ M = M(1) \]
1085 IF H = 45 THEN J = (1 + F) \times J(1): \[ K = (1 + F) \times K(1): \] \[ L = L(1): \] \[ M = M(1) \]
1086 IF H = 46 THEN J = (1 - F) \times J(1): \[ K = (1 - F) \times K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1087 IF H = 47 THEN J = J(1): \[ K = (1 - F) \times K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1088 IF H = 48 THEN J = (1 + F) \times J(1): \[ K = (1 - F) \times K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1089 IF H = 49 THEN J = (1 - F) \times J(1): \[ K = K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1090 IF H = 50 THEN J = J(1): \[ K = K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1091 IF H = 51 THEN J = (1 + F) \times J(1): \[ K = K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1092 IF H = 52 THEN J = (1 - F) \times J(1): \[ K = (1 + F) \times K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1093 IF H = 53 THEN J = J(1): \[ K = (1 + F) \times K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1094 IF H = 54 THEN J = (1 + F) \times J(1): \[ K = (1 + F) \times K(1): \] \[ L = (1 + F) \times L(1): \] \[ M = M(1) \]
1095 IF H = 55 THEN J = (1 - F) \times J(1): \[ K = (1 - F) \times K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1096 IF H = 56 THEN J = J(1): \[ K = (1 - F) \times K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1097 IF H = 57 THEN J = (1 + F) \times J(1): \[ K = (1 - F) \times K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1098 IF H = 58 THEN J = (1 - F) \times J(1): \[ K = K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1099 IF H = 59 THEN J = J(1): \[ K = K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1100 IF H = 60 THEN J = (1 + F) \times J(1): \[ K = K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1101 IF H = 61 THEN J = (1 - F) \times J(1): \[ K = (1 + F) \times K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1102 IF H = 62 THEN J = J(1): \[ K = (1 + F) \times K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1103 IF H = 63 THEN J = (1 + F) \times J(1): \[ K = (1 + F) \times K(1): \] \[ L = (1 - F) \times L(1): \] \[ M = (1 + F) \times M(1) \]
1104 IF H = 64 THEN J = (1 - F) \times J(1): \[ K = (1 - F) \times K(1): \] \[ L = L(1): \] \[ M = (1 + F) \times M(1) \]
1105 IF H = 65 THEN J = J(1): \[ K = (1 - F) \times K(1): \] \[ L = L(1): \] \[ M = (1 + F) \times M(1) \]
1106 IF H = 66 THEN J = (1 + F) \times J(1): \[ K = (1 - F) \times K(1): \] \[ L = L(1): \] \[ M = (1 + F) \times M(1) \]
1107 IF H = 67 THEN J = (1 - F) \times J(1): \[ K = K(1): \] \[ L = L(1): \] \[ M = (1 + F) \times M(1) \]
1130 FOR I = 1 TO N
1140 D = L * EXP(-J * X(I)) + M * EXP(-K * X(I)) - Y(I)
1150 S = S + D * D
1160 NEXT I
1170 PRINT #1, "H"; H; "J"; J; "K"; K; "L"; L; "M"; M; "S"; S
1180 NEXT H
1190 CLOSE #1

1500 DATA .75, .45, .45, .55, .05, .35, .95, .05, .85, .75, .35, .65
1501 DATA .25, .95, .55, .45, .15, .65, .65, .35, .35, .05, .75, .25
1502 DATA .65, .85, .05, .95, .45, .15, .15, .85, .95, .55, .85, .15
1503 DATA .55, .25, .25, .75

2000 REM SINDHUJAYARAJAN'S DATA OF RUN #7 OF THE REACTION OF 0.3251 M P-TOLUIDINE
2001 REM WITH 0.001M CHLORANIL IN THF AT 25.0 DEG MONITORED AT 555 NM IN 1 CM CELL
2002 REM ZINF = 0.924
2003 REM DATA 30, .361, 60, .406, 90, .434, 120, .455, 150, .475, 180, .493
2004 REM DATA 210, .509, 240, .525, 270, .540, 300, .554, 330, .568, 360, .581
2005 REM DATA 390, .593, 420, .604, 450, .615, 480, .625, 510, .636, 540, .646
2006 REM DATA 570, .655, 600, .664, 630, .673, 660, .682, 690, .689, 720, .697
2007 REM DATA 750, .705, 780, .711, 810, .718, 840, .725, 870, .730, 900, .736

2100 REM LOWRY & TRAILL'S DATA ON THE MUTAROTATION OF ALUMINIUM BENZOYL CAMPHOR IN
2101 REM CABON TETRACHLORIDE AT 20 DEG. C. (1931): ZINF = 1244.5
2102 DATA 0.9, 962, 1.1, 1031, 1.7, 1100, 2.1, 1159, 2.3, 1200, 2.8, 1234
2103 DATA 3.1, 1259.5, 3.5, 1287, 4, 1301, 4.5, 1319, 4.9, 1327, 5.3, 1333.5
2104 DATA 5.8, 1338, 6.2, 1340, 6.7, 1340, 7.3, 1338, 8.0, 1335.5
2105 DATA 8.5, 1332.5, 9.2, 1326, 10.1, 1322.5, 11.4, 1312, 13.2, 1300
2106 DATA 14.8, 1291, 16.7, 1281.5, 18.4, 1275.5, 20, 1271.5, 23.7, 1261
2107 DATA 29, 1253.5, 37, 1247.5, 51, 1245
### TWO-STEP : PRODUCT FORMATION DATA

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**SR - 1.2**
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# TWO-STEP: PRODUCT FORMATION DATA

\( K = 2, \quad KS = 0.1, \quad KF = 0.2, \quad DT = 0.94 \)

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SR - 1. 8
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SR - 1.10
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SR - 1 . 11
**TWO-STEP : PRODUCT FORMATION DATA**

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SR - I . 12
## TWO-STEP: PRODUCT FORMATION DATA

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SR – I . 13
## TWO-STEP PRODUCT FORMATION DATA

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SR - II .4
# TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR - II.7
# TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR - II.8
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SR-II 9
**TWO-STEP: CO-PRODUCT CONCENTRATION DATA**

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**SR - II. 10**
# TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR - II 11
**TWO-STEP: CO-PRODUCT CONCENTRATION DATA**

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SR - II. 13
### Two-Step: Co-Product Concentration Data

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SR - II. 14
### TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR - II .15
## TWO - STEP : CO-PRODUCT CONCENTRATION DATA

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**SR – II .16**
## TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR- II .17
## TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR - II. 18
### TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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## TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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\end{align*} \]

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SR - II . 20
## Two-Step: Co-Product Concentration Data

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SR - II. 21
## TWO-STEP: CO-PRODUCT CONCENTRATION DATA

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SR - II . 22
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SR - II . 24
## INTERMEDIATE CONCENTRATION DATA

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**SR - III. 5**

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**SR - III. 6**
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### SR - III . 9

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**SR - III . 12**
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**SR** - III. 13

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**SR** - III. 14
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**SR – III . 16**
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SR – III . 19
### THREE-STEP: PRODUCT FORMATION DATA

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SR. IV - 1
THREE-STEP: PRODUCT FORMATION DATA

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SR . IV - 2
THREE-STEP: PRODUCT FORMATION DATA

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SR . IV - 9
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SR . IV - 13
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SR . IV - 18
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SR . IV - 21
### THREE-STEP: PRODUCT FORMATION DATA

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SR . IV - 22
THREE-STEP: PRODUCT FORMATION DATA

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SR . IV - 23
### TWO-STEP : SYSTEM PROPERTY DATA

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**SR - V.1**
### TWO-STEP: SYSTEM PROPERTY DATA

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**SR - V.2**
## TWO-STEP: SYSTEM PROPERTY DATA

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**SR-V. 3**
## TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 4
### TWO-STEP: SYSTEM PROPERTY DATA

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**SR - V. 5**
## TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 6
## TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 7
## TWO-STEP: SYSTEM PROPERTY DATA

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\( \text{SR-V.9} \)
## TWO-STEP : SYSTEM PROPERTY DATA

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### TWO-STEP: SYSTEM PROPERTY DATA

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SR-V. 11
## TWO-STEP : SYSTEM PROPERTY DATA

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TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 13
## TWO-STEP: SYSTEM PROPERTY DATA

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## TWO-STEP: SYSTEM PROPERTY DATA

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SR – V. 15
## Two-Step: System Property Data

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# Two-Step: System Property Data

For the given system, the property data is presented in two steps: N = 16 (70% reaction) and N = 24 (80% reaction). The table below contains the values for various sets and simulations. The columns represent different properties or variables, and the rows correspond to different sets and simulations.

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**SR - V. 17**
# TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 18
## TWO-STEP: SYSTEM PROPERTY DATA

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SR-V. 19
## TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 20
## TWO-STEP SYSTEM PROPERTY DATA

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**SR - V. 21**
## TWO-STEP: SYSTEM PROPERTY DATA

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**SR-V. 22**
## TWO-STEP : SYSTEM PROPERTY DATA

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**SR - V. 23**
## TWO - STEP : SYSTEM PROPERTY DATA

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**SR - V. 24**
### TWO - STEP : SYSTEM PROPERTY DATA

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SR - V. 25
### TWO-STEP: SYSTEM PROPERTY DATA

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**SR - V. 26**
## TWO-STEP: SYSTEM PROPERTY DATA

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**SR - V. 28**
### TWO-STEP: SYSTEM PROPERTY DATA

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**SR-V. 29**
## TWO-STEP SYSTEM PROPERTY DATA

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SR – V. 30
## TWO-STEP: SYSTEM PROPERTY DATA

\( k = 7, \; k_s = 0.1, \; k_f = 0.7, \; c_s = 1.2, \; c_f = -0.2, \; d_t = 0.75 \)

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SR-V. 31
## TWO-STEP : SYSTEM PROPERTY DATA

\[ K = 7, \quad KS = 0.1, \quad KF = 0.7, \quad CS = 0.95, \quad CF = 0.05, \quad DT = 0.65 \]

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SR - V. 32
## TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 33
## TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 34
## TWO-STEP : SYSTEM PROPERTY DATA

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### TWO-STEP : SYSTEM PROPERTY DATA

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**SR - V.36**
## TWO-STEP: SYSTEM PROPERTY DATA

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SR-V. 37
## TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 38
### TWO-STEP: SYSTEM PROPERTY DATA

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**TWO-STEP : SYSTEM PROPERTY DATA**

\[ \kappa = 10. \]

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# TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 41
### TWO-STEP: SYSTEM PROPERTY DATA

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\[ SR - V. \ 42 \]
# TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 43
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SR - V. 45
## TWO-STEP: SYSTEM PROPERTY DATA

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### TWO-STEP SYSTEM PROPERTY DATA

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**SR - V. 47**
## TWO-STEP SYSTEM PROPERTY DATA

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SR - V. 48
## TWO - STEP : SYSTEM PROPERTY DATA

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SR - V. 49
## TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 51
## TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 53
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# Two-Step: System Property Data

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**SR - V. 56**
# TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 57
**TWO-STEP : SYSTEM PROPERTY DATA**

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## TWO-STEP: SYSTEM PROPERTY DATA

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SR-V. 59
# TWO-STEP: SYSTEM PROPERTY DATA

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SR - V. 60
# TWO-STEP : SYSTEM PROPERTY DATA

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SR-V. 61
### TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 62
### TWO-STEP: SYSTEM PROPERTY DATA

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SR - V . 65
## Two-Step: System Property Data

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*SR - V.66*
## TWO-STEP : SYSTEM PROPERTY DATA

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SR - V. 67
### TWO-STEP: SYSTEM PROPERTY DATA

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SR – V. 68 & 69
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SR - V. 70 & 71
### TWO-STEP : SYSTEM PROPERTY DATA

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