Thermal Decomposition of Viscose Rayon in the Presence of Inorganic Additives. A Kinetic Study

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Synopsis

Viscose rayon, like many other cellulosic materials, has a thermal decomposition reaction. The rate of change of weight loss of this material is very high at a narrow range of temperatures. When viscose rayon is impregnated with inorganic additives, there is a shift in the temperature of maximum rate of weight loss (T_{max}) towards the lower side of the temperature. This effect, due to the addition of ammonium chloride, calcium chloride, and a mixture of calcium chloride and ammonium chloride, was studied in the temperature range 200–400°C through thermogravimetry and the changes observed in the values of activation energy, order of reaction, and char yield are presented in this paper.

INTRODUCTION

Many researchers[1-3] carried out the thermal decomposition studies on the commonest forms of cellulosic materials. Addition of certain classes of inorganic additives and their effect on increasing the char yield also had been reported.[1,4-7] Many authors[1,5-7] have published results on the effect of different additives on the thermal decomposition of viscose rayon.

The most commonly accepted mechanism for thermal degradation of cellulose was proposed by Tang and Bacon[3] and is given below:

Stage I: Physical desorption of water (25–150°C)

Stage II: Dehydration from the cellulose unit (150–240°C)

Stage III: Thermal cleavage of the glycosidic linkage and scission of other C—O bonds via a free radical reaction (240–400°C).

Stage IV: Aromatization (400°C and above)

It has been reported[8] that it is preferable to have the dehydration reaction completed to the extent possible at lower temperatures so that the cellulose ring is stabilized against its decomposition into combustible compounds. Consequently, a product of higher char yield is obtained. This advancement of dehydration reaction can be achieved by impregnation with inorganic additives like chlorides of alkaline earth metals.[9] It had also been observed that addi-

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Journal of Applied Polymer Science, Vol. 41, 2783–2811 (1990)
 CCC 0021-8995/90/11-122783-29$04.00

tion of a depolymerization inhibitor like ammonium chloride enhanced the char yield.[9]

We conducted the above studies with a viscose rayon fabric obtained from Indian commercial sources and present the results in this paper.

EXPERIMENTAL

The material used for the studies was viscose rayon fabric of Indian origin. The rayon fabric was washed with warm water to remove the sizing materials applied during weaving. The washed fabric was air-dried. This is designated as RN.

Impregnation with additives calcium chloride, ammonium chloride, and a mixture of calcium chloride and ammonium chloride was carried out by immersing the fabric in 0.5 *M* solutions of the corresponding additives for 15 min followed by air drying. The rayon fabrics impregnated with calcium chloride, ammonium chloride, and a mixture of calcium chloride and ammonium chloride are designated as RC, RA, and RM, respectively.

Thermograms of RN, RC, RA, and RM were obtained using a thermal analyzer (DuPont model 990). The pyrolysis was carried out in an inert atmosphere of ultra high pure nitrogen at a flow rate of 60 mL/min. The heating rate used was 5°C/min, and the pyrolysis was conducted up to 400°C.

RESULTS

The thermograms (TG) and derivative thermograms (DTG) obtained are shown in Figures 1–4. The weight and rate of weight loss vs. temperature are given in the figures. The shift in T_{max} and change in char yield after decomposition up to 400°C are listed in Table I.

Evaluation of Kinetic Parameters

Based on Coats and Redfern,[10] for calculation of E and n, the following equations can be used:

$$\log_{10}\left[\frac{1-(1-\alpha)^n}{T^2(1-n)}\right] = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2\cdot 3RT} \qquad (1)$$

for all values of n, except $n = 1$. When $n = 1$, we get

$$\log_{10}\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right] = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2\cdot 3RT} \qquad (2)$$

where α = fraction of rayon decomposed at any time t, n = order of reaction, A = frequency factor (min^{-1}), R = gas constant, T = absolute temperature (K), E = activation energy (kcal/mol), and a = linear heating rate, dT/dt (deg/min).

The FORTRAN program was generated for solving eqs. (1) and (2) and values of E and n were obtained. The values of E and correlation coefficient obtained

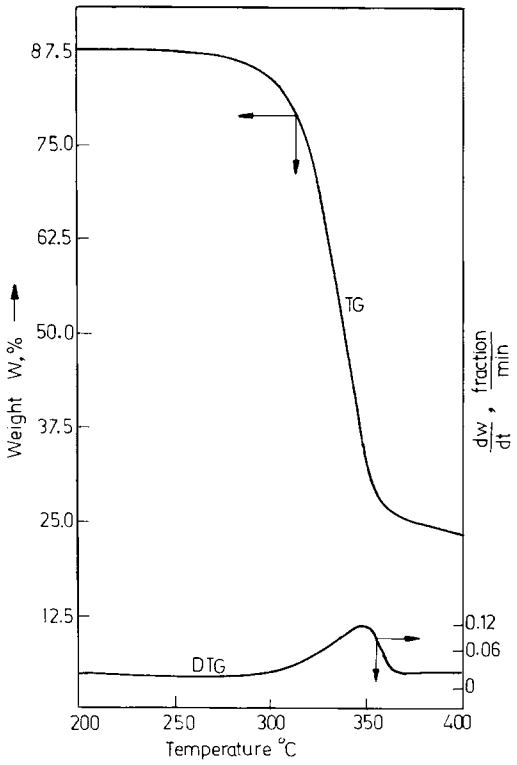

Fig. 1. Thermogram (TG) and derivative thermogram (DTG) of viscose rayon (RN).

by solving eq. (2), solution when $n = 1$, are given in Table II. Table III gives the values E and n obtained by solving eq. (1) by an iteration method when n is not equal to 1. To enable the readers to understand the variation in values of E and the correlation coefficient obtained for each increment for n tried in the iteration, the same is presented in Tables IV and V for the two systems which needed the iteration. In Figure 5, the variation of correlation coefficient with the values of n is shown graphically.

DISCUSSION

As mentioned earlier, it can be observed from Figure 1 and Table I that the T_{max} value for RN is 350°C. This temperature was shifted to lower side when the rayon fabric was impregnated with inorganic additives. The shift in T_{max} can be noticed from DTG curves given in Figures 2, 3, and 4 and the T_{max} values listed in Table I. Although only one peak was observed for RN (Fig. 1), RC (Fig. 2), and RM (Fig. 4), an additional peak at 205°C for higher rates of weight loss was observed for RA (Fig. 3). This can be attributed to a transformation starting within the compound ammonium chloride at 185°C.[11] The same peak in the DTG for RM (Fig. 4) has merged with the shifted T_{max}. The shifting of T_{max} to a lower side indicates the advancement of the intramolecular dehydration reaction (Stage II).

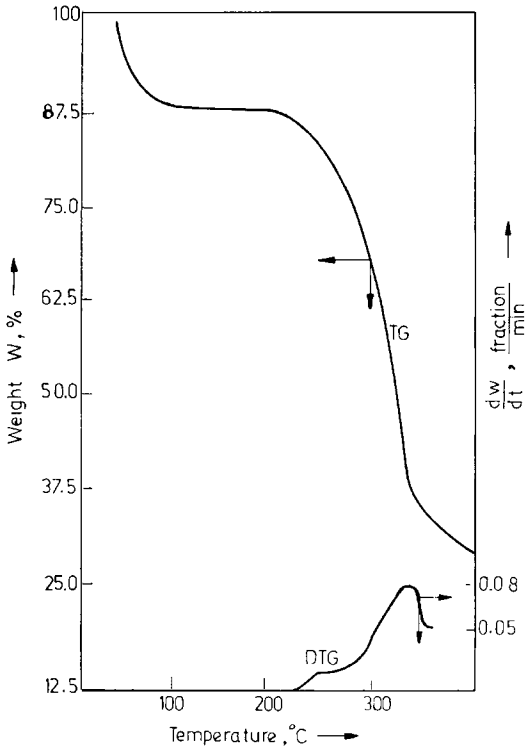

Fig. 2. Thermogram (TG) and derivative thermogram (DTG) of viscose rayon + $CaCl_2$ (RC).

From the char yield data presented in Table I, it can be seen that an increase in char yield had resulted in all the additive impregnated systems. The char includes about 1% inorganic residue in all the three additive impregnated systems. The increased char yield of 30.0% for RC compared to the value of 24.0% for RN can be attributed to the advancement of dehydration reaction. The higher char yield of 29.95% for RA compared to that of RN is the result of inhibition of the depolymerization reaction (Stage III). Ammonium chloride can decompose into ammonia and hydrogen chloride in the temperature range studied and provide an acidic atmosphere during decomposition. The inhibition lowers the formation of flammable volatiles and results in lesser loss of carbon from the char. This is in line with the study reported by Shindo et al.,[12] where increased char yields were obtained when decomposition of rayon was carried out in hydrogen chloride atmosphere. The highest char yield of 38.75% noticed for RM is believed to be the result of the combined effects of the advancement of dehydration and inhibition of depolymerization.

The pyrolysis of viscose rayon is a complex reaction and cannot be fit to a single order, as may be seen from the reaction scheme explained earlier.[3] Broido[13] in his theoretical treatment had observed that the cellulose decomposition can be roughly compared to follow the first order during a significant portion of its weight loss. However, we have visualized the thermal degradation reaction in the temperature range of 200–400°C as an overall reaction in order to avoid complexity. The changes in E and n were worked out for the overall

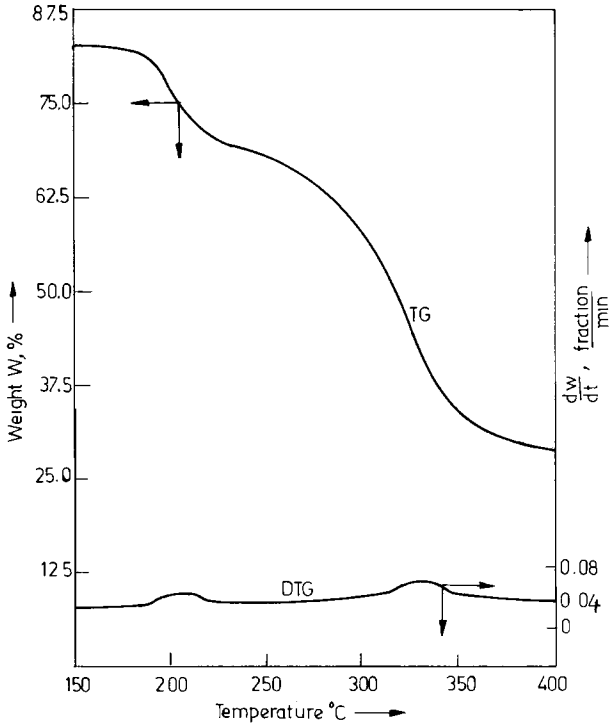

Fig. 3. Thermogram (TG) and derivative thermogram (DTG) of rayon + NH_4Cl (RA).

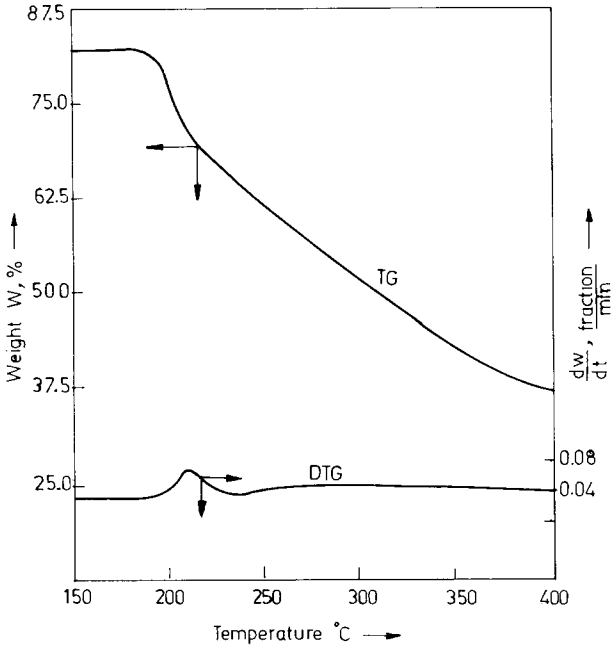

Fig. 4. Thermogram (TG) and derivative thermogram (DTG) of rayon + $CaCl_2$ + NH_4Cl (RM).

TABLE I
Changes in T_{max} and Char Yield Due to Additives

System	System designation	Temperature of maximum rate of decomposition (°C), T_{max}	Char yield at 400°C (%)
Viscose rayon	RN	350	24.00
Viscose rayon + 0.5 *M* $CaCl_2$	RC	338	30.00
Viscose rayon + 0.5 *M* NH_4Cl	RA	337	29.95
Viscose rayon + 0.5 *M* $CaCl_2$ + 0.5*M* NH_4Cl	RM	210	38.75

TABLE II
Activation Energy and Correlation Coefficient Values When n = 1, Solution as per Eq. (2)

System	System designation	Activation energy E (kcal/mol)	Correlation coefficient
Viscose rayon (neat)	RN	35.140	0.9867
Viscose rayon + 0.5 *M* $CaCl_2$	RC	19.538	0.9864
Viscose rayon + 0.5 *M* NH_4Cl	RA	12.203	0.9416
Viscose rayon + 0.5 *M* NH_4Cl + 0.5 *M* $CaCl_2$	RM	12.906	0.9017

TABLE III
Values of Activation Energy, Correlation Coefficient, and Order of Reaction When n is Not Equal to 1, Solution as per Eq. (1), by Iteration Technique

System	System designation	Activation energy E (kcal/mol)	Correlation coefficient	Order of reaction, n
Viscose rayon + 0.5 *M* NH_4Cl	RA	15.545	0.9602892	1.52
Viscose rayon + 0.5 *M* NH_4Cl + 0.5 *M* $CaCl_2$	RM	21.881	0.9637819	2.40

degradation reaction, using the Coats and Redfern method and solving the eqs. (1) and (2) as mentioned earlier. In our attempt to estimate the kinetic parameters, we first used eq. (2) and computed the values of E and correlation coefficient for all the systems and the same is shown in Table II. It can be seen that RN and RC have better correlation coefficient values of 0.98, meaning that they follow first order to a good extent with 98% points fitting into a straight line. From Table II, it can also be observed that addition of calcium chloride had resulted in lowering of activation energy to 19.538 kcal/mol against 35.140 kcal/mol for RN.

Since the systems RA and RM have correlation coefficients of 0.9416 and 0.9017, respectively, it is evident that they are deviating from first order to a

TABLE IV
Computation of n and E by Iteration for Viscose Rayon + 0.5 M NH_4Cl + 0.5 M $CaCl_2$ System (RM)

Order assumed, n	Activation energy E (kcal/mol)	Correlation coefficient
0	10.696	0.8499780
0.2	11.141	0.8610380
0.4	11.647	0.8731259
0.6	12.229	0.8861693
0.8	12.898	0.8999123
1.0	13.667	0.9138437
1.2	14.546	0.9272015
1.4	15.536	0.9391155
1.6	16.635	0.9488554
1.8	17.831	0.9560409
2.0	19.112	0.9606911
2.2	20.466	0.9631205
2.22	20.605	0.9632583
2.24	20.745	0.9633789
2.26	20.885	0.9634828
2.28	21.025	0.9635704
2.30	21.167	0.9636423
2.32	21.308	0.9636989
2.34	21.451	0.9637407
2.36	21.593	0.9637682
2.38	21.737	0.9637817
2.40	21.881	0.9637819
2.42	22.025	0.9637690

TABLE V
Computation of n and E by Iteration for Viscose Rayon + 0.5 M NH_4Cl System (RA)

Order assumed, n	Activation energy E (kcal/mol)	Correlation coefficient
0	9.867	0.8930203
0.2	10.304	0.9042956
0.4	10.810	0.9159828
0.6	11.400	0.9277276
0.8	12.089	0.9388992
1.0	12.893	0.9485795
1.2	13.818	0.9557433
1.4	14.864	0.9596297
1.42	14.975	0.9598256
1.44	15.086	0.9599867
1.46	15.199	0.9601133
1.48	15.313	0.9602056
1.50	15.429	0.9602641
1.52	15.545	0.9602892
1.54	15.662	0.9602814
1.56	15.780	0.9602413
1.58	15.899	0.9601695
1.60	16.019	0.9600662
1.80	17.266	0.9574914

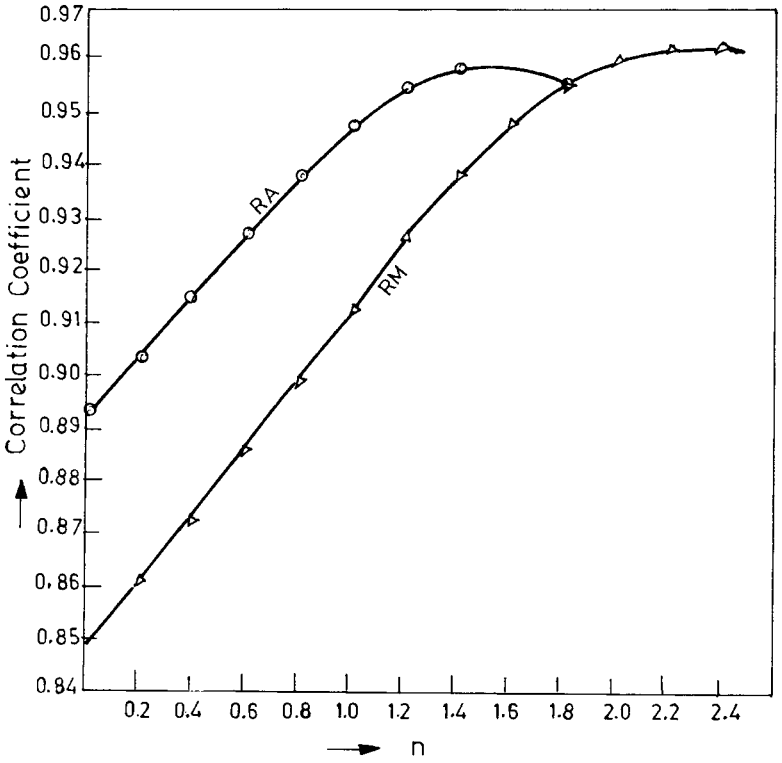

Fig. 5. Variation of correlation coefficient with order of reaction.

great extent. Hence, to obtain the correct values of n, eq. (1) was solved, resorting to an iteration technique as mentioned earlier. The values of n, E, and correlation coefficient obtained simultaneously from the program output are given in Table III. From Table III, it may be noticed that n changes to 1.52 and 2.40 and E is lowered to 15.545 and 21.881 kcal/mol, respectively, for RA and RM. These changes can be attributed to changes in mechanism of overall thermal degradation like advancement of intramolecular dehydration and inhibition of the depolymerization reactions as mentioned earlier.

It may also be observed from Tables IV and V that the maximum correlation coefficient values that could be obtained for RA and RM are 0.9602892 and 0.9637819, respectively. Higher correlation coefficient values can be obtained when a closer range of temperature than 200–400°C is taken up for study.

CONCLUSIONS

1. The thermal degradation reaction of viscose rayon studied in the temperature range of 200–400°C is observed to follow first order with an activation energy of 35.14 kcal/mol.
2. Impregnation with inorganic additives calcium chloride, ammonium chloride, and a mixture of calcium chloride and ammonium chloride results

in lowering of activation energy to 19.538, 15.545, and 21.881 kcal/mol, respectively.

3. Although the order of reaction is not changed due to addition of calcium chloride, a change in order of 1.52 and 2.40 was observed with respect to rayon impregnated with ammonium chloride and rayon impregnated with a mixture of calcium chloride and ammonium chloride, respectively.
4. Char yield is increased from 24.0% for neat rayon to 30.0, 29.95, and 38.75% for rayon impregnated with calcium chloride, ammonium chloride, and a mixture of calcium chloride and ammonium chloride, respectively.

Mr. K. Parthasarathy of Computer Division, VSSC, is gratefully acknowledged for his assistance in generating the Computer programs. The suggestions given by Dr. B. K. Sarkar, Director, Materials and Metallurgy Group, VSSC, in the preparation of manuscript is also acknowledged. We express our sincere thanks to the Director, VSSC, for granting permission for bringing out this publication.

APPENDIX A: PROGRAM LISTING FOR CALCULATION OF η, E, AND ERROR ANALYSIS

```
      PROGRAM CHEMIC ( INPUT,OUTPUT )
      DIMENSION T ( 50 ),W ( 50 ),X ( 50 ),Y ( 50 )
      REAL L ( 50 )
C     ENTER NO. OF OBSERVATIONS,
      PRINT *,''==========================================''
      PRINT *,''ENTER NR.OBS''
      READ *,N
C     ENTER THE OBSERVATIONS
      DO 4 JK=1,N
      READ *,T ( JK ),W ( JK )
4     CONTINUE
      N = N - 1
      H=0.0
      IR=N-1
      N = N - 1
      ITSAMP= N - 2
      PRINT *, ''ENTER T DISTR. VALUE FOR '',ITSAMP,'' SAMPLES''
      READ *,ATSTAT
      PRINT *,''++++++++++++++++++++++++++++++++++++++++++++''
      PRINT *,''      ''
      PRINT *,''NUMBER OF SAMPLES = '',N
      PRINT *,''   ''
6     A = 0.0
      B=0.0
      C=0.0
      D=0.0
      E=0.0
      PRINT *,''**********************************************''
      PRINT *,''      ''
      PRINT *,''ORDER = '',H
      PRINT *,''    ''
      PRINT *,''**********************************************''
      PRINT *,''       ''
```

```
      L(1)=0.0
      PREVAL = 0.0
C     CALCULATION OF INTEGRAL BY TRAPEZOIDAL RULE
      DO 5 I=1,IR
      K=I+1
      X(K)=1/T(K)
      RK = 1/(((1-W(K))**H)*(T(K)*T(K)))
      RI = 1/(((1-W(I))**H)*(T(K)*T(K)))
      L(K) = PREVAL + ((W(K)-W(I))/2)*(RI+RK)
      Y(K)=ALOGIO(L(K))
      PRINT *,X(K),Y(K)
      A = A + X(K)
      B = B + X(K)**2
      C = C + Y(K)
      D = D + Y(K)**2
      E = E + (X(K) * Y(K))
      PREVAL = L(K)
5     CONTINUE
      PRINT *,''   ''
      PRINT *,''**********************************************''
      PRINT *,''       ''
C     CALCULATION OF CORRELATION COEFFCT. AND REGRESSION LINE
      F=A/N
      G=C/N
      AJ=B-((A**2)/N)
      AK=SQRT(AJ/(N-1))
      AL=D-((C**2)/N)
      AM=SQRT(AL/(N-1))
      O=E-((A*C)/N)
      R=O/SQRT(AJ*AL)
      PRINT *,''CORRELATION='',R
      P=O/AJ
      Q=G-(P*F)
      PRINT *,''EQ IS''
      PRINT *,''Y='',Q,''+'',P,''X''
      ENERGY=4.575*P
      PRINT *,''ENERGY='',ENERGY
      PRINT *,''   ''
      PRINT *,''**********************************************''
      PRINT *,''      ''
C      ERROR CALCULATION
      SAMPNO = N
       ERREST = SQRT((D-(Q*C)-(F*E))/SAMPNO)
       PRINT *,''STANDARD ERROR OF ESTIMATE IS '',ERREST
C      CALCULATION OF THE SUM OF ERROR SQUARES
       ISTART = 2
      ERRSQR = 0.0
      IFSAMP = N+ISTART-1
       DO 20 IL = ISTART,IFSAMP
        CALY = Q+(P*X(IL))
        DIFFY = (CALY-Y(IL))*(CALY-Y(IL))
        ERRSQR = ERRSQR + DIFFY
20     CONTINUE
       PRINT *,''ERROR SUM OF SQUARES '',ERRSQR
C      CALCULATION OF SIGNIFICANCE OF R
       STERR = (1-(R*R))/(SQRT(SAMPNO))
       PRINT *, ''STANDARD ERROR ESTIMATE FOR CORRELATION IS'',STERR
```

```
C       TEST OF SIGNIFICANCE OF R
        TSTAT = (R/SQRT(1-(R*R)))*(SQRT(SAMPNO-2))
        PRINT *,''OBSERVED T STATISTIC VALUE IS'',TSTAT
        IF(ABS(TSTAT).LE.ATSTAT) GO TO 10
        PRINT *,''R IS STATISTICALLY SIGNIFICANT''
        GO TO 11
10      PRINT *,''R IS NOT SIGNIFICANT''
11      IEH = H
        PRINT *,''    ''
        PRINT *,''    ''
        PRINT *,''    ''
        IF(ABS(R).GE.0.98.OR.IEH.GE.2) GO TO 52
        H = H+0.2
        GO TO 6
52      PRINT
        *,''++++++++++++++++++++++++++++++++++++++++++++++++''
        STOP
        END
```

APPENDIX B: ERROR ESTIMATE FOR THE CORRELATION AND STATISTICAL SIGNIFICANCE

In the automatic processing of non-isothermal kinetic data, the modified Coats–Redfern method[10] uses the equation

$$\log \int_0^{\alpha} \frac{d\alpha}{f(\alpha)T^2} = \log \frac{AR}{aE} - \frac{E}{2.303R}\frac{1}{T}$$

For the correct value of n, the plot $\log \int_0^{\alpha} d\alpha/(1-\alpha)^n T^2$ values against $1/T$ values should give a straight line whose slope and intercept allows the calculation of activation energy and preexponential factor A. For the calculation of the integral, the trapezoidal rule is used. The program allows the selection of n for the evaluation of the integral. The program calculates the regression line and correlation value for the different values of n. The errors introduced in the process involves two kinds:

1. Experimental error in calculating the weight loss
2. Error involved in evaluating the integral by trapezoidal rule

On account of this, we may not be able to get an exact straight line as per theoretical results for a value of n but only a close fit. The correlation coefficient gives the goodness of fit.

The correlation coefficient indicates that any prediction will not be exactly correct. The actual value might be above or below the predicted value based on the regression equation. This error is measured by the standard error of estimate[14] designated by

$$Sy \cdot x = \sqrt{\frac{\Sigma Y^2 - a(\Sigma Y) - b(\Sigma XY)}{N-2}}$$

If the values in a frequency distribution are normally distributed about the mean $\bar{X}$, then

$\bar{X} \pm 1s$ encompasses about 68.3% of the values.

$\bar{X} \pm 2s$ encompasses about 95.5% of the values.

$\bar{X} \pm 3s$ encompasses about 99.7% of the values.

Likewise, in the regression line, if the values are normally distributed about the line, then

$\bar{Y} \pm 1\ (Sy \cdot x)$ includes 68.3% of the Y values, etc. where $\bar{Y}$ refers to the predicted value.

In the programme the standard error of estimate is shown for the values of n.

Another metric, i.e., error sum of squares[15] of the difference is the actual Y value and the predicted Y values are also shown, which helps to measure the variance around the regression line and calculate the confidence interval for slopes and intercept of the line.

Also, the standard error of the correlation[16] given by $1 - r^2/\sqrt{n}$ is calculated and shown. Finally, in order to establish the statistical significance of the correlation, the test statistic[15]

$$r\sqrt{n-2}/\sqrt{1-r^2}$$

is used.

The program is run on a Cyber 170/730 machine, which is a 60-bit machine and hence computational errors are not significantly accounted for. The program listings are also shown below. The program output for systems RM and RA are given in Tables VI and VII, respectively.

Computer Output of Error Analysis for System RM

```
14
423 0.
443 0.00685
```

TABLE VI
Error Analysis Data for System RM (Viscose Rayon + 0.5 M NH_4Cl + 0.5 M $CaCl_2$)

Order assumed, n	Activation energy E (kcal/mol)	Correlation coefficient	Standard error of estimate	Error sum of squares	Standard error estimate for correlation	Observed test statistic value
0	10.696	0.8499780	0.33869	1.3765	0.08011	5.1020
0.2	11.141	0.8610380	0.33615	1.3559	0.07465	5.3542
0.4	11.647	0.8731259	0.33223	1.3245	0.06860	5.6637
0.6	12.229	0.8861693	0.32666	1.2804	0.06197	6.0477
0.8	12.898	0.8991234	0.31929	1.2233	0.05489	6.5259
1.0	13.667	0.9138437	0.31025	1.5511	0.04759	7.1166
1.2	14.546	0.9272015	0.30019	1.0814	0.04050	7.8279
1.4	15.536	0.9391155	0.29040	1.0120	0.03408	8.6429
1.6	16.635	0.9488554	0.28275	0.9594	0.02877	9.5040
1.8	17.831	0.9560409	0.27939	0.9367	0.02482	10.3101
2.0	19.112	0.9606911	0.28215	0.9553	0.02224	10.9429
2.2	20.466	0.9631205	0.29210	1.0238	0.02089	11.3191
2.22	20.605	0.9632583	0.29350	1.0337	0.02082	11.3416
2.24	20.745	0.9633789	0.29497	1.0441	0.02075	11.3613
2.26	20.885	0.9634828	0.29652	1.0551	0.02069	11.3784
2.28	21.025	0.9635704	0.29814	1.0666	0.02064	11.3928
2.30	21.167	0.9636423	0.29982	1.0787	0.02060	11.4047
2.32	21.308	0.9636989	0.30158	1.0914	0.02057	11.4141
2.34	21.451	0.9637407	0.30341	1.1047	0.02055	11.4211
2.36	21.593	0.9637682	0.30531	1.1186	0.02053	11.4256
2.38	21.737	0.9638179	0.30728	1.1330	0.02053	11.4279
2.40	21.881	0.9637819	0.30931	1.1481	0.02053	11.4279
2.42	22.025	0.9637690	0.31141	1.1637	0.02053	11.4258

TABLE VII
Error Analysis Data for System RA (Viscose Rayon + 0.5 *M* NH_4Cl)

Order assumed, *n*	Activation energy *E* (kcal/mol)	Correlation coefficient	Standard error of estimate	Error sum of squares	Standard error estimate for correlation	Observed test statistic value
0	9.867	0.8930203	0.25489	0.77967	0.05846	6.2752
0.2	10.304	0.9042956	0.24937	0.74622	0.05261	6.6984
0.4	10.810	0.9159828	0.24273	0.70701	0.04646	7.2195
0.6	11.400	0.9277276	0.23511	0.66337	0.04021	7.8598
0.8	12.089	0.9388992	0.22719	0.61939	0.03419	8.6261
1.0	12.893	0.9485795	0.22055	0.58373	0.02892	9.4764
1.2	13.818	0.9557433	0.21805	0.57058	0.02498	10.272
1.4	14.864	0.9596297	0.22332	0.59851	0.02283	10.789
1.42	14.975	0.9598256	0.22441	0.60433	0.02272	10.817
1.44	15.086	0.9599867	0.22560	0.61078	0.02263	10.840
1.46	15.199	0.9601133	0.22691	0.61788	0.02256	10.858
1.48	15.313	0.9602056	0.22833	0.62564	0.02251	10.871
1.50	15.429	0.9602641	0.22987	0.63409	0.02248	10.880
1.52	15.545	0.9602892	0.23152	0.64323	0.02247	10.883
1.54	15.662	0.9602814	0.23329	0.65310	0.02247	10.882
1.56	15.780	0.9602413	0.23517	0.66370	0.02249	10.877
1.58	15.899	0.9601695	0.23717	0.67505	0.02253	10.866
1.60	16.019	0.9600662	0.23929	0.68716	0.02259	10.851
1.80	17.266	0.9574914	0.26669	0.85354	0.02402	10.496

```
463 0.01370
483 0.2397
503 0.3493
523 0.4315
543 0.5410
563 0.6507
583 0.7123
603 0.7945
623 0.8767
643 0.9383
663 0.9794
673 1.
1.812
 ==========================================
 ENTER NR.OBS
 ENTER T DISTR. VALUE FOR 10 SAMPLES
 ++++++++++++++++++++++++++++++++++++++++++

 NUMBER OF SAMPLES = 12

 ******************************************

 ORDER = 0.

 ******************************************

 .002257336343115 -7.457116880954
 .002159827213823 -7.174840879647
```

```
.002070393374741 -5.984801929618
.001988071570577 -5.833037174427
.001912045889101 -5.752194318164
.001841620626151 -5.669445476464
.001776198934281 -5.604361884797
.001715265866209 -5.573810930693
.001658374792703 -5.538488426442
.001605136436597 -5.507816418834
.001555209953344 -5.487467318223
.001508295625943 -5.475167408466

*******************************************

CORRELATION=-.8499780374489
EQ IS
Y=-1.625714667426+-2338.103016495X
ENERGY=-10696.82130046

*******************************************

STANDARD ERROR OF ESTIMATE IS .3386934109357
ERROR SUM OF SQUARES 1.376558719332
STANDARD ERROR ESTIMATE FOR CORRELATION IS.08011812778287
OBSERVED T STATISTIC VALUE IS-5.102076858451
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = .2

*******************************************

.002257336343115 -7.456818263054
.002159827213823 -7.174255828267
.002070393374741 -5.972922998862
.001988071570577 -5.815547658285
.001912045889101 -5.730224116264
.001841620626151 -5.640923801527
.001776198934281 -5.568352029943
.001715265866209 -5.533153096625
.001658374792703 -5.490798938424
.001605136436597 -5.451457635879
.001555209953344 -5.422564849329
.001508295625943 -5.402004251314

*******************************************

CORRELATION=-.8610380061574
EQ IS
Y=-1.413928899875+-2435.251298969X
ENERGY=-11141.27469279

*******************************************

STANDARD ERROR OF ESTIMATE IS .3361531643933
ERROR SUM OF SQUARES 1.355987399179
STANDARD ERROR ESTIMATE FOR CORRELATION IS.0746553019179
```

```
OBSERVED T STATISTIC VALUE IS-5.354225794827
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = .4

*******************************************

.002257336343115 -7.456519439968
.002159827213823 -7.173670364117
.002070393374741 -5.960748389346
.001988071570577 -5.797651079346
.001912045889101 -5.707684649376
.001841620626151 -5.611442980614
.001776198934281 -5.530706633263
.001715265866209 -5.490315890314
.001658374792703 -5.43979572617
.001605136436597 -5.389711537703
.001555209953344 -5.349149810776
.001508295625943 -5.315247692682

*******************************************

CORRELATION=-.8731259296517
EQ IS
Y=-1.174107205753+-2545.98722925X
ENERGY=-11647.89157382

*******************************************

STANDARD ERROR OF ESTIMATE IS .3322303943234
ERROR SUM OF SQUARES 1.324524418947
STANDARD ERROR ESTIMATE FOR CORRELATION IS.06860396644583
OBSERVED T STATISTIC VALUE IS-5.663787640421
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = .6

*******************************************

.002257336343115 -7.456220411696
.002159827213823 -7.173084487181
.002070393374741 -5.948277713361
.001988071570577 -5.779349641393
.001912045889101 -5.684578049694
.001841620626151 -5.580995269556
.001776198934281 -5.49138701971
.001715265866209 -5.445231213703
.001658374792703 -5.385303505371
.001605136436597 -5.322072256823
.001555209953344 -5.265896208071
.001508295625943 -5.211109661521
```

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*********************************************

CORRELATION=-.8861693520511
EQ IS
Y=-.9007673321071+-2673.026784104X
ENERGY=-12229.09753727

*********************************************

STANDARD ERROR OF ESTIMATE IS .3266605075925
ERROR SUM OF SQUARES 1.280485046643
STANDARD ERROR ESTIMATE FOR CORRELATION IS.06197967130848
OBSERVED T STATISTIC VALUE IS-6.047791079754
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = .8

*********************************************

.002257336343115 -7.455921178238
.002159827213823 -7.172498197445
.002070393374741 -5.935510986265
.001988071570577 -5.760648051788
.001912045889101 -5.66090723003
.001841620626151 -5.549574628722
.001776198934281 -5.450359228615
.001715265866209 -5.397840491701
.001658374792703 -5.327165414756
.001605136436597 -5.248063320662
.001555209953344 -5.171485866996
.001508295625943 -5.085351080698

*********************************************

CORRELATION=-.8999123476929
EQ IS
Y=-.5880175720412+-2819.291662111X
ENERGY=-12898.25935416

*********************************************

STANDARD ERROR OF ESTIMATE IS .3192911875601
ERROR SUM OF SQUARES 1.22336234944
STANDARD ERROR ESTIMATE FOR CORRELATION IS.05489381882991
OBSERVED T STATISTIC VALUE IS-6.525941509278
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = 1.

*********************************************

.002257336343115 -7.455621739595
```

```
.002159827213823 -7.171911494894
.002070393374741 -5.922448626402
.001988071570577 -5.741543499089
.001912045889101 -5.636675849336
.001841620626151 -5.517176764152
.001776198934281 -5.407594645363
.001715265866209 -5.348096312261
.001658374792703 -5.265249206235
.001605136436597 -5.167267577219
.001555209953344 -5.06474176459
.001508295625943 -4.933965071383

**********************************************

CORRELATION=-.9138437600777
EQ IS
Y=-.2303867799359+-2987.496304361X
ENERGY=-13667.79559245

**********************************************

STANDARD ERROR OF ESTIMATE IS .3102573915852
ERROR SUM OF SQUARES 1.155115788403
STANDARD ERROR ESTIMATE FOR CORRELATION IS.04759952232537
OBSERVED T STATISTIC VALUE IS-7.116645648033
R IS STATISTICALLY SIGNIFICANT


**********************************************

ORDER = 1.2

**********************************************

.002257336343115 -7.455322095768
.002159827213823 -7.171324379515
.002070393374741 -5.909091452834
.001988071570577 -5.722045628274
.001912045889101 -5.611888274097
.001841620626151 -5.483799155985
.001776198934281 -5.363070574319
.001715265866209 -5.295963858694
.001658374792703 -5.199452949602
.001605136436597 -5.079357986186
.001555209953344 -4.944781862377
.001508295625943 -4.754195563158

**********************************************

CORRELATION=-.9272015744324
EQ IS
Y=-.1759901687017+-3179.557603133X
ENERGY=-14546.47603433

**********************************************

STANDARD ERROR OF ESTIMATE IS .3001975914404
ERROR SUM OF SQUARES 1.081423126877
```

```
STANDARD ERROR ESTIMATE FOR CORRELATION IS.04050032474709
OBSERVED T STATISTIC VALUE IS-7.827977994241
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = 1.4

*******************************************

.002257336343115 -7.455022246758
.002159827213823 -7.170736851295
.002070393374741 -5.895440680908
.001988071570577 -5.702156513892
.001912045889101 -5.986549536235
.001841620626151 -5.44944107377
.001776198934281 -5.316770730331
.001715265866209 -5.241422048308
.001658374792703 -5.129709750899
.001605136436597 -4.98412495748
.001555209953344 -4.811156979787
.001508295625943 -4.545458521175

*******************************************

CORRELATION=-.93911559356
EQ IS
Y=.6323020487052+-3396.061913337X
ENERGY=-15536.98325352

*******************************************

STANDARD ERROR OF ESTIMATE IS .2904032933432
ERROR SUM OF SQUARES 1.012008873409
STANDARD ERROR ESTIMATE FOR CORRELATION IS.03408153543088
OBSERVED T STATISTIC VALUE IS-8.642993058968
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = 1.6

*******************************************

.002257336343115 -7.454722192567
.002159827213823 -7.170148910221
.002070393374741 -5.881497915703
.001988071570577 -5.681880631479
.001912045889101 -5.560665288151
.001841620626151 -5.414103578457
.001776198934281 -5.268685627977
.001715265866209 -5.184464304295
.001658374792703 -5.05599103098
.001605136436597 -4.881495681601
.001555209953344 -4.663930533135
.001508295625943 -4.309594130885
```

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*********************************************

CORRELATION=-.9488554216299
EQ IS
Y=1.136721442527+-3636.096214759X
ENERGY=-16635.14018252

*********************************************

STANDARD ERROR OF ESTIMATE IS .2827580887618
ERROR SUM OF SQUARES .9594256411233
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02877322893993
OBSERVED T STATISTIC VALUE IS-9.504087615361
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = 1.8

*********************************************

.002257336343115 -7.454421933195
.002159827213823 -7.169560556279
.002070393374741 -5.867265143445
.001988071570577 -5.661222827579
.001912045889101 -5.534241755591
.001841620626151 -5.377789511059
.001776198934281 -5.218812851033
.001715265866209 -5.125098908345
.001658374792703 -4.978308030348
.001605136436597 -4.771541868231
.001555209953344 -4.5036723216
.001508295625943 -4.050267919281

*********************************************

CORRELATION=-.9560409286574
EQ IS
Y=1.685005587149+-3897.548134997X
ENERGY=-17831.28271761

*********************************************

STANDARD ERROR OF ESTIMATE IS .2793948059021
ERROR SUM OF SQUARES .9367374907804
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02482194585636
OBSERVED T STATISTIC VALUE IS-10.31010911495
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = 2.

*********************************************
```

```
.002257336343115 -7.454121468644
.002159827213823 -7.168971789459
.002070393374741 -5.852744720973
.001988071570577 -5.640188288717
.001912045889101 -5.507285688982
.001841620626151 -5.340503468204
.001776198934281 -5.167157189164
.001715265866209 -5.063348907761
.001658374792703 -4.896711383223
.001605136436597 -4.654474374361
.001555209953344 -4.331368460193
.001508295625943 -3.771924419771

*******************************************

CORRELATION=-.9606911366505
EQ IS
Y=2.271631440684+-4177.671926184X
ENERGY=-19112.84906229

*******************************************

STANDARD ERROR OF ESTIMATE IS .2821567769589
ERROR SUM OF SQUARES .9553493614064
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02224892584684
OBSERVED T STATISTIC VALUE IS-10.94293823916
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = 2.2

*******************************************

.002257336343115 -7.453820798916
.002159827213823 -7.168382609748
.002070393374741 -5.837939363382
.001988071570577 -5.618782509674
.001912045889101 -5.479804313876
.001841620626151 -5.302251764972
.001776198934281 -5.113730634433
.001715265866209 -4.999251580257
.001658374792703 -4.811288808643
.001605136436597 -4.530625761775
.001555209953344 -4.148278261595
.001508295625943 -3.478866257319

*******************************************

CORRELATION=-.9631205153171
EQ IS
Y=2.890861186463+-4473.619203091X
ENERGY=-20466.80785414

*******************************************

STANDARD ERROR OF ESTIMATE IS .2921019022013
```

```
ERROR SUM OF SQUARES 1.02388225523
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02089975440064
OBSERVED T STATISTIC VALUE IS-11.31917386929
R IS STATISTICALLY SIGNIFICANT


*****************************************
```

Computer Output of Error Analysis for System RA

```
14
423 0.
443 0.00565
463 0.0393
483 0.1751
503 0.2259
523 0.2598
543 0.3051
563 0.3785
583 0.5028
603 0.7288
623 0.8588
643 0.9322
666 0.9831
673 1.
1.812
 ==========================================
 ENTER NR.OBS
 ENTER T DISTR. VALUE FOR 10 SAMPLES
 ++++++++++++++++++++++++++++++++++++++++++++

 NUMBER OF SAMPLES = 12

 *****************************************

 ORDER = 0.

 *****************************************

 .002257336343115 -7.540759004627
 .002159827213823 -6.731042469392
 .002070393374741 -6.114710670672
 .001988071570577 -6.013830314391
 .001912045889101 -5.961542014799
 .001841620626151 -5.904401838197
 .001776198934281 -5.830384845456
 .001715265866209 -5.734355467995
 .001658374792703 -5.608173796509
 .001605136436597 -5.552843076207
 .001555209953344 -5.526144754847
 .001501501501501 -5.509721438641

 *****************************************

 CORRELATION=-.8930203629869
 EQ IS
 Y=-2.040730139849+-2156.852490987X
 ENERGY=-9867.600146265
```

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*********************************************

STANDARD ERROR OF ESTIMATE IS .2548985458132
ERROR SUM OF SQUARES .7796792238907
STANDARD ERROR ESTIMATE FOR CORRELATION IS.05846093844529
OBSERVED T STATISTIC VALUE IS-6.27528073026
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = .2

*********************************************

.002257336343115 -7.540512862721
.002159827213823 -6.729322391912
.002070393374741 -6.10658390681
.001988071570577 -6.003323849031
.001912045889101 -5.949461563903
.001841620626151 -5.890214646306
.001776198934281 -5.81262615808
.001715265866209 -5.709773695082
.001658374792703 -5.566759418197
.001605136436597 -5.498006220414
.001555209953344 -5.460900499003
.001501501501501 -5.433180925343

*********************************************

CORRELATION=-.9042956353567
EQ IS
Y=-1.837988726621+-2252.386045518X
ENERGY=-10304.66615825

*********************************************

STANDARD ERROR OF ESTIMATE IS .2493707573198
ERROR SUM OF SQUARES .7462292952744
STANDARD ERROR ESTIMATE FOR CORRELATION IS.05261087119339
OBSERVED T STATISTIC VALUE IS-6.69849714296
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = .4

*********************************************

.002257336343115 -7.540266581391
.002159827213823 -6.727597023662
.002070393374741 -6.098349023803
.001988071570577 -5.992679235062
.001912045889101 -5.937214063876
.001841620626151 -5.875807830847
.001776198934281 -5.794519361639
```

```
.001715265866209 -5.684447148507
.001658374792703 -5.522479977145
.001605136436597 -5.437536054291
.001555209953344 -5.386567079751
.001501501501501 -5.340275845744

*****************************************

CORRELATION=-.9159828861277
EQ IS
Y=-1.604692005542+-2362.936187357X
ENERGY=-10810.43305716

*****************************************

STANDARD ERROR OF ESTIMATE IS .2427305268937
ERROR SUM OF SQUARES .7070173042343
STANDARD ERROR ESTIMATE FOR CORRELATION IS.04646958149778
OBSERVED T STATISTIC VALUE IS-7.219509087649
R IS STATISTICALLY SIGNIFICANT


*****************************************

ORDER = .6

*****************************************

.002257336343115 -7.540020160636
.002159827213823 -6.725866359465
.002070393374741 -6.090005370709
.001988071570577 -5.981896420282
.001912045889101 -5.924799681788
.001841620626151 -5.861181434222
.001776198934281 -5.77606268829
.001715265866209 -5.658361029969
.001658374792703 -5.475135840374
.001605136436597 -5.370890233647
.001555209953344 -5.301852360979
.001501501501501 -5.226016228518

*****************************************

CORRELATION=-.9277276562798
EQ IS
Y=-1.33413169066+-2491.835720827X
ENERGY=-11400.14842278

*****************************************

STANDARD ERROR OF ESTIMATE IS .2351190859874
ERROR SUM OF SQUARES .6633718151406
STANDARD ERROR ESTIMATE FOR CORRELATION IS.04021862267686
OBSERVED T STATISTIC VALUE IS-7.859801808535
R IS STATISTICALLY SIGNIFICANT


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```
ORDER = .8

*******************************************

.002257336343115 -7.539773600457
.002159827213823 -6.724130394265
.002070393374741 -6.081552344616
.001988071570577 -5.970975427433
.001912045889101 -5.912218683151
.001841620626151 -5.846335640163
.001776198934281 -5.757254637493
.001715265866209 -5.631501443393
.001658374792703 -5.424539600723
.001605136436597 -5.297583548485
.001555209953344 -5.205573435539
.001501501501501 -5.084899949433

*******************************************

CORRELATION=-.9388992814905
EQ IS
Y=-1.019222740217+-2642.607507034X
ENERGY=-12089.92934468

*******************************************

STANDARD ERROR OF ESTIMATE IS .227192773772
ERROR SUM OF SQUARES .619398677447
STANDARD ERROR ESTIMATE FOR CORRELATION IS.03419880603356
OBSERVED T STATISTIC VALUE IS-8.62617418011
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = 1.

*******************************************

.002257336343115 -7.539526900853
.002159827213823 -6.722389123131
.002070393374741 -6.072989391845
.001988071570577 -5.959916353989
.001912045889101 -5.899471430794
.001841620626151 -5.831270771959
.001776198934281 -5.738093979163
.001715265866209 -5.603855511719
.001658374792703 -5.37052392744
.001605136436597 -5.217225337633
.001555209953344 -5.096796452312
.001501501501501 -4.912095695075

*******************************************

CORRELATION=-.9485795576073
EQ IS
Y=-.6538586642037+-2818.288653849X
```

```
ENERGY=-12893.67059136

*********************************************

STANDARD ERROR OF ESTIMATE IS .2205559402395
ERROR SUM OF SQUARES .5837390733002
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02892433133362
OBSERVED T STATISTIC VALUE IS-9.476474225256
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = 1.2

*********************************************

.002257336343115 -7.539280061825
.002159827213823 -6.720642541251
.002070393374741 -6.064316009069
.001988071570577 -5.948719371771
.001912045889101 -5.886558383488
.001841620626151 -5.815987290269
.001776198934281 -5.718579755855
.001715265866209 -5.575411491442
.001658374792703 -5.31294956642
.001605136436597 -5.12955370935
.001555209953344 -4.974967760155
.001501501501501 -4.705061028211

*********************************************

CORRELATION=-.9557433822569
EQ IS
Y=-.2346992665742+-3020.538479341X
ENERGY=-13818.96354299

*********************************************

STANDARD ERROR OF ESTIMATE IS .2180560750626
ERROR SUM OF SQUARES .5705814224633
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02498615713061
OBSERVED T STATISTIC VALUE IS-10.27297555412
R IS STATISTICALLY SIGNIFICANT


*********************************************

ORDER = 1.4

*********************************************

.002257336343115 -7.539033083373
.002159827213823 -6.71889064394
.002070393374741 -6.055531744343
.001988071570577 -5.937384726387
.001912045889101 -5.873480094316
.001841620626151 -5.80048579053
```

```
.001776198934281 -5.698711283969
.001715265866209 -5.546158882981
.001658374792703 -5.251712805871
.001605136436597 -5.034460557
.001555209953344 -4.8399993256
.001501501501501 -4.464660545715

*******************************************

CORRELATION=-.9596297406279
EQ IS
Y=.2375963262732+-3249.023286162X
ENERGY=-14864.28153419

*******************************************

STANDARD ERROR OF ESTIMATE IS .2233299549953
ERROR SUM OF SQUARES .5985152255728
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02283730955142
OBSERVED T STATISTIC VALUE IS-10.78911738518
R IS STATISTICALLY SIGNIFICANT


*******************************************

ORDER = 1.6

*******************************************

.002257336343115 -7.538785965499
.002159827213823 -6.717133426634
.002070393374741 -6.046636198041
.001988071570577 -5.925912736499
.001912045889101 -5.86023720882
.001841620626151 -5.784766999976
.001776198934281 -5.678488153965
.001715265866209 -5.516088534925
.001658374792703 -5.186751666976
.001605136436597 -4.932002443484
.001555209953344 -4.692280774159
.001501501501501 -4.194909963941

*******************************************

CORRELATION=-.9600666290089
EQ IS
Y=.7586077621921+-3501.535705667X
ENERGY=-16019.52585342

*******************************************

STANDARD ERROR OF ESTIMATE IS .2392988774766
ERROR SUM OF SQUARES .687167433137
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02259519972553
OBSERVED T STATISTIC VALUE IS-10.85170478552
R IS STATISTICALLY SIGNIFICANT
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*********************************************

ORDER = 1.8

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.002257336343115 -7.538538708203
.002159827213823 -6.715370884897
.002070393374741 -6.037629023694
.001988071570577 -5.914303792929
.001912045889101 -5.84683046291
.001841620626151 -5.768831774308
.001776198934281 -5.657910229616
.001715265866209 -5.485192740155
.001658374792703 -5.118050136574
.001605136436597 -4.822395108329
.001555209953344 -4.532614370274
.001501501501501 -3.901535462361

*********************************************

CORRELATION=-.9574914899024
EQ IS
Y=1.321675490483+-3774.754985263X
ENERGY=-17269.50405758

*********************************************

STANDARD ERROR OF ESTIMATE IS .2666992536611
ERROR SUM OF SQUARES .853541902837
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02402067144938
OBSERVED T STATISTIC VALUE IS-10.49656113672
R IS STATISTICALLY SIGNIFICANT


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ORDER = 2.

*********************************************

.002257336343115 -7.538291311485
.002159827213823 -6.713603014413
.002070393374741 -6.028509928721
.001988071570577 -5.90255835759
.001912045889101 -5.833260680568
.001841620626151 -5.752681094011
.001776198934281 -5.636977646292
.001715265866209 -5.453465321925
.001658374792703 -5.045639937103
.001605136436597 -4.705992810345
.001555209953344 -4.362095202
.001501501501501 -3.590376413437

*********************************************

CORRELATION=-.9526926604107
EQ IS
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Y=1.919641928708+-4065.116192242X
ENERGY=-18597.90657951

*******************************************

STANDARD ERROR OF ESTIMATE IS .3041455217868
ERROR SUM OF SQUARES 1.110053981081
STANDARD ERROR ESTIMATE FOR CORRELATION IS.02666685480467
OBSERVED T STATISTIC VALUE IS-9.912235455907
R IS STATISTICALLY SIGNIFICANT


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ORDER = 2.2

*******************************************

.002257336343115 -7.538043775347
.002159827213823 -6.711829810995
.002070393374741 -6.019278675068
.001988071570577 -5.890676962274
.001912045889101 -5.819528771343
.001841620626151 -5.736316060366
.001776198934281 -5.615690808321
.001715265866209 -5.42090170809
.001658374792703 -4.969599604913
.001605136436597 -4.583256744178
.001555209953344 -4.18197262102
.001501501501501 -3.266402196479

*******************************************

CORRELATION=-.9465050448626
EQ IS
Y=2.54599429307+-4369.380051269X
ENERGY=-19989.91373456

*******************************************

STANDARD ERROR OF ESTIMATE IS .3493503170515
ERROR SUM OF SQUARES 1.464547728287
STANDARD ERROR ESTIMATE FOR CORRELATION IS.03005922216447
OBSERVED T STATISTIC VALUE IS-9.275530385389
R IS STATISTICALLY SIGNIFICANT


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Received November 14, 1989
Accepted February 16, 1990