LIST OF SYMBOLS AND ABBREVIATIONS

While different authors have used different sets of symbols in the fields of spectrophotometry, equilibria and chemical kinetics, in the present work it was necessary to allocate a limited number of symbols for topics falling under the above fields as well as statistics, while avoiding exotic symbols and styles. Consideration had also to be paid for the symbols and abbreviations to be used in writing the computer programs. Lower case symbols are not mostly used. Even then, some had to be allotted to more than one term, property or quantity, and the exact assignment has on such occasions to be inferred from the context. A few symbols, used in certain sections of the thesis are defined locally.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>A</td>
<td>Intercept in linear regression; a parameter in non-linear regression.</td>
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<tr>
<td>A</td>
<td>Reactant in a two-step, consecutive reaction; its concentration.</td>
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<tr>
<td>A₀</td>
<td>Initial concentration of the reactant A in a two-step, consecutive reaction.</td>
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<tr>
<td>AA</td>
<td>Correction applied to parameter A at the end of an iteration in non-linear routines.</td>
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<tr>
<td>Abs.</td>
<td>Absorbance unit</td>
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<tr>
<td>B</td>
<td>The regression coefficient in linear regression, i.e., the slope; a parameter in non-linear regression.</td>
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<tr>
<td>B</td>
<td>The intermediate in a two-step, consecutive reaction; its concentration.</td>
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<tr>
<td>BA</td>
<td>Bromanil; 2,3,5,6-tetrabromo-1,4-benzoquinone, an acceptor</td>
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<tr>
<td>BB</td>
<td>Correction applied to the parameter B at the end of an iteration in non-linear routines.</td>
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</table>
C Acceptor; its (initial) concentration. Also, in the method of residuals, the number of (positive) residuals obtained.

C The product in a two-step, consecutive reaction; its concentration.

CA chloranil; 2,3,5,6-tetrachloro-1,4-benzoquinone, an acceptor.

D Donor; its initial concentration.

DE the standard error in the estimated molar extinction coefficient.

DK the standard error in the estimated formation constant.

E Molar extinction coefficient of the charge-transfer complex, unless specified otherwise.

EA Electron affinity of the acceptor.

ET energy of charge-transfer transition.

F multiplier to alter the step-size during iterations.

FA partial derivative of the trial function with respect to the parameter A in Deming’s method.

FB partial derivative of the trial function with respect to the parameter B in Deming’s method.

FO The objective or trial function defined in terms of deviations.

f a function.

fε dielectric constant function (Kirkwood function).

H coding for the various non-linear methods.

HOMO highest occupied molecular orbital (of donor).

I index variable in programs.

ID ionization potential of the donor.

J dissociation constant ( = 1/K) of a complex; an index variable in the program for the method of residuals.

K the formation (or association) constant of a complex, assumed to be bimolecular unless otherwise specified.
\( K_{\text{rel}} \)  relative formation constant \((K / K_0)\)

\( k \)  rate co-efficient, first-order unless otherwise stated.

\( k_f \)  rate coefficient of the faster step in consecutive reactions (upper case used in the program)

\( k_s \)  rate coefficient of the slower step in consecutive reactions (upper case used in the program)

\( L \)  a parameter in the general form of the rate equation for two-step, consecutive, first-order reactions.

LUMO  lowest unoccupied molecular orbital (of acceptor)

\( l \)  path length or cell size

\( M \)  a parameter in the general form of the rate equation for two-step, consecutive, first-order reactions. an index variable in programs.

MEK  methyl ethyl ketone, used as a solvent

\( N \)  the total number of readings in a series.

\( n \)  refractive index of the solvent

\( P \)  used in the Nelder-Mead routine.

\( Q \)  defined in Deming’s method.

\( QQ \)  defined in Deming’s method.

\( R \)  Pearson’s correlation coefficient, a measure of the goodness of fit in linear regression; represented as \( r \) in Parts A and B

\( S \)  Sum of squares of deviations.

\( S \)  the solvent

\( T \)  time interval between successive readings \((\Delta T)\), in de Prony’s method; also, a quantity defined in Deming’s method;

\( t \)  (reaction) time

THF  tetrahydrofuran, used as a solvent

\( U \)  lag time in a kinetic run, i.e., the time elapsed after initiating the reaction before taking the first (absorbance) reading.

\( U (I) \)  a residual (in the method of residuals).
V a parameter in the general form of the rate equation for two-step, consecutive, first-order reactions.

W a parameter in the general form of the rate equation for two-step, consecutive, first-order reactions.

X a variable, conventionally the independent one.

x the equilibrium concentration of the complex.

Y a variable, conventionally the dependent one.

Z the absorbance of a equilibrium or reaction mixture. (also refers to the Kosower's solvent polarity parameter in Part-B)

$Z_0$ the initial or zero-time absorbance of a reaction mixture.

$Z_\infty$ the infinite-time absorbance of a reaction mixture

$Z_{\text{INF}}$ the infinite-time absorbance of a reaction mixture (in programs)

$\gamma$ extent of reaction with respect to product formation in a two-step, consecutive, first-order reaction.

$\Delta G^0$ Gibb's free energy of formation

$\Delta T$ the uniform time interval between successive readings

$\varepsilon$ the dielectric constant of a medium

$\rho$ Hammett's reaction parameter

$\sigma$ Hammett's substituent parameter

$\lambda_{\text{CT}}$ wavelength of the charge-transfer absorption maximum

$\tau$ dimensionless time parameter defined by Swain as $k_1t$

$\psi_N$ wave function (ground state)

$\psi_E$ wave function (excited state)