APPENDIX I

A. Derivation for the Overall Equilibrium Constant for the Equilibration of Cr(salen)(H₂O)₂⁺ Complexes when X⁻ = NCS⁻, N₃⁻, C₂H₅N, C₃H₄N₂ and C₆H₄NO₂⁻

The equilibrium constant measurements for the complexation of NCS⁻, N₃⁻ and other nucleophiles with trans- Cr(salen)(H₂O)₂⁺ were carried out in the u.v.-region, where outersphere complexes of the Cr(salen)(H₂O)₂⁺, X⁻ also absorb. The equilibria involved in the overall process can be written as in (A-1),

\[ C + X^- \xrightleftharpoons{K_{OS}}^{K_{IS}} C, X^- \xrightleftharpoons{K_{OS}}^{K_{IS}} D + H₂O \ldots \quad (A-1) \]

where the complexes Cr(salen)(H₂O)₂⁺ and Cr(salen)(H₂O)X are denoted as C and D and other nucleophiles such as NCS⁻, N₃⁻ etc. as X⁻ (referred as X⁻⁻ in the text) respectively. From (A-1) it follows that

\[ K_{OS} = \frac{[C, X^-]}{[C][X^-]} \quad \ldots \quad (A-2) \]

and

\[ K_{IS} = \frac{[D]}{[C, X^-]} \quad \ldots \quad (A-3) \]
where equilibrium constants are expressed as a function of concentration variables.

The total metal concentration, \( M_T \), can be written as in (A-4),

\[
M_T = [C] + [C, X^-] + [D] \quad \ldots \quad (A-4)
\]

where \([C]\), \([C, X^-]\) and \([D]\) are the equilibrium concentrations of the complex \([\text{Cr(salen)(H}_2\text{O)}_2]^+\), the ion-pair \([\text{Cr(salen)(H}_2\text{O)}_2]^+ \cdot X^-\) and the complexes \([\text{Cr(salen)(H}_2\text{O)}X(1-n)^+]\) respectively. Substituting (A-2) and (A-3) in (A-4),

\[
M_T = [C] + K_{OS} [C] [X^-] + K_{OS} K_{IS} [X^-] [C] \quad \ldots \quad (A-5)
\]

equation (A-5) is obtained, which can be rearranged to (A-6),

\[
[C] = \frac{M_T}{1 + K_{OS} [X^-] + K_{OS} K_{IS} [X^-]} \quad \ldots \quad (A-6)
\]

The absorbance prior to any complexation (inner or outer-sphere),
\[ A_0 = \varepsilon_0 [C]_0 = \varepsilon_0 \varepsilon_T \quad \ldots \quad (A-7) \]

where \( \varepsilon_0 \) is the absorption coefficient for the complex \( \text{Cr(salen)}(H_2O)_2^+ \) and the concentrations of \([C, X^-]\) and \([D]\) are zero. The total absorbance after the overall equilibration \((A-1)\) is attained,

\[ A = \varepsilon_0 [C] + \varepsilon_1 [C, X^-] + \varepsilon_2 [D] \quad \ldots \quad (A-8) \]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the absorption coefficients for the ion-pairs \([\text{Cr(salen)}(H_2O)_2^+, X^-]\) and the complexes \([\text{Cr(salen)}(H_2O)_2X(n-1)^+]\) respectively. Substituting \((A-2)\) and \((A-3)\) in \((A-8)\),

\[ A = \varepsilon_0 [C] + \varepsilon_1 K_{OS} [C] [X^-] + \varepsilon_2 K_{OS} K_{IS} [C] [X^-] \quad \ldots \quad (A-9) \]

equation \((A-9)\) is obtained.

Replacing \([C]\) in \((A-9)\) with \(M_T\) as defined in \((A-6)\),

\[ A = \frac{(\varepsilon_0 + \varepsilon_1 K_{OS} [X^-] + \varepsilon_2 K_{OS} K_{IS} [X^-]) M_T}{1 + K_{OS} [X^-] + K_{OS} K_{IS} [X^-]} \quad \ldots \quad (A-10) \]
equation (A-10) is derived. The total absorbance change,

\[
A - A_0 = \frac{( \varepsilon_0 + \varepsilon_1 K_{OS}[X^-] + \varepsilon_2 K_{OS}K_{IS}[X^-] ) I_T}{1 + K_{OS}[X^-] + K_{OS}K_{IS}[X^-]} - \varepsilon_0 I_T
\]

... (A-11)

can be written as in (A-11) which in turn can be rearranged to (A-12).

\[
A - A_0 = \frac{(K_{OS}(\varepsilon_1 - \varepsilon_0) + K_{OS}K_{IS}(\varepsilon_2 - \varepsilon_0))[X^-] M_T}{1 + K_{OS}[X^-] + K_{OS}K_{IS}[X^-]}
\]

... (A-12)

Denoting

\[K_{OS}(\varepsilon_1 - \varepsilon_0) + K_{OS}K_{IS}(\varepsilon_2 - \varepsilon_0)\]
as \(P\)

equation (A-12) gives (A-13),

\[
A - A_0 = \frac{P[X^-] M_T}{1 + (K_{OS} + K_{OS}K_{IS})[X^-]}
\]

... (A-13)

which can be written as in (A-14),
\[(A-A_0)^{-1} = \frac{1}{P \left[X^-\right] M_T} + \frac{K_{OS} + K_{OS} K_{IS}}{P M_T} \ldots \ (A-14)\]

Therefore plots of \((A-A_0)^{-1}\) against \([X^-]^{-1}\) at constant \(M_T\) are linear and the intercept/slope ratio of such plots gives \(K_{OS} + K_{OS} K_{IS}\), a quantity denoted as overall equilibrium constant in Chapter IV.

**B. Derivation of Equilibrium Constant for Complexation of NCS⁻ and other ligands with \([Cr(salen)(H_2O)_2]^+\)**

The equilibrium process for the reaction of NCS⁻ and other ligands with \([Cr(salen)(H_2O)_2]^+\) was carried out under the acid conditions where the complex undergoes partial dissociation (as evident from acid dependent spectrum). In this derivation the conjugate base has been assigned the formulation \([Cr(salen)OH(H_2O)]\) for the sake of unambiguity. The equilibria involved in the overall process can be written as in \((A-15)\),
\[
\left[ (H_2O)_2 T^{+} \right] + [X^-] \xrightleftharpoons[K_1]{K_2} \left[ (H_2O)_2 T (X) \right] + \text{H}_2
\]

\[
\text{H}^+ \quad \frac{K_a}{K_k} \quad \text{H}^- \quad \ldots \quad (A-15)
\]

\[
\left[ H_2O \text{T OH} \right] [X^-] \xrightleftharpoons[K_2]{K_1} \left[ (H_2O)_2 T (X^-) \right] + \text{H}_2\text{O}
\]

where \((H_2O)_2 T\) stands for \(\text{Cr(salen)(H}_2\text{O})_2^{+}\) and \(\text{H}_2\text{O}\text{TOH}\) for the conjugate base, \(\text{H}_2\text{OTX}\) for \(\text{Cr(salen)(H}_2\text{O})X\), \(\text{OHTX}\) for the \(X^-\) derivative of the conjugate base and \(K_a'\) and \(K_a\) are dissociation constants. The equilibrium constants can be written as in (A-16) to (A-18).

\[
K_1 = \frac{[(H_2O)_2T(X)]}{\left[(H_2O)_2T\right][X^-]} \quad \ldots \quad (A-16)
\]

\[
K_2 = \frac{[\text{OH}_2\text{T}(X)]}{\left[\text{OH}_2\text{T}\right][X^-]} \quad \ldots \quad (A-17)
\]

\[
K_a = \frac{[\text{OH}_2\text{OH} \text{T}][\text{H}^+]}{\left[\text{OH}_2\text{OH} \text{T}^{+}\right]} \quad \ldots \quad (A-18)
\]

The total metal concentration, \(M_T\), at zero time (i.e., in the absence of any added \(X^-\)) is as in (A-19),

\[
M_T = [T(H_2O)_2] + [\text{TOH}(H_2O)] \quad \ldots \quad (A-19)
\]
where \([T(H_2O)_2]^+\) and \([T(OH)(OH)_2]^-\) are the concentrations of 
\([Cr(salen)(H_2O)_2]^+\) and \([Cr(salen)(H_2O)(OH)]^-\) at zero time.
Substituting (A-18) in (A-19)

\[
M_T = \frac{[T(H_2O)_2]^+ ([H^+] + K_a)}{[H^+]} \quad \ldots \quad (A-20)
\]

The total metal concentration, \(M_T\), at the completion of the overall equilibrium process is expressed as in (A-21)

\[
M_T = [T(H_2O)_2]^+ + [T(OH)(H_2O)] + [T(H_2O)] + [T(OH)(OH)_2]^- \quad \ldots \quad (A-21)
\]

where \([T(H_2O)_2]^+\), \([T(OH)(H_2O)]\), \([T(H_2O)]\) and \([T(OH)(OH)_2]^-\) equilibrium concentrations of \([Cr(salen)(H_2O)_2]^+\),
\([Cr(salen)(OH)(H_2O)]\), \([Cr(salen)(H_2O)X]\), \([Cr(salen)(OH)(OH)_2]^-\) respectively. Substituting (A-16), (A-17) and (A-18) in (A-21),

\[
T = [T(H_2O)_2]^+ \left( 1 + [H^+]^{-1} K_a + K_1 [X] + K_a X_2 [X] [H^+]^{-1} \right) \quad \ldots \quad (A-22)
\]
equation (A-22) is obtained. Hence the equilibrium concentration \(T(OH)_2^+\) can be expressed as in (A-23)
\[ [T(H_2O)_2^+] = \frac{[H^+] M_T}{[H^+] + K_a + (K_1 [H^+] + K_2 K_a) [X^-]} \quad \ldots \quad (A-23) \]

The total absorbance, \( A_0 \) at zero time is written as in (A-24)

\[ A_0 = \varepsilon_1 [T(H_2O)_2^+] + \varepsilon_2 [T(OH)(OH_2)] \quad \ldots \quad (A-24) \]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the absorption coefficients of \( \text{Cr(salen)}(H_2O)_2^+ \) and \( \text{Cr(salen)}(OH)H_2O \) respectively. Substituting (A-20) and (A-18) in (A-24), equation (A-25) is obtained.

\[ A_0 = \frac{(\varepsilon_1 [H^+] + \varepsilon_2 K_a) M_T}{[H^+] + K_a} \quad \ldots \quad (A-25) \]

At any one \([H^+]\) and \([\text{Cr(III)}]\), the term \( \varepsilon_1 [H^+] + \varepsilon_2 K_a \) in equation (A-25) is a constant and therefore \( A_0 \) can be expressed as a function of \( \varepsilon_0 \) (an average absorption coefficient for a mixture of \( \text{Cr(salen)}(H_2O)_2^+ \) and \( \text{Cr(salen)}(H_2O)(OH) \) at a particular \([H^+]\) and denoted as \( A_0 = \varepsilon_0 M_T \). From (A-25), equation (A-26) is derived.

\[ \varepsilon_0 ([H^+] + K_a) = \varepsilon_1 [H^+] + \varepsilon_2 K_a \quad \ldots \quad (A-26) \]
The total absorbance at the attainment of the equilibration in the overall process shown in (A-15), is as shown in (A-27).

\[
A = \varepsilon_1 \left[ (\text{TH}_2\text{O})_2^+ \right] + \varepsilon_2 \left[ (\text{TOH}) \right] + \varepsilon_3 \left[ \text{TOH}_2\text{X} \right] + \varepsilon_4 \left[ \text{TOHX} \right]
\]

... (A-27)

where \( \varepsilon_3 \) and \( \varepsilon_4 \) are absorption coefficients for \([\text{Cr} \text{(salen)}(\text{OH}_2)^\text{X}]\) and \([\text{Cr} \text{(salen)}\text{OH} \text{X}^-]\) respectively. Substituting (A-16), (A-17) and (A-18) in (A-27) at any one \([\text{H}^+]\), (A-28) is obtained.

\[
A = \left( \varepsilon_1 [\text{H}^+] + \varepsilon_2 K_a + \varepsilon_3 K_1 [\text{X}^-] [\text{H}^+] + \varepsilon_4 K_a K_2 [\text{X}^-] \right) \left[ \text{TH}_2\text{O}_2^- \right][\text{H}^+]^{-1}
\]

... (A-28)

Replacing \([\text{T(OH}_2)_2^-]\) by \(M^\text{T}\) as in (A-23), (A-28) can be written as in (A-29).

\[
A = \frac{\left( \varepsilon_1 [\text{H}^+] + \varepsilon_2 K_a + \varepsilon_3 K_1 [\text{X}^-][\text{H}^+] + K_a \varepsilon_4 K_2 [\text{X}^-] \right) M^\text{T}}{[\text{H}^+] + K_a + K_1 [\text{X}^-][\text{H}^+] + K_a K_2 [\text{X}^-]}
\]

... (A-29)

The net absorbance change \((A-A_0) = \Delta A\), therefore is as in (A-30).
\[ \Delta A = \frac{(\varepsilon_1 [\text{H}^+] + \varepsilon_2 K_a) + \varepsilon_3 K_1 [X^-][\text{H}^+] + K_a \varepsilon_4 K_2 [X^-] M_T}{[\text{H}^+] + K_a + K_1 [X^-][\text{H}^+] + K_a K_2 [X^-]} \quad \varepsilon_o M_T \]

\[ \Delta A = \frac{(K_1 (\varepsilon_3 - \varepsilon_o) [\text{H}^+] + K_a K_2 (\varepsilon_4 - \varepsilon_o) [X^-]) M_T}{[\text{H}^+] + K_a + K_1 [X^-][\text{H}^+] + K_a K_2 [X^-]} \]

Substituting (A-26) in (A-30), (A-31) is obtained.

Denoting \( \Delta A (M_T)^{-1} \) as \( (\varepsilon_{\text{obs}} - \varepsilon_o) \) and \([\text{H}^+] + K_a \) as \( Q \)
\( [\text{H}^+] K_1 (\varepsilon_3 - \varepsilon_o) + K_a K_2 (\varepsilon_4 - \varepsilon_o) \) as \( R \) and \( K_1 [\text{H}^+] + K_2 K_a \) as \( S \) (A-31) can be written simply as in (A-32).

\[ (\varepsilon_{\text{obs}} - \varepsilon_o) = \frac{R [X^-]}{Q + S [X^-]} \quad \ldots \quad (A-32) \]

It follows that

\[ (\varepsilon_{\text{obs}} - \varepsilon_o)^{-1} = \frac{Q}{R [X^-]} + \frac{S}{R} \quad \ldots \quad (A-33) \]

and the plots of \( (\varepsilon_{\text{obs}} - \varepsilon_o)^{-1} \) against \( [X^-]^{-1} \) at any particular \([\text{H}^+]\) are linear and the ratio of intercept to slope gives \( S/Q \).
where \((S/Q)\) is therefore an apparent equilibrium constant, \(K_{\text{app}}\), for the equilibria involved in the overall process \((A-15)\).

Equation \((A-33)\) can be written as \((A-35)\).

\[
\frac{S}{Q} = \frac{K_1 [H^+] + K_2 K_a}{[H^+] + K_a} \quad \cdots \quad (A-34)
\]

\[
(\varepsilon_{\text{obs}} - \varepsilon_0)^{-1} = \left(\frac{1}{K_{\text{app}}[X]} + 1\right) \frac{1}{N} \quad \cdots \quad (A-35)
\]

and from the changes of absorbance for the equilibration involved in the overall process in \((A-15)\), an apparent equilibrium constant, \(K_{\text{app}}\), for the equilibration with a mixture of \([\text{Cr(salen)}(H_2O)_2^+]\) and its conjugate base can be calculated at each \([H^+]\). The values of \(K_1\) and \(K_2\) can be obtained by the treatment of \(K_{\text{app}}\) according to \((A-34)\).
APPENDIX II

TREATMENT OF DATA

A. Introduction

The rate of a reaction is assumed to be given by the rate of passage through a transition state, and a system in the transition state is an activated complex. Under most conditions the activated complex is in equilibrium with the reactants. The transition state theory\textsuperscript{169} gives the rate constant (k) for a simple bimolecular reaction expressed in the form of (T-1),

\[
k = \frac{P \cdot kT \cdot k^*}{h} \quad \ldots \quad (T-1)
\]

where \( k \) and \( h \) are Boltzmann's and Planck's constants respectively and \( k^* \) has the dimensions of an equilibrium constant (\( k^* \) is related to the true equilibrium constant for the activated complex \( K = [AB^*]/[A][B] \) by a factor of \( (2\pi m^* kT)^{\frac{1}{2}} (\delta / h) \) where \( m^* \) is the effective mass of the activated complex and defines the transition state configuration). The transmission coefficient, \( P \), is the probability of the activated complex proceeding to products and its value is taken to be unity. The parameters free
energy of activation $\Delta G^*$, activation enthalpy $\Delta H^*$ and
activation entropy $\Delta S^*$ are defined as in (T-2)

$$K^* = e^{-\Delta G^*/RT} = e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \quad \ldots \quad (T-2)$$

and hence (T-3) may be derived

$$k = \frac{kT}{h} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \quad \ldots \quad (T-3)$$

Rate constants, $k$, and activation parameters together with
their errors were generally evaluated using least-squares
computer programmes. Similarly whenever equilibrium constants
were measured by spectrophotometric methods, statistical
treatments using computer programmes were made.

The data for all the systems were computed using
computer programmes based on the Los Alamos Scientific
Laboratory report$^{152}$. They have been adapted for use in the
IBM 370 computer at the Iowa State University, Ames, Iowa,
by Dr. J.H. Epperson and his group workers$^{153}$. 
B. Computer Programme for Kinetic Parameters

The programme was used to analyse the kinetic data which conform to (T-4)

\[ k_{eq} = k_{-r} + k_{s} K_{a} [H^{+}]^{-1} + (k_{r} + k_{g} K_{a} [H^{+}]^{-1}) [\cdot]^{-1} \]  

... (T-4)

which can be rearranged to (T-5)

\[ k_{eq} = \frac{k_{-r} [H^{+}] + k_{s} K_{a} + k_{r} [H^{+}] [X^{-}] + k_{g} K_{a} [X^{-}]}{[H^{+}]} \]  

... (T-5)

One of the following polynomials, (T-6) and (T-7) were used to analyse the \( k_{eq} \) data.

\[ Y = \frac{\sum n_{i} P_{i+1} X_{1}^{P_{i+1}} X_{2}^{P_{i+2}}}{\sum n_{k} P_{k+1} X_{1}^{P_{k+1}} X_{2}^{P_{k+2}}} \]  

... (T-6)

\[ Y = \Sigma P_{i}^{(X)} P_{i+1}^{(X)} + \frac{n_{j} P_{j}^{(X)}}{\Sigma P_{k}^{(X)}} \]  

... (T-7)

By suitable choice of various constants in the above
equations, various systems investigated could be fitted to two subroutines.

The parameter, $k_{eq}$, in equations (T-4) to (T-9) were measured quantities and this data along with $[H^+]$, temperature, $[X^-]$ and estimates of equilibrium constant, individual rate constants and activation parameters $\Delta H^*$ and $\Delta S^*$ were used in computation. Estimates of activation parameters were obtained by rearranging (T-3) to (T-8)

$$\log \left( \frac{k}{T} \right) = 10.32 + \frac{\Delta S^*/R}{\Delta H^*/RT} \quad \ldots \quad (T-8)$$

and plotting $\log \left( \frac{k}{T} \right)$ against $1/T$, where $\log k / h = 10.32$ and $2.303R = 4.57$ kcal.mol.$^{-1}$ The LALS programmes solved one of the simultaneous equations in (T-6) and (T-7) and fitted the various quantities in a non-linear least-squares manner to one of the following expressions, whichever of these was applicable.

$$k_{-r} = \frac{kT}{h} e^{-\Delta H_{1}^*/RT} e^{\Delta S_{1}^*/K} \quad \ldots \quad (T-9)$$

$$k_{-s} K_2' = \frac{kT}{h} e^{-\Delta H_{2}^*/RT} e^{\Delta S_{2}^*/R} \quad \ldots \quad (T-10)$$
\[ k_r = \frac{kT}{h} e^{-\frac{\Delta H^*_3}{RT}} e^{\frac{\Delta S^*_3}{R}} \]  \hspace{1cm} \ldots \quad (T-11)

\[ k_{sK_a} = \frac{kT}{h} e^{-\frac{\Delta H^*_4}{RT}} e^{\frac{\Delta S^*_4}{R}} \]  \hspace{1cm} \ldots \quad (T-12)

An iterative procedure was used to obtain accurate values of activation parameters \( \Delta H^* \) and \( \Delta S^* \) with their standard errors.
APPENDIX III

Model Listings for the Treatment of $k_{eq}$ Data on the

A. Simultaneous fit of $k_{eq}$ data to two concentration variables, $[H^+]$ and $[NCS^-]$.

The rate data, $k_{eq}$, were fitted using an IBM 370 computer according to (T-6) of Appendix II. When NCS$^-$ is the coordinating ligand, the contribution of the $k_{eq}$ in eq. (T-4) of Appendix II is $\sim 10\%$. A satisfactory simultaneous fit of $k_{eq}$ to (T-6) was obtained as shown in the following example.
RATE CONSTANT VS CONCENTRATION

VALUE OF DETERMINANT = 1.12021E7

ITERATIONS

RATE CONSTANT VS CONCENTRATION

\[ y = f(x_1, x_2) = 5CLY - 5CLY + 5CLY \]


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EXACT LEAST SQUARES EQUATIONS

FITTED EQUATIONS

\[ y = 2.323E-03 \cdot x_1 - 2.323E-03 \cdot x_2 + 2.323E-03 \]

\[ y = 1.24E-04 \cdot x_1 - 1.24E-04 \cdot x_2 + 1.24E-04 \]

\[ y = 4.927E-04 \cdot x_1 - 4.927E-04 \cdot x_2 + 4.927E-04 \]

\[ y = 1.843E-04 \cdot x_1 - 1.843E-04 \cdot x_2 + 1.843E-04 \]

\[ y = 7.82E-05 \cdot x_1 - 7.82E-05 \cdot x_2 + 7.82E-05 \]

\[ y = 2.31E-04 \cdot x_1 - 2.31E-04 \cdot x_2 + 2.31E-04 \]

\[ y = 4.06E-04 \cdot x_1 - 4.06E-04 \cdot x_2 + 4.06E-04 \]

\[ y = 7.43E-04 \cdot x_1 - 7.43E-04 \cdot x_2 + 7.43E-04 \]

\[ y = 1.42E-03 \cdot x_1 - 1.42E-03 \cdot x_2 + 1.42E-03 \]

\[ y = 2.25E-03 \cdot x_1 - 2.25E-03 \cdot x_2 + 2.25E-03 \]

\[ y = 3.01E-03 \cdot x_1 - 3.01E-03 \cdot x_2 + 3.01E-03 \]

\[ y = 3.20E-03 \cdot x_1 - 3.20E-03 \cdot x_2 + 3.20E-03 \]

\[ y = 3.35E-03 \cdot x_1 - 3.35E-03 \cdot x_2 + 3.35E-03 \]

\[ y = 3.60E-03 \cdot x_1 - 3.60E-03 \cdot x_2 + 3.60E-03 \]

\[ y = 3.70E-03 \cdot x_1 - 3.70E-03 \cdot x_2 + 3.70E-03 \]

\[ y = 3.79E-03 \cdot x_1 - 3.79E-03 \cdot x_2 + 3.79E-03 \]

\[ y = 3.86E-03 \cdot x_1 - 3.86E-03 \cdot x_2 + 3.86E-03 \]

\[ y = 3.91E-03 \cdot x_1 - 3.91E-03 \cdot x_2 + 3.91E-03 \]

\[ y = 3.99E-03 \cdot x_1 - 3.99E-03 \cdot x_2 + 3.99E-03 \]

\[ y = 4.06E-03 \cdot x_1 - 4.06E-03 \cdot x_2 + 4.06E-03 \]

\[ y = 4.23E-03 \cdot x_1 - 4.23E-03 \cdot x_2 + 4.23E-03 \]

\[ y = 4.39E-03 \cdot x_1 - 4.39E-03 \cdot x_2 + 4.39E-03 \]

\[ y = 4.54E-03 \cdot x_1 - 4.54E-03 \cdot x_2 + 4.54E-03 \]

\[ y = 4.68E-03 \cdot x_1 - 4.68E-03 \cdot x_2 + 4.68E-03 \]

\[ y = 4.82E-03 \cdot x_1 - 4.82E-03 \cdot x_2 + 4.82E-03 \]
B. Stepwise fits of $k_{eq}$ data to the concentration variables $[H^+]$ and $[X^-]$.

The rate data, $k_{eq}$, were fitted to $[X^-]$ initially at each $[H^+]$ using an IBM 370 computer according to (T-7) of Appendix II also in cases where $k_{-r}$ was small in magnitude. The fit of $k_{eq}$ to $[X^-]$ at each $[H^+]$ gave the values of the forward rates $k_r[H^+] + k_sK_a$ (from the slope) and the reverse rates $k_{-r}[H^+] + k_{-s}K'_a$ (from the intercepts) which were denoted as $P_2$ and $P_1$ respectively. The analysis of $P_2$ and $P_1$ using (T-7) of Appendix II as a function of $[H^+]$, gave the individual values of $k_r$, $k_sK_a$, $k_{-r}$ and $k_{-s}K'_a$ along with their respective standard deviations as shown in the example. In general the method A was preferred.
MODEL LISTING FOR AZIDE SYSTEM

VALUE OF DETERMINANT = 3.23777756 E-01


3 ITERATIONS

MODEL LISTING FOR AZIDE SYSTEM

FUNCTION IS Y = POLY + POLY/POLY

THIS PROBLEM CONTAINS 0 DATA POINTS, 1 INDEPENDENT VARIABLES, AND 6 PARAMETERS. THE FIRST 0 VARIABLES WILL BE FITTED.


<table>
<thead>
<tr>
<th>K</th>
<th>GLE Estimate</th>
<th>Final Value of</th>
<th>Std. Err. of</th>
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</thead>
<tbody>
<tr>
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<td>1.3530465E+02</td>
<td>1.19625554E-03</td>
<td>1.1749786E-01</td>
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<tr>
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<tr>
<td>2</td>
<td>1.0000000E+00</td>
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MATRIX OF CORRELATIONS NOT CALLED FOR PARAMETERS

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<tr>
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<th>2</th>
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</thead>
<tbody>
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</tr>
<tr>
<td>2</td>
<td>-0.8511088</td>
<td>1.0000000E+00</td>
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MODEL LISTING FOR AZIDE SYSTEM

VALUE OF DETERMINANT = 3.23777756 E-01


3 ITERATIONS
RATE CONSTANT VS WEIGHT CONCENTRATION

<table>
<thead>
<tr>
<th>WEIGHT</th>
<th>x</th>
<th>DEPENDENT VARIABLE</th>
<th>INDEPENDENT VARIABLE</th>
<th>WEIGHTED DEPENDENT VARIABLE</th>
<th>UNWEIGHTED DEPENDENT VARIABLE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.00000E-02</td>
<td>5.00000E-02</td>
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<tr>
<td>3</td>
<td>1.00000E+00</td>
<td>1.00000E+00</td>
<td>1.00000E+00</td>
<td>1.00000E+00</td>
<td>1.00000E+00</td>
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<tr>
<td>4</td>
<td>2.00000E+00</td>
<td>1.00000E+00</td>
<td>2.00000E+00</td>
<td>2.00000E+00</td>
<td>2.00000E+00</td>
</tr>
</tbody>
</table>

MATRIX OF CORRELATIONS BETWEEN GIVEN VARIABLES

| 1   | 1.0000 | -0.857 | 0.994 |
| 2   | -0.857 | 1.0000 |
P ONE VS INVERSE ACID CONCENTRATION AZIDE
PLUE OF DETERMINANT = 1.92898455-11

3 ITERATIONS

P ONE VS INVERSE ACID CONCENTRATION AZIDE

NOTICE IS y = POLY + POLY + POLY

THIS PROBLEM CONTAINS 4 DATA POINTS, 1 INDEPENDENT VARIABLE(s), AND 6 PARAMETER(s) (4 OF WHICH MUST BE 0).


<table>
<thead>
<tr>
<th>KTH PARAMETER</th>
<th>KTH PARAMETER</th>
<th>KTH PARAMETER</th>
<th>KTH PARAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000000E+00</td>
<td>1.000000E+00</td>
<td>1.000000E+00</td>
<td>1.000000E+00</td>
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</tbody>
</table>

MATRIX OF CORRELATIONS BETWEEN ALL PARAMETERS

1  1.000  -0.657
2  -0.657  1.000

P ONE VS INVERSE ACID CONCENTRATION AZIDE

<table>
<thead>
<tr>
<th>WEIGHT</th>
<th>INDEPENDENT VARIABLE</th>
<th>DEPENDENT VARIABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000000E+00</td>
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<td>1.000000E+00</td>
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<tr>
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<td>1.000000E+00</td>
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<tr>
<td>5.125000E-01</td>
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<td>1.000000E+00</td>
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<tr>
<td>3.437500E-01</td>
<td>1.000000E+00</td>
<td>1.000000E+00</td>
</tr>
</tbody>
</table>
P THREE VS INVERSE ACID CONCENTRATION  

VALUE OF DETERMINANT = 1.53407E+04

3 ITERATIONS

P THREE VS INVERSE ACID CONCENTRATION  

FUNCTION IS Y = POLY + POLY/POLY

THIS PROBLEM CONTAINS 5 DATA POINTS, 1 INDEPENDENT VARIABLE(s) AND 5 PARAMETER(s) OF THE MODEL contains:


<table>
<thead>
<tr>
<th>SELECTED</th>
<th>KTH PARAMETER</th>
<th>FINAL VALUE</th>
<th>KTH PARAMETER</th>
<th>KTH PARAMETER</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>1.000000E+00</td>
<td>2.585683E-09</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.000000E+00</td>
<td>1.000000E+00</td>
<td>2.585683E-09</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.000000E+00</td>
<td>1.000000E+00</td>
<td>2.585683E-09</td>
<td></td>
</tr>
</tbody>
</table>

MATRIX OF CORRELATIONS BETWEEN FREE PARAMETERS

1 - 0.364  
2 - 0.364  1.000

P THREE VS INVERSE ACID CONCENTRATION  

<table>
<thead>
<tr>
<th>WEIGHT</th>
<th>INDEPENDENT VARIABLES</th>
<th>2.428544E-02</th>
<th>2.428544E-02</th>
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</thead>
<tbody>
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<td>5</td>
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<td>3.0000E+00</td>
<td>2.428544E-02</td>
</tr>
</tbody>
</table>