THIN-SOURCE CONCENTRATION
DEPENDENT DIFFUSION

VOLUME II

BY

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THESIS

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CHAPTER 8

RESULTS AND INTERPRETATIONS

I. Preliminaries

At the end of Chapter 6, Sec. V, the grand minimizing functional for the non-linear equation, capable of handling a multiple time correlation, was presented. Denoting a set of 'N' measured profiles by:

$$(S_1), (S_2), (S_3), \dots (S_N)$$

a "two-time" correlation examining the propagation $(S[\text{Initial}]) \rightarrow (S[\text{Final}])$ involves 1-term in the ϕ^2 -function. Thus, 'NK' terms in ϕ^2 is an "NK+1"-time correlation, composed of subunit 2-time correlations. Given 'N' measured profiles, many different correlations are possible. Some examples of "3-time" correlations would be:

Sequential:	$(S_1) \rightarrow (S_2); (S_2) \rightarrow (S_3)$	$S_1 \rightarrow S_2 \rightarrow S_3$
Alternating:	$(S_1) \rightarrow (S_3); (S_2) \rightarrow (S_4)$	$S_1 \rightarrow S_3, S_2 \rightarrow S_4$
Pinned:	$(S_2) \rightarrow (S_4); (S_3) \rightarrow (S_4)$	$(S_2, S_3) \rightarrow S_4$

(the last column being a shortened notation). Clearly for even 4 or 5 measured profiles, the totality of correlations, each of which is a separate non-linear analysis, is quite large. Thus, in this work, we will concentrate on the 'sequential' correlations, which should show how the non-linear effects change as the concentration decreases, and the 'pinned' correlations which show how easily a given final state is reached from various (different time) "initial" states.

Each subunit 2-time correlation uses an initial state $[C(x, \Gamma_0; k_j^0)]$ which is propagated forward to give a state $[C(x, \Gamma(k_j); k_j^0)]$ which can then be compared to a measured final state $[C(x, \Gamma_0; k_j)]$. As outlined in Chapter 6, the propagated state:

$$C(x, \Gamma(k_j); k_j^0) = \phi_0(x) + \alpha\phi_1(x) + \alpha^2\phi_2(x) + \beta\phi_3(x) \quad (8.01)$$

can be derived in accordance with 6 independent models; each model being a distinct calculation for the various correlations (p=pre-picked number):

Model	Code	D(C)-function	C(α, β)
(1).	<I000>	D_0	$\phi_0(x)$
(2).	<II00>	$D_0(1+\alpha C)$	$\phi_0(x) + \alpha\phi_1(x)$
(3).	<AII0>	$D_0(1+\alpha C)$	$\phi_0(x) + \alpha\phi_1(x) + \alpha^2\phi_2(x)$
(4).	<I00I>	$D_0(1+\beta C^2)$	$\phi_0(x) + \beta\phi_3(x)$
(5).	<AIII>	$D_0(1+\alpha C + \beta C^2)$	$\phi_0(x) + \alpha\phi_1(x) + \alpha^2\phi_2(x) + \beta\phi_3(x)$
(6).	<AIIZ>	$D_0(1+\alpha C + p\alpha^2 C^2)$	$\phi_0(x) + \alpha\phi_1(x) + \alpha^2[\phi_2(x) + p\phi_3(x)]$

Because the grand minimizing function $\phi^2(D)$ is a polynomial in both (α, β) , the best value of $\phi^2(D)$ for a given value of D is simply the root of a (cubic in α , quadratic in β) polynomial. A numerical calculation, in contrast, would involve first constructing successive "small" Δt advancements in time, calculating each next approximate profile. This would need to be done 'M' times (where 'M' is a large number) to give a finite time difference $(t_F - t_R)$ between the initial and final state $(M\Delta t = (t_F - t_R))$. This whole process would have to be repeated for each distinct value of (α, β) , while a search in the (α, β) -plane were performed. Each $\phi^2(D)$, which the analytical method reaches immediately, replaces this three dimensional numerical iteration.

At every value of D , a maximizing functional:

$$\Omega(D) \equiv (1/\phi^2(D))^{1/2} \equiv "[1/\text{MIN.FUNC.}]" \quad (8.02)$$

can be used to give a "goodness-of-fit" number (a value of $\Omega(D)=50$ matches the final state to 2%). Since the best-fit values $(D_o, \alpha(D_o), \beta(D_o))$ are to be determined, not only is the value $\Omega(D_o)$ important, but, also, the full analytic structure of the $\Omega(D)$ function, which shows how the best-fit value compares with other D -values. Concurrent with a determination of $\Omega(D)$, the analysis also gives the functions $\alpha(D)$ and $\beta(D)$.

As noted before (at the end of Chapter 4, Sec. II), because the non-linear equation cannot scale with concentration (to change total diffusant amount: $\int \tilde{C}(x, t_i) dx = N(i)$ is to change the values of $\alpha, \beta, \dots$), in this thesis, plots will be presented not of the normalization-dependent functions: $\alpha(D)$, $\beta(D)$, but of the normalization-independent functions:

$$\alpha_o(D) = \alpha(D)/\bar{N}; \quad \beta_o(D) = \beta(D)/\bar{N} \quad (8.03)$$

where $\bar{N}$ is an average normalization. Since each multiple time correlation is made of subunit 2-time correlations, the ' $\bar{N}$ ' will be the average for each individual correlation of the "initial" and "final" state 'areas'. Thus, with $C(x, \Gamma(k_j); k_j^o)$ representing the $(k_j^o)^{\text{th}}$ -state propagated forward to match the $(k_j)^{\text{th}}$ -state (via $\Gamma(k_j)$), the α_o and β_o for this correlation will then be:

$$\alpha_o N(k_j^o, k_j) = \alpha \quad (8.04a)$$

$$\beta_o [N(k_j^o, k_j)]^2 = \beta \quad (8.04b)$$

where the following definitions were used:

$$N(k_j^0, k_j) \equiv .5[N(k_j^0) + N(k_j)] \quad (8.05a)$$

$$\int \tilde{C}(x, t_k) dx \equiv N(k), \quad \int C(x, t_k) \equiv \hat{1}. \quad (8.05b)$$

In this manner, not only are all three parameters α_o, β_o, D_o made independent of state, but also a correction is made for the experimental situation of not having every state with equal diffusant amounts.

Since the parameter β_o has the same units as α_o^2 , the plots in this work will present graphs of $\Omega(D)$, $\alpha_o(D)$ and $\epsilon(D)$ where

$$\epsilon(D) \equiv [|\beta_o(D)|]^{1/2} \text{sign}(\beta_o(D)) \quad (8.06)$$

so that the ratio 'r' (Chapter 3, Sec. VI) is simply

$$r = \pm [\epsilon(D)/\alpha_o(D)]^2 \equiv \beta_o(D)/[\alpha_o(D)]^2. \quad (8.07)$$

All tabulated "ALPHA" and "BETA" values will be α_o and β_o values ($\epsilon(D)$ is plotted but not tabulated).

* * *

Not only can the functions $[\Omega(D), \alpha_o(D), \epsilon(D)]$ be obtained from this non-linear analysis, but, also, once the "best-fit" values $[D_o, \Omega(D_o), \alpha_o(D_o), \beta_o(D_o)]$ have been determined, one can take the measured initial-state profile, $C_R(x, t_R)$, and construct the propagated state profile: $C_R(x, t_F)$. This then can be directly compared pictorially to the measured final state $C_F(x, t_F)$. Since each propagated state can be written as Eq. (8.01), having values D_o, α_o, β_o allows one to plot the linear-equation part of the propagated state ($\phi_o(x, t) = \text{"order-1"}$) as well as each non-linear correction [$\alpha\phi_1(x, t) = \text{"order-}\alpha\text{"}$, $\beta\phi_3(x, t) = \text{"order-}\beta\text{"}$].

One can further do a simulation for other times 't' to examine how the propagated state $\hat{C}_R(x,t)$ behaves for times between t_R and t_F , as well as for times beyond t_F .

These comparisons (of $\hat{C}_R(x,t_F)$ with $C_F(x,t_F)$) and "simulations" (i.e., $\hat{C}_R(x,t)$ for general times 't') will often be presented as both [C vs. x]-plots and as [$\ln C$ vs. x^2]-plots, even though, as noted before, the $\phi^2(D)$ function inherently minimizes error on a [C vs. x]-plot; thus, large deviations must occur in the tail region of a [$\ln C$ vs. x^2]-graph.⁵²

* * *

We note that each raw data-fit for each experimental time ' t_R ' is written (see examples in Table <8.1>) in terms of the coefficients $B(2M)$ where:

$$C_R(x, t_R) = \sum B(2M) \hat{H}_{2M}(x/x_R) \exp-(x/x_R)^2 \equiv \sum B_p \hat{H}_{2p}(x/x_R) \exp-(x/x_R)^2 \quad (8.08)$$

$$\hat{H}_{2p}(y) \equiv (-1)^p H_{2p}(y) p!/(2p)!; \hat{H}_{2p}(0) = 1. \quad (8.09)$$

The $\hat{H}_{2p}$ representation is chosen so that convergence of the series can be easily ascertained from a scan of the $B(2M)$ -coefficients. Also [NPI, NPA, NPB] are used as universal designations of the number of polynomials, respectively, in each series: [order-1, order- α , order- $(\alpha^2$ or $\beta)$] and it represents a calculation involving (see Chapter 4, Sec. VIII) the following truncation of large 'p' values:

$$g(p, 1) \quad p=(0, \text{NPI}-1)$$

$$g(p, 2) \quad p=(0, \text{NPA}-1)$$

$$g(p, 3) \quad p=(0, \text{NPB}-1).$$

When "re-coupling" is done (Chapter 4, Sec. VII) giving a propagated state (see Eq. 4.90)

$$\hat{C}_R(x, t > t_R) = \sum_{m=0}^{m(\max)} G_m(\Gamma) H_{2m}(z) \exp -z^2, \quad (8.10)$$

$m(\max) \equiv NPI-1$ is consistently used. Since in principle $m(\max) \rightarrow \infty$, this is a possibly critical approximation which can be ameliorated in the following manner: If an $(NI+1)$ polynomial fit is a "good" fit to the experimental data: $\{B_0, B_1 \dots B_{NI}\} \neq 0$, one can force $NPI > (NI+1)$ by introducing and setting the following: $\{B_{NI+1}, \dots B_{NPI-1}\} \equiv 0$, which then allows a calculation where $m(\max) > NI$. We summarize this in a Polynomial Code (P.C.) which we can attach to any "state". It will be of the form:

State-label([NI+1], NPI, NPA, NPB)

as for example: "S1(4,6,9,9)". Finally, to keep our notation consistently interpretable, we note that 'NI' and 'N1' are used interchangeably to indicate number of non-gaussian terms in the raw experimental data-fit.

II. The S-dataset, Average Temperature: 674.2°C

The S-dataset represents the median temperature of this investigation. The 6-polynomial and 4-polynomial fits are given here (Fig. [8.1a] to [8.1d]). Direct comparison of the 4- and 6-polynomial fits (as by overlaying them, since they are plotted on same scale axes) would show that they are virtually identical on both a $[C \text{ vs. } x]$ -graph as well as on a $[\ln C \text{ vs. } x^2/t^*]$ -graph. Recall that t^* is a time which has been "warm-up" corrected. As given in Chapter 7 (Sec. I), throughout the data analysis, we choose:

$$t^* = t[\text{expt1.}] - .072[\text{tu-units}]. \quad (8.11)$$

We re-emphasize that t^* is used only for $[\ln C \text{ vs. } x^2/t^*]$ -graphing, and t^* is not used in any analyses.

The first calculations presented here used the following polynomial "code":

$$\text{P.C. (S-data)} = (4, 6, 9, 9).$$

Table <8.1> shows the actual information "file" that was used as input into the "program" outlined in Chapter 6.

* * *

A. The (S2)→(S3) Correlation

Fig. [8.2a] through [8.2f] show plots of $[\Omega(D) \text{ vs. } D]$, $[\alpha_o(D) \text{ (undashed line) vs. } D]$, and $[\epsilon(D) \text{ (dashed line) vs. } D]$ for each of the 6 models (I000, ..., AIIZ). There is a significant improvement in data-fitting for practically every non-linear model, including the I00I-model ($D(C) = D_o(1 + \beta C^2)$), which is a model not expected to be motivated by the

Figure 8.1a. This dataset is given the label 'S' in text. Average temperature: 674°C. The 6-polynomial fits to the raw data plotted on [C vs. x]-axes with individual profiles labelled as follows:

Label	Diffusion Time (tu*)	Temperature (°C)	Total Area [†] (Amt*)
S1	$t_1=0.810$	674.8	5.37
S2	$t_2=1.530$	673.9	5.08
S3	$t_3=2.97$	673.6	5.21
S4	$t_4=5.85$	674.4	6.00

[†]The 'Total Area' under the [C vs. x]-curve corresponds to the prediffusion surface concentration of impurity atoms.

*Throughout this chapter, the units used to label axes are:

Distance: 1 xu = 10⁻⁶ μm

Time: 1 tu = 10⁻⁴ sec.

Diffusivity: 1 du = 10⁻¹⁰ cm²/sec = 1 xu²/tu

Concentration: 1 cu = 1 nanomole/cm² micron = 1 Amt./xu

Total Area: 1 Amt. = 10⁻¹⁰ nanomoles/cm² = 6.023 × 10¹⁵ Atoms/cm²

Figure 8.1b. [$\ln C$ vs. x^2/t^*]-plot of the 6-polynomial fits to the raw data in the 'S'-dataset. Recall 't*' is a "warm-up corrected" time used only for graphic presentation where:

$$t^* = t(\text{exptl.}) - .072(tu)$$

On these axes, gaussian profiles and constant diffusivity would have plotted as a family of parallel straight lines.

Fig. 8.1 Raw data-fits

Figure 8.1c and 8.1d. These show the 4-polynomial fits to the raw data in the 'S'-dataset. These are virtually indistinguishable from the 6-polynomial fits.

Fig. 8.1 Raw data-fits

```

4  =#DATASETS TO CORRELATE
***
CA-A-S1      =SAMPLE LABEL (3A5)
7-10-77; 12:03 =DATE & TIME SAMPLE IN FURNACE (15A1)
      0100 SEC =FURNACE DURATION
      948.00   =FURNACE TEMP; DEG. KELVIN
      56, 80   =#SLICES:DATA-KEPT&W/TAI
      8.93374/ =XR PARAMETER OF CHOICE
      8.9337, .1044 =XRC+/-JDX, XR=LIMITING SLOPE
3  =MODE: 1=STD.H(2M) 2=HH(2M)COEF(X**2)=1 3=H0(2M)=(1,X=0)
1  =#-SERIES REP.STATE
6  =NPI =#POLYNS IN FIT; MODE=(3)
      .27007662E-01 =RESIDUAL ERROR (FRACTIONAL)
      .53754562E+01 =TOTAL AREA (RNZ-COEFF)
      .63152624E-01 =B( 0)
      -.23186433E-02 =B( 2)
      .12019651E-02 =B( 4)
      .40979327E-03 =B( 6)
      .00000000E+00 =B( 8)
      .00000000E+00 =B(10)
9  =NPA (POLYNS ORDER ALPHA)
9  =NPB (POLYNS ORDER BETA)
***
CA-A-S2      =SAMPLE LABEL (3A5)
7-21-77; 12:13 =DATE & TIME SAMPLE IN FURNACE
      15300 SEC =FURNACE DURATION
      947.10   =FURNACE TEMP; DEG. KELVIN
      51, 73   =#SLICES:DATA-KEPT&W/TAI
      9.191900 =XR PARAMETER OF CHOICE
      9.1919, .0297 =XRC+/-JDX, XR=LIMITING SLOPE
3  =MODE: 1=STD.H(2M) 2=HH(2M)COEF(X**2)=1 3=H0(2M)=(1,X=0)
1  =#-SERIES REP.STATE
6  =NPI =#POLYNS IN FIT; MODE=(3)
      .16160932E-01 =RESIDUAL ERROR (FRACTIONAL)
      .50792063E+01 =TOTAL AREA (RNZ-COEFF)
      .61378998E-01 =B( 0)
      -.16351757E-01 =B( 2)
      .25723208E-02 =B( 4)
      .12516010E-02 =B( 6)
      .00000000E+00 =B( 8)
      .00000000E+00 =B(10)
9  =NPA
9  =NPB
***
CA-A-S3      =SAMPLE LABEL (3A5)
7-21-77; 00:19 =DATE & TIME SAMPLE IN FURNACE
      29700 SEC =FURNACE DURATION
      946.80   =FURNACE TEMP; DEG. KELVIN
      62, 87   =#SLICES:DATA-KEPT&W/TAI
      12.001952 =XR PARAMETER OF CHOICE
      12.0020, .1779 =XRC+/-JDX, XR=LIMITING SLOPE
3  =MODE PARAMETER
1  =#-SERIES REP.STATE
6  =NPI =#POLYNS IN FIT; MODE=(3)
      .16978628E-01 =RESIDUAL ERROR (FRACTIONAL)
      .52174384E+01 =TOTAL AREA (RNZ-COEFF)
      .47008153E-01 =B( 0)
      -.14391853E-01 =B( 2)
      .20719210E-02 =B( 4)
      .35402489E-03 =B( 6)
      .00000000E+00 =B( 8)
      .00000000E+00 =B(10)
9  =NPA
9  =NPB
***
CA-A-S4      =SAMPLE LABEL (3A5)
7-19-77; 23:54 =DATE & TIME SAMPLE IN FURNACE
      58500 SEC =FURNACE DURATION
      947.60   =FURNACE TEMP; DEG. KELVIN
      67, 103  =#SLICES:DATA-KEPT&W/TAI
      16.782661 =XR PARAMETER OF CHOICE
      16.7827, .0965 =XRC+/-JDX, XR=LIMITING SLOPE
3  =MODE PARAMETER
1  =#-SERIES REP.STATE
6  =NPI =#POLYNS IN FIT; MODE=(3)
      .17375786E-01 =RESIDUAL ERROR (FRACTIONAL)
      .59934851E+01 =TOTAL AREA (RNZ-COEFF)
      .33617410E-01 =B( 0)
      -.67245987E-02 =B( 2)
      -.35521803E-04 =B( 4)
      -.34479869E-03 =B( 6)
      .00000000E+00 =B( 8)
      .00000000E+00 =B(10)
9  =NPA
9  =NPB
***

```

physics presented in Chapter 3. What is surprising is that the AIIZ-model $\{D(C) = D_0(1+\alpha C+5(\alpha C)^2); 'C' \text{ calculated to order-}\alpha^2\}$ is the poorest fit, aside from the linear equation. This AIIZ-model, recall, is the closest approximation to the 'standard' model of:

$$D(C) = D_0 \{(\alpha C) + [1+(\alpha C)^2]^{1/2}\}. \quad (8.12)$$

The full order- (α^2, β) [AIII]-model also has two distinct "peaks", although one is "sharper". This means that there are two alternate sets of values which seem to match the data. Whereas one believes that a unique value of $(D_0, \alpha_0, \beta_0 \dots)$ is driving the physical system, that condition only necessitates that at those particular values, the fit is "good". Unfortunately, "spurious" additional "good-fits" are not disallowed.

Applying the criterion that, sharp peaks in $\Omega(D)$ aside, any value of $\Omega(D) > 100$ (1% datafit) must be regarded as qualitatively consistent with our experimental data, examining Fig. [8.2e] (the AIII-model) shows that the entire range $D=(13, 28+)$ is a "window" of allowed D_0 values. This requires the utmost caution for those who would do a numerical calculation. Here, the analytic method presents an order-by-order analysis, and it gives a very clear relationship between the approximations used in the calculation of the propagated state, $\hat{C}_R(x, t)$, and the approximations used in the $D(C)$ function. The main difficulty in a numerical calculation is that the degree of approximation in the final (numerically) propagated state is not known. It possibly could be as good as only a first order analytic calculation. Or worse, because of the large "window" of allowed values found by the analytic method, a numerical method, being more restricted, may falsely converge on a given D -value in this window and

Figures 8.2a through 8.2f. These show the results of the S2(4,6,9,9)→S3(4,6,9,9) correlation. The numbers, "(4,6,9,9)", correspond to numbers of polynomials at which series were truncated, as explained in the text.

The individual figures plot [Ω vs. D]; D =diffusivity and Ω =maximizing functional, with peaks in Ω and the associated values of α_0 and ϵ denoted by a small cross (+). Each figure (8.2a, 8.2b,...) corresponds to one of 6 possible models:

Model	$D(C)$	Comments
I000	D_0	Linear equation
I00I	$D_0(1+\beta C^2)$	$D(C)$ is a quadratic diffusivity NOT motivated by Chapter 3; $\alpha_0=0$
II00	$D_0(1+\alpha C)$	$C(x,t)$ calculated to order (α); $\beta_0=0$
AIIO	$D_0(1+\alpha C)$	$C(x,t)$ calculated to order (α^2); $\beta_0=0$
AIII	$D_0(1+\alpha C+\beta C^2)$	$C(x,t)$ calculated to order (α^2, β); α and β are free parameters
AIIZ	$D_0(1+[\alpha C]+.5[\alpha C]^2)$	Power series expansion of the 'Standard' $D(C)$ model; $\beta_0=.5\alpha_0^2$

The [Ω vs. D]-plot has a purely numerical vertical scale, and a horizontal scale set in diffusivity units ($1 \text{ du}=10^{-10} \text{ cm}^2/\text{sec}$). A value $\Omega=50$ corresponds to the 'S2'-state, propagated, matching the 'S3'-datafit curve to 2%; $\Omega=100$ corresponds to a 1% match.

For each D -value, the best $\alpha_0(D)$, $\epsilon(D)$ values are also plotted. Recall:

$$\epsilon(D) \equiv [|\beta_0(D)|]^{1/2} \text{sign}[\beta_0(D)]$$

so that $\epsilon(D)$ and $\alpha_0(D)$ have the same units, which are inverse concentration (concentration being in cu-units; $1 \text{ cu}=1 \text{ nanomole}/\text{cm}^2 \text{ microns}$). Also note that it is the normalization-independent non-linearity parameters, $\alpha_0(D)$ and $\epsilon(D)$, that are being plotted. The horizontal axis is the same as for the $\Omega(D)$ -function.

Throughout the rest of this chapter, the $\alpha_0(D)$ and $\epsilon(D)$ plots will have the same vertical scale as here, with the same range: $(-25, +25)$.

Fig. 8.2 $S2(4,6,9,9) \rightarrow S3(4,6,9,9)$

Fig. 8.2

present that value as a unique answer, but it would then be a value primarily determined by the approximations of the numerical procedure.

As given earlier, once a "best-fit" set of values ($\Omega(D_0)$, D_0 , $\alpha_0(D_0)$, $\beta_0(D_0)$) has been found, the actual propagated state $\hat{C}_R(x, t_F)$ can be constructed from $C_R(x, t_R)$. This is shown in Fig. [8.3a] and [8.3b] using the (S2)→(S3) correlation; [8.3a] showing the linear-contribution compared to the total of the 3 non-linear contributions; [8.3b] plotting each non-linear contribution separately. The order- α part is seen to "move" additional atoms from a region of high concentration to a region of lower concentration. The order- α^2 term is seen to "redistribute" matter from regions of high gradients to regions of lower gradients. The order- β term is small in this case and seems not as easily amenable to direct interpretation. One also sees a tendency towards cancellation of the various non-linear terms. The order- α term by itself, near $x=0$, is about a 10% correction on the concentration, the total non-linear correction being about 7%.

Table <8.2> presents the (S2)-initial-state as:

$$C_R(x, t_R) = \sum_{IP=1} G1(IP) H_{2(IP-1)}(x/x_R) \exp-(x/x_R)^2 \quad (8.13)$$

as well as a direct representation of the (S2)-propagated state evaluated at $\Gamma(D_0)=1+4D_0(t_F-t_R)/x_R^2$ (best-fit, AIII-model):

$$\hat{C}_R(x, t_F) = \sum_{IP=1} \{G1(IP) + \alpha_0 G2(IP) + \alpha_0^2 G3A(IP) + \beta_0 G3B(IP)\} \times H_{2(IP-1)}(x/x_N) \exp-(x/x_N)^2 \quad (8.14)$$

where $x_N^2 = \Gamma x_R^2$ and where the normalization (dependence on $\bar{N}$ with $\alpha \equiv \alpha_0 \bar{N}$, $\beta \equiv \beta_0 \bar{N}^2$) has been shifted from (α, β) into the functions $(G2, G3A, G3B)$.

Figures 8.3a and 8.3b. S2(AIII-propagated). This presents the propagated function, beginning with the 'S2'-datafit, using the best (D_0, α_0, β_0) values found using the AIII-model. As outlined in the text, every propagated state, to order- (α^2, β) , can be written as:

$$\hat{C}_R(x, t) = \phi_0(x, t) + \alpha\phi_1(x, t) + \alpha^2\phi_2(x, t) + \beta\phi_3(x, t).$$

The $\phi_0(x, t)$ is the linear part (denoted "L.P." in Fig. 8.3a). The other three non-linear contributions, added together, are also plotted (and denoted "N.L." in Fig. 8.3a). Each non-linear contribution is also plotted separately on an expanded scale (Fig. 8.3b), along with the notation.

$$\theta(\alpha) = [\text{order-}\alpha] \equiv \alpha\phi_1(x, t)$$

$$\theta(\alpha^2) = [\text{order-}\alpha^2] \equiv \alpha^2\phi_2(x, t)$$

$$\theta(\beta) = [\text{order-}\beta] \equiv \beta\phi_3(x, t)$$

$$\theta(1) = [\text{order-}1] \equiv \phi_0(x, t)$$

The vertical scale is concentration; the horizontal scale is distance (xu-units). Both Fig. 8.3a and 8.3b have identical horizontal axes, so only the lower axis is labelled. Similar plots, using the exact same abbreviations as introduced here, appear throughout Chapter 8.

Note that the non-linear effects (Fig. 8.3b) tend to be of opposite sign, thus partially cancelling. This is found to be consistently so throughout most of this analysis. In this particular case, because the order- β contribution is small, and comparable in size to the experimental errors, a β -value cannot be assigned with confidence.

Fig. 8.3 S2(AIII-propagated)

TABLE 8.2

(S2)-DATAFIT STATE

GAMMA= 1.00000 NPOLY= 6 XN= 9.19190

IF	G1(IP)	G2(IP)	G3A(IP)	G3B(IP)
1	.6138E-01	0.0	0.0	0.0
2	.8176E-02	0.0	0.0	0.0
3	.2144E-03	0.0	0.0	0.0
4	-.1043E-04	0.0	0.0	0.0
5	.0000E+00	0.0	0.0	0.0
6	.0000E+00	0.0	0.0	0.0

G1, G2, G3A, G3B COEFFICIENTS EVALUATED AT X=0.0:

1	.6138E-01	0.0	0.0	0.0
2	-.1635E-01	0.0	0.0	0.0
3	.2572E-02	0.0	0.0	0.0
4	.1252E-02	0.0	0.0	0.0
5	.0000E+00	0.0	0.0	0.0
6	.0000E+00	0.0	0.0	0.0

ALPHA= .3534E+01

BETA=-.2414E+01

(S2)-PROPAGATED FOWARD

GAMMA= 1.99809 NPOLY+ 6 XN= 12.99312

1	.4342E-01	.0000E+00	.0000E+00	.0000E+00
2	.2895E-02	.4247E-03	-.5333E-05	.9336E-04
3	.3798E-04	-.2334E-04	.2415E-05	.1550E-04
4	-.9250E-06	.6495E-06	-.2220E-06	.5866E-07
5	.0000E+00	-.1267E-07	.1128E-07	.5188E-08
6	.0000E+00	.2138E-09	-.3986E-09	-.1742E-09

G1, G2, G3A, G3B COEFFICIENTS EVALUATED AT X=0.0:

1	.4342E-01	.0000E+00	.0000E+00	.0000E+00
2	-.5789E-02	-.8493E-03	.1067E-04	-.1867E-03
3	.4558E-03	-.2801E-03	.2898E-04	.1860E-03
4	.1110E-03	-.7794E-04	.2664E-04	-.7039E-05
5	.0000E+00	-.2128E-04	.1894E-04	.8715E-05
6	.0000E+00	-.6465E-05	.1205E-04	.5266E-05

ALPHA= .3534E+01

BETA=-.2414E+01

Fig. [8.4a] and [8.4b] present on both $[C \text{ vs. } x]$ -axes and $[\ln C \text{ vs. } x^2]$ -axes, the comparison between the (S2)-propagated and (S3)-datafit states. On the $[C \text{ vs. } x]$ -plot, they are indistinguishable, with only a small "tail" deviation on a $[\ln C \text{ vs. } x^2]$ -plot.

For comparison to this AIII-model ($D_o=14.64$, $\alpha_o=3.53$, $\beta_o=-2.41$, $\Omega(D_o)=2810.$), the best linear equation fit is given next ($D_o=20.7$, $\Omega(D_o)=36.8$), again comparing the (S2)-propagated-(linear equation) and the (S3)-datafit states (Fig. [8.5a], [8.5b]). The most striking characteristic of this "best" linear equation fit is the extraordinary lack of curvature on the $[\ln C \text{ vs. } x^2]$ -plot of the propagated state (Fig. [8.5b]).

In Fig. [8.4c], we present on a $[\ln C \text{ vs. } x^2/t^*]$ -plot, the results of a simulation. Starting from the (S2)-state (time $t_2=1.53$), using the best-fit values of (D_o, α_o, β_o) as derived from the AIII-model (S2) $\rightarrow$ (S3) correlation, Fig. [8.4c] shows the profile obtained from propagating forward in time, as well as a small amount backward in time ($t_{1.5}=1.109$).

The times used are:

$$t_{1.5}=1.109, \quad t_2=1.53, \quad t_3=2.97, \quad t_4=5.85, \quad t_5=11.59, \quad t_6=23.04$$

and these times almost exactly obey (for "corrected" times $t^*=t-.072$), the relationship.

$$t_{.5(n+m)}^* = [t_n^* t_m^*]^{1/2} \quad (8.15)$$

as was the intent when the original experimental times (t_2, t_3, t_4) were chosen. The actual (S3)-datafit is also shown for comparison to the (S2)-propagated states.

Fig. [8.5c] shows the same simulation (for the same set of times as the AIII-model simulation), except it uses the D_o -value derived from

Figure 8.4a. The S2-propagated state, using the AIII-model [quadratic (in C) diffusivity, 'C' calculated to order- (α^2, β)], is compared to the polynomial fit to the raw dataset 'S3'. The best-fit values found from the non-linear analysis were used to construct S2-propagated, and they were:

$$D_0 = 14.64, \alpha_0 = 3.53, \beta_0 = 2.41, \Omega = 2810.$$

"S2(prop.)" is an abbreviation for 'S2-propagated' and "S3(data.)" is an abbreviation for 'S3-datafit'. In this case, the propagated and datafit curves are indistinguishable, on [C vs. x]-axes, so only one curve appears on the plot.

The lower part of Fig. 8.4a (and 8.4b) uses the same horizontal axis as the (respective) upper part of each figure. In Fig. 8.4a, the vertical scale, labelled " Δ_1 " corresponds to the fractional deviation of the propagated-(initial)-state compared to the datafit-(final)-state. Thus,

$$\Delta_1 \equiv 1 - [C(x, \text{propagated}) / C(x, \text{datafit})],$$

or, using the notation of the text: $\Delta_1 \equiv 1 - \hat{C}_R(x, t_F) / C_F(x, t_F)$. A value of $\Delta_1 = .01$ corresponds to a 1% deviation, $\Delta_1 = .05$ corresponding to a 5% deviation. The [Δ_1 vs. x]-plot has a horizontal line drawn at $\Delta_1 = 0.0$.

Figure 8.4b. This plots the same functions as Fig. 8.4a, but on a [$\ln C$ vs. x]-axes, emphasizing "curvature" or the non-gaussian properties of a profile. It also emphasizes the deep-penetration region where, as noted in the text, a deviation is expected because of the minimizing function $\phi^2(D)$ used. In the lower part of Fig. 8.4b, the vertical scale, labelled " Δ_2 ", corresponds to:

$$\Delta_2 \equiv \ln[C(x, \text{propagated}) / C(x, \text{datafit})],$$

or, in the text notation: $\Delta_2 \equiv \ln[\hat{C}_R(x, t_F) / C_F(x, t_F)]$. The vertical axis for Δ_2 , consistently is unlabelled, and corresponds exactly to the Δ_1 axis marking, i.e., in Fig. 8.4b, the Δ_2 -scale are $(-.01, +.01)$. A horizontal line of $\Delta_2 = 0.0$ is also drawn.

Throughout this chapter, a plot on [C vs. x], [$\ln C$ vs. x^2], or [$\ln C$ vs. x^2/t^*]-axes will use the representation:

solid line = forward (in time) propagation of a given initial state

dashed line = polynomial raw-data fit

dotted line = backward (in time) propagation of a given initial state.

As noted in the text, this method does not converge for backward-time propagation, and these dotted curves emphasize that result

Figure 8.4c. This shows the propagation of the 'initial' state (here, the 'S2'-state, at time $t_2 = 1.530$; curve denoted by "(S2): t_2 " in figure) for the various times:

$$t_{1.5} = 1.109, t_3 = 2.97, t_4 = 5.85, t_5 = 11.59, t_6 = 23.04$$

as detailed in text. Plotted also, for comparison, is the 'final' state datafit (here, the 'S3'-state, at time $t_3 = 2.97$; curve denoted by "(S3): t_3 " in figure). This propagation uses the same model and values of the parameters as Fig. 8.4a. Note that as a non-linear propagation (AIII-model), as one progresses in time, a family of 'curved'-profiles (on [$\ln C$ vs. x^2/t^*]-axes) are generated. The dot-dash line shows $D_0 = 14.64$ and one sees the longer time limiting slopes are not far from this value.

Fig. 8.4 S2(AIII-prop.) vs. S3

Figure 8.5a and 8.5b. For comparison to Figure 8.4, these show the best linear-equation fit ("I000-model"), using the best-values found of:

$$D_0 = 20.7, \quad \Omega(D_0) = 36.8,$$

which is a 3% fit. Although the magnitude of this deviation does not appear as large on a $[C \text{ vs. } x]$ -plot, the propagated profile has the wrong shape, as seen easily in Fig. 8.5b, which is a $[\ln C \text{ vs. } x^2]$ -plot. The $[\ln C]$ -plot shows a clear tendency for the best linear equation fit to match the initial slope.

Figure 8.5c. This shows the propagation of the S2-state using the best D_0 -value obtained from the non-linear analysis (AIII-model), which was $D_0=14.64$, but where the non-linearity parameters have been set to zero. This plot is on the same axes as Figure 8.4c, with the same simulated times. Comparison of Fig. 8.4c with 8.5c clearly shows the effect of the non-linear corrections. Not only are the non-linear penetrations deeper, but the linear equation propagation shows a family of almost gaussian curves, whereas the non-linear propagation shows a persistence of curvature, as explained in the text.

Fig. 8.5 S2(1000-prop.) vs. S3

the AIII-model, and has all the non-linear parameters set to zero. Again, as with (S2)-propagated state of Fig. [8.5b], one sees the linear equation propagation converging into a gaussian very rapidly. In contrast, the AIII-model, for forward time-propagation, shows a neat family of curved penetration profiles, even noticeable in the longest simulated time ($t_6 = 23.04$) which is 4 times longer than the longest experimental time chosen (at this temperature). This persistence of curvature in the AIII-model (and it should appear in all the non-linear models), and its conspicuous "absence" in the linear-equation simulation (it is there, as seen with the aid of a straight-edge, but greatly reduced, compared to the non-linear cases) is primarily the manifestation of the fact that the non-gaussian terms in the linear equation solution ($q_p = B_p H_{2p} (x/x_R)^2$) decay as ($t^{-p-1/2}$); but every non-gaussian q_p -term, in every non-linear model, acquires a leading term that decays as ($t^{-3/2}$).

One also sees in the AIII-model a strong "dip" in the profile on a [$\ln C$ vs. x^2/t^*]-graph for the backward-time propagation (time: $t_{1.5} = 1.109$ this is an attempt to run time "backwards" from the (S2)-state). On a [C vs. x]-graph, this strong "dip" would appear as a "double-hump" (peak and shoulder) in the penetration profiles at large concentrations (near $x=0$). As state (S1) (time = $t_1 = .810 < t_{1.5}$) was measured and shows none of this "double-hump" structure, it is an indication that this procedure [which begins with a measured initial state profile $C_R(x, t_R)$ and constructs a propagated profile $\hat{C}_R(x, t)$ for $t > t_R$], even though it is analytically continuable into the $t < t_R$ domain, does not converge to the "physical" profile for $t < t_R$. The reason for this is that the propagated state (as seen in Chapter 6) is expressed as a series analogous to a series in ($t^{-n}, n \geq .5$),

and the large 'n' terms in this series, which decay faster and faster in a forward-time propagation, become unstable (arbitrarily large) in a backward-time propagation.

* * *

The physical models presented in Chapter 3 to describe the expected concentration-dependent diffusion of $\text{Ca}^{++} \rightarrow \text{NaCl}$ seemed to allow 'r' values (Eq. (8.07)) of either $r=0$ or $.4 \leq r \leq .5$. The (S2)→(S3) correlation not only gives a poor fit to the 'standard' model ($r=.5$), but because $\epsilon(D) < 0$ in the AIII-model, one has here that $r < 0$. As this solution has a $\beta(D_0)$ contribution that is small compared to the order- α and order- α^2 terms, judgement as to whether this is a physical $\beta_0 < 0$ situation or not will be reserved till more correlations and analyses for different temperatures are presented. The local maxima in $\Omega(D)$ (Fig. [8.2a] to [8.2f]), and the associated $\alpha_0(D)$, $\epsilon(D)$ values at those points, are denoted by a cross (+). The list of these "best-fit" values are presented as a part of Table <8.3> under the sub-heading "S2(4,6,9,9)→S3(4,6,9,9)." The table shows, for the AIII-model:

$$r(\text{S2} \rightarrow \text{S3}) = -.193.$$

Aside from whether $\beta_0 < 0$ is reasonable or not, especially allowing for the fact that this method is essentially perturbative and the β_0 contribution might not be accurate until a calculation to order ' γ ' is done [i.e., $D(C) = D_0(1 + \alpha C + \beta C^2 + \gamma C^3)$ or $D_0(1 + \alpha C + \beta C^2 + \gamma C^4)$ for approximating models as $D(C) = D_0(\alpha C + [1 + (\alpha C)^2]^{1/2})$ which have no γC^3 term], one thing that is required for these systems (as $\text{Ca}^{++} \rightarrow \text{NaCl}$) is that $\alpha > 0$. These "global" restrictions (as $\alpha > 0$ or $\beta > 0$) can easily be handled within the framework of this analysis.

Figure 8.6a. This figure shows, co-plotted on the same axes, the maximizing function, $\Omega(D)$, for various non-linear diffusion models.

Figure 8.6b and 8.6c. These show the effect of global restrictions on the non-linearity parameters (e.g., $\alpha > 0$ or $\beta > 0$), as explained in the text.

NOTE: Figures 8.7 through 8.46 are explained in the text, but the axes and labelling exactly follow the forms presented in Figures 8.1 through 8.6, thus, separate captions are not given for most of the following graphs.

Fig. 8.6

An unrestricted non-linear parameter (as α or β) might give rise to a local maximum in $\Omega(D)$ for some 'unphysical' (outside the domain of a given model) value of the non-linearity parameter. In these cases, setting the parameter to the last "physically acceptable" value gives the proper modified $\Omega(D)$ values. Specifically, given $\alpha(D) > 0$, then when α would have gone negative, it is set to zero, giving a transition from an AIII-model to an IOOI-(pure β)-model. Similarly a $\beta > 0$ restriction, when β would have gone negative, on being replaced by $\beta = 0$, gives a transition from an AIII-model to an AII0-model. Fig. [8.6a] to [8.6c] show this restriction as applied to the AIII-model, ($S_2 \rightarrow S_3$) correlation. In Fig. [8.6a], the $\Omega(D)$ for the various models are co-plotted. In [8.6b], the $\alpha > 0$ is applied. The sharp break in the resultant $\Omega(D)$ is a result of the sharp drop-off in $\Omega(D)$ -IOOI-model function. At the change-in-models point, $\Omega(D)$ is both continuous with a continuous slope. This continuity is shown in its less striking manner with a $\beta > 0$ restriction (Fig. [8.6c]). Here, the transition point is barely noticeable, but it has changed the global $\Omega(D)$ maximum in Fig. [8.6c].

A final point worth mentioning (see Fig. [8.2e]) is the spontaneous generation of additional curves on the $\alpha_0(D)$ and $\epsilon(D)$ plots, characteristically involving the AIII-model. Recalling (Chapter 6, Sec. V) that $\phi^2(D)$ to order- (α^2, β) is inherently a quartic in α , quadratic in β expression, one determines α by the roots of a cubic. When the cubic has 3 real roots, three β values and $\Omega(D)$ values will also be generated. This appears as sudden "side-branches" on the $\alpha_0(D)$ and $\epsilon(D)$, as well as on the $\Omega(D)$ plots. The α -values, as roots of a cubic, guarantee only a local extremum in $\phi^2(D, \alpha)$ which, as a quartic in ' α ', means 2 local minima and one local

maximum in ϕ^2 (as a function of α for a given value of 'D'). Characteristically, one of the 2 local minima and the local maximum correspond to such large values of ϕ^2 that they are totally ignorable minimum values on an $\Omega(D)$ plot. The $\Omega(D)$ will show, then, as a function of D, the characteristic one physically relevant branch and two ignorable side branches (even though the 'relevant' branch may have its own maxima and minima as a function of D).

* * *

Having presented the full $S2(4,6,9,9) \rightarrow S3(4,6,9,9)$ calculation, we next present two cognates to it. It was originally thought that to maintain a consistent level of approximation, $NPI \equiv Nl$ could always be taken (see Eq. (8.08) to (8.101)). Since the 4 and 6 polynomial raw datafits seemed virtually indistinguishable, whether $Nl=4$ or $Nl=6$ was taken should not matter in terms of any analysis, since they pictorially represent the same state accurately. The $\Omega(D)$ functions for the correlations:

$$S2(4,4,8,8) \rightarrow S3(4,4,8,8); \quad S2(6,6,9,9) \rightarrow S3(6,6,9,9)$$

are given in Fig. [8.7] and [8.8] respectively, with the $\alpha_o(D)$ and $\epsilon(D)$ functions also shown for the AIII- and AIIZ-models. The $\Omega(D)$ are quite similar except for the AIII-model where the major difference (in the region important to $\Omega(D)$) is in the $\epsilon(D)$ functions.

Comparing both to the previous $S2(4,6,9,9) \rightarrow S3(4,6,9,9)$ calculation, one finds that the $\alpha_o(D)$ and $\epsilon(D)$ are practically identical for the (4,6,9,9) and the (6,6,9,9) calculation, the $\Omega(D)$ functions being the same shape but with possibly a difference in height, but giving similar D_o -values. The real difference, then, is not due to $Nl=(\# \text{ polynomials in datafit states})$ but rather to different NPI-values, i.e., to different truncations at the

Fig. 8.7 $S2(4,4,8,8) \rightarrow S3(4,4,8,8)$

Fig. 8.8 $S2(6,6,9,9) \rightarrow S3(6,6,9,9)$

"recoupling" stage (Chapter 4, Sec. VII); thus, some care must be exercised in the 'NPI'-choice.

Table <8.3> lists the "best-fit" values of the (S2)→(S3) correlation for each of the 3 calculations: P.C.=(4,4,8,8), P.C.=(4,6,9,9) and P.C.=(6,6,9,9), giving all local maxima of $\Omega(D)$ and the associated (D_o, α_o, β_o) -values, the last column indicating if an $\alpha_o > 0$ or $\beta_o > 0$ restriction was applied.

In most of the following work (beyond the (S2)→(S3) correlation), for a 4 or 6 polynomial datafit, NPI=6 will be used as a general "middle-range" NPI-polynomial-number value.

* * *

B. The (S1)→(S2) Correlation

Fig. [8.9a] through [8.9f] show plots of $[\Omega(D) \text{ vs. } D]$ and $[\alpha_o(D), \epsilon(D) \text{ vs. } D]$ for each of the models (I000...AIIZ). As with the (S2)→(S3) calculation, this presentation is of the calculation:

$$S1(4,6,9,9) \rightarrow S2(4,6,9,9)$$

and the AIII-model here gives a best-fit solution with a value $r=+.173$. Fig. [8.11a] and [8.11b] show the non-linear resolution of the propagated (S1)-state while Fig. [8.10a] and [8.10b] show the direct comparison between this (S1)-propagated state and the (S2)-datafit state. A significant deviation, as expected, is seen in the "tail" of the $[\ln C \text{ vs. } x^2]$ -graph, whereas on a $[C \text{ vs. } x]$ -plot, where least squares minimization is done, the propagated- and data- states are indistinguishable. Because the non-linearities prevent the non-gaussian terms from decaying faster than $(t^{-3/2})$, the shape of the (S1)-propagated state, including the tail

TABLE 8.3

*** S1=>S2: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
1.	0.8100	0.8100
2.	1.5300	1.5300

S1(4,4,8,8) => S2(4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.920	.0000E+00	.0000E+00	.6162E+02	N,N
=I100	14.893	.1108E+01	.0000E+00	.8430E+02	N,N
=I001	17.920	.0000E+00	-.5222E+01	.8761E+02	N,N
=A110	3.037	.3943E+02	.0000E+00	.1201E+03	N,N
=A110	14.641	.1282E+01	.0000E+00	.8482E+02	N,N
=A111	4.046	.2264E+02	.2609E+02	.9346E+03	N,N
=A11Z	9.848	.4717E+01	.1113E+02	.9475E+02	N,N
=A11Z	13.632	.1799E+01	.1619E+01	.8497E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

S1(4,6,9,9) => S2(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.677	.0000E+00	.0000E+00	.6142E+02	N,N
=I100	15.677	.7498E+00	.0000E+00	.7522E+02	N,N
=I001	17.677	.0000E+00	-.2643E+01	.7306E+02	N,N
=A110	7.010	.1029E+02	.0000E+00	.6629E+02	N,N
=A110	15.343	.9290E+00	.0000E+00	.7695E+02	N,N
=A111	9.010	.6021E+01	.6804E+01	.8231E+03	N,N
=A11Z	11.010	.3676E+01	.6755E+01	.1308E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 106

S1(6,6,9,9) => S2(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.920	.0000E+00	.0000E+00	.6549E+02	N,N
=I100	15.397	.8843E+00	.0000E+00	.9291E+02	N,N
=I001	17.920	.0000E+00	-.3181E+01	.9028E+02	N,N
=A110	7.073	.1000E+02	.0000E+00	.6425E+02	N,N
=A110	15.145	.1054E+01	.0000E+00	.9666E+02	N,N
=A111	9.596	.5263E+01	.6129E+01	.4641E+03	N,N
=A11Z	11.614	.3229E+01	.5212E+01	.1574E+03	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

*** S2=>S3: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
2.	1.5300	1.5300
3.	2.9700	2.9700

S2(4,4,8,8) => S3(4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	20.450	.0000E+00	.0000E+00	.3681E+02	N,N
=I100	15.403	.2432E+01	.0000E+00	.1888E+03	N,N
=I001	22.721	.0000E+00	-.1576E+02	.3923E+03	N,N
=A110	14.141	.3712E+01	.0000E+00	.2639E+03	N,N
=A111	11.365	.6241E+01	.5357E+01	.4916E+04	N,N
=A111	21.964	.2511E+00	-.1465E+02	.4421E+03	N,N
=A11Z	13.889	.3420E+01	.5847E+01	.9198E+02	N,N

D-CALC.RANGE=(.1000E-01, .2802E+02) #PTS= 112

S2(4,6,9,9) => S3(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	20.695	.0000E+00	.0000E+00	.3680E+02	N,N
=I100	15.650	.2291E+01	.0000E+00	.1641E+03	N,N
=I001	22.460	.0000E+00	-.1400E+02	.2639E+03	N,N
=A110	13.884	.3968E+01	.0000E+00	.2425E+03	N,N
=A111	14.641	.3534E+01	-.2414E+01	.2810E+04	N,N
=A11Z	15.145	.2634E+01	.3470E+01	.7172E+02	N,N

D-CALC.RANGE=(.1000E-01, .2802E+02) #PTS= 112

S2(6,6,9,9) => S3(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	20.442	.0000E+00	.0000E+00	.3459E+02	N,N
=I100	15.145	.2558E+01	.0000E+00	.2773E+03	N,N
=I001	22.460	.0000E+00	-.1478E+02	.7458E+03	N,N
=A110	14.136	.3722E+01	.0000E+00	.1347E+03	N,N
=A111	16.154	.2595E+01	-.5232E+01	.2229E+04	N,N
=A111	22.208	.1032E+00	-.1446E+02	.9296E+03	N,N
=A11Z	15.397	.2478E+01	.3069E+01	.6213E+02	N,N

D-CALC.RANGE=(.1000E-01, .2802E+02) #PTS= 112

mismatch, remains for quite a long time. This is shown in Fig. [8.12a] which is a $[\ln C \text{ vs. } x^2/t^*]$ presentation of a simulation using the best (D_o, α_o, β_o) values (as determined by the (S1)→(S2) correlation, AIII-model) and gives profiles propagated from the (S1)-state (time: $t_1=.810$) for the times:

$$t_{.5} = .597, t_{1.0} = .810, t_2 = 1.53, t_3 = 2.97, t_4 = 5.85, t_5 = 11.592.$$

The dashed "tails" we have appended to these simulation profiles are probably closer to the shape one would have found if the tail region of (S1)-propagated had matched the (S2)-datafit closer. The near origin ($x^2=0$ region) on Fig. [8.12a] show an "upturn", similar to the "dip" of the backward propagated (time= $t_{1.5}$)-state in the simulation given in Fig. [8.4c], but it is less severe here. Whereas in Fig. [8.4c], the large "dip" profile becomes, on a $[C \text{ vs. } x]$ -graph, a "double-hump" profile, this less severe "upturn" of Fig. [8.12a] does not show a stark "double-hump" behavior, as one can see in Fig. [8.12b] which is a $[C \text{ vs. } x]$ -plot of the propagations presented in [8.12a]. Whereas an "untrained eye" might tend to envision any profile as "very close to gaussian" if it exhibits a monotonic decay beginning with zero slope at the origin, the $[\ln C \text{ vs. } x^2/t^*]$ -plots emphasize that the $[C \text{ vs. } x]$ -profiles are, in no range of 'x', gaussian-like.

Finally, the "best-fit" values of $(D_o, \Omega(D_o), \alpha_o, \beta_o)$ for the various models are given in Table <8.3> alongside the (S2)→(S3) results. The calculations were for these alternate polynomial numbers:

$$S1(6,6,9,9) \rightarrow S2(6,6,9,9); \quad S1(4,4,8,8) \rightarrow S2(4,4,8,8)$$

in addition to $S1(4,6,9,9) \rightarrow S2(4,6,9,9)$ calculation presented here.

* * *

Fig. 8.9 $S1(4,6,9,9) \rightarrow S2(4,6,9,9)$

Fig. 8.9

Fig. 8.10 S1(AIII-prop.) vs. S2

Fig. 8.11 S1(AIII-prop.)

Fig. 8.12 SI(AIII-propagated)

C. The (S3)→(S4) Correlation

The $[\Omega(D) \text{ vs. } D]$ and $[\alpha_o(D), \epsilon(D)) \text{ vs. } D]$ -functions for the correlation S3(4,6,9,9)→S4(4,6,9,9) is shown in Fig. [8.13a] to [8.13f]. The $\Omega(D)$ -function for the AIII-model is actually broader in width than for the other correlations presented. This is probably due to the long-time penetration profiles being less curved, thus making it increasingly difficult to specify a given narrow range of admissible $[D, \alpha(D), \beta(D)]$ values. The "best-fit" AIII-model also gives a ' β_o ' which is quite negative compared to the corresponding α_o value, and the ratio 'r' at that point is: $r=4.92$, which may be connected to this broader AIII-model peak.

Fig. [8.14a] and [8.14b] show the non-linear resolution of the (S3)-propagated state at this value of (D_o, α_o, β_o) . As this profile has a large β_o -term, the effect of the β_o -contribution is a bit clearer. This non-linear β_o -term has one region above and one below the $C=0$ line, similar to the α -term; however, it seems to not change the $x=0$ concentration appreciably compared to the change it gives in deeper x -values. Figs. [8.15a] and [8.15b] show the comparison of (S3)-propagated with the (S4)-datafit. The propagated state is significantly more curved than the (S4)-state, the sharp curving being a precursor to the propagated state crossing the $C=0$ line in the tail region. This behavior will be characteristic of propagations which have a large negative 'r' value. Fig. [8.15c] shows a simulation using these best AIII-model values, starting with state (S3) (time $t_3=2.97$), and showing the expected profiles for the times:

$$t_{2.5} = 2.128, t_3 = 2.97, t_4 = 5.85, t_5 = 11.59, t_6 = 23.04, t_7 = 45.87.$$

The deep-tail curving down in the simulated states slowly heals out, leaving

Fig. 8.13 $S3(4,6,9,9) \rightarrow S4(4,6,9,9)$

Fig. 8.13

Fig. 8.14 S3(AIII-propagated).

Fig. 8.15 S3(AIII-prop.) vs. S4

TABLE 8.4

*** S3=>S4: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
3.	2.9700	2.9700
4.	5.8500	5.8500

S3(4,4,8,8) => S4(4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	15.902	.0000E+00	.0000E+00	.3105E+02	N,N
=I100	11.109	.3757E+01	.0000E+00	.4617E+03	N,N
=I001	18.424	.0000E+00	-.2757E+02	.9811E+02	N,N
=A110	10.100	.5677E+01	.0000E+00	.1986E+03	N,N
=A111	11.614	.4104E+01	-.6322E+01	.2337E+03	N,N
=A11Z	10.605	.4175E+01	.8715E+01	.6310E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

S3(4,6,9,9) => S4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	16.010	.0000E+00	.0000E+00	.3104E+02	N,N
=I100	11.010	.3851E+01	.0000E+00	.3746E+03	N,N
=I001	18.010	.0000E+00	-.2486E+02	.1356E+03	N,N
=A110	11.010	.4377E+01	.0000E+00	.7430E+02	N,N
=A111	14.510	.1903E+01	-.1593E+02	.1926E+03	N,N
=A11Z	12.010	.2887E+01	.4166E+01	.4909E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113

S3(6,6,9,9) => S4(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	15.902	.0000E+00	.0000E+00	.2621E+02	Y,N
=I100	10.352	.4572E+01	.0000E+00	.1443E+03	N,N
=I001	18.424	.0000E+00	-.2882E+02	.7650E+02	N,N
=A110	10.857	.4531E+01	.0000E+00	.4840E+02	N,N
=A111	14.641	.2017E+01	-.1960E+02	.9597E+02	N,N
=A11Z	11.866	.2976E+01	.4428E+01	.3692E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

*** S1=>S4.DAT: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
1.	0.8100	0.8100
4.	5.8500	5.8500

S1(4,4,8,8) => S4(4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.010	.0000E+00	.0000E+00	.2537E+02	N,N
=I100	12.260	.2815E+01	.0000E+00	.3191E+03	N,N
=I001	18.760	.0000E+00	-.2479E+02	.6214E+02	N,N
=A110	12.260	.3786E+01	.0000E+00	.5866E+02	N,N
=A111	13.010	.3862E+01	-.1089E+02	.1815E+03	N,N
=A11Z	12.760	.2821E+01	.3978E+01	.4016E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113

S1(4,6,9,9) => S4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	16.911	.0000E+00	.0000E+00	.2537E+02	N,N
=I100	12.875	.2389E+01	.0000E+00	.7906E+03	N,N
=I001	18.172	.0000E+00	-.1979E+02	.1147E+03	N,N
=A110	13.379	.2511E+01	.0000E+00	.4337E+02	N,N
=A111	14.641	.2044E+01	-.1129E+02	.2774E+03	N,N
=A11Z	13.884	.1918E+01	.1839E+01	.3556E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

S1(6,6,9,9) => S4(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.163	.0000E+00	.0000E+00	.2285E+02	N,N
=I100	12.370	.3068E+01	.0000E+00	.2418E+03	N,N
=I001	19.433	.0000E+00	-.2445E+02	.6472E+02	N,N
=A110	13.127	.2936E+01	.0000E+00	.3671E+02	N,N
=A111	15.397	.2191E+01	-.1564E+02	.1000E+03	N,N
=A11Z	13.884	.2057E+01	.2117E+01	.3088E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

a profile whose limiting slope closely matches the D_o value given by the non-linear analysis. That limiting slope may be quantitatively valid in the longer time diffusion runs is easily believed. Finally, the "best-fit" (D_o, α_o, β_o) values for each model are given in Table <8.4>.

* * *

D. The (S1)→(S4) Correlation

In all the correlations presented so far, each gives an excellent datafit once the non-linear terms are taken into account. However, they, as individual correlations, converge upon different values of the parameters: D_o, α_o, β_o . This could indicate the possibilities:

(1). The dominant diffusion process changes as one changes the diffusion time and/or diffusion temperature. This could mean that each simple model (as those given in Chapter 3) could each have its region of "operation", or that other processes entirely are occurring. Either would render the entire diffusion process significantly more complicated than this work had sought to handle analytically.

(2). The $D(C)$ -function could even be the same throughout the time and temperature domain, but each distinct measurement would be emphasizing a different portion of this $D(C)$ -function.

For this case (and for Case-(1)), one could expect that each "pair" correlation would converge to different "best-fit" (D_o, α_o, β_o)-values.

(3). Since the only guarantee one has is that the propagated-state and the measured final data-state must agree (i.e., $\Omega(D_o)$ is large), it does not automatically preclude, due to experimental errors, that there is a nearby state in the (D, α, β) -hyperspace which happens to give a better fit.

Since the $\Omega(D_0)$ at the global maximum point has been characteristically >100 , it is possible that some other value $(D'_0, \alpha'_0, \beta'_0)$ with $\Omega(D'_0) > 100$ (but with $\Omega(D'_0) < \Omega(D_0)$) may be closer to the "correct" value.

This work cannot distinguish between Case-(1) or Case-(2), but it can distinguish whether Case-(3) is occurring or not. The gist of the test is as follows:

Case-(1) and (2) both give values of (D_0, α_0, β_0) which are irreconcilable. There should be no value in the entire (D, α, β) -hyperspace that can even approximately handle a multiple-time correlation. On the other hand, Case-(3) is reconcilable because each 2-time correlation gives "too-good" a fit, and a multiple-time correlation can then find an overall (D_0, α_0, β_0) which is less accurate for each subunit 2-time comparison, but which becomes a good fit over a now broader range. Thus, we examine some multiple-time and quasi-multiple time correlations to test if Case-(3) is indeed the situation at hand.

The first part of this test is to do a 2-time correlation with widely separated times. Here, the (S1)→(S4) correlation was done and Fig. [8.16a] to [8.16f] show that, indeed, a "good match" between (S1)-propagated and (S4) can be found; Fig. [8.17c] then shows (S1)-state (time: $t_1 = .810$) propagated (AIII-model) for the times:

$$t_{.5} = .597, t_{1.0} = .810, t_2 = 1.53, t_3 = 2.97, t_4 = 5.85, t_5 = 11.59$$

$$t_6 = 23.04.$$

The $\beta_0 < 0$ value indicates (similar to the (S3)→(S4) correlation) that the deep-tail region of the simulation states in Fig. [8.17c] is lower than it should actually be. What is noteworthy is the extent to which any slope

Fig. 8.16 $S1(4,6,9,9) \rightarrow S4(4,6,9,9)$

Fig. 8.16

Fig. 8.17

Fig. 8.18 Using (S1)+(S4) values

on the $[\ln C \text{ vs. } x^2/t^*]$ -graph is an inaccurate measure of D_0 . Since $D = \text{constant}$ would have been a family of parallel straight lines, curvature aside, the deviations from parallel are of themselves strong indications of the c.d.d. process operating. Returning to this "test", having "pinned" the propagation to match the initial (S1)-state and the final (S4)-state, we next compare how well the (S1)-propagated state matches each intermediate time state ((S2) and (S3)). The comparison of (S1)-propagated with these intermediate states is shown in Fig. [8.18a] to [8.18d]; the explicit comparison of (S1)-propagated with (S4) is given in [8.17a] and [8.17b]. The generally poor comparison of the best (S1) $\rightarrow$ (S4) values with the intermediate states [(S2) and (S3)] indicate that situation-(3) is probably not operating.

The second part of this test involves the correlation (S1) $\rightarrow$ (S2) $\rightarrow$ (S3) $\rightarrow$ (S4) and is detailed next. These (S1) $\rightarrow$ (S4) $\Omega(D)$ maxima are also listed as part of Table <8.4> alongside the (S3) $\rightarrow$ (S4) results.

E. Other S-data Correlations

To continue to examine the general behavior as well as to help ascertain a more "complete" picture, other correlations were done, for some (4,6,9,9) and (6,6,9,9) polynomial cases. The results of these are given in Table <8.5a> and <8.5b>, but without the additional graphical presentations that were given earlier. Of particular importance is the full sequential multiple-time correlation: (S1) $\rightarrow$ (S2) $\rightarrow$ (S3) $\rightarrow$ (S4), which continues the "test" of part (D).

The $[\Omega(D) \text{ vs. } D]$ -plots are given in Fig. [8.19a] to [8.19f] for a P.C.=(6,6,9,9). The AIII-model compared to the linear equation still gives

the characteristic lowering of the best D_0 -value. There is a gradual shift of the peak of $\Omega(D)$ to lower and lower D_0 -values as one goes from the I000-model to the II00-model, to the AII0-one, and finally to the AIII-model. However, the sharpness of the peaks, characteristic of the single 2-time correlations, is no longer present. This multiple-time analysis does give a positive value of 'r', with:

$$r(4,6,9,9) = +.252, \quad r(6,6,9,9) = +.202 .$$

Thus, we find the general characteristics of the non-linear analysis remain, but one cannot find a sharp best-fit peak in $\Omega(D)$, indicating that the c.d.d. process is present but that the non-linear parameters derived from the approximate expansion of the $D(C)$ function:

$$D(C) \approx D_0(1 + \alpha C + \beta C^2) \quad (8.16)$$

are not universal (constant). Both this conclusion and the previous one support the idea that Case-(1) or Case-(2), as given earlier is operating. There is no region of the (D_0, α, β) -parameter-space which can give a "good-fit" to the data over the entire range of times that were experimentally measured. Noticing that the best AIII-model D_0 -values found for the whole set of correlations do not seem to vary over a wide range means that the lack of a sharp peak in the multiple-time correlation studies is mainly due to the inability to match the non-linear parameters over the whole data range (S1) to (S4).

Finally, each propagated state for this multiple-time correlation is shown in Fig. [8.20] resolved into its linear and non-linear parts. Again, one sees the characteristic persistence of the non-linear terms throughout the entire time-range.

Fig. 8.19 (S1+S2+S3+S4) (6,6,9,9)

Fig. 8.19

Fig. 8.20 S1→S2→S3→S4 (AIII-propagation)

TABLE 8.5A

*** S-DATA: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
1.	0.8100	0.8100
2.	1.5300	1.5300
3.	2.9700	2.9700
4.	5.8500	5.8500

(S1 => S2 => S3 => S4) (4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	18.172	.0000E+00	.0000E+00	.3013E+02	N,N
=I100	13.632	.2278E+01	.0000E+00	.4306E+02	N,N
=I001	18.929	.0000E+00	-.9905E+01	.3559E+02	N,N
=A110	13.127	.2911E+01	.0000E+00	.4308E+02	N,N
=A111	9.091	.6965E+01	.1299E+02	.5028E+02	N,N
=A11Z	10.605	.4802E+01	.1153E+02	.4716E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

(S1 => S2 => S3 => S4) (4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	18.010	.0000E+00	.0000E+00	.3015E+02	N,N
=I100	14.510	.1750E+01	.0000E+00	.3974E+02	N,N
=I001	18.510	.0000E+00	-.6250E+01	.3383E+02	N,N
=A110	13.010	.3030E+01	.0000E+00	.4101E+02	N,N
=A111	11.510	.4261E+01	.4573E+01	.4465E+02	N,N
=A11Z	12.260	.3404E+01	.5795E+01	.4286E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113

(S1 => S2 => S3 => S4) (6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	18.172	.0000E+00	.0000E+00	.2820E+02	N,N
=I100	13.884	.2098E+01	.0000E+00	.3866E+02	N,N
=I001	18.677	.0000E+00	-.7344E+01	.3235E+02	N,N
=A110	12.623	.3371E+01	.0000E+00	.3926E+02	N,N
=A111	11.866	.3960E+01	.3164E+01	.4069E+02	N,N
=A11Z	12.623	.3125E+01	.4882E+01	.3883E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

(S1, S2, S3) => S4 (4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	16.760	.0000E+00	.0000E+00	.2680E+02	N,N
=I100	12.260	.2925E+01	.0000E+00	.1390E+03	N,N
=I001	19.010	.0000E+00	-.2499E+02	.6106E+02	N,N
=A110	12.010	.4019E+01	.0000E+00	.6669E+02	N,N
=A111	13.260	.3381E+01	-.9316E+01	.1028E+03	N,N
=A11Z	12.510	.2984E+01	.4453E+01	.4471E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113

(S1, S2, S3) => S4 (4,6,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	16.911	.0000E+00	.0000E+00	.2681E+02	N,N
=I100	12.623	.2642E+01	.0000E+00	.1218E+03	N,N
=I001	18.424	.0000E+00	-.2079E+02	.8156E+02	N,N
=A110	13.127	.2747E+01	.0000E+00	.4710E+02	N,N
=A111	14.641	.2171E+01	-.1185E+02	.1063E+03	N,N
=A11Z	13.632	.2086E+01	.2176E+01	.3830E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

(S1, S2, S3) => S4 (6,6,8,8) NOT DONE

TABLE 8.5B

S1(4,4,8,8) => S3(4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	19.260	.0000E+00	.0000E+00	.3172E+02	N,N
=I100	14.510	.2222E+01	.0000E+00	.2060E+03	N,N
=I001	20.510	.0000E+00	-.1671E+02	.2453E+03	N,N
=A110	12.010	.5268E+01	.0000E+00	.3031E+03	N,N
=A111	11.380	.7041E+01	-.4933E+01	.6338E+03	N,N
=A112	18.010	.9432E+00	-.1152E+02	.5183E+03	N,N
=A11Z	14.010	.2811E+01	.3950E+01	.6330E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113
D-CALC.RANGE=(.1000E+02, .1280E+02) #PTS= 141 (A111-MODEL)

S1(4,6,9,9) => S3(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	19.260	.0000E+00	.0000E+00	.3172E+02	N,N
=I100	15.010	.1909E+01	.0000E+00	.1309E+03	N,N
=I001	20.010	.0000E+00	-.1220E+02	.2513E+03	N,N
=A110	14.010	.3051E+01	.0000E+00	.9939E+02	N,N
=A111	13.510	.3762E+01	-.3905E+01	.1960E+04	N,N
=A112	22.260	-.7336E+00	-.1663E+02	.4324E+03	N,N
=A11Z	15.260	.1990E+01	.1980E+01	.5346E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113

S1(6,6,9,9) => S3(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	19.433	.0000E+00	.0000E+00	.3009E+02	N,N
=I100	14.893	.1986E+01	.0000E+00	.1891E+03	N,N
=I001	19.938	.0000E+00	-.1273E+02	.7846E+03	N,N
=A110	14.136	.2934E+01	.0000E+00	.8127E+02	N,N
=A111	14.136	.3156E+01	-.4204E+01	.1873E+04	Y,N
=A112	20.442	-.1501E+00	-.1373E+02	.2563E+04	N,N
=A11Z	15.397	.1911E+01	.1826E+01	.4871E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

S2(4,4,8,8) => S4(4,4,8,8)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.163	.0000E+00	.0000E+00	.2628E+02	N,N
=I100	12.623	.2891E+01	.0000E+00	.4670E+03	N,N
=I001	19.686	.0000E+00	-.2534E+02	.6799E+02	N,N
=A110	11.866	.4466E+01	.0000E+00	.8251E+02	N,N
=A111	13.127	.3904E+01	-.8835E+01	.2098E+03	N,N
=A11Z	12.370	.3207E+01	.5142E+01	.4591E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

S2(4,6,9,9) => S4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.010	.0000E+00	.0000E+00	.2628E+02	N,N
=I100	12.760	.2758E+01	.0000E+00	.2177E+04	N,N
=I001	19.260	.0000E+00	-.2236E+02	.1074E+03	N,N
=A110	13.010	.3061E+01	.0000E+00	.4900E+02	N,N
=A111	15.260	.2102E+01	-.1294E+02	.2190E+03	N,N
=A11Z	13.760	.2143E+01	.2296E+01	.3848E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 113

S2(6,6,9,9) => S4(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	17.163	.0000E+00	.0000E+00	.2285E+02	N,N
=I100	12.370	.3068E+01	.0000E+00	.2418E+03	N,N
=I001	19.433	.0000E+00	-.2445E+02	.6472E+02	N,N
=A110	13.127	.2936E+01	.0000E+00	.3671E+02	N,N
=A111	15.397	.2191E+01	-.1564E+02	.1000E+03	N,N
=A11Z	13.884	.2057E+01	.2117E+01	.3088E+02	N,N

D-CALC.RANGE=(.1000E-01, .2801E+02) #PTS= 112

III. The T-dataset, Average Temperature: 724.2° C

Having presented a "complete" non-linear analysis program using the S-dataset, we present next a shortened version using the T-dataset. The calculation here uses:

$$P.C.(T\text{-dataset}) = (6,6,9,9)$$

and the raw datafits are given in Fig. [8.21a] and Fig. [8.21b]. The $\Omega(D), \alpha_o(D), \beta(D)$ for the T2-T3 correlations and the various models is given in Fig. [8.22a] to [8.22f]. Again, the AIII-model is an excellent datafit. What is surprising, in contrast to the entire S-dataset analysis, is that the AIIZ-model also is an excellent fit. Fig. [8.23a] and [8.23b] show the non-linear resolution of the T2-propagated state. This shows how the β -term compares to the α^2 -term when $\beta_o \approx \frac{1}{2}\alpha_o^2$. They almost follow each other, with the β -term smaller near $x=0$ and larger than the α^2 -term in the deeper penetration region. Fig. [8.24] is a simulation, using the best AIII-model values, examining the time-propagation of the T2-state (time: $t_2=0.816$) for the times $(t_{1.5}, t_3, t_4, t_5)$ which are:

$$t_{1.5}=0.603, t_2=0.816, t_{2.5}=1.114, t_3=1.53, t_4=2.982, t_5=5.808, t_6=11.664$$

the "corrected" times $(t^*=t-.072)$ obeying a relationship similar to Eq. (8.16). Note, again, the persistence of curvature even for long times, as well as the non-parallelism indicative of $D \neq \text{constant}$ on the $[\ln C \text{ vs. } x^2/t^*]$ -plot.

Fig. [8.25] through [8.27] present a similar analysis for the T3-T4 correlation. Again, the AIIZ-model, which is the best cognate to "standard" model, shows a good datafit (as does, of course, the AIII-model). A simulation using times $(t_{2.5}, t_4, t_5, t_6)$ as given above is also included.

In Fig. [8.28a] to [8.28f], the results of the 3-time correlation (T2→T3→T4) are given. As with the 2-time correlations, both the AIII-model and the AIIZ-model give equivalently good datafits, and both are significant improvements over the linear equation. Noteworthy, also, is that the pure β -model is at most a negligible improvement over the linear equation, and as one gives through the sequence of models:

$$I000 \rightarrow I100 \rightarrow A110 \rightarrow (AIII \text{ or } AIIZ)$$

the "best-fit" gets progressively better. The 3-time correlation (AIII-model) gives:

$$D_0 = 19.19, \alpha_0 = 3.41, \beta_0 = 3.96, \Omega(D_0) = 142., r = .341$$

while the AIIZ-model gives:

$$D_0 = 19.53, \alpha_0 = 3.16, \beta_0 = 4.94, \Omega(D_0) = 130., r = .500.$$

Finally, Figs. [8.29a] and [8.29b] show T2-propagated compared to the T3-datafit; [8.29c] and [8.29d] show the T3→T4 comparison; both use the best AIII-model (3-time correlation) values. Notice that the fractional deviations of the propagated and datafit states (in [8.29a] and [8.29c]) are oscillatory with almost a fixed amplitude and frequency over most of the penetration depth. This represents, to first order, a systematic slice-thickness variation due to the relaxation of the microtone stage. Thus, even down to the details of the deviations, this dataset presents the non-linear analysis working at its best. Concurrently, it is the "standard" model working also at its best, showing that the method presented in Chapters 4-6 is indeed capable of viably approximating the difficult D(C)-functions dictated by the physics of the c.d.d. process.

Figures 8.21a and 8.21b. This dataset is given the label 'T' in text. Average temperature: 724°C. The 6-polynomial fits to the raw data are plotted on both [C vs. x]-axes and [$\ln C$ vs. x^2]-axes, with individual profiles labelled as follows:

Label	Diffusion Time (tu)	Temperature (°C)	Total Area
T2	0.816	724.5	6.76
T3	1.530	724.0	5.00
T4	2.98	724.0	4.66

Fig. 3.21 Raw data-fits

Fig. 8.22 T2(6,6,9,9)→T3(6,6,9,9)

Fig. 8.22

Fig. 8.23 T2(AIII-propagated)

Fig. 8.24 T2(AIII-propagated)

Fig. 8.25 $T3(6,6,9,9) \rightarrow T4(6,6,9,9)$

Fig. 8.25

Fig. 8.26

Fig. 8.27 T3(AIII-Propagated)

Fig. 8.28 (T2→T3→T4) (6,6,9,9)

Fig. 8.28

Fig. 8.29 Using T2→T3→T4 Values

TABLE B.6

*** T-DATA: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
2.	0.8160	0.8160
3.	1.5300	1.5300
4.	2.9820	2.9820

T2(4,6,9,9) => T3(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	30.635	.0000E+00	.0000E+00	.6057E+02	N,N
=I100	25.250	.1288E+01	.0000E+00	.2975E+03	N,N
=I001	31.308	.0000E+00	-.5744E+01	.3114E+03	N,N
=A110	23.904	.1820E+01	.0000E+00	.5181E+03	N,N
=A111	21.885	.2532E+01	.1632E+01	.1028E+04	N,N
=A112	22.558	.2218E+01	.2461E+01	.2499E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 105

T2(6,6,9,9) => T3(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	30.343	.0000E+00	.0000E+00	.7855E+02	N,N
=I100	26.677	.8688E+00	.0000E+00	.1396E+03	N,N
=I001	31.010	.0000E+00	-.3759E+01	.1370E+03	N,N
=A110	26.010	.1103E+01	.0000E+00	.1508E+03	N,N
=A111	19.677	.3350E+01	.5288E+01	.6578E+03	N,N
=A112	20.010	.3193E+01	.5099E+01	.5943E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 106

T2(4,6,9,9) => T4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	24.914	.0000E+00	.0000E+00	.9834E+02	N,N
=I100	22.222	.1217E+01	.0000E+00	.3179E+03	N,N
=I001	25.250	.0000E+00	-.8434E+01	.2895E+03	N,N
=A110	21.885	.1444E+01	.0000E+00	.3644E+03	N,N
=A111	18.520	.3363E+01	.8613E+01	.1586E+04	N,N
=A112	17.173	.4432E+01	.9822E+01	.3463E+03	N,N
=A11Z	20.875	.1959E+01	.1919E+01	.4082E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 105

T2(6,6,9,9) => T4(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	25.010	.0000E+00	.0000E+00	.1130E+03	N,N
=I100	23.010	.8037E+00	.0000E+00	.1607E+03	N,N
=I001	25.010	.0000E+00	-.5105E+01	.1524E+03	N,N
=A110	22.677	.9798E+00	.0000E+00	.1645E+03	N,N
=A111	16.677	.4653E+01	.1593E+02	.2121E+04	N,N
=A112	15.677	.5676E+01	.1611E+02	.3136E+03	N,N
=A11Z	22.677	.9866E+00	.4867E+00	.1669E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 106

2

2

(T2 => T3 => T4) (4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	27.606	.0000E+00	.0000E+00	.4374E+02	N,N
=I100	22.558	.1659E+01	.0000E+00	.8774E+02	N,N
=I001	27.943	.0000E+00	-.5096E+01	.4976E+02	N,N
=A110	20.875	.2582E+01	.0000E+00	.1003E+03	N,N
=A111	19.193	.3408E+01	.3958E+01	.1416E+03	N,N
=A112	19.529	.3145E+01	.4944E+01	.1298E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 105

(T2 => T3 => T4) (6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	27.343	.0000E+00	.0000E+00	.4746E+02	N,N
=I100	23.343	.1312E+01	.0000E+00	.6965E+02	N,N
=I001	27.677	.0000E+00	-.2806E+01	.4939E+02	N,N
=A110	22.343	.1833E+01	.0000E+00	.7508E+02	N,N
=A111	18.343	.3760E+01	.7170E+01	.1475E+03	N,N
=A112	18.343	.3760E+01	.7070E+01	.1475E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 106

T2(4,6,9,9) => T4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	26.260	.0000E+00	.0000E+00	.6802E+02	N,N
=I100	23.231	.1063E+01	.0000E+00	.2359E+03	N,N
=I001	27.270	.0000E+00	-.6708E+01	.2695E+03	N,N
=A110	22.222	.1592E+01	.0000E+00	.3326E+03	N,N
=A111	20.202	.2501E+01	.2476E+01	.1126E+04	N,N
=A112	32.991	-.1295E+01	-.1510E+02	.6708E+03	N,N
=A11Z	20.539	.2298E+01	.2640E+01	.6800E+03	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 105

T2(6,6,9,9) => T4(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	26.343	.0000E+00	.0000E+00	.7878E+02	N,N
=I100	26.343	.0000E+00	.0000E+00	.7878E+02	N,N
=I100	24.010	.7704E+00	.0000E+00	.1338E+03	N,N
=I001	27.010	.0000E+00	-.5131E+01	.1357E+03	N,N
=A110	18.010	.4297E+01	.0000E+00	.9621E+02	N,N
=A111	23.343	.1077E+01	.0000E+00	.1449E+03	N,N
=A112	19.010	.3048E+01	.4916E+01	.1199E+04	N,N
=A11Z	19.010	.3070E+01	.4712E+01	.1031E+04	N,N

D-CALC.RANGE=(.1000E-01, .3501E+02) #PTS= 106

Finally, for the various correlations and various models, the "best-fit" values, T-dataset, are given in Table <8.6>.

* * *

IV. The U-dataset, Average Temperature: 774.9° C

These are the highest temperature data taken. Fig. [8.30a] and [8.30b] show the 5-polynomial raw data fits. Out of the series [U1A, U2A, U3, U4], the [U3] dataset seems to be an "anomalous" profile, when plotted on [$\ln C$ vs. x^2/t^*]-axes. The intrinsic curved penetration profile seems "expected" for a c.d.d. process, but the average penetration depth appears as if the diffusion time or temperature were a fair bit less than recorded. This also occurred for one other diffusion run, the [R4]-profile in the [R1,R2,R3,R4,R5; Temp.=624.7°C]-series. The procedure chosen for handling both these cases is as follows:

Since both [U3] and [R4] appear as curved profiles, we introduce an ad hoc time correlation for these states using the state-before and the state-after to "pinpoint" the proper "effective-time".

If the [U3]-data were totally ignored, the "longest-time" correlation would be the (U2A)→(U4) correlation. The $\Omega(D)$, $\alpha(D)$, $\beta(D)$ functions for this are given in Fig. [8.31a] to [8.31f]. A 3-time correlation using (U2A)→(U3)→(U4) can do no better than these results, since any [U3]-dataset will introduce an extra constraint on the diffusion process between times t_2 (for U2A) and t_4 (for U4). The 3-time correlation is then performed for various trial times: $\hat{t}_3$. When $\hat{t}_3$ comes as close to the non-linear behavior dictated by the (U2A)→(U4) correlation, the AIII-model should show a strong maximum as a function of $\hat{t}_3$. This is indeed the case, as shown

Figures 8.30a and 8.30b.[†] This dataset is given the label 'U' in text. Average temperature: 775°C. The 5-polynomial fits to the raw data are plotted on both [C vs. x]-axes and [$\ln C$ vs. x^2]-axes, with individual profiles labelled as follows:

Label	Diffusion Time (tu)	Temperature (°C)	Total Area
U1A	.276	775.2	4.53
U2A	.456	774.8	4.69
U3	.816	774.6	5.64
U4	1.530	774.9	5.41

[†] See also Fig. 8.33.

Fig. 8.30 Raw data-fits

Fig. 8.31 $U2A(5,5,8,8) \rightarrow U4(5,5,8,8)$

Fig. 8.31

Fig. 8.32 $U2A \rightarrow U3(\hat{t}_3) \rightarrow U4$

Fig. 8.33 Raw data $U3(\hat{t}_3 = .680)$

in Fig. [8.32]. The maxima for these plots are included in the U-data Table <8.7a>, and the "best" time thus found was:

$$\hat{t}_3(U3) = .680$$

(the "original" times being $t_1(U1A)=.276$, $t_2(U2A)=.456$, $t_3(U3)=.816$, $t_4(U4)=1.53$). This modified $\hat{t}_3$ is used in place of t_3 and a new plot of the penetration profiles on $[\ln C \text{ vs. } x^2/t^*]$ -axes is given in Fig. [8.33].

* * *

The $U2A(t_2) \rightarrow U3(\hat{t}_3) \rightarrow U4(t_4)$ correlation results are given in Fig. [8.34a] to [8.34f]. Much like the T-dataset, the AIIZ-model is a good fit, in addition to the AIII-model, and the succession

$$I000 \rightarrow II00 \rightarrow AII0 \rightarrow (AIII \text{ or } AIIZ)$$

gives increasingly better fits. The AIII-model for this 3-time correlation gives:

$$D_o = 47.0, \alpha_o = 3.534, \beta_o = 10.13, \Omega(D_o) = 536, r = .811$$

and the AIIZ-model has 2 maxima:

$$D_o = \begin{Bmatrix} 43.0 \\ 57.0 \end{Bmatrix}, \alpha_o = \begin{Bmatrix} 4.736 \\ 1.528 \end{Bmatrix}, \beta_o = \begin{Bmatrix} 11.21 \\ 1.17 \end{Bmatrix}, \Omega(D_o) = \begin{Bmatrix} 223. \\ 153. \end{Bmatrix}, r = .500$$

The non-linear resolution of the (U2A)-propagated profile for the AIII-model is given in Fig. [8.36a] and [8.36b]. For the (U3)-propagated state, this is shown in [8.38a] and [8.38b]. The comparisons, respectively, to U3 (for U2A-propagated) and U4 (for U3-propagated) are presented in [8.35] and [8.37].

Also given are the 2-time correlations: $(U1A) \rightarrow (U2A)$, $(U2A) \rightarrow (U3)$, $(U3) \rightarrow (U4)$ in Fig. [8.39] through [8.41] for the AIII and AIIZ-models. The maxima of $\Omega(D)$ and the associated D_o, α_o, β_o values for each model, for

Fig. 8.34 $(U2A \rightarrow U3(\hat{t}_3 = .680) \rightarrow U4)(5, 5, 8, 8)$

Fig. 8.34

Fig. 8.35 Using $U2A \rightarrow U3(\hat{t}_3) \rightarrow U4$ Values

Fig. 8.36 U2A(AIII-prop.)

Fig. 8.37 Using $U2A \rightarrow U3(t_3) \rightarrow U4$ Values Fig. 8.38 $U3(t_3, AIII\text{-prop.})$ $D_0 = 47.0$

Fig. [8.39] $\text{U1A}(5,5,8,8) \rightarrow \text{U2A}(5,5,8,8)$

Fig. [8.40] $U2(5,5,8,8) \rightarrow U3(5,5,8,8), (\hat{t}_3 = .680)$

Fig. 8.41 $U_3(5,5,8,8) \rightarrow U_4(5,5,8,8)$, $(\hat{t}_3 = .680)$

TABLE 8.7A

*** U-DATA: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
1A.	0.2760	0.2760
2A.	0.4560	0.4560
3.	0.8160	0.6800 (WHEN NOTED)
4.	1.5300	1.5300

U2A(3,5,8,8) => U3(3,5,8,8) TIME(3)= 0.680

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	TIME(3)
=AIII	37.010	.7617E+01	.1479E+02	.3818E+02	0.620
=AIII	38.010	.6879E+01	.1508E+02	.5968E+02	0.640
=AIII	41.010	.5485E+01	.1399E+02	.1218E+03	0.660
=AIII	43.010	.4728E+01	.1281E+02	.2234E+03	0.670
=AIII	45.010	.4100E+01	.1152E+02	.3455E+03	0.675
=AIII	47.010	.3534E+01	.1013E+02	.5355E+03	0.680
=AIII	50.010	.2803E+01	.7983E+01	.5165E+03	0.685
=AIII	55.010	.1802E+01	.4395E+01	.3698E+03	0.690
=AIII	65.010	.2818E+00	-.2567E+01	.2360E+03	0.700
=AIII	75.010	-.8423E+00	-.8935E+01	.1873E+03	0.710
=AIII	85.010	-.1729E+01	-.1464E+02	.1605E+03	0.720
=AIII	97.010	-.2626E+01	-.2087E+02	NOT FOUND	>0.740

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99

!PEST TIME(3,ADJUSTED)= 0.680

U1A(3,5,8,8) => U2A(3,5,8,8)

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	77.907	.0000E+00	.0000E+00	.1101E+03	N,N
=I100	69.364	.7355E+00	.0000E+00	.1079E+04	N,N
=I001	78.913	.0000E+00	-.3315E+01	.1028E+04	N,N
=AII0	34.687	.9069E+01	.0000E+00	.4206E+02	N,N
=AII0	68.861	.8205E+00	.0000E+00	.1385E+04	N,N
=AIII	62.328	.1508E+01	.2325E+01	.1141E+05	N,N
=AIII	90.472	-.7649E+00	-.6924E+01	.1739E+05	N,N
=AIIZ	49.261	.3517E+01	.6183E+01	.2382E+03	N,N
=AIIZ	67.856	.9181E+00	.4214E+00	.1537E+04	N,N

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 98

U1A(5,5,8,8) => U2A(5,5,8,8)

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	77.804	.0000E+00	.0000E+00	.1048E+03	N,N
=I100	69.721	.7185E+00	.0000E+00	.1252E+04	N,N
=I001	78.814	.0000E+00	-.3458E+01	.2126E+04	N,N
=AII0	35.371	.8771E+01	.0000E+00	.4197E+02	N,N
=AII0	68.711	.8456E+00	.0000E+00	.2378E+04	N,N
=AIII	64.670	.1255E+01	.1368E+01	.6751E+04	N,N
=AIII	85.886	-.4788E+00	-.5695E+01	.4828E+04	N,N
=AIIZ	49.515	.3470E+01	.6021E+01	.2352E+03	N,N
=AIIZ	66.690	.1044E+01	.5447E+00	.2364E+04	N,N

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 98

U2A(3,5,8,8) => U3(3,5,8,8) TIME(3)= 0.680

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	72.010	.0000E+00	.0000E+00	.2457E+03	N,N
=I100	68.010	.4279E+00	.0000E+00	.1333E+04	N,N
=I001	73.010	.0000E+00	-.2103E+01	.8832E+03	N,N
=AII0	20.010	.2114E+02	.0000E+00	.3035E+02	N,N
=AII0	68.010	.4374E+00	.0000E+00	.1455E+04	N,N
=AIII	60.010	.1347E+01	.3924E+01	.7151E+04	N,N
=AIII	95.010	-.1555E+01	-.1040E+02	.1543E+05	N,N
=AIIZ	40.010	.5306E+01	.1408E+02	.1832E+03	N,N
=AIIZ	68.010	.4392E+00	.9646E-01	.1372E+04	N,N

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99

U2A(5,5,8,8) => U3(5,5,8,8) TIME(3)= 0.680

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	73.010	.0000E+00	.0000E+00	.2094E+03	N,N
=I100	73.010	.0000E+00	.0000E+00	.2094E+03	N,N
=I100	68.010	.4711E+00	.0000E+00	.1095E+04	N,N
=I001	73.010	.0000E+00	-.2515E+01	.1108E+04	N,N
=AII0	20.010	.2122E+02	.0000E+00	.3102E+02	N,N
=AII0	67.010	.5748E+00	.0000E+00	.1246E+04	N,N
=AIII	59.010	.1521E+01	.4036E+01	.1412E+05	N,N
=AIII	94.010	-.1471E+01	-.1059E+02	.8680E+04	N,N
=AIIZ	40.010	.5328E+01	.1419E+02	.2016E+03	N,N
=AIIZ	67.010	.5784E+00	.1673E+00	.1360E+04	N,N

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99

U3(3,5,8,8) => U4(3,5,8,8) TIME(3)= 0.680

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	66.010	.0000E+00	.0000E+00	.6476E+02	N,N
=I100	56.010	.1570E+01	.0000E+00	.8006E+03	N,N
=I001	67.010	.0000E+00	-.1102E+02	.1615E+04	N,N
=AII0	37.010	.8433E+01	.0000E+00	.7237E+02	N,N
=AII0	55.010	.1912E+01	.0000E+00	.1075E+04	N,N
=AIII	51.010	.2755E+01	.2991E+01	.9659E+04	N,N
=AIII	70.010	-.3588E+00	-.1358E+02	.4677E+04	N,N
=AIIZ	50.010	.2975E+01	.4426E+01	.9475E+03	N,N

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99

U3(5,5,8,8) => U4(5,5,8,8) TIME(3)= 0.680

MODEL	ID	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	65.010	.0000E+00	.0000E+00	.9634E+02	N,N
=I100	59.010	.9738E+00	.0000E+00	.2691E+03	N,N
=I001	66.010	.0000E+00	-.6930E+01	.2841E+03	N,N
=AII0	35.010	.9748E+01	.0000E+00	.5970E+02	N,N
=AII0	58.010	.1174E+01	.0000E+00	.2846E+03	N,N
=AIII	46.010	.3021E+01	.1033E+02	.5876E+04	N,N
=AIII	87.010	-.2177E+01	-.2371E+02	.7866E+03	N,N
=AIIZ	43.010	.4800E+01	.1152E+02	.4869E+03	N,N
=AIIZ	57.010	.1368E+01	.9363E+00	.2929E+03	N,N

D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99

TABLE 8.7B

U2A => U3 => U4) (3,5,8,8) TIME(3)= 0.680						U2A(5,5,8,8) => U4(5,5,8,8)					
MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?	MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B > 0?
=I000	68.010	.0000E+00	.0000E+00	.7195E+02	N,N	=I000	66.010	.0000E+00	.0000E+00	.6956E+02	N,N
=I100	59.010	.1191E+01	.0000E+00	.1362E+03	N,N	=I100	60.010	.1033E+01	.0000E+00	.2588E+03	N,N
=I001	66.010	.0000E+00	-.4963E+01	.9072E+02	N,N	=I001	68.010	.0000E+00	-.7608E+01	.3024E+03	N,N
=A110	58.010	.1423E+01	.0000E+00	.1390E+03	N,N	=A110	44.010	.6092E+01	.0000E+00	.9356E+02	N,N
=A111	50.010	.2926E+01	.6909E+01	.2123E+03	Y,N	=A110	59.010	.1299E+01	.0000E+00	.2804E+03	N,N
=A112	46.010	.3959E+01	.7837E+01	.1632E+03	N,N	=A111	49.010	.3373E+01	.7951E+01	.2636E+04	N,N
=A11Z	54.010	.2141E+01	.2292E+01	.1581E+03	N,N	=A111	83.010	-.1607E+01	-.2025E+02	.7703E+03	N,N
D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99						=A11Z	47.010	.4019E+01	.8078E+01	.4400E+03	N,N
***						=A11Z	58.010	.1463E+01	.1071E+01	.2957E+03	N,N
D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99											
U2A(5,5,8,8) => U3(5,5,8,8) TIME(3)= 0.680						U1A(3,5,8,8) => U4(3,5,8,8)					
MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?	MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B > 0?
=I000	67.010	.0000E+00	.0000E+00	.8141E+02	N,N	=I000	67.701	.0000E+00	.0000E+00	.5972E+02	N,N
=I100	60.010	.9872E+00	.0000E+00	.1349E+03	N,N	=I100	59.618	.1311E+01	.0000E+00	.6079E+03	N,N
=I001	68.010	.0000E+00	-.4027E+01	.9552E+02	N,N	=I001	71.742	.0000E+00	-.1107E+02	.9805E+03	N,N
=A110	59.010	.1192E+01	.0000E+00	.1401E+03	N,N	=A110	56.587	.2124E+01	.0000E+00	.2377E+04	N,N
=A111	47.010	.3534E+01	.1013E+02	.5355E+03	N,N	=A111	56.587	.2137E+01	-.2124E+00	.5509E+04	N,N
=A11Z	43.010	.4736E+01	.1121E+02	.2231E+03	N,N	=A111	67.701	.4691E+00	-.8014E+01	.6079E+04	N,N
=A11Z	57.010	.1528E+01	.1168E+01	.1533E+03	N,N	=A11Z	54.567	.2394E+01	.2865E+01	.2778E+03	N,N
D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99						D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 98					
***						***					
U1A(5,5,8,8) => U3(5,5,8,8) TIME(3)= 0.680						U1A(5,5,8,8) => U4(5,5,8,8)					
MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?	MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B > 0?
=I000	74.010	.0000E+00	.0000E+00	.1234E+03	N,N	=I000	68.010	.0000E+00	.0000E+00	.8027E+02	N,N
=I100	68.010	.6030E+00	.0000E+00	.8126E+03	N,N	=I100	61.010	.1012E+01	.0000E+00	.2556E+03	N,N
=I001	75.010	.0000E+00	-.2652E+01	.6782E+03	N,N	=I001	70.010	.0000E+00	-.7658E+01	.3450E+03	N,N
=A110	46.010	.4988E+01	.0000E+00	.5969E+02	N,N	=A110	49.010	.4470E+01	.0000E+00	.1831E+03	N,N
=A110	68.010	.6394E+00	.0000E+00	.1118E+04	N,N	=A110	60.010	.1300E+01	.0000E+00	.2907E+03	N,N
=A111	62.010	.1273E+01	.2252E+01	.1113E+05	N,N	=A111	52.010	.2800E+01	.5184E+01	.2687E+04	N,N
=A111	84.010	-.6259E+00	-.6040E+01	.1636E+05	N,N	=A111	81.010	-.1130E+01	-.1590E+02	.7843E+03	N,N
=A11Z	51.010	.3026E+01	.4577E+01	.1702E+03	N,N	=A11Z	51.010	.3128E+01	.4893E+01	.1065E+04	N,N
=A11Z	67.010	.7391E+00	.2731E+00	.1142E+04	N,N	=A11Z	58.010	.1626E+01	.1321E+01	.3128E+03	N,N
D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99						D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99					
***						***					
U2A(3,5,8,8) => U4(3,5,8,8)						U2A & U3) (5,5,8,8) => U4(5,5,8,8) TIME(3)= 0.680					
MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?	MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B > 0?
=I000	66.690	.0000E+00	.0000E+00	.6192E+02	N,N	=I000	66.010	.0000E+00	.0000E+00	.9117E+02	N,N
=I100	57.598	.1521E+01	.0000E+00	.6516E+03	N,N	=I100	60.010	.9531E+00	.0000E+00	.2050E+03	N,N
=I001	69.721	.0000E+00	-.1231E+02	.1037E+04	N,N	=I001	67.010	.0000E+00	-.6708E+01	.1935E+03	N,N
=A110	55.577	.2136E+01	.0000E+00	.1498E+04	N,N	=A110	59.010	.1185E+01	.0000E+00	.2050E+03	N,N
=A111	53.556	.2546E+01	.1824E+01	.6248E+04	N,N	=A111	49.010	.3202E+01	.8502E+01	.3060E+03	N,N
=A111	68.711	.9409E-01	-.1123E+02	.6566E+04	N,N	=A111	91.010	-.2409E+01	-.2576E+02	.2721E+03	N,N
=A11Z	52.546	.2712E+01	.3677E+01	.4926E+03	N,N	=A11Z	46.010	.4153E+01	.8622E+01	.2007E+03	N,N
D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99						=A11Z	58.010	.1353E+01	.9154E+00	.2101E+03	N,N
***						D-CALC.RANGE=(.1000E-01, .9801E+02) #PTS= 99					
***						***					

these, and as well as for a P.C.=(3,5,8,8) calculation, are given in Table <8.7a> and <8.7b>.

* * *

V. The R-dataset, Average Temperature: 624.7°C

The R-dataset, with 5 distinct diffusion times, has purposely the longest-time penetration (R5) of any of the temperature runs. Plots of the raw datafits on [C vs. x]-axes are given in Fig. [8.42a]. The (R4)-profile, similar to the (U3)-profile, is an anomalously shallow penetration. A correction (similar to the one done with (U3)) using the (R3)→(R5) correlation to find a best adjusted time: $\hat{t}_4$ gives:

$$\hat{t}_4(R4) = 8.90$$

(the original times being: $t_1(R1)=1.638$, $t_2(R2)=3.15$, $t_3(R3)=6.21$, $t_4(R4)=12.24$, $t_5(R5)=24.57$). The [$\ln C$ vs. x^2/t^*]-plots using this adjusted $t_4^*=8.828$ time ($t_4^*=\hat{t}_4-.072$) are given in Fig. [8.42b]. The correlations given here use:

$$P.C.(R1,R4,R5) = (4,6,9,9); \quad P.C.(R2,R3) = (6,6,9,9).$$

Plots are given in Fig. [8.43a] to [8.43p] of the AIII- and AIIZ-models; however, the results of all the models (I000 to AIIZ) giving "best-fit" values of $(D_0, \Omega(D_0), \alpha_0, \beta_0)$ for each correlation studied are included in Table <8.8a> and <8.8b>. What is noteworthy is that for every correlation except those involving (R5), the AII0-model ($\beta \equiv 0$) gives a better fit than the AIIZ-model, indicating, as was seen in the S-dataset, that the "standard" D(C) function may not be operating except for the very longest time diffusion run. Because $\Gamma(D)$ is linear in both 'D' and time 't', the introduction

Figures 8.42a and 8.42b. This dataset is given the label 'R' in text. Average temperature: 625°C. The polynomial fits to the raw data are plotted on both [C vs. x]-axes and [$\ln C$ vs. x^2]-axes, with individual profiles labelled as follows:

Label	Diffusion Time (tu)	Temperature (°C)	Total Area	#Poly
R1	1.638	624.0	4.80	4
R2	3.15	624.5	5.33	6
R3	6.21	624.0	4.69	6
R4	8.90 [†]	625.0	3.60	4
R5	24.57	625.0	4.62	4

[†]This is an adjusted time. See Chapter 8 text for details and end of Part B, Sec. II, Ch. 7.

Fig. 8.42 Raw data-fits

[a],[b]: $\text{R3}(6,6,9,9) \rightarrow \text{R5}(4,6,9,9)$
 [c],[d]: $\text{R3}(6,6,9,9) \rightarrow \text{R4}(4,6,9,9) \rightarrow \text{R5}(4,6,9,9)$

Fig. 8.43

[e], [f]: R3(6,6,9,9)→R4(4,6,9,9)
 [g], [h]: R4(4,6,9,9)→R5(4,6,9,9)

Fig. 8.43

[i],[j]: R1(4,6,9,9)→R2(6,6,9,9)
 [k],[l]: R2(6,6,9,9)→R3(6,6,9,9)

Fig. 8.43

[m], [n]: R1(4,6,9,9) $\rightarrow$ R3(6,6,9,9)
 [o], [p]: R2(6,6,9,9) $\rightarrow$ R4(4,6,9,9)

Fig. 8.43

TABLE 8.8A

*** R-DATA: SUMMARY OF RESULTS

	EXPTL.TIME	ADJ.TIME
1.	1.6380	1.6380
2.	3.1500	3.1500
3.	6.2100	6.2100
4.	12.2400	8.9000 (WHEN NOTED)
5.	24.5700	24.5700

R3(6,6,9,9) => (R4 => R5) (4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	TIME(4)
=AIII	4.510	.1033E+02	.2885E+02	.7429E+02	8.80
=AIII	4.510	.1021E+02	.2901E+02	.7613E+02	8.90
=AIII	4.510	.1009E+02	.2911E+02	.7404E+02	9.00
=AIII	4.677	.9284E+01	.2630E+02	.6955E+02	9.10

D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106
 !-REST TIME(4,ADJUSTED)= 8.90

R1(4,6,9,9) => R2(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	12.843	.0000E+00	.0000E+00	.4758E+02	N,N
=I100	11.510	.7717E+00	.0000E+00	.5336E+02	N,N
=I001	13.177	.0000E+00	-.3658E+01	.5335E+02	N,N
=AII0	11.343	.9165E+00	.0000E+00	.5342E+02	N,N
=AIII	8.843	.2870E+01	.4805E+01	.5420E+02	N,N
=AIII	13.677	-.2412E+00	-.4668E+01	.5341E+02	N,N
=AIIZ	8.510	.3233E+01	.5225E+01	.5413E+02	N,N
=AIIZ	11.010	.1124E+01	.6318E+00	.5347E+02	N,N

D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106

R1(6,6,9,9) => R2(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	12.798	.0000E+00	.0000E+00	.4793E+02	N,N
=I100	11.621	.7064E+00	.0000E+00	.5333E+02	N,N
=I001	13.135	.0000E+00	-.3503E+01	.5337E+02	N,N
=AII0	11.452	.8410E+00	.0000E+00	.5339E+02	N,N
=AIII	8.592	.3105E+01	.5481E+01	.5448E+02	N,N
=AIII	13.976	-.3684E+00	-.5190E+01	.5342E+02	N,N
=AIIZ	8.423	.3316E+01	.5497E+01	.5442E+02	N,N
=AIIZ	11.116	.1045E+01	.5463E+00	.5344E+02	N,N

D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 105

R2(6,6,9,9) => R3(6,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	7.750	.0000E+00	.0000E+00	.3854E+02	N,N
=I100	5.899	.2571E+01	.0000E+00	.6742E+02	N,N
=I001	8.760	.0000E+00	-.1592E+02	.6864E+02	N,N
=AII0	4.385	.6845E+01	.0000E+00	.1170E+03	N,N
=AIII	4.217	.7125E+01	.2739E+01	.1239E+03	N,N
=AIII	9.938	-.8278E+00	-.2047E+02	.6942E+02	N,N
=AIIZ	5.058	.3968E+01	.7871E+01	.6577E+02	N,N

D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 105

R3(6,6,9,9) => R4(4,6,9,9) TIME(4)=8.9

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	8.843	.0000E+00	.0000E+00	.3505E+02	N,N
=I100	6.177	.5109E+01	.0000E+00	.5445E+02	N,N
=I001	10.510	.0000E+00	-.4246E+02	.5744E+02	N,N
=AII0	4.010	.1562E+02	.0000E+00	.1108E+03	N,N
=AIII	3.843	.1554E+02	.1647E+02	.1368E+03	N,N
=AIIZ	5.010	.7719E+01	.2979E+02	.5710E+02	N,N

D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106

R4(4,6,9,9) => R5(4,6,9,9) TIME(4)=8.9

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	7.343	.0000E+00	.0000E+00	.7382E+02	N,N
=I100	7.177	.4648E+00	.0000E+00	.7472E+02	N,N
=I001	7.343	.0000E+00	-.2652E+00	.7383E+02	N,N
=AII0	4.677	.1157E+02	.0000E+00	.4916E+02	N,N
=AII0	7.177	.4823E+00	.0000E+00	.7491E+02	N,N
=AIII	4.677	.7068E+01	.5554E+02	.3905E+03	N,N
=AIII	12.010	-.3650E+01	-.8815E+02	.9876E+02	N,N
=AIIZ	4.510	.9131E+01	.4169E+02	.1146E+03	N,N
=AIIZ	7.177	.4810E+00	.1157E+00	.7494E+02	N,N

D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106

TABLE 8.8B

```

R1(4,6,9,9) => R3(4,6,9,9)
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I000    9.510    .0000E+00    .0000E+00    .3679E+02    N,N
=I100    7.677    .1827E+01    .0000E+00    .6874E+02    N,N
=I001    10.010   .0000E+00    -.1306E+02   .7096E+02    N,N
=A110    6.677    .3905E+01    .0000E+00    .7619E+02    N,N
=A111    6.677    .4035E+01    -.1369E+01   .7756E+02    N,N
=A111    10.177   -.1761E+00    -.1364E+02   .7149E+02    N,N
=A112    7.343    .2427E+01    .2946E+01    .5926E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106
***
R1(6,6,9,9) => R3(6,6,9,9)
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I000    9.433    .0000E+00    .0000E+00    .3695E+02    N,N
=I100    7.750    .1756E+01    .0000E+00    .6891E+02    N,N
=I001    9.938    .0000E+00    -.1253E+02   .7144E+02    N,N
=A110    6.741    .3772E+01    .0000E+00    .7650E+02    N,N
=A111    6.741    .3880E+01    -.1193E+01   .7760E+02    N,N
=A111    10.106   -.1232E+00    -.1333E+02   .7148E+02    N,N
=A112    7.246    .2554E+01    .3261E+01    .5942E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 105
***
R2(6,6,9,9) => R4(4,6,9,9) TIME(4)=8.9
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I000    8.177    .0000E+00    .0000E+00    .2768E+02    N,N
=I100    6.343    .2931E+01    .0000E+00    .4721E+02    N,N
=I001    9.343    .0000E+00    -.3005E+02   .6033E+02    N,N
=A110    5.177    .6798E+01    .0000E+00    .9875E+02    N,N
=A111    5.343    .8022E+01    -.1519E+02   .9629E+03    N,N
=A111    11.843   -.1932E+01    -.4671E+02   .7281E+02    N,N
=A112    5.510    .4531E+01    .1026E+02    .4537E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106
***
R3(6,6,9,9) => R5(4,6,9,9)
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I000    7.343    .0000E+00    .0000E+00    .6535E+02    N,N
=I100    7.010    .8034E+00    .0000E+00    .7027E+02    N,N
=I001    7.510    .0000E+00    -.7326E+01   .6988E+02    N,N
=A110    5.010    .8522E+01    .0000E+00    .8532E+02    N,N
=A110    7.010    .8500E+00    .0000E+00    .7098E+02    N,N
=A111    5.010    .5674E+01    .2752E+02    .3414E+03    N,N
=A111    11.510   -.4532E+01    -.6434E+02   .9586E+02    N,N
=A112    4.843    .6833E+01    .2334E+02    .2173E+03    N,N
=A112    6.843    .1204E+01    .7254E+00    .7135E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106
***
R3(6,6,9,9) => R5(6,6,9,9)
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I100    6.909    .1030E+01    .0000E+00    .8548E+02    N,N
=I001    7.582    .0000E+00    -.1045E+02   .8591E+02    N,N
=A110    5.058    .8115E+01    .0000E+00    .8263E+02    N,N
=A110    6.909    .1101E+01    .0000E+00    .8739E+02    N,N
=A111    5.058    .5612E+01    .2507E+02    .2867E+03    N,N
=A111    11.116   -.4107E+01    -.6090E+02   .1329E+03    N,N
=A112    5.058    .6182E+01    .1911E+02    .2017E+03    N,N
=A112    6.741    .1460E+01    .1065E+01    .8841E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 105
***
R3(6,6,9,9) => (R4 => R5) (4,6,9,9) TIME(4)=8.9
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I000    7.510    .0000E+00    .0000E+00    .3846E+02    N,N
=I100    6.677    .2248E+01    .0000E+00    .4513E+02    N,N
=I001    7.843    .0000E+00    -.1534E+02   .4035E+02    N,N
=A110    4.677    .1165E+02    .0000E+00    .6218E+02    N,N
=A111    4.510    .1021E+02    .2901E+02    .7613E+02    N,N
=A112    4.677    .8578E+01    .3679E+02    .7163E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106
***
(R3(6,6,9,9) & R4(4,6,9,9)) => R5(4,6,9,9) TIME(4)=8.9
MODEL    DO      A=ALPHA    B=BETA      1/MIN.FUNC  A,B>0?
=I000    7.343    .0000E+00    .0000E+00    .6920E+02    N,N
=I100    7.177    .4759E+00    .0000E+00    .7193E+02    N,N
=I001    7.510    .0000E+00    -.7194E+01   .7175E+02    N,N
=A110    5.010    .8832E+01    .0000E+00    .5723E+02    N,N
=A110    7.010    .8570E+00    .0000E+00    .7235E+02    N,N
=A111    5.177    .5209E+01    .3083E+02    .9748E+02    N,N
=A111    9.510    -.2614E+01    -.4119E+02   .7379E+02    N,N
=A112    5.010    .6718E+01    .2256E+02    .8625E+02    N,N
=A112    7.010    .8505E+00    .3617E+00    .7247E+02    N,N
D-CALC.RANGE=(.1000E-01, .1751E+02) #PTS= 106
***

```


of an adjusted time (as t_4^*) will only affect the scale on the D-axis. It cannot affect either the shape of $\alpha_o(D)$, $\beta_o(D)$, $\Omega(D)$, or the best-fit values of these parameters. The "adjusted time" changes only the "best-fit" D_o -value. We note further that, whereas a time "adjustment" affects only the scale on the D-axis for a 2-time correlation, a normalization "adjustment" affects only the scale of $\alpha_o(D)$ (and $\epsilon(D)$). Neither correction is capable of altering the shape of $\Omega(D)$, $\alpha_o(D)$, or $\epsilon(D)$.

* * *

VI. The Q-dataset, Average Temperature: 574.4°C

This is the lowest temperature diffusion run. Fig. [8.44a] to [8.44d] show the [C vs. x]-graphs and the [$\ln C$ vs. x^2/t^*]-graphs of the raw datafits for 4 and 7 polynomials, using both:

$$P.C.(Q\text{-data}) = (4,6,9,9); \quad P.C.(Q\text{-data}) = (7,7,9,9).$$

The $P.C.=(7,7,9,9)$ results are plotted. The raw datafits on a logarithmic plot emphasize the extreme non-linearities which are expected at this low temperature, although the unusual deep tail region may largely be an artifact of the polynomial number. The AIII- and AIIZ-model $\Omega(D)$ functions are shown for a variety of correlations in Fig. [8.45]. The "good-fits" here all involve the longest time (Q4)-dataset, indicative again, of extreme non-linearity. The (Q3)→(Q4) correlation being one of these "good-fits", the non-linear resolution of the (Q3)-propagated state is given in [8.46c] and [8.46d], the comparison of this (Q3)-propagated state with the (Q4)-datafit being given in Fig. [8.46a] and [8.46b]. Also, the I000- and AIII-model $\Omega(D)$ -functions are shown in Fig. [8.45i] and [8.45j] for

Figure 8.44a through 8.44d. This dataset is given the label 'Q' in text. Average temperature: 574°C. Both 7-polynomial and 4-polynomial fits to the raw data are presented, plotted both on [C vs. x]-axes and [$\ln C$ vs. x^2]-axes. Note the deviations in the tail (large x^2) region on Fig. 8.44b compared with 8.44d. The individual profiles are labelled as follows:

Label	Diffusion Time (tu)	Temperature (°C)	Total Area
Q1	4.05	575.3	5.56
Q2	8.01	574.3	5.44
Q3	15.93	574.3	6.41
Q4	31.77	574.7	4.88

Fig. 8.44 Raw data-fits

Fig. 8.44

[a],[b]: $Q1(7,7,9,9) \rightarrow Q2(7,7,9,9)$
 [c],[d]: $Q2(7,7,9,9) \rightarrow Q3(7,7,9,9)$

Fig. 8.45

[e], [f]: $Q1(7,7,9,9) \rightarrow Q4(7,7,9,9)$
 [g], [h]: $Q2(7,7,9,9) \rightarrow Q4(7,7,9,9)$

Fig. 8.45

Fig. 8.45 (Q2→Q3→Q4) (7,7,9,9)

Fig. 8.45

Fig. 8.46

*** Q-DATA: SUMMARY OF RESULTS

TABLE B.9

	EXPTL.TIME	ADJ.TIME
1.	4.0500	4.0500
2.	8.0100	8.0100
3.	15.9300	15.9300
4.	31.7700	31.7700

G1(4,6,9,9) => Q2(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	8.082	.0000E+00	.0000E+00	.3278E+02	N,N
=I100	6.064	.2277E+01	.0000E+00	.1207E+03	N,N
=I001	8.839	.0000E+00	-.1241E+02	.8361E+02	N,N
=A110	6.064	.2570E+01	.0000E+00	.6671E+02	N,N
=A111	7.325	.1266E+01	-.7265E+01	.9938E+02	N,N
=A112	6.316	.1981E+01	.1962E+01	.5120E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 112

G1(7,7,9,9) => Q2(7,7,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	8.010	.0000E+00	.0000E+00	.2893E+02	N,N
=I100	5.760	.2661E+01	.0000E+00	.1066E+03	N,N
=I001	8.885	.0000E+00	-.1387E+02	.7576E+02	N,N
=A110	5.885	.2828E+01	.0000E+00	.5412E+02	N,N
=A111	7.260	.1398E+01	-.8520E+01	.8843E+02	N,N
=A112	6.260	.2016E+01	.2032E+01	.4203E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 113

Q2(4,6,9,9) => Q3(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	6.316	.0000E+00	.0000E+00	.3592E+02	N,N
=I100	4.677	.2926E+01	.0000E+00	.4353E+03	N,N
=I001	6.821	.0000E+00	-.1996E+02	.8639E+03	N,N
=A110	4.298	.4406E+01	.0000E+00	.1631E+03	N,N
=A111	6.316	.6340E+00	-.1639E+02	.1845E+04	N,N
=A112	5.307	.2206E+01	-.9160E+01	.1124E+04	N,N
=A112	4.677	.2985E+01	.4455E+01	.6757E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 112

Q2(7,7,9,9) => Q3(7,7,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	6.260	.0000E+00	.0000E+00	.3167E+02	N,N
=I100	4.635	.3015E+01	.0000E+00	.6552E+02	N,N
=I001	6.885	.0000E+00	-.2048E+02	.6754E+02	N,N
=A110	3.885	.5948E+01	.0000E+00	.9293E+02	N,N
=A111	3.885	.6206E+01	-.3244E+01	.9955E+02	N,N
=A112	4.510	.3387E+01	.5735E+01	.5117E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 113

Q3(4,6,9,9) => Q4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	3.289	.0000E+00	.0000E+00	.2797E+02	N,N
=I100	2.028	.6824E+01	.0000E+00	.3277E+03	N,N
=I001	4.046	.0000E+00	-.5193E+02	.2486E+03	N,N
=A110	1.902	.8724E+01	.0000E+00	.7369E+02	N,N
=A111	3.163	.2573E+01	-.3796E+02	.7863E+03	N,N
=A112	2.280	.4633E+01	.1073E+02	.4235E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 112

Q3(7,7,9,9) => Q4(7,7,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	3.385	.0000E+00	.0000E+00	.2283E+02	N,N
=I100	2.010	.7748E+01	.0000E+00	.7176E+02	N,N
=I001	4.385	.0000E+00	-.6231E+01	.8498E+02	N,N
=A110	1.760	.1142E+02	.0000E+00	.6278E+02	N,N
=A111	2.135	.1005E+02	-.3271E+02	.4359E+03	N,N
=A112	2.260	.5271E+01	.1389E+02	.3246E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 113

Q1(4,6,9,9) => Q4(4,6,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	4.677	.0000E+00	.0000E+00	.2196E+02	N,N
=I100	3.542	.3377E+01	.0000E+00	.1450E+03	N,N
=I001	11.992	-.1653E+02	.0000E+00	.3320E+02	N,N
=I001	5.433	.0000E+00	-.4096E+02	.1067E+03	N,N
=A110	3.668	.3594E+01	.0000E+00	.7484E+02	N,N
=A111	4.298	.3201E+01	-.2838E+02	.9595E+03	N,N
=A112	3.794	.2720E+01	.3699E+01	.3000E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 112

Q1(7,7,9,9) => Q4(7,7,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	4.760	.0000E+00	.0000E+00	.1883E+02	N,N
=I100	3.510	.3651E+01	.0000E+00	.5100E+02	N,N
=I001	5.635	.0000E+00	-.4837E+02	.7707E+02	N,N
=A110	3.760	.3476E+01	.0000E+00	.2741E+02	N,N
=A111	4.260	.5504E+01	-.4418E+02	.1038E+03	N,N
=A112	3.885	.2630E+01	.3458E+01	.2427E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 113

Q2(7,7,9,9) => Q4(7,7,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	4.260	.0000E+00	.0000E+00	.1912E+02	N,N
=I100	3.010	.4723E+01	.0000E+00	.5196E+02	N,N
=I001	5.010	.0000E+00	-.5946E+02	.8045E+02	N,N
=A110	3.010	.5602E+01	.0000E+00	.3221E+02	N,N
=A111	3.260	.7683E+01	-.4543E+02	.2047E+03	N,N
=A112	3.260	.3707E+01	.6873E+01	.2552E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 113

(Q2 => Q3 => Q4) (7,7,9,9)

MODEL	DO	A=ALPHA	B=BETA	1/MIN.FUNC	A,B>0?
=I000	4.760	.0000E+00	.0000E+00	.1541E+02	N,N
=I100	3.010	.5453E+01	.0000E+00	.2118E+02	N,N
=I001	5.135	.0000E+00	-.2158E+02	.1665E+02	N,N
=A110	2.510	.9517E+01	.0000E+00	.2200E+02	N,N
=A111	2.510	.9793E+01	-.3502E+01	.2200E+02	N,N
=A112	2.885	.5701E+01	.1625E+02	.2000E+02	N,N

D-CALC.RANGE=(.1000E-01, .1401E+02) #PTS= 113

the 3-time correlation $(Q2) \rightarrow (Q3) \rightarrow (Q4)$. As before, each model, for each Q-data correlation, has the maxima in $\Omega(D)$ presented with the (D_0, α_0, β_0) -values, here in Table <8.9>.

In addition to the extreme behavior of the penetration profiles, it is noteworthy that $\beta_0 < 0$ for every AIII-model correlation performed, again indicating a most severe deviation from the "standard" model.

* * *

VII. Arrhenius Plots

In the last section we have seen that the non-linear analysis method constructed in this work is indeed capable of giving excellent agreement with experimentally measured penetration profiles over a wide range of times and temperatures. The two-time correlation studies show a significant increase in "goodness-of-fit" using a non-linear equation compared to the $D=\text{constant}$ equation. The approximation of a given $D(C)$ -function by:

$$D(C) = D_0 (1 + \alpha C + \beta C^2) \quad (8.17)$$

which necessitates at least an equivalent level of approximation in constructing $C(z, \Gamma)$:

$$C(z, \Gamma) = \phi_0(z, \Gamma) + \alpha \phi_1(z, \Gamma) + \alpha^2 \phi_2(z, \Gamma) + \beta \phi_3(z, \Gamma) \quad (8.18)$$

has been shown to be sufficient to match practically every detail of a "curved" (on $[\ln C \text{ vs. } x^2]$ -axes) profile except in the deep "limiting-slope" region; as well as to match the details of the profile shape for a $[C \text{ vs. } x]$ -plot.

The multiple-time correlations, however, show a decrease in "goodness-of-fit" and this indicates that the "true" $D(C)$ function is a strongly changing function of anneal time. As noted earlier, this can be due to either the $D(C)$ function being a strong function of concentration, or the behavior of the system being governed in each concentration region by dominance of a different type of physical process. But, as the $D(C)$ here is so rapidly changing a function, a correlation using two states ($S[\text{Initial}] \rightarrow S[\text{Final}]$) where ' $S[\text{Initial}]$ ' and ' $S[\text{Final}]$ ' have very different diffusion times, should be inaccurate because it ignores the changes in what drives the system for the intermediate times. Thus, in this section we concentrate on the sequential correlations (state $(N) \rightarrow \text{state}(N+1)$) in the further analyses.

* * *

Fig. [8.47] is an Arrhenius plot ($\ln D_0$ vs. $10^3/T(K)$) plot of the diffusivity D_0 obtained from the AIII-model non-linear analysis for the various temperatures and for the sequential-type correlations. Since no segregation is made of the short-time correlations (as $(S1) \rightarrow (S2)$) or long-time ones (as $(S3) \rightarrow (S4)$), the general clustering of values of D_0 (for a given temperature) in a small region indicates that the D_0 values are not strongly changing. This is an important "success" of this analysis. Ideally, the D_0 values should have been all the same point (since the corrections for non-linearities have been made) but the approximation of $D(C)$ as a parabolic function, being inexact, has given rise to the scatter. The fact that the scatter here is not great (where any limiting slope or linear equation analysis would have given a totally different answer, with even

Figure 8.47. Arrhenius plot of the $D_0(T)$ values obtained after correcting for the non-linear diffusion process, using a quadratic (in C) diffusivity:

$$D(C) = D_0(T) \cdot (1 + \alpha C + \beta C^2).$$

The points plotted are analysis results primarily from the sequential correlations, where each state at a given time is propagated forward, non-linearly, to match the next larger time data state.

The squares correspond to using initial data fits containing ≈ 6 polynomials; the triangles to using ≈ 4 polynomials. The critical "recoupling" stage[†] for these points has ≈ 6 polynomials. For the 'S'-dataset, the results of a 4 polynomial calculation at this "recoupling" stage are also given (indicated by diamonds on plot). The 3 filled-in symbols ('S'-dataset) are explained in text.

[†] See Ch. 4, Sec. VII; Ch. 8, end of Sec. I; and end of part A, Sec. II, Ch. 8.

Fig. 8.47

Figure 8.48. Plots the same information as Figure 8.47, but on an expanded scale, with each point labelled, and with each point corresponding to a labelled entry in Table 8.10 and indicated by the letters A,B,C,... The numbers associated with each dataset (as "T(1.003)") correspond to values of $[10^3/T(^{\circ}\text{K})]$.

Fig. 8.48

TABLE 8.10

AIII-MODEL SUMMARY (SEE FIG. 8.4B)

PT.	CORRO.	DO	ALPHA	BETA	FIT.RATIO	#POLY
U-DATA: TEMP.=774.9°C						
A.	U1A=>U2A	64.670	.1255E+01	.1368E+01	.6442D+02	[5,5]
B.	U2A=>U3	59.010	.1521E+01	.4036E+01	.7046D+02	[5,5]
C.	U3=>U4	46.010	.3821E+01	.1033E+02	.6099D+02	[5,5]
D.	U2A=>U4	49.010	.3373E+01	.7951E+01	.2977D+02	[5,5]
E.	U2A-U3-U4	47.010	.3534E+01	.1013E+02	.6577D+01	[5,5,5]
F.	U1A=>U2A	62.328	.1508E+01	.2325E+01	.1034D+03	[3,3]
G.	U2A=>U3	60.010	.1347E+01	.3824E+01	.2910D+02	[3,3]
H.	U3=>U4	51.010	.2755E+01	.2991E+01	.1492D+03	[3,3]
I.	U2A=>U4	53.556	.2546E+01	.1824E+01	.1009D+03	[3,3]
J.	U2A-U3-U4	50.010	.2926E+01	.6909E+01	.2951D+01	[3,3,3]
T-DATA: TEMP.=724.2°C						
A.	T2=>T3	19.677	.3350E+01	.5288E+01	.8374D+01	[6,6]
B.	T3=>T4	16.677	.4653E+01	.1593E+02	.1877D+02	[6,6]
C.	T2=>T4	19.010	.3048E+01	.4916E+01	.1522D+02	[6,6]
D.	T2-T3-T4	18.343	.3760E+01	.7170E+01	.3108D+01	[6,6,6]
E.	T2=>T3	21.885	.2532E+01	.1632E+01	.1697D+02	[4,4]
F.	T3=>T4	18.520	.3363E+01	.8613E+01	.1613D+02	[4,4]
G.	T2=>T4	20.202	.2501E+01	.2476E+01	.1655D+02	[4,4]
H.	T2-T3-T4	19.193	.3408E+01	.3958E+01	.2992D+01	[4,4,4]
S-DATA: TEMP.=674.2°C						
A.	S1=>S2	9.596	.5263E+01	.6129E+01	.7087D+01	[6,6]
B.	S2=>S3	16.154	.2595E+01	-.5232E+01	.6444D+02	[6,6]
C.	S3=>S4	14.641	.2017E+01	-.1960E+02	.3662D+01	[6,6]
D.	* * *	10.352	.4572E+01	.0000E+00	.5506D+01	[6,6]
E.	S1=>S2	9.010	.6021E+01	.6804E+01	.1340D+02	[4,4]
F.	S2=>S3	14.641	.3534E+01	-.2414E+01	.7636D+02	[4,4]
G.	S3=>S4	14.510	.1903E+01	-.1593E+02	.6205D+01	[4,4]
H.	* * *	11.010	.3851E+01	.0000E+00	.1207D+02	[4,4]
I.	S2=>S3	11.365	.6241E+01	.5357E+01	.1336D+03	<4,4>
J.	S3=>S4	11.614	.4104E+01	-.6322E+01	.7527D+01	<4,4>
K.	* * *	11.109	.3717E+01	.0000E+00	.1487D+02	<4,4>
* = BEST BETA = 0.0 MODEL (IN EACH CASE: IIUO-MODEL)						
R-DATA: TEMP.=624.7°C						
A.	R2=>R3	4.217	.7155E+01	.2739E+01	.3215D+01	[6,6]
B.	R3=>R4	3.843	.1554E+02	.1647E+02	.3903D+01	[6,4]
C.	R4=>R5	4.677	.7068E+01	.5554E+02	.5290D+01	[4,4]
D.	R2=>R4	5.343	.8022E+01	-.1519E+02	.3479D+02	[6,4]
E.	R3=>R5	5.010	.5674E+01	.2752E+02	.5224D+01	[6,4]
F.	R3-R4-R5	4.510	.1021E+02	.2901E+02	.1979D+01	[6,4,4]
Q-DATA: TEMP.=574.4°C						
A.	Q1=>Q2	7.260	.1358E+01	-.8520E+01	.3067D+01	[7,7]
B.	Q2=>Q3	3.885	.6206E+01	-.3244E+01	.3143D+01	[7,7]
C.	Q3=>Q4	2.135	.1005E+02	-.3271E+02	.1909D+02	[7,7]
D.	Q1=>Q2	7.325	.1266E+01	-.7265E+01	.3032D+01	[4,4]
E.	Q2=>Q3	5.307	.2206E+01	-.9160E+01	.3129D+02	[4,4]
F.	Q3=>Q4	3.163	.2573E+01	-.3796E+02	.2811D+02	[4,4]

CODE (UNDER HEADING: *#POLY*):

([6,] OR [,6])=P.C.(6,6,9,9); ([4,] OR [,4])=P.C.(4,6,9,9)

([7,] OR [,7])=P.C.(7,7,9,9); (<4, > OR < ,4>)=P.C.(4,4,8,8)

FIT.RATIO =

MAX.FUNC.(BEST NON-LINEAR.EQN.FIT)/MAX.FUNC.(BEST LINEAR.EQN.FIT)

greater scatter), means that even in this extreme non-linearity limit this method is capable of being quantitatively accurate for "real" experimental situations.

To avoid clutter, the points in [8.47] have not been explicitly labelled, but they have been labelled and re-plotted on an expanded scale in Fig. [8.48]. The numerical values associated with the points of Fig. [8.48] are taken directly from the previously presented tables and are collected in Table <8.10>. For the (U3) and (R4) datasets which involved a time-adjustment, the following correlation results were both plotted:

1. (R3)→(R5) (R3)→(R4[$\hat{t}_4=8.90$])→R5
2. (U2A)→(U4); (U2)→(U3[$\hat{t}_3=.680$])→U4.

In addition, because the (S3)→(S4) correlation has an unusually large ratio 'r' ($r \approx -4.9$); the best $\beta=0$ model is also plotted (it is the II00-model, which, note, is a better 1st-order fit than the best 2nd-order (AIII-model) fit). We are inherently suspicious of large 'r'-values because they indicate a β -term dominated fit which is then primarily a model of: $D(C)=D_0(1+\beta C^2)$ with the α -term at most a small correction. Since this model is nowhere motivated by the physics, large 'r'-values (which are all, incidentally, large negative values) are discounted.

* * *

Since the 2-time correlations work quite well compared to most multiple-time correlations, it has been taken as an indication of a strongly changing $D(C)$ function operating. This gives an emphasis to the sequential-time correlations and gave an Arrhenius-type plot with post-non-linear-analysis values of D_0 which, as Fig. [8.47] showed, are similar

for the entire range of diffusion times at each temperature. If this interpretation is well-founded, the longest time correlations should give the most reliable measure of D_0 . The D_0 values for these long-time correlations have thus been abstracted from [8.47] and are plotted in Fig. [8.49], using the P.C.=(6,6,9,9) results [Q:(7,7,9,9); U:(5,5,8,8)].

The most striking behavior of [8.49] is the two distinct straight "lines" that together fit the data. The upper part of Fig. [8.49] is composed of:

- (1). A solid-line curve representing a least-squares fit to the points (indicated by a small square symbol) which are "best" D_0 (AIII-model) values.
- (2). A dashed-line curve representing a least-squares fit to the points (denoted by a small cross) which are the best linear-equation D_0 -values for the same correlations as in the solid-curve.

The lower part of [8.49] is a plot of $(\alpha_0)^{-1}$ for the same long-time correlations (the $(\alpha_0)^{-1}$ -scale is on the right-side of [8.49], the diffusivity scale on the left).

In each case, the data are well-represented by two straight lines joined, indicating that two processes are operating, each with its own activation energy. We express each of the curves in [8.49] in terms of the form:

$$"X" = "X_0" \cdot \exp\{-U[(kT)^{-1} - (kT_m)^{-1}]\} \quad (8.19)$$

where T_m =melting-point (NaCl:801°C), U =activation-energy, and where ' X_0 ' represents the value of the quantity ' X ' at the melting point. We denote the two separate regions: (H.T.)='High-Temperature Region', (L.T.)='Lower-Temperature Region.'

Figure 8.49. The upper two of the 3 curves are plots of $D_o(T)$ abstracted from Figure 8.47, using the long-time correlations. The diffusivity scale (du units = 10^{-10} cm²/sec) is on the left border.

The upper (dashed-line) curve, along with marked crosses, corresponds to the linear equation $D_o(T)$ result for these long-time correlations. The lower of the two curves, a solid line with marked small squares, corresponds to the $D_o(T)$ found after corrections have been made for the non-linearity, using the quadratic (in C) diffusivity.

The lowest of the three curves, is a plot of $[\alpha_o]^{-1}$ vs. Temperature using the scale on the right border (cu units = 1 nanomole/cm²micron)

The points plotted, abstracted from Table 8.10, are:

$10^3/T(^{\circ}K)$	Correlation	Model	D_o	α_o	$\Omega(D_o)$	#Poly [†]
.954	U2A→U4	AIII	49.0	3.37	2636.	[5,5]
		I000	66.0	0.0	88.6	
	U2A→U3→U4	AIII	47.0	3.53	535.5	[5,5,5]
		I000	67.0	0.0	81.4	
1.003	T2→T3→T4	AIII	18.3	3.76	147.5	[6,6,6]
		I000	27.3	0.0	47.5	
1.056	S3→S4	II00	10.4	4.57	144.3	[6,6]
		I000	15.9	0.0	26.2	
1.114	R3→R5	AIII	5.0	5.67	341.4	[6,4]
		I000	7.3	0.0	65.4	
	R3→R4→R5	AIII	4.5	10.2*	76.1	[6,4,4]
		I000	7.5	0.0	38.5	
1.180	Q3→Q4	AIII	2.14	10.1	435.9	[7,7]
		I000	3.34	0.0	22.8	

* $[\alpha_o]^{-1}$ not plotted for this point

[†]The "Poly" follows the form given in Table 8.10

Fig. 8.49

The D_0 (limiting-concentration diffusivity) obtained from the non-linear (AIII-model) analysis, as a function of temperature, is:

$$D_0(\text{H.T.}) = 75.45 \exp(-1.69 \pm 0.02 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.20a)$$

$$D_0(\text{L.T.}) = 45.76 \exp(-1.06 \pm 0.04 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.20b)$$

where the units are in du-units ($1 \text{ du} = 10^{-10} \text{ cm}^2/\text{sec}$). In the high-temperature region (here the T-dataset and U-dataset), not only was this AIII-model a good-fit, but the AIIZ-(cognate to the "standard")-model was also a good-fit. This was not true for most of the lower temperature correlations, and this lower temperature region is exactly the region where the lines in [8.49] show a definite "break" compared to the H.T.-region.

In the "standard" model, and in most of the models given in Chapter 3, the non-linearity parameter, α_0 , is proportional to the inverse of $[v_0]$ (cation vacancy concentration in the absence of impurities). Thus, the quantity $[\alpha_0]^{-1}$ was also plotted, as a function of temperature. The fits are given by:

$$[\alpha_0]^{-1}(\text{H.T.}) = .30 \exp(-0.15 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.21a)$$

$$[\alpha_0]^{-1}(\text{L.T.}) = .35 \exp(-0.32 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.21b)$$

The concentrations (.30, .35), expressed in cu-units ($1 \text{ cu} = 1 \text{ nanomole}/\text{cm}^2 \cdot \text{micron}$) correspond to, respectively, (81 p.p.m., 94 p.p.m) at the melting-point. The "standard" model (see Chapter 3, Sec. VI: "Summary of Models") has :

$$\alpha_0 = m/2[\hat{v}_0], \quad [\hat{v}_0] = \left[\begin{array}{l} \text{Total cation vacancy concentration} \\ \text{including divacancies} \end{array} \right] \quad (8.22)$$

where m =(charge mismatch)=1 (for $\text{Ca}^{++} \rightarrow \text{NaCl}$). This then gives

$$[\hat{v}_0] \text{ (at melting point)} = (40-47 \text{ p.p.m.}).$$

This is somewhat lower than the value estimated by Dreyfus and Nowick⁵³ (251 p.p.m. at melting point), and slightly higher than a more recent value of Allnatt and Pantelis⁵⁴ of 32 p.p.m. We believe it to be an underestimation for the following reason: The parameters (D_o, α_o, β_o) are closely coupled in the non-linear solution and the general trends can be established:

(1). Every $D(C)=D_o(1+\beta C^2)$ model gave a $\beta < 0$ value, and concurrently a $D_o(\text{pure } \beta\text{-model}) > D_o(\text{best linear equation fit})$

(2). Every $\beta=0$ model had a primary maximum in the $\alpha > 0$ region and concurrently gave a $D_o(\text{pure } \alpha\text{-model}) < D_o(\text{linear equation})$. Thus, if a "best-fit" (D_o, α_o)-value has a D_o that was high compared to similar measurements (at, say, a nearby diffusion anneal time), then it will concurrently have an α_o -value which is "too-low" and vice-versa. The exact amount of variation may be difficult to quantify and is beyond the scope of this present work.

With knowledge of this basic "trade-off" between the various parameters, we note the following: The parameter 'r', which equals .5 in the standard model, has the U-data values (AIII-model) of:

$$r(U2A \rightarrow U3(t_3) \rightarrow U4) = .811 \quad r(U2A \rightarrow U4) = .699$$

whereas for the T-data, it is:

$$r(T2 \rightarrow T3 \rightarrow T4) = .507$$

The standard model, which assigns the equivalence: $\alpha_o = m/2[\hat{v}_o]$, assigns $r=.5$ (with some extensions of Chapter 3 giving $.4 \leq r \leq .5$ or $r=0$). Since the U-dataset has good fits with incredibly large $\Omega(D_o)$ ($\sim 10^4$ in some cases), it is quite believable that one has the "real" (D_o, α_o, β_o) close to the

value specified by the maximum of $\Omega(D)$. This is further evidenced by the U-dataset giving 'r' values 40-60% greater than $r=.5$, and (as noted at the end of Chapter 3) values of $r>.5$ are not easily interpreted within the framework of Chapter 3 models.

We, therefore, for purposes of determining $[\hat{v}_0]$ by using $\alpha_0 = m/2[\hat{v}_0]$, turn to the (D_0, α_0, β_0) -values of the AIIZ-model where $r=.5$ is rigorously enforced. These "best-fits" have an $\Omega(D)[\text{AIIZ-model}] < \Omega(D)[\text{AIII-model}]$, but, as noted earlier, the AIIZ-model also gives "good" fits (within experimental error) for the T-data and U-data sets. We believe that the $D(C)$ as dictated by the "standard" model is indeed the majority effect operating at these higher temperatures, reasonably free of other possible non-linear effects, the success of the AIIZ-model being the primary evidence of this.

Fig. [8.50a] shows the AIIZ-model results for the various U-data and T-data correlations; [8.50b] shows the same results on an expanded scale with labelled points, the values associated with the points being given in Table <8.11>. Fig. [8.50a] also shows an exponential-type fit to the long term correlations, and in [8.50c] we plot the $[\alpha_0]^{-1}$ -values for these. This gives a modified high-temperature D_0 -function and a modified $[\alpha_0]^{-1}$:

$$D_0(\text{H.T.}) \doteq 98.42 \exp(-2.01 \text{ eV})[(kT)^{-1} - (kT_m)^{-1}] \quad (8.23)$$

$$[\alpha_0]^{-1}(\text{H.T.}) = 1.03 \exp(-1.63 \text{ eV})[(kT)^{-1} - (kT_m)^{-1}], \quad (8.24)$$

the (1.03)-value corresponding to a melting point vacancy concentration of (via $[\hat{v}_0] = .5 [\alpha_0]^{-1}$, see also end of Sec. III, Chapter 2):

$$[\hat{v}_0] \text{ (at melting point)} = 139 \text{ p.p.m.}$$

Figure 8.50. Alternate high temperature $D_o(T)$ function using the specific quadratic diffusivity (AIIZ-model):

$$D(C) = D_o(T) \cdot (1 + [\alpha C] + .5[\alpha C]^2),$$

which is the small series expansion of the 'standard' $D(C)$ model with vacancy equilibration with extended defects (see Chapter 3, Sec. I). In this model $[\alpha_o]^{-1} = .5[v_o]$ where $[v_o]$ = intrinsic vacancy concentration.

Fig. 8.50a shows the $D_o(T)$ values obtained primarily from the sequential correlations. The square and triangle data points follow notation of Fig. 8.47.

Arrows mark the three longer-time correlations, which give the $D_o(T)$ line plotted. The $[\alpha_o]^{-1}$ for these points, plotted as a function of $[10^3/T^\circ(K)]$, are shown in Fig. 8.50c.

Fig. 8.50b shows the same results as Fig. 8.50a, but on an expanded scale, with labelled points corresponding to entries in Table 8.11. The units on all axes match those of Fig. 8.47 also.

The AIIZ-model results are not plotted for lower temperatures because this restricted $\beta = .5\alpha^2$ model does not give a good datafit in that region. See text for details.

The points which were used to determine the lines in Figs. 8.50a and 8.50c, abstracted from Table 8.11, are:

$10^3/T(^{\circ}K)$	Correlation	Model	D_o	α_o	$\Omega(D_o)$	#Poly
.954	U2A→U4	AIIZ	58.0	1.46	295.7	[5,5]
	U2A→U3→U4		57.0	1.53	153.3	[5,5,5]
1.003	T2→T3→T4	AIIZ	18.3	3.77	147.5	[6,6]

Fig. 8.50

TABLE 8.11

AIIZ-MODEL SUMMARY (SEE FIG. 8.50)

PT.	CORRO.	DO	ALPHA	BETA	FIT.RATIO	#POLY
U-DATA; TEMP.=774.9°C						
A.	U1A=>U2A	66.690	.1044E+01	.5447E+00	.2256D+02	[5,5]
B.	U2A=>U3	67.010	.5784E+00	.1673E+00	.6786D+01	[5,5]
C.	U3=>U4	57.010	.1363E+01	.9363E+00	.3040D+01	[5,5]
D.	U2A=>U4	58.010	.1463E+01	.1071E+01	.3339D+01	[5,5]
E.	U2A-U3-U4	57.010	.1523E+01	.1168E+01	.1883D+01	[5,5]
AA.	U1A=>U2A	49.515	.3470E+01	.6021E+01	.2244D+01	[5,5]
BB.	U2A=>U3	40.010	.5328E+01	.1419E+02	.1006D+01	[5,5]
CC.	U3=>U4	43.010	.4800E+01	.1152E+02	.5054E+01	[5,5]
DD.	U2A=>U4	47.010	.4019E+01	.8078E+01	.4968D+01	[5,5]
EE.	U2A-U3-U4	43.010	.4736E+01	.1121E+02	.2740D+01	[5,5]
F.	U1A=>U2A	67.856	.9181E+00	.4214E+00	.1396E+02	[3,3]
G.	U2A=>U3	68.010	.4392E+00	.9646E-01	.5584D+01	[3,3]
H.	U3=>U4	50.010	.2975E+01	.4426E+01	.1464E+02	[3,3]
I.	U2A-U3-U4	54.010	.2141E+01	.2292E+01	.2197D+01	[3,3]
FF.	U1A=>U2A	49.261	.3517E+01	.6183E+01	.2163D+01	[3,3]
GG.	U2A=>U3	40.010	.5306E+01	.1408E+02	.7456E+00	[3,3]
HH.	U3=>U4	(NO ALTERNATE PEAK)				
II.	U2A-U3-U4	46.010	.3959E+01	.7837E+01	.2268D+01	[3,3]
T-DATA; TEMP.=724.2°C						
A.	T2=>T3	20.010	.3193E+01	.5099E+01	.7566D+01	[6,6]
B.	T1=>T4	15.677	.5676E+01	.1611E+02	.2775D+01	[6,6]
BB.	"	22.677	.9866E+00	.4867E+00	.1477D+01	[6,6]
C.	T2=>T4	19.010	.3070E+01	.4712E+01	.1309E+02	[6,6]
D.	T2-T3-T4	18.343	.3767E+01	.7096E+01	.3108D+01	[6,6]
E.	T2=>T3	22.558	.2218E+01	.2461E+01	.4126D+01	[4,4]
F.	T3=>T4	20.875	.1959E+01	.1919E+01	.4151D+01	[4,4]
FF.	"	17.173	.4432E+01	.9822E+01	.3522D+01	[4,4]
G.	T2=>T4	20.539	.2298E+01	.2640E+01	.3108D+01	[4,4]
H.	T2-T3-T4	19.529	.3145E+01	.4944E+01	.2968D+01	[4,4]

NOTE: DOUBLE LETTERS (AS "AA") DENOTE SECOND PEAK IN AIIZ-MODEL AND ARE NOT PLOTTED

F. Comparison with Other Workers

The results of the (AIII-model) best non-linear equation results as shown in Fig. [8.49] are compared with the results of Slifkin and Brebec,⁵⁵ Mitchell,^{44,45} and Beniere et al.;⁵⁶ as shown in Fig. [8.51].

The results of Slifkin and Brebec were taken with intentionally high specific activity tracer, to assure a minimum amount of Ca-impurity. That curve indicates the following diffusivity:

$$D_o(T) = 74.9 \exp(-1.62 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}]. \quad (8.25)$$

The high-temperature portion of this work gave:

$$D_o(T) = 75.45 \exp(-1.69 \pm 0.02 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.26)$$

which closely matches the Slifkin result in this high temperature range, even though the tracer amounts used here were purposely very large. The linear-equation curve of Fig. [8.49] serves as a reference to the extreme non-linearity of the present data. Thus, guided by Slifkin's result, we see the viability of this analysis method for handling non-linear diffusion.

The results of Mitchell are also given, that diffusivity function being:

$$D_o(T) = 63.6 \exp(-1.60 \pm 0.04 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}]. \quad (8.27)$$

This value is lower than Slifkin's result, and used a Ca-impurity concentration that was not deliberately chosen "low" or "high", in conjunction with an approximate procedure to correct for the non-linearities. Lazarus⁵⁷ notes that the Mitchell-Feit procedure tended to "over-correct", i.e., to give low D_o -values. We further note here that even though Mitchell purposely did not use a low-concentration of tracer, the present data have been taken at even higher concentrations, approximately 5-20 times the

Figure 8.51. Plots of $D_0(T)$ functions, compared with prior measurements of Slifkin, Mitchell, and Beniere. The present work uses the quadratic (in C) diffusivity, unrestricted ' β '. For full comparison with Beniere's line, the low temperature portion of the present work has been drawn extrapolated to the melting point.

Fig. 8.51

concentrations used in determining the Mitchell line. We have kept track of the total impurity amount used (and this is expressed as "Total area under (C vs. x)-curve" or "Renormalization Coefficient" -- see Chapter 2, Sec. III; Chapter 4, Sec. II; and Table <8.1>) and these "areas", i.e.:

$$\int \tilde{C}(x, t_i) dx = N(i) \quad (8.28)$$

ranged in this experiment from about 4-6, with most clustering near 5 Amounts. This corresponds to a surface concentration of:

$$5 \text{ Amounts} = 50 \text{ nanomoles/cm}^2 = 3.01 \times 10^{16} \text{ Atoms/cm}^2.$$

As mentioned earlier, the concentrations of this experiment were purposely chosen so high, because we sought to see if this method would be capable of handling extreme non-linearities (it had been believed at this project's inception that the method of Feit et al. and Mitchell et al. was capable of handling the low to moderate concentration values).

Finally, the results of Beniere et al. are also shown, with the diffusivity function:

$$D_o(T) = 42.1 \exp(-1.14 \pm 0.01 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}]. \quad (8.29)$$

Beniere's results have often been questioned, being quite at odds with the values of Mitchell and Slifkin. Beniere et al. used limiting slope to determine D_o , and tracer of rather low specific activity (i.e., high Ca-impurity concentrations). What is unusual is that the activation energy of Beniere's work closely matches the low temperature curve found here of:

$$D_o(T) = 45.76 \exp(-1.06 \pm 0.04 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.30)$$

This unexpected concurrence of two "anomalous" results we view as further evidence of a second process operating, and this will be considered in the next section.

* * *

VIII. A Speculation

The distinct "break-point" on the Arrhenius plots is the first evidence of 2 processes operating: one at high-temperatures, and one at lower temperatures. The success of the AIIZ-model (which is the small power-series expansion of the "standard" D(C)-model) in the high-temperature region and its sudden inadequacy as a datafitting model in the lower temperatures is a second indication of a possible 2-process situation. The third evidence comes from the examination of Fig. [8.51], where the high temperature-region matches the expected $D_0(T)$ curve, and the low-temperature part seems part of the same "family" as Beniere's results. The fourth evidence is derived from the details of the present analysis procedure.

In reviewing the $[\Omega(D), \alpha_0(D), \epsilon(D)]$ -plots for the various correlations and temperatures, one sees the consistent appearance of "side-branches" in the AIII-model. Recalling that the minimizing functional $\phi^2(D, \alpha, \beta)$ is inherently a quartic in α , there must be either one or three α -values corresponding to extreme of $\phi^2(D, \alpha, \beta)$; this allows the appearance of these branches in the AII0-, AIII-, and AIIZ-models. We note that the side branches are uncommon in the AII0-model, and, whenever present in the AIII-model, they are associated with a value $\beta < 0$. This connection between

Figure 8.52. This shows a typical case, using the AIII-model (T2→T3 correlation), where the $\phi^2(D)$ -function, being a quartic in α_0 , has only one single principle minimum. The "side-branches" on the (AIII)-plot correspond to local extrema of $\phi^2(D)$ at such large values of α_0 , that they are totally ignorable.

side-branches and $\beta < 0$ is further enforced by the fact that the AIIZ-model ($\beta = .5\alpha^2$ so by construction, $\beta > 0$) never was seen to develop these branches, although it also has a cubic determining α .

The shape of the $\alpha(D)$ and $\beta(D)$ functions can be divided into two general categories: those where the side-branches come "close" to the main-branch (as shown in Fig. [8.53] which is the (R2)→(R4) correlation), and those where the side-branches are "far" from the main branch (as shown in Fig. [8.52] which is the (T2)→(T3) correlation).

In the cases where the side branches are not close to the main-branch, $\phi^2(D)$ develops a local maximum and local minimum at values of $\phi^2(D)$ so large (indicating a very poor fit) so that these side-branches are totally ignorable. Such is the case shown in [8.52]; the $[\phi^2(\alpha, D)$ vs. $\alpha]$ -plot is qualitative in nature, but still shows how the physically relevant (small value of $\phi^2(\alpha, D)$) region compares with the "side-branch" region.

Fig. [8.53], where the side-branches are close to the main-branch, is more interesting. Visual inspection shows that "branch-2" of the side-branches seems almost a continuation of "branch-1". Simultaneously, "branch-1" developed a corner-like region (the down-dipping branch labelled "branch-1A").

Indeed, if "branch-2" represents a continuation of the same physical phenomena as "branch-1", then the non-linear diffusion process is showing a sudden transition to a new type of behavior. At this transition point, the α_0 -value which gave a global minimum in $\phi^2(\alpha, D)$ as a function of α (i.e., "branch-1"), becomes a local maximum in $\phi^2(\alpha, D)$ as a function of α (i.e., "branch-2"). This is very reminiscent of a (2nd-order) phase

Figure 8.53. This shows a typical case, using the AIII-model ($R_2 \rightarrow R_4$ correlation), where the equation determining α_0 has a point where there are three real, close-valued numbers for α_0 . In these cases, $\phi^2(D, \alpha)$, viewed as a function of α_0 , develops a broad flat region, indicating a whole range of values of α_0 being nearly equivalent "good-fits" to the data. Away from this region, a new "branch" on the $\alpha_0(D)$ -plot becomes associated with the best-fit values, indicating a transition from one type of non-linear behavior, to another type of non-linear behavior. The transition point is viewed as supporting the "two-process" view of non-linear diffusion in this extremely high impurity limit. See text for details.

Fig. 8.52

Fig. 8.53

transition with the $\Phi^2(\alpha)$ -minimizing-functional acting the role of a Free Energy, and ' α_0 ' being akin to an order parameter. This new process (as seen in [8.53]) raises D_0 and lowers α_0 from what it would have been had this process not been operating. As $[\alpha_0]^{-1}$, in the standard model, is proportional to the limiting vacancy concentration (i.e., $[v+]$ as $C \rightarrow 0$), the lowering of α_0 for the "new-process" indicates an increase in the "background" vacancy concentration and thereby gives a larger D_0 .

* * *

We speculate as to the origin of this second process. The low temperature results found here, taken along with Beniere's data, almost appear as part of the same "family" of curves. Both look suspiciously like diffusion in doped crystals. The usual "doped" diffusion experiment is as follows: One investigates homovalent ion diffusion in a crystal doped with a small uniformly dispersed amount of heterovalent impurity. The impurity concentration= $[k]$ is constant and the vacancy concentration is:

$$[v+] = [v_0] + [k]. \quad (8.31)$$

The $[v_0]$ (thermally activated vacancy concentration) is a strong function of temperature, while $[k]$ is not, so that at low temperatures $[v+] \approx [k]$ and at high temperatures $[v+] \approx [v_0] = \exp(-G^F/2kT)$, G^F being the Shottky-pair formation energy. The homovalent ion then has a diffusivity:

$$D_0(\text{ion}) \sim [v+] \exp(-G^m(\text{ion})/kT) \quad (8.32)$$

which gives a high-temperature Arrhenius-plot region characterized by a slope $-[G^m(\text{ion}) + G^F/2]$ and a low-temperature region with slope $-[G^m(\text{ion})]$.

In order to bring this situation over to heterovalent ion diffusion, one needs the equivalent of a low-temperature approximately uniform enhancement of vacancy concentration. Recall the c.d.d. process is naturally a vacancy concentration enhancement, but a non-uniform one (which follows the impurity concentration profile). Since the $(v+)$ are highly mobile, the reason they follow the impurity concentration profile is to maintain local charge neutrality. Using the fact that this necessitates a vacancy concentration gradient which becomes more extreme at lower temperatures, we speculate that at lower temperatures or high impurity concentrations the vacancies do indeed break free from their following of the impurity profile. Noting that the entire set of models (presented in Chapter 3) totally ignores association (binding of $(v+)-(Ca^{++})$ pairs), it means the models have vacancies not bound to any particular (Ca) -site, but constrained to move in a 2-dimensional plane perpendicular to the diffusion direction. What we are suggesting here is that the vacancies also have an ability to move in that third direction, the direction of diffusion. The process we envision is as follows:

Some vacancies, instead of being totally constrained to move in a plane, "leak-out" in the diffusion direction. This creates a microscale charge imbalance. Where the vacancies left, new $(v+)$ can form to maintain local charge neutrality. The region where the vacancies that migrated wind up also is charge imbalanced. Two things can happen there:

- (1). The vacancy is absorbed, thus maintaining the status quo (i.e., this is the standard situation where the vacancy concentration follows the impurity concentration)

- (2). The vacancy continues, but being a charge imbalance, it helps

along the creation of a (v-) to maintain local charge neutrality.

We believe that choice-2 may operate when the impurity concentration is sufficiently large so as to create a large (v+)-vacancy gradient. Examining the simplest "standard" model, one sees built into it the natural suppression of local (v-) concentrations. Choice-2 has the simultaneous effect of allowing the (v-)-concentration to increase from its suppressed state, while simultaneously allowing a lowering of (v+)-gradients.

Choice-2 is a model in which the high-impurity concentration is acting like an "engine" for vacancy production, as well as giving the system a method by which it can reduce the non-linearity of the system. A reduction in non-linearity is not demanded, but is aesthetic in the following sense: All non-linear phenomena embody some form of "feedback" or self-coupling, and thus they have large tendencies to become unstable (viz. the difficulty of performing most non-linear analyses). A reduction in non-linearity is, in that context, a path closer to stability.

The previously assumed condition which the process, as given above, would change is local vacancy equilibrium. The condition:

$$[\hat{v}+][\hat{v}-] = K_0(T) \quad (8.33)$$

no longer holds exactly. The postulated process which allows an increase in the "background" vacancy concentration, and gives behavior consistent with both the present results and those of Beniere, and properly operates only in the limit of low temperature and high concentration (combined); allowing also:

- (1). a reduction in (v+)-gradient
- (2). a return of (v-)-concentration closer to its $[v_0(C=0)]$ value
- (3). a reduction of non-linearity in the diffusing system. It

is a limit where vacancy equilibrium is breaking down, since this process increases both local $[v+]$ and $[v-]$ concentrations. We finally note that formal solution of this type of model would involve coupled concentration-dependent diffusion equations (at least one equation for the impurity $[C]$ and one for $[v+]$) which is beyond the scope of the present models.

* * *

IX. Further Comments

(1). This entire method is quasi-perturbative. The "quasi-" is used to express the fact that many of the (AIII-model) best-fits give values of D_0 which are "far" from the linear equation values [and in some cases with an α_0 -(AIII-model) quite different from the first non-linear correction α_0 -(II00-model)]. Thus, it is not fully perturbative which would have required a slow convergence onto a new solution as one successively "turns-on" more correction terms. This nature of the non-linear solution can be most easily seen by examining the $\Omega(D)$ -functions for the various models and correlations.

However, this method is perturbative in the sense that the approximation $D(C)=D_0(1+\alpha C+\beta C^2\dots)$ is used; and also because the β -term has been found usually to give a small contribution to the penetration-profile compared to the α -term. This is seen by examining the non-linear resolution of the (propagated-state) concentration profiles presented in the previous sections.

(2). The AIII-model results giving a β_0 -value for each of the various correlations, have not been graphically presented as a $\beta_0(T)$ -Arrhenius type plot, although the results are tabulated along with the

"best-fit" ($\Omega(D_0), \alpha_0(D_0), D_0$)-values. The reason is that we have found it difficult to assign a precise meaning to the β -term. On one hand, when the β -contribution on the "non-linear resolution"-plots is not small, it has corresponded consistently to large negative 'r'-values (as with the (S3)→(S4) correlation), which is indicative of $D(C) \approx D_0(1 - |\beta|C^2)$, a diffusivity form not motivated by the physical models presented in Chapter 3. But, when this was not true, the β -term was small compared to the contribution of the α -terms in the penetration profile; thus, one could not, with the data taken here, accurately determine β . Indeed, examining even the AIII-model long-diffusion-time results (presented in Table <8.10>), one sees the β -values still follow no general trend. It may be that a calculation of $C(z, \Gamma)$ to higher order than (α^2, β) is necessary to pin down a better value of β . However, the general smallness of the β -term [when $\beta > 0$, or when the α -terms were not small] indicates that for the types of $D(C)$ functions encountered physically, operating in the laboratory with real systems, the higher order terms in $D(C)$ may not be as important as the higher order terms in the propagated state $\hat{C}_R(x, t_F)$.

(3). Reviewing the simulation studies presented (Fig. [8.4c], [8.12a], [8.15c], [8.17c], [8.24], [8.27]), once the best (D_0, α_0, β_0) -values are found, the propagation for intermediate times show a long-time convergence to parallel lines in the limiting slope region for long times. Taken along with the earlier result (Fig. [8.4], [8.5]) which compares propagation via a linear and non-linear equation, we can develop this powerful cogent test:

- A. The measurement of penetration profiles for two distinct diffusion times are necessary. If both show similar curvature, this persistence of curvature indicates that a non-linear phenomenon is operating even in that time range.

- B. If the limiting slopes are nearly parallel (on a $[\ln C \text{ vs. } x^2/t^*]$ -plot, using a warm-up time correction), the value of D_0 is probably close to that value. Only if they are not parallel or if the profiles seem to belong to different families of curves, need a non-linear analysis be performed to determine D_0 .

The part-"B" comes about from the a posteriori observation that the non-linear diffusion equation solution does not seem to alter the long-time limiting slope, although, as [8.17c] shows, for short times, the non-linearities have a significant effect on limiting slope.

We finally note that, in terms of determining the average penetration depth of a profile, the linear equation is inoperative. Once again, this is a "history" effect, the average depth being determined by all the diffusion motion previous to the "current" time, non-linearities included.

X: Conclusions

The aim of this work has been to investigate, both analytically and experimentally, the occurrence of non-gaussian ("curved" on $[\ln C \text{ vs. } x^2]$ -axes) penetration profiles as found in heterovalent metal ion diffusion in strongly ionic crystals.

(1). First and foremost, when a non-gaussian profile is observed, one must perform at least a diffusion experiment involving the same amount of tracer and two different diffusion times (Chapter 1, Sec. II).

(2). We began by seeking a method to handle non-gaussian profiles when $D=\text{constant}$, and discussed the "generalization" of the 'thin-source' solution. It is a series in $(t^{-p-1/2})$ multiplied by $[H_{2p}(z) \exp(-z^2)]$; H_{2p} = Hermite polynomials (Chapter 2, Sec. II). This was found to be totally

inadequate to describe the diffusion process when the curved profiles are experimentally observed (Chapter 8, Sec. II). Even though an arbitrary initial state could be matched, the propagation is totally incorrect.

(3). We found that the mathematical idealization ($\delta(x)$) of a "thin-source" for the $D=\text{constant}$ problem can never be used as an initial condition on any $D(C)$ problem (Chapter 1, Sec. III); and furthermore, one must do an experiment involving finite not-small times.

(4). The "limiting-slope" ansatz was found to replace a $D(C)$ problem with an inequivalent $D_0(t)$ -time dependent diffusivity (Chapter 1, Sec. IV), and it can give incorrect results even when $D=\text{constant}$ (Appendix I, Sec. 3), irrespective of the number of decades of data taken.

(5). We reviewed the "standard" $D(C)$ -model as believed applicable for a system as $(\text{Ca}^{++}) \rightarrow \text{NaCl}$, the function being:

$$D(C) = D_0 \left(\frac{1}{2}K + \left[1 + \left(\frac{1}{2}K \right)^2 \right]^{1/2} \right), \quad K = [C]/2[v_0] \quad (8.34)$$

$[C]$ =Impurity (Ca^{++}) concentration, $[v_0]$ =Vacancy concentration as $(C \rightarrow 0)$. It necessitates both mobile $[(v+), (v-)]$ -vacancies as well as a fair amount of dislocations and grain boundaries to serve as vacancy sources or sinks. Based on a simple model (Chapter 3, Sec. II), the average equilibration time τ with defects was found to be:

$$\begin{aligned} \tau &\sim n^{-1} (\text{point defects}), \quad \tau \sim n^{-3/2} (\text{dislocations, low density}), \\ \tau &\sim n^{-2} (\text{domain walls}), \end{aligned}$$

where 'n' was the concentration of lattice-sites occupied by the particular defect type. This showed that the equilibration of a point defect $(v+)$ with extended defects is much slower than point-defect--point-defect equilibration. We were thus led to propose the process:

as a fundamental process for maintaining the equilibrium constraint; with

$$[\hat{v}+] [\hat{v}-] = K_0(T) , \quad (8.36)$$

inherent in the "standard" model, as a possible second process.

This allowed us to derive a set of extensions of the "standard" model; each remained a $D(C)$ function (Chapter 3, Sec. III and VI), and using the small 'C' expansion

$$D(C) = D_0(1 + \alpha C + \beta C^2) \quad (8.37)$$

the parameters (D_0, α, β) were different for each case. The models could be separated into 3 classes, depending on $r = \beta/\alpha^2$:

$$r = 0, \quad r = .5, \quad .4 \leq r < .5 \quad (8.38)$$

The extent of non-linearity present in a system is mirrored in α , the processes (given that it is one of those in Chapter 3) are differentiated by 'r'.

(6). In attempting to handle diffusion when both free $(v+)$ -vacancies and divacancies contribute, we clarified the relationship between mobility, hopping frequency, and diffusivity. We found that (Chapter 3, Sec. IV-V):

$$D \sim (\sum \mu(i)n(i)) \quad (8.39)$$

is correct, where $\mu(i)$ and $n(i)$ are the mobility and fractional-site-occupation of the defect species (i); but to double a species' mobility does not double the diffusivity due to that species. Doubling the hopping frequency halves the average visitation time, giving no net gain.

Specifically, for $(v+)$ and (d) contributing to the $(Ca^{++}) \rightarrow NaCl$ process:

$$D \sim v_C = \gamma_0 (\exp(-G^m(Ca^{++})/kT) [n(v+) + Q(T)n(d)] \quad (8.40a)$$

$$Q(T) = \frac{\exp[-G^m(Cl^-) - G^m(Na^+)]/kT}{\exp-G^m(Na^+)/kT + \exp-G^m(Cl^-)/kT} \quad (8.40b)$$

(7). We attempted an analysis of the D(C)-problem by examining the "polynomial"-diffusivity:

$$D(C) = D_0(1+\alpha C+\beta C^2 \dots) \quad (8.41)$$

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial}{\partial x}(1+\alpha C+\beta C^2+\dots) \frac{\partial C}{\partial x} \quad (8.42)$$

which is a non-linear partial-differential equation in 2 independent variables.

First and foremost, to change the normalization (Chapter 4, Sec.II):

$$\int \tilde{C}(x,t_1) dx = N(i) \quad (8.43)$$

is to change the non-linear parameters; thus, a concentration-dependent diffusion study requires the two different diffusion time states to have the same initial surface concentration of impurities.

Secondly, one can change from using the dynamical variables (x,t) into using (D, z) as dynamical variables (Chapter 4, Sec. IV), where:

$$z^2 = x^2 / \Gamma x_R^2 \quad (8.44a)$$

$$\Gamma = 1 + 4D(t_F - t_R) / x_R^2 \quad (8.44b)$$

and where (x_R) is an arbitrary parameter used to describe an initial state, and ($t_F - t_R$) is the time difference between the given initial state and a final state.

A solution to this (or any D(C) problem) must be able to:

- (1). Handle an arbitrary initial state (Chapter 1, Sec. IV)
- (2). Conserve total amount: $\int \tilde{C}(x,t_1) dx = N(i)$ [indep. of time] (Chapter 4, Sec. I).

We have constructed a solution to the following problems:

$$D(C) = D_0(1+\alpha C) \quad (\text{Chapter 4, Sec. V-VII}) \quad (8.45a)$$

$$D(C) = D_0(1+\gamma RC^R) \quad (\text{Chapter 5, and Appendix V}) \quad (8.45b)$$

$$D(C) = D_0(1+\alpha C+\beta C^2+\dots) \quad (\text{Chapter 5}) \quad (8.45c)$$

and demonstrated that each indeed obeys rigorous conservation of mass and each allows an arbitrary initial state.

We decoupled the non-linearities using the (di-) orthogonal function set

$$C(z, \Gamma) = \sum_{m,n} g_{m,n}(\Gamma) H_{2m}(z\sqrt{n}) \exp(-nz^2) \quad (8.46)$$

and the system is recursive. One calculates $g_{m,n}$ using $g_{m',n'}$ ($n' < n$). The gaussian term decays as $(g_{0,1}) \sim \Gamma^{-1/2}$, and all non-linear terms decay as $\Gamma^{-3/2}$ (Chapter 6, end of Sec. III). Thus all series converge. Comparing this non-linear equation decay of non-gaussian terms via $\Gamma^{-3/2}$ to $\Gamma^{-(p+1/2)}$ for equivalent non-gaussian terms in the linear equation solution gives rise to a "persistence of curvature" as the fundamental "earmark" of a $D(C)$ process (Chapter 8, Sec. II).

This solution naturally expresses $C(z, \Gamma)$ as a polynomial series in non-linearity parameters (Chapter 4, Sec. VIII). The procedure set-up is used explicitly to calculate $C(z, \Gamma)$, the propagated-forward state, for:

$$D(C) = D_0(1+\alpha C+\beta C^2) \quad (8.47)$$

(Chapter 5, and Appendix V), and it is reduced to a substitution of formulae into formulae situation. The substitution for $C(z, \Gamma)$ calculated to order- (α^2, β) has also been explicitly carried out (Chapter 6, Sec. I-III). The final algebra (Chapter 6, Sec. IV) is presented in a form for easy

evaluation via computer. An extension to handle a multiple-time correlation (more than 1 pair of data-sets) is also constructed (Chapter 6, Sec. V). This is the form used here to fit experimental data.

(8). The essential experiment for a D(C) situation is a multiple diffusion-time experiment, which has not often been done in the field. We have, thus, for the system $(\text{Ca}^{++})\text{-NaCl}$ investigated the diffusion for various times, using approximate initial surface concentrations of:

$$\int \tilde{C}(x, t_i) dx = N(i) \approx 5 \text{ Amounts} = 3 \times 10^{16} \text{ atoms/cm}^2. \quad (8.48)$$

This is a regime of expected high non-linearities, and we studied the system in the temperature range ($\sim 575^\circ\text{C} - 775^\circ\text{C}$).

We found that, with each two-time correlation, over the entire temperature range, except for correlations between the shortest time data, an excellent agreement between non-linearly-propagated state and measured final-data state was obtained.

The values of (D_0, α, β) were found by minimizing the error on a $[C \text{ vs. } x]$ -plot, in contrast to the more common procedure of using $[\ln C \text{ vs. } x^2]$ -graphs (Appendix I, Sec. 9); but the final match consistently reproduced the "curvature" on the $[\ln C \text{ vs. } x^2]$ -plot, although not the apparent limiting slope (Chapter 8, Sec. II-VI). This is expected from using $[C \text{ vs. } x]$ -plots which match, in order of decreasing importance (Chapter 2, Sec. V):

- A. The total area (normalization)
- B. The extent of the profile (average penetration)
- C. The detailed shape of the profile
- D. Rarely is the apparent limiting slope matched.

The success in matching the "curvature" of each profile is the primary success of this entire methodology.

The "best-fit" values were different for the different correlations, although the D_0 -(limiting concentration diffusivity)-values were closely clustered on an Arrhenius plot (Chapter 8, Sec. VIII). The (α, β) -values varied somewhat more from correlation to correlation, indicating that the small polynomial approximation:

$$D(C) \doteq D_0(1 + \alpha C + \beta C^2) \quad (8.49)$$

is not sufficient if one requires the same values of (D_0, α, β) for the entire time range from shortest-time to longest-time. Thus, the test involving $r = \beta/\alpha^2$ could not be done giving consistent results.

(9). The following general trend was observed in the non-linear propagation of the experimentally measured profiles:

- A. Given data for two different diffusion times, the persistence of curvature on a $[\ln C \text{ vs. } x^2]$ -graph indicates the presence of non-linearities even in that time range;
- B. Only if both profiles appear to be members of the same "family" of curves, and if they have the same apparent limiting slope on a $[\ln C \text{ vs. } x^2/t^*]$ -graph, can the D_0 (limiting slope) be approximately accurate;
- C. In neither case can D_0 , by itself, predict the average penetration depth of the profile into the crystal.

(10). Using the quadratic (in C) diffusivity:

$$D(C) = D_0(1 + \alpha C + \beta C^2), \quad (8.50)$$

with $C(x, t)$ found to order- (α^2, β) , neglecting higher-order terms, it is found that:

- A. D_0 , by itself, with no non-linear corrections, gives a poor

datafit, except at the highest temperature;

- B. $D(C)=D_0(1+\alpha C)$ gives an improved datafit, with the amount of improvement diminishing at lower temperatures;
- C. $D(C)=D_0(1+[\alpha C]+.5[\alpha C]^2)$ is a good datafit at high temperatures, but is barely better than D_0 at lower temperatures;
- D. $D(C)=D_0(1+\alpha C+\beta C^2)$, with both α and β adjustable, gives good datafits over the entire range of temperature and time, except for the shortest diffusion times.

(11). The $D_0(T)$ Arrhenius plot for the $D(C)=D_0(1+\alpha C+\beta C^2)$ function, after corrections for the non-linearity have been made, shows a distinct high-temperature (H.T) and lower-temperature (L.T.) region, with:

$$D_0(\text{H.T.}) = .642 \exp[-(1.69 \pm .02 \text{ eV})/kT] \text{ cm}^2/\text{sec.} \quad (8.51a)$$

$$D_0(\text{L.T.}) = .431 \times 10^{-3} \exp[-(1.06 \pm .04 \text{ eV})/kT] \text{ cm}^2/\text{sec.} \quad (8.51b)$$

An alternate form for these functions, emphasizing D_0 (melting point) is:

$$D_0(\text{H.T.}) = 75.5 (\times 10^{-10} \text{ cm}^2/\text{sec.}) \exp-(1.69 \pm .02 \text{ eV})[(kT)^{-1} - (kT_m)^{-1}]$$

$$D_0(\text{L.T.}) = 45.8 (\times 10^{-10} \text{ cm}^2/\text{sec.}) \exp-(1.06 \pm .04 \text{ eV})[(kT)^{-1} - (kT_m)^{-1}] \quad (8.52a, 8.52b)$$

where T_m = melting temperature (NaCl: 801°C). The high-temperature function closely matches the $D_0(T)$ function obtained from a low impurity concentration experiment by Slifkin⁵⁵ and it is similar to a result obtained by Mitchell *et al.*^{44,45} The lower temperature part is similar to a result obtained by Beniere, who also used large total impurity amounts, though probably not quite as large as those used in this work. This lower-temperature function, combined with the sudden failure of the $D(C)=D_0(1+[\alpha C]+.5[\alpha C]^2)$ model at these temperatures, indicates the onset of a second

diffusion process, one which would operate only at extremely high impurity concentrations. This low-temperature behavior has been shown to be consistent with a breakdown of the conditions assumed for local vacancy equilibrium (Chapter 8, Secs. VII and VIII).

(12). Using the high-temperature data, where $D(C) = D_0(1 + [\alpha C] + 5[\alpha C]^2)$ is a good datafit, using the fact that $[\alpha_0]^{-1}$ is proportional to the intrinsic vacancy concentration for this model, an alternate, but less reliable $D_0(T)$ function is obtained:

$$D_0(\text{H.T.}) = 98.4 (\times 10^{-10} \text{ cm}^2/\text{sec.}) \exp(-2.01 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.53)$$

but it concurrently gives an $[\alpha_0]^{-1}$ function of temperature:

$$[\alpha_0]^{-1}(\text{H.T.}) = 1.03 (\text{cu-units}) \exp(-1.63 \text{ eV}) [(kT)^{-1} - (kT_m)^{-1}] \quad (8.54)$$

which extrapolates to a melting point total intrinsic cation vacancy concentration of approximately 140 p.p.m. (Chapter 8, Sec. VII).

* * *

APPENDIX I

ADDITIONAL NOTES

1. Note on $C(x, t=0)$ with an $x=(0, \infty)$ Domain (ref. 3)

The solution to the $D=D_0$, $C(x, t=0) = \hat{1}\delta(x)$ problem as written (Eq. 1.06) is normed to $\hat{1}$ on the double-infinite interval $x=(-\infty, +\infty)$. A cognate solution for diffusion of a normed 'thin-source' on a surface into the semi-infinite interval $x=(0, \infty)$ is given as:

$$C(x, t) = \hat{1}(\pi D_0 t)^{-1/2} \exp(-x^2/4D_0 t) \quad (I.01)$$

which does, of course, obey:

$$\int_{x=0}^{\infty} C(x, t) dx = \hat{1} \quad (I.02)$$

The common error which is present in practically all the literature is that this solution converges to a δ -function as $t \rightarrow 0$. The proper convergence on the $x=(0, \infty)$ interval is:

$$\lim_{t \rightarrow 0} C(x, t) = 2\delta(x) \cdot \hat{1} \quad (I.03)$$

the reason being that $\delta(x)$ is patently symmetric. Taking the $t \rightarrow 0$ limit bears out this factor of 2 explicitly.

* * *

2. Note on Domains of Orthogonal Functions (ref. 7)

The importance of the domain in determining the type of orthogonal functions one must use is easily apparent from this example: Consider

the time development of the following exactly equivalent initial configurations:

Case 1 develops to $\bar{C}(t=\infty) = \frac{1}{2}C_A$ and requires a finite sine-cosine series for analysis. Case 2 on the semi-infinite interval develops as a sum of 2 error-functions.

If a solution to the linear equation is written as the integral of a given state, over a kernel function, the fact that the kernel will be domain specific can be easily seen by applying any given kernel to these two similar situations involving the time evolution of a finite rectangular source of length x_A in the two domains $x=(0, 2x_A)$ and $x=(0, \infty)$. If the given propagator yield is correct results for the latter (using reflection symmetry for the $x=(-\infty, 0)$ part) it will not for the former.

* * *

3. An Example of Limiting Slope ($\hat{D}_0$) Bearing "History Marks" (ref.10)

As a short example, we demonstrate that while $\tilde{D}_0(t)$ does not bear "history marks," $\hat{D}_0(t)$ does. Suppose one took a sample and suddenly at time t_0 uniformly heated it from an initial temperature T_1 to a new temperature T_2 (assume, for simplicity, normal diffusion, i.e., a constant diffusivity at a given temperature) then with $D(T_1)=D_1$ and $D(T_2)=D_2$, one has:

$$\tilde{D}_0(t) = D_1 + (D_2 - D_1)\theta(t - t_0) \quad (\text{I.04})$$

$$\theta(t - t_0) = \begin{cases} 1 & t > t_0 \\ 0 & t < t_0 \end{cases} \quad (\text{I.05})$$

Using

$$\tilde{D}_o(t)dt = d(\hat{D}_o(t) \cdot t) \quad (I.06)$$

$$\int_{\bar{t}=0}^t \tilde{D}_o(\bar{t})d\bar{t} = \int_{\bar{t}=0}^t d(\hat{D}_o(\bar{t}) \cdot \bar{t}) = \hat{D}_o(t) \cdot t \quad (I.07)$$

one can find:

$$\hat{D}_o(t) \cdot t = D_1 t + (D_2 - D_1) \int_{\bar{t}=0}^t \theta(\bar{t} - t_o) d\bar{t} \quad (I.08)$$

$$= \begin{cases} D_1 t & \text{if } t < t_o \\ D_1 t + (D_2 - D_1)(t - t_o) & \text{if } t > t_o \end{cases} \quad (I.09)$$

A plot of $\hat{D}_o(t)$ is thus:

We remind the reader that $\hat{D}_o(t)$ would be the actual limiting slope measured by the standard procedure, as a function of anneal time 't', even though the diffusivity in this example for $t > t_o$ is indubitably D_2 . This "error" (of $\hat{D}_o(t) \neq D_2$) remains even if one takes more decades of data (i.e., uses the deeper and deeper penetration region) and occurs solely because $\hat{D}_o(t)$ bears the "history" of being at D_1 during the time $t=(0, t_o)$. In this sense, the most standard method is the most unreliable one of all.

* * *

4. Note On Boundedness and Convergence (ref. 18)

There is a corollary on boundedness worth mentioning here. Suppose $C(x, t_R)$ as an initial profile (in the domain $x=(-\infty, \infty)$) has the property $[C(x, t_R) = 0 \text{ if } |x| > x_s \text{ for some } x_s]$, as true for many physical sources for some time t_R in their existence, it a fortiori has a "tail" that decreases faster than $A \exp(-(x/x_A)^2)$ for any value of x_A ; then any value may be chosen for the expansion parameter x_R !

The analysis for the $D=\text{constant}$ case presented here one can see naturally stays within the bounds of gaussian-type functions, and this will be true even for our non-linear analysis.

What this means is the following: As long as one can parameterize the initial state as a Hermite series, i.e., some x_R exists which gives a convergent series representation, once the solution to the linear or non-linear equation is constructed which tells in what manner said state propagates forward in time, it can be examined to see what values of (x_F) are allowed in the representation of the final state as:

$$C(x, t_F) = \sum_{m=0}^{NF} \tilde{B}_m H_{2m}(x/x_F) \exp(-(x/x_F)^2). \quad (I.10)$$

One will find that the range of x_F allowed as an expansion parameter is the same for a study via $D=D_0$ or $D=D(C)$ (with $\lim_{C \rightarrow 0} D(C)=D_0$). Thus, if the expansion is constructable at any time t_R , it is constructable for all times $t > t_R$.

* * *

One has the added condition $\int C dx = 1$. A natural question is: Does a normalizable sufficiently non-oscillatory function allow a Hermite series representation? The answer is: no. A good counter example is $C(x, t_R) \sim [x_R / (x^2 + x_R^2)]$ which gives $B_1, B_2, \dots = \infty$. The reason, of course, being

that this type function has a long "tail" and an initial profile of such type is inaccessible from a 'thin-source'. Some long range interaction involving a totally non-diffusive process would have been required to create a concentration profile of such a type. These are still analyzable by the propagator if one is restricted to the linear equation, that propagator, as mentioned before, allowing concentration profiles up to and including those of the form:

$$C(x, t_R) < A \exp(x/x_A) \quad (I.11)$$

which are even totally unnormalizable! Propagators, at least those which are writable as an integral over a kernel function (Eq. 2.01), of course, do not exist for non-linear equations, because a kernel needs each member of the orthogonal function set to propagate independently of all others, which is true only for the particular orthogonal function set which is the linear equation solution, and for no other set. Non-linearities effectively couple different members of the orthogonal function set, and thus, they allow any particular coefficient of, say, the m^{th} -orthogonal-function-member (as $H_m(z) \exp(-z^2)$) to grow from zero; and the kernel, integrating over zero times a function at the initial time, would then have to give out a finite result to match the later-time finite coefficient -- which is impossible.

* * *

5. Some Comments on Divacancies and Mobilities (ref. 32)

A. On $D \sim (\sum \mu(i)n(i))$:

This phenomenology is interesting because it is a variant on $J = -D \partial C / \partial x$ where the usual extension is to use $J_i = \sum_j D_{ij} \partial C_j / \partial x$, i.e., having one species flux depending on many species' diffusivities and concentration

gradients. Here, it is almost the inverse: $D_j = \sum K_{ij} J_i$; i.e., having D of one species depend on the flux of many (other) species.

* * *

B. On $\mu(d)$:

In a crystal geometry where a 'two'-defect, such as a divacancy, would necessarily have to disassociate at some stage in order to have the cluster move a finite amount, one may not expect $\mu(d)$ to be roughly independent of the binding energy.

* * *

C. On Reduced Mobility:

There are two interesting 'extensions' of this reduced mobility formulation. One is that true extended defects (as dislocations) viewed as an array of bound point-defects (although the "binding" is a strain field and not electrostatic attraction) would have a mobility

$$[1/\mu(\text{total})] = \sum_i^N [1/\mu_i] \quad (\text{I.12})$$

and as N gets large, $\mu(\text{total})$ for the array approaches zero. The other is that in the diffusion of multiply ionized species (as $\text{Fe}^{+++} \rightarrow \text{NaCl}$), there may be an onset of clustering: Formation of $(v^+)-(M^{+++})-(v^+)$ complexes and their mobility could be less than a simple $(M^{++})-(v^+)$ or $(M^{+++})-(v^+)$ complex.

* * *

6. On the Transformation $[x, t] \rightarrow [z^2 = x^2/4D, t]$ (ref. 38)

To go from (x, t) to (z, w) where $z = z(x, t)$ and $w = w(x, t)$ are given one uses standard Jacobians of transformation:

$$(I.13) \quad \frac{\partial}{\partial t} = \frac{\partial z}{\partial t} \frac{\partial}{\partial z} + \frac{\partial w}{\partial t} \frac{\partial}{\partial w}, \quad \frac{\partial}{\partial x} = \frac{\partial z}{\partial x} \frac{\partial}{\partial z} + \frac{\partial w}{\partial x} \frac{\partial}{\partial w}$$

but the terms $(\frac{\partial z}{\partial w})$, $(\frac{\partial x}{\partial w})$, $(\frac{\partial t}{\partial w})$ are still expressed as functions

of (x, t) and not (z, w) . A clearer formalism is to begin with $x = x(z, w)$,

$t = t(z, w)$ and use:

$$(I.14) \quad \frac{\partial}{\partial z} = \frac{\partial x(z, w)}{\partial z} \frac{\partial}{\partial x} + \frac{\partial t(z, w)}{\partial z} \frac{\partial}{\partial t}, \quad \frac{\partial}{\partial w} = \frac{\partial x(z, w)}{\partial w} \frac{\partial}{\partial x} + \frac{\partial t(z, w)}{\partial w} \frac{\partial}{\partial t}$$

or in matrix form:

$$(I.15) \quad \begin{pmatrix} \frac{\partial w}{\partial z} & \frac{\partial w}{\partial t} \\ \frac{\partial x}{\partial z} & \frac{\partial x}{\partial t} \end{pmatrix} = \begin{pmatrix} \frac{\partial w}{\partial x} & \frac{\partial w}{\partial t} \\ \frac{\partial x}{\partial x} & \frac{\partial x}{\partial t} \end{pmatrix} \equiv \bar{M} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial t} \end{pmatrix}$$

$$(I.16) \quad \bar{M}^{-1} = \frac{1}{\det(\bar{M})} \begin{pmatrix} \frac{\partial w}{\partial t} & -\frac{\partial w}{\partial x} \\ -\frac{\partial z}{\partial t} & \frac{\partial z}{\partial x} \end{pmatrix}$$

Then:

$$(I.17) \quad \begin{pmatrix} \frac{\partial}{\partial t} \\ \frac{\partial}{\partial x} \end{pmatrix} = \bar{M}^{-1} \begin{pmatrix} \frac{\partial w}{\partial z} \\ \frac{\partial x}{\partial z} \end{pmatrix}$$

gives a right-hand-side entirely a function of (z, w) . For the transformation $(x, t) \rightarrow (z = x^2/4D, t)$, $w = t$ one has $t(z, w) = w$, $x(z, w) = z^{1/2}$,

$$\underline{M} = \begin{pmatrix} (4D_o w)^{1/2} & 0 \\ z(D_o/w)^{1/2} & 1 \end{pmatrix} \quad (I.18)$$

$$\underline{M}^{-1} = \frac{1}{(4D_o w)^{1/2}} \begin{pmatrix} 1 & 0 \\ -z(D_o/w)^{1/2} & (4D_o w)^{1/2} \end{pmatrix} \quad (I.19a)$$

$$\frac{\partial}{\partial x} = (1/4D_o w)^{1/2} \frac{\partial}{\partial z}, \quad \frac{\partial}{\partial t} = -\frac{z}{2w} \frac{\partial}{\partial z} + \frac{\partial}{\partial w} \quad (I.19b)$$

This transforms

$$\frac{\partial}{\partial t} C = D_o \frac{\partial}{\partial x} (1 + \gamma f(C)) \frac{\partial}{\partial x} C \quad (I.20)$$

into:

$$\left(-\frac{z}{2w} \frac{\partial}{\partial z} + \frac{\partial}{\partial w}\right) C = D_o \left(\frac{1}{4D_o w}\right) \frac{\partial}{\partial z} (1 + \gamma f(C)) \frac{\partial}{\partial z} C \quad (I.21)$$

and now replacing $w=t$ giving $C(z,t)$ instead of $C(x,t)$, one has:

$$4t \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} (1 + \gamma f(C)) \frac{\partial C}{\partial z} + 2z \frac{\partial C}{\partial z} \quad (I.22)$$

* * *

7. Note on an Integral (ref. 46)

Gradshteyn and Ryzhik⁴⁷ give the incorrect value of this integral (Eq. 7.374-4, their text; Eq. (4.88) here) Pre-1977 versions of their tables have a factor $(2^{-m+1/2})$, whereas a factor of (2^{+n}) is correct. Taking the $(m \rightarrow 0, n \rightarrow 0)$ limit makes this error apparent. They reference the Bateman Manuscript Project,⁴⁸ where integrals are written in terms of the polynomials:

$$He_m(x) = 2^{-m/2} H_m(2^{-1/2} x), \quad (I.23)$$

the $He_m(x)$ being orthogonal with respect to the weighting function

$[\exp(-x^2/2)]$. A typographic error, dropping the 'e' in ' $He_m(x)$ ' occurs in two integrals in the Bateman Project: Eqs. 16.5(20) and 16.5(21), one of those equations being this integral. W. N. Bailey⁴⁹ has the correct value of this integral, and at the suggestion of this author, post-1977 versions of Gradshteyn and Ryzhik have been corrected.

* * *

8. On deriving Some Integrals with Hermite Polynomials (ref. 50)

The defining formula:

$$H_m(x) \exp(-x^2) = (-1)^m \left(\frac{d}{dx}\right)^m \exp(-x^2) \quad (I.24)$$

can give many powerful formulae for calculations with Hermite polynomials.

First, using the translation operator

$$\left[\exp(-t \frac{\partial}{\partial x})\right] \Psi(x) = \Psi(x-t) \quad (I.25)$$

gives:

$$\left[\exp(-t \frac{\partial}{\partial x})\right] \exp(-x^2) = \exp(-(x-t)^2) \quad (I.26)$$

$$\int \frac{1}{n!} (-t \frac{\partial}{\partial x})^n \exp(-x^2) = \int \frac{1}{n!} (-t)^n (-1)^n H_n(x) \exp(-x^2) \quad (I.27)$$

thus, giving the "generating function" relationship

$$\int \frac{1}{n!} t^n H_n(x) = \exp(-t^2 - 2tx). \quad (I.28)$$

Substituting 'ax' for 'x' gives

$$\frac{1}{n!} H_n(ax) \exp(-ax)^2 = \left[\frac{\text{coeff.}}{\text{of } (t)^n}\right] \exp(-t-ax)^2. \quad (I.29)$$

Any $f(t)$, expanded as a Taylor series, gives:

$$\left[\frac{\text{coeff.}}{\text{of } (t)^n}\right] f(t) = \frac{1}{n!} \left[\left(\frac{\partial}{\partial t}\right)^n f(t)\right]_{(t=0)} \quad (I.30)$$

thus, demonstrating that:

$$H_n(ax) \exp(-ax)^2 = \left[\text{Limit}_{t \rightarrow 0}\right] \left(\frac{\partial}{\partial t}\right)^n \exp(-t-ax)^2 \quad (I.31)$$

* * *

One can proceed to derive many integrals, one important uncommon one being:

$$J'(m,n) = \int x^{2m+n} H_n(x) \exp(-x^2) dx \quad (I.32)$$

(for $-n < m < 0$ this integral vanishes by orthogonality)

$$J'(m,n) = \left[\lim_{a \rightarrow 1} \right] \int x^{2m+n} (-1)^n \left(\frac{\partial}{\partial(ax)} \right)^n \exp(-(ax)^2) dx \quad (I.33)$$

treating 'a' as the variable in the derivative, and x as a parameter:

$$\begin{aligned} J'(m,n) &= \left[\lim_{a \rightarrow 1} \right] (-1)^n \int x^{2m} \left(\frac{\partial}{\partial a} \right)^n \exp(-(ax)^2) dx \quad (I.34) \\ &= \left[\lim_{a \rightarrow 1} \right] (-1)^n \left(\frac{\partial}{\partial a} \right)^n [a^{-2m-1}] \int \xi^{2m} \exp(-\xi^2) d\xi \\ &= \left[\lim_{a \rightarrow 1} \right] (-1)^n (-2m-1)(-2m-2)\dots(-2m-n) [a^{-2m-n-1}] \Gamma(m+\frac{1}{2}) \end{aligned}$$

thus, giving:

$$J'(m,n) = \int x^{2m+n} H_n(x) \exp(-x^2) dx = \frac{(2m+n)!}{(2m)!} \Gamma(m+\frac{1}{2}) \quad (I.35)$$

By a similar method, one can evaluate:

$$\begin{aligned} J''(m,n;y) &= \int x^{2m+n} H_n(yx) \exp(-x^2) dx = \quad (I.36) \\ &(-1/y)^n \Gamma(m+\frac{1}{2}) \left[\lim_{a \rightarrow 1} \right] \left(\frac{\partial}{\partial a} \right)^n (1+a^2 y^2 - y^2)^{-(2m+1)/2} \end{aligned}$$

Replacing the $a \rightarrow 1$ limit by $b \rightarrow 0$ ($b=a-1$) gives

$$J''(m,n;y) = (-1/y)^n \Gamma(m+\frac{1}{2}) \left[\lim_{b \rightarrow 0} \right] \left(\frac{\partial}{\partial b} \right)^n (1+2by^2 + b^2 y^2)^{-m-1/2} \quad (I.37)$$

and defining $z=by$,

$$J''(m,n;y) = (-1)^n \Gamma(m+\frac{1}{2}) \left[\lim_{z \rightarrow 0} \right] \left(\frac{\partial}{\partial z} \right)^n (1+2zy+z^2)^{-m-1/2} \quad (I.38)$$

Using the definition of Gegenbauer polynomials: $\frac{C_p^k}{p}(y)$:

$$(1+2yz+z^2)^{-k} = \sum_{p=0}^{\infty} \frac{C_p^k}{p}(y) (-1)^p z^p; \quad \frac{C_p^k}{p}(1) = \binom{2k+p-1}{p} \quad (I.39)$$

$$C_{-n-m}^{m+1/2}(y) = (-1)^m (1-y^2)^{-m/2} 2^{-m} P_n^m(y) [\sqrt{\pi}/\Gamma(m+\frac{1}{2})] \quad (I.40)$$

and using:

$$\lim_{z \rightarrow 0} \left(\frac{\partial}{\partial z} \right)^n z^p = n! \delta(n=p) \quad (I.41)$$

the factors of $\Gamma(m+\frac{1}{2})$ and $(-1)^n$ cancel, giving:

$$J''(m,n;y) = \sqrt{\pi} (-1)^m n! P_{m+n}^m(y) / [4(1-y^2)]^{m/2} \quad (I.42)$$

where $P_{m+n}^m(y)$ is an associated Legendre polynomial.

* * *

Another usage of the simpler integral $J'(m,n)$ is to allow easy re-expressing of power series and Hermite polynomial series. Specifically, given:

$$\sum_{m=0}^N B_m H_{2m}(z) \exp(-z^2) \equiv \sum_{m=0}^N \gamma_m z^{2m} \exp(-z^2) \quad (I.43)$$

The integral $J'(m,n)$ allows derivation of the quasi-symmetric relations:

$$H_{2p}(z) = \sum_{m=0}^p (-1)^{p-m} 2^{2m} \frac{(2p)!}{(2m)!(p-m)!} z^{2m} \quad (I.44)$$

$$\gamma_m = \sum_{p=m}^N (-1)^{p-m} 2^{2m} \frac{(2p)!}{(2m)!(p-m)!} B_p \quad (I.45)$$

as well as their inverses:

$$z^{2m} = \sum_{p=0}^m 2^{-2m} \frac{(2m)!}{(2p)!(m-p)!} H_{2p}(z) \quad (I.46)$$

$$B_p = \sum_{m=p}^N 2^{-2m} \frac{(2m)!}{(2p)!(m-p)!} \gamma_m \quad (I.47)$$

* * *

9. Note on Data-Fitting on [C vs. x]-Axes
Compared to [lnC vs. x^2]-Axes (ref. 52)

This work, by using a ϕ^2 -function minimization, and thereby minimizing error or a [C vs. x]-graph, is in sufficient contradistinction to the practically universal usage of function-fitting on [lnC vs. x^2]-graphs. We, therefore, summarize here most of the basic arguments for this.

(1). An orthogonal function set does not exist for a [lnC vs. x^2]-graph. Remembering that orthogonal function set members are oscillatory with no net area, except the first "fundamental" member of the set, this means that the $f(x)=0$ line is crucial to the orthogonal function set. The $C=0$ line is indeed a strong physical dividing point, but the $\ln C=0$ point is not. The example (Eq. (2.21)) showing the divergence of limiting intercept for (polynomial) $\times$ (gaussian) functions further shows the difficulty of writing a converging function series to approximate a given function in the entire $x^2=(0,\infty)$ range on a [lnC vs. x^2]-graph.

(2). A best data-fit on a [lnC vs. x^2]-graph does not inherently respect preservation of normalization. The normalization preservation is not only dictated by the physics of the diffusion process, but it is needed for the unambiguous definition of the non-linear parameters (as seen in Chapter 8, Sec. I).

(3). Beyond the question of simple normalization preservation, is the question of the values of the $\{B_p\}$ parameters in the expansion

$$C(x, t_R) = \sum B_p H_{2p}(x/x_R) \exp-(x/x_R)^2. \quad (I.48)$$

One could choose $B_0 = \hat{1}/(\pi^{1/2} x_R)$ thereby respecting normalization, and choose the $(B_1, B_2, \dots)$ -set by minimizing error on a [lnC vs. x^2]-plot.

However, such a procedure no longer results in a system obeying the orthogonal function properties (as outlined in Chapter 2, Sec. I).

(4). Given any $D(C)$ function and an initial profile $C(x)$, the development of this profile on a $[(f(y)=\ln C) \text{ vs. } (y=x^2)]$ -graph when compared to the development of a cognate profile $\tilde{f}(y)$ of the exact same shape on a $[\ln C \text{ vs. } x^2]$ -graph (where $f_0 = \text{constant}$):

$$\tilde{f}(y) = f(y) + f_0 \quad (\text{I.49})$$

has the property that $\tilde{f}(y)$ must span the entire spectrum of $D(C) \approx D_0$ (as $f_0 \rightarrow -\infty$) to $D(C) \rightarrow \infty$ (as $f_0 \rightarrow +\infty$) and, thus, the shape on a $[\ln C \text{ vs. } x^2]$ -graph cannot be a prime determining parameter of the time evolution of the profile.

(5). The ϕ^2 -minimizing functional methodology has been shown to effectively replace the "limiting slope" concept for the linear diffusion equation (see Chapter 2, Sec. V), thus demonstrating that this methodology must be at least as good as the standard one using $[\ln C \text{ vs. } x^2]$ -graphs. Indeed, the cautions on limiting slope (Chapter 1, Sec. IV) demonstrate additional weakness with a $[\ln C \text{ vs. } x^2]$ -oriented methodology.

(6). The non-linear equation was decoupled in a manner totally obeying the $\int C dx = 1$ constraint by using the non-"linearly independent" set:

$$C(x,t) = \sum g_{m,n}(t) H_{2m}(z/\sqrt{n}) \exp(-(nz)^2). \quad (\text{I.50})$$

The calculation of each $g_{m,n}(t)$ strongly relies on knowledge of the set of numbers $\{B_p, x_R\}$ from the initial state. The fact that (within the context of continuous functions) each ' B_p ' is an invariant, not changing with the number of polynomials in a fit (a truth only if each B_p is the coefficient of a member of an orthogonal function set), seems to strongly

indicate that if this were changed (as with determining the B_p from a "best fit" on a $[\ln C \text{ vs. } x^2]$ -graph), it would cascade into a larger change in the $g_{m,n}(t)$ functions, thereby

(A). either making the $g_{m,n}(t)$ inaccurate or even patently incorrect

(B). or unknowingly recoupling the $g_{m,n}(t)$ together again in such a manner so that the determination of $g_{m,n}(t)$ recursively from 'previous' $g_{m',n'}(t)$ would no longer be correct.

It is for all these reasons [as well as the previously mentioned one (Chapter 2, Sec. V) that the diffusion process naturally involves C , VC , and such terms] that the ϕ^2 -methodology which inherently minimizes error on a $[C \text{ vs. } x]$ -graph, is used and believed to be the cornerstone of the correct data-fitting procedure.

APPENDIX II

ON THE CONVERGENCE OF SOME SERIES OF HERMITE POLYNOMIALS

The critical question to be answered here is: Under what conditions does the series:

$$f(x) \approx \sum B_m H_{2m}(x/x_R) \exp-(x/x_R)^2 \quad (\text{II.01})$$

truly approximate $f(x)$? As mentioned before, if $f(x)$ has a sufficiently slowly decaying "tail", even though $\int f(x)dx=1$, some coefficients diverging ($B_m \rightarrow \infty$) can occur. But, since one does not expect such states from a "thin-source," this problem is of no concern here.

In the long time limit, for any $D(C)$ process, $D(C) \rightarrow D_0$ so one expects to remain within the domain of gaussian-like functions.

Thus, the question can be simplified to: Can every gaussian-like $f(x)$ be expanded as a Hermite polynomial series? The simplest case would be :

$$(1/\pi^{1/2} x_A) \exp-(x/x_A)^2 = \sum B_m H_{2m}(x/x_R) \exp-(x/x_R)^2 \quad (\text{II.02})$$

One then seeks the range of possible x_R values to get a converging sequence, given x_A . Multiplying both sides by $H_{2p}(x/x_R) d(x/x_R)$ and integrating, gives:

$$\pi^{1/2} 2^{(2p)} (2p)! B_p = (1/\pi^{1/2} x_A) \int H_{2p}(x/x_R) \exp-(x/x_A)^2 d(x/x_R). \quad (\text{II.03})$$

Defining $a=(x_A/x_R)$, $\xi=(x/x_A)$ the resulting integral is tabulated, giving:

$$\pi^{1/2} 2^{(2p)} (2p)! B_p = (1/\pi^{1/2} x_R) [\pi^{1/2} (a^2-1)^p (2p)!/p!] \quad (\text{II.04})$$

Substituting for B_p back into the original equation, one gets:

$$(1/\pi^{1/2} x_A) \exp-(x/x_A)^2 = \quad (II.05)$$

$$(1/\pi^{1/2} x_R) \sum (1/p!) ([a^2-1]/4)^p H_{2p}(x/x_R) \exp-(x/x_R)^2.$$

Evaluating both sides as $x \rightarrow \infty$, gives: $0 = 0$. This limit gives no new information. Evaluating both sides as $x \rightarrow 0$, gives:

$$(1/x_A) = (1/x_R) \sum (1/p!) ([a^2-1]/4)^p H_{2p}(0) \quad (II.06)$$

$$\begin{aligned} a-1 &= \sum (1/p!) ([a^2-1]/4)^p (-1)^p 2^p (2p-1)!! \\ &= \sum ([1-a^2]/2)^p (2p-1)!!/p! \end{aligned} \quad (II.07)$$

CASE 1: $a < 1$

Define $z = [1-a^2]/2, (z > 0)$ and one gets:

$$(1-2z)^{-1/2} = \sum z^p (2p-1)!!/p! \quad (II.08)$$

Of course, the right-hand-side is just the power series representation for $(1-2z)^{-1/2}$. The domain of convergence is:

$$z < 1/2; (1-a^2)/2 < 1/2, \text{ i.e., } a^2 > 0 \quad (II.09)$$

CASE 2: $a > 1$:

Define $z = [a^2-1]/2, (z > 0)$ and one gets:

$$(1+2z)^{-1/2} = \sum (-1)^p z^p (2p-1)!!/p! \quad (II.10)$$

The domain of convergence is again

$$z < 1/2; (a^2-1)/2 < 1/2, \text{ i.e., } a^2 < 2. \quad (II.11)$$

The ratio test in each case is the same

$$\frac{|\text{Term 'p'}|}{|\text{Term 'p-1'}|} = \frac{z^p (2p-1)!! (p-1)!}{p! z^{p-1} (2p-3)!!} = \frac{z(2p-1)}{p} < 1 \quad (II.12)$$

which gives $z < (\frac{1}{2})(1 + \frac{1}{2p} + \dots)$ (as 'p' gets large, this clearly shows $z < \frac{1}{2}$).

The full domain of 'a' is thus, $2 > a^2 > 0$, which (using $a = x_A/x_R$) gives:

$$\infty > x_R > 2^{-1/2} x_A. \quad (\text{II.13})$$

Finally, by taking an arbitrary number of derivatives on both sides, one does not change the domain of convergence. Thus, one has:

Given any function which has a tail that decays faster than $A \cdot \exp-(x/x_A)^2$, for some A, x_A , it will have a converging series representation

$$\sum B_m H_{2m}(x/x_R) \exp-(x/x_R)^2 \quad (\text{II.14})$$

for $\infty > x_R > 2^{-1/2} x_A$.

A final comment: It was demonstrated in (Sec. II, Chapter 2) that the function $B(x/x_0)^2 \exp-(x/x_0)^2$ possesses a limiting slope $(-1/x_0^2)$ on a $[\ln C \text{ vs. } x^2]$ -graph, but the limiting intercept diverges. This is also true for $(x/x_0)^n$ where $n = \text{integer}$. This means that for a given B, x_0 , there is no finite value for 'A' which obeys over the entire x range

$$|A \exp-(x/x_0)^2| > |B(x/x_0)^n \exp-(x/x_0)^2| \quad (\text{II.15})$$

however, it will be true that for any $\epsilon > 0$, and any finite n, that there exists a finite 'A' such that:

$$|A \exp-x^2/(x_0 + \epsilon)^2| > |B(x/x_0)^n \exp-(x/x_0)^2| \quad (\text{II.16})$$

APPENDIX III

CREATING A CONTINUOUS DATAFIT FROM DISCRETE DATA

This section seeks to demonstrate the method by which the expansion:

$$C(x, t_R) = \sum B_m H_{2m}(x/x_R) \exp-(x/x_R)^2 \quad (\text{III.01})$$

can be created from raw data consisting of 'N' ordered pairs: $\{C_i, x_i; i=1, 2, \dots, N\}$. Since this work is implicitly written on the $x=(-\infty, \infty)$ interval with only even-parity functions being used, the arguments will be presented for that restriction.

Much of this entire appendix is derived from Peter Beckmann's book "Orthogonal Polynomials for Engineers and Physicists." One important difference between Beckmann's book and this work is the following:

Consider a set of functions: $Q_n(y)$ orthogonal with respect to the weighting function $w(y)$. This means that:

$$\int Q_n(y) Q_m(y) w(y) dy = \delta(m=n) / (\Lambda_m)^2 \quad (\text{III.02})$$

where $(\Lambda_m)^2$ is a normalization. The treatment in Beckmann is given for the case where an arbitrary function $C(y)$ is approximated by the sequence:

$$C(y) \approx \sum \bar{B}_m Q_m(y) \quad (\text{III.03})$$

whereas here, still considering $Q_m(y)$ and $w(y)$ as before, one will try to

approximate the arbitrary function $C(y)$ by the series:

$$C(y) \approx \sum \bar{B}_m Q_m(y) w(y) \quad (\text{III.04})$$

* * *

A basic theorem is the following: given the interval (as: $y = (-Y_I, Y_I)$), and the standardization (e.g., $Q_n(0) = 1$ or (coeff. y^n in Q_n) $= 2^n$), and the weighting function $w(y)$; the $Q_n(y)$, given they are polynomials in y , are totally determined. The interval $y = (-Y_I, Y_I)$ can allow $Y_I \rightarrow \infty$, but that may involve additional mathematical subtleties.

For $w(y) = \exp(-(x/x_R)^2)$ and [coeff. y^n in $Q_n(y)$] $= 2^n$ and $y = (-\infty, \infty)$, $Q_n(y) \equiv H_n(y)$. For any other $w(y)$ under consideration, Y_I will be finite.

The next theorem is that: All orthogonal function sets have a recurrence relation of the type:

$$Q_{n+1}(y) + U_n(y) Q_n(y) + V_n(y) Q_{n-1}(y) = 0. \quad (\text{III.05})$$

For orthogonal polynomials, the restriction is even more severe. Irrespective of the weighting function $w(y)$ or the interval, if one uses the standardization [coeff. y^n in Q_n] $= 1$, one must have the form:

$$Q_{n+1}(y) = (y - E_n) Q_n(y) - (A_{n-1}/A_n)^2 Q_{n-1}(y) \quad (\text{III.06})$$

(with $Q_0 = 1$ and $Q_{-1} = 0$) and where E_n are constants, and the $(A_n)^2$ are the normalizations, as given before. An explicit representation for E_n is:

$$E_n = (A_n)^2 \int y [Q_n(y)]^2 w(y) dy \quad (\text{III.07})$$

and an alternate representation of the $(A_n)^2$ is:

$$1/(A_n)^2 = \int y^n [Q_n(y)] w(y) dy. \quad (\text{III.08})$$

We note that the functions $Q_n(y) = H_n(y)/2^n$ would obey the relation:

$$Q_{n+1}(y) = yQ_n(y) - \frac{1}{2}nQ_{n-1}(y). \quad (\text{III.09})$$

Finally, the parameters $\{\bar{B}_m\}$ in the equation:

$$C(y) \approx \sum \bar{B}_m Q_m(y) w(y) \quad (\text{III.10})$$

are determined by:

$$\int C(y) Q_n(y) dy = \sum \bar{B}_m \int Q_m(y) Q_n(y) w(y) dy = \bar{B}_n / (A_n)^2. \quad (\text{III.11})$$

* * *

One now generalizes the situation to handle discrete data. We suppose 'N' data points have been taken $\{C_i, x_i; i=(1,N)\}$ from which $\{y_i = x_i/x_R\}$ can be found. We use implicit "mirror" symmetry for the $x-(-\infty, 0)$ interval and will expand $C(y)$ only in even parity functions.

Without loss of generality, the following weighting function is admissible:

$$w(y) = \sum_{i=N}^{+N} \delta(y-y_i) \exp(-y^2) \quad (\text{III.12})$$

Since this is NOT a gaussian, the $Q_n(y)$ set are not (ordinary) Hermite polynomials, but some generalized polynomials of a discrete variable. Notice also, that since the $\{y_i\}$ are distinct points, $w(y)$ necessarily spans a finite interval, thus, the domain is:

$$y = [-\max\{y_i \text{ set}\}; + \max\{y_i \text{ set}\}] \quad (\text{III.13})$$

The orthogonality integral now becomes:

$$\sum_{i=-N}^{+N} Q_n(y_i) Q_m(y_i) \exp(-y_i^2) = \delta(m-n) / (A_m)^2. \quad (\text{III.14})$$

Because the $w(y)$ is explicitly an even function,

$$E_n = (A_n)^2 \int y [Q_n(y)]^2 w(y) dy = 0 \quad (\text{III.15})$$

since it is an integral over an odd function. Thus:

$$Q_{n+1}(y) = yQ_n(y) - (A_{n-1}/A_n)^2 Q_{n-1}(y) \quad (\text{III.16})$$

$$1/(A_n)^2 = \int y^n [Q_n(y)] w(y) dy = \sum_{i=-N}^{+N} (y_i)^n [Q_n(y_i)] \exp(-y_i)^2 \quad (\text{III.17})$$

One begins with $Q_{-1}=0$, $A_{-1}=0$, $Q_0=1$ and then calculates A_0 . This generates $Q_1(y)$ which in turn gives A_1 . A_1 along with A_0 uniquely specify $Q_2(y)$. The process can then be continued indefinitely. In such a manner, the continuous functions $Q_n(y)$ can be generated and they will depend only on the values $\{y_i; i=(-N, N)\}$ and not on the values of $\{C_i; i = (-N, +N)\}$ where $C(y_i) = C(-y_i)$. Instead of determining $\bar{B}_m$ via:

$$C(y) = \sum \bar{B}_m Q_m(y) w(y) \quad (\text{III.18})$$

since one does not want to use

$$w(y) = \sum_{i=-N}^{+N} \delta(y-y_i) \exp(-y_i)^2 \quad (\text{III.19})$$

in this expression for $C(y)$, the series approximation sought is:

$$C(y) = \sum \bar{B}_m Q_m(y) \exp(-y)^2 \quad (\text{III.20})$$

This gives:

$$\sum_{i=-N}^{+N} C(y) \delta(y-y_i) = \sum \bar{B}_m Q_m(y) w(y) \quad (\text{III.21})$$

$$\int \left[\sum_{i=-N}^N C(y) \delta(y-y_i) \right] Q_n(y) dy = \sum \bar{B}_m \left[\int Q_m(y) Q_n(y) w(y) dy \right] \quad (\text{III.22})$$

$$\sum_{i=-N}^N C(y_i) Q_n(y_i) = \bar{B}_n / (A_n)^2, \quad (\text{III.23})$$

thus, given the data $C(y_i)$, the parameters $\{\bar{B}_n\}$ are determined. Using $C(y_i) = C(-y_i)$, one expects to need only $Q_m(y)$ for $m=\text{even}$, i.e.,

$$C(y) \approx \sum_{m=0}^{NI} \bar{B}_{2m} Q_{2m}(y) \exp-y^2. \quad (\text{III.24})$$

An $(NI+1)$ polynomial fit $m=(0, NI)$ can be re-expressed in terms of $H_{2m}(y)$ since an explicit form for the $Q_{2m}(y)$ has been given via this analysis method. A simple transformation takes one from the $\{Q_{2m}(y)\}$ -set to the $\{H_{2m}(y)\}$ -set. Writing the $Q_{2m}(y)$ as:

$$Q_{2m}(y) = \sum_{n=0}^m k(m,n) y^{2n} \quad (\text{III.25})$$

(where the $k(m,n)$ are "known"), one has:

$$\sum_{m=0}^{NI} \bar{B}_{2m} \sum_{n=0}^m k(m,n) y^{2n} \exp-y^2 \approx \sum_{n=0}^{NI} B_n H_{2n}(y) \exp-y^2 \quad (\text{III.26})$$

$$\sum_{n=0}^{NI} y^{2n} \left[\sum_{m=n}^{NI} \bar{B}_{2m} k(m,n) \right] \exp-y^2 \approx \sum_{n=0}^{NI} B_n H_{2n}(y) \exp-y^2. \quad (\text{III.27})$$

Multiplying both sides by $H_{2p}(y) dy$ and integrating gives:

$$\pi^{1/2} 2^{2p} (2p)! B_p = \sum_{n=0}^{NI} \left[\sum_{m=n}^{NI} \bar{B}_{2m} k(m,n) \right] \int y^{2n} H_{2p}(y) \exp-y^2 dy. \quad (\text{III.28})$$

Using:⁵⁰

$$\int x^{2m+n} H_n(x) \exp-(x^2) dx = \frac{(2m+n)!}{(2m)!} \Gamma(m+\frac{1}{2}) \delta(m \geq 0) \quad (\text{III.29})$$

results in:

$$\pi^{1/2} 2^{2p} (2p)! B_p = \sum_{n=0}^{NI} \left[\sum_{m=n}^{NI} \bar{B}_{2m} k(m,n) \right] \frac{(2n)!}{(n-p)!} \Gamma\left(\frac{n-p+1}{2}\right) \delta(n \geq p), \quad (\text{III.30})$$

thus, determining the $\{B_p\}$ parameters.

The transformation from the $\{\bar{B}_{2m}\}$ -set to the $\{B_p\}$ -set is a necessary step. In the limit of continuous data, the $\{B_p\}$ would not change going from an $(NI+1)$ -polynomial fit to an $(NI+2)$ -polynomial fit. For this reason (each B_p being an "invariant"), it is the $\{B_p\}$ numbers that couple directly to the analysis procedure. Because data is taken as discrete pairs: (C_i, x_i) , the discrete pair approximation to $C(x)$ makes the set $\{\bar{B}_{2m}\}$ falsely the invariants. However, even though the $\{B_p\}$ -set cannot be invariant when one changes the number of polynomials in a fit, they should be almost invariant. This then provides an unambiguous test of "goodness-of-fit": A "good fit" to the discrete data, coupled with a "reasonable" choice of ' x_R ' will yield $\{B_p\}$ parameters that are almost independent of the number of polynomials in the fit. If this is not obeyed, one should change the value of ' x_R ' and recalculate.

One computational caution: The orthogonality sum (Eq. (III.14)) for the $\{Q_{2m}\}$ -set embodies $(m+1)$ restrictions on each (Q_{2m}) -polynomial. Because of the finite accuracy of any computer, this orthogonality relation will become more severely violated for larger and larger order polynomials, due entirely to round-off errors. This limits, in practice, the number of polynomials in a fit to 10-15 at most. In this work 5 or 6 polynomials in a datafit proved sufficient to generate a fit within experimental error (1%-2%).

* * *

As a final note in this section, the analysis method given in this thesis begins with an initial state

$$C_R(x, t_R) = \sum_{m=0}^{NI} B_m H_{2m}(x/x_R) \exp-(x/x_R)^2 \quad (\text{III.31})$$

and the linear or non-linear analysis gives a propagated state:

$$\hat{C}_R(x, t_F) = \sum_{p=0}^{p(\max)} G_p(\Gamma) H_{2p}(z) \exp-(z^2) \quad (\text{III.32})$$

where $\Gamma = 1 + 4D_o(t_F - t_R)/x_R^2$ and where the functional form $G_p(\Gamma)$ depends on the set $\{B_m; m=(0, NI)\}$. The primary calculation has been to specify $G_p(\Gamma)$ and z . To get the actual profile $\hat{C}_R(x, t_F)$, one needs to do a sum on the Hermite-polynomial series. One need not re-express each $H_{2p}(z)$ = (explicit polynomial in z) and then sum the resulting polynomial in z . One can "telescope-down" the series [much like $S = (1+z+z^2+\dots+z^n)$ can be "telescoped-down" by comparing (S) to (zS)]. For the series:

$$C = \sum_{K=0}^N G_K H_{2K}(z) \exp-z^2, \quad (\text{III.33})$$

to evaluate 'C' at any given point 'z', one needs only to do the following N-step loop (see Beckmann⁵⁸):

```

G(0), G(1),...G(N) = (given)
Z = (given)
A1 = 0, A2 = 0
DO K = 0, N
  A3 = (2Z) (A2) - 2(A1) (2N - 2K + 2)
  A1 = A2, A2 = A3
  A3 = G(N-K) + (2Z)(A2) - 2(A1) (2N - 2K + 1)
  A1 = A2, A2 = A3
CONTINUE
C = (A3) EXP-(Z2)

```

* * *

APPENDIX IV

INTEGRALS OF $\Gamma^v (\ln \Gamma)^m$

One seeks:

$$\Phi(v, m, q; \Gamma, \Gamma_0) = \int_{(\Gamma_0)}^{(\Gamma)} \dots \int \Gamma^v (\ln \Gamma)^m (d\Gamma)^{q+1} = \quad (\text{IV.01})$$

$$\int_{\Gamma_1=\Gamma_0}^{\Gamma} d\Gamma_1 \int_{\Gamma_2=\Gamma_0}^{\Gamma_1} d\Gamma_2 \dots \int_{\Gamma_{q+1}=\Gamma_0}^{\Gamma_q} d\Gamma_{q+1} (\Gamma_{q+1})^v (\ln(\Gamma_{q+1}))^m$$

where (v =real number) and (m =integer ≥ 0). The $(q+1)$ -fold integral for these types of limits can be replaced by a single integral of the form⁵⁹:

$$\Phi(v, m, q; \Gamma, \Gamma_0) = \frac{1}{q!} \int_{W=\Gamma_0}^{\Gamma} (\Gamma-W)^q (W)^v (\ln W)^m dW. \quad (\text{IV.02})$$

The integrands differ by a function $f(W)$ whose integral vanishes at both $(W=\Gamma_0)$ and $(W=\Gamma)$. Expanding the binomial:

$$\Phi = \frac{(-1)^q}{q!} \sum_{p=0}^q \binom{q}{p} (-\Gamma)^{q-p} \int_{W=\Gamma_0}^{\Gamma} (\Gamma-W)^p (W)^v (\ln W)^m dW, \quad (\text{IV.03})$$

and using $x = \ln W$, $e^x = W$, $dW = e^x dx$, one gets:

$$\Phi = \frac{(-1)^q}{q!} \sum_{p=0}^q \binom{q}{p} (-\Gamma)^{q-p} \int_{x=x_1}^{x_2} x^m \exp[(p+v+1)x] dx \quad (\text{IV.04})$$

where the limits (x_1, x_2) are $(\ln \Gamma_0, \ln \Gamma)$. There are two cases. First,

if both ($v=\text{integer}$) and ($p+v+1=0$):

$$\int_{x=x_1}^{x_2} x^m dx = \frac{1}{(m+1)} [(\ln \Gamma)^{m+1} - (\ln \Gamma_o)^{m+1}] \delta(p+v+1=0) \quad (\text{IV.05})$$

Otherwise:

$$\int_{x=x_1}^{x_2} x^m \exp[(p+v+1)x] dx = (p+v+1)^{-(m+1)} \int_{s=s_1}^{s_2} s^m e^s ds (1-\delta(p+v+1=0)) \quad (\text{IV.06})$$

where the limits (s_1, s_2) are $[(p+v+1)\ln \Gamma_o, (p+v+1)\ln \Gamma]$. It is easily verified by taking derivatives of both sides, that:

$$\int s^m e^s ds = (-1)^m m! \sum_{r=0}^m \frac{(-1)^r}{r!} s^r e^s \quad (\text{IV.07})$$

and using:

$$[s^r e^s]_{s_1}^{s_2} = (p+v+1)^r [\Gamma^{p+v+1} (\ln \Gamma)^r - \Gamma_o^{p+v+1} (\ln \Gamma_o)^r] \quad (\text{IV.08})$$

this results in:

$$\begin{aligned} \int_{x=x_1}^{x_2} x^m \exp[(p+v+1)x] dx = & \quad (\text{IV.09}) \\ & \delta(p+v+1=0) [(\ln \Gamma)^{m+1} - (\ln \Gamma_o)^{m+1}] / (m+1) + \\ & (1-\delta(p+v+1=0)) \frac{(-1)^m m!}{(p+v+1)^{m+1}} \sum_{r=0}^m \frac{(-1)^r}{r!} (p+v+1)^r [\Gamma^{p+v+1} (\ln \Gamma)^r - \Gamma_o^{p+v+1} (\ln \Gamma_o)^r] \end{aligned}$$

Since one does a sum on the index 'p' from $p=(0, q)$, a particular value of 'p' will satisfy $\delta(p+v+1=0)$ only if $v=\text{negative-integer}$ in range $(-1, -q-1)$

and then $p=+|v|-1$. Thus:

$$\begin{aligned} \Phi(v, m, q; \Gamma, \Gamma_0) &= \delta(v=\text{integer}) \delta(-1 \leq v \leq -(q+1)) \times \\ &\frac{(-1)^{|v|-1}}{(m+1)q!} \left[\binom{q}{|v|-1} \Gamma^{q-|v|+1} [(\ln \Gamma)^{m+1} - (\ln \Gamma_0)^{m+1}] + \right. \\ &(-1)^m \frac{m!}{q!} \sum_{p=0}^q \binom{q}{p} (-1)^p (1 - \delta(p+v+1=0)) \Gamma^{q-p} \times \\ &\left. \sum_{r=0}^m \frac{(-1)^r}{r!} \left[\frac{1}{p+v+1} \right]^{m-r+1} [\Gamma^{p+v+1} (\ln \Gamma)^r - \Gamma_0^{p+v+1} (\ln \Gamma_0)^r] \right] \end{aligned} \quad (\text{IV.10})$$

APPENDIX V

COUPLING COEFFICIENTS FOR THE $D = D_0(1+\alpha C)$ AND $D = D_0(1+\gamma C^R)$ PROBLEMS1. Representation of the $\Theta(\dots)$ Functions

In this section we consider that integral, whose parameters are entirely indices and contain no physical parameters, and whose value represents the strength of coupling between the different models of the linear equation via non-linearities. This integral, denoted by:

$$\Theta(m_1, m_2, \dots, m^*(R+1), n_1, n_2, \dots, n^*(R+1); p, n)$$

has the explicit representation:

$$\Theta(m_1, m_2, \dots, m^*(R+1), n_1, n_2, \dots, n^*(R+1); p, n) = \quad (V.01)$$

$$\begin{aligned} & (n^{1/2} 2^{2p} (2p)!)^{-1} \prod_{q=1}^{R+1} \delta((n^* q) a_q^2 = 1) \delta(a_1^2 + a_2^2 + \dots + a_{R+1}^2 = 1) \times \\ & \text{Limit}_{t_1 \dots t_{R+1} \rightarrow 0} \int H_{2p}(\xi) \prod_{j=1}^{R+1} \left(\frac{\partial}{\partial t_j} \right)^{2m^* j} \left[\sum_{i=1}^{R+1} a_i \frac{\partial}{\partial t_i} \right]^2 \exp - \left[\sum_{k=1}^{R+1} [t_k - a_k \xi]^2 \right] d\xi. \end{aligned}$$

Since each (t_i) is independent,

$$\left(\frac{\partial}{\partial t_i} \right) \left(\frac{\partial}{\partial t_j} \right) = \left(\frac{\partial}{\partial t_j} \right) \left(\frac{\partial}{\partial t_i} \right) \quad (V.02)$$

and the set $\{t_i\}$ spans an $(R+1)$ -dimensional rectilinear hyperspace.

Examining the exponent, one has:

$$(\sum (t_k - a_k \xi)^2) = \sum (t_k)^2 - 2\xi \sum (a_k t_k) + \sum (a_k)^2 \xi^2. \quad (V.03)$$

Using $[\sum (a_k)^2 = 1]$, and completing the square:

$$(\sum (t_k - a_k \xi)^2) = [\xi - \sum (a_k t_k)]^2 + \sum (t_k)^2 - (\sum a_k t_k)^2, \quad (V.04)$$

with:

$$z = \sum (a_k t_k) \quad (V.05a)$$

$$F^2 = \sum (t_k)^2 \quad (V.05b)$$

$$f^2 = F^2 - z^2 \quad (V.05c)$$

the integral appearing in $\Theta(\dots)$, denoted ' I_0 ', is:

$$I_0 = \int H_{2p}(\xi) \dots d\xi \quad (V.06)$$

$$\prod_{j=1}^{R+1} \left(\frac{\partial}{\partial t_j} \right)^{2m^*j} \left[\sum a_i \frac{\partial}{\partial t_i} \right]^2 (\exp - f^2) \times$$

$$\int H_{2p}(\xi) \exp - [\xi - z]^2 d\xi.$$

Using :

$$\int H_{2p}(\xi) \exp - [\xi - z]^2 d\xi = \pi^{1/2} 2^{2p} z^{2p} \quad (V.07)$$

gives:

$$I_0 = \pi^{1/2} 2^{2p} \prod_{j=1}^{R+1} \left(\frac{\partial}{\partial t_j} \right)^{2m^*j} \left[\sum a_i \frac{\partial}{\partial t_i} \right]^2 z^{2p} \exp - f^2 \quad (V.08)$$

viewing each (t_i) as a vector, the vector

$$|z\rangle = \sum a_i |t_i\rangle$$

corresponds then to a specific direction in this $(R+1)$ -dimensional space.

Because $[\sum a_i^2 = 1]$, $|z\rangle$ is normed (i.e., $\langle z|z\rangle = 1$). A unitary transformation between the set $\{t_i\}$ and a set $\{z_i\}$ (with ' $z' \equiv z_{R+1}$ ') could be performed.

Since it would be a norm-preserving transformation:

$$F^2 = \sum_{k=1}^{R+1} (t_k)^2 \equiv \sum_{k=1}^{R+1} (z_k)^2 \quad (V.09)$$

from which follows:

$$f^2 = F^2 - z^2 \equiv \sum_{k=1}^R (z_k)^2. \quad (V.10)$$

Since each of the set $\{z_i\}$ are independent rectilinear coordinates, (z) and (f) are now linearly independent.

Next, examining

$$[\sum a_i \frac{\partial}{\partial t_i}]^2 Q(z, f); Q(z, f) \equiv z^{2p} \exp -f^2, \quad (V.11)$$

since each $[\sum a_i \frac{\partial}{\partial t_i}]$ term is composed only of constants and first-derivatives, this gives:

$$[\sum a_i \frac{\partial}{\partial t_i}] Q(z, f) = \frac{\partial Q}{\partial z} [\sum a_i \frac{\partial}{\partial t_i}] z + \frac{\partial Q}{\partial f} [\sum a_i \frac{\partial}{\partial t_i}] f. \quad (V.12)$$

one term is:

$$[\sum a_i \frac{\partial}{\partial t_i}] z = [\sum a_i \frac{\partial}{\partial t_i}] [\sum a_j t_j] = [\sum a_i a_j \frac{\partial}{\partial t_i} (t_j)]. \quad (V.13)$$

But, since the (t_i) and (t_j) coordinates are independent:

$$\frac{\partial}{\partial t_i} (t_j) = \delta(i=j) \quad (V.14)$$

giving:

$$[\sum a_i a_j \frac{\partial}{\partial t_i} (t_j)] = [\sum a_i a_j \delta(i=j)] = [\sum a_i^2] = 1. \quad (V.15)$$

Thus, re-expressing $[\sum a_i \frac{\partial}{\partial t_i}]$ in terms of $\{z_i\}$ with $'z' \equiv z_{k+1}$:

$$[\sum a_i \frac{\partial}{\partial t_i}] \equiv \frac{\partial}{\partial z}. \quad (V.16)$$

Eq. (V.16) uses $(z, t_1, t_2, \dots)$ being rectilinear and $[\sum a_i \frac{\partial}{\partial t_i}] z = 1$ ($\equiv \frac{\partial}{\partial z} z$).

This means, concurrently, that since (f) and (z) are independent, that:

$$\frac{\partial f}{\partial z} = 0. \quad (V.17)$$

This is easily checked for via: $\frac{1}{2}f \frac{\partial f}{\partial z} = \frac{\partial}{\partial z}(f^2)$ and:

$$\begin{aligned} \frac{\partial}{\partial z}(f^2) &= \frac{\partial}{\partial z} [\sum (t_j)^2 - z^2] = [\sum a_i \frac{\partial}{\partial t_i}] [\sum (t_j)^2] - \frac{\partial}{\partial z}(z^2) = \\ &[2 \sum a_i t_j \frac{\partial}{\partial t_i}(t_j)] - 2z = [2 \sum a_i t_i] - 2z = 0. \end{aligned} \quad (V.18)$$

Thus:

$$I_0 = \pi^{1/2} 2^{2p} \prod_{j=1}^{R+1} \left(\frac{\partial}{\partial t_j} \right)^{2m^*j} (\exp - f^2) \left(\frac{\partial}{\partial z} \right)^2 [z^{2p}] \quad (V.19)$$

The next step is critical to this entire work. When $p=0$, $z^{2p}=1$, then:

$$\frac{\partial^2}{\partial z^2} (z^0) = 0 \quad (V.20)$$

Thus:

$$O(m_1, m_2, \dots, m^*(R+1), n_1, n_2, \dots, n^*(R+1); p=0, n) = 0 \quad (V.21)$$

This vanishing, recall, was critical to both the normalization preservation condition:

$$\int C(x, t) dx = 1 \quad (V.22)$$

as well as effecting a full decoupling of the $g(p, n)$ equations.

Finally,

$$O(m_1, m_2, \dots, m^*(R+1), n_1, n_2, \dots, n^*(R+1); p>0, n) =$$

$$\left(\prod_{q=1}^{R+1} \delta(n^*q) a_q^2 = 1 \right) \delta(a_1^2 + a_2^2 + \dots + a_{R+1}^2 = 1) \times$$

$$\lim_{t_1 \dots t_{R+1} \rightarrow 0} \left[\prod_{j=1}^{R+1} \left(\frac{\partial}{\partial t_j} \right)^{2m^*j} \right] (z^{2(p-1)} / (2p-2)!) \exp - f^2 \quad (V.23)$$

An alternate form for $\Theta(\dots)$ is possible. Using:

$$I(m_1, m_2, \dots, m^*(R+1), p; a_1, a_2, \dots, a_{R+1}) = \int H_{2m_1}(a_1 \xi) H_{2m_2}(a_2 \xi) \dots H_{2m^*(R+1)}(a_{R+1} \xi) \times \\ \delta(a_1^2 + a_2^2 + \dots + a_{R+1}^2 = 1) H_{2p}(\xi) \exp(-\xi^2) d\xi, \quad (V.24)$$

and using

$$H_{2q}(a_j \xi) \exp(-(a_j \xi)^2) = \lim_{t_j \rightarrow 0} \left(\frac{\partial}{\partial t_j} \right)^{2q} \exp(-(t_j - a_j \xi)^2); \quad (V.25)$$

following the same steps, with the same definition of (f^2) and (z) , this gives:

$$I(m_1, m_2, \dots, m^*(R+1), p; a_1, a_2, \dots, a_{R+1}) = \delta(a_1^2 + a_2^2 + \dots + a_{R+1}^2 = 1) \\ \pi^{1/2} 2^{2p} \lim_{t_1 \dots t_{R+1} \rightarrow 0} \left[\prod_{j=1}^{R+1} \left(\frac{\partial}{\partial t_j} \right)^{2m^*j} \right] z^{2p} \exp(-f^2) \quad (V.26)$$

In terms of this,

$$\Theta(m_1, m_2, \dots, m^*(R+1), n_1, n_2, \dots, n^*(R+1); p, n) = \\ (\pi^{1/2} 2^{2(p-1)} (2p-2)!)^{-1} \left[\prod_{q=1}^{R+1} \delta((n^*q) a_q^2 = 1) \right] \times \\ I(m_1, m_2, \dots, m^*(R+1), (p-1); a_1, a_2, \dots, a_{R+1}). \quad (V.27)$$

The remainder of this section will be a calculation of both functions

$$I(m, n, p; a, b), \quad I(p_1, p_2, p_3, p; a, b, c),$$

which are required for a full solution to the

$$D(C) = D_0 (1 + \alpha C + \beta C^2) \quad (V.28)$$

problem. Data are analyzed only for $C(z, \Gamma)$ taken out to order $-(\alpha^2, \beta)$,

thus, the only values of n required are $n=(1,2,3)$. Still, the $I(\dots)$ functions will be calculated for arbitrary n , and thus will embody a full solution (to all orders) of the quadratic (in concentration) diffusivity.

Finally, to be consistent with previous notations, the integrals which appear in the minimizing functionals (see Eqs. (2.35) and (6.116)) were denoted $I_{m,n}(a,b)$ and

$$I_{m,n}(a,b) \equiv I(m,n,p=0;a,b) \quad (V.29)$$

2. On $I(m,n,p;a,b)$

One starts with:

$$I(m,n,p;a,b) = \int H_{2m}(a\xi) H_{2n}(b\xi) H_{2p}(\xi) \delta(a^2+b^2=1) \exp(-\xi^2) d\xi =$$

$$\pi^{1/2} 2^{2p} \delta(a^2+b^2=1) \lim_{t_1, t_2 \rightarrow 0} \left(\frac{\partial}{\partial t_1} \right)^{2m} \left(\frac{\partial}{\partial t_2} \right)^{2n} z^{2p} \exp(-y^2) \quad (V.30)$$

where necessarily:

$$\begin{pmatrix} at_1 + bt_2 = z \\ t_1^2 + t_2^2 = z^2 + y^2 \end{pmatrix}. \quad (V.31)$$

Two unitary transformations from (t_1, t_2) to (z, y) are possible:

$$1. \quad \begin{pmatrix} z \\ y \end{pmatrix} = \begin{pmatrix} a & b \\ -b & a \end{pmatrix} \begin{pmatrix} t_1 \\ t_2 \end{pmatrix}; \quad \begin{pmatrix} \frac{\partial}{\partial t_1} \\ \frac{\partial}{\partial t_2} \end{pmatrix} = \begin{pmatrix} a \frac{\partial}{\partial z} - b \frac{\partial}{\partial y} \\ b \frac{\partial}{\partial z} + a \frac{\partial}{\partial y} \end{pmatrix} \quad (V.32a)$$

$$2. \begin{pmatrix} y \\ z \end{pmatrix} = \begin{pmatrix} b & -a \\ a & b \end{pmatrix} \begin{pmatrix} t_1 \\ t_2 \end{pmatrix}; \quad \begin{cases} \frac{\partial}{\partial t_1} = a \frac{\partial}{\partial z} + b \frac{\partial}{\partial y} \\ \frac{\partial}{\partial t_2} = b \frac{\partial}{\partial z} - a \frac{\partial}{\partial y} \end{cases} \quad (\text{V.32b})$$

The integral $I(\dots)$ should be independent of which one is chosen. We keep 'track' of both via:

$$\left(\frac{\partial}{\partial t_1}\right)^{2m} \left(\frac{\partial}{\partial t_2}\right)^{2n} = \left(a \frac{\partial}{\partial z} \pm b \frac{\partial}{\partial y}\right)^{2m} \left(b \frac{\partial}{\partial z} \mp a \frac{\partial}{\partial y}\right)^{2n} \quad (\text{V.33})$$

As a linear transformation, it obeys:

$$\left(\frac{\partial}{\partial z}\right) \left(\frac{\partial}{\partial y}\right) = \left(\frac{\partial}{\partial y}\right) \left(\frac{\partial}{\partial z}\right) \quad (\text{V.34a})$$

$$\text{Limit}_{t_1, t_2 \rightarrow 0} [\quad] \equiv \text{Limit}_{z, y \rightarrow 0} [\quad] . \quad (\text{V.34b})$$

Expanding the binomials:

$$\left(a \frac{\partial}{\partial z} \pm b \frac{\partial}{\partial y}\right)^{2m} = \sum_{s1=0}^{2m} \binom{2m}{s1} (\pm b \frac{\partial}{\partial y})^{2m-s1} \left(a \frac{\partial}{\partial z}\right)^{s1} \quad (\text{V.35a})$$

$$\left(b \frac{\partial}{\partial z} \mp a \frac{\partial}{\partial y}\right)^{2n} = \sum_{s2=0}^{2n} \binom{2n}{s2} (\mp a \frac{\partial}{\partial y})^{2n-s2} \left(b \frac{\partial}{\partial z}\right)^{s2} , \quad (\text{V.35b})$$

and using 's'=s1+s2, this gives two equivalent expressions:

$$\sum_{s1=0}^{2m} \sum_{s2=0}^{2n} K(s1, s2) = \sum_{s=0}^{2(m+n)} \sum_{(s1)} \delta(\min[2m, s] \geq s1 \geq \max[0, s-2n]) K(s1, s-s1) \quad (\text{V.36})$$

$$= \sum_{s=0}^{2(m+n)} \sum_{(s2)} \delta(\min[2n, s] \geq s2 \geq \max[0, s-2m]) K(s-s2, s2) \quad (\text{V.37})$$

These can be used to give:

$$\begin{aligned} \left(\frac{\partial}{\partial t_1}\right)^{2m} \left(\frac{\partial}{\partial t_2}\right)^{2n} &= \sum_{s1=0}^{2m} \sum_{s2=0}^{2n} \binom{2m}{s1} \binom{2n}{s2} a^{2n+s1-s2} b^{2m+s2-s1} (\pm 1)^{s1} (\mp 1)^{s2} \times \\ &\quad \left(\frac{\partial}{\partial y}\right)^{2(m+n)-(s1+s2)} \left(\frac{\partial}{\partial z}\right)^{s1+s2} \end{aligned} \quad (\text{V.38})$$

$$= \left[\sum_{s=0}^{2(m+n)} \sum_{(s1)} \binom{2m}{s1} \binom{2n}{s-s1} a^{2n+2s1-s} b^{2m-2s1+s} (\bar{\pm}1)^s (-1)^{s1} \right] \times$$

$$\left[\sum_{s=0}^{2(m+n)} \sum_{(s2)} \binom{2m}{s-s2} \binom{2n}{s2} a^{2n-2s2+s} b^{2m+2s2-s} (\pm 1)^s (-1)^{s2} \right] \times$$

$$\left(\frac{\partial}{\partial y} \right)^{2(m+n)-s} \left(\frac{\partial}{\partial z} \right)^s \quad (V.39a, V.39b)$$

Notice that the ambiguity of allowable orthogonal transformations is now mirrored entirely in the term $(\bar{\pm}1)^s$ (or $(\pm 1)^s$). The integral must be symmetric or interchange of (m,n) simultaneously with (a,b) , i.e.,

$$I(m,n,p;a,b) = I(n,m,p;b,a) . \quad (V.40)$$

That this is indeed so, can be seen by noticing that the label transformation just takes one from Eq. (V.39a) to Eq. (V.39b). Using Eq. (V.39a), one has:

$$I(m,n,p;a,b) = \pi^{1/2} 2^{2p} a^{2n} b^{2m} \delta(a^2+b^2=1)$$

$$\sum_{s=0}^{2(m+n)} (\bar{\pm}1)^s (b/a)^s \text{Limit}_{y,z \rightarrow 0} \left[\left(\frac{\partial}{\partial y} \right)^{2(m+n)-s} \left(\frac{\partial}{\partial z} \right)^s z^{2p} \exp -y^2 \right] \times$$

$$\sum_{(s1)} \delta(\min[2m,s] \geq s1 \geq \max[0,s-2n]) (-1)^{s1} \binom{2m}{s1} \binom{2n}{s-s1} (a/b)^{2s1} . \quad (V.41)$$

Since (y,z) are independent coordinates, the $z \rightarrow 0$ Limit can be immediately evaluated:

$$\text{Limit}_{z \rightarrow 0} \left[\left(\frac{\partial}{\partial z} \right)^s z^{2p} \right] = (2p)! \delta(s=2p) . \quad (V.42)$$

For this to be satisfied requires $2(m+n) \geq 2p$ so that a term in the 's'-sum will be able to satisfy the restriction $\delta(s=2p)$. The $y \rightarrow 0$ Limit is also evaluated:

$$\text{Limit}_{y \rightarrow 0} \left[\left(\frac{\partial}{\partial y} \right)^{2(m+n)-2p} \exp -y^2 \right] = \text{Limit}_{y \rightarrow 0} [H_{2(m+n-p)}(y) \exp -y^2]$$

$$= H[2(m+n-p)] \quad (V.43)$$

where we have used the definition:

$$H_{2p}(y=0) \equiv H[2p] . \quad (V.44)$$

Notice also that $(+1)^s \delta(s=2p) = +1$, thus removing any effect due to choice of possible unitary transformations. Finally:

$$I(m,n,p;a,b) = \quad (V.45)$$

$$\pi^{1/2} 2^{2p} (2p)! a^{2(n-p)} b^{2(m+p)} \delta(a^2+b^2=1) \delta(m+n \geq p) H[2(m+n-p)] \times \\ \int \delta(\min[2m, 2p] \geq s \geq \max[0, 2p-2n]) (-1)^s \binom{2m}{s} \binom{2n}{2p-s} (a/b)^{2s} .$$

Defining:

$$F(m, r_2, r_1; x) = \sum_{(n)} \delta(\min[r_2, m] \geq n \geq \max[0, m-r_1]) \times \\ \binom{r_2}{n} \binom{r_1}{m-n} (-1)^n (x)^{2n} \quad (V.46)$$

one has:

$$I(m,n,p;a,b) = \pi^{1/2} 2^{2p} (2p)! a^{2(n-p)} b^{2(m+n)} \delta(a^2+b^2=1) \delta(m+n \geq p) \times \\ H[2(m+n-p)] F(2p, 2m, 2n; (a/b)) \quad (V.47)$$

* * *

3. On $I(p_1, p_2, p_3, p; a, b, c)$

One starts with:

$$I(p_1, p_2, p_3, p; a, b, c) = \quad (V.48)$$

$$\int H_{2p_1}(a\xi) H_{2p_2}(b\xi) H_{2p_3}(c\xi) H_{2p}(\xi) \exp(-\xi^2) d\xi \delta(a^2+b^2+c^2=1) = \\ \pi^{1/2} 2^{2p} \delta(a^2+b^2+c^2=1) \lim_{t_1, t_2, t_3 \rightarrow 0} \left(\frac{\partial}{\partial t_1} \right)^{2p_1} \left(\frac{\partial}{\partial t_2} \right)^{2p_2} \left(\frac{\partial}{\partial t_3} \right)^{2p_3} z^{2p} \exp-(r^2+s^2)$$

where necessarily:

$$at_1 + bt_2 + ct_3 = z \quad (V.49)$$

$$t_1^2 + t_2^2 + t_3^2 = r^2 + s^2 + z^2 \quad (V.50)$$

There is a 1-dimensional arbitrariness in the choice of unitary transformations which will fulfill these conditions. We choose the following particular transformation with:

$$|z\rangle = a|t_1\rangle + b|t_2\rangle + c|t_3\rangle, \quad (V.51)$$

the vector $|r\rangle \sim |z\rangle \times |t_3\rangle$ is then perpendicular to the (z, t_3) plane and picks out a direction in the (t_1, t_2) plane. The normed $|r\rangle$ is:

$$|r\rangle = k(b|t_1\rangle - a|t_2\rangle); \quad k = (a^2 + b^2)^{-1/2}. \quad (V.52)$$

Finally, with $|r\rangle$ and $|z\rangle$ perpendicular, the last direction chosen is:

$$\begin{aligned} |s\rangle &= |z\rangle \times |r\rangle \\ &= kac|t_1\rangle + kbc|t_2\rangle - (1/k)|t_3\rangle \end{aligned} \quad (V.53)$$

and it is easily verified that $|s\rangle$ is normed.

Summarizing the transformation as:

$$\begin{pmatrix} r \\ s \\ z \end{pmatrix} = \begin{pmatrix} kb & -ka & 0 \\ kac & kbc & -1/k \\ z & b & c \end{pmatrix} \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} \quad (V.54)$$

it is easily verified that the determinant of the matrix is 1. The constraint $a^2 + b^2 + c^2 = 1$ gives $1 = k^2(1 - c^2)$ and thus, only (a, b) are independent. Using:

$$\frac{\partial}{\partial t_1} = \frac{\partial r}{\partial t_1} \frac{\partial}{\partial r} + \frac{\partial s}{\partial t_1} \frac{\partial}{\partial s} + \frac{\partial z}{\partial t_1} \frac{\partial}{\partial z} \quad (V.55)$$

and similar equations for $(\frac{\partial}{\partial t_2})$ and $(\frac{\partial}{\partial t_3})$, this gives:

$$I(p_1, p_2, p_3, p; a, b, c) = \pi^{1/2} 2^{2p} \delta(a^2 + b^2 + c^2 = 1) \times$$

$$\lim_{r, s, z \rightarrow 0} (kb \frac{\partial}{\partial r} + kac \frac{\partial}{\partial s} + a \frac{\partial}{\partial z})^{2p_1} (-ka \frac{\partial}{\partial r} + kbc \frac{\partial}{\partial s} + b \frac{\partial}{\partial z})^{2p_2} \times$$

$$(-\frac{1}{k} \frac{\partial}{\partial s} + c \frac{\partial}{\partial z})^{2p_3} z^{2p} \exp(-(r^2 + s^2)) . \quad (V.56)$$

As an orthogonal transformation, all the derivatives commute:

$$(\frac{\partial}{\partial r})(\frac{\partial}{\partial s})(\frac{\partial}{\partial z}) = (\frac{\partial}{\partial z})(\frac{\partial}{\partial s})(\frac{\partial}{\partial r}) . \quad (V.57)$$

Thus, the derivative operators can be treated as if they were algebraic quantities during algebraic operations. Specifically, with:

$$u \equiv \frac{\partial}{\partial r} , v \equiv \frac{\partial}{\partial s} , w \equiv \frac{\partial}{\partial z} \quad (V.58)$$

the following algebraic expression is next simplified:

$$J1 \equiv (kbu + kacv + aw)^{2p_1} (-kau + kbcv + bw)^{2p_2} (-[v/k] + cw)^{2p_3}$$

$$= k^{2(p_1+p_2)} a^{2p_1} b^{2p_2} ([bu/a] + cv + [w/k])^{2p_1} \times$$

$$(-[au/b] + cv + [w/k])^{2p_2} (-[v/k] + cw)^{2p_3} . \quad (V.59)$$

Expanding binomially the terms:

$$J2 \equiv ([bu/a] + (cv + [w/k]))^{2p_1} (-[au/b] + (cv + [w/k]))^{2p_2} =$$

$$\sum_{m_1=0}^{2p_1} \sum_{m_2=0}^{2p_2} \binom{2p_1}{m_1} \binom{2p_2}{m_2} (cv + [w/k])^{m_1+m_2} \times$$

$$[bu/a]^{2p_1-m_1} [-au/b]^{2p_2-m_2} =$$

$$\sum_{m=0}^{2(p_1+p_2)} \sum_{(m_1)} \delta(\min[2p_1, m] \geq m_1 \geq \max[0, m-2p_2]) \binom{2p_1}{m_1} \binom{2p_2}{m-m_1} \times$$

$$(cv + [w/k])^m [bu/a]^{2p_1-m_1} [-au/b]^{2p_2-m+m_1} . \quad (V.60)$$

Simplifying:

$$[bu/a]^{2p_1-m_1} [-au/b]^{2p_2-m+m_1} = \quad (V.61)$$

$$(-1)^m (b/a)^{2(p_1-p_2)+m} u^{2(p_1+p_2)-m} (-1)^{m_1} (a/b)^{2m_1},$$

one notes that the variable (u) is independent of the (m₁)-sum. Thus:

$$J_2 = (b/a)^{2(p_1-p_2)} \sum_{m=0}^{2(p_1+p_2)} (cv+[w/k])^m u^{2(p_1+p_2)-m} (-1)^m \left(\frac{b}{a}\right)^m \sum_{(m_1)} \delta(\min[2p_1, m] \geq m_1 \geq \max[0, m-2p_2]) \binom{2p_1}{m_1} \binom{2p_2}{m-m_1} (-1)^{m_1} (a/b)^{2m_1}. \quad (V.62)$$

Using

$$F(m, r_2, r_1; x) = \sum_{(n)} \delta(\min[r_2, m] \geq n \geq \max[0, m-r_1]) \times \binom{r_2}{n} \binom{r_1}{m-n} (-1)^n (x)^{2n}, \quad (V.63)$$

one gets:

$$J_2 = (b/a)^{2(p_1-p_2)} \sum_{m=0}^{2(p_1+p_2)} (cv+[w/k])^m u^{2(p_1+p_2)-m} (-1)^m \left(\frac{b}{a}\right)^m \times F(m, 2p_1, 2p_2; (a/b)). \quad (V.64)$$

Thus:

$$a^{2p_1} b^{2p_2} (b/a)^{2(p_1-p_2)} = a^{2p_2} b^{2p_1} \quad (V.65)$$

$$J_1 = k^{2(p_1+p_2)} a^{2p_2} b^{2p_1} \sum_{m=0}^{2(p_1+p_2)} (cv+[w/k])^m (-[v/k]+cw)^{2p_3} \times (-1)^m \left(\frac{b}{a}\right)^m u^{2(p_1+p_2)-m} F(m, 2p_1, 2p_2; (a/b)). \quad (V.66)$$

Expanding the remaining binomials gives:

$$(cv+[w/k])^m (-[v/k]+cw)^{2p3} = \quad (V.67)$$

$$\sum_{q1=0}^m \sum_{q2=0}^{2p3} \binom{m}{q1} \binom{2p3}{q2} (cv)^{m-q1} (-v/k)^{2p3-q2} (w/k)^{q1} (cw)^{q2} =$$

$$\sum_{q1=0}^m \sum_{q2=0}^{2p3} \binom{m}{q1} \binom{2p3}{q2} (c)^{m-q1+q2} (-1)^{q2} (1/k)^{2p3+q1-q2} \times$$

$$v^{m+2p3-(q1+q2)} w^{(q1+q2)}.$$

Using:

$$\sum_{m=0}^{2(p1+p2)} \sum_{q1=0}^m \sum_{q2=0}^{2p3} K(m, q1, q2) = \quad (V.68)$$

$$\int \delta(2(p1+p2+p3) \geq q \geq 0) \delta(\min[2(p1+p2), q] \geq q1 \geq \max[0, q-2p3]) \times$$

$$\delta(2(p1+p2) \geq m \geq q1) K(m, q1, q-q1)$$

gives:

$$J1 = k^{2(p1+p2)} a^{2p2} b^{2p1} \int \delta(2(p1+p2+p3) \geq q \geq 0) \times$$

$$\delta(\min[2(p1+p2), q] \geq q1 \geq \max[0, q-2p3]) \delta(2(p1+p2) \geq m \geq q1) \times$$

$$\binom{m}{q1} \binom{2p3}{q-q1} c^{m-2q1+q} (-1)^{q-q1} k^{-2p3-2q1+q} (-1)^m \left(\frac{b}{a}\right)^m \times$$

$$v^{m+2p3-q} w^q u^{2(p1+p2)-m} F(m, 2p1, 2p2; (a/b)). \quad (V.69)$$

One notes that the variables (u,v,w) are independent of the (q1)-sum, thus using:

$$\delta(\min[2(p1+p2), q] \geq q1 \geq \max[0, q-2p3]) \delta(2(p1+p2) \geq m \geq q1) = \quad (V.70)$$

$$\delta(2(p1+p2) \geq m \geq \max[0, q-2p3]) \delta(\min[2(p1+p2), q, m] \geq q1 \geq \max[0, q-2p3])$$

one gets:

$$\begin{aligned}
 J_1 = & k^{2(p_1+p_2)} a^{2p_2} b^{2p_1} \int \delta(2(p_1+p_2+p_3) \geq q \geq 0) (-1)^q w^q \\
 & \int \delta(2(p_1+p_2) \geq m \geq \max[0, q-2p_3]) c^{m+q} k^{q-2p_3} (-1)^m (b/a)^m \\
 & v^{m+2p_3-q} u^{2(p_1+p_2)-m} F(m, 2p_1, 2p_2; (a/b)) \\
 & \int \delta(\min[2(p_1+p_2), q, m] \geq q_1 \geq \max[0, q-2p_3]) \times \\
 & \binom{m}{q_1} \binom{2p_3}{q-q_1} (-1)^{q_1} (1/kc)^{2q_1} .
 \end{aligned} \tag{V.71}$$

Since $2(p_1+p_2) \geq m$; $\min[2(p_1+p_2), q, m] = \min[q, m]$ this gives:

$$\begin{aligned}
 & \int \delta(\min[q, m] \geq q_1 \geq \max[0, q-2p_3]) \times \\
 & \binom{m}{q_1} \binom{2p_3}{q-q_1} (-1)^{q_1} (1/kc)^{2q_1} = F(q, m, 2p_3; (1/kc))
 \end{aligned} \tag{V.72}$$

This finally gives:

$$\begin{aligned}
 J_1 = & k^{2(p_1+p_2)} a^{2p_2} b^{2p_1} \int \delta(2(p_1-p_2+p_3) \geq q \geq 0) (-1)^q w^q \\
 & \int \delta(2(p_1+p_2) \geq m \geq \max[0, q-2p_3]) c^{m+q} k^{q-2p_3} (b/a)^m \\
 & (-1)^m v^{m+2p_3-q} u^{2(p_1+p_2)-m} \\
 & F(m, 2p_1, 2p_2; (a/b)) F(q, m, 2p_3; (1/kc)) .
 \end{aligned} \tag{V.73}$$

Re-introducing the derivative operators, one has:

$$\begin{aligned}
 I(p_1, p_2, p_3, p; a, b, c) = & \\
 \pi^{1/2} 2^{2p} \delta(a^2 + b^2 + c^2 = 1) \text{Limit}_{r, s, z \rightarrow 0} (J_1 \text{ operator}) z^{2p} \exp(-(r^2 + s^2)) .
 \end{aligned} \tag{V.74}$$

The derivative operator (J_1) gives terms of the form:

$$\begin{aligned}
 & \left(\frac{\partial}{\partial z}\right)^q \left(\frac{\partial}{\partial s}\right)^{m+2p_3-q} \left(\frac{\partial}{\partial r}\right)^{2(p_1+p_2)-m} z^{2p} \exp(-(r^2 + s^2)) = \\
 & (2p)! \delta(q=2p) H[m+2p_3-2p] H[2(p_1+p_2)-m] .
 \end{aligned} \tag{V.75}$$

$$\delta(2(p_1+p_2+p_3) \geq q \geq 0) (-1)^q \delta(q=2p) = \delta(p_1+p_2+p_3 \geq p) \quad (V.76)$$

and using $H[m=\text{odd integer}]=0$ which restricts 'm'=even, one gets (with $m=2n$):

$$\begin{aligned} I(p_1, p_2, p_3, p; a, b, c) &= \pi^{1/2} 2^{2p} (2p)! \delta(a^2 + b^2 + c^2 = 1) \times \\ &\quad k^{2(p_1+p_2)} a^{2p_2} b^{2p_1} \delta(p_1+p_2+p_3 \geq p) \\ &\quad \sum \delta((p_1+p_2) \geq n \geq \max[0, p-p_3]) c^{2(n+p)} k^{2(p-p_3)} (b/a)^{2n} \\ &\quad H[2(p_3-p+n)] H[2(p_1+p_2-n)] \\ &\quad F(2n, 2p_1, 2p_2; (a/b)) F(2p, 2n, 2p_3; (1/kc)) \end{aligned} \quad (V.77)$$

* * *

4. Alternate Forms for the I(...) Functions

Usage of the function $F(m, r_2, r_1; x)$ has one drawback. The argument x used is either (a/b) or $(1/kc)$ and as $b \rightarrow 0$ or $c \rightarrow 0$, $F(\dots)$ diverges. There are enough coefficients that are zero to prevent a true singularity, however, since $I(\dots)$ is finite in these limits, an 'expanded' function may be more suited for computation:

$$F_1(m, r_2, r_1; x, p_1, n_1; y, p_2, n_2) \equiv \quad (V.78)$$

$$\begin{aligned} &\sum_{(n)} \delta(\min[m, r_2] \geq n \geq \max[0, m-r_1]) \times \\ &\quad \binom{r_2}{n} \binom{r_1}{m-n} (-1)^n x^{(2n)(p_1)+n_1} y^{(2n)(p_2)+n_2} \end{aligned}$$

In terms of this, one has:

$$\begin{aligned} I(m, n, p; a, b) &= \pi^{1/2} 2^{2p} (2p)! \delta(a^2 + b^2 = 1) \delta(m+n \geq p) \times \\ &\quad H[2(m+n-p)] F_1(2p, 2m, 2n; a, 1, 2(n-p); b, -1, 2(m+p)) \end{aligned} \quad (V.79)$$

Now, neither $a \rightarrow 0$ nor $b \rightarrow 0$ poses any problems.

Also, converting to $F_1(\dots)$ notation, one has:

$$I(p_1, p_2, p_3, p; a, b, c) = \quad (V.80)$$

$$\pi^{1/2} 2^{2p} (2p)! \delta(a^2 + b^2 + c^2 = 1) \delta(p_1 + p_2 + p_3 \geq p) \times$$

$$\sum \delta(p_1 + p_2 \geq n \geq \max[0, p - p_3]) H[2(p_3 - p + n)] H[2(p_1 + p_2 - n)]$$

$$F_1(2n, 2p_1, 2p_2; a, +1, 2(p_2 - n); b, -1, 2(p_1 + n)) \times$$

$$F_1(2p, 2n, 2p_3; k, -1, 2(p_1 + p_2 + p - p_3); c, -1, 2(n + p)) .$$

It can easily be shown that each limit $a \rightarrow 0$, $b \rightarrow 0$, $c \rightarrow 0$ is now permitted, but the simultaneous limit $(a \rightarrow 0, b \rightarrow 0)$ is not permitted because $k \rightarrow \infty$, and the original transformation matrix which rotated (t_1, t_2, t_3) into (r, s, z) becomes undefined.

APPENDIX VI

NOTES ON $(\text{Sc}^{+++}) \rightarrow (\text{NaCl})$ DIFFUSION

Part of the original experiment had planned to use the tracer Sc^{46} which is a trivalent species and a strong γ -emitter (whereas Ca^{45} is a β -emitter). In preparation for this, a magnifying telescope was set-up which allowed all tracer handling to be done at arm's length while permitting high accuracy in alignments and volumetric readings. Although the physical distance is not needed for Ca^{45} , it is desirable for visual-oriented work with γ -sources, the eyes being the second most sensitive part of the body to radiation.

However, the Scandium project was halted because of difficulty in getting Sc^{46} to be deposited on the NaCl crystals. The vacuum deposition method essentially involves drying a tracer amount onto a refractory metal "boat" made of tantalum, molybdenum, or tungsten. Then, by ohmic heating to a high temperature, the tracer evaporates and then condenses onto the crystal surfaces in the evaporator.

It was originally thought that Sc^{46} diffused into the foils faster than it evaporated off, causing the difficulty. Use of a mix of tracer with NaCl as a source which dried into highly radioactive salt crystals, succeeded in getting a few percent of Sc^{46} tracer off the foils.

As the Sc^{46} was in the form of ScCl_3 in HCl , and ScCl_3 has a sublimation point of 800°C - 850°C , evaporation from a small quartz ampoule and from an alumina crucible were also tried -- both with negligible success, although the alumina porosity could have accounted for the failure of that test.

The real "problem" was found by attempting evaporation of reagent grade ScCl_3 in the form of $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$. It was noticed that a concentrated ScCl_3 solution, on gentle heating, turned molasses-like, hinting at the formation of a hydroxide. Direct heating of $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ (which is a white powder) under vacuum also created a bubbling transition upon gentle heating, leaving a slightly whiter compound that was impervious to further evaporation, even at extremely high temperatures. Indeed, the sequence of reactions:

was verified. ScCl_3 is one of the few hydrated metal-chlorides that decompose to the oxide upon heating.⁶⁰ Notice that the hydrated form $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ always contains enough water to allow this reaction to go to completion (it necessitating only $1.5\text{H}_2\text{O}$ per ScCl_3).

Dehydration of the hydrated chloride was considered, as for example, by using a "water scavenger" 2,2-dimethoxypropane which operates by:

creating an anhydrous salt (denoted " MX_n ") along with acetone and methanol. However, even if a layer of anhydrous ScCl_3 were successfully deposited on a crystal, any small amount of moisture could easily adsorb onto the surface so that the diffusion anneal, by being at an elevated temperature, would create the same problem: Sc_2O_3 on the crystal surface. Thus, since the crystals are exposed to atmospheric pressure (taking them from the evaporator

to be sealed in quartz ampoules), usage of even a dried nitrogen or argon atmosphere with even p.p.m. water impurity could give ample time for a hydrated ScCl_3 layer to form. For this reason, the $(\text{Sc}^{+++}) \rightarrow (\text{NaCl})$ work was abandoned.

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LIST OF REFERENCES

1. A. Fick, Ann. Phys. Leipzig 170, 59 (1859)
2. W. Jost, Diffusion in Solids, Liquids, Gases (Academic Press, New York, 1960) p. 33-35
3. Appendix I, Sec. 1, this work
4. S. J. Rothman, N. L. Peterson, A. L. Laskar, and L. C. Robinson, J. Phys. Chem. Solids 33, 1061 (1972)
5. B. Tuck and M. A. H. Kadhim, J. Mat. Sci. 7, 581 (1972)
6. A. B. Lidiard, Philos. Mag. 46, 1218 (1955)
7. Appendix I, Sec. 2, this work
8. J. Crank, Mathematics of Diffusion (Oxford-Clarendon Press, London, 1956) p. 13
9. M. J. Lighthill, Fourier Analysis and Generalized Functions (Cambridge Univ. Press, Cambridge, 1958)
10. S. J. Rothman, L. W. Barr, A. H. Rowe, and P. G. Selwood, Phil. Mag. 14, 501 (1966)
11. Appendix I, Sec. 3, this work
12. Jost, op. cit.
13. P. Beckmann, Orthogonal Polynomials for Engineers and Physicists (Golem Press, Boulder, Colo., 1973) p. 107-110
14. M. J. Turunen, Phys. Stat. Sol. (a) 31, 489 (1975)
15. A. Erdelyi, Higher Transcendental Functions (McGraw-Hill, New York, 1954)
16. Beckmann, op. cit. p. 47-51
17. Beckmann, Ibid. p. 229
18. Lighthill, op. cit.
19. Appendix I, Sec. 4, this work
20. W. N. Bailey, J. London Math. Soc. 23, 291 (1948)

21. W. F. Ames, Nonlinear Ordinary Differential Equations in Transparent Processes (Academic Press, New York, 1968)
22. H.T. Davis, Introd. to Nonlinear Differential and Integral Equations (Dover Press, New York, 1962)
23. A. C. Scott, F. Y. F. Chu, D. W. McLaughlin, Proc. IEEE 61, 1443 (1973)
24. L. A. Girifalco, Atomic Migration in Solids (Blaisdell Pub. Co. (1964) p. 68 ff.
25. C. P. Flynn, Point Defects and Diffusion (Oxford-Clarendon Press, London, 1972) p. 65 ff.
26. J. Bardeen and C. Herring, in Imperfections in Nearly Perfect Solids, ed. by W. Shockley et al., (John Wiley Co., New York, 1952)
27. D. Mapother, H. N. Crooks, and R. J. Maurer, J. Chem. Phys. 18, 1231 (1950)
28. N. Laurance, Phys. Rev. 120, 57 (1960)
29. R. G. Fuller, Phys. Rev. 142, 524 (1966)
30. W. J. Fredericks, in Diffusion in Solids: Recent Developments (Academic Press, New York, 1975) p. 381-444
31. L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, Trans. Faraday Soc. 56, 697 (1960)
32. Appendix I, Sec. 5, this work
33. C. R. A. Catlow et al., Abstracts of the 1977 Defects in Insulating Crystals Conference, p. 73-74
34. J. R. Manning, Diffusion Kinetics for Atoms in Crystals (D. VanNostrand Co., New Jersey, 1968) p. 37-49
35. P. L. Meyer, Introd. Probability and Statistical Applications (Addison-Wesley Pub. Co., Reading, Mass., 1965) p. 146-169
36. L. Boltzmann, Ann. Physik Leipzig 53, 959 (1894)
37. C. Matano, Japan. J. Physics 8, 109 (1933)
38. Appendix I, Sec. 6, this work
39. J. R. Philip, Australian J. Phys. 13, 1 (1960)
40. A. D. Pelton and T. H. Etsell, Acta Metall. 20, 1269 (1972)
41. M. Ghezzi, J. Electrochem. Soc. 119, 977 (1972)
42. M. Ghezzi, J. Electrochem. Soc. 120, 1123 (1973)

43. F. Beniere, M. Beniere, and M. Chemla, J. Chem. Phys. 56, 549 (1972)
44. M. D. Feit, J. L. Mitchell, and D. Lazarus, Phys. Rev. B 8, 1715 (1973)
45. J. L. Mitchell and D. Lazarus, Phys. Rev. B 12, 734 (1975)
46. Appendix I, Sec. 7, this work
47. I. S. Gradshteyn and I. M. Ryzhik, Tables of Integrals Series and Products (Academic Press, New York, 1973) p. 837
48. H. Bateman, Tables of Integral Transforms, Vol. II (McGraw-Hill, New York, 1954) p. 291
49. W. N. Bailey, op. cit.
50. Appendix I, Sec. 8, this work
51. J. L. Mitchell, PhD Thesis, Univ. of Illinois at Urbana-Champaign (1974) (unpublished)
52. Appendix I, Sec. 9, this work
53. R. W. Dreyfus and A. S. Nowick, J. Appl. Phys. 33, 473 (1962)
54. A. R. Allnatt and P. Pantelis, Solid State Comm. 6, 309 (1968)
55. L. Slifkin and G. Brebec, C.E.A. Report R3769 (1969)
56. F. Beniere, M. Beniere, and M. Chemla, Comp. Rend. C 268, 1461 (1969)
57. Private Communication with Dr. D. Lazarus
58. Beckmann, op. cit. p. 120-124
59. Gradshteyn and Ryzhik, op. cit. p. 620
60. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (Interscience, New York, 1966) p. 577, p. 1061

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Etiam nunc perstat.