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An Analysis of Multi-component, Chemical Transport Crystal Growth

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Abstract

The chemical transport crystal growth of binary compounds in closed containers is analyzed for transport properties under conditions of multi-component, gas phase diffusion controlled kinetics. The Stefan-Maxwell transport equations for multi-component gaseous diffusion are integrated and related to phase equilibria at ends of the transport path to predict diffusion fluxes and component concentrations along the transport path. The analysis allows the prediction of interdiffusion contributions to the transport flux.

Introduction

Chemical transport reactions are well recognized for their importance in crystal growth (1, 2). These reactions are appropriate for the growth of metal chalcogenides because of the high vapor pressure of the chalcogen element and because many metal chalcogenides vaporize incongruently. Through chemical transport in which low vapor pressure component elements of the compound react with a halogen to form a volatile halide, the crystal growth temperature can be greatly reduced below that required for direct crystal growth by sublimation-condensation.

The reaction chamber commonly considered in theories of closed-system chemical transport is a tube of constant cross-section placed in a temperature gradient. The tube contains a solid source chemical S at one end and a seed crystal or auto-nucleated crystals of S at the other. The central part of the tube is initially evacuated and filled with I_o moles of a transport agent A_1 before the tube is sealed and raised to the operating temperatures. Gaseous reaction products between A_1 and S are then formed which are transported by diffusion caused by the thermal gradient.

Previous analyses of closed-tube, diffusion controlled chemical transport reactions in a thermal gradient have been presented by Schaefer et al. (3, 4) and by Mandel and Lever (5-9). Schaefer et al. (3, 4) analyzed the transport case for the simple reaction involving two vapor species

$$iS_{(s)} + jA_{1(g)} \rightleftharpoons k\,A_{2(g)} \qquad (1)$$

with the limitations of equimolal counterdiffusion and a combined diffusion coefficient. They used the simple Fick's Law

$$N_i = -D_i \frac{dc_i}{dz} \tag{2}$$

to describe the diffusion for the case of j = k. For j ≠ k the flow term introduced in the system was approximated to unity. They discussed the system involving three vapor species,

$$iS_{(s)} + jA_{1(g)} \rightleftharpoons kA_{2(g)} + \ell A_{3(g)} \tag{3}$$

but did not attempt a solution.

Mandel (5) followed a more rigorous approach improving on that of Schaefer by eliminating the need for a combined diffusion coefficient for all the species and by treating cases involving more than two vapor species. Mandel, however, still used the basic Fick's diffusion relation

$$N_i = -\frac{D_i}{RT}\frac{\partial p_i}{\partial z_i} \tag{4}$$

which does not take into account the flow term caused by an increase in the gas phase molar concentration on reaction. Multicomponent diffusion involving a flow term is best expressed by the standard Stefan-Maxwell equations (10)

$$x_i = \sum_{j=1}^{n} \frac{1}{CD_{ij}} (x_i N_j - x_j N_i) \ . \tag{5}$$

Later, Mandel and Lever (6) attempted to justify simplification of the above equation by defining an "average diffusion coefficient"

for each species which would, in its very definition, take into account the flow term. Approximations of the partial pressures of the vapor species would then reduce this "average diffusion coefficient" to the diffusion coefficient of the species in a mixture as needed in their earlier paper (5).

Mandel (5) also treats the effect of surface reaction rates on the product formation rate. Subsequently, Lever (7) treats the problem of multiple reaction equilibria for vapor transport. Here thermal diffusion is neglected and the flow is expressed very simply in terms of the diffusion coefficient and a simple parameter describing the overall gas composition without reference to individual molecular species. Mandel (9) extends this to transport of several solids by using coupling parameters that can be determined from an (N-1) dimensional equation set where N is the number of equilibria. In a later work Lever (8) also treats the problem of a single heterogeneous equilibrium and transport. None of these studies has treated the effect of multicomponent interdiffusion on chemical transport and transport flow.

In the analyses of diffusion in multicomponent gas mixtures the most fundamental gas phase transport equations are the Stefan Maxwell equations (Eqn. 5), as formulated by Curtis and Hirschfelder (10). We have used these as our basis for a more rigorous solution to the transport problem. The major improvement over previous researchers is (i) that we do not approximate the flow term and (ii) that we use simple binary diffusivities of the species involved. We do not take recourse to the "average

diffusion coefficients" of Mandel and Lever, nor do we approximate the partial pressure profiles of the gaseous species.

We consider the diffusion-limited steady-state transport in this paper. Since we have not taken into account the limitations due to surface reaction and nucleation of the product crystals, the product rate predicted will necessarily be an upper limit of the experimental rate. The approximation we use is that diffusivity and the total concentration is constant because of the slight variation of temperature along the tube.

Integration of the Stefan-Maxwell Equations

The heterogeneous reaction equilibrium which applies at the solid-gas interfaces has the general form

$$S_{(s)} + \nu_1 A_{1(g)} \rightleftharpoons \nu_2 A_{2(g)} + \nu_3 A_{3(g)} \tag{6}$$

where ν_i are rational stoichiometric coefficients of the species A_i. A_1 is the transport agent and A_2, A_3 are the intermediate products.

The equilibrium constant for the above reaction is

$$K = \frac{P_2^{\nu_2} P_3^{\nu_3}}{P_1^{\nu_1}} \tag{7}$$

where P_i are the partial pressures of species A_i. The temperature dependence of K can be deduced from free energy calculations.

During steady-state chemical transport the mass flux of the product S, N_S, is related to mass fluxes of the gas phase species by

$$N_S = -\nu_1^{-1} N_1 = \nu_2^{-1} N_2 = \nu_3^{-1} N_3 \tag{8}$$

If the mean free path between molecular collisions is small compared to the dimensions of the transport tube, the total pressure within the tube is independent of position. Thus,

$$\begin{aligned} &\sum P_i(z) = P(z) = P_t \\ \text{or} \quad &\sum x_i(z) = 1, \qquad 0 \leqslant z \leqslant L \end{aligned} \tag{9}$$

where the total pressure P_t is specified by the extent of reaction at the source temperature T_1, and x_i is the mole fraction of species A_i in the vapor phase.

Diffusion of the various gaseous species along the transport path can now be deduced from the Stefan-Maxwell equations,

$$\nabla x_i = \sum_{j=1}^{3} \frac{1}{CD_{ij}} (x_i N_j - x_j N_i), \quad i=1,2,3. \tag{10}$$

Combining Eqs. (9) and (10), we can eliminate one species, say x_3, and represent Eq. (10) in a linear form,

$$\nabla x_i = a_{i1} x_1 + a_{i2} x_2 + b_i, \quad i=1,2. \tag{11}$$

Using Eq. (8) and the fact that $D_{ij} = D_{ji}$, the coefficients in Eq. (11) are found to be as follows:

$$a_{11} = \frac{N_S}{C}\left(\frac{\nu_2}{D_{12}} + \frac{\nu_3 - \nu_1}{D_{13}}\right) \qquad a_{21} = -\frac{N_S}{C}\nu_2\left(\frac{1}{D_{12}} - \frac{1}{D_{23}}\right)$$

$$a_{12} = \frac{N_S}{C}\nu_1\left(\frac{1}{D_{12}} - \frac{1}{D_{13}}\right) \qquad a_{22} = \frac{N_S}{C}\left(\frac{-\nu_1}{D_{12}} + \frac{\nu_2+\nu_3}{D_{23}}\right)$$

$$b_1 = \frac{N_S}{C}\frac{\nu_1}{D_{13}} \qquad b_2 = -\frac{N_S}{C}\frac{\nu_2}{D_{23}}$$

Eq. (11) can be represented in matrix form as

$$\nabla x = \underline{A}\,\underline{x} + \underline{B} \tag{12}$$

where $\nabla x = \begin{bmatrix} \nabla x_1 \\ \nabla x_2 \end{bmatrix}$, $A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$, $\underline{x} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$ and $\underline{B} = \begin{bmatrix} b_1 \\ b_2 \end{bmatrix}$

The solutions to the homogeneous parts of Eq. (12) are

$$x_1 = \lambda_1 e^{m_1 z} + \lambda_2 e^{m_2 z} \tag{13}$$

$$x_2 = \lambda_3 e^{m_1 z} + \lambda_4 e^{m_2 z} \tag{14}$$

where $$m_1, m_2 = \frac{a_{11}+a_{22}}{2} \pm \frac{1}{2}\sqrt{(a_{11}+a_{22})^2 + 4(a_{21}a_{12}-a_{11}a_{22})}$$

It can be shown that λ_3 and λ_4 are related to λ_1 and λ_2 by

$$\lambda_3 = \frac{a_{21}}{m_1-a_{22}}\lambda_1 = \frac{m_1-a_{11}}{a_{12}}\lambda_1 ,$$

and $$\lambda_4 = \frac{a_{21}}{m_2-a_{22}}\lambda_2 = \frac{m_2-a_{11}}{a_{12}}\lambda_2 .$$

The general solution to the nonhomogeneous Eq. (12) is

$$\underline{x} = \underline{\lambda} e^{\underline{A}z} - \underline{A}^{-1}\underline{B} \tag{15}$$

where $\underline{\lambda}$ is a vector containing arbitrary constants.

Addition of the vector $\underline{A}^{-1}\underline{B}$ to the solutions (13) and (14) then gives the solution to Eq. (12):

$$x_1 = \lambda_1 e^{m_1 z} + \lambda_2 e^{m_2 z} + \frac{a_{22}b_1-a_{12}b_2}{a_{21}a_{12}-a_{11}a_{22}} \tag{16}$$

$$x_2 = \frac{a_{21}\lambda_1}{m_1-a_{22}} e^{m_1 z} + \frac{a_{21}\lambda_2}{m_2-a_{22}} e^{m_2 z} + \frac{a_{11}b_2-a_{21}b_1}{a_{21}a_{12}-a_{11}a_{22}} \tag{17}$$

$$x_3 = 1 - x_1 - x_2 \tag{18}$$

The roots m_1 and m_2 are generally complex and require that they be expressed in terms of trigonometric functions.

If we assume that m_i are complex with real and imaginary parts defined by

$$m_1 = s + ir$$

$$m_2 = s - ir$$

where $s = \frac{a_{11}+a_{22}}{2}$ and $r = \frac{1}{2}\sqrt{(a_{11}+a_{22})^2+4(a_{21}a_{12}-a_{11}a_{22})}$

then the concentrations of the gaseous species can be expressed as

$$x_1 = \alpha_1 + e^{sz}(c_1 \cos rz + c_2 \sin rz) \tag{19}$$

$$x_2 = \alpha_2 + e^{sz}(c_3 \cos rz + c_4 \sin rz) \tag{20}$$

$$x_3 = 1 - x_1 - x_2 \tag{21}$$

where $\alpha_1 = \frac{a_{22}b_1-a_{12}b_2}{a_{21}a_{12}-a_{11}a_{22}}$

$$\alpha_2 = \frac{a_{11}b_2-a_{21}b_1}{a_{21}a_{12}-a_{11}a_{22}}$$

$$c_1 = \lambda_1 + \lambda_2 , \quad c_2 = \lambda_1 - \lambda_2$$

$$c_3 = \left(\frac{\lambda_1}{m_1-a_{22}} + \frac{\lambda_2}{m_2-a_{22}}\right)a_{21}, \quad c_4 = \left(\frac{\lambda_1}{m_1-a_{22}} - \frac{\lambda_2}{m_2-a_{22}}\right)a_{21} .$$

Note that c_3 and c_4 are dependent on c_1 and c_2 by the relation

$$c_3 = \left(\frac{c_1 t - r c_2}{r^2+t^2}\right)a_{21} \quad \text{and} \quad c_4 = \left(\frac{c_2 t + r c_1}{r^2+t^2}\right)a_{21}$$

where $t = s - a_{22}$.

Formulation of the Chemical Transport Boundary Value Problem

To obtain a particular solution to the above general solutions for x_1, x_2 and x_3, i.e., Eq. 19-21, we must know N_S (which is implicit in the constants a_{11}, a_{12}, etc.), c_1, c_2 and C, the total concentration of all gaseous species in the ampoule. Accordingly, we need four equations to obtain these four quantities. These equations can be derived from:

i) Conversion at the source. (This gives us C, the total concentration.)

ii) Transport agent conservation in the ampoule.

iii) The equilibrium condition at the source end.

iv) The equilibrium condition at the product end.

i) Conversion at the source:

At temperature T_1 the source reaction given by Eq. 6 has the equilibrium constant,

$$K_1 = \left.\frac{P_2^{\nu_2} P_3^{\nu_3}}{P_1^{\nu_1}}\right|_{z=0} = \left.\frac{x_2^{\nu_2} x_3^{\nu_3}}{x_1^{\nu_1}}\right|_{z=0} \bullet (CRT_1)^{\Pi} \tag{22}$$

where $\Pi = \nu_2 + \nu_3 - \nu_1$.

If y is the extent of reaction at the source for the reaction of Eq. (6), and if the initial feed concentration of the transport agent is $\varepsilon = I_0/(\hat{a}L)$, where L is the tube length and $\hat{a}$ the tube cross sectional area, then the concentration of the transport species are given by

$$A_1 = (1-y)\,\varepsilon = Cx_1 \tag{23}$$

$$c_2 = \varepsilon\, y\, \frac{\nu_2}{\nu_1} = Cx_2 \tag{24}$$

$$\text{and } c_3 = \varepsilon\, y\, \frac{\nu_3}{\nu_1} = Cx_3 \tag{25}$$

Replacing the values of x_1, x_2 and x_3 in Eq. 22 by Eq. 23-25, we obtain

$$K_1 = \left(\frac{\nu_2}{\nu_1}\right)^{\nu_2} \left(\frac{\nu_3}{\nu_1}\right)^{\nu_3} \frac{y^{(\nu_2+\nu_3)}}{(1-y)^{\nu_1}} \quad (\varepsilon RT_1)^{\Pi} \tag{26}$$

Since the mole fractions of the gaseous species must sum to unity, it is necessary that

$$\frac{(1-y)\,\varepsilon}{C} + \frac{\varepsilon y}{C}\frac{\nu_2}{\nu_1} + \frac{\varepsilon y}{C}\frac{\nu_3}{\nu_1} = 1. \tag{27}$$

As a consequence, the extent of reaction is simply,

$$y = \frac{\nu_1}{\Pi}\ \frac{C}{\varepsilon} - 1. \tag{28}$$

Combining Eq. (26) and Eq. (28) we obtain

$$K_1 = \frac{\nu_2^{\nu_2}\nu_3^{\nu_3}\left(\frac{\varepsilon RT}{\Pi}\right)^{\Pi}\left(\frac{C}{\varepsilon} - 1\right)^{\nu_2+\nu_3}}{\left[\Pi - \nu_1\left(\frac{C}{\varepsilon} - 1\right)\right]^{\nu_1}} . \tag{29}$$

Knowing the equilibrium constant at the source end from free energy considerations the total concentration C in the ampoule can be obtained by inverting Eq. 29.

ii) Transport agent requirements:

The transport agent A_1 reacts with the solid S to form volatile intermediates which, after transport to the other end of the tube, react to give back the original compounds A_1 and S. The number of moles of the transport agent species must be conserved, whether as A_1 or in some fraction of A_2 and A_3. This conservation condition is then

$$\varepsilon AL = I_0 = C\hat{a} \int_0^L \left[x_1(z) + \gamma_2 x_2(z) + \gamma_3 x_3(z)\right] dz \qquad (30)$$

where $\gamma_i = \dfrac{\text{atoms of species } A_1 \text{ in } A_i}{\text{atoms of species } A_1 \text{ forming a molecule of } A_1}$

For example, in the reactive transport of ZnS with iodine as a transport agent, the reaction equation is

$$ZnS + I_2 \rightleftharpoons ZnI_2 + \tfrac{1}{2}S_2$$

and the ratio of γ_2, the atoms of species I in molecule of ZnI_2 to γ_3, the atoms of species I in molecules of I_2 is unity. Similarly, for the reactive transport of Fe_2S_3 with iodine with the reaction equation

$$Fe_2S_3 + 3I_2 \rightleftharpoons 2FeI_3 + \tfrac{3}{2}S_2,$$

the values of γ_2 and γ_3 are 3/2 and 0, respectively.

Generally, for the reaction in Eq. (6) only one of the products A_2 or A_3 contains the transport agent species, and especially when the transport agent is an element. We can write the general transport equation such that $\gamma_3 = 0$. Thus, for a typical case the conservation condition becomes,

$$\frac{I_0}{\hat{a}C} = \int_0^L (x_1 + \gamma_2 x_2)\, dz$$

In terms of the constants c_i this condition becomes

$$\frac{I_0}{\hat{a}C} = L(\alpha_1 + \gamma_2\alpha_2) + \frac{(c_1 + \gamma_2 c_3)}{r^2 + s^2}\left[s(e^{sL}\cos rL - 1) + re^{sL}\sin rL\right]$$

$$+ \frac{c_2 + \gamma_2 c_4}{r^2 + s^2}\left[se^{sL}\sin rL - r(e^{sL}\cos rL - 1)\right]$$

where c_3 and c_4 can be expressed in terms of c_1 and c_2. (31)

iii) Equilibrium at the source end:

Equilibrium at the source end requires the reaction Eq. 6 with

$$K_1 = \left.\frac{x_2^{\nu_2} x_3^{\nu_3}}{x_1^{\nu_1}}\right|_{z=0} (CRT_1)^{\Pi}.$$

This equation reduces to

$$K_1 = \frac{\left[\alpha_2 + \frac{a_{21}(tc_1 - rc_2)}{r^2 + t^2}\right]^{\nu_2}\left[1 - \alpha_1 - \alpha_2 - c_1 - \frac{a_2}{r^2 + t^2}(tc_1 - rc_2)\right]^{\nu_3}}{\alpha_1 + c_1^{\nu_1}} (CRT_1)^{\Pi} \tag{32}$$

iv) Equilibrium at the product end:

Similarly, equilibrium at the product end of the reaction vessel requires

$$K_2 = \left.\frac{x_2^{\nu_2} x_3^{\nu_3}}{x_1^{\nu_1}}\right|_{z=L} (CRT_2)^{\Pi}$$

In terms of the constants c_i, this equation becomes

$$K_2 = \left[\alpha_2 + \frac{a_{21}}{r^2 + t^2} e^{sL} \quad (c_1 t - c_2 r) \cos rL + (c_1 r + c_2 t) \sin rL\right]^{\nu_2}$$

$$\times \left[1 - \alpha_1 - \alpha_2 - e^{sL} \left\{\left[c_1 + \frac{a_{21}}{r^2 + t^2} (c_1 t - c_2 r)\right] \cos rL\right.\right.$$

$$\left.\left. + \left[c_2 + \frac{a_2}{r^2 + t^2} (c_1 r + c_2 t)\right] \sin rL\right\}\right]^{\nu_3}$$

$$\times \left[\frac{(CRT_2)^{\Pi}}{(\alpha_1 + e^{sL} (c_1 \cos rL + c_2 \sin rL)^{\nu_1}}\right] \tag{33}$$

Once C is calculated from Eq. 29, the system of three non-linear algebraic simultaneous equations Eqs. 31-33 can be solved for c_1, c_2 and N_S.

Results

The chemical transport of a number of binary metal chalcogenides with halogen transport agents was studied by numerical simulation under a variety of transport conditions. The total molar concentration and extent of reaction were calculated from Eqs. 28 and 29 for a fixed source temperature and feed concentration of the transport agent. The species concentrations and product flux along the transport path were than calculated by solving Eqs. 31-33 simultaneously for the variables c_1 , c_2 and N_S for a fixed temperature gradient and species interdiffusivities. The method of computation used was to first set the initial approximate variable values within their respective ranges, and then to seek a minimum error for the equation set by unconstrained minimization using the Newton Raphson method with internally approximated gradients.

The computed results of the simulated transport problems were examined for dependence of the product flux on the halogen feed concentration, the interdiffusion coefficients and the imposed temperature gradient. In general the following results were found:

i) For a given temperature gradient and a fixed crystal growth temperature the product flux increased with the concentration of transport agent feed. The rate of increase decreases with increasing feed concentration, and reaches a maximum when the mole fraction of the transport agent predominates over other species mole fractions within the ampoule.

ii) The product flux increases essentially linearly with increasing temperature gradient imposed along the transport path, for

a fixed path length and halogen feed concentration. The linear rate of increase tends to decrease slightly for $\Delta T > 100°K$.

iii) The interdiffusion coefficient influences the transported product flux most significantly in the region of the transport path where $K \simeq 1$. The variation in product flux is within 25% of that when interdiffusion effects are absent.

iv) The concentration profiles along the transport path were found to be nearly linear in all transport simulations. The non-linearity depends to a large extent on unequal interdiffusion coefficients, as well as on other factors. As a general rule, the non-linearity increases with both iodine feed and temperature gradient.

The effect of interdiffusion coefficient variation was explored for a hypothetical metal dichalocogenide with scalable physical properties transported with iodine as a transport agent along a temperature difference of 25°C. The interdiffusion coefficients were varied for each of three values of the equilibrium constants at the product end, K_2 . The interdiffusion coefficients enter into the constants a_{ij} and b_i which in turn fix the values of the transport parameters r , s , c_1 and c_2 . It was found, however, that c_1 is approximately equal to 2, whereas c_2 has a value near -1 for metal dichalocogenide transport. The normalized molar product flux was found to vary as much as 25% for fixed values of equilibrium constants at the ends of the transport path.

Table 1. Dependence of normalized product flux on transport parameters r and s.

K_2	$r \times 10^4$	$s \times 10^4$	N_S*
8.92	1.1	2.6	0.178
8.92	2.0	4.8	0.164
8.92	3.5	8.4	0.141
1.66	5.0	12.7	6.91
1.66	9.5	23.8	6.17
1.66	16.5	41.9	5.55
0.185	9.7	24.6	4.65
0.185	19.5	49.3	4.57
0.185	38.4	97.1	4.34

*normalized product flux, [moles $cm^{-2} hr^{-1} (25°K)^{-1} atm^{-1} \times 10^5$]

Discussion

The results of the numerical simulation studies are consistent with expectations based on simpler predictions of the product flux dependence on transport conditions where transport flow and interdiffusion effects are omitted. For the transport problem which includes interdiffusion and flow, result (i) above is consistent with the effect of increasing halogen mole fraction on allowable concentrations of other species. The near linear dependence of product flux on temperature gradient is also expected, since the interdiffusivities are assumed independent of temperature in the present model.

The significant result of the present study is that of (iii) above, which is that interdiffusion and transport flow effects can influence the predicted product flux for the chemical transport process. The major effect is expected in the region where $K \approx 1$ because the vapor phase is truly multicomponent in this range. When K differs significantly from unity one or two of the species dominate in the vapor phase, and chemical transport is then limited by diffusion of other species through this simpler vapor.

The superiority of our model over the analysis of previous researchers is derived from the exactness of the concentration profile and the consequent improvement in the product rate. The approximations of the flow terms, diffusion coefficients and concentration profiles in the previous analyses are avoided. The product flux is an implicit variable in the problem which is solvable by numerical techniques. A computer program has been compiled for the transport of binary chalcogenides by halogens,

$$MX + Ha_2 \rightleftharpoons M\,Ha_2 + \frac{1}{2}X_2 \qquad (34)$$

where M is the divalent metal, Ha the halogen and X the chalcogen. For Eq. 34, $\nu_1 = 1$, $\nu_2 = 1$, $\nu_3 = \frac{1}{2}$, $\gamma_2 = 1$ and $\gamma_3 = 0$. The results for ZnS and MnS transport by I_2 will be tabulated and discussed in a later paper.

Our model still assumes no variation of diffusivities D_{ij} and total concentration C with a variation in temperature. However, assuming a linear temperature variation along the ampoule, we can link the variations of C and D_{ij} to z and examine the errors thus caused.

A linear variation of temperature with distance, coupled with the boundary conditions gives us

$$T = \frac{(T_2 - T_1)}{L} z + T_1 \qquad (35)$$

$$\text{and} \quad \frac{dT}{dz} = \frac{T_2 - T_1}{L} = \frac{\Delta T}{L} = k_1 \qquad (36)$$

Assuming an ideal gas variation at constant pressure,

$$CT = \frac{P}{R} = k_2 \tag{37}$$

$$\text{and} \quad T\frac{dC}{dz} + C\frac{dT}{dz} = 0. \tag{38}$$

Combining Eqs. 36 and 38, we obtain

$$\ell n\ C = -\ \ell n(k_1 z + T_1) + \ell n\ k_3 \tag{39}$$

$$\text{or} \quad C = \frac{k_3}{k_1 z + T_1}. \tag{40}$$

At the source end, for $z = 0$ and $T = T_1$, if the total concentration is C_1 as found by Eq. 29, then

$$c_1 = \frac{k_3}{T_1} \tag{41}$$

$$C = \frac{c_1}{1 + \frac{z}{L}\frac{\Delta T}{T_1}}. \tag{42}$$

If $\frac{z}{L} = \xi$ and $\frac{\Delta T}{T_1} = \delta$, then

$$C = \frac{c_1}{1 + \xi\delta}. \tag{43}$$

If $\xi\delta$ is small, then $C = c_1$ which is our assumption in the text, is always 1. Hence, if δ is small, the error is small. However, we can use Eq. 43 to further require the model. We have used Eqs. 29, 30, 32 and 33 to generate the solution to the transport problem. In Eq. 29 and 32 we can directly use c_1 as found above. In Eq. 33 we can use c_2 instead of C, where

$$c_2 = \frac{c_1}{1 + \delta} .$$

Only Eq. 30 will have to be transformed to

$$\frac{I_0}{a} = \int_0^L (Cx_1 + \gamma_2 Cx_2 + \gamma_3 Cx_3)\, dz , \tag{44}$$

The individual terms under the integral sign can be integrated separately and will involve integrations of the form

$$\beta_1 = \int_0^L \frac{e^{sz} \cos rz}{(1 + z \frac{\delta}{L})} dz \quad \text{and} \quad \beta_2 = \int_0^L \frac{e^{sz} \sin rz}{(1 + \frac{z}{L} \delta)} dz ,$$

These can be found from any integration tables. However, since $C \propto \frac{1}{T}$ and $D_{ij} \propto T^{1.8}$ it is not possible to offset the variation of C with T. If we combine both the quantities, then $(CD_{ij}) \propto T^{0.8} \propto z^{0.8}$. Since incorporation of variation of D_{ij} with z will complicate the problem, it is better to eliminate the variation of C with T in the main problem.

The simulation of the chemical transport of metal chalcogen compounds including interdiffusion effects has several incentives. In addition to comparing the suitability of different halogens and other compounds as transport agents, the solution method proposed allows a prediction of the product compound formation rate for diffusion controlled transport under different conditions of temperature, initial transport agent concentration and choice of transport agent. The method outlined above allows a prediction of the concentration profiles for various species along the transport path,

can provide the total pressure in the transport tube, and can provide data for predicting the optimum conditions for crystal growth.

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