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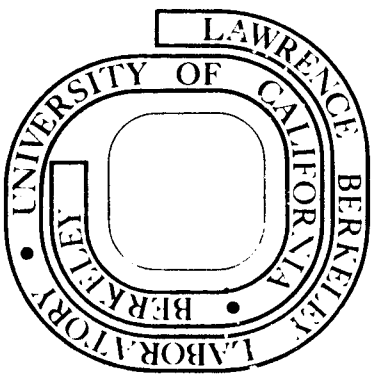

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Chemical Transport Analysis of ZnS Crystal Growth

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Abstract

Crystal growth of ZnS by the closed tube chemical transport method was explored by numerical simulation with iodine as a transport agent. An analysis of diffusion controlled kinetics based on integration of the Stefan-Maxwell equations for multi-component diffusion is utilized to calculate the transport flux as a function of transport agent concentration and temperature gradient along the transport path. The product flux increases approximately linearly with temperature gradient along the transport path for fixed initial iodine concentration, but tends to a saturation value as the initial iodine concentration is increased for a fixed temperature gradient.

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Introduction

Zinc sulfide is of considerable importance as an electronic material because of its phosphorescence and photoconduction properties. Strain free single crystals and thin films exhibiting bulk properties are needed for physical property studies and electro-optical device applications. The chemical transport crystal growth method is well suited for crystal growth of this compound, but conditions must be established for successful application of this method. In this paper the chemical transport of ZnS with iodine is simulated for transport properties under diffusion-controlled kinetics.

Although ZnS can be grown in single crystal form by the sublimation-condensation method of Piper and Polich[1]) which has proven so commercially successful for the growth of CdS , the vapor pressure of ZnS lies significantly below that of CdS , and much higher temperatures are required, > 1300°C . In the presence of a transport agent such as iodine, however, the equilibrium constant for the reaction with ZnS is increased, and the transport reaction can be carried out at significantly lower temperatures.

That ZnS crystals can be successfully grown by chemical transport reactions has been known for some time, and crystal growth with a number of transport agents have been studied. Deville successfully transported ZnS with H_2 in 1861[2]). Lorenz found transport successful with NH_4Cl [3]). Recent transport studies have been conducted with iodine[4-7]), HCl [8-10]) , Cl_2 [10]) as transport agents. These studies which are summarized in Table I show that both the zink blende and wurtzite structures as well as

Table I

Experimental Conditions for Crystal Growth of ZnS by Chemical Transport

Transport Agent	T source(°C)	T growth(°C)	Crystal Form	Maximum Dimensions (mm)	Reference
I	1000	750	Z*, polyhedra	8×8×10	4,5
I	1300	1150	Z, hexagonal	3×3×8	4,5
I	1050	770	Z, polyhedra	3×3×3	6
I	1050	900	Z, prisms	2-7	7
HCl	1050	940	Z, disordered	2×2×6	8
HCl	1000	760-970	Z, plates	1×10×10	9
HCl	1100	1020	P†, needles	1×1×15	9
HCl,Cl_2	1200	1060	W‡, prisms	5×5×10	10

*Z = Zink blende
‡W = Wurtzite
†P = Polytype

polytypes can be produced by different transport reactions, whereas the zink blende structure is the equilibrium phase at high temperature.

The transport rate of grown crystals is seldom reported in experimental studies of chemical transport. Schaefer et al.[11]) developed an approximate theory relating the transport rate to crystal growth parameters which uses an approximate diffusion coefficient[5]), and neglects the transport flow produced by transport reactions which change the number of moles in the vapor phase. Mandel[12]) and Lever[13]) have studied multi-component transport reactions, but also employ a simplified diffusion expression[12]). Recently the present authors introduced a new approach to diffusion-controlled multi-component chemical transport in which the Stefan-Maxwell equations for multi-component diffusion are solved simultaneously assuming equilibrium gas-solid reactions at the ends of the transport path[14]). This approach is applied here to explore the simulation of ZnS transport. Iodine was chosen as a transport agent because this halogen offers nucleation control during crystal growth; for the related problem of chemical transport of ZnSe , only iodine has been found to control nucleation and allow the growth of large single crystals[15]).

Diffusion-Controlled Transport of II-VI Compounds

Single crystals of the divalent chalcogenides can be grown in the vapor phase by chemical transport with various transport agents halogens. With free halogens as transport agents, the temperatures of transport are considerably reduced below those required for sublimation. If I_2

is added, the gaseous metal is bound in the iodide form, and the equilibrium is consequently shifted in favor of the gaseous participant in the reaction. The general reaction can be represented by

$$MX_{(s)} + I_{2(g)} = MI_{2(g)} + 0.5\ X_{2(g)}$$

Here we designate the gas phase species I_2, MI_2 and X_2 by the subscripts 1, 2 and 3 respectively, and x_i the mole fraction of species i in the vapor phase.

The multicomponent Stefan-Maxwell diffusion equations are[16])

$$\nabla x_i = \sum_{j=1}^{3} \frac{1}{c\hat{D}_{ij}} (x_i N_j - x_j N_i) \qquad i = 1\ ,\ 2\ ,\ 3\ . \qquad (1)$$

where

$$\sum_{i-1}^{3} x_i(z) = 1\ .$$

and where N_i is the molar flux of the species i with respect to fixed coordinates, c is the total molar concentration, and $\hat{D}_{ij}$ is the binary diffusion coefficient for the species pair i, j, and z is the distance along the ampoule. Because of the above constraint, only two of the set of equations (1) for the species MI_2, S_2 and I_2 are independent. These have been shown[14]) to reduce to the form in terms of the product flux J

$$\nabla x_1 = a_1 x_1 + b_1 x_2 + d_1$$

$$\nabla x_2 = a_2 x_1 + b_2 x_2 + d_2$$

where

$$a_1 = \frac{J}{c}\left(\frac{1}{\hat{D}_{12}} - \frac{1}{2\hat{D}_{13}}\right) \qquad a_2 = \frac{J}{c}\left(\frac{1}{\hat{D}_{23}} - \frac{1}{\hat{D}_{21}}\right)$$

$$b_1 = \frac{J}{c}\left(\frac{1}{\hat{D}_{12}} - \frac{1}{\hat{D}_{13}}\right) \qquad b_2 = \frac{J}{c}\left(\frac{3}{2\hat{D}_{23}} - \frac{1}{\hat{D}_{21}}\right)$$

$$d_1 = \frac{J}{c\hat{D}_{13}} \qquad d_2 = -\frac{J}{c\hat{D}_{23}} .$$

The integrated solutions for these equations are

$$x_1 = \frac{b_2 d_1 - b_1 d_2}{a_2 b_1 - a_1 b_2} + \lambda_1 e^{m_1 z} + \lambda_2 e^{m_2 z}$$

$$x_2 = \frac{a_1 d_2 - a_2 d_1}{a_2 b_1 - a_1 b_2} + \frac{a_2 \lambda_1}{m_1 - b_2} e^{m_1 z} + \frac{a_2 \lambda_2}{m_2 - b_2} e^{m_2 z}$$

$$x_3 = 1 - x_1 - x_2$$

where

$$m_1 , m_2 = \frac{(a_1 + b_2)}{2} \pm \frac{1}{2}\sqrt{(a_1 + b_2)^2 - 4(a_1 b_2 - a_2 b_1)} .$$

Generally, it has been found that the discriminent is negative and so the roots are imaginary. Then we can represent the solutions as

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

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

$$x_3 = 1 - x_1 - x_2$$

where r and s are given by

$$r = (m_1 - m_2)/2 \qquad s = (m_1 + m_2)/2$$

$$c_1 = \lambda_1 + \lambda_2 \qquad c_2 = (\lambda_1 - \lambda_2)$$

$$c_3 = a_2\left[\frac{\lambda_1}{m_1 - b_2} + \frac{\lambda_2}{m_2 - b_2}\right] \qquad c_4 = a_2\left[\frac{\lambda_1}{m_1 - b_2} - \frac{\lambda_2}{m_2 - b_2}\right]$$

$$\alpha_1 = \frac{b_2 d_1 - b_1 d_2}{a_2 b_1 - a_1 b_2} \quad \text{and} \quad \alpha_2 = \frac{a_1 d_2 - a_2 d_1}{a_2 b_1 - a_1 b_2}\,.$$

To obtain a particular solution to the above general solutions for x_1, x_2 and x_3 we must know the values of the quantities λ_1, λ_2 and J which is implicit in the constants a_1, b_1 ... etc. These three unknowns require three equations which are

i) the heterogeneous equilibrium at the source end,

$$K_1 = K_{z=0} = \left.\frac{x_2 x_3^{1/2}}{x_1}\right|_{z=0} (cRT_1)^{1/2} \qquad (2)$$

ii) the heterogeneous equilibrium at the product end

$$K_2 = K_{z=L} = \left.\frac{x_2 x_3^{1/2}}{x_1}\right|_{z=L} (cRT_2)^{1/2} \qquad (3)$$

iii) and the overall iodine balance in the closed tube: If ε is the concentration of I_2 initially fed to the system (moles/cm^3) and if A is the uniform cross section area of the tube, then

$$A\varepsilon L = Ac \int_0^L (x_1 + x_2)dz \ . \qquad (4)$$

We also need to know the total concentration of all gaseous species in the tube, c. This is obtained from the relation derived from the transport equation[14],

$$K_1 = \frac{\left(\frac{c}{\varepsilon} - 1\right)^{3/2}}{3 - \frac{2c}{\varepsilon}} (4RT_1\varepsilon)^{1/2} \ . \qquad (5)$$

Once c is calculated from Eq. 5, the system of three non-linear algebraic simultaneous equations, Eqs. 2, 3 and 4 can be solved for the unknowns λ_1, λ_2 and J.

Thermodynamic Calculations

For the transport reaction between ZnS and I_2,

$$ZnS_{(s)} + I_{2(g)} = ZnI_{2(g)} + \frac{1}{2} S_{2(g)}$$

the free energy change for the reaction at the temperature of interest is

$$\Delta G^{\circ}_{T,rxn} = \Delta G^{\circ}_{f,ZnI_{2(g)}} - \Delta G^{\circ}_{f,ZnS_{(s)}}$$

since $\Delta G^{\circ}_{f,I_{2(g)}} = \Delta G^{\circ}_{f,S_{2(g)}} = 0$.

We are interested in finding the free energy of reaction at high temperatures. Thus, heat capacities, the heats of fusion and heats of vaporization, must be added to the values for ΔG°_{f} at 298°K. For most metal halides, however, the heat capacities are not well known at higher temperatures, and it is therefore useful to approximate the free energy as those at 298°K. The change in ΔH_{298} and ΔS_{298} is such that the errors tend to balance out. A detailed discussion of the errors involved in this approximation is presented by Brewer[17]).

For ZnI_2 we have found the heats and entropies of formation for the gaseous state from

$$\Delta G^{\circ}_{f(g)} = \Delta G^{\circ}_{f(s)} + \Delta G^{\circ}_{(melting)} + \Delta G^{\circ}_{vap} .$$

where, to obtain the free energy of vaporization, we have utilized Kelley's method[20]),

$$\Delta G_{vap} = \Delta H_{o} - \Delta C_{p} T \ln T + IT$$

and

$$\Delta H_{vap} = \Delta H_{o} + \Delta C_{p} T .$$

Here ΔH_o is

$$\Delta H_o = T_b(\Delta S_v - \Delta C_p)$$

$$I = \Delta C_p \ln T_1 + (\Delta C_p - \Delta S_v)$$

and ΔS_v is the entropy of vaporization at the boiling point, T_b. This equation given above is valid for the entire liquid range, but must be modified for the solids. Since ΔC_p data was not available for $ZnI_{2(s)}$ and $ZnI_{2(s)}$, the value $\Delta C_p = -10$ was used, as suggested by Kelley[18]).

Following this procedure, then, we find for $ZnS_{(s)}$,

$$\Delta H^\circ_{298} = -60.7 \text{ kcal/mole}$$

$$\Delta S^\circ_{298} = -23.4 \text{ cal/mole } ^\circ K$$

and

$$\Delta G^\circ_{T,ZnS_{(s)}} - 60.7 + 0.0234\ T\ .$$

For ZnI_2 at 1000°K

$$\Delta G - \Delta H_{298} = 28.1\ T\ , \text{ at } 1000^\circ K$$

$$\Delta H_{298} = -64.7 \text{ kcal/mole}$$

and

$$\Delta G_{ZnI_2(\ell)} = 0.0281\ T - 64.7\ .$$

For the vaporization of $ZnI_{2(\ell)}$ with $T_b = 1000°K$,

$$\Delta S_v = 23 \ , \ \Delta H_o = 33000 \ ,$$

and

$$I = \Delta C_p \ \ell n \ T - 0.1021 \ T = -102.076$$

$$\Delta G_{vap} = 33 + .010 \ T \ \ell n \ T - 0.1021 \ T \ .$$

Finally, the expression for the free energy of reaction becomes

$$\Delta G_{T,rxn} = \Delta G_{ZnI_2(g)} - \Delta G_{ZnS(s)}$$

$$\Delta G_{T,rxn} = -0.0974 \ T + 0.01 \ T \ \ell n \ T + 29.0 \ \text{kcal/mole} \ . \qquad (6)$$

Determination of Vapor-Phase Diffusivity

For ordinary diffusion in low-density, multi-component vapors where Lennard Jones potential function parameters are unknown, the binary diffusion coefficients can be determined by the relation develcped by Slattery and Bird[19],

$$\hat{D}_{AB} = a\left(\frac{T}{\sqrt{T_{c_A} T_{c_B}}}\right)^b P^{-1}\left(P_{c_A} P_{c_B}\right)^{1/3}\left(T_{c_A} T_{c_B}\right)^{5/12}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}$$

where P_{c_i} and T_{c_i} are the critical pressure and temperature of species i , and M_i the molecular weight of species i . The constants are found to be $a = 2.745 \times 10^{-4}$ and $b = 1.823$ for nonpolar

gas pairs, and the accuracy is about 8%. The critical temperature and pressure of ZnI_2 were calculated to be 1549°K and 37.5 atm, respectively by the method of Meissner and Redding[20]. We have used this relation to estimate the binary diffusivities.

Results

The chemical transport of ZnS with iodine was simulated numerically by solving Eqs. 2-5 for the transport variables c, λ_1, λ_2, and J. The total concentration of gaseous species, c, was first calculated from Eq. 5, and then Eqs. 2-4 were solved simultaneously for λ_1, λ_2 and J by an unconstrained minimization technique utilizing the Newton Raphson iterative method with internally approximated gradients. These equations were solved on a CDC 6600 computer at the Lawrence Berkeley Laboratory.

The results of computational simulation of crystal growth at different temperatures indicate the general results that the transport flux, and therefore the crystal growth rate, increases monatonically with both the temperature difference from source to deposition zones, ΔT, and with the concentration of iodine feed, the initial iodine concentration, placed in the ampoule. The computed results of the chemical transport crystal growth simulation corresponding to growth at 1100°K are summarized in Table II for source-to-growth temperature differences of 25, 50 and 100°K, and for iodine feed concentrations from 0.1 to 20×10^{-6} moles/cm^3.

The variation of the transported ZnS product flux on ΔT for fixed iodine feed concentrations is shown in Fig. 1. The rate dependence

Table II. ZnS transport by Iodine. Product rates of fromation for various transport conditions.

Source Temp, T_1 (°K)	Product Temp, T_2 (°K)	Iodine Feed (moles/cc)$\times 10^6$	Pressure in ampoule (atm.)	Conversion in reaction at source	Total concn. in ampoule (moles/cc)$\times 10^6$	Product Rate (Gm/sq.cm/hr)$\times 10^3$
1125	1100	.100	.0135	.9676	.1484	.2384
		.200	.0270	.9550	.2955	.3255
$K_{1125} = 1.994$	$K_{1100} = 1.662$	.500	.0669	.9315	.7329	.4813
		1.000	.1327	.9070	1.453	.6337
		2.000	.2624	.8753	2.875	.8150
		5.000	.6437	.8209	7.052	1.087
		10.000	1.264	.7699	13.85	1.297
		20.000	2.475	.7111	27.11	1.488
1150	1100	.100	.0137	.9722	.1486	.4351
		.200	.0273	.9613	.2961	.5956
$K_{1150} = 2.369$	$K_{1100} = 1.662$	.500	.0679	.9408	.7352	.8848
		1.000	.1347	.9192	1.469	1.170
		2.000	.2668	.8909	2.891	1.514
		5.000	.6556	.8417	7.104	2.037
		10.000	1.289	.7946	13.97	2.452
		20.000	2.528	.7393	27.39	2.838

Table II (Continued)

Source Temp, T_1 (°K)	Product Temp, T_2 (°K)	Iodine Feed (moles/cc)$\times 10^6$	Pressure in ampoule (atm.)	Conversion in reaction at source	Total concn. in ampoule (moles/cc)$\times 10^6$	Product Rate (Gm/sq.cm/hr)$\times 10^3$
1200	1100	.100	.0140	.9791	.1490	.7367
		.200	.0280	.9708	.2971	1.012
		.500	.0696	.9549	.7387	1.514
$K_{1200} = 3.248$	$K_{1100} = 1.662$	1.000	.1385	.9379	1.469	2.017
		2.000	.2748	.9154	2.915	2.633
		5.000	.6775	.8750	7.187	3.597
		10.000	1.336	.8351	14.18	4.387
		20.000	2.627	.7868	27,87	5.155

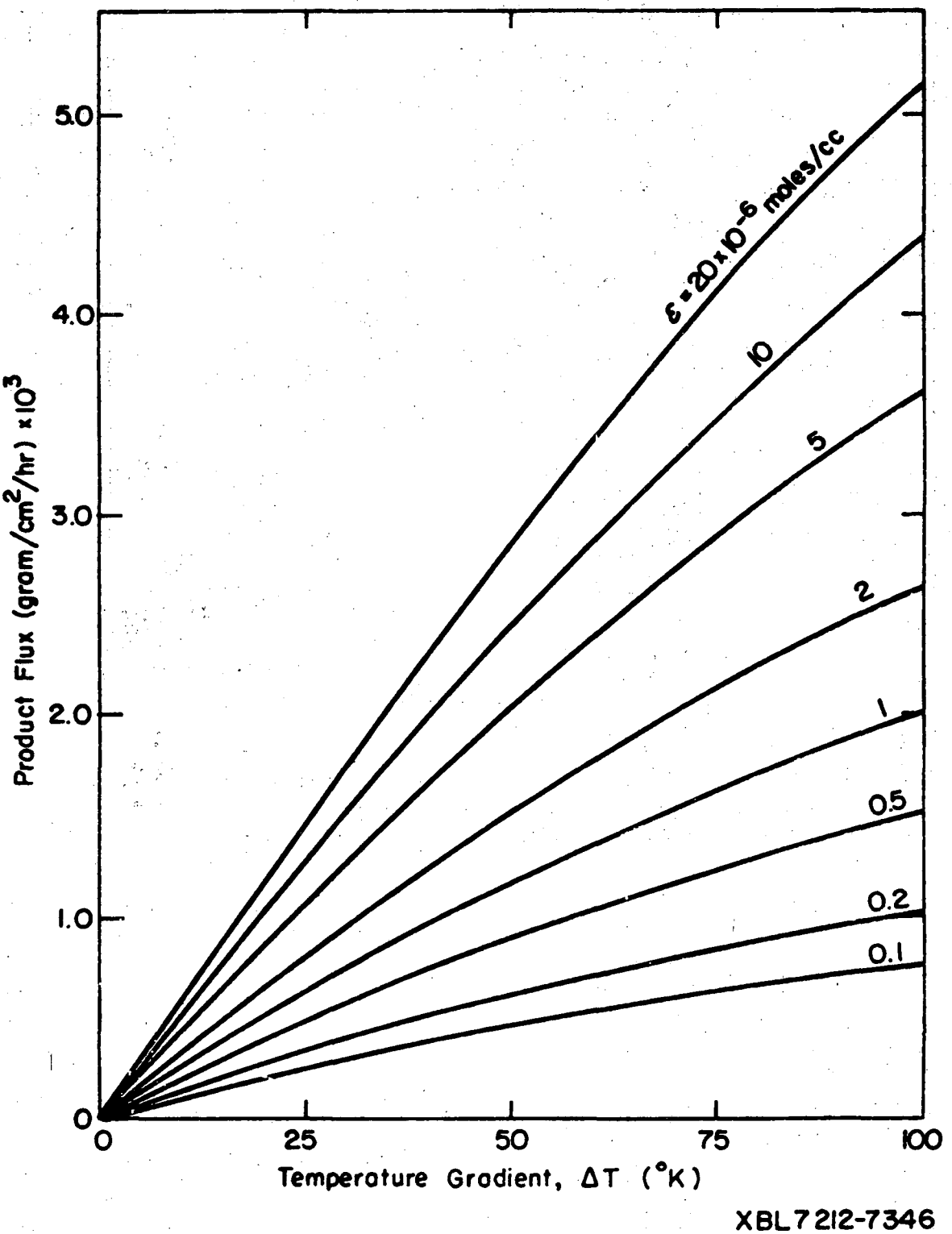

Fig. 1. Product flux of chemically transported ZnS as a function of the temperature difference along the transport path for fixed iodine feed concentrations, and a growth temperature of 1100°K.

is nearly linear with the temperature difference ΔT with a slope decreasing gradually with increasing ΔT.

The transported product flux dependence on iodine feed concentration at fixed ΔT is shown in Fig. 2. The product flux increases monatonically with feed concentration, but with a rate of increase which tends to decrease rapidly to small values for iodine feed exceeding 5×10^{-6} moles/cm^3.

Discussion

The results of the chemical transport study indicates that the high temperature diffusion-controlled transport of ZnS with I_2 is rate controlled by the counter diffusion of I_2 through a vapor phase containing principally ZnI_2 and S_2. The data summarized in Table II indicates that the extent of conversion of I_2 to ZnI_2 at the ZnS source temperature is large. As the iodine feed concentration increases from small values the extent of conversion initially falls rapidly until the build-up of sulfur pressure impedes the forward transport reaction. When the transport agent concentration is large ($> 10^{-5}$ moles/cm^3), the vapor phase concentration of I_2 is on the same order of magnitude as ZnI_2 and S_2, and the effects of multi-component interdiffusion and transport flow which are accounted for in the present model become important.

Changes in the growth temperature were shown to produce similar results in the simulation study. The major limitation on transport of ZnS with I_2 is the boiling point of ZnI_2, ~ 1000°K, which

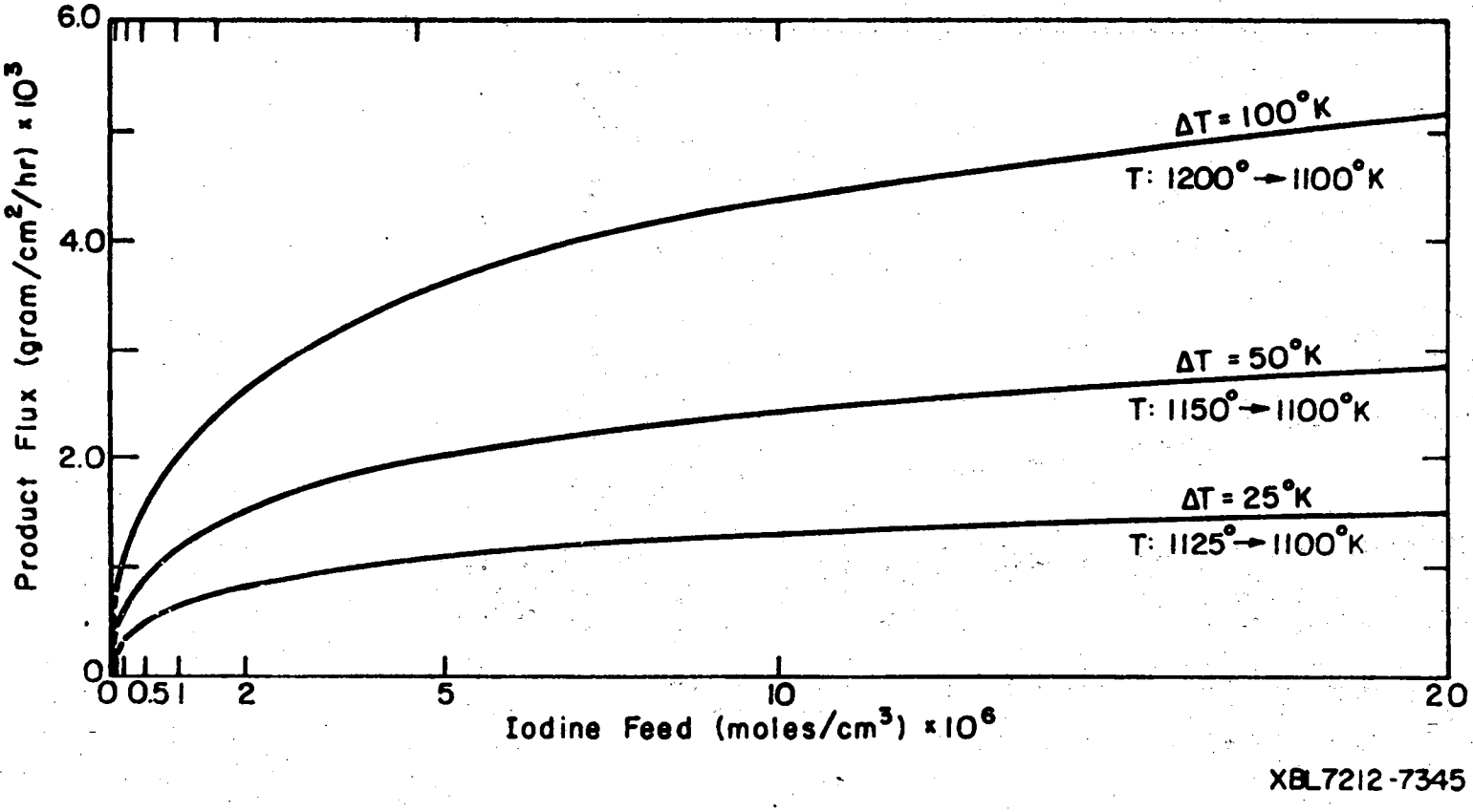

Fig. 2. Product flux of chemically transported ZnS as a function of the iodine feed concentration for fixed temperature differences, ΔT, along the transport path.

must be exceeded to prevent condensation of $ZnI_{2(\ell)}$ on the growing crystals and consequent interference with the transport growth mechanism. For transport temperatures above 1000°K the free energy of reaction, Eq. 6 , does not change sign with increasing temperature, and consequently the equilibrium constant for the transport reaction, K , is always greater than unity.

The parameters required for the calculation of concentration profiles along the transport path are summarized in Table III for crystal growth at 1100°K. The concentrations of the various gaseous species as a function of position along the ampoule involve exponential and trigonometric function dependence. For binary metal chalcogenides these functions are

$$x(I_2) = -2 + (c_1 \cos rz + c_2 \sin rz) \exp (sz)$$

$$x(MI_2) = 2 + (c_3 \cos rz + c_4 \sin rz) \exp (sz)$$

$$x(S_2) = I - x(I_2) - x(MI_2)$$

where x is the mole fraction z the distance along the ampoule. The nonlinearity of the concentration profiles is indicated by varying magnitudes of r and s . The values in these quantities over the range of conditions studied correspond to nearly linear concentration gradients. As a general rule, the nonlinearity increases with both iodine feed and temperature gradient. The effect of ZnS transport by a sublimation-condensation transport mechanism is not taken into account in the present analysis. This parallel reaction

Table III. ZnS transport by Iodine. Parameters for concentration profiles along the closed ampoule.

Source Temp, T_1 (°K)	Product Temp, T_2 (°K)	Iodine Feed (moles/cc)$\times 10^6$	r	s	c_1	c_2	c_3	c_4
1125	1100	.100	.00009	.00023	2.0219	-.8651	-1.3482	-.1563
$K_{1125} = 1.994$	$K_{1100} = 1.662$	.200	.00013	.00032	2.0304	-.8692	-1.3541	-.1568
		.500	.00019	.00047	2.0467	-.8768	-1.3651	-.1577
		1.000	.00025	.00062	2.0640	-.8849	-1.3769	-.1587
		2.000	.00032	.00080	2.0868	-.8954	-1.3923	-.1600
		5.000	.00042	.00106	2.1270	-.9139	-1.4195	-.1624
		10.000	.00050	.00127	2.1662	-.9316	-1.4459	-.1649
		20.000	.00058	.00146	2.2131	-.9527	-1.4775	-.1680
1150	1100	.100	.00017	.00042	2.0187	-.8646	-1.3464	-.1556
$K_{1150} = 2.369$	$K_{1100} = 1.662$	.200	.00023	.00058	2.0261	-.8684	-1.3515	-.1558
		.500	.00034	.00086	2.0402	-.8757	-1.3613	-.1563
		1.000	.00045	.00114	2.0554	-.8834	-1.3718	-.1568
		2.000	.00058	.00147	2.0755	-.8935	-1.3856	-.1575
		5.000	.00079	.00198	2.1114	-.9112	-1.4103	-.1591
		10.000	.00095	.00238	2.1470	-.9283	-1.4346	-.1608
		20.000	.00109	.00276	2.1903	-.9488	-1.4641	-.1632

Table III (Continued)

Source Temp, T_1 (°K)	Product Temp, T_2 (°K)	Iodine Feed (moles/cc)$\times 10^6$	r	s	c_1	c_2	c_3	c_4
1200	1100	.100	.00028	.00070	2.0141	-.8638	-1.3436	-.1546
$K_{1200} = 3.248$	$K_{1100} = 1.662$	.200	.00038	.00097	2.0197	-.8673	-1.3477	-.1545
		.500	.00057	.00144	2.0305	-.8740	-1.3556	-.1542
		1.000	.00076	.00192	2.0422	-.8811	-1.3641	-.1540
		2.000	.00100	.00251	2.0580	-.8904	-1.3754	-.1538
		5.000	.00136	.00343	2.0870	-.9068	-1.3959	-.1539
		10.000	.00166	.00419	2.1163	-.9227	-1.4165	-.1544
		20.000	.00195	.00492	2.1530	-.9418	-1.4420	-.1554

becomes important at low ionine concentrations. The effect of thermal convection in addition to sublimation transport and chemical transport could also contribute to enhancement of the transport rate over that calculated in this study.

The limitations on the accuracy of our results stem principally from errors in the thermodynamic data, and from errors in estimating diffusivity. Both of these are inevitable because of the exploratory applications to which chemical transport is applied. In addition, there is a great probability of multiple reactions. Sulfur is assumed present only in the form of S_2. This is true to a large extent because at high temperatures the polymers S_4, S_6, S_8 break down into S_2 and the equilibrium heavily favors S_2. Also, the dissociation of iodine, $I_2 = 2I$, was neglected at this temperature. We have lumped the monatomic iodine with the diatomic molecule in this study, as the concentration of I does not exceed a few % of the I_2 concentration at typical transport temperatures.

The present analysis of chemical transport 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. In particular, the method properly accounts for interdiffusion effects and transport flow, and allows a prediction of the concentration profiles for various species along the transport path. This method has potential in general for predicting the optimum conditions for crystal growth.

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