Irreversible and Reversible Reaction Fronts in Quasichemical Theory of Multicomponent Diffusion

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- ☑ **Introduction**
- ❑ Model
- ❑ Results
- ❑ Cu Diffusion in PbS
- ❑ Summary

Introduction

The concept of a reaction front is used in

- physics
- chemistry
- materials science
- biology
- geology

Introduction

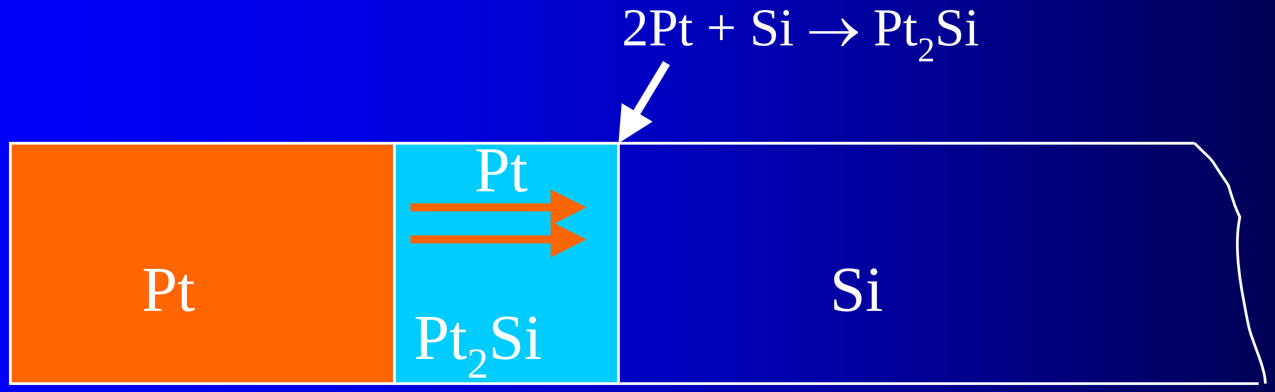
Examples of systems with <u>initially separated components</u>:

- Diffusion flames (Y. B. Zeldovich, 1949)
- Internal oxidation of metals (C. Wagner, 1959)
- Gas absorption with chemical reactions in liquids (P. V. Danckwerts, 1970, G. Astarita, 1967)
- New phase formation in solids (G. V. Kidson, 1961, U. Gösele and K. N. Tu,1984)
- Multicomponent diffusion in semiconductors (V. I. Fistul and M. I. Sinder, 1984)

Examples

Example 1.

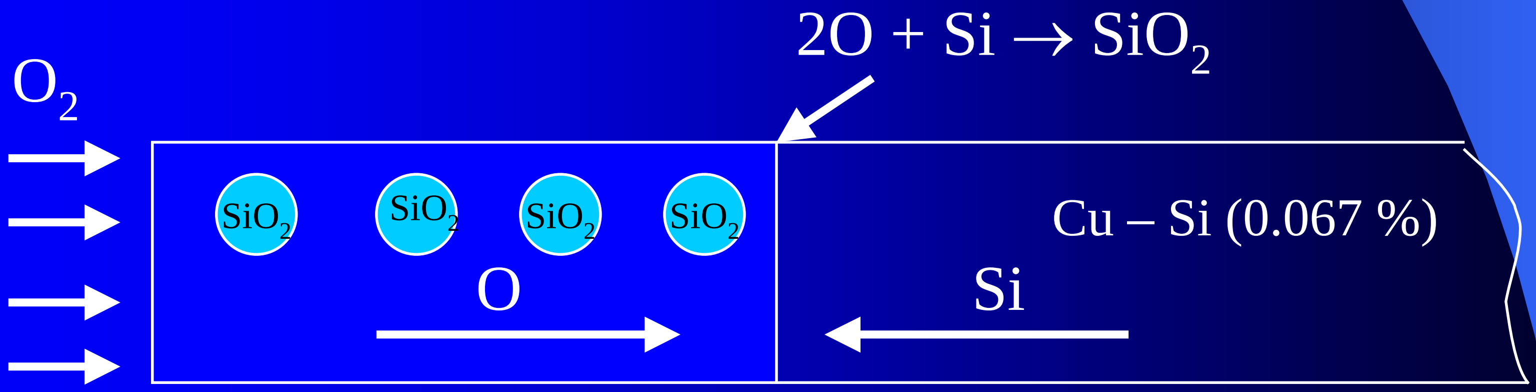
Silicide formation in thin-film by metal-silicon reaction: Pt_2Si formation in the system Pt film/Si(111), T =323 ^oC, t = 25 min.



Examples

Example 2.

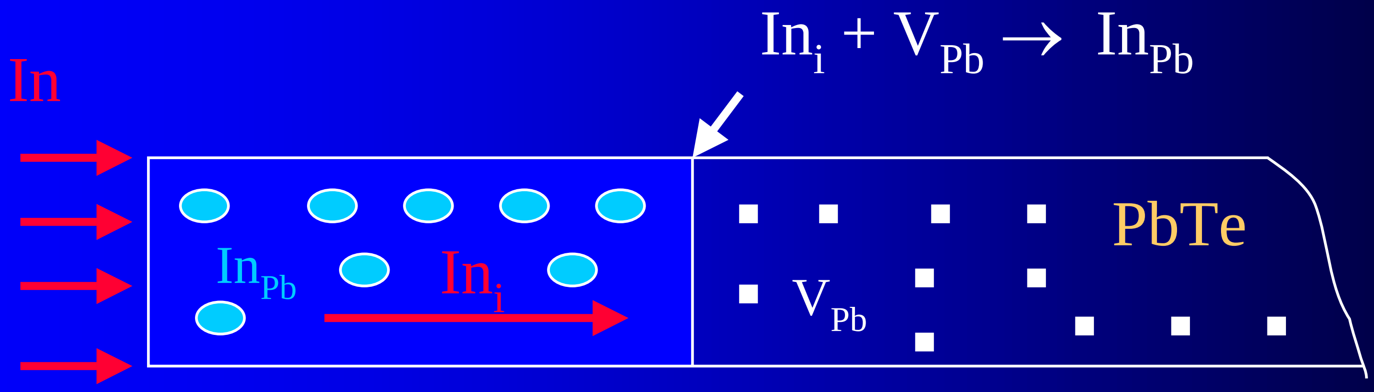
Internal oxidation of alloys: oxidation of the alloy Cu – Si (0.067 %) at 725 ^{o}C, t = 100 h.



Examples

Example 3.

Multi-components diffusion in semiconductors: In diffusion in PbTe with high concentration of vacancies of lead, V_{Pb} at 700°C, t = 10 h.



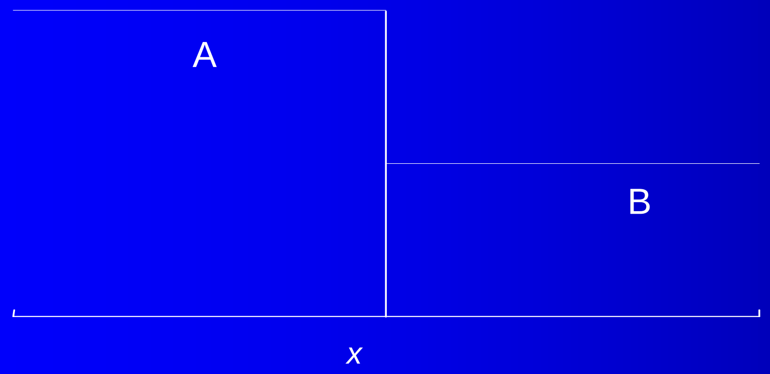
Introduction

Recently some new aspects of the reaction front concept have been revealed on the basis of a **simple model** .

(M. Sinder and J. Pelleg, 1999, 2000,

Z. Koza, 2002)

Introduction (Cont.)



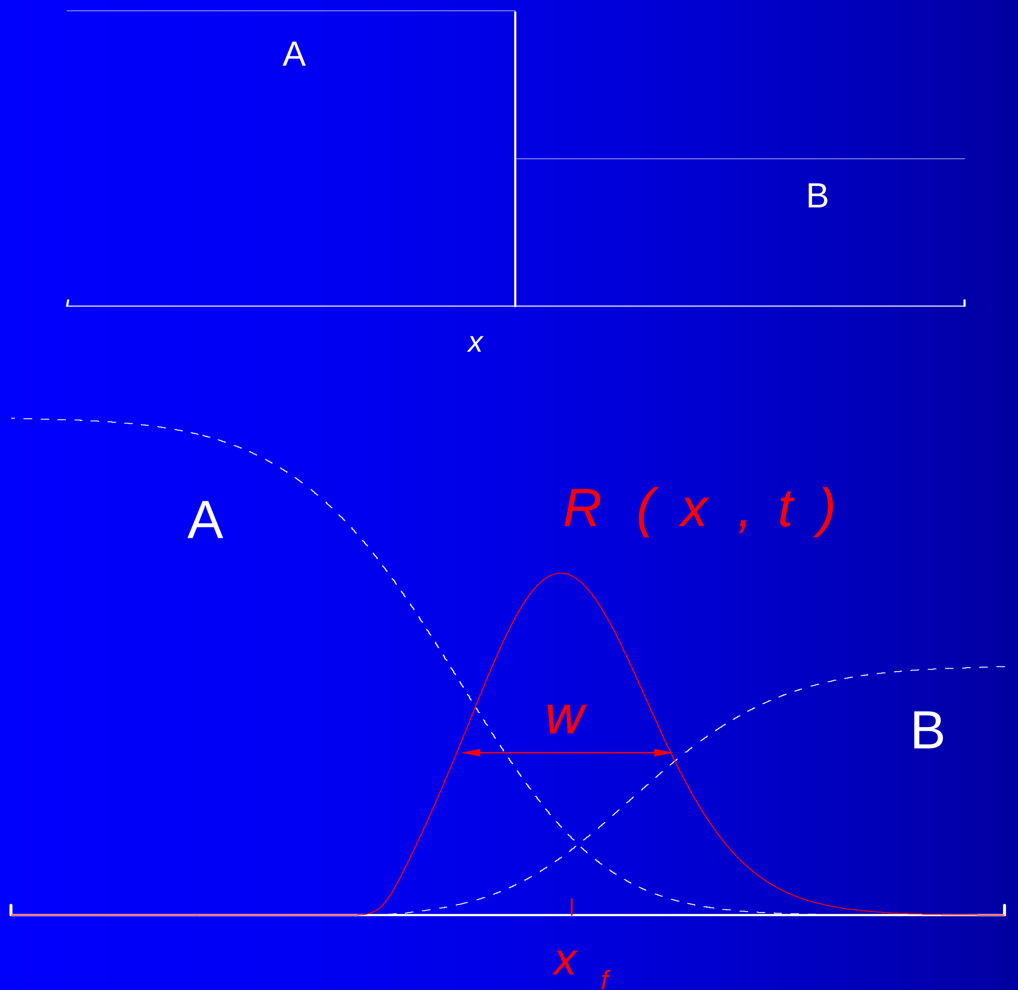
Two geometries, where the **initial separation of the componentts** can be realized.

Introduction (Cont.)

- Two components, A and B are uniformly distributed on opposite sides of an impenetrable barrier, which is removed at time $t = 0$.

  The two components start to mix and react by a single reversible reaction $A + B \leftrightarrow C$.
- The diffusion coefficients of components are constant, i.e., independent of the spatial location and component concentrations.
- A penetrates into B and vice versa. The dynamics of the system is described as a temporal evolution of the reaction front.

Characteristic properties of the reaction front



- $x_f(t)$ - center of the reaction front,
- $w(t)$ - width of the reaction front,
- $R(x_f, t)$ - reaction rate at x_f,
- $R(t) = \int R(x, t)dx$ - global reaction rate.

Introduction (Cont.)

- The main achievement was the suggestion of a way to calculate the reaction rate for the reversible reaction case .
- By this way it was shown:

  i) the reaction rate $R(x, t)$ of A + B $\leftrightarrow$ C may be either $R > 0$ or $R < 0$;

  ii) a limit of the solution when $K \rightarrow 0$ is identical to the long time solution $t \rightarrow \infty$ of the irreversible A + B $\rightarrow$ C reaction (K is the reversible reaction constant). This is valid only if $R \geq 0$.

Introduction (Cont.)

- Idea:

  The study of the long-time behavior of the irreversible reactions system

  considering an appropriate limit for the solution of the reversible reactions system.

Objective

Work is devoted to the study of a system with the two reversible reactions $A + B \leftrightarrow C$ and $C + B \leftrightarrow S$.

Our analysis is applied for diffusion in the Cu/PbS system.

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Model

The two components A and B start to mix and react by A + B ↔ C and C + B ↔ S reactions.

The equations of the model are regular equations of “ diffusion + reaction “ in quasistaionary approximation.

Equations of the model

$$ab = K_1 c \qquad bc = K_2 s$$

$$\frac{\partial (a + c + s)}{\partial t} = D_A \frac{\partial^2 a}{\partial x^2} + D_C \frac{\partial^2 c}{\partial x^2} + D_S \frac{\partial^2 s}{\partial x^2}$$

$$\frac{\partial (b + c + 2s)}{\partial t} = D_B \frac{\partial^2 a}{\partial x^2} + D_C \frac{\partial^2 c}{\partial x^2} + 2D_S \frac{\partial^2 s}{\partial x^2}$$

Model (Cont.)

Parameters of the model:

- the diffusion constants D_A, D_B, $D_{C,}$, $D_{S,}$ of A, B, C, S;
- the initial concentrations, a_0 and b_0 , of A and B;
- the reversible reaction constants K_1 and K_2.

Model (Cont.)

- The essentially new element are the expressions for the rates R_1 and R_2 of the reactions:

A + B $\leftrightarrow$ C and

C + B $\leftrightarrow$ S

$$R_1 = D_A \frac{\partial^2 a}{\partial x^2} - \frac{\partial a}{\partial t}$$

$$R_2 = -D_S \frac{\partial^2 s}{\partial x^2} + \frac{\partial s}{\partial t}$$

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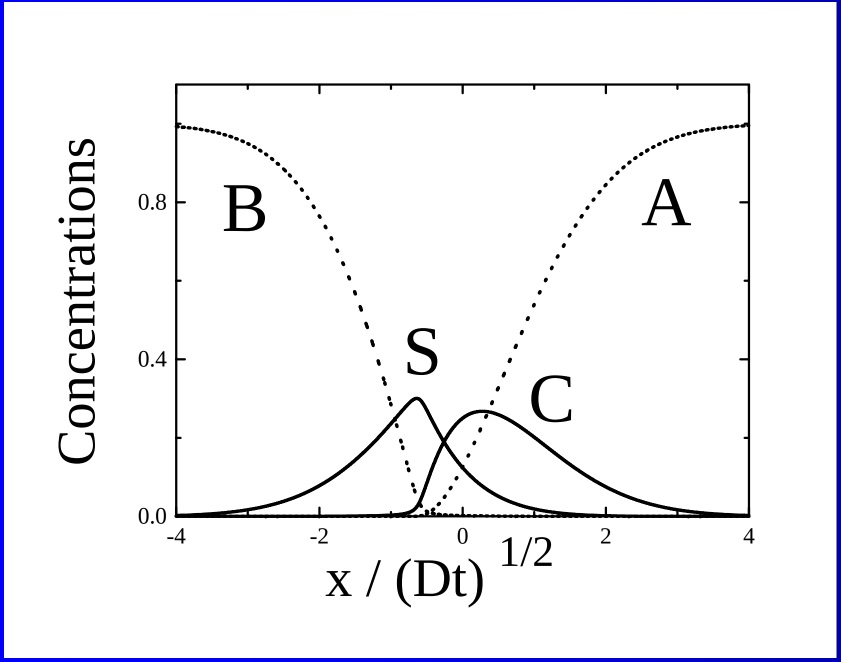
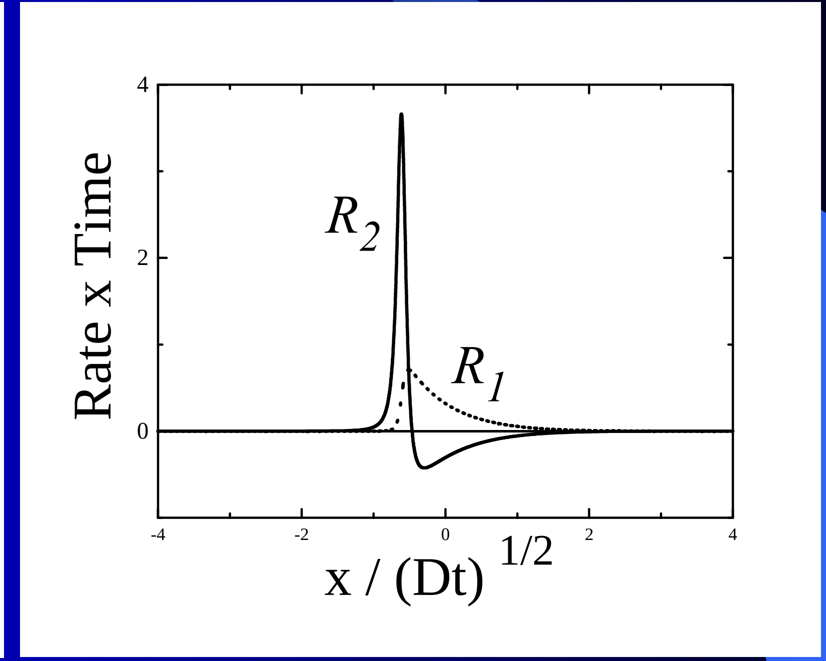
Results

- For the same diffusion constants the solution is reduced to a cubic equation. Through routine formulas, profiles of the components and the reaction rates are calculated and investigated for arbitrary values of K_1 and K_2 and initial concentrations a_0 and b_0.

Results

The solution when $K_1/K_2 = 1/4$ and the values of K_1, K_2 are small is shown below:





Results

Special limiting cases are obtained by assuming values K_1 and K_2 either tending to zero or to infinity:

- i) $K_1 \to \infty$ and $K_2 \to \infty$: independent interdiffusion of A and B;
- ii) $K_1 \to 0$ and $K_2 \to \infty$: A + B → C reaction front;
- iii) $K_1 \to \infty$, $K_2 \to 0$ and $K_1 K_2 \to 0$: A + 2B → S reaction front;
- iv) $K_1 \to \infty$, $K_2 \to 0$ and $K_1 K_2 \to \infty$: independent interdiffusion of A and B;
- v) $K_1 \to 0$, $K_2 \to 0$ and $K_1 / K_2 \to 0$: two consequent reaction fronts B + C → S and S + A → 2C;
- vi) $K_1 \to 0$, $K_2 \to 0$ and $K_1 / K_2 \to \infty$: A + 2B → S reaction front.

Results

Patterns for special cases when one or two reactions are irreversible. The requirement of non-negativity of the "irreversible" reaction rate is examined:

- a) A + B → C and C + B ↔ S ($K_1 = 0$, $K_2 > 0$);
  If K_2 is large ($K_2 >> K_{2c}$): irreversible A + B → C reaction front;
  If K_2 is small ($K_2 << K_{2c}$): two consecutive fronts of the reversible B + C ↔ S and the irreversible S + A → 2C reactions exist.
  K_{2c} is constant, which can be evaluated from the solution.
- b) A + B ↔ C and C + B → S ($K_1 > 0$, $K_2 = 0$):
  an irreversible A + 2B → S reaction front pattern.
- c) A + B → C and C + B → S ($K_1 = 0$, $K_2 = 0$):
  irreversible A + 2B → S reaction front pattern. The result is confirmed by direct numerical calculations (S. M. Cox and M.D. Finn, 2001).

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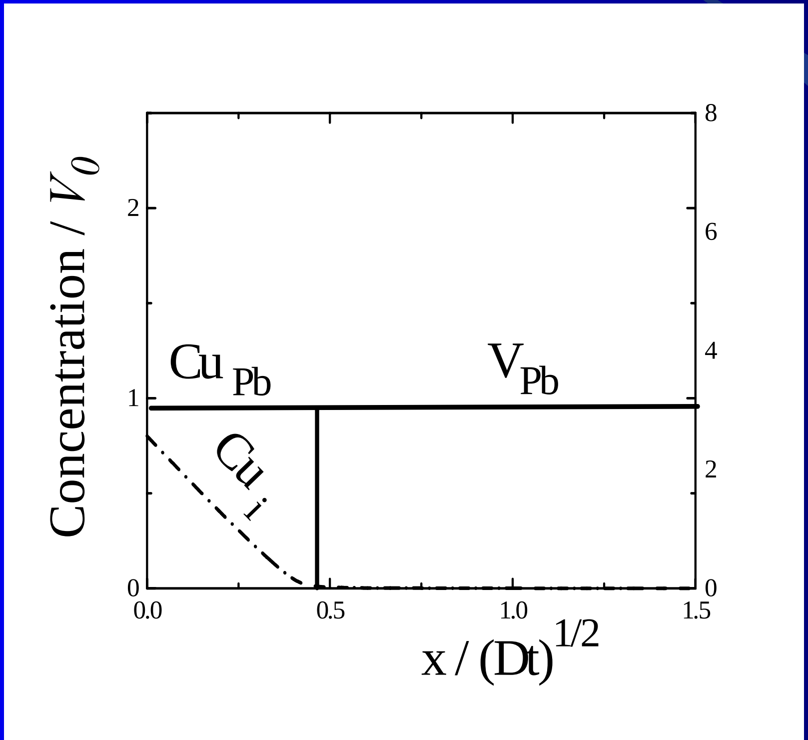
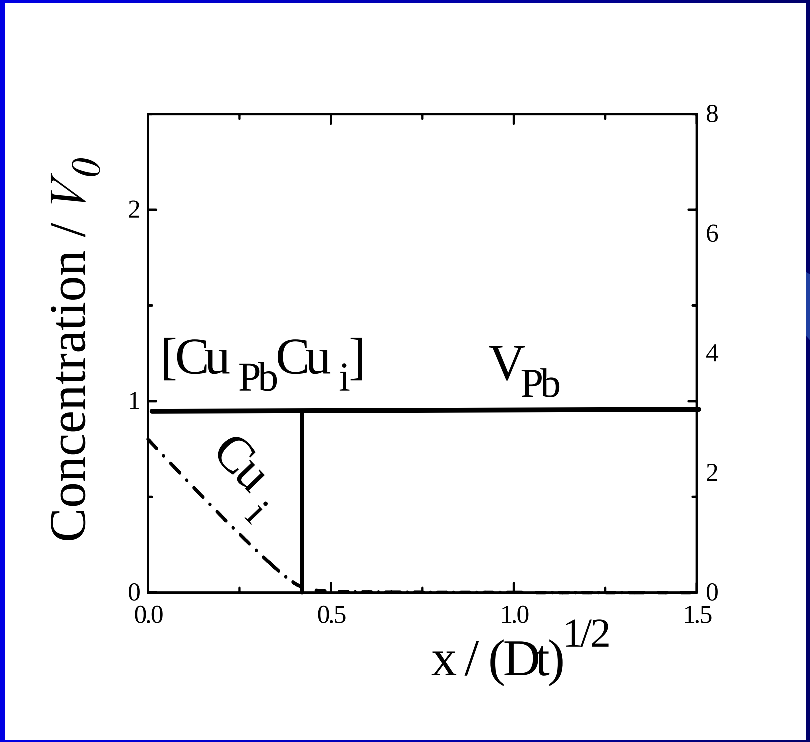
Cu Diffusion in PbS

- Model of interstitial Cu diffusion in PbS (J. Bloem and F.A. Kröger, 1957)
- Cu atoms may occupy
  interstitial sites, Cu_i ,
  Pb sub-lattice sites, Cu_{Pb}
  or be associated in pairs, $[Cu_{Pb}\ Cu_i]$.
- Two limits of pairs association: weak or strong association.
- At low temperatures only Cu_i is mobile.
- If an interstitial Cu_i meets a V_{Pb} vacancy it immediately occupies the vacancy site.

Cu Diffusion in PbS



Weak pair association profiles



Strong pair association profiles.

Cu Diffusion in PbS

- How do the pictures change if the mobility of the other components, V_{Pb}, Cu_{Pb} and [Cu_{Pb} Cu_i] are taken into account?
- This is important for diffusion at high temperatures.

Cu Diffusion in PbS

- The model of Cu diffusion in PbS corresponds to the schema of two quasi-chemical reactions

$$Cu_i + V_{Pb} \rightarrow Cu_{Pb}$$
$$Cu_{Pb} + Cu_i \leftrightarrow [Cu_{Pb}\,Cu_i]$$

- This is equivalent to the analyzed system of the reactions if

$A \equiv V_{Pb}$ $B \equiv Cu_i$ $C \equiv Cu_{Pb}$ $S \equiv [Cu_{Pb}Cu_i]$.

Cu Diffusion in PbS

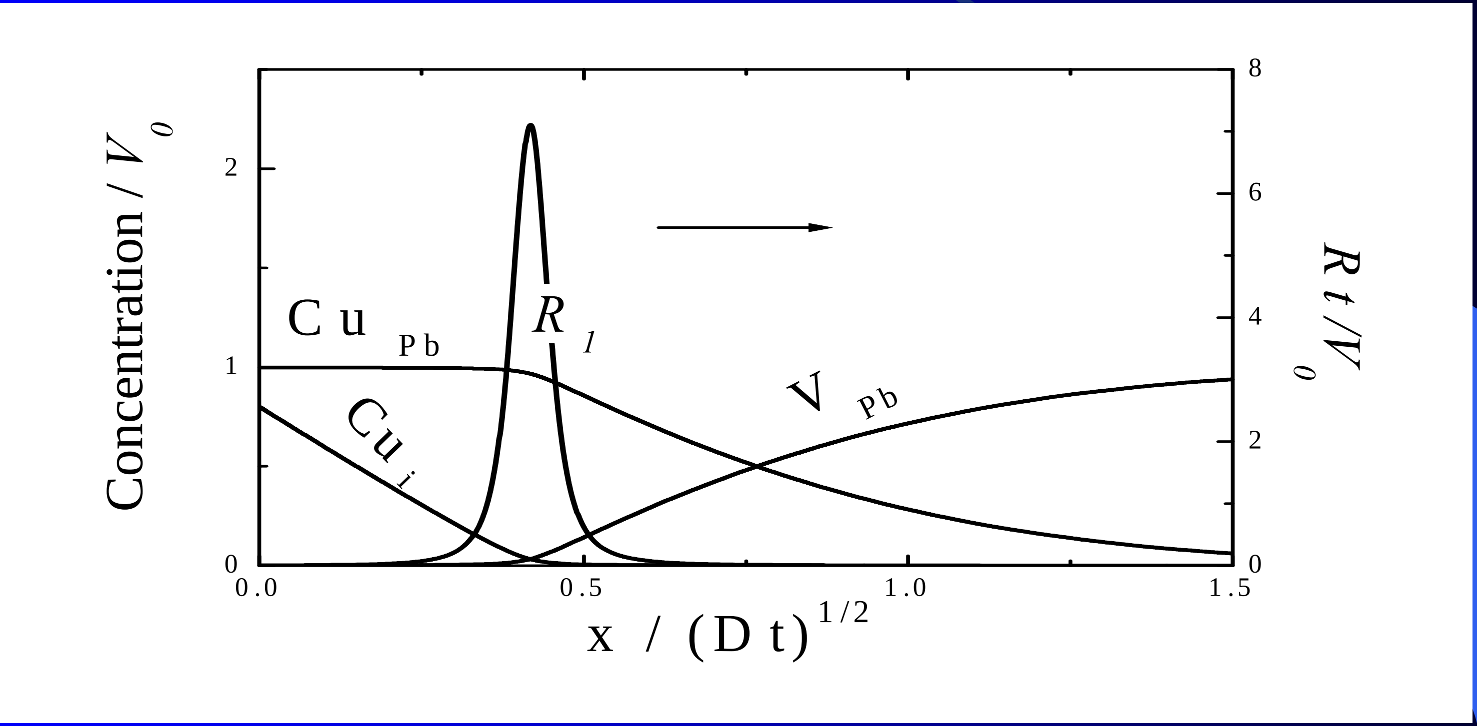
From the results we have two possible cases:

- a) Pairs association is weak (K_2 is large):
  One irreversible $Cu_i + V_{Pb} \rightarrow Cu_{Pb}$ reaction front exist.

- b) Pairs association is strong (K_2 is small):
  Two reaction fronts are present:
  the reversible $Cu_{Pb} + Cu_i \leftrightarrow [Cu_{Pb}\ Cu_i]$
  and the irreversible $[Cu_{Pb}\ Cu_i] + V_{Pb} \rightarrow 2\ Cu_{Pb}$.

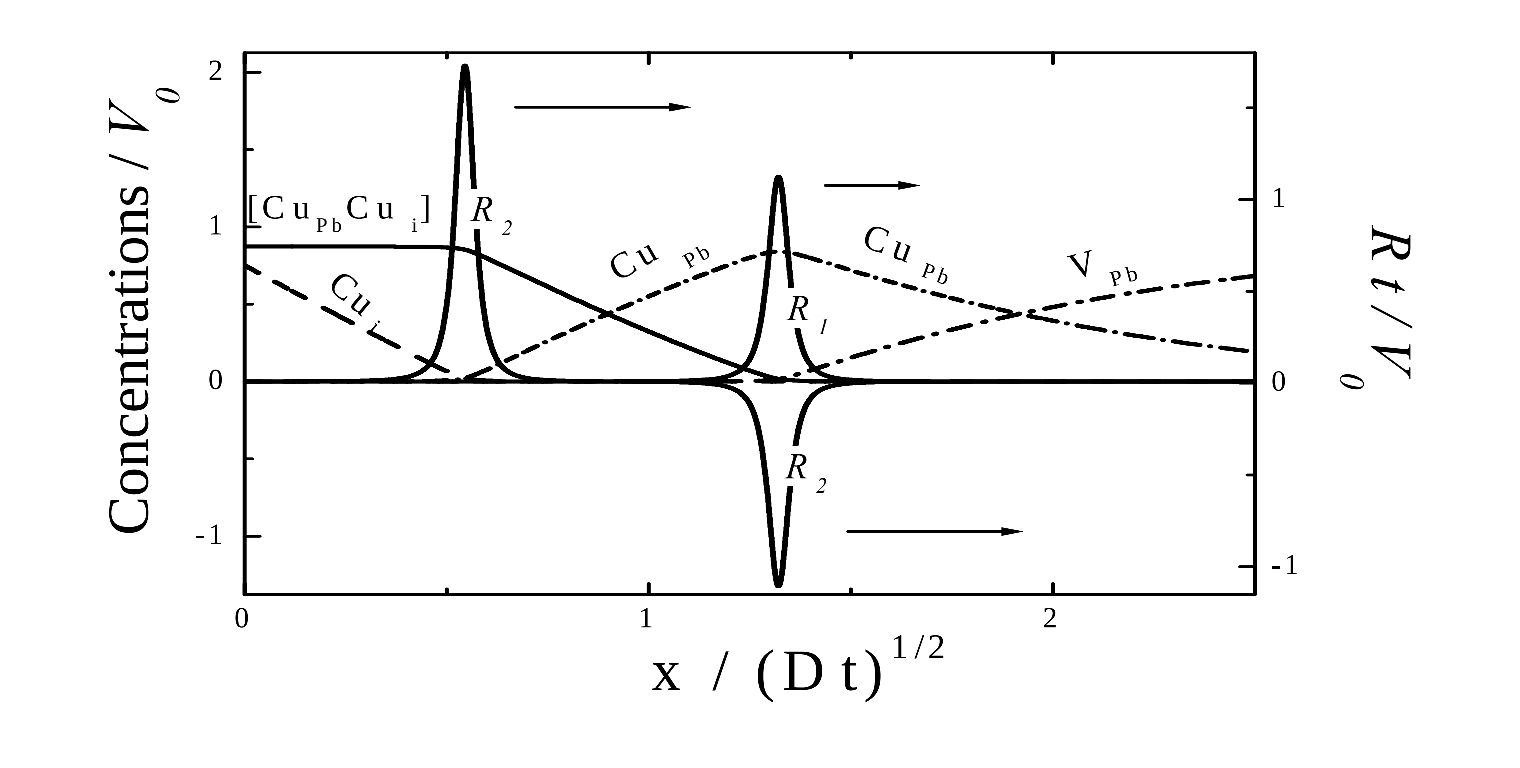
It is assumed that the flow of vacancies (free and bond) equal zero at the external boundary of the specimen.

Cu Diffusion in PbS



Weak pair association profiles

Cu Diffusion in PbS



Strong pair association profiles.

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Summary

- The system with initially separated components and two reversible reactions A + B $\leftrightarrow$ C and C + B $\leftrightarrow$ S is studied.
- The long-time behavior of the irreversible or the partly irreversible reactions system is predicted.
- The model is used to the description of Cu diffusion in PbS.

Where to Get More Information

- M. Sinder and J. Pelleg, Phys. Rev. E, **60**, R6259 (1999)
- M. Sinder and J. Pelleg, Phys. Rev. E, **61**, 4935 (2000)
- Z. Koza, Phys. Rev. E **66**, 011103 (2002)

Thank You!

Questions?