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WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
27 February - 17 March 1989

"Flow Models:
- Diffusion
- Advection
- Convection"

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MASS TRANSPORT MECHANISM VIA THE VAPOUR PHASE

Example: Molecular Sublimation in a closed ampoule

$AB_{solid} \rightleftharpoons AB_{vap}$.

$T_{source} > T_{crystal}$

T_s	T_{cr}
↑	↑
Evaporation	Condensation (Crystal Growth)
$AB_{sol.} \rightarrow AB_{vap.}$	$AB_{vap} \rightarrow AB_{sol.}$

1) Only the ideally pure material present.

NO IMPURITIES IN THE VAPOUR

Gas flow only due to Stefan's flow (ADVECTION)

Change of volume due to Evaporation and Crystallization (expansion at the source; contraction at the crystal surface → pumping action)

volume flow (Poiseuille)

[illegible]

2) Impurities present in the vapour phase.

Up to now almost always the case (Residual Gases; Desorption from glass surfaces; Desorption during ampoule sealing)

Advection + diffusion

↓

Vapour + Impurity molecules move as a whole, from source to crystal. IMPURITIES ARE REJECTED FROM THE CRYSTAL. They slowly diffuse back to the source through the vapour phase. This impedes strongly the mass transport of the vapour molecules

RESULT: PARTIAL PRESSURE GRADIENTS NEAR THE CRYSTAL

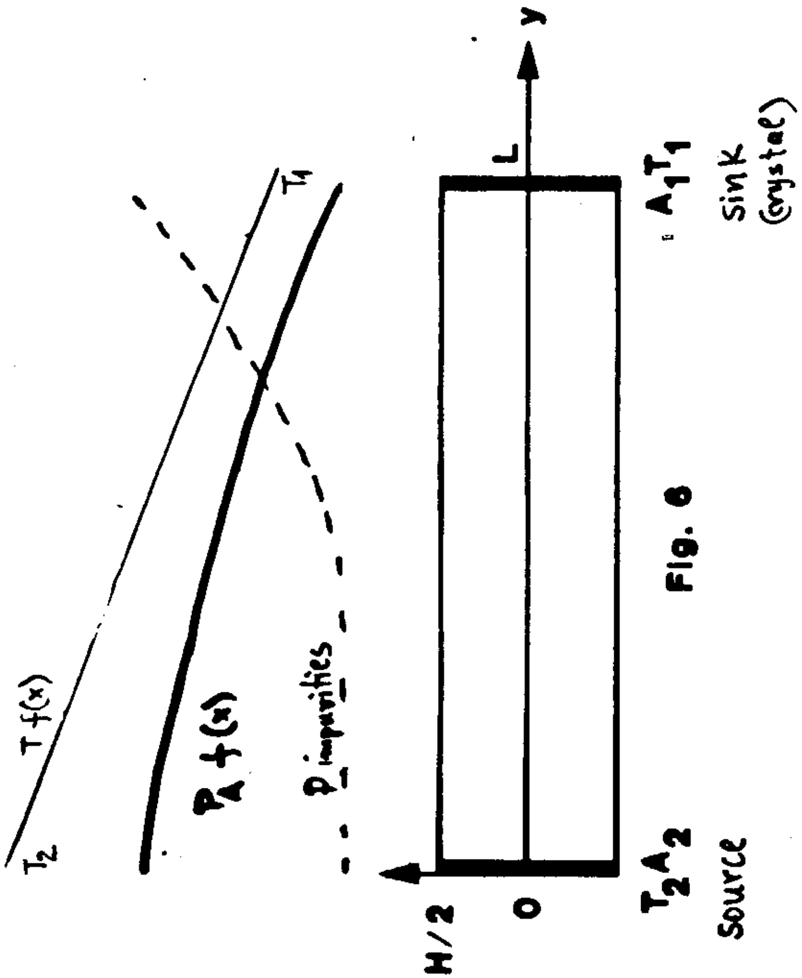


Fig. 6

- **Ideally pure systems (no gaseous impurities)**

Mass transport → advective flow (Stefan's flow) → Very high rate ($LGR > 10^{-5}$ cm/s)

↑

expansion of substance during evaporation

- **In the presence of gaseous impurities** → Slow mass transp. due to diffusion ($LGR \sim 10^{-6}$ cm/s)

Net flux of transported species A

sum: flow term + diffusion term

$$J_A = \frac{U}{RT} p_A - \frac{D}{RT}\frac{dp_A}{dx}$$

} build up of a partial pressure gradient ΔP along ΔT

1D- Model

Flux of A: $J_A = \frac{U}{RT} P_A - \frac{D}{RT} \frac{dP_A}{dx}$ (1)

Flux of impurity Z: → zero

$J_Z = \frac{U}{RT} P_Z - \frac{D}{RT} \frac{dP_Z}{dx} = 0$ (2)

otherwise incorporation to the crystal.

Adding (1) and (2) $P_A + P_Z = P$: total pressure

$J_A = \frac{U}{RT} P - \frac{D}{RT} \frac{dP}{dx}$ (3)

$\frac{dP}{dx} \ll 1$ no actual total pressure gradient.

$J_A = \frac{U}{RT} P$ (4)

Subst (4) in (1)

$J_A = \frac{J_A}{P} P_A - \frac{D}{RT} \frac{dP_A}{dx}$ (1')

rearange (1')

↓

$$\frac{dP_A}{P_A - P} = \frac{J_A RT}{D P} dx$$

integrate $x=0 \rightarrow x=L$

$$\ln\left\{\frac{P_A(L) - P}{P_A(0) - P}\right\} = J_A \frac{RTL}{DP}$$

Dependense of growth rate J on partial pressure gradient and total P.

changing to concentrations

$$\frac{1 - X_A(x)}{1 - X_A(0)} = \exp Pe \frac{x}{L}$$

(Pe) = PECLET NUMBER

relative weight

Convective / advective flow / diffusion

$$Pe = \frac{UL}{D_{AZ}} = \frac{J_A}{C} \cdot \frac{L}{D_{AZ}}$$

- $Pe \leq 1$ diffusion dominates; linear dependence of partial pressures (source→sink)

Calculation 1D- Model Rosenberger et al

Experimental confirmation: R. Cadoret et al for α- HgI_2

First
Experimental measurement,
Partial pressure gradient nearly linear (Diffusion dominating)

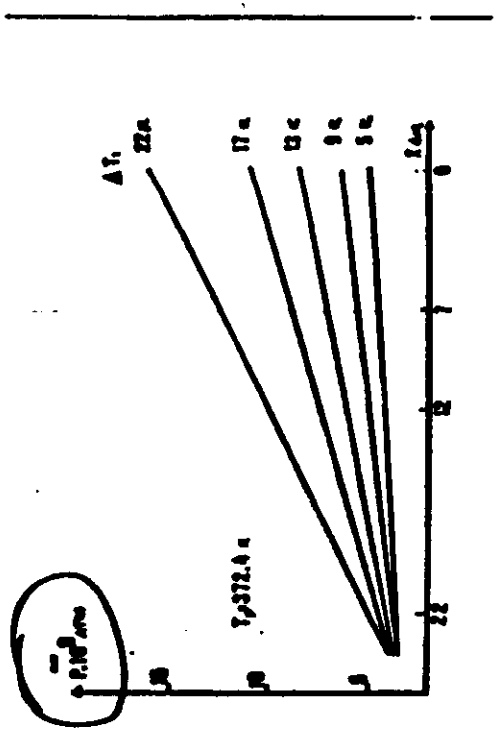


FIG. 5.4 HgI_2 partial pressure as a function of the position x with resp to the source for different temperature differences ΔT between source sink. (After OMALY et al., 1981).

Low impurity content.
- $Pe \gg 1$, 1-D Model

Non linear Partial Pressure Curves. Strong curvature near the crystal.

Build up of impurity in front of the crystal

Figure

2D-Model numerical solution (F. Rosenberger et al)

Very important:
Viscous interaction of diffusive-advective flow with ampoule walls

Stefan tube experiments (diff. induced binary flows) → Mass average velocity zero at the walls

$$U = \Sigma_i c_i U_i = 0$$

No slip condition
- For crystal growth $U_A \neq 0$
- then also $U_B \neq 0$

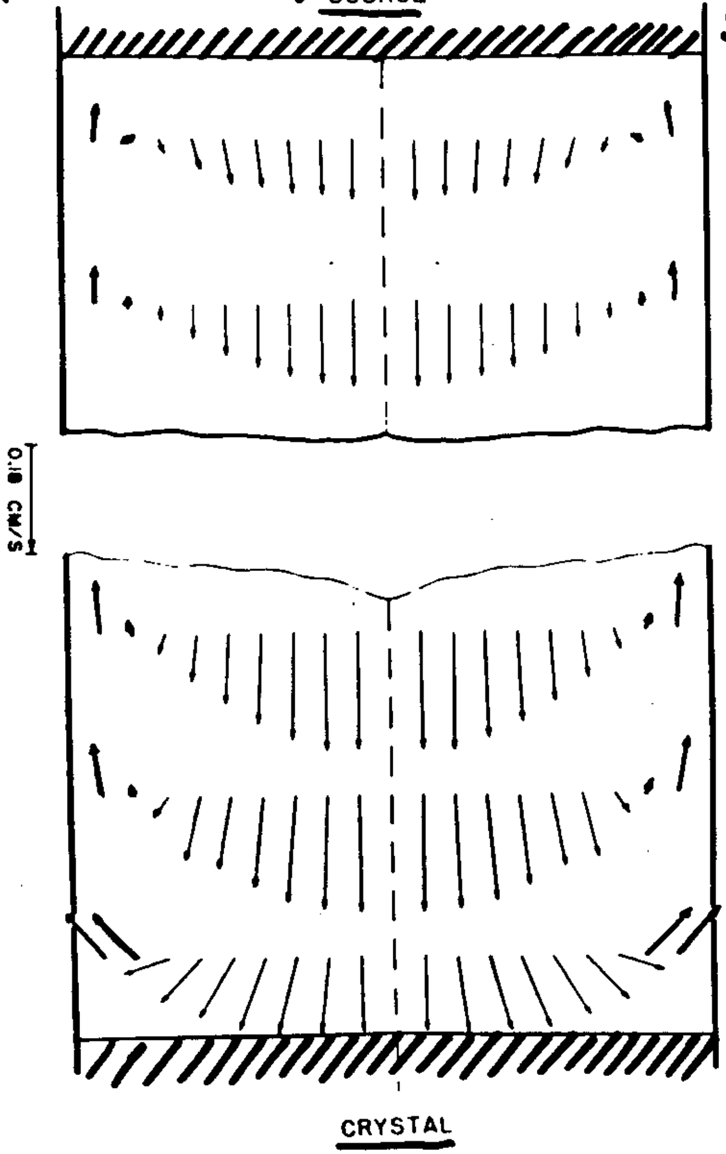
→ $U = 0$

Impurity not stagnant. RECIRCULATION FLOW EVEN in (μg)

CONCLUSION: MEANINGFUL SPACE EXPERIMENTS ONLY WITH VERY PURE SYSTEM.

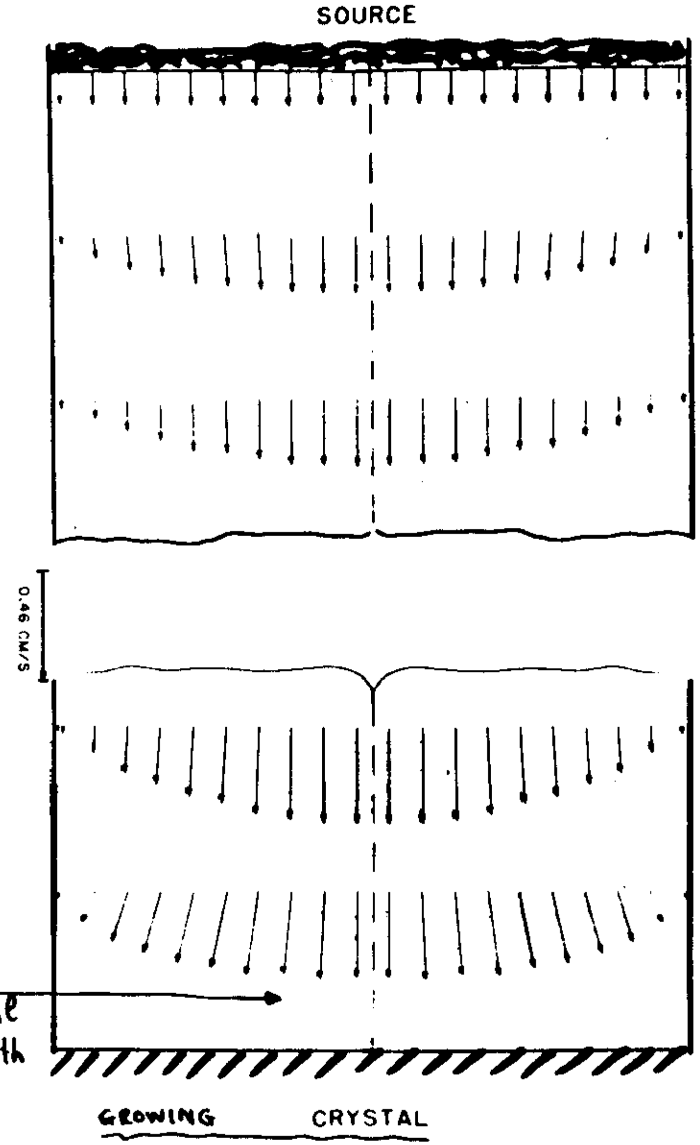
After F. Rosenberger et al J. Cryst. Growth 51 (1981) 413

Calculated velocity distribution of the impurity component H_2 during the diffusion of α-HgI_2 molecules from the source to the crystal under zero gravity (induced recirculation of impurity)



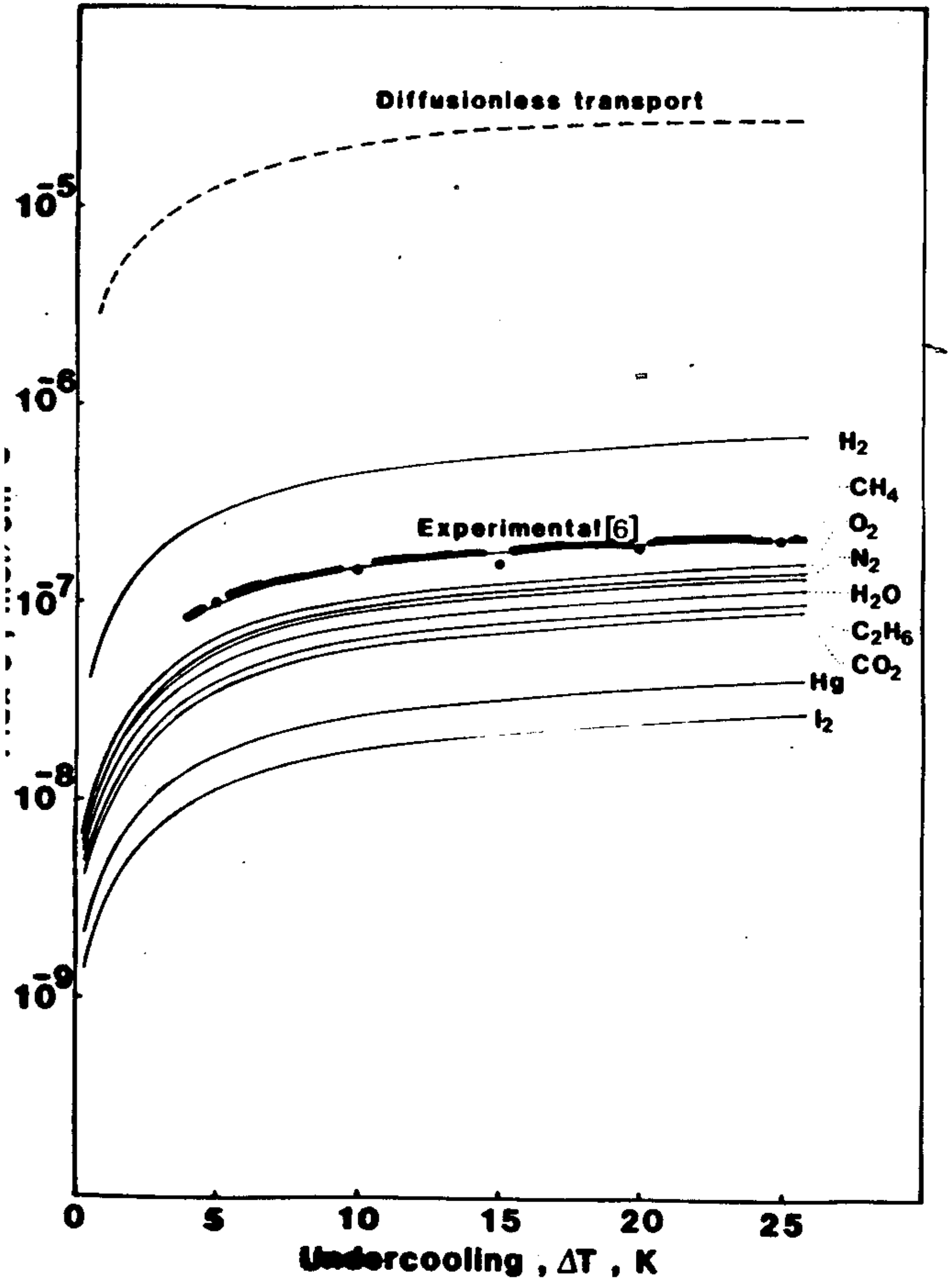
Solutal gradients near the walls.

MASS AVERAGE VELOCITY (IODINE - HYDROGEN)



Proportional to the growth flux

After PIECHOTKA (based on Faktor + Garrett / Rosenberger)



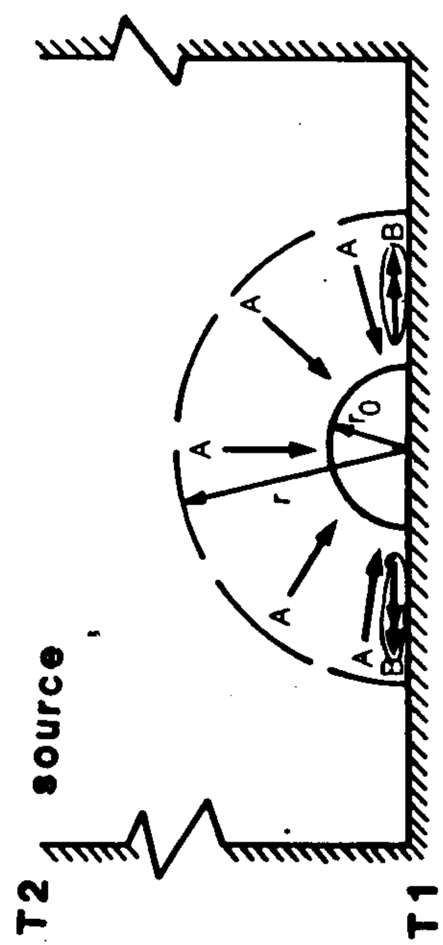


Fig. 8

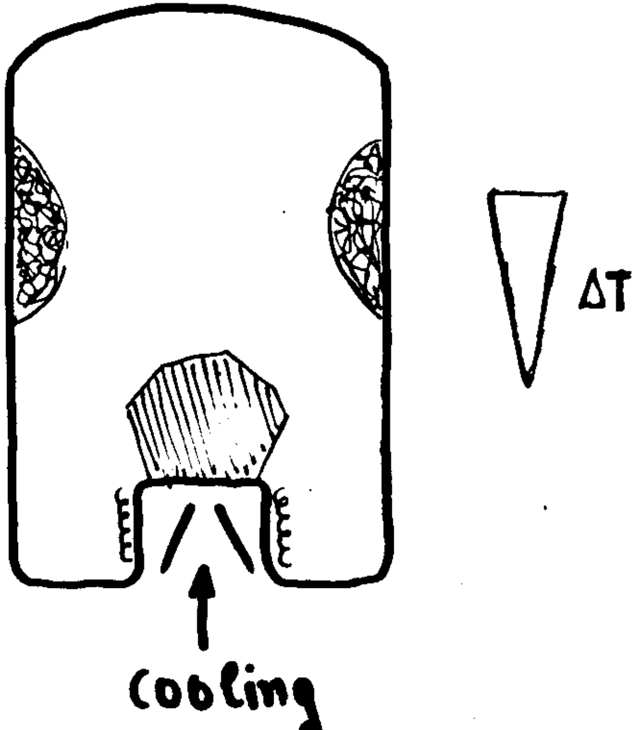
- Recirculation flow of impurity.
- Crystal should not cover the front of the ampoule.

Nucleation Control

Seeded Growth

Formation of seed in situ

(NASA-Design) SL-3
EG+G



Up to 500g! crystals (α-HgI_2)

Drawback → Temperature of the growth interface unknown

SLIDES