INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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SMR/382- 13

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

"Nonstoichiometry"

E. KALDIS
ETH
Zurich, Switzerland

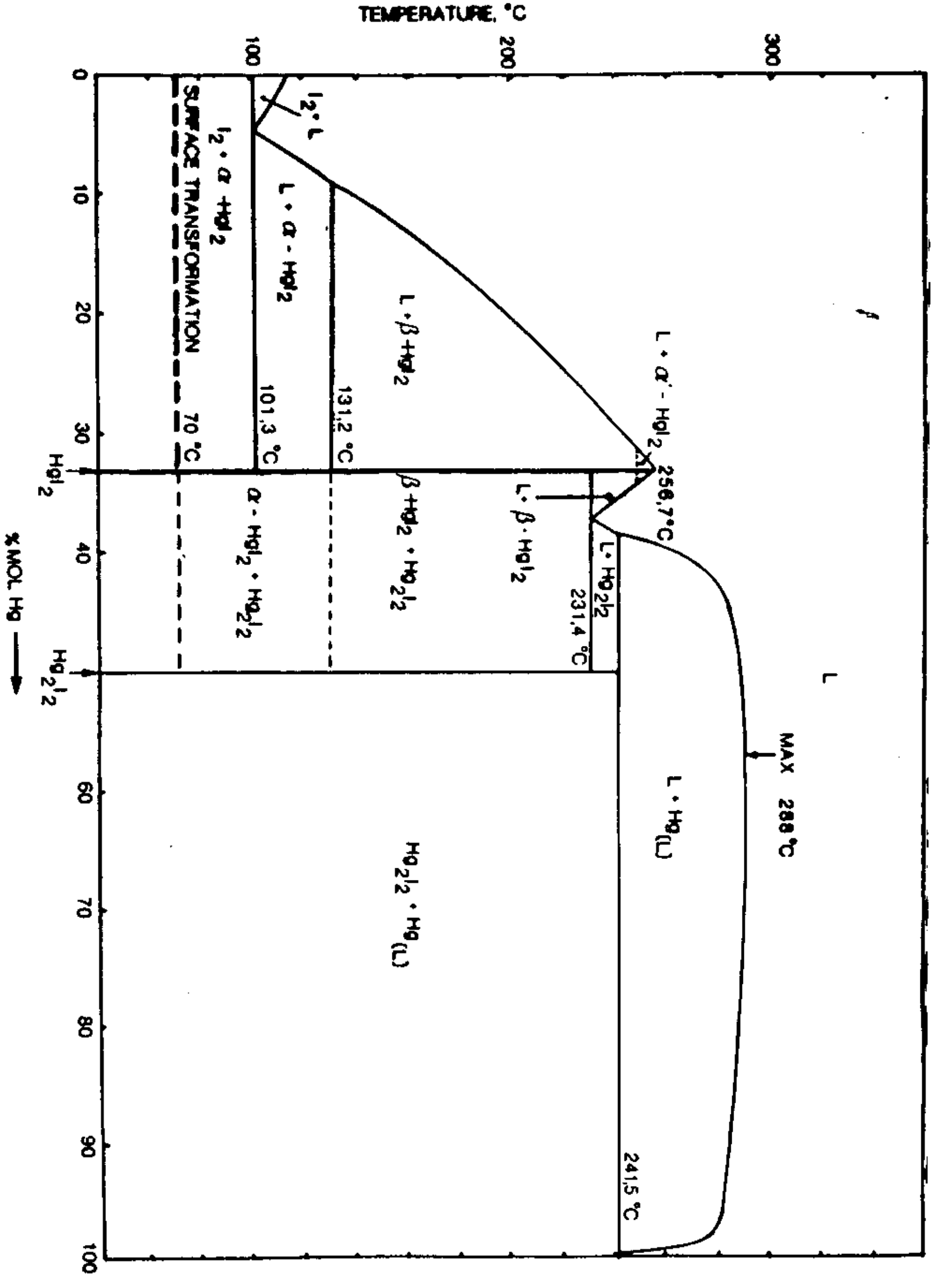
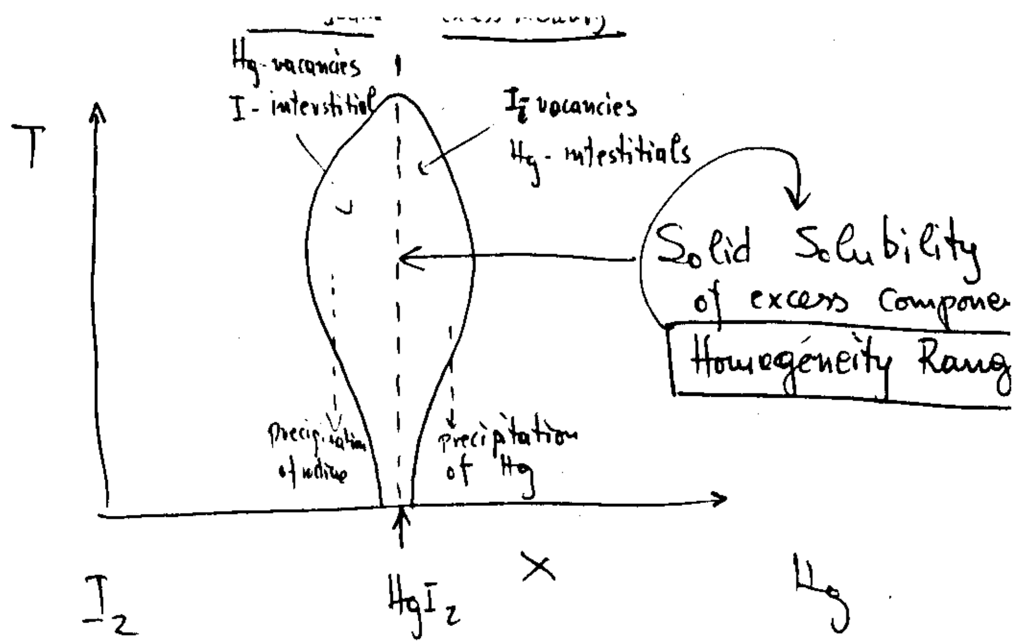


FIG. 2.1 T-x phase diagram of the system Hg-I. Solid line according to thermal analysis made by DWORSKY, KOMAREK, 1970, dashed lines after TOUBEKTSIS et al., 1985 (α*-phase) and PIECHOTKA, KALDIS, 1986 (surface transition).



4. Nonstoichiometry

Contradicting views in the literature.

Chemical analysis not sensitiv enough.

Best approach Nicolau (density measurements) → both sides possible

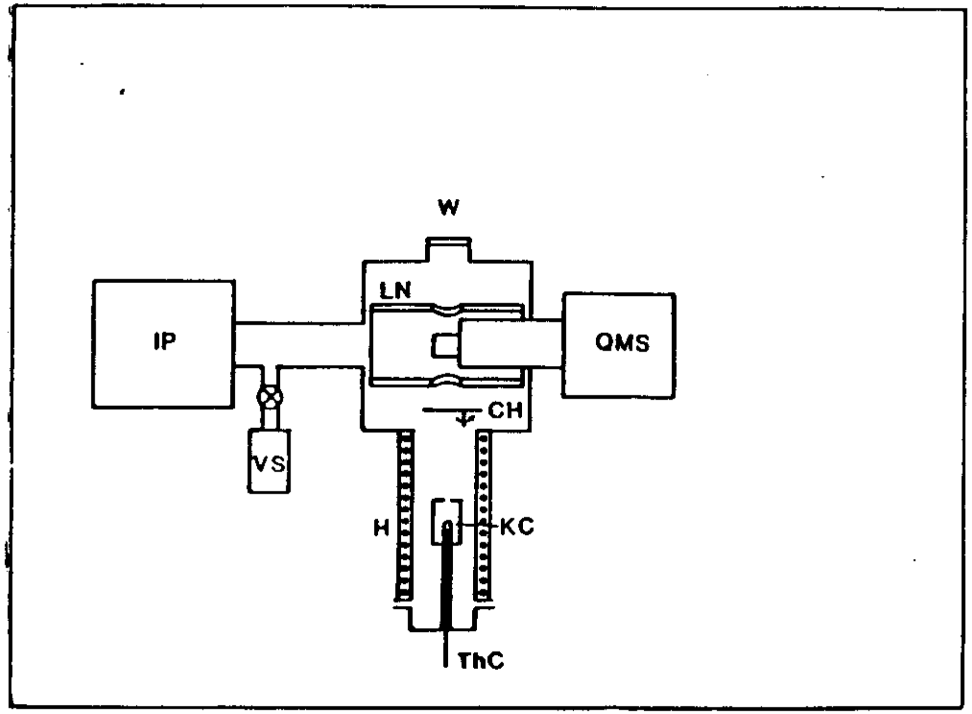
New approach for a qualitative but clear decision.

Total evaporation measurements (Piechotka, Kaldis)
J. Less Comm. Metals 1986
J. Electroch. Soc. 1986

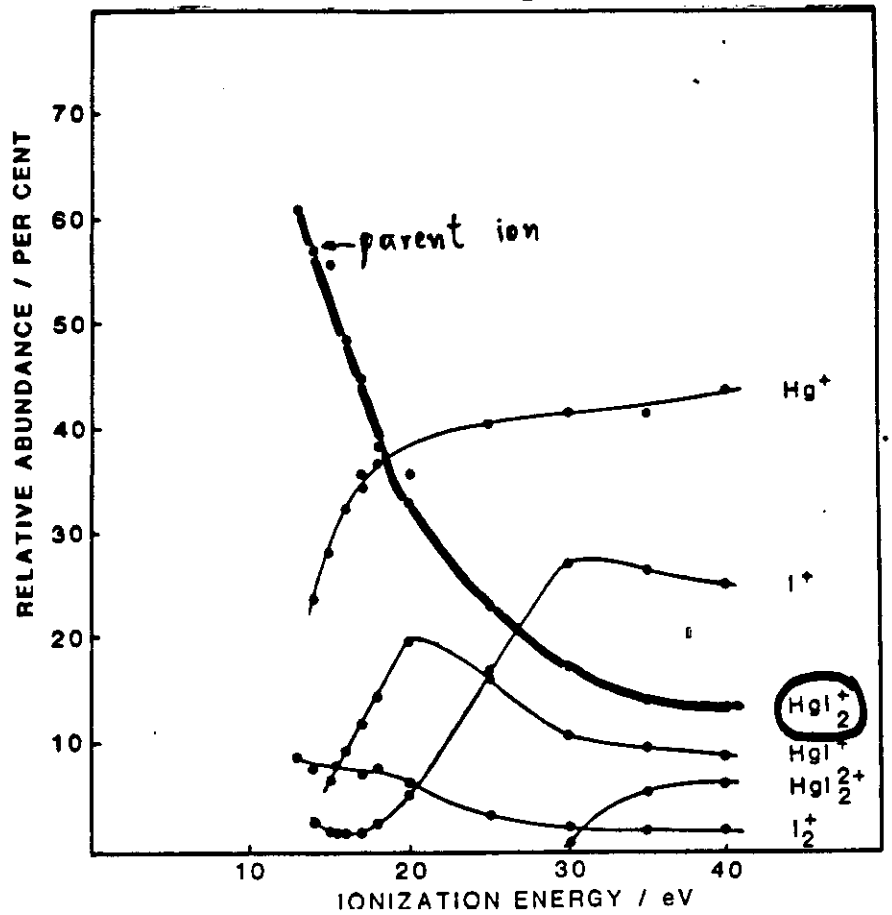
Condition: congruent evaporation
→ has to be proved.
↓
For this → study of evaporation necessary

UHV - Evaporation Apparatus

- Chopped Molecular Beam
- Quadrupol Mass Spectrometer (cross beam)
- Ion Getter and Absorption Pumps



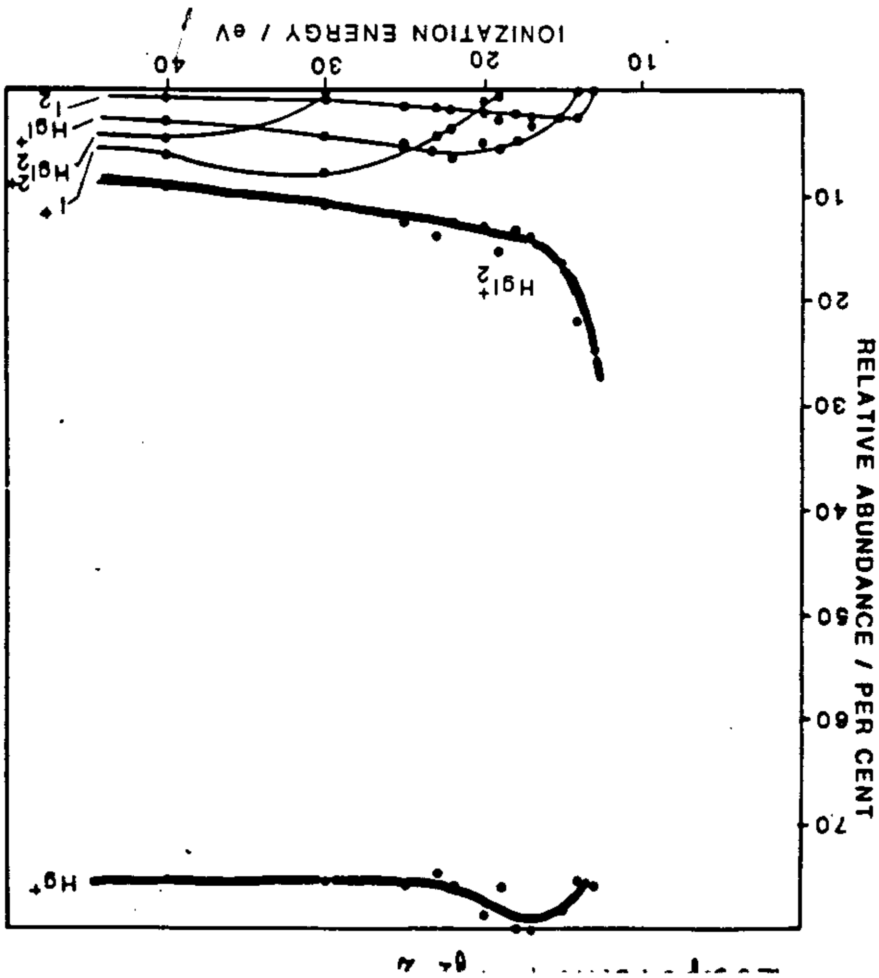
Investigation of the evaporation reaction



Parent-Ion: only HgI_2^+

Evaporation Reaction

$\boxed{HgI_{2}(s) \rightleftharpoons HgI_{2}(v)}$



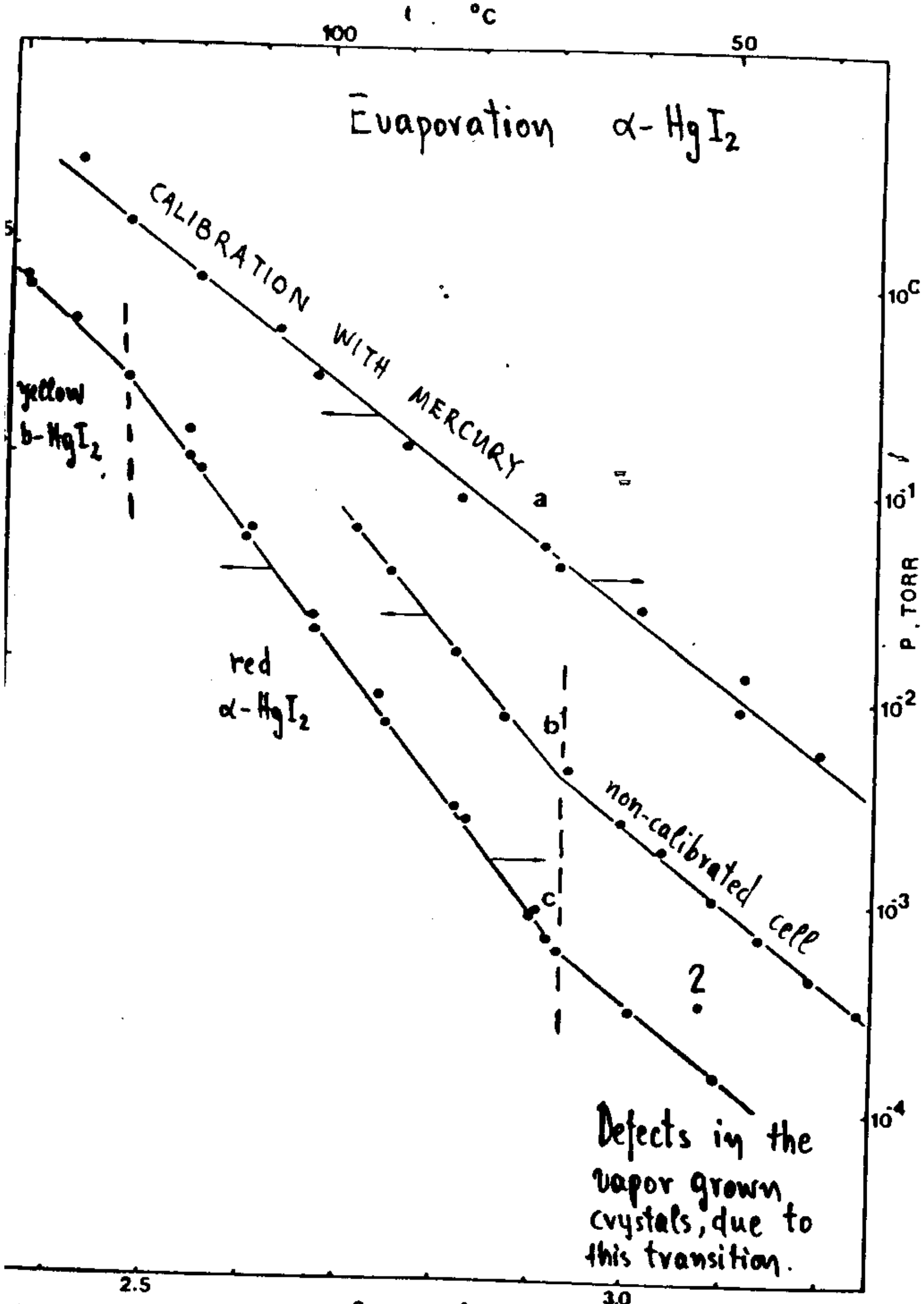
Two parent ions
- Hg^+
- HgI_2^+

Evaporation Reaction

$Hg_2I_2(s) \rightleftharpoons HgI_2(s) + Hg(v)$

$\downarrow$

$HgI_2(v)$



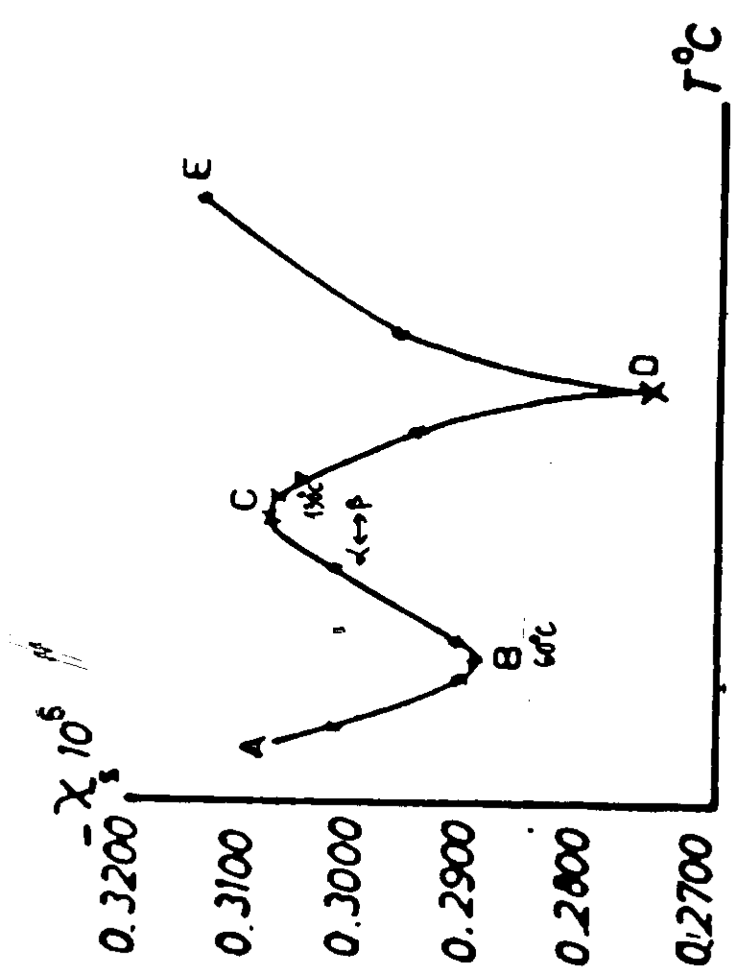


Fig. 1a. Temperature dependence of the magnetic susceptibility of HgI_2 after the author.

M. Mikhail et al
J. Phys+Chem. Solids 36 (1975) 1033

L.F. Strakhof et al
Soviet Phys. Sol. State
10(8), 1970 (1969)

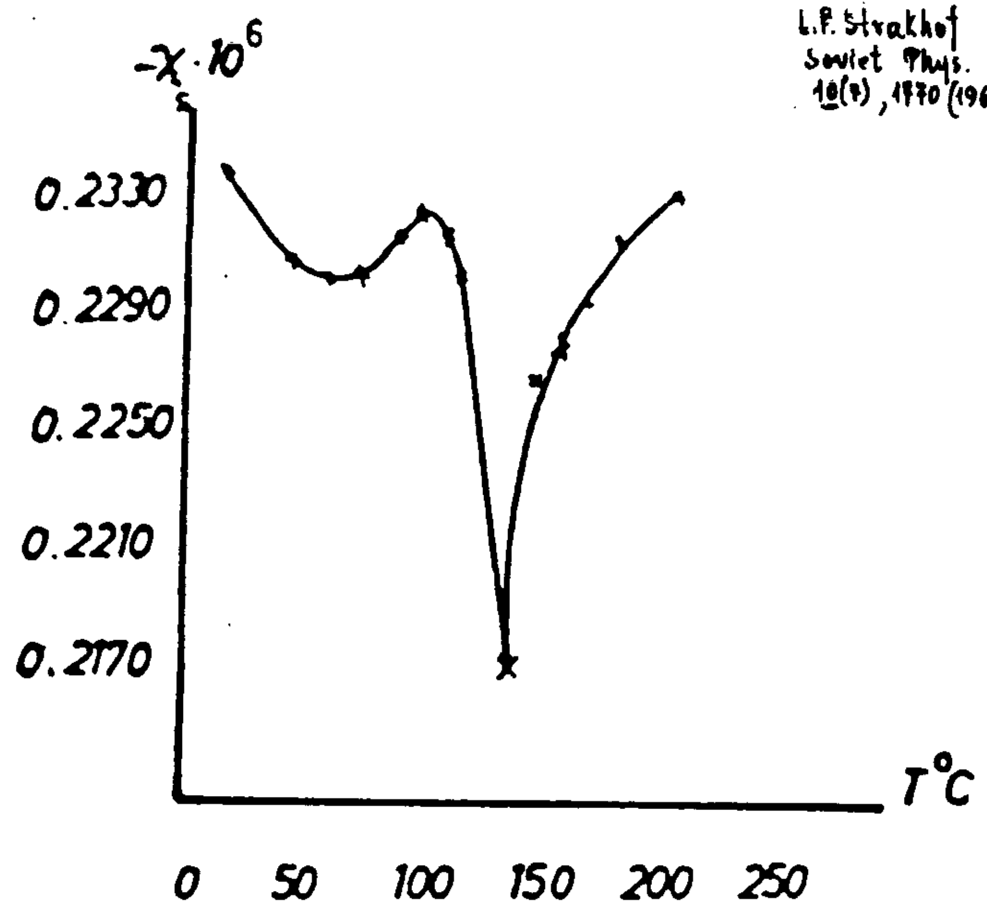
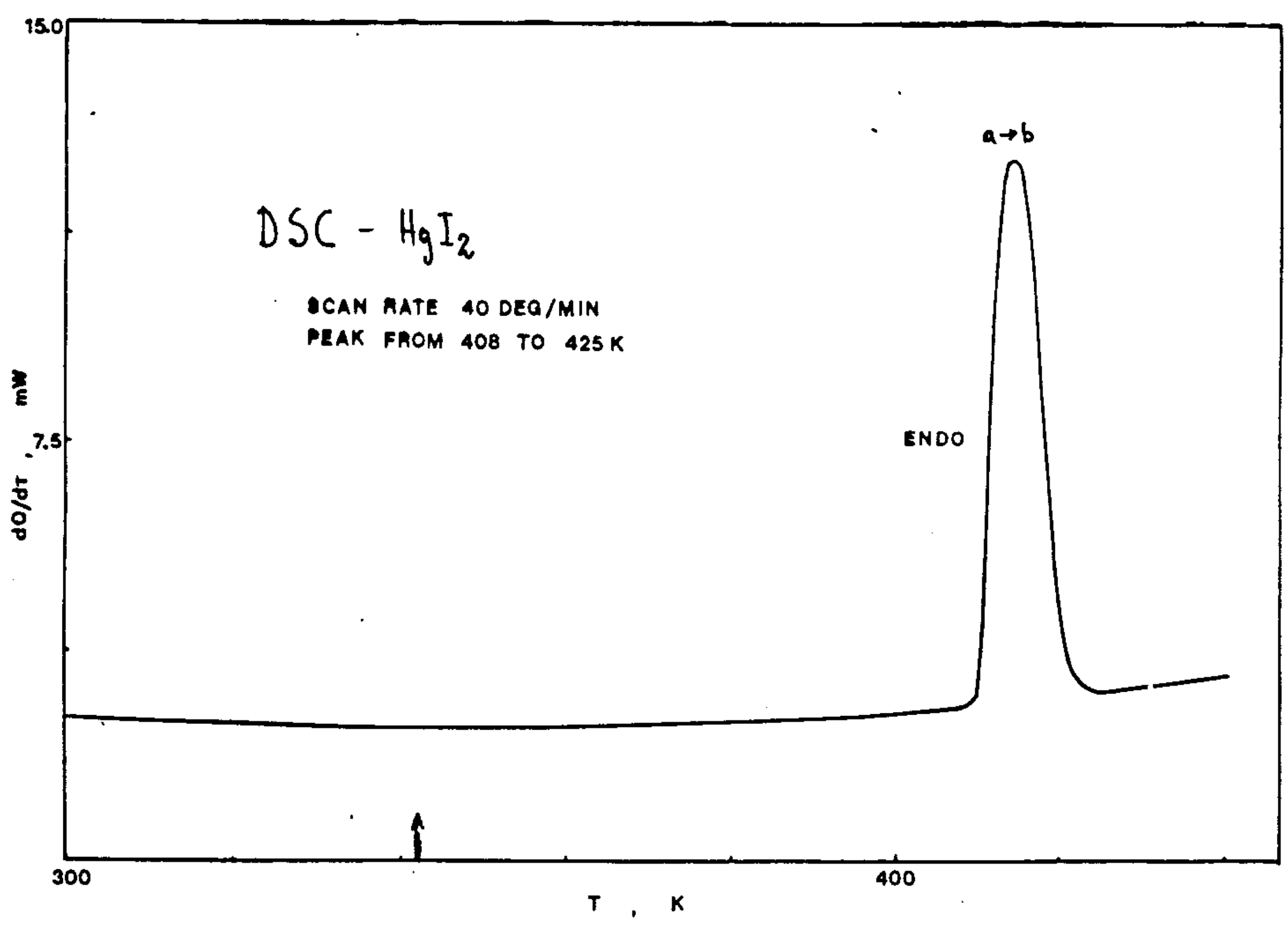


Fig. 1b. Temperature dependence of the magnetic susceptibility of HgI_2 (uncorrected for ferromagnetic impurities) after Strakhov



Nonstoichiometry

To find if (solid solubility) exists ~~table~~

~~excess stoich~~

Doping with Fe

Hg

Hydrocarbons.

Does the evaporation enthalpy change?

ΔH_{evap}.

(Slope of the evaporation curve).

If not → No solubility.

If only the evaporation sees the effect

and the DSC not

↓

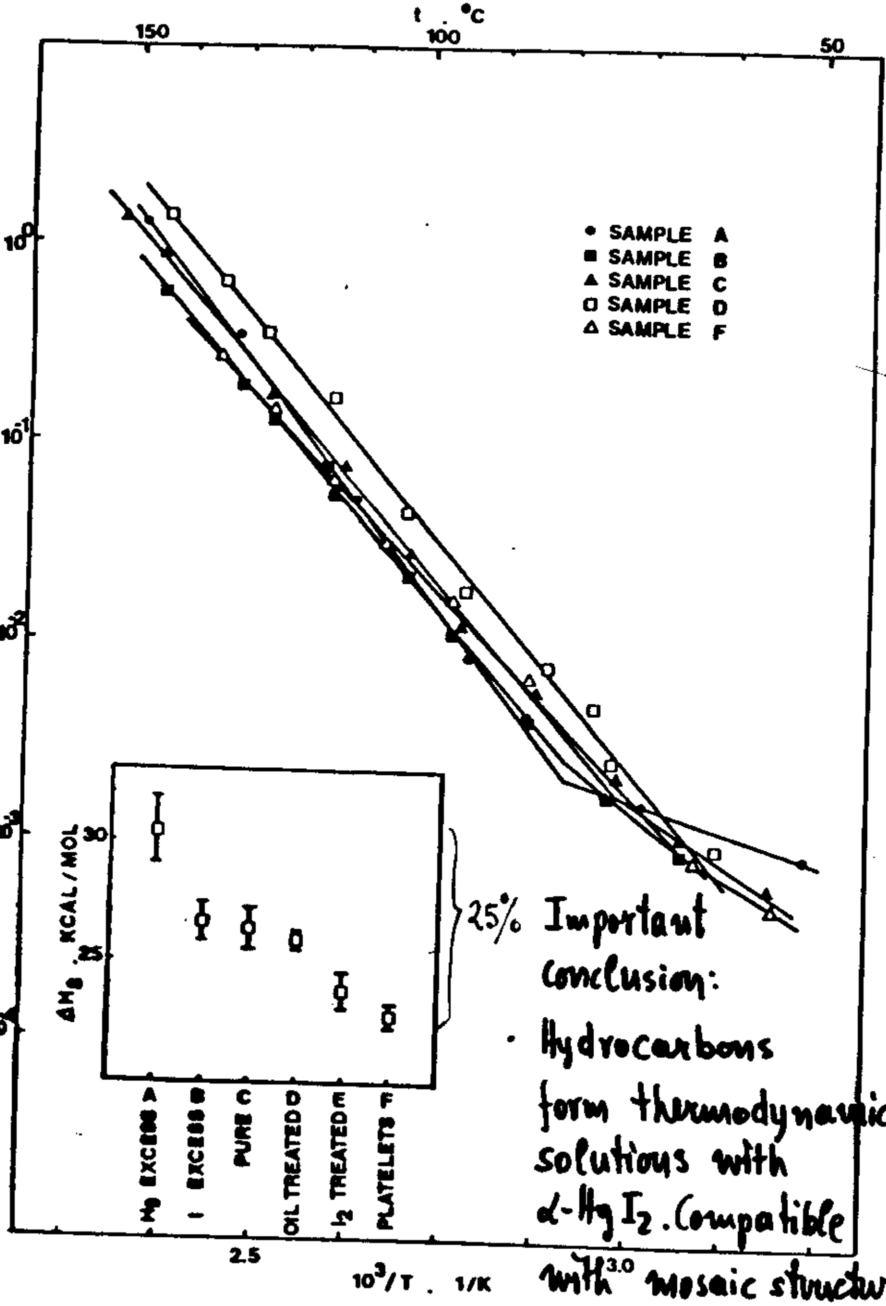
we must assume that it is a surface effect

z.B. A surface reconstruction.

This is in agreement with the industry EG+G (detector fabrication). They find a high concentration of defects at the surface of the crystals.

Surface parts are cut away.

Evaporation Enthalpies: Dopants dissolved in the lattice of α-HgI_2



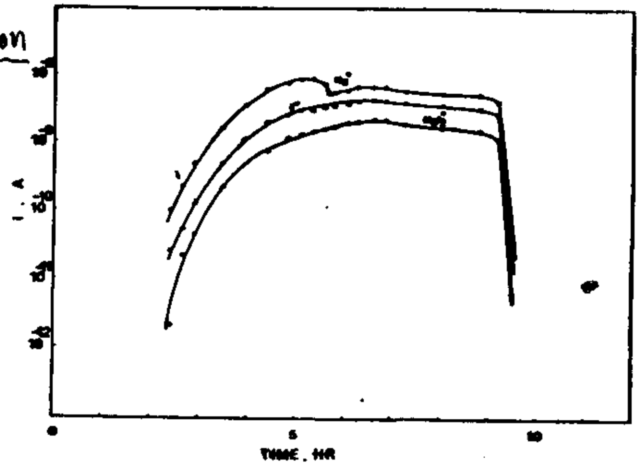
25% Important conclusion:

- Hydrocarbons form thermodynamic solutions with α-HgI_2. Compatible with mosaic structure model?

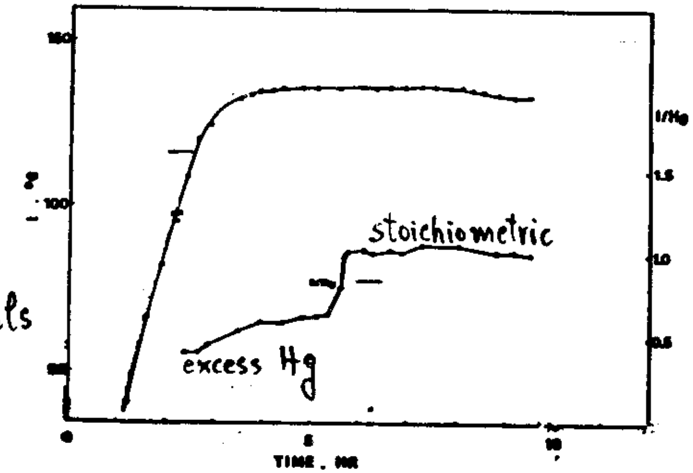
Evaporation of pure α-HgI_2 {with excess of Hg dissolved in the lattice.}

Total Evaporation

Ionization Current as a function of time

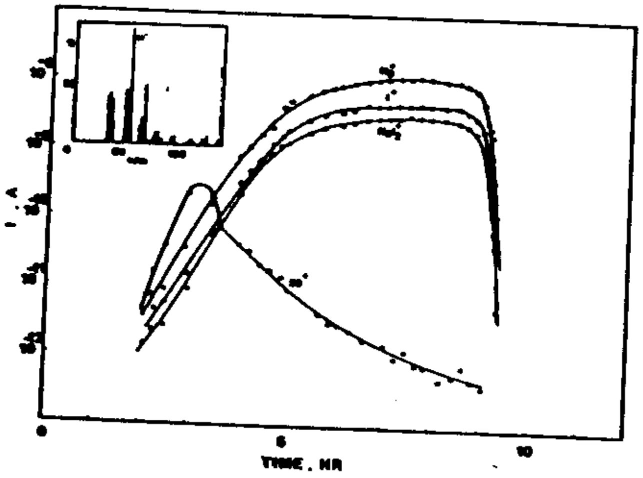


Ratio of the I/Hg Signals



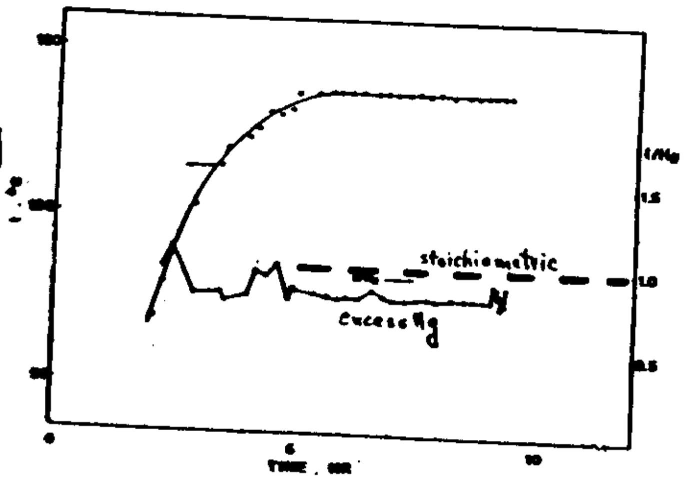
Evaporation of HC-doped α-HgI_2 {with excess Hg}, dissolved in the lattice

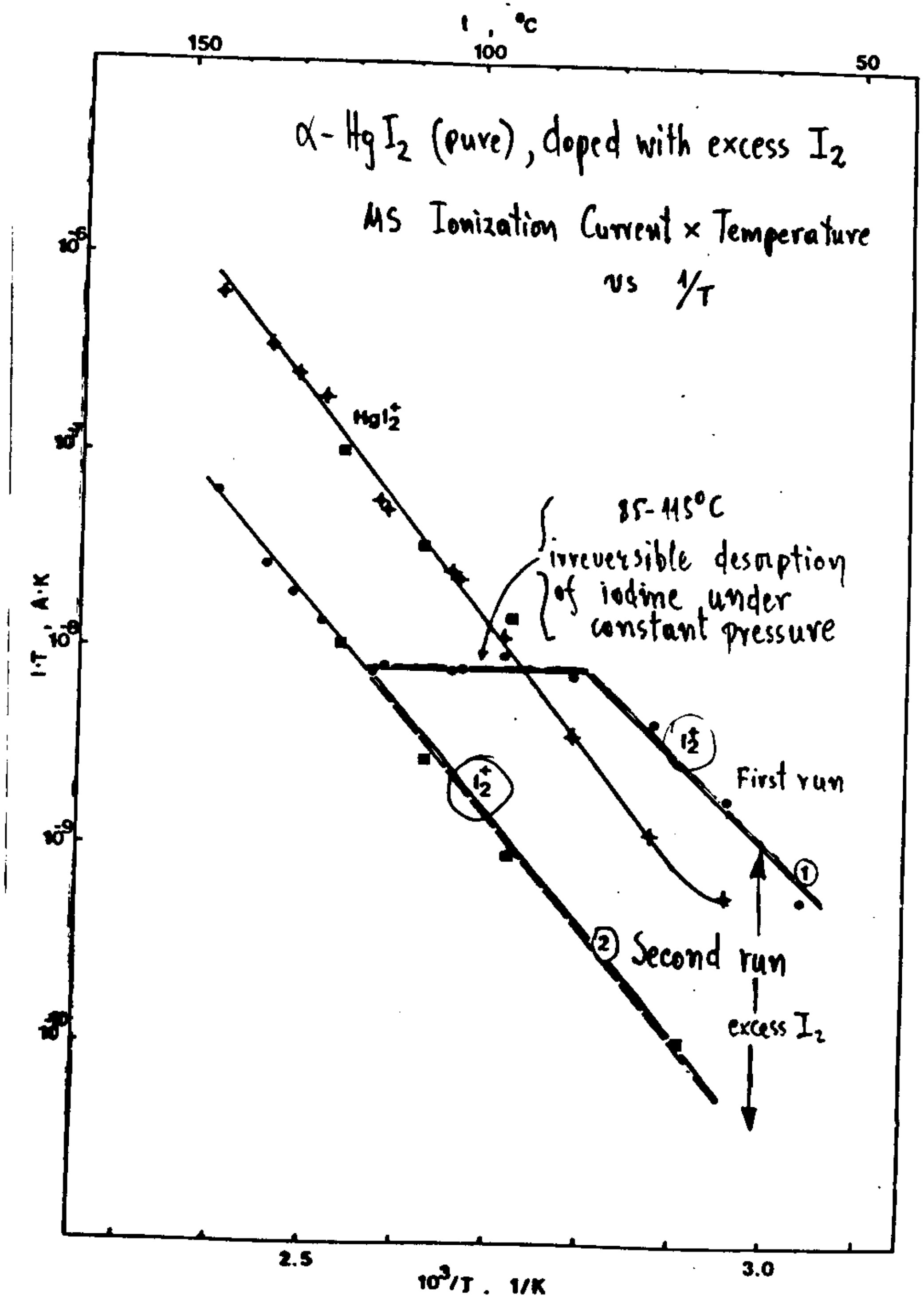
Total Evaporation



nstoichiometry FIXED

I/Hg ratio





Conclusions

- We know the evaporation reaction

- We know that both types of nonstoichiometry are possible

  For detector fabrication

- In principle self doped detectors can be produced ad demand

- Except if hydrocarbons are present,

  the negative importance of

  hydrocarbons is, therefore, particularly [illegible]

- A very surface annealing is present [illegible] [illegible] [illegible]